R. C. Larock

Organomercury Compounds in Organic Synthesis

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Paul Helquist

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Volume 22

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To

George Zweifel
For inspiring an interest in organometallic chemistry.

Herbert C. Brown
For showing me how to productively explore those interests.

Henry Gilman
For his kindness and encouragement in my early years in academia.

Preface

The field of organometallic chemistry has enjoyed explosive growth in recent years. During this time a rapidly increasing number of metals have found utility in organic synthesis as the corresponding organometallic compounds. The subject of "Organic Synthesis by Means of Transition Metal Complexes" was reviewed in the first volume of this series of monographs. This volume deals primarily with the application of organomercury compounds in organic synthesis (exclusive of solvomercuration-demercuration reactions), but will of necessity involve a number of reactions of other organometallics as well.

Organomercurials are among the oldest known organometallics and were perhaps the first to have an entire book devoted to their chemistry, when Whitmore wrote an American Chemical Society monograph on the subject in 1921. Subsequently, two very detailed monographs on the subject have appeared. In 1967 "The Organic Compounds of Mercury", volume 4 in the series "Methods of Elemento-Organic Chemistry" appeared and this was followed in 1974 by Houben Weyl's full volume, Band XIII/2b, devoted entirely to the organometallic compounds of mercury. These books cover the entire field of organomercury chemistry.

The purpose of the present monograph and one entitled "Solvomercuration-Demercuration" which will appear later in this series is not just to update the work in this area, but to place special emphasis on the application of organomercury compounds in organic synthesis. In order to accomplish this objective, it will be necessary to review the major methods by which organomercurials can be prepared. Due to the space limitations of this monograph, only those procedures which appear to be reasonably general in scope and which provide organomercurials of use in organic synthesis will be covered. Similar restrictions have been placed on the synthetic applications of these reagents which will be discussed. Those reactions which appear limited in scope, but provide a unique synthetic transformation will be only briefly discussed. Reactions in which mercuric salts are employed strictly as oxidants and in

which carbon-mercury bond formation is not involved have been completely omitted. The exceedingly important application of solvomercuration-demercuration reactions for the Markovnikov functionalization of alkenes and alkynes will not be covered in this volume due to a shortage of space. This topic will be covered instead in a separate volume in this series entitled "Solvomercuration-Demercuration".

My own personal interest in the application of organomercurials in organic synthesis goes back to my graduate school days when I first became involved in the development of new synthetic routes to organomercurials via organoboranes. In 1976 I wrote a chapter entitled "Organomercurials as Reagents and Intermediates in Organic Synthesis" for a book entitled "New Applications of Organometallic Reagents in Organic Synthesis". That chapter was subsequently pared down to a brief review article in Angewandte Chemie which appeared in 1978. The response to that article has encouraged me to undertake the writing of this monograph, which will finally provide the space necessary to cover the subject in the detail that seems desirable. The subject matter has necessarily been edited and I apologize in advance to those authors whose work may have been slighted, or worse yet completely overlooked. The references cited in this monograph represent thorough coverage of the chemical literature through 1980 and the majority of important works which appeared in journals readily accessible in the United States from 1981 to mid 1983. An abbreviated version of this book was published in Tetrahedron Reports in 1982.

I wish to thank Iowa State University for the sabbatical leave necessary to complete a major portion of this book, and the chemistry faculty at the California Institute of Technology for their warm hospitality during that leave. I also wish to express my appreciation to my own graduate students for both their patience and their scientific and technical assistance in the writing of this manuscript. In particular, I wish to thank Drs. Douglas Leach and Constance Fellows for assistance in translating the French and Russian literature respectively. Finally, this entire project would have been impossible without the outstanding professional assistance of two very fine secretaries, Miss Helen Tranter and especially Mrs. Denise Junod, whose help is greatly appreciated.

Ames, Iowa
May, 1984

Richard C. Larock

Table of Contents

Abbreviations

The following abbreviations have been used in this book.

Ac	acetyl
Ar	aryl
n-Bu	*n*-butyl
i-Bu	isobutyl
s-Bu	*sec*-butyl
t-Bu	*tert*-butyl
Bz	benzoyl
CIDNP	chemically induced dynamic nuclear polarization
d	day(s)
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
Et	ethyl
h	hour(s)
HMPA	hexamethylphosphoramide
m	minute(s)
Me	methyl
NBS	*N*-bromosuccinimide
Ph	phenyl
PNB	*p*-nitrobenzoyl
n-Pr	*n*-propyl
i-Pr	isopropyl
R	alkyl
THF	tetrahydrofuran
THP	tetrahydropyranyl
TLC	thin layer chromatography
Ts	*p*-toluenesulfonyl

I. Introduction

Edward Frankland reported the first organomercury compound, methylmercuric iodide (CH_3HgI), in 1852 only three years after his discovery of the first organometallic compound [1, 2]. Several other organomercury compounds were discovered soon thereafter, but the accidental death of two of the co-workers of Frankland's successor in 1865 and 1866 effectively brought a halt to activity in this field until the discovery of the mercuration of aromatic compounds by Dimroth [3] just before the turn of the century.

The early 1900's saw the first application of organomercury compounds as fungicides, and organomercurials have played an important role, especially as agricultural seed dressings, ever since. This important application has not been without its misfortunes also, as treated grain has on occasion been accidently used as food instead of seed, resulting in mercury poisoning [4, 5]. More recently great public concern has been raised by the presence of mercury in the environment [6–9]. Biological methylation of mercury leads to methylmercury compounds whose high toxicity resulted in entensive organomercury poisoning in Minamata, Japan in the 1950's [10, 11]. Such incidents are cited as a warning to the reader that organomercurials should be handled with respect.

However, the vast majority of organomercurials are fairly high melting crystalline solids whose handling requires no undue precautions. They are generally of sufficiently reduced volatility that they can be easily weighed out in air on the laboratory bench and transferred to the reaction vessel. Since the most efficient use of organomercurials in synthesis requires that all organic groups attached to mercury be utilized, organomercurials of the type RHgX are most commonly used. These are also less volatile than the diorganomercurials R_2Hg. The most common organomercurials of the type RHgX are the organomercuric halides, although acetates, hydroxides and nitrates are sometimes used. The halides are generally much higher melting and much less powerful skin irritants than these other more ionic salts.

With these precautions in mind, one finds that organomercurials possess a number of very attractive characteristics making them desirable as reagents or intermediates in organic synthesis. A tremendous number of organomercurials encompassing a wide range of structural types are already known. Alkyl-, alkenyl-, alkynyl-, aryl- and carboalkoxymercurials are known, as are many polymercurated compounds. Furthermore, a substantial number of organomercurials are presently commercially available. Most organomercurials are extremely stable up to temperatures well above their melting

points and can be routinely stored in air with no deterioration. Most compounds are also quite stable to protic solvents, dilute acids and even rather strong bases. This remarkable chemical stability allows one to incorporate essentially all important organic functional groups in these organometallics. The vast majority of these compounds are fairly high melting solids which can be readily recrystallized (often from ethanol) and thus easily purified. This is important when one is concerned about the isomeric purity of such compounds as the vinyl- or arylmercurials. These characteristics thus allow one to run synthetic reactions employing organomercurials under a wide variety of reaction conditions.

The early part of the twentieth century saw the development of the more reactive organometallic reagents, such as the organolithium and -magnesium compounds. These reagents accommodate very little in the way of functionality. We are now seeing a rebirth of interest in the organometallic chemistry of the less reactive main group elements and the transition metals. The modern synthetic organic chemist is increasingly concerned about the chemo-, regio- and stereoselectivity of a reagent. This has heightened interest in transition metal organometallic reagents which often exhibit substantially different reactivity patterns from main group organometallic reagents. Much of the current interest in organomercurials stems from the ease with which these compounds undergo transmetallation reactions with transition metal salts, particularly palladium. Thus, many of the more interesting newer developments in organomercury chemistry involve the organometallic chemistry of other metals as well.

While the majority of this monograph will be devoted to synthetic applications of organomercury compounds, particularly those involving carbon—carbon bond formation, it will first be necessary to review the major methods of preparing these compounds. Chapter II covers a number of the more important methods, but it is out of necessity limited in scope and the reader is encouraged to consult more detailed monographs [12, 13] for more details. Only when one comprehends the wide variety of synthetic routes by which these compounds can be prepared can one fully appreciate the numerous synthetic possibilities which exist for these compounds. The remaining chapters will cover the more important reactions of organomercurials, starting with one of the oldest and mechanistically one of the most thoroughly studied reactions of organomercurials, halogenation. Subsequent chapters describe the conversion of organomercurials into heteroatom-containing compounds, followed by the highly important carbon—carbon bond forming reactions. The final chapter describes the use of organomercurials as divalent carbon transfer reagents.

The synthetically very valuable solvomercuration-demercuration reactions will be covered in a separate monograph entitled "Solvomercuration-Demercuration". The increasingly important chemistry of compounds containing silicon, germanium and tin bonded directly to mercury will also not be discussed. The synthesis of other organometallic reagents by organomercury transmetallation reactions has also for the most part been omitted, although this area has over the years provided one of the

most important applications of organomercurials. Only those transmetallation reactions which lead directly to organic products of interest to the synthetic organic chemist will be discussed. Let's see now how organomercury compounds are best prepared.

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II. Preparation of Organomercury Compounds

A. Introduction

A full appreciation of the synthetic potential of organomercurials requires a thorough understanding of the methods available for their preparation. The following sections discuss a number of the most important methods, but by no means all. Emphasis is on those methods which have proven generality, proceed in good yield, provide unique structural types or chemical transformations, and provide organomercurials which have subsequently proven useful in organic synthesis. Newer methods which have yet to pass these tests are reported only when their synthetic potential warrants such attention. After an initial section on the direct conversion of organic halides to organomercurials, a variety of transmetallation reactions will be discussed. These methods are followed by the extremely important mercuration reactions of alkanes, unsaturated hydrocarbons and aromatic compounds. The very valuable solvomercuration reaction will be only briefly introduced at this point and then covered in depth in a separate monograph in this series. This chapter concludes with a variety of elimination reactions which lead directly to organomercury compounds.

B. Direct Mercuration of Organic Halides

The direct reaction of metallic mercury and organic halides is of limited synthetic utility. Although methylmercuric iodide, the first organomercurial ever prepared, is readily available by this route (Eq. 1) [1, 2], ethyl [3–5], *n*-propyl [2] and *n*-amyl [1] iodides give only low yields. Mercurous iodide has been found to catalyse the reaction with methyl iodide [6]. The reaction of ethyl iodoacetate and mercury gives the corresponding organomercuric iodide but in only very low yield (Eq. 2) [7].

$$CH_3I + Hg \xrightarrow{h\nu} CH_3HgI \qquad (1)$$

$$EtOCCH_2I + Hg \longrightarrow EtOCCH_2HgI \qquad (2)$$

A number of polyhaloalkanes also yield organomercurials upon direct reaction with mercury. Methylene iodide affords either the mono- or dimercurated product depending upon the amount of metallic mercury available (Eq. 3) [2, 8–12]. Addition of mercurous iodide again facilitates

reaction [9]. It appears that iodoform reacts in a similar fashion (Eq. 4) [9]. On the other hand, the mixed halides Cl_2CHI [13], Cl_2CHBr [13], Cl_3CI [13, 14] and Cl_3CBr [13, 14] afford only the corresponding dichloromethyl- and trichloromethylmercuric halides respectively, and $HCCl_3$, $HCBr_3$ and CCl_4 provide no organomercurial at all [15]. Perfluoroalkyl iodides and bromides also react (Eqs. 5–7).

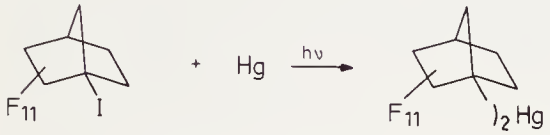
$$CH_2I_2 \xrightarrow{Hg} ICH_2HgI \xrightarrow{Hg} CH_2(HgI)_2 \tag{3}$$

$$HCI_3 + 3Hg \longrightarrow HC(HgI)_3 \tag{4}$$

$$R_fI + Hg \xrightarrow[\Delta]{h\nu} R_fHgI \tag{5 [16–18]}$$

$$EtOCCF_2CFCF_3 + Hg \longrightarrow EtOCCF_2CFCF_3 \tag{6 [19, 20]}$$

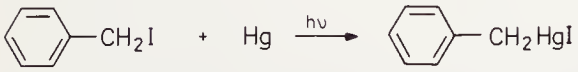
(Br; HgBr)



(7) [21]

A large number of allylic halides have been reported to give the corresponding allylmercuric halides upon direct reaction with mercury: $H_2C{=}{=}CHCH_2I$ [22, 23], $H_2C{=}CClCH_2I$ [24], $ClCH{=}CClCH_2I$ [24], $Cl_2C{=}{=}CHCH_2I$ [13, 14, 25], $Cl_2C{=}CClCH_2I$ [24], $Cl_2C{=}CClCH_2Br$ [24], $Cl_2C{=}CBrCH_2I$ [24], $Cl_2C{=}C(CH_3)CH_2I$ [13, 25], $H_2C{=}CHCH_2Br$ [7, 26] and $C_6H_5CH{=}CHCH_2Br$ [7]. However, $H_2C{=}CClCCl_2Br$, $Cl_2C{=}{=}CHCH_2Br$ and $H_2C{=}CBrCCl_3$ are all reported to give the same product, $Cl_2C{=}CClCH_2HgBr$ [24]. Propargyl iodide also reacts readily with mercury upon photolysis. Contrary to the literature report [27], we have obtained the allenic mercurial from this reaction (Eq. 8). A wide variety of benzylic halides undergo a smooth reaction with mercury to give the corresponding organomercurials (Eqs. 9–11).

$$HC{\equiv}CCH_2I + Hg \xrightarrow{h\nu} H_2C{=}C{=}CHHgI \tag{8}$$

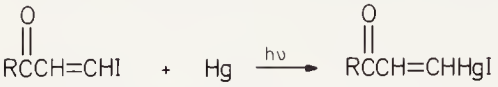


(9) [6]

(10) [28]

(11) [7, 26, 29–33]

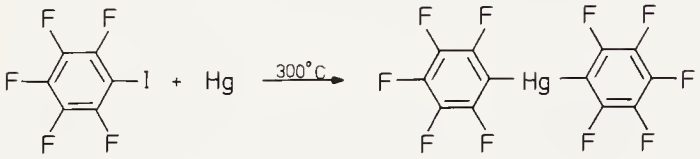
Organomercurials have also been prepared from metallic mercury and vinyl and acetylenic iodides (Eqs. 12, 13). Starting with the *trans*-alkenyl iodide, one apparently obtains primarily the *cis*-organomercurial [35]. This product can in turn be isomerized to the *trans*-compound.



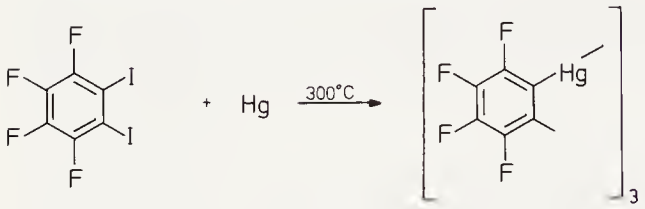
(12) [34, 35]

(13) [36]

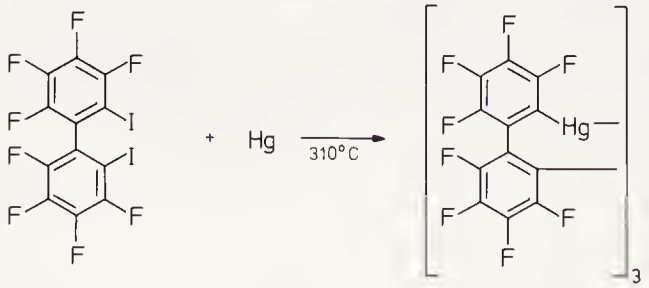
Aryl iodides do not generally react well with metallic mercury [7, 26, 37], but perfluoroaryl iodides do give rise to arylmercurials at elevated temperatures (Eqs. 14–16).



(14) [38, 39]



(15) [40]

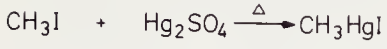


(16) [39, 41, 42]

Other than the following example, organic chlorides are generally inert towards metallic mercury (Eq. 17) [43]. However, the addition of anions to the reactions of metallic mercury and alkyl or aryl iodides, bromides and even chlorides, sufficiently activates the mercury that organomercurials can be obtained even without additional photolysis [44, 45]. Unfortunately however, the yields are usually rather low.

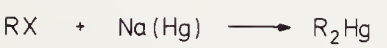
(17)

Finally, there are several isolated examples of alkylmercuric salts being formed directly by the interaction of mercuric or mercurous salts with alkyl halides. However, only the following example appears preparatively useful (Eq. 18) [46].



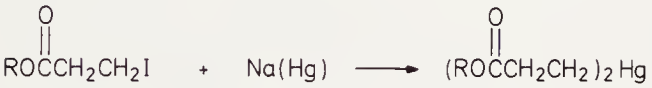
$$CH_3I + Hg_2SO_4 \xrightarrow{\Delta} CH_3HgI \qquad (18)$$

Mercury amalgams have also proven quite useful in the synthesis of organomercurials. Alkyl iodides and bromides react readily with sodium amalgam containing a low percentage of sodium (<0.5%) to give good yields of the corresponding dialkylmercury compounds (Eq. 19) [47–69]. Experimental details have been closely examined [60]. Alkyl chlorides generally



$$RX + Na(Hg) \longrightarrow R_2Hg \qquad (19)$$

give only low yields, but dimethyl and diethyl sulfate react well [70]. These reactions are best run in carbonyl-containing solvents. Ester groups are accommodated as long as the halogen is not alpha to the carbonyl group (Eq. 20) [71, 72]. For some reason the reactions of cyclohexyl iodide [74], trichloromethyl bromide [13, 25] and $Cl_2C{=}CClCH_2Br$ [24] only proceed as far as the corresponding alkylmercuric iodide and bromides respectively.

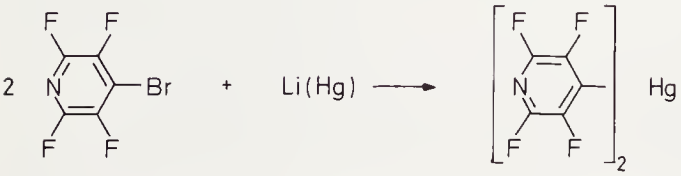


$$ROCCH_2CH_2I + Na(Hg) \longrightarrow (ROCCH_2CH_2)_2Hg \qquad (20)\ [72, 73]$$

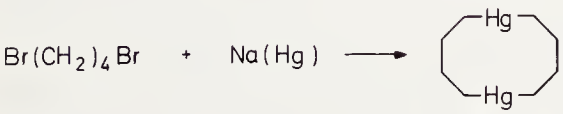
Amalgams of other metals, particularly cadmium, have also been employed [75, 76]. *Bis*-(trideuteromethyl)mercury [77], *bis*-(trifluoromethyl)-mercury [75], and *bis*-(pentafluoroethyl)mercury [76] have been prepared from the corresponding iodides in this manner.

Aryl halides generally require higher temperatures and higher percentages of sodium in the amalgam, but again generally give good yields (Eq. 21) [67, 78–103]. This has proved to be one of the more important routes to arylmercurials. Lithium amalgam may also be employed as illustrated by the following example (Eq. 22) [104].

$$2\,ArBr + Na(Hg) \longrightarrow (Ar)_2Hg \qquad (21)$$

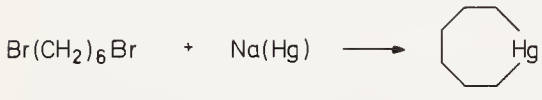


$$2 \left[\begin{array}{c} F \quad F \\ N \\ F \quad F \end{array}\right]\!\!-Br + Li(Hg) \longrightarrow \left[\begin{array}{c} F \quad F \\ N \\ F \quad F \end{array}\right]_2 Hg \qquad (22)$$

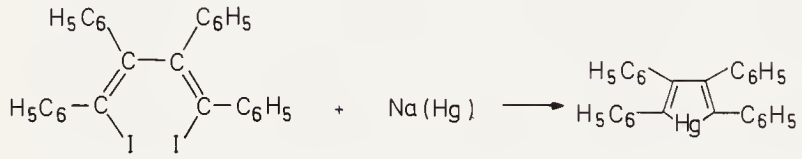


$$Br(CH_2)_4Br + Na(Hg) \longrightarrow \underset{Hg}{\overset{Hg}{\square}} \qquad (23)\ [108]$$

α,ω-Dihaloalkanes provide cyclic and polymeric organomercurials whose structures are of considerable interest (Eqs. 23, 24) [105–110]. Tetraphenylmercurole has also reportedly been prepared in this manner (Eq. 25) [111]. 1,2-Dibromo-, -dichloro- and -diiodobenzene give large ring arylmercurials of structures *1* or *2*, depending on the solvent and amalgam used [42, 112–118]. Structures such as *3* have also been proposed [113, 114, 117], but recently these results have been disputed [42, 119]. 1,2-Dibromonaphthalene [120], 1-bromo-2-fluoronaphthalene [120], *o*-fluorobromobenzene [42, 115] and 5-fluoro-6-bromo-1,2,4-trimethylbenzene [115] react with lithium or sodium amalgam to give compounds with structures presumably analogous to *2*, but bromopentafluorobenzene [121] affords only *bis*-(pentafluorophenyl)-mercury.



(24) [108]



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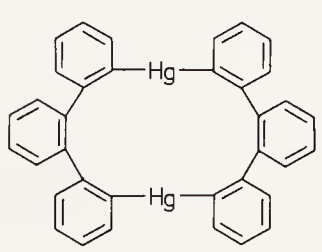

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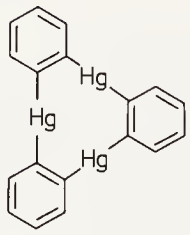

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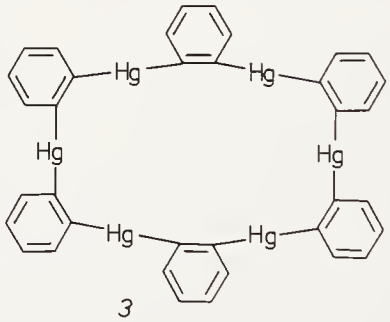
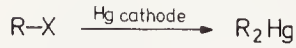


3

The electrochemical synthesis of organometallic compounds is quite general and has proved useful in the synthesis of organomercurials [122]. Electrochemical reduction of organic halides at a mercury cathode provides diorganomercurials often in excellent yield (Eq. 26). Benzyl chloride [123], iodide [124], bromide [123, 125] and substituted bromides [125]; *n*-decyl bromide [126] and iodide [126–128]; 1-iodo-1-methyl-2,2-diphenylcyclopropane [129]; ethyl [130], *n*-butyl [130] and 2-cyanoethyl [131] iodides; 1-chloro-5,5-dimethylcyclohexen-3-one [132]; and pentafluoroiodobenzene [133] all afford the corresponding organomercurials. The yields of diethyl- and di-*n*-butylmercury are quantitative, but diphenylmercury cannot be prepared in this manner. Both dialkylmercurials [134–137] and alkylmercury



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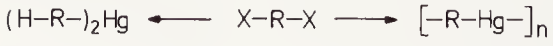


(27)

polymers [138] have been reported upon electrolysis of 1,ω-dihalides (Eq. 27). 1,2-Dihalobenzenes give rise to *o*-phenylenemercury trimer [139, 140].

The electrochemical reduction of ketones provides di-*sec*-alkylmercurials, but only in low yields (Eq. 28) [141–149]. Benzaldehyde is the only aldehyde to have been reduced in this manner and the yield was only 6.5% [148]. Methyl vinyl ketone is reduced at the carbon—carbon double bond (Eq. 29) [149].

$$R_2CO \xrightarrow{\text{Hg cathode}} (R_2CH)_2Hg \tag{28}$$

$$CH_2{=}CHC(=O)CH_3 \xrightarrow{\text{Hg cathode}} Hg(CH_2CH_2C(=O)CH_3)_2 \tag{29}$$

C. Organomagnesium and -Lithium Procedures

The preparation of organomagnesium reagents from organic halides (Eq. 30), and subsequent reaction with mercuric halides provides one of the most important and widely used methods for the synthesis of organomercurials (Eqs. 31, 32). In regards to organic synthesis, however, these reactions are of relative unimportance. They suffer two major disadvantages. First of all, the high reactivity of the organomagnesium reagents themselves severely limits the ability to incorporate functional groups in the organomercurial.

$$RX + Mg \longrightarrow RMgX \tag{30}$$

$$RMgX + HgX_2 \longrightarrow RHgX \tag{31}$$

$$RMgX + RHgX \longrightarrow R_2Hg \tag{32}$$

More importantly, the tremendous synthetic versatility of the initial organomagnesium compounds greatly reduces the number of subsequent organomercury reactions which would have any practical synthetic utility. For these reasons, the discussion of this approach to organomercurials will be rather brief. Previous monographs [150, 151] cover these reactions in considerably greater detail, including tables of almost every organomercurial ever prepared in this fashion.

This approach to organomercurials is both very convenient and extremely versatile. Essentially any organomagnesium compound can be used, including primary, secondary and tertiary alkyl, cycloalkyl and aralkyl, as well as alkenyl groups. Aryl compounds are also readily prepared, but the number of other versatile methods for the preparation of these compounds greatly reduces the significance of this route. For example, the reaction of aryl halides and sodium amalgam discussed earlier (Sect. II B) provides excellent yields

of diarylmercurials. Many aromatic compounds also undergo direct mercuration with electrophilic mercury salts (Sect. II K). One can also readily obtain arylmercuric salts directly via aryldiazonium salts (Sect. II L).

Since the organomagnesium compounds are most easily prepared in either diethyl ether or tetrahydrofuran (THF), the subsequent reaction with the mercuric halide is most commonly run in these solvents as well. THF reportedly gives better yields [152], but it can be difficult to separate from low boiling dialkylmercurials. Xylene [5] and heptane [153] have also been employed. The organomagnesium solution should be freed of excess magnesium before addition of the mercuric halide or else reduction of the halide salt can occur.

Any of the mercury halides, mercuric chloride, bromide or iodide, can be employed in the mercuration step. However, it is best to use the mercuric halide salt containing the same halide as the organomagnesium compound when attempting to prepare an organomercuric halide. Otherwise mixtures of organomercuric halides result and separation can be difficult [154–156]. Mercuric chloride has been used most often since it is readily available and ether soluble. It has a tendency, however, to form clumps during the reaction unless efficient stirring is employed. On the other hand, mercuric bromide reportedly reacts more smoothly and gives alkylmercuric halides of greater purity [157]. Should halide exchange later become desirable, the halide present in the final product can be readily replaced by conversion to the hydroxide and treatment with the appropriate halo acid (Eq. 33) [157]. Upon work-up, unreacted mercuric chloride is more readily removed from the product due to its high solubility in water. Mercuric bromide is less soluble and mercuric iodide is best removed by carefully washing the product with aqueous potassium iodide.

$$\mathrm{RHgX} \xrightarrow{\mathrm{KOH}} \mathrm{RHgOH} \xrightarrow{\mathrm{HY}} \mathrm{RHgY} \tag{33}$$

As indicated previously, the reaction can be employed to prepare either the organomercuric halide or the diorganomercurial depending on the amounts of reagents employed [154, 158, 159]. Mixed diorganomercury compounds of the type RHgR′ can be prepared as well, if one starts with an organomercuric halide and a different organomagnesium compound [160]. In the preparation of diorganomercurials, any halide may be utilized, but the second alkylation is generally slower due to the insolubility of the intermediate RHgX, and one must usually employ elevated temperatures [154, 161, 162] and make certain to stir effectively, if one desires high yields of product. Excess organomagnesium compound [154] and prolonged reaction times [161] do not appear necessary [162], and THF gives improved yields due to the increased solubility of the mercurials [152]. In the preparation of di-*tert*-alkylmercurials, the reaction must be run at room temperature due to the low thermal stability of the product. The success of the organomagnesium approach to organomercurials can best be measured by the numerous applications of this reaction in the references already cited, as well as a number of other works [163–165].

Organolithium reagents have also found extensive utilization in the preparation of organomercurials. They react with mercuric salts under conditions essentially identical to those of Grignard reagents to give either mono- or diorganomercury compounds depending on the stoichiometry of the reaction (Eqs. 34, 35). Diethyl ether or THF is commonly employed as the solvent

$$RLi + HgX_2 \longrightarrow RHgX + LiX \tag{34}$$

$$RLi + RHgX \longrightarrow R_2Hg + LiX \tag{35}$$

and either mercuric chloride or bromide as the mercury salt. Since organolithium reagents are commonly prepared from the corresponding organic halide and metallic lithium, in preparing organomercuric halides one must be careful to utilize the same halide in both steps of the synthesis or mixtures can result (Eqs. 36, 37). With regard to eventual synthetic organic

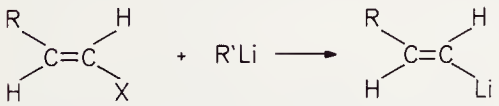
$$RX + 2Li \longrightarrow RLi + LiX \tag{36}$$

$$RLi + HgX_2 \longrightarrow RHgX + LiX \tag{37}$$

applications, these reactions are subject to exactly the same limitations as the Grignard procedures. Organolithium reagents will accommodate very few important organic functional groups. Furthermore, organolithium reagents themselves possess considerable synthetic versatility making it unlikely that many new applications of the resultant organomercurials will be found which will make this circuitous approach worthwhile.

In general, organolithium reagents have been used much less frequently than Grignard reagents for the synthesis of organomercurials. Few alkylmercurials have ever been prepared in this manner, presumably because of the greater ease of preparation of the alkyl Grignard reagents. Bridgehead bicyclic alkylmercurials are a notable exception however [166, 167]. A number of alkenylmercury compounds have also been prepared from organolithium reagents. This may be due in part to the availability of these reagents by either the direct lithiation or metal halogen exchange of alkenyl halides (Eqs. 38, 39). The versatility of the latter procedure is nicely illustrated by the following

(38)



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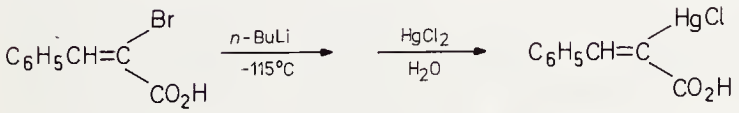
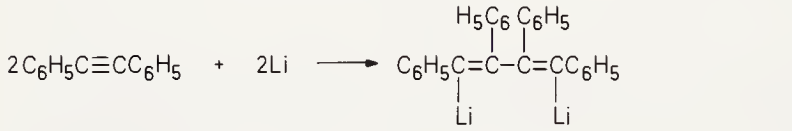


(40)

synthesis (Eq. 40) [168]. When mercuration is carried out at temperatures below 10 °C, the alkenyl lithium reactions generally proceed with clean stereochemical retention of configuration. Each of the following simple alkenylmercurials has been prepared in this manner: $(CF_2=CF)_2Hg$ [169], *cis*-$CH_3CH=CHHgBr$ [170–172], *trans*-$CH_3CH=CHHgBr$ [170–172], *cis,cis*-$(CH_3CH=CH)_2Hg$ [173], *trans,trans*-$(CH_3CH=CH)_2Hg$ [173], *cis,trans*-$(CH_3CH=CH)_2Hg$ [173], $CH_2=CH(CH_3)HgCl$ [174], $CH_2=CH(CH_3)HgBr$ [174].  [175].  [175], $CH_2=CH(C_6H_5)HgCl$ [176], *cis*-$C_6H_5CH=C(C_6H_5)HgCl$ [177], *trans*-$C_6H_5CH=C(C_6H_5)HgCl$ [177], *cis, cis*-$[C_6H_5CH=C(C_6H_5)]_2Hg$ [177] and *trans,trans*-$[C_6H_5CH=C(C_6H_5)]_2Hg$ [177]. The readily available 1,4-dilithium reagent derived from diphenylacetylene and lithium metal (Eq. 41) reportedly gives either the 1,4-*bis*-chloromercurio derivative [178] or the mercuracyclopentadiene [111] (Eq. 42). The structure of this latter compound has apparently never been determined. Should the compound exist as drawn, it would be an interesting example of an organomercury compound in which the C—Hg—C bond angle deviates drastically from the usual colinear arrangement.



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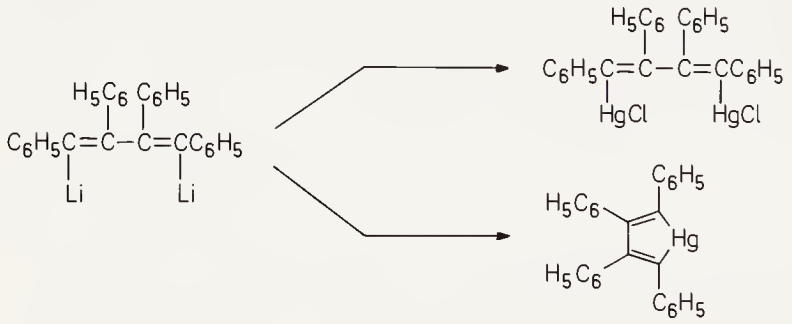
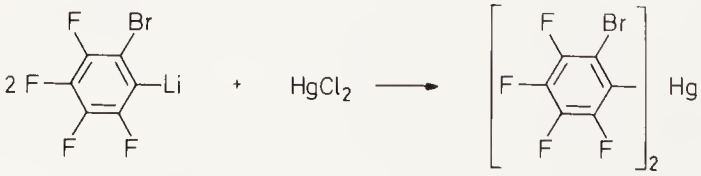


(42)

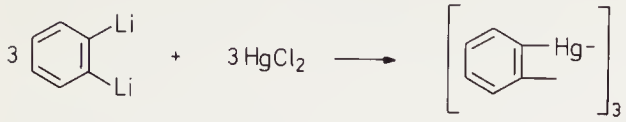
Although a number of simple arylmercury compounds have been prepared from the corresponding aryl lithium reagents [179–188], the sodium amalgam approach to these compounds is much more commonly employed. The lithium approach finds greatest utility in the preparation of the much less readily available polyhalogenated arylmercurials (Eq. 43) [189–192]. The



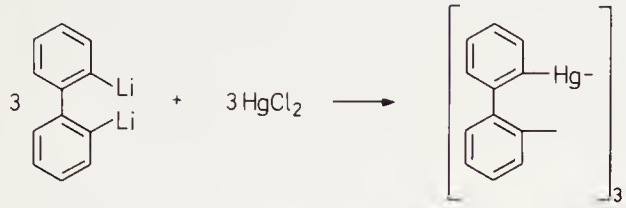
(43)

mercuration of dilithiated aromatics provides some interesting cyclic aromatic mercury compounds (Eq. 44–48). Although each of the polymeric organomercurials was originally assigned an alternate structure, it now appears that

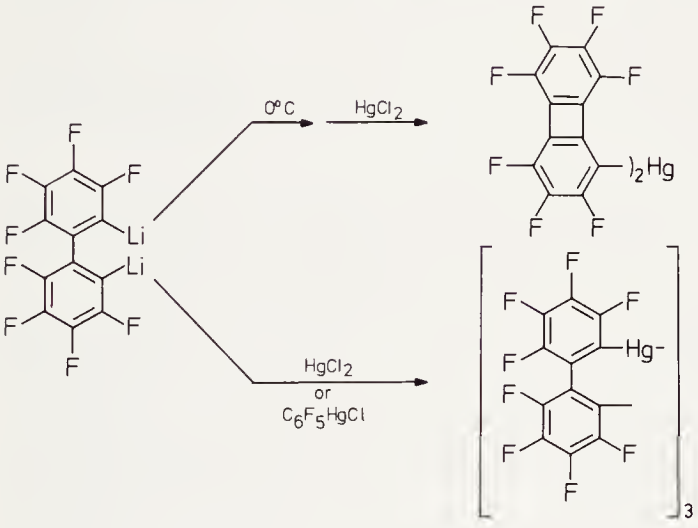
they are all cyclic trimers [42]. The structure of the last compound seems highly questionable in view of the trimeric nature of the products obtained in equations 44, 45 and 47.



(44) [113]

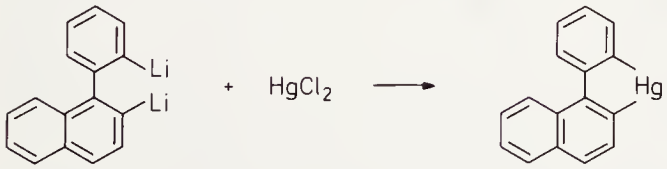


(45) [42, 193, 194]



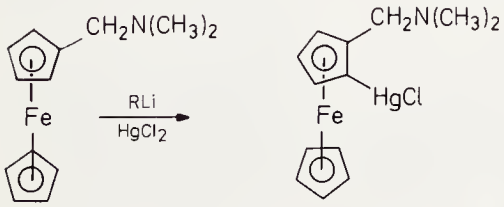
(46) [192]

(47) [42, 195]



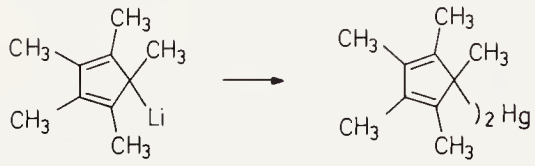
(48) [196]

The direct lithiation and mercuration of ferrocenes has provided a wide variety of ferrocenylmercurials which in turn have proven valuable as synthetic intermediates (Eq. 49) [197–202].



(49) [197]

Perhaps the most important application of organolithium compounds in the preparation of organomercurials derives from those compounds possessing acidic hydrogens which are readily lithiated by alkyl lithium reagents. Compounds such as cyclopentadienes [201, 203, 204], indene [205–207], carboranes [208–211], and phosphorus [212] and sulfur [213–215] compounds have been mercurated in this fashion (Eqs. 50–57).



(50) [203]

(51) [207]

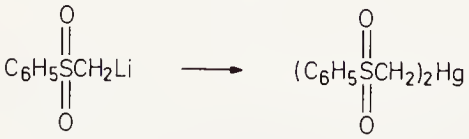
(52) [208]

$$NCCH_2Li \longrightarrow NCCH_2HgCl \qquad (53)\ [216]$$

(54) [212]

$$C_6H_5SCH_2Li \longrightarrow (C_6H_5SCH_2)_2Hg \qquad (55)\ [213]$$

$$(PhS)_2CHLi \longrightarrow [(PhS)_2CH]_2Hg \qquad (56)\ [214]$$



(57) [215]

Organolithium compounds have also been reacted with mercury(I) salts [217] and metallic mercury [113, 121, 218–227] to obtain organomercury compounds (Eqs. 58, 59). However, the yields are often low using these procedures

$$2RLi + Hg_2X_2 \longrightarrow R_2Hg + Hg + 2LiX \qquad (58)$$

$$2RLi + Hg \longrightarrow R_2Hg + Li(Hg) \qquad (59)$$

and they do not appear to offer any advantages over the use of mercury(II) salts. It is at first glance rather surprising that the latter reaction proceeds at all, since the reverse reaction of organomercurials and lithium metal is reportedly one of the best ways to prepare organolithium reagents (Eq. 60)

[228]. Apparently the formation of lithium-mercury amalgam in Equation 59 results in a shift in the equilibrium which favors organomercurial formation.

$$R_2Hg + 2Li \longrightarrow 2RLi + Hg \quad (60)$$

In spite of numerous examples of the utilization of organomagnesium and -lithium reagents in the preparation of organomercurials, this approach has found only limited applications in organic synthesis. Probably the most important application of this type of carbanion displacement reaction is in the synthesis of α-haloorganomercury compounds (Eq. 61). The resultant organomercurials are valuable divalent carbon transfer reagents whose synthesis and utility will be discussed in detail in Chapter X.

$$C_6H_5HgCl + HCBr_3 + KO\text{-}t\text{-}Bu \longrightarrow C_6H_5HgCBr_3 \quad (61)$$

D. Organoboranes

The mercuration of organoboron compounds is one of the oldest known routes to organomercurials, but only in recent years has this approach developed into one of real synthetic utility. With the many rapid advances in organoboron chemistry in the last 25 years, this route is now one of the more convenient routes to a wide variety of organomercurials. This aspect of organoboron chemistry has recently been reviewed [229].

As long ago as 1881, Michaelis and Becker reported that *p*-tolyl- and phenylboronic acids react rapidly and quantitatively with mercuric chloride to give the corresponding arylmercuric chloride (Eq. 62) [230]. A number of

$$ArB(OH)_2 + HgCl_2 + H_2O \longrightarrow ArHgCl + B(OH)_3 + HCl \quad (62)$$

other arylboronic acids have been reported to react in a similar fashion [94, 231–239], including 2-furan- [240] and 2-thiopheneboronic acids [240, 241], as well as substituted ferrocenyl- [197, 242–244], ruthenocenyl [245] and tricarbonylmetal cyclopentadienylboronic [246, 247] acids. Mercuric acetate [237], mercuric bromide [236, 248] and mercuric hydroxide [249, 250] may also be employed. With the latter reagent, diarylmercurials are usually obtained (Eq. 63). Phenylmercuric nitrate and perchlorate also react with

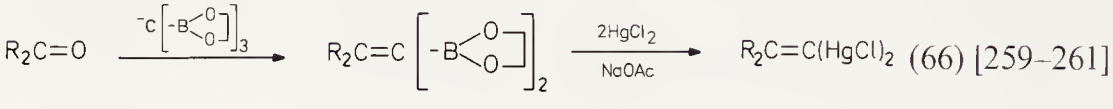
$$2ArB(OH)_2 + HgO \longrightarrow Ar_2Hg \quad (63)$$

phenylboronic acid to generate diphenylmercury [251, 252]. This approach has been employed in the synthesis of unsymmetrical organomercurials (Eq. 64) [253–255].

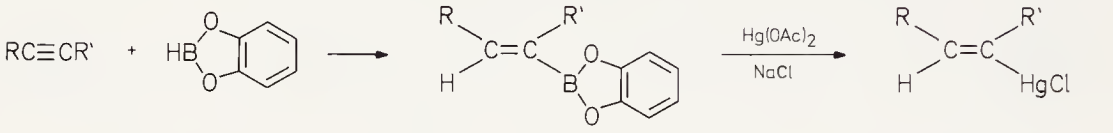
$$RHgX + ArB(OH)_2 \longrightarrow RHgAr \quad (64)$$

Vinylboronic acids also undergo facile stereospecific transmetallation by mercuric halides to give excellent yields of the corresponding vinylmercuric halides (Eq. 65). *trans*-β-Chlorovinyl- [256], *cis*- and *trans*-propenyl- [257], and styrylmercuric [258] halides have been prepared in this manner. With the recent development of new routes to vinylboronic esters, these procedures have taken on new meaning (Eqs. 66, 67). This latter hydroboration

$$RCH{=}CHB(OH)_2 + HgX_2 \longrightarrow RCH{=}CHHgX \qquad (65)$$

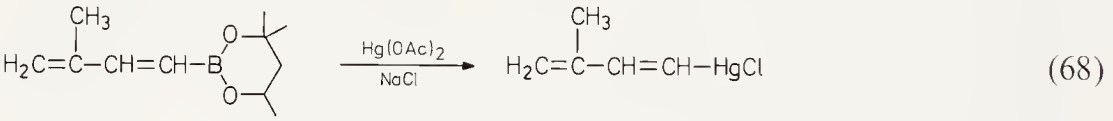


(66) [259–261]



(67) [262]

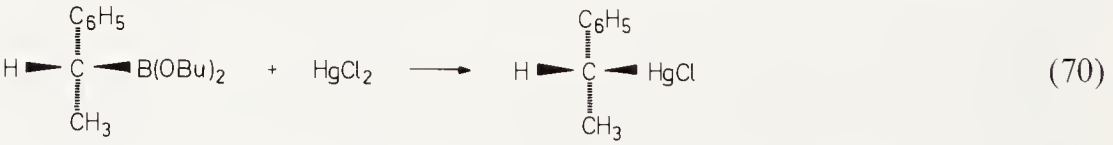
approach using 1,3,2-benzodioxaborole provides a highly regio- and stereoselective synthesis of vinylmercurials from simple terminal and internal acetylenes which proceeds in excellent yields. Dienyl- and allenylboronic esters react similarly (Eqs. 68, 69) [263].



(68)

$$(CH_3)_2C{=}C{=}CH{-}B(OMe)_2 \longrightarrow (CH_3)_2C{=}C{=}CH{-}HgCl \qquad (69)$$

Benzyl- [235] and substituted benzylboronic [264] esters, as well as substituted α-phenethylboronic [265] esters also undergo mercuration by mercuric chloride. This reaction apparently proceeds with predominant retention of configuration, although low optical purities were obtained due to racemization of the product (Eq. 70) [266]. Simple alkylboronic acids apparently



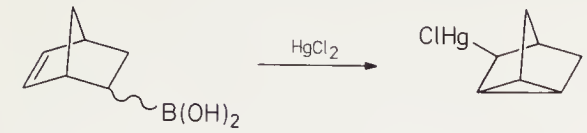
(70)

react only very slowly with mercuric chloride if at all [236, 249, 265, 267], but excellent yields of alkylmercurials can be obtained upon heating briefly with mercuric acetate in acetic acid (Eq. 71) [236]. The kinetics of mercuride-

$$RB(OH)_2 + Hg(OAc)_2 \longrightarrow RHgOAc \xrightarrow{NaCl} RHgCl \qquad (71)$$

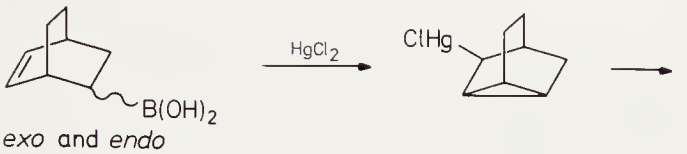
boronation have recently been examined [268]. No secondary alkylboronic acids or esters have ever been reported to react [265], except for the above

benzylic ester (Eq. 70) and the following bicyclic compounds whose reactions apparently proceed through initial attack of the mercury salt at the double bond (Eqs. 72, 73).



exo and *endo*

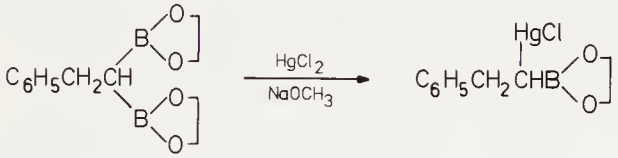
(72) [251, 269–271]



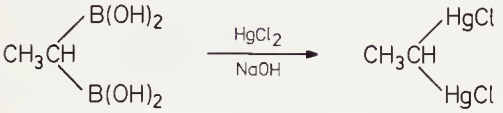
exo and *endo*

(73) [272, 273]

Polymercurated alkanes can also be prepared from the corresponding boronic acids and esters. *gem*-Diboronic acids or esters may be either mono- or dimercurated (Eqs. 74, 75). Similarly, we have employed a hydroboration-

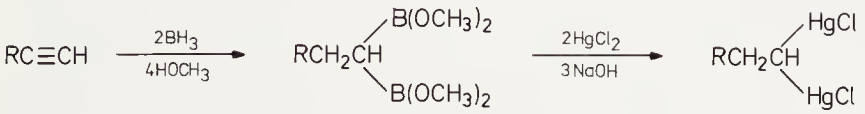


(74) [274]



(75) [275]

mercuration sequence to obtain 1,1-*bis*-chloromercurioalkanes in 58–77% yield (Eq. 76) [276]. Tri- and tetramercuriomethanes have been prepared in like fashion (Eqs. 77, 78) [277, 278].



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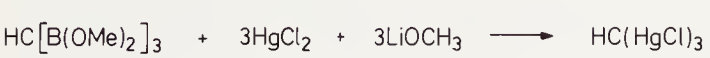

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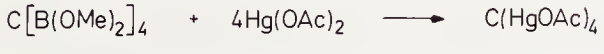


(78)

Diarylborinic acids [237, 279] and anhydrides [280, 281], triarylboranes [282, 283], tetraalkynyl- [258] and tetraarylborate [182, 282, 284–290] anions all undergo facile mercuration with mercuric salts (Eqs. 79–81). Tetraalkyl- and tetraarylborate anions also react with mercury salts to give dialkyl- and diarylmercury compounds [290–292]. The electrolysis of tetraalkylborates

at a mercury cathode also affords dialkylmercury compounds [293]. None of these reactions, however, appear to be of any practical synthetic utility, since the requisite organoboron compounds are not readily available and the products are more easily prepared by more direct routes.

$$Ar_2BOH + 2HgX_2 \longrightarrow 2ArHgX \tag{79}$$

$$Ar_3B + 3HgX_2 \longrightarrow 3ArHgX \tag{80}$$

$$Ar_4B^{\ominus} + 4HgX_2 \longrightarrow 4ArHgX \tag{81}$$

On the other hand, the mercuration of trialkylboranes provides a highly convenient route to the corresponding alkylmercurials. This is a direct result of the ready availability of these organoboranes by simple hydroboration procedures (Eq. 82) [294]. Shortly after the discovery of the hydroboration

$$3RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2)_3B \tag{82}$$

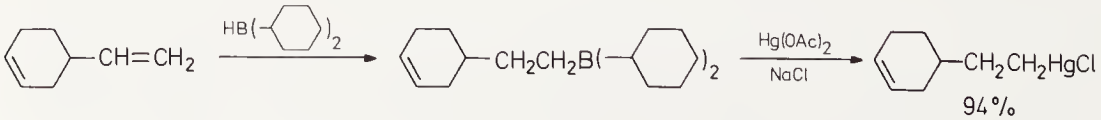
reaction in 1956, Honeycutt and Riddle reported that triethyl- and tri-*n*-butylborane react readily with mercuric acetate or mercuric oxide at 60–80 °C to give the corresponding dialkylmercurials [283, 295]. Subsequent patents indicate that both trialkyl- and trialkenylboranes undergo this reaction [296–300]. Triallylboron also reacts [301]. Unfortunately, from that work neither the stoichiometry nor the scope of the reaction was evident. Primary trialkylboranes undergo a very rapid reaction with mercuric acetate at room temperature to transfer all three alkyl groups from boron to mercury to give the corresponding alkylmercurials (Eqs. 83, 84) [302]. Work-

$$R_3B + 3Hg(OAc)_2 \longrightarrow 3RHgOAc + B(OAc)_3 \tag{83}$$

$$3RHgOAc + 3NaCl \longrightarrow 3RHgCl \tag{84}$$

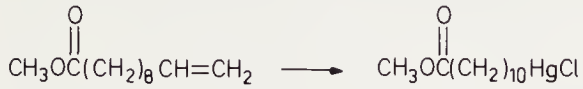
up with aqueous sodium chloride provides near quantitative yields of the desired alkylmercuric chlorides. This reaction has provided a useful synthesis of 1,3-dimercury and other 1,3-dimetallic compounds (Eq. 85) [303]. The low reactivity of secondary alkylboron groups in this reaction allows selective hydroboration-mercuration to be achieved (Eq. 86) [302]. Functional groups are readily accommodated providing obvious advantages over Grignard or

$$H_2C{=}C{=}CH_2 \xrightarrow[\substack{Hg(OAc)_2\\NaCl}]{BH_3} ClHg(CH_2)_3HgCl \xrightarrow[2\ Mg/MgBr_2]{1.\ 2RLi} BrMg(CH_2)_3MgBr \tag{85}$$



(86)

organolithium routes (Eq. 87). Tufariello and Hovey have subsequently confirmed our results on the facile mercuration of primary trialkylboranes [304, 305]. This reaction has been established to proceed with inversion of configuration (Eq. 88) [306, 307].



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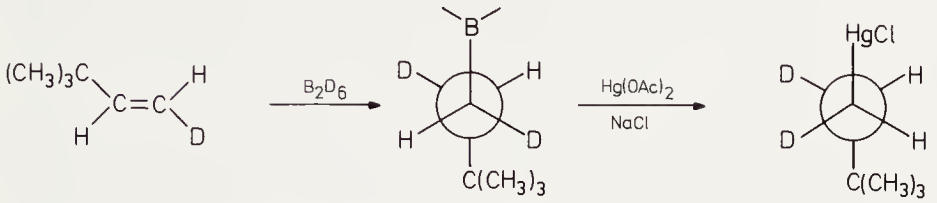
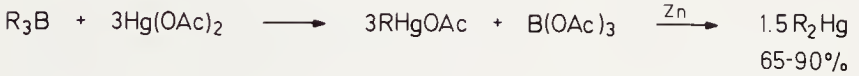


(88)

Dialkylmercurials can be conveniently prepared by symmetrization of the monoalkyl mercury compounds with magnesium (Eq. 89) [308], or by direct symmetrization of the alkylmercuric acetates with zinc dust (Eq. 90) [309]. Utilization of lesser amounts of mercuric acetate accomplishes the same objective, but elevated temperatures and/or excess trialkylborane are required (Eq. 91). These difficulties are overcome by utilizing dicyclohexylborane as the hydroborating agent (Eqs. 92, 93).

(89)



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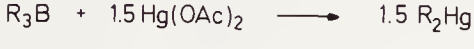

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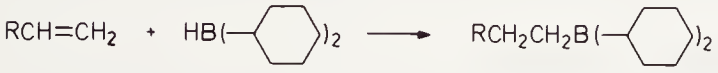

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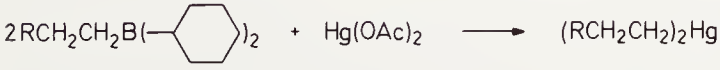


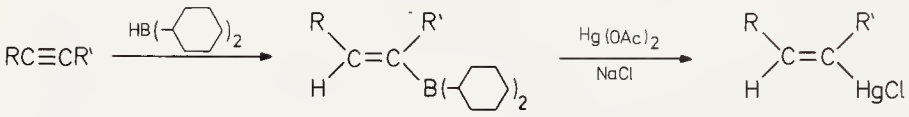
(93)

The mercuration of tri-*sec*-alkylboranes is much more difficult [310]. Examination of a variety of mercury(II) salts with a series of representative tri-*sec*-alkylboranes established that only the reactions of tricyclopentyl- and tricyclohexylborane with mercuric benzoate were synthetically useful and only two of the three alkyl groups were transferred from boron to mercury. More bulky tri-*sec*-alkylboranes reacted only exceedingly slowly. Subsequently, it was observed that mercury(II) methoxide would react with a variety of tri-*sec*-alkylboranes at room temperature in THF or in refluxing methanol with transfer of one of the three alkyl groups (Eq. 94) [311]. Yields were later doubled by using mercury(I) *tert*-butoxide in *tert*-butanol (Eq. 95) [312].

$$R_3B + Hg(OCH_3)_2 \longrightarrow RHgOCH_3 \quad (94)$$

$$R_3B + 2Hg_2(O\text{-}t\text{-}Bu)_2 \longrightarrow 2\,RHgO\text{-}t\text{-}Bu \quad (95)$$

The ease with which vinylboranes are obtained from acetylenes via hydroboration also opens up a convenient new route to vinylmercurials. Consecutive treatment of either terminal or internal acetylenes with dicyclohexylborane, mercuric acetate and finally aqueous sodium chloride provides a convenient "one-pot" regio- and stereospecific synthesis of vinylmercuric chlorides (Eq. 96) [313]. Excellent yields of vinylmercurials are obtained from terminal acetylenes (R′ = H), but internal acetylenes give lower yields and the earlier mentioned 1,3,2-benzodioxabole procedure is preferable (Eq. 67) [262]. Trialkenylboranes and dialkenylboron halides are also reported to react with mercuric oxide, mercuric acetate or mercuric halides to give dialkenylmercury compounds [296–300]. The stoichiometry and scope of these reactions remain to be established.



(96)

While a large number of reactions of mercury salts and organoboron compounds have been reported to lead to organomercurials, only those routes utilizing organoboranes prepared by hydroboration or condensation reactions appear preparatively useful. Methods employing organoboranes derived from Grignard and organolithium reagents clearly have no advantage over direct mercuration of these organometallics. However, hydroboration-mercuration procedures developed in recent years have provided valuable new routes to a large variety of alkyl- and vinylmercurials, including functionally substituted compounds, which are not easily prepared by any other method.

E. Other Transmetallation Reactions

Few other organometallic reagents have proved as useful as those of magnesium, lithium or boron. However, transmetallation reactions involving organoaluminum, -silicon, -tin, -lead, -zinc and -palladium compounds appear to have significant synthetic utility. Reactions of the organometallic compounds of the remaining elements of the periodic table are of only very limited utility. Few of these organometallics are readily available via procedures which are sufficiently unique that their subsequent conversion to organomercurials would have a synthetic advantage over the other methods outlined in this chapter.

The use of organoaluminum compounds in the synthesis of organomercurials has attracted considerable attention, because of the ease with which these organometallics are prepared industrially from simple olefins and aluminum metal, and because of the great interest in simple alkylmercuric salts as fungicides and seed disinfectants [314]. Simple mono-, di- and trialkylalu-

minum compounds, as well as the sesquichlorides and sodium chloride adducts, all react with mercuric chloride, bromide and acetate to transfer all available organic groups from aluminum to mercury, thereby providing the corresponding alkylmercuric salts in excellent yields (Eqs. 97–101) [315–321].

$$R_3Al + 3HgX_2 \longrightarrow 3RHgX \quad (97)$$

$$R_2AlCl + 2HgX_2 \longrightarrow 2RHgX \quad (98)$$

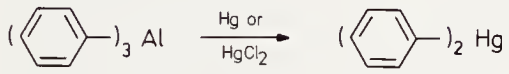
$$RAlCl_2 + HgX_2 \longrightarrow RHgX \quad (99)$$

$$R_3Al_2Cl_3 + 3HgX_2 \longrightarrow 3RHgX \quad (100)$$

$$RAlCl_2 \cdot NaCl + HgX_2 \longrightarrow RHgX \quad (101)$$

Analogous reactions using trialkylaluminum compounds and mercuric chloride, bromide and acetate can be employed to prepare dialkylmercury compounds directly, although it is not obvious if all three alkyl groups can be transferred (Eq. 102) [318, 322–325]. Triphenylalane reacts with both mercuric chloride [326] and metallic mercury [327] to afford diphenylmercury (Eq. 103). Dialkylmercury compounds are also available from electrolysis of alkali metal alanate salts at a mercury anode (Eqs. 104, 105) [328, 329].

$$R_3Al + HgX_2 \longrightarrow R_2Hg \quad (102)$$



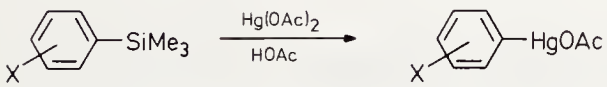
(103)

$$NaAl(C_2H_5)_4 \xrightarrow{Hg} (C_2H_5)_2Hg \quad (104)$$

$$Na[CH_3AlCl_3] \longrightarrow (CH_3)_2Hg \quad (105)$$

Although numerous examples of the conversion of organothallium(III) compounds to organomercurials are known, few if any of these reactions possess real synthetic utility. In fact, in many instances the organothallium compounds have been prepared by transmetallation reactions of other organometallic compounds discussed in this chapter, or they originate from organomercurials themselves.

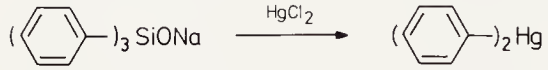
Organosilanes can also provide a valuable source of organomercurials. Aryltrimethylsilanes are readily cleaved by mercuric acetate in acetic acid (Eq. 106) [330–335]. The relative rates of reaction of a variety of sub-



(106)

stituted arylsilanes and the overall kinetics of the reaction are consistent with an electrophilic aromatic substitution reaction. Ferrocenyltrimethylsilanes

behave similarly [336]. Siloxy- [337] and phenoxysilanes [338, 339] also afford arylmercurials, but the latter reaction reportedly proceeds by an electron transfer process (Eqs. 107, 108). Arylsilanes are apparently much more reactive if they contain fluorine on silicon (Eqs. 109, 110) [340–342].



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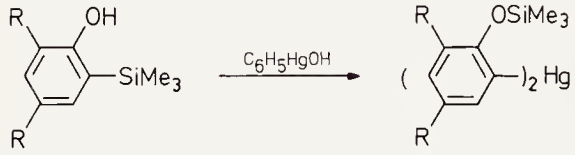

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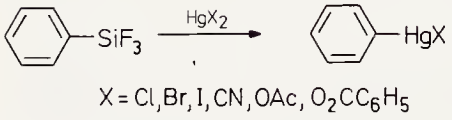
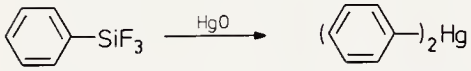
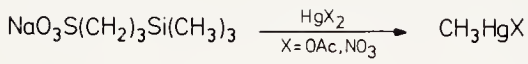


(109) [341, 342]



(110) [341, 342]

The picture for alkylsilanes is very similar. Although tetraethylsilane fails to react with mercuric chloride in refluxing ethanol and gives only a 15% yield of ethylmercuric chloride at 140 °C [343], mercuric acetate or nitrate react readily with tetraalkylsilanes (Eq. 111) [344]. If the organosilane is first treated with fluoride anion, even mercuric chloride reacts (Eqs. 112, 113). Alkyl-, allyl-, vinyl- and phenylsilanes are all reactive under these conditions.



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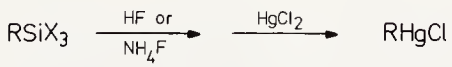
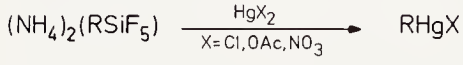
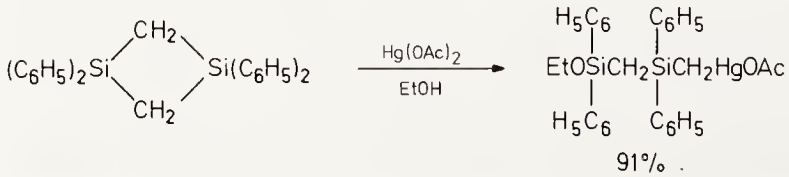


(112) [340, 345, 346]



(113) [340, 347]

1,3-Disilacyclobutanes also undergo mercuration to give monomeric, dimeric or oligomeric organomercurials depending upon the substituents on silicon and the mercury salts employed (Eq. 114) [348–351].



(114) [350]

Organotin compounds are somewhat more reactive towards mercury salts than the corresponding organosilanes. For example, simple primary, secondary and benzylic tetraalkylstannanes react readily with mercuric chloride, iodide and acetate to give good yields of the corresponding alkylmercuric salts (Eq. 115) [343, 352–365]. The mechanism of these reactions has been

$$R_4Sn \xrightarrow[X = Cl, I, OAc]{HgX_2} RHgX \qquad (115)$$

extensively studied by Abraham and co-workers and all data is consistent with a bimolecular electrophilic substitution reaction [354–365]. Mercurous acetate [366] and nitrate [367] afford the corresponding dialkylmercurials (Eq. 116). Although only one alkyl group is generally transferred from tin, it appears that more groups can be transferred as evidenced by the following successful reactions (Eqs. 117–119).

$$2R_4Sn + Hg_2X_2 \xrightarrow[X = OAc, NO_3]{} R_2Hg + 2R_3SnX + Hg \qquad (116)$$

$$R_4Sn \xrightarrow{\text{excess } Hg_2(NO_3)_2} 2RHgNO_3 \qquad (117)\ [367]$$

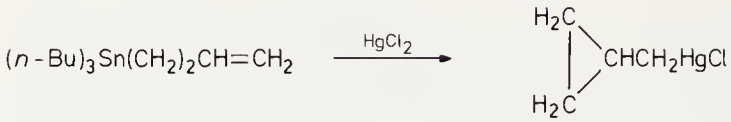
$$R_3SnX \xrightarrow[X = Cl, OAc]{HgX_2} RHgX \qquad (118)\ [368–370]$$

$$R_3SnNO_3 \xrightarrow{RHgNO_3} R_2Hg \qquad (119)\ [367]$$

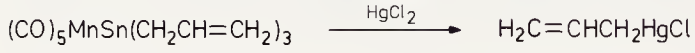
The mercuration of a number of mixed organostannanes has been examined. In all mixed alkylmethylstannanes studied to date, except 1,1-dimethylstannacyclopentane [371], the methyl group reacts preferentially [343, 355, 371, 372]. In $RSnMe_3$ the following relative reactivities have been reported: $R = H_2C{=}CHCH_2 > H_2C{=}CH > C_6H_5 > CH_3$ [373, 374]. In alkylarylstannanes it is the aryl group which always undergoes cleavage and both arylmercuric salts and diarylmercurials can be formed depending on the stoichiometry of the reaction and the arylstannane employed [353, 375 to 380]. As many as three aryl groups can be transferred to mercury.

A wide variety of aryltin compounds have been converted into arylmercurials using mercuric halides, mercuric acetate and mercuric oxide: Ar_4Sn [352, 381–384], Ar_3SnCl [385], Ar_3SnO_2CR [368], $(Ar_3Sn)_2O$ [385], Ar_2SnCl_2 [381, 382, 386–388], $ArSnCl_3$ [381, 382, 386–388] and $ArSnO_2H$ [389]. All aryl groups can be transferred under the right conditions. When sodium hydroxide is added to these reactions diarylmercurials are generally isolated.

Alkenylstannanes are probably the most valuable organotin compounds for the synthesis of organomercurials. Although 3-butenyl- and allylstannanes afford organomercurials (Eqs. 120, 121), vinylstannanes are far more important as intermediates in organomercurial synthesis. Each of the following types of vinylstannane has afforded vinylmercurials: $(vinyl)_4Sn$ [393],

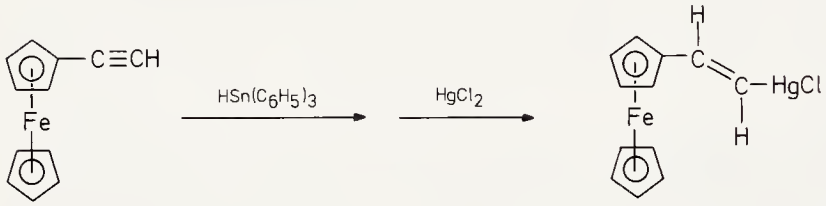


(120) [390, 391]

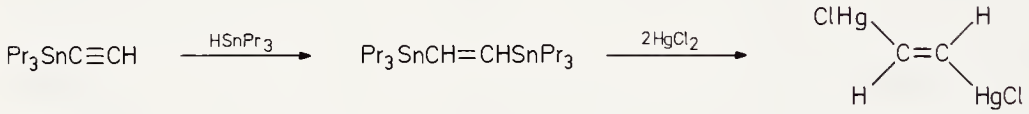


(121) [392]

$(vinyl)_3SnR$ [394], $(vinyl)_3SnCl$ [395], $(vinyl)_2SnR_2$ [394, 396], $(vinyl)_2SnX_2$ (X = Cl, Br) [171, 395, 397–400], $(vinyl)SnR_3$ [401–403], $(vinyl)SnCl_3$ [171, 399] and $(vinyl)SnO_2H$ [399]. The reaction of trialkylvinylstannanes is of special importance in view of the ease with which these compounds can be prepared by hydrostannation of acetylenes (Eqs. 122, 123). This approach parallels the hydroboration-mercuration approach described earlier, and will probably only be of interest where the regio- or stereochemistry of hydrostannation differs from hydroboration.

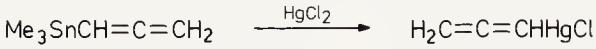


(122) [403]



(123) [402]

Allenyl- and alkynylmercurials can also be prepared from organotin compounds, although these reactions appear to be of little synthetic utility (Eqs. 124, 125) [404–406].



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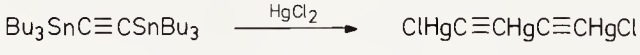
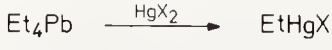


(125)

While methods for the synthesis of organolead compounds are less well developed than those of silicon or tin, the vast quantities of tetraethyllead that have been produced industrially as a gasoline additive and the commercial significance of ethylmercury salts as fungicides and seed disinfectants have substantially increased interest in this route to organomercurials [407]. Thus, tetraethyllead reacts with mercuric chloride, mercuric



(126)

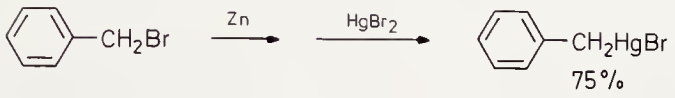
acetate or mercuric oxide in the presence of acetic acid, phosphoric acid or phenols to give the corresponding ethylmercuric salts (Eq. 126) [343, 352, 408–413]. Mercurous nitrate gives dialkylmercury compounds [414]. In similar

fashion, triethyllead chloride and acetate also alkylate mercury(II) salts [352, 415].

Phenylmercurials are just as readily available via tetraphenyllead and mercuric acetate or mercuric chloride (in the presence or absence of sodium hydroxide) [382, 408, 416, 417]. Aryl-, diaryl- and triaryllead chlorides and acetates have also been shown to react, thus establishing that all four aryl groups can be transferred from lead to mercury to form either arylmercuric salts or diarylmercury compounds [382, 415, 418].

Divinyllead dichlorides react with metallic mercury to afford vinylmercuric chlorides, but this reaction is of no preparative significance [395].

The reaction of dimethyl- and diethylzinc with mercuric chloride or organomercuric halides provided one of the first routes to dimethyl- and diethylmercury [419–423]. Nowadays this approach generally has been supplanted by the more convenient organomagnesium or -lithium procedures. However, this approach still appears useful for the synthesis of benzylic, allylic and propargylic mercury halides (Eqs. 127–129) [424–427].

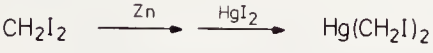


(127)

(128)

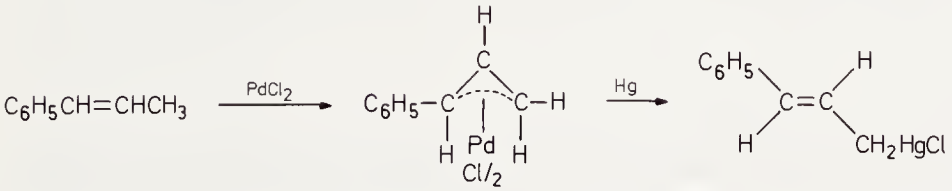
(129)

It is also valuable for the synthesis of α-haloorganomercurials as outlined later in Chapter X (Eq. 130) [428–430].



(130)

The reaction of π-allylpalladium compounds and either metallic mercury [431–434] or mercuric salts [435] provides an alternate route to allylic mercurials which gains its significance in the fact that π-allylpalladium

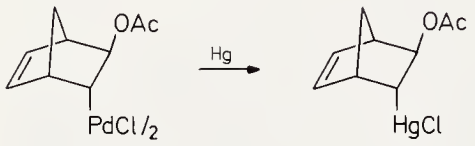


(131)

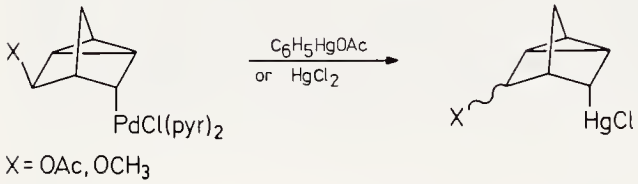
halides are readily available directly from olefins (Eq. 131). Polycyclic organomercurials are available in like fashion (Eqs. 132–134).

Several other miscellaneous transition metal routes to organomercurials deserve brief comment. Organocopper compounds have recently proved useful as intermediates in the synthesis of vinylmercurials (Eq. 135) [440].

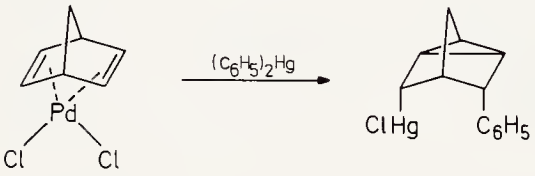
Organochromium compounds are useful in the synthesis of α-haloorganomercurials as described later in Chapter X (Eq. 136). Although of no application in preparative chemistry, the transfer of organic groups from organocobalt compounds to mercury is of great biological and mechanistic interest [441–468]. It is by this route that methylmercury compounds are formed in the environment.



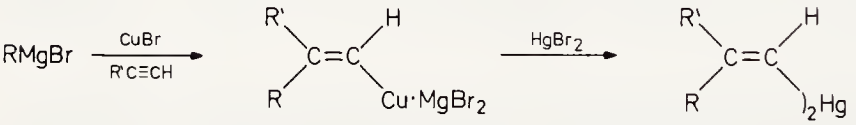
(132) [436]



(133) [437, 438]



(134) [437, 439]



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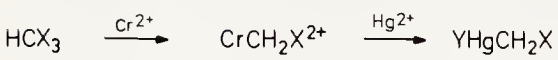
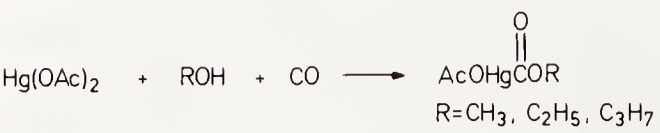


(136)

Finally, it should be noted that organic compounds of each of the following elements have been employed in the preparation of organomercurials: Na, Ti, Zr, V, Cr, Fe, Ag, Au, Cd, P, As, Sb and Bi. However, none of these approaches appears to offer any advantages to the chemist interested in synthetic applications of the resulting organomercurials.

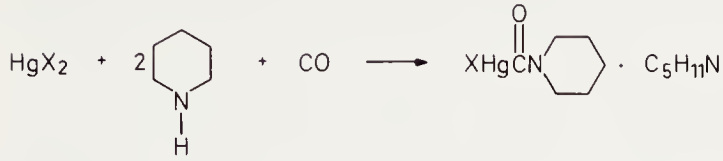
F. Mercuration of Carbon Monoxide

Alcohol solutions of mercuric acetate have been observed to slowly absorb carbon monoxide to generate the corresponding carboalkoxymercurial in high yield (Eq. 137) [469, 470]. Addition of halide anions gives the



(137)

corresponding easily isolable, stable organomercuric halides. While the exact structure of these compounds was originally debated [471–473], infrared and nuclear magnetic resonance data [474] are consistent with the above structures, as is the majority of the known chemistry of these compounds [469]. Some thirty-five years after the discovery of these compounds, an analogous reaction of piperidine and mercuric chloride or bromide was reported (Eq. 138) [475]. The resulting complex could be freed of the additional



(138)

equivalent of piperidine by simply washing with potassium hydroxide and ether. By using mercuric acetate, one obtains the corresponding diorganomercurials instead (Eq. 139) [476]. A variety of secondary amines have been

(139)

employed in this reaction. The chemistry of these carbonylmercurials has proven quite interesting, as we will see in subsequent chapters of this book.

G. Mercury Substitution in Activated C—H Containing Compounds

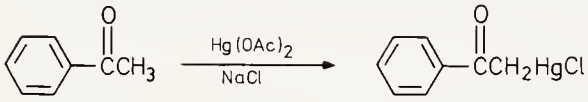
A number of organic compounds contain bonds sufficiently acidic that the hydrogen is readily replaced by mercury to form organomercurials. Electrophilic mercury salts or basic mercury salts have both been employed to effect this transformation. Many of the first organomercurials were prepared in this way. Unfortunately, many of those early compounds have still not been fully characterized and one can only guess at their structures.

Cyclopentadiene is one of the simplest hydrocarbons to have been mercurated due to its relatively high acidity. Mercuric chloride, with and without sodium acetate [477–479]; mercuric acetate [477, 479]; mercuric oxide plus amines [480]; and $Hg[N(SiMe_3)_2]_2$ [481] have all been employed in these reactions. Mono- [478, 479], di- [477], tetra- [479] and hexamercurated [479] species, as well as dicyclopentadienylmercury [478, 480, 481], have all been isolated or inferred from elemental analysis. Cyclopentadienyl- and substituted cyclopentadienylmercury compounds are also readily prepared from the corresponding lithium, sodium and thallium salts as well [203, 204, 206, 482–486]. In similar fashion, pentachlorocyclopentadiene has been mercurated by mercuric methoxide [487]. Although the structure of these mercury com-

pounds has been the center of some controversy, most evidence points to them being fluxional sigma bonded species.

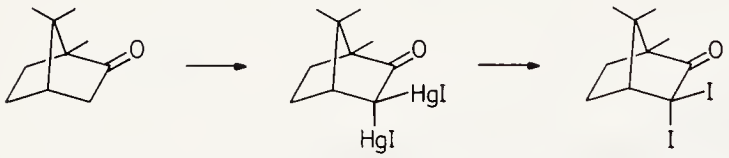
The mercuration of simple aldehydes and ketones is easily effected under a wide variety of reaction conditions. In the late 1800's these reactions were studied by several different groups and many new compounds were reported. Slight variations in reaction conditions often led to new products with different melting points and elemental analyses. Limited only by their imaginations, the chemists of the day reported many fanciful structures to match their analyses. With today's better understanding of mechanism and bonding, it is clear that few of these earlier reported structures are correct. This fascinating era in organomercury chemistry is nicely summarized in Whitmore's early treatise on the organic compounds of mercury [488].

The first simple, well-characterized, correctly identified organomercurial derived from the mercuration of a carbonyl compound would appear to be the compound obtained from acetophenone by Dimroth in 1902 (Eq. 140)



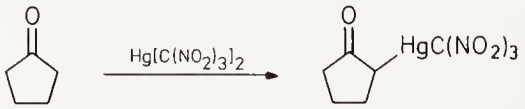
(140)

[489, 490]. Several years later the mercuration of camphor was reported to give an homologous series of dimercurials, all of which could be iodinated to give the same diiodocamphor compound (Eq. 141) [491–493].



(141)

Over forty years passed then before a general procedure was reported for the mercuration of ketones [494]. Using a combination of mercuric oxide, mercuric nitrate and calcium sulfate, and quenching with potassium iodide, one can obtain low yields of the corresponding α-iodomercury ketones. While isopropyl methyl ketone gave only the more highly substituted organomercurial in 30% yield, 2-butanone gives 19% of the 1-iodomercury compound and 7% of the 3-substituted product. Subsequently, $Hg[C(NO_2)_3]_2$ was reported to mercurate acetone and cyclopentanone in quantitative yield (Eq. 142) [495, 496]. More recently ClHgOAc or $ClHgNH_2$/HOAc have been reported to mercurate cyclic ketones to afford the corresponding α-chloromercury compounds [497], and $Hg[N(SiMe_3)_2]_2$ has been observed to provide good yields of a variety of analogous diorganomercurials [498].



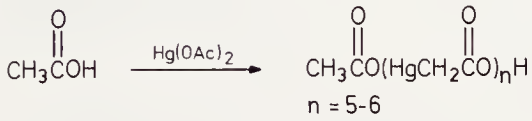
(142)

The products from the mercuration of aldehydes have still not been fully characterized [499–501]. They appear to be highly mercurated, polymeric

structures. Simple α-chloromercury aldehydes are best prepared by solvomercuration procedures to be discussed later.

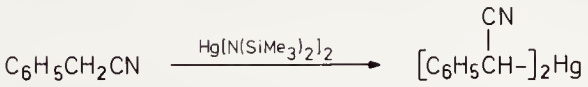
The mercuration of ethanol and a number of other alcohols with mercuric oxide and sodium hydroxide was first reported by Hofmann to give the same product as the mercuration of acetaldehyde and propionaldehyde [502, 503]. This "mercarbide" was suggested to be a hexamercurated ethane derivative, but has more recently been shown to be a derivative of tetramercuriomethane [504]. Similarly, mercuric chloride and ethanol were first reported to give a tetramercurated ethane [505] which more recently has been shown to be a methane derivative [506]. These discrepancies only serve to illustrate the errors common to much of the early literature in this area. A thorough reinvestigation of this entire area using today's modern means of structure elucidation is sorely needed.

The mercuration of acetic acid has been examined by several workers and various structures have been reported [507]. Best present evidence suggests that polymeric monomercurated products of the following type are obtained (Eq. 143) [508, 509], which can apparently be cleaved to the corresponding monomers by a variety of anions [510]. All attempts to mercurate esters have so far failed [494], while acetamide mercurates on nitrogen and not carbon [511].

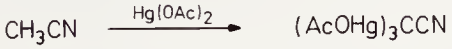


(143)

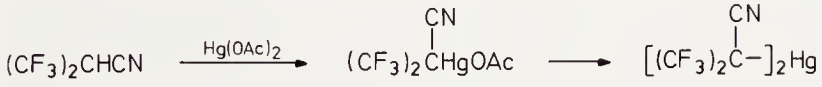
Cyano groups are also sufficiently activating to allow facile mercuration as indicated by the following examples (Eqs. 144–148).



(144) [498]



(145) [216]



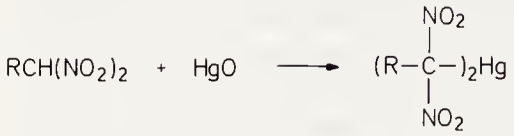
(146) [512, 513]

(147) [514–516]

(148) [517]

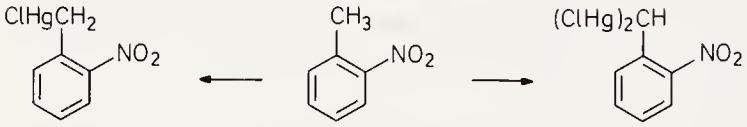
Nitro groups behave similarly. Mercuration of simple nitroalkanes occurs readily, but is complicated by rearrangement to highly explosive mercury fulminates [518–520]. Additional nitro groups afford more stable organo-

mercurials (Eqs. 149, 150) [521–525]. *o*-Nitrotoluene reportedly affords mono- or dimercurated species depending upon reaction conditions (Eq. 151) [526].



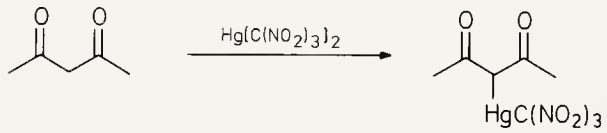
(149) [521]

(150) [522]

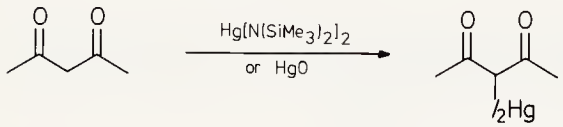


(151)

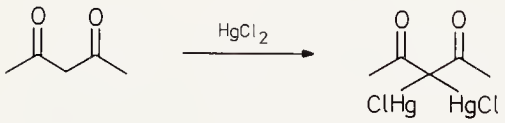
A large number of organomercurials have been prepared by mercuration of doubly activated C—H containing compounds. For example, the mercuration of acetylacetone has been extensively studied and both mono- and dimercury compounds have been isolated (Eqs. 152–154). A variety of metal



(152) [495, 496]



(153) [527–529]



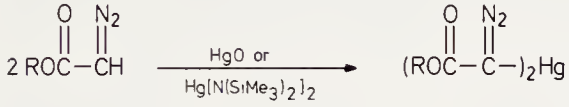
(154) [530–532]

acetylacetonates can also be used to prepare these same organomercurials [432, 531, 533, 534]. A number of related mercurated β-diketones are also available by procedures identical to those outlined above [527, 528, 534, 535–542]. The major interest in these compounds has centered on their structures. Although mercury-oxygen bonded structures have been occasionally suggested for some of these compounds [528, 536, 538, 539], most evidence, including IR, NMR and x-ray crystallographic data, indicates that these compounds exist almost exclusively as the carbon bonded species [527, 528, 537, 538, 540, 543–545].

Numerous other methylene doubly activated compounds have also been mercurated, including diacids [546], diesters [71, 495, 496, 546–552], diamides [550–552], ketoesters [494–496, 546, 547, 552–558], ketoamides [534, 551, 552], nitroesters [495, 496, 525, 559, 560], disulfones [542, 561], diphosphonates

[562], phosphonate esters [562], cyanophosphonates [562], cyanoesters [563, 564] and cyanoamides [563].

The mercuration of diazo compounds has also been extensively studied. Three different groups have examined the mercuration of diazomethane, and several different products have been claimed, although few are well characterized [565–567]. Best evidence exists for replacement of both hydrogens by mercury [567, 568]. On the other hand, organomercurials derived from alkyl diazoacetates [566–570] have been known since 1895 [569], and their crystal structures [571, 572] and numerous reactions have been reported (Eqs. 155, 156). Use of mercuric chloride instead of these basic mercury salts affords a polymercurated compound [573]. Reactions identical to those involving the mercury bases have also been reported for numerous diazoketones [566, 569, 574–577]; diazonitriles [566, 568]; diazophosphorus [578, 579], -arsenic [580] and -nitro [581] compounds; as well as simple diazoalkanes [566, 568].



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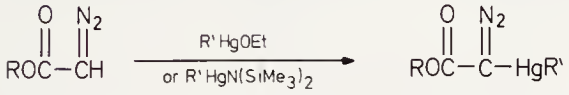
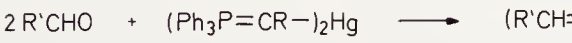


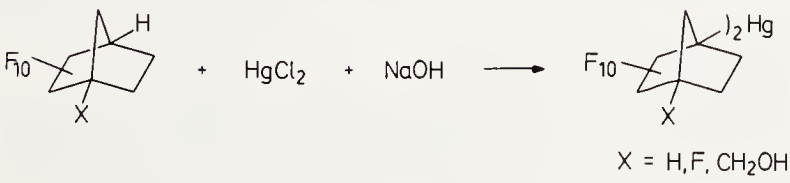
(156)

Although the mercuration of many phosphorus [582–594], arsenic [587, 591, 593], nitrogen [593] and sulfur [593] ylids has been reported, few of these reactions are of real significance to the synthetic organic chemist. Of primary interest are the Wittig reactions of some of these ylids which provide an interesting route to vinylmercurials (Eq. 157) [589–591].



(157)

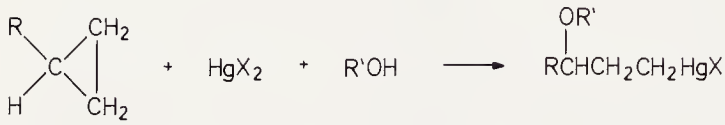
Finally, it should be noted that highly halogenated organic compounds can frequently be mercurated under basic conditions. The majority of the highly useful α-haloalkylmercurial divalent carbon transfer reagents discussed in detail in Chapter X are prepared in this fashion. Polyfluorinated arenes react analogously (see Sect. K). Even fluorinated bicyclic alkanes of the following type are sufficiently acidic to be mercurated under basic conditions (Eq. 158) [167, 595]. Certain carboranes are also acidic enough to be mercurated under neutral or basic conditions [596, 597].



(158)

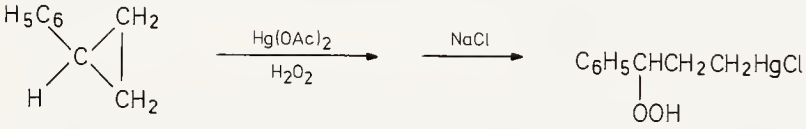
H. Mercuration of Cyclopropanes

The reaction of electrophilic mercury salts, nucleophilic solvents and cyclopropanes provides a very useful route to γ-substituted alkylmercuric salts (Eq. 159) [598]. Mercuric acetate and either water or methanol are most

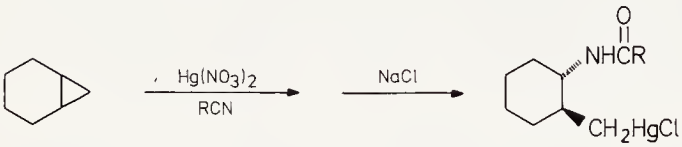


(159)

commonly employed in this reaction. On occasions mercury(II) trifluoroacetate [599–602], trinitromethyl [496, 603], nitrate [602, 604, 605], sulfate [602] and perchlorate [602] have been used, or catalytic amounts of perchloric acid have been added to promote reaction [606–609]. Even phenylmercuric acetate has been employed [610, 611]. Hydrogen peroxide [612, 613] and nitriles [604, 605] also serve as suitable nucleophiles and afford the corresponding hydroperoxide- and amide-containing organomercurials (Eqs. 160, 161). The structures of the resulting organomercurials have been most commonly determined by reductive cleavage of the mercury and determination of the structure of the resulting product.



(160)

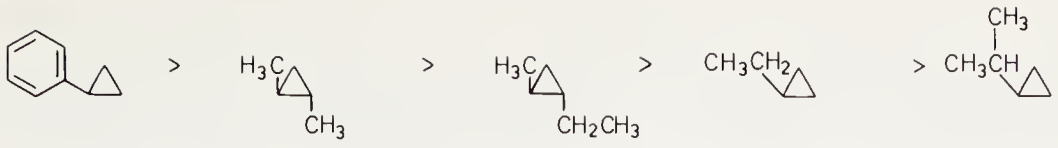


(161)

The large number of cyclopropanes for which mercuration products have been reported are summarized in Table 2.1. As indicated, the reaction proceeds with alkyl, aryl, hydroxy and alkoxy substituted cyclopropanes, as well as polycyclic hydrocarbons. In many studies the primary emphasis has been on the relative rates of mercuration and the stereochemistry of substitution. Where no effort has been made to isolate or characterize the resulting organomercurial, this work has been omitted from Table 2.1. This is not to say that organomercurials could not be isolated if one so desired.

As indicated, the rates of mercuration of many of these cyclopropanes have been studied and the following relative reactivities reported:

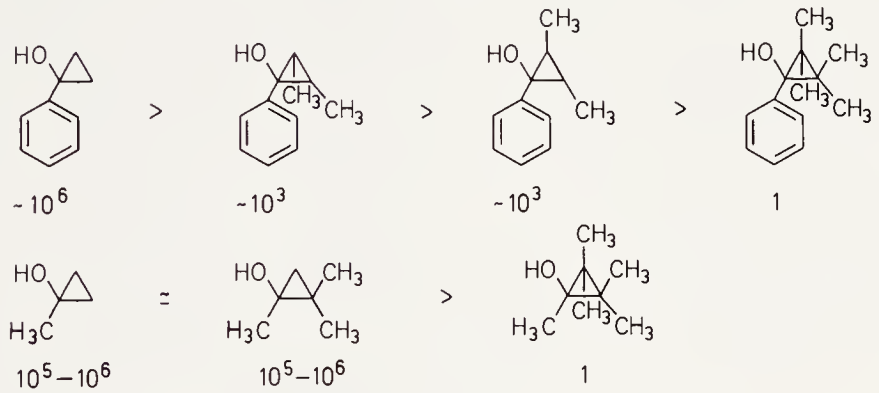
(Ref. 657)



(Ref. 658)

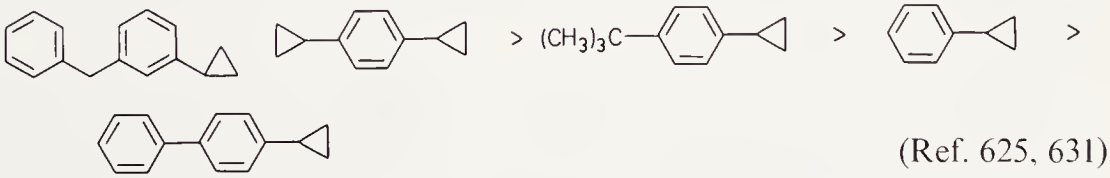
(Ref. 659)

Although increasing substitution appears to facilitate reaction, the position and number of groups is extremely important. Highly alkylated compounds tend to react much slower, apparently due to steric hindrance to attack [601, 640]. For example, introduction of a methyl group *at the site of mercury substitution* actually decreases the rate of reaction by a factor of $\sim 10^3$ as indicated by the following relative rates [640]:

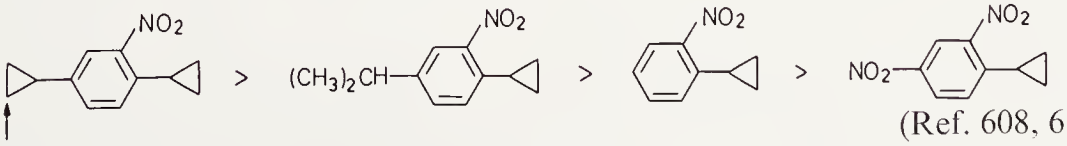


Groups such as a phenyl or β-silyl group which can stabilize a developing positive charge favor the reaction, while electron-withdrawing ketone [658] and ester [659] groups severely retard the reaction.

The effect of aromatic substituents on the rate of reaction of arylcyclopropanes has also been studied. As expected, electron-donating groups increase the rate of reaction and electron-withdrawing groups slow it down [660–662]. Using σ^+ constants, a ϱ value of -3.2 has been obtained for this reaction [662]. The following relative reactivities have also been reported:



(Ref. 625, 631)



(Ref. 608, 632)

Table 2.1. Mercuration of Cyclopropanes

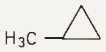
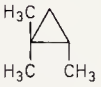
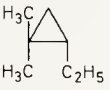
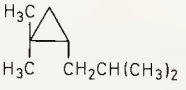
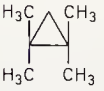
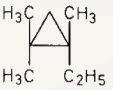
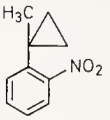
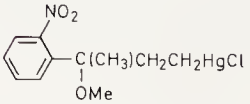
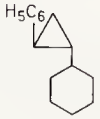
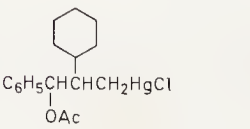
Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
1		$Hg(OAc)_2$	H_2O	$CH_3CHCH_2CH_2HgX$ (OH); X = Cl, Br, SCN	80–85	614
2			ROH R = H, Me	$(CH_3)_2CCH_2CH_2HgX$ (OR); X = Cl, Br, I, CN, SCN	62–92	614
3			H_2O	$CH_3CHCH(CH_3)CH_2HgOAc$ (OH)	—	615
4			ROH R = H, Me, Et	$(CH_3)_2CCH(CH_3)CH_2HgX$ (OR); X = Cl, Br, I, OAc, CN, SCN	62–92	616, 617
5			H_2O	$(CH_3)_2CCH(C_2H_5)CH_2HgX$ (OH); X = Cl, Br	—	618
6				$(CH_3)_2CCHCH_2HgOAc$ (CH(CH3)2; OH)	—	618
7				$(CH_3)_2CCHCH_2HgBr$ ($CH_2CH(CH_3)_2$; OH)	—	618
8			ROH R = H, Me, Et	$(CH_3)_2CC(CH_3)_2CH_2HgX$ (OR); X = Cl, Br, I, OAc, CN, SCN	56–96	619
			H_2O	$(CH_3)_2CC(CH_3)_2CH_2HgOAc$ (OH)	76	620
9				Mixture	—	621
10			MeOH		20	607
11			HOAc		47, 50	622, 623

Table 2.1. (continued)

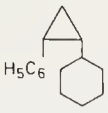
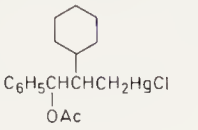
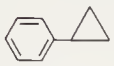
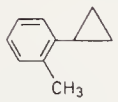
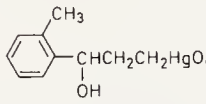
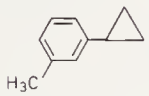
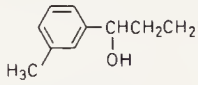
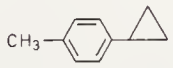
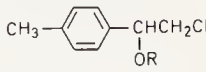
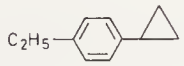
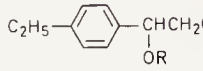
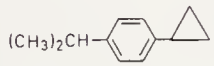
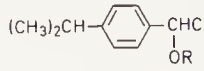
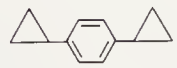
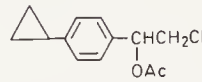
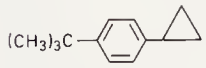
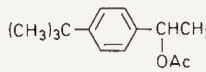
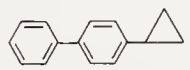
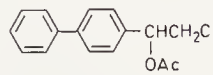
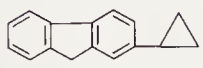
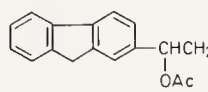
Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
12					40	622
13			ROH R = H, Me	$C_6H_5CHCH_2CH_2HgCl$ OR	71, 82	624
			H_2O_2	$C_6H_5CHCH_2CH_2HgCl$ OOH	55, 56	612, 613
			HOAc	$C_6H_5CHCH_2CH_2HgOAc$ OAc	—	625, 626
		$Hg[C(NO_2)_3]_2$	MeOH	$C_6H_5CHCH_2CH_2HgC(NO_2)_3$ OMe	75	496, 603
14		$Hg(OAc)_2$	H_2O		~100	627
15					~100	627
16			ROH R = H, Me	 X = Cl, Br, OAc	54-84	628
17				 X = Cl, Br, I, OAc	—	629
18				 X = Cl, Br, OAc, SCN	—	630
19			HOAc		—	625
20					—	625
21					—	625
22					—	631

Table 2.1. (continued)

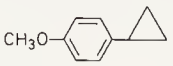
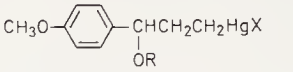
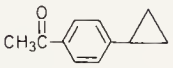
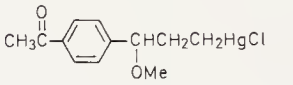
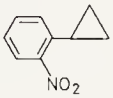
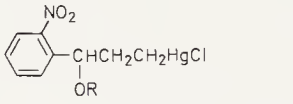
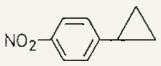
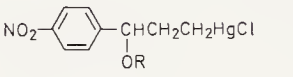
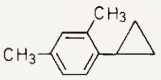
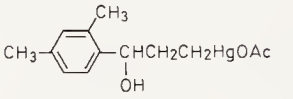
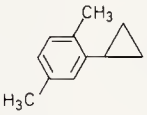
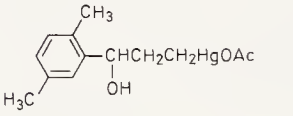
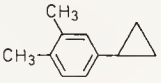
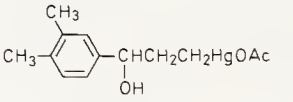
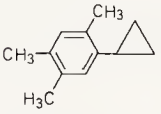
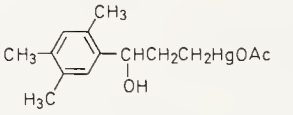
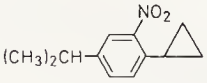
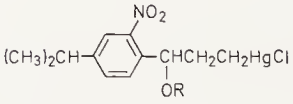
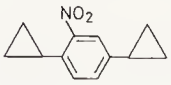
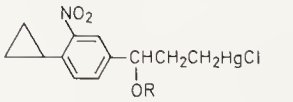
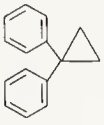
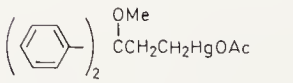
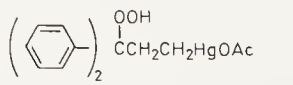
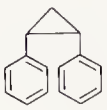
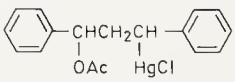
Entry	Cyclopropone	Mercury salt	Nucleophile	Orgonomercurial	% Yield	Ref.
23			ROH R = H, Me, Ac	 X = Cl, Br, I, OAc, CN, SCN	45-92	626, 628
24			MeOH		55	608
25			ROH R = Me, Ac		26-50	606, 608
26					56-72	606, 608
27			H_2O		~100	627
28					~100	627
29					~100	627
30					~100	627
31			ROH R = Me, Ac		63, 66	608, 632
32					87, 53	608, 632
33			MeOH		30	633
			H_2O_2		46.5	613
34			HOAc		12, 20, 30	623, 634, 635

Table 2.1. (continued)

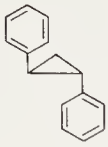
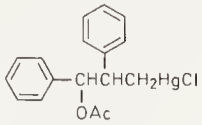
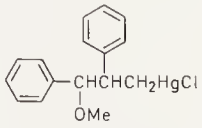
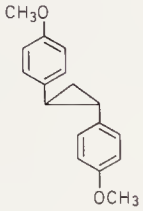
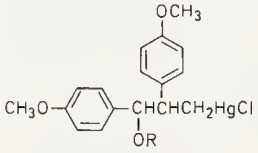
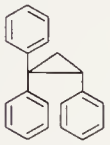
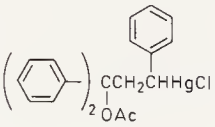
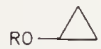
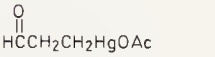
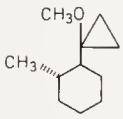
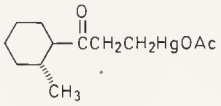
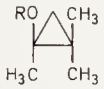
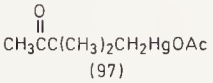
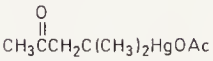
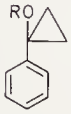
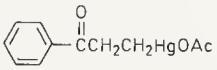
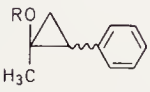
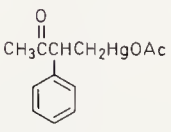
Entry	Cyclapropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
35					21	609, 623, 635
			MeOH		40	635
36		HgX_2 X = OAc, NO_3	ROH R = H, Me, Ac		10-95	636
37		$Hg(OAc)_2$	HOAc		16, 24	637
38	 R = $COCH_3$, COC_2H_5, $-C_6H_5$, $-C_6H_2(CH_3)_3$-2,4,6		H_2O		—	638
39					—	639
40	 R = H, Me		HOAc	 (97) +  (3)	—	640
41	 R = H, Me				100	640
42	 R = H, Me			 (75-77) +	—	640, 641

Table 2.1. (continued)

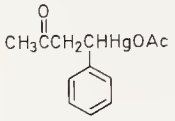
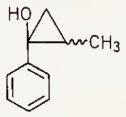
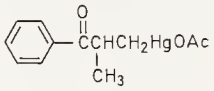
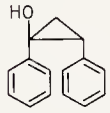
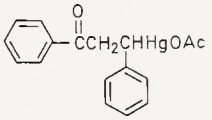
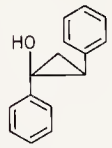
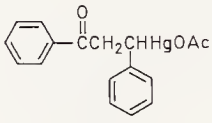
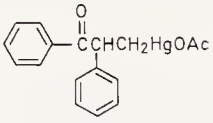
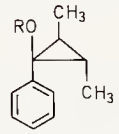
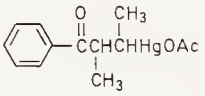
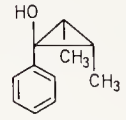
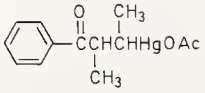
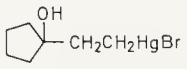
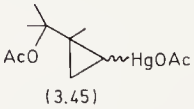
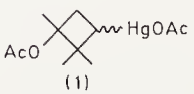
Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
				 (23-25)		
43					—	640
44					~68	641
45				 (88) +  (12)	—	641
46	 R = H, Me				85	640
47					—	640
48			H_2O		34	642
49			—		—	643
50			—	 (3.45) +  (1)	—	644

Table 2.1. (continued)

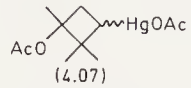
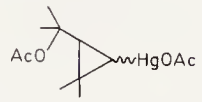
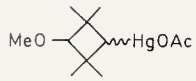
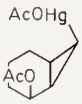
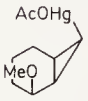
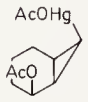
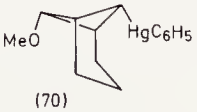
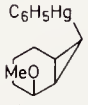
Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
			MeOH	 (13.5) +  (4.07) +  (1.0)	97	644
51			—		—	644
			MeOH		6	644
52			—		80	610, 645
			MeOH	 (49-56) +  (31-32) +  (13-16)	40 — —	610, 645
		C_6H_5HgOAc	MeOH	 (70) +  (30)	—	610, 611

Table 2.1. (continued)

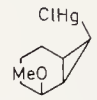
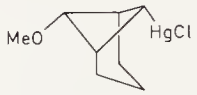
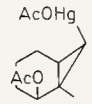
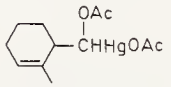
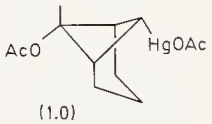
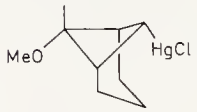
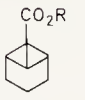
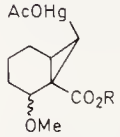
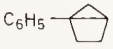
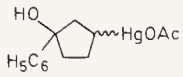
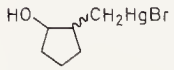
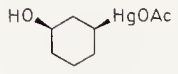
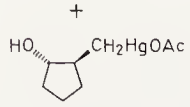
Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
		$HgCl_2$	NaOMe/MeOH	 (3) +  (2)	— —	611
53		$Hg(OAc)_2$	—	 (5.5) +  (1.2) +  (1.0)	60 (as RHgCl) — —	645
			MeOH		75	610, 645
54	 R = Me, Et				—	610, 645
55			H_2O		82	646
56					—	647
57					60	646
				 (63) +  (37)	~95	648

Table 2.1. (continued)

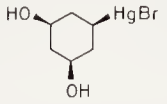
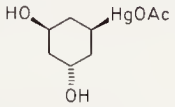
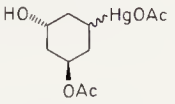
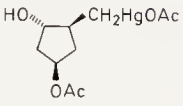
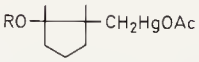
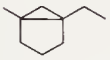
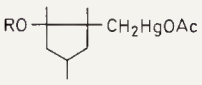
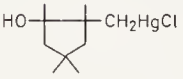
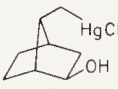
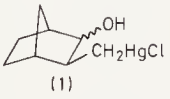
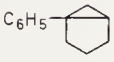
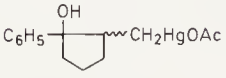
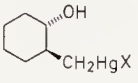
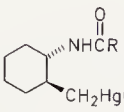
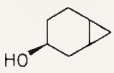
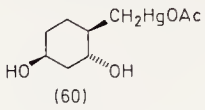
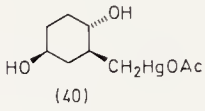
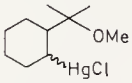
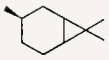
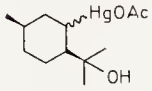
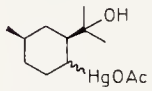
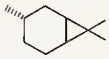
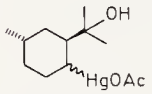
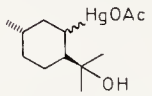
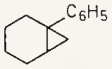
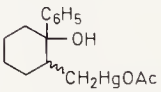
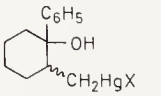
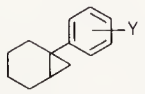
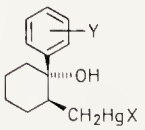
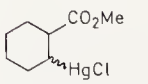
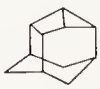
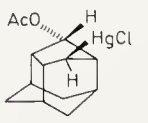
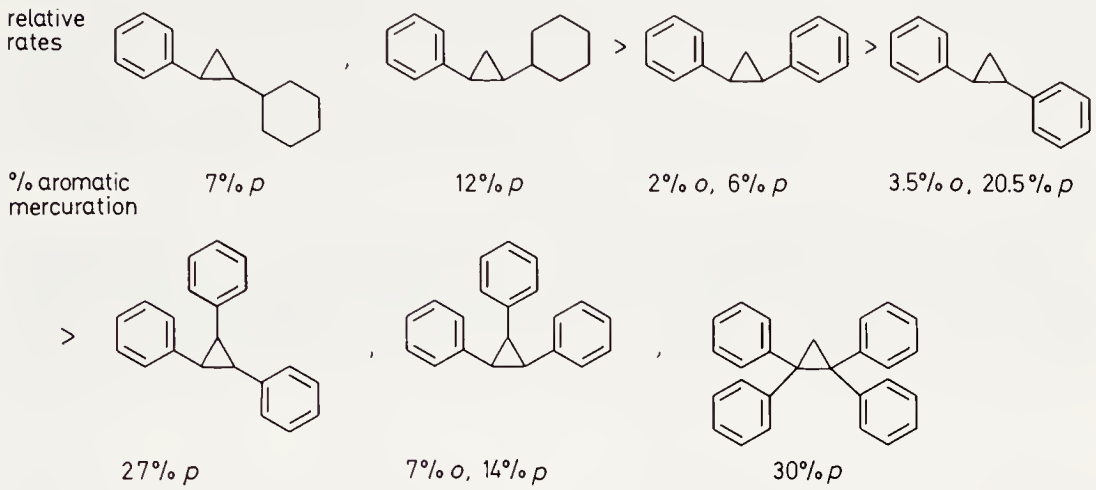
Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
58					56	648
59					~51	648
60				 (59) +  (39)	~68	648
61			ROH R = H, Me		80,92	649
62				possible mixture	—	649
63					—	649
64			H_2O		—	650
65				 (9) +  (1)	84	651
66					73	647
67				 X = Cl, OAc	83,86	646, 652
			RCN R = Me, Ph		32,18	604, 605

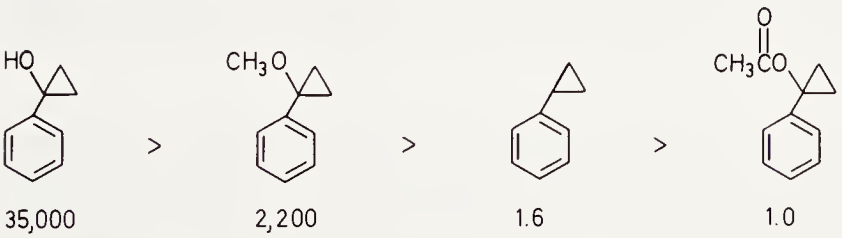
Table 2.1. (continued)

Entry	Cyclopropane	Mercury salt	Nucleophile	Organomercurial	% Yield	Ref.
68			H_2O	 (60) +  (40)	~98	648
69			MeOH	 *cis* : *trans* = 17:83	90	652
70			H_2O	 (90) +  (10)	~65	653
71				 (95) +  (5)	~60	653
72					70	647
		HgX_2 X = OAc, O_2CCF_3, SO_4, NO_3, ClO_4			—	602, 654
73	 Y = *p*-Me, *m*-Cl	HgX_2 X = OAc, O_2CCF_3			—	654
74		$HgCl_2/HgO$	MeOH		88	655
75		$Hg(OAc)_2$	HOAc		95	656

Increasing alkyl [601, 622, 623] or aryl [623, 634, 635, 637, 658] substitution on the arylcyclopropane three membered ring results in slower reactions and increasing amounts of aromatic mercuration products, apparently due to steric hindrance. The triphenyl- [623, 635, 663] and tetraphenylcyclopropanes [637] listed give only aromatic mercuration products.

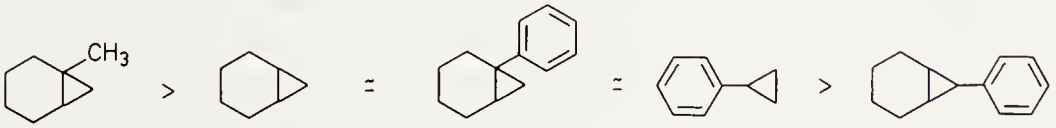


In oxygen-substituted cyclopropanes, cyclopropyl alcohols are more reactive than the corresponding esters or ethers [640]. From the literature it would appear that alkyl ethers are more reactive than esters, which in turn are more reactive than aromatic ethers [638, 640]. The oxymercuration of cyclopropyl vinyl ether proceeds via initial attack on the carbon—carbon double bond [638]. The cyclopropanol produced is then cleaved in a second step. The following relative rates give a good indication of the high reactivity of some of these compounds [640]:



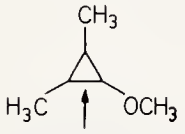
While an ester group apparently has little effect on the rate, a methyl ether group increases the rate by a factor of $\sim 10^3$ and an alcohol group by $\sim 10^4$.

The relative rates of reaction of a variety of norcarane derivatives have also been examined [664]. The accessibility of the cyclopropane appears to play a dominant role in these reactions.

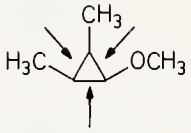


The direction of cyclopropane ring opening, and the stereochemistry of both the mercury and nucleophilic substitution reactions have been the primary interest in much of the work carried out to date on the mercuration of cyclopropanes. The results are consistent with the mercury electrophile attacking the least substituted carbon of the least substituted bond of the cyclopropane, with ring opening occurring in the direction which would lead to the most stable carbonium ion. If two or three of the bonds have the same number of substituents, a cis substituted bond is more readily attacked than a trans substituted bond. The only major exceptions to this mode of ring cleavage seem to be certain phenyl substituted cyclopropanes (Table 2.1; entries 34, 37, 42, 44 and 45), where the mercury becomes attached to the more substituted carbon bearing the phenyl group.

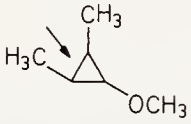
Mercury substitution can occur with either retention or inversion, as can trapping of the carbonium ion by the nucleophile. The stereochemistry of mercury substitution is highly dependent on the stereochemistry of the cyclopropane as nicely illustrated by the following examples [600, 601]. The



only one
cis disubstituted bond
90% retention



three equal
cis disubstituted bonds
60% retention
(statistical is 66%)



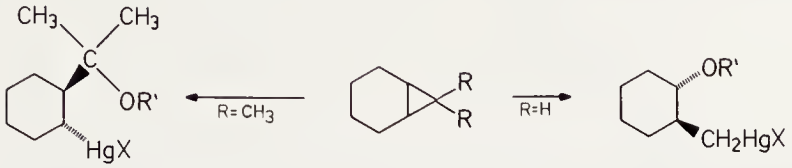
only one
cis disubstituted bond
90% inversion

trend is similar for the analogous 2,3-dimethylphenylcyclopropanes. In *cis*-1,2,3-trimethylcyclopropane, where all bonds are equal, it has been observed that inversion is preferred over retention by 62:38. Numerous other examples also exist which are consistent with this picture [600, 601, 640]. A corner mercurated cyclopropane has been suggested as an intermediate [601].

The stereochemistry of the concomitant nucleophilic substitution has also been studied, and in all cases the reaction proceeds with a very high degree, if not exclusive, inversion [600, 601]. The only major exceptions are alkylphenylcyclopropanes [600, 601, 622, 665]. Optically active *trans*-1,2-dimethylcyclopropane undergoes nucleophilic ring opening with at least 85% inversion, and quite possibly 100% inversion [615].

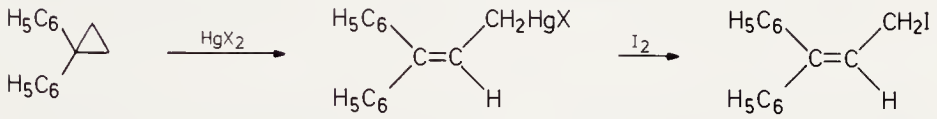
The direction of ring cleavage in bicyclic hydrocarbons has received considerable attention. Bicyclobutanes apparently undergo preferential attack at the least hindered bridgehead carbon, unless electron-withdrawing groups are present [666], and afford both cyclopropyl- and cyclobutylmercurials depending on reaction conditions [610, 611, 643–646]. Bicyclopentanes afford exclusively cyclopentylmercurials [646, 647], while bicyclo[3.1.0]hexanes give both cyclopentylmethyl- and cyclohexylmercurials [646–651]. The latter compounds are formed by a double inversion process [648]. In the bicyclo[4.1.0] system, cleavage always proceeds so as to leave the cyclohexyl ring intact. Both cyclohexyl- and cylohexylmethylmercurials have been ob-

served depending on the substitution pattern (Eq. 162). In the former organomercurials, a fair degree of stereospecificity has been observed [652, 653], while the stereospecificity of the latter reaction has been found to be highly dependent on the solvent, the mercury salt employed and the amount of nucleophile present [602].



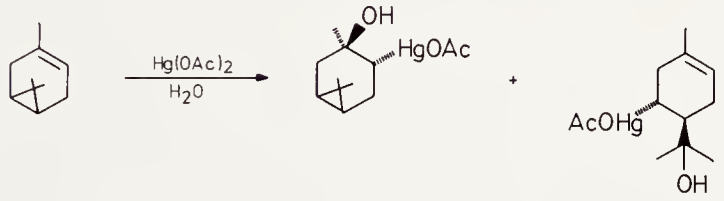
(162)

In a number of cases the mercuration of cyclopropanes has been reported to produce products different from those described above. For example, 1,1-diphenylcyclopropane apparently reacts with mercuric trifluoroacetate in nitrile solvents to generate an allylmercurial which cannot be isolated, but gives the expected allyl iodide upon iodination (Eq. 163) [599].



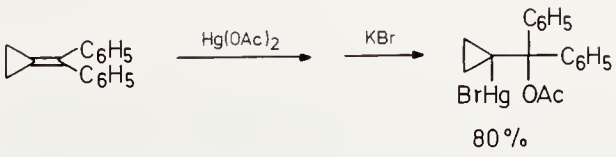
(163)

The mercuriation of a number of unsaturated cyclopropanes has been examined. For example, 3-carene undergoes oxymercuration at both the carbon—carbon double bond and the cyclopropane ring, and the latter organomercurial can be isolated (Eq. 164) [667]. Alkylidenecyclopropanes

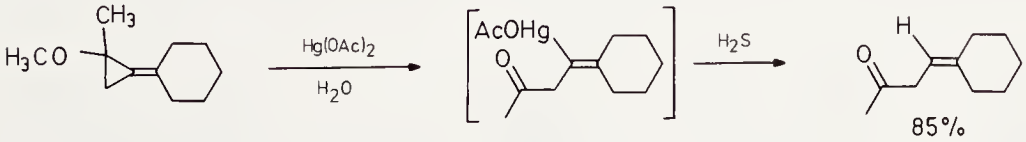


(164)

appear to undergo initial attack at the double bond, although ring cleavage products are usually observed (Eqs. 165–168). Benzocyclopropene affords an

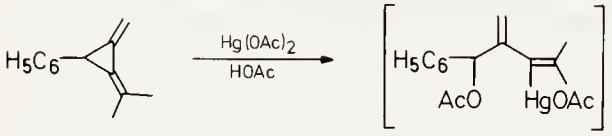


(165) [668]

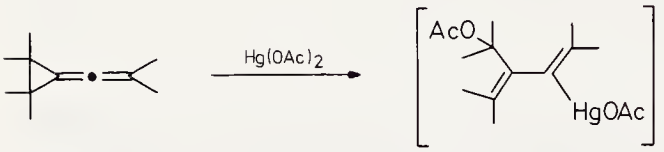


(166) [669]

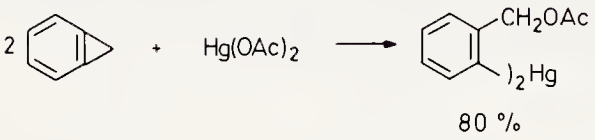
arylmercurial (Eq. 169) [672]. Cyclopropenes undergo ring opening to give predominantly vinylmercurials (Eqs. 170, 171) [673].



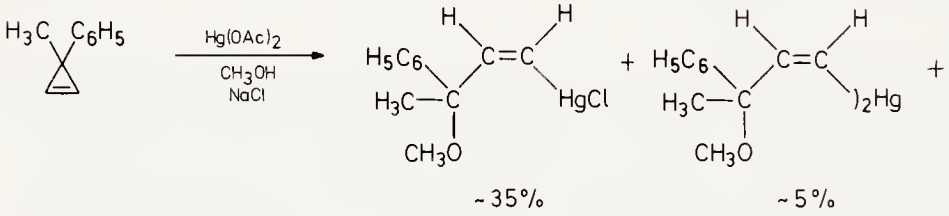
(167) [670]



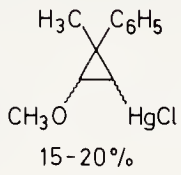
(168) [671]

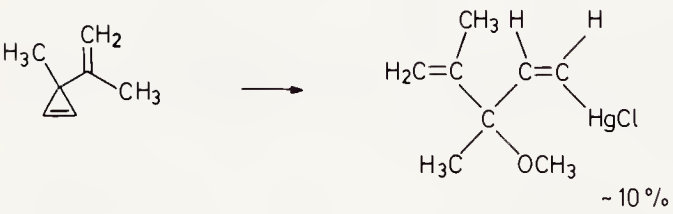


(169)



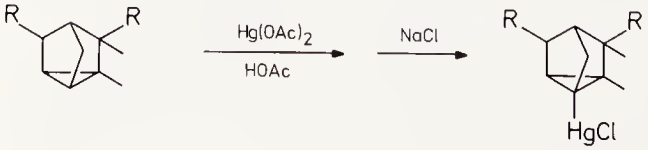
(170)





(171)

Contrary to all the above reactions, the highly hindered polycyclic hydrocarbons tricyclene and longicyclene react via cyclopropyl hydrogen substitution rather than ring opening (Eq. 172) [674, 675].



(172)

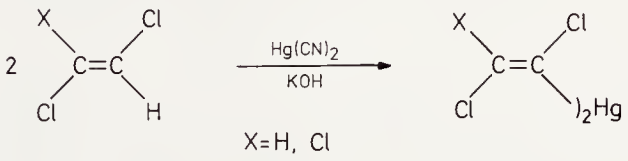
I. Mercuration of Alkenes

A large number of different mercury salts will add to alkenes to generate organomercurials (Eq. 173). When nucleophilic solvents are present, the sol-

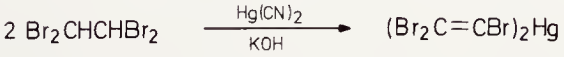
$$RCH{=}CH_2 + HgX_2 + Y^- \longrightarrow RCH(Y)CH_2HgX \qquad (173)$$

vent is frequently incorporated in the organomercurial. Subsequent borohydride-induced free radical addition of these alkyl groups to alkenes has recently become a very valuable new reaction which will be covered in Chapter VII. Reductive demercuration of these organomercurials also provides a very valuable method for the Markovnikov addition of a wide variety of HY (Y=OH, OR, O_2R, O_2CR, NR_2, NHCOR, N_3 and NO_2) to alkenes. This topic will be discussed in detail in a separate monograph entitled "Solvomercuration-Demercuration". At this time, only those reactions of alkenes which lead directly to alkenylmerucurials and certain useful carbonyl-containing organomercurials will be discussed.

trans-1,2-Dichloroethylene [676] and trichloroethylene [677, 678] react readily with mercuric cyanide and potassium hydroxide to give the corresponding divinylmercurials (Eq. 174), while *cis*-1,2-dichloroethylene [676, 679–681] apparently undergoes elimination to chloroacetylene which is converted into the corresponding dialkynylmercurial. Under similar conditions, 1,1,2,2-tetrabromoethane evidently undergoes elimination to tribromoethylene which subsequently mercurates (Eq. 175) [678, 679].

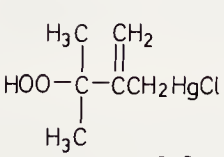


(174)

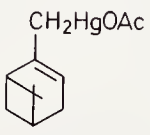


(175)

A number of other olefins have been reported to react with mercuric salts, such as $Hg(OAc)_2$ or $Hg(O_2CCF_3)_2$, to afford either allylic mercurials or alkenylmercurials directly. The following allylic mercurials have been prepared in this manner:

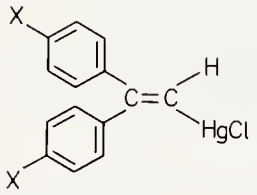


40%[682]

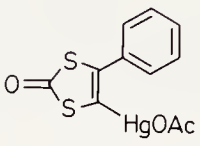


– %[683]

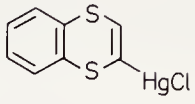
More common is alkenylmercurial formation:



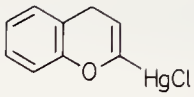
X = H 85 % [684]
CH_3 91 %
Cl 95 %



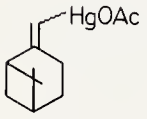
— % [685]



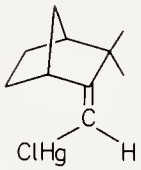
79 % [686]



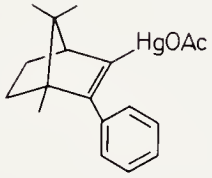
50 % [687]



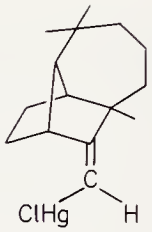
— % [683]



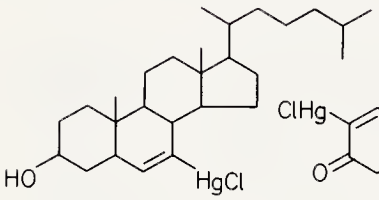
22 % [688]



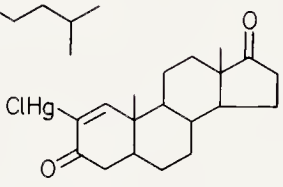
— % [683, 689]



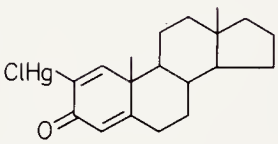
14 % [688]



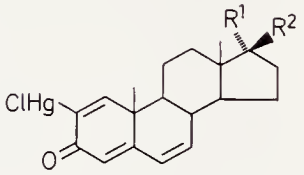
20 % [690]



12 % [691]

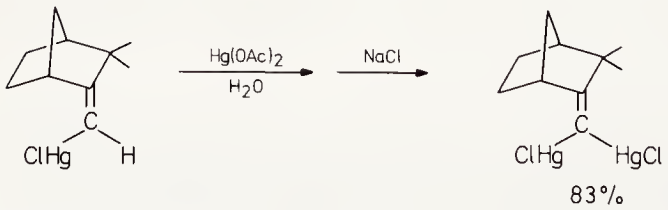


44 % [691]

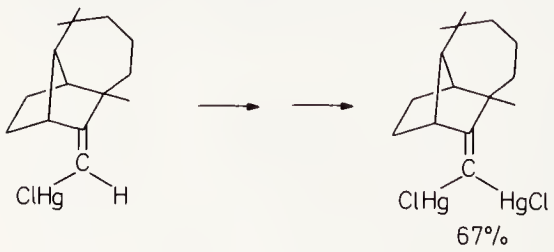


R^1	R^2	Ref.
O	O	691
H	OH	691
H	OAc	691
H	O_2CEt	692,693
CH_3	OH	692,693

Two of the above alkenylmercurials have also been reported to undergo further mercuration to afford dimercurials (Eqs. 176, 177) [688, 694]. Although few of these reactions have been run under ideal conditions, this



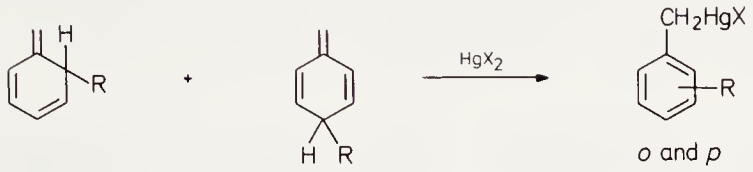
(176)



(177)

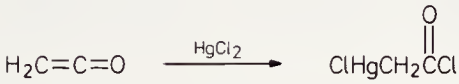
approach appears to provide a valuable route to alkenylmercurials, a class of compounds for which a number of new synthetic applications have been reported recently.

The mercuration of trienes of the following type results in benzylic mercurials (Eq. 178) [695–700].

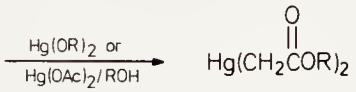


(178)

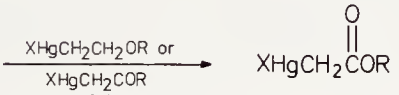
The mercuration of oxygenated olefins leads to a variety of useful carbonyl-containing organomercurials. Some of these have been examined as possible divalent carbon transfer reagents and will be discussed later in Chapter X. Ketene, for example, undergoes mercuration to afford a variety of ester-containing organomercurials (Eqs. 179–183). Ketene dimer also



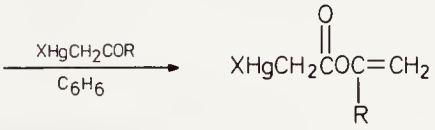
(179) [701]



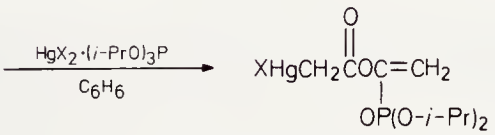
(180) [702]



(181) [703]

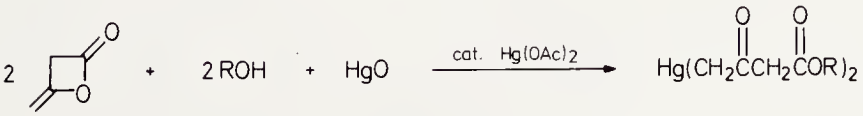


(182) [703]



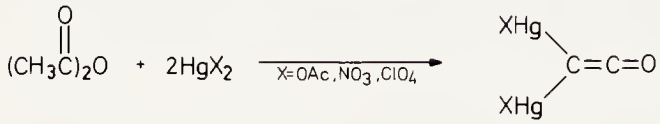
(183) [704]

undergoes mercuration to provide excellent yields of γ-mercurated β-keto esters (Eq. 184) [705, 706]. Recently, mercurated ketenes themselves have

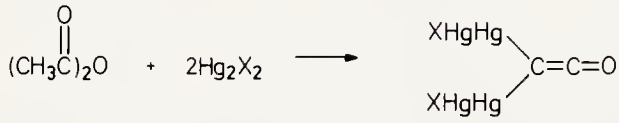


(184)

been obtained from acetic anhydride or isopropenyl acetate (Eqs. 185, 186) [707]. Mercurous salts provide what is apparently the first stable, isolable organomercury(I) compound.

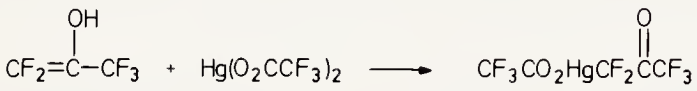


(185)

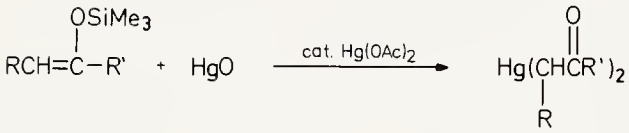


(186)

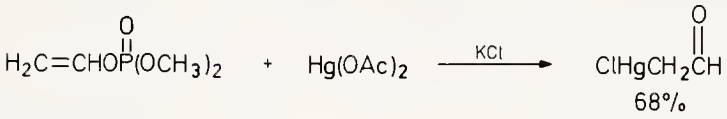
The mercuration of an enol [708, 709], or enol silanes [710–715] or phosphates [716] provides a highly convenient route to α-mercury carbonyl compounds, while enol acetates afford either carbonyl compounds [717–720] or the corresponding acetals [721] (Eqs. 187–191). Analogous reactions with



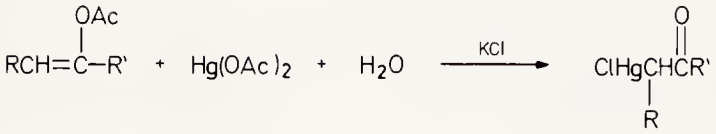
(187)



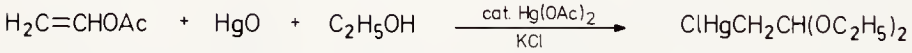
(188)



(189)

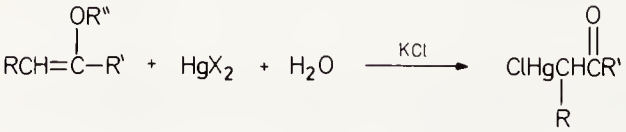


(190)

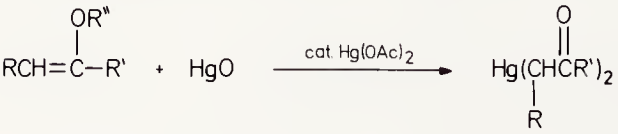


(191)

vinyl ethers yield either carbonyl-containing alkylmercuric salts [496, 603, 638, 718, 722–725] or dialkylmercurials [721, 723, 726–728], as well as

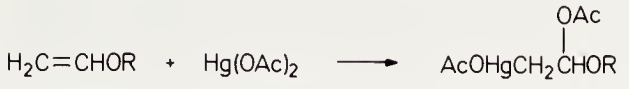


(192)

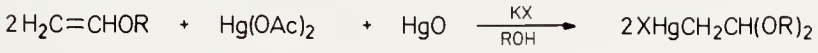


(193)

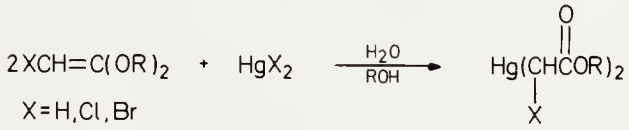
acylals [729] or acetals [721, 723] (Eqs. 192–195). Ketene acetals reportedly give mono-, di- or trimercurated compounds depending on the starting material and reaction conditions (Eqs. 196–199). Only the second and third



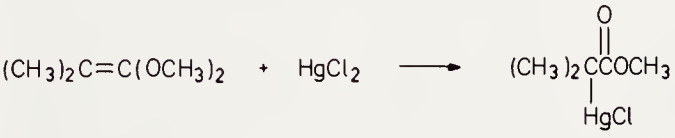
(194)



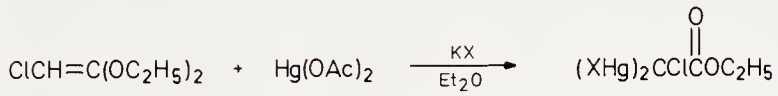
(195)



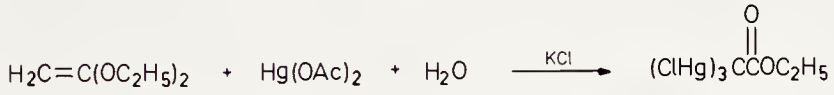
(196) [723, 730]



(197) [731]

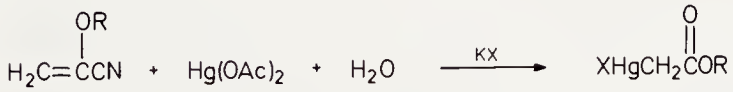


(198) [730]



(199) [730]

of these reactions (Eqs. 197, 198) go in good yield and the trimercurated ester (Eq. 199) was not fully characterized. Simple monomercurated acetic esters are best obtained from the corresponding cyanovinyl ether (Eq. 200) [732]. Unfortunately, this approach is apparently not applicable to the synthesis of other mercurated esters.

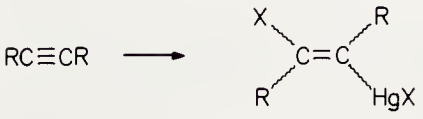


(200)

J. Mercuration of Alkynes

Alkynes can react in two entirely different ways with mercury salts depending upon the reaction conditions employed. Under basic conditions alkynes possessing a terminal hydrogen undergo facile mercuration to afford dialkynylmercurials (Eq. 201). Under acidic or neutral conditions mercury salts usually add to the carbon—carbon triple bond (Eq. 202).

(201)



(202)

The conversion of alkynes to dialkynylmercurials is a well known reaction which has often been used to help characterize terminal alkynes [733]. In fact, it has been suggested as an analytical method for the determination of alkynes [734]. The reaction is commonly run using alkaline mercuric iodide or cyanide solutions and usually affords excellent yields of organomercurial (Eq. 203) [733]. The versatility of this reaction is illustrated by the

$$2RC{\equiv}CH \xrightarrow[\substack{K_2HgI_4\\ \text{or}\\ Hg(CN)_2}]{NaOH} (RC{\equiv}C)_2Hg \qquad (203)$$

following complete listing of alkynes ($RC{\equiv}CH$) which have been employed in this reaction: R = H [678, 735], CH_3 [733, 736], CD_3 [737], C_2H_5 [733], *n*-C_4H_9 [733, 738], *i*-C_4H_9 [739], *t*-C_4H_9 [733], *n*-C_5H_{11} [733],  [733], *n*-C_8H_{17} [733], *n*-$C_{11}H_{23}$ [740, 741], *n*-$C_{13}H_{27}$ [741], *n*-$C_{15}H_{31}$ [741], *n*-$C_{16}H_{33}$ [741], $C_6H_5CH_2$ [733, 739], $C_6H_5CH_2CH_2$ [733], *m*-$CH_3OC_6H_4CH_2CH_2$ [742], $CH_3OCH_2CH_2$ [743], $C_2H_5OCH_2CH_2$ [743, 744], *n*-$C_4H_9OCH_2CH_2$ [743], $BrCH_2CH_2OCH_2CH_2$ [743], $C_6H_5OCH_2$ [733, 745], *p*-$CH_3OC_6H_4O(CH_2)_3$ [744], *o*-$CH_3OC_6H_4O(CH_2)_5$ [744], CF_3 [746, 747], C_2F_5 [748], $F(CH_2)_n$ n = 3–7 [749], $H_2C{=}CHCHOH$ [750], *trans*-$CH_3CH{=}CHCHOH$ [750], C_6H_5CHOH [739, 750, 751], 3,4-$(CH_3O)_2C_6H_3CHOH$ [751], 3,4-$(CH_2O_2)C_6H_3CHOH$ [751],  [752], $H_2C{=}CH$ [753], *cis* and *trans* $CH_3CH{=}CH$ [754], *cis* and *trans* *n*-$C_6H_{13}CH{=}CH$ [755], *trans* *n*-$C_3H_7CH{=}CH(CH_2)_4$ [756], $F_2C{=}CH$ [757], *cis*(?)*n*-$C_4H_9SCH{=}CH$ [758], $H_2C{=}CH(CH_2)_8CO_2CH_2$ [759], $H_2C{=}CHCH{=}CH$ [760], $HC{\equiv}C$ [761], $CH_3C{\equiv}C$ [761, 762], $C_2H_5C{\equiv}C$ [761], *n*-$C_3H_7C{\equiv}C$ [761], *n*-$C_4H_9C{\equiv}C$ [761], $C_6H_5C{\equiv}C$ [761, 763], $(C_6H_5)_2COHC{\equiv}C$ [764], *n*-$C_4H_9C{\equiv}CCH_2$ [765, 766], *n*-$C_3H_7C{\equiv}C(CH_2)_4$ [756], *n*-$C_4H_9C{\equiv}CCH_2C{\equiv}CCH_2$ [766], C_6H_5 [36, 733, 738, 739, 767–770], *m*-$CH_3C_6H_4$ [738], *p*-$CH_3C_6H_4$ [733, 739], *p*-$CH_3OC_6H_4$ [733, 739], *p*-$(CH_3)_2NC_6H_4$ [771], *p*-FC_6H_4 [738], *m*-ClC_6H_4 [738], *p*-ClC_6H_4 [738, 739], *p*-BrC_6H_4 [739], *p*-$NO_2C_6H_4$ [739, 772], 2,4-$(CH_3)_2C_6H_3$ [738], 2,6-$(CH_3)_2C_6H_3$ [738], 3-Br-2,4,6-$(CH_3)_3C_6H$ [773], 1-naphthyl [774, 775], 2-naphthyl [739, 776], 2-furyl [733, 739], 5-bromo-3-furyl [733], 2-thienyl [776], 3-pyridyl [739], Cl [678, 733], Br [679, 733], C_6H_5S [777] and *p*-$CH_3C_6H_4S$ [681, 778]. It is noteworthy that fluoroacetylene apparently undergoes addition of mercuric iodide to generate an alkenylmercurial instead (Eq. 204) [779].

$$2FC{\equiv}CH + K_2HgI_4 \longrightarrow (IFC{=}CH)_2Hg \qquad (204)$$

Several other variations in this general procedure have been reported. Organic amines and either mercuric acetate [770, 780], mercuric chloride [769] or M_2HgX_4 (M = Na, K) [781] have been employed with equally good results. The rate of the latter reaction is dependent on the base strength and

concentration of the amine, and the acidity of the alkyne hydrogen [781]. Mercuric acetate in acetic acid [753], chloroform [782] or methanol [783] has also been reported to mercurate terminal alkynes, but these conditions more commonly give products of addition to the triple bond. The reagent $Hg[N(SiMe_3)_2]_2$ also appears excellent for mercurating terminal acetylenes [498].

Mixed alkynylmercury compounds are also readily prepared from organomercuric salts and alkynes under basic conditions (eqs. 205–207).

$$RHgX + HC{\equiv}CH \longrightarrow RHgC{\equiv}CH \qquad (205)\ [784]$$

$$RHgX + HC{\equiv}CH \xrightarrow{KOH} RHgC{\equiv}CHgR \qquad (206)\ [785\text{–}789]$$

$$RHgX + HC{\equiv}CR' \xrightarrow{LiNH_2} RHgC{\equiv}CR' \qquad (207)\ [255, 739]$$

Several other types of substrates also give dialkynylmercury compounds. Iodoalkynes react with either metallic mercury [36] or alkaline mercuric iodide or cyanide [790] to give the corresponding organomercurials (Eq. 208).

$$RC{\equiv}CI \xrightarrow[HgX_2/OH^-]{Hg\ or} (RC{\equiv}C)_2Hg \qquad (208)$$

Several vinyl halides have also been reported to react with basic mercury salts to yield dialkynylmercurials, presumably via elimination to the corresponding alkyne (Eq. 209) [676, 679–682, 772, 791].

$$ClCH{=}CHCl \xrightarrow[KOH]{Hg(CN)_2} (ClC{\equiv}C)_2Hg \qquad (209)\ [676, 679\text{–}681]$$

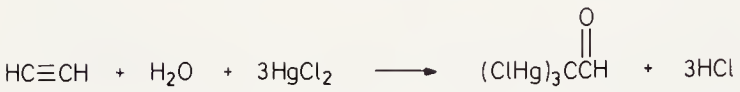
The mercuration of alkynes under neutral or acidic conditions generally results in entirely different products. Under these conditions, addition of the mercury salt to the carbon—carbon triple bond usually occurs and organomercurials can frequently be isolated. Under strongly acidic conditions, however, protonolysis of the resulting organomercurial is common. This approach, first reported by Kucherov in 1881, provides a very useful method for the catalytic hydration of acetylenes and will be discussed in more detail in the monograph entitled "Solvomercuration-Demercuration" (Eq. 210) [792, 793]. It has found wide application in organic

$$RC{\equiv}CH + H_2O \xrightarrow{cat.\ Hg^{++}} RC(=O)CH_3 \qquad (210)$$

synthesis and several interesting variations of the original procedure have recently been reported [794, 795]. This general approach can also be used for the synthesis of ketals [796–798] or enol esters [799–801] (Eq. 211).

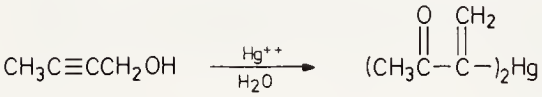
$$\begin{matrix} OR' \\ | \\ RCCH_2R \\ | \\ OR' \end{matrix} \xleftarrow[R'OH]{cat\ Hg^{++}} RC{\equiv}CR \xrightarrow[R'CO_2H]{cat.\ Hg^{++}} \begin{matrix} O_2CR' \\ | \\ RC{=}CHR \end{matrix} \qquad (211)$$

Under more or less neutral conditions, organomercurials can frequently be isolated from these reactions. The organomercurials isolated from the reaction of acetylene and various mercury salts have been extensively studied. Keiser first reported the formation of an organomercurial upon addition of acetylene to aqueous solutions of mercuric chloride [735]. Although the exact nature of this compound was the center of considerable debate, the best available evidence would suggest that it is trichloromercurioacetaldehyde (Eq. 212) [505, 802–806]. Similar uncertainty exists today over the nature

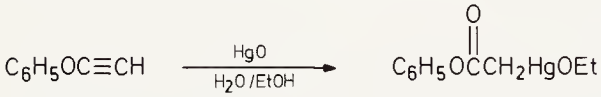


(212)

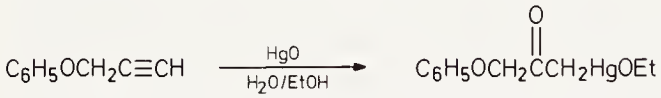
of the products derived from the reaction of acetylene and mercuric nitrate [555, 807–810], nitrite [811] and chlorate [811], as well as the reaction of propyne [802, 812] and phenylacetylene [806, 813] with aqueous mercuric chloride. The latter reactions have been suggested to give α-polymercurated ketones similar to trichloromercurioacetaldehyde [802, 806]. The only other α-mercurated ketones to actually be isolated from the aqueous mercuration of an alkyne appear to be the following (Eqs. 213–215).



(213) [814]



(214) [745]



(215) [745]

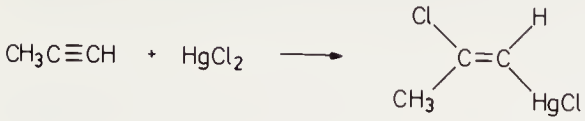
The reaction of acetylene and mercuric chloride in concentrated hydrochloric acid affords an entirely different organomercurial, *trans*-β-chlorovinylmercuric chloride (Eq. 216) [815–820]. This compound has been used

(216)

extensively in studies on the reactivity of vinylmercurials. The cis isomer can be prepared by the non-aqueous reaction of acetylene and mercuric chloride at 90–100 °C [821], or by free radical [822] or photochemical [823] isomerization of the trans isomer [818, 819, 824]. Both isomers are readily symmetrized to divinylmercurials upon treatment with ammonia [817, 819, 822, 825].

A large number of other alkynes have been observed to add mercuric chloride to afford β-chlorovinylmercurials. For example, propyne reacts at low temperatures to give an unstable trans addition product (Eq. 217) [826].

While 4-octyne fails to react with mercuric chloride even upon heating, cyclooctyne gives a 52% yield of vinylmercurial (Eq. 218) [827]. Vinylacetylene



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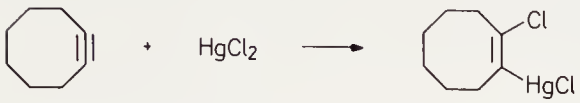
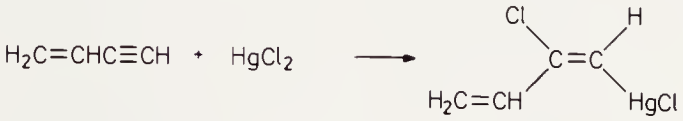


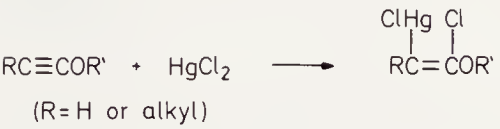
(218)

also affords a stable organomercurial adduct, whose structure appears to have been originally misassigned (Eq. 219) [826, 828–830]. Mercuric chloride



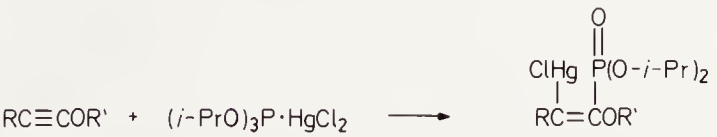
(219)

addition to alkynyl ethers also affords unstable organomercurials, whose stereochemistry has not been reported (Eq. 220) [831–833]. When the reaction



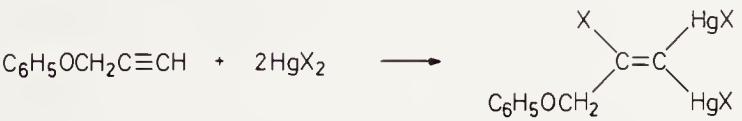
(220)

is run in the presence of triisopropylphosphite, vinylphosphonate mercurials are isolated (Eq. 221) [832–834].



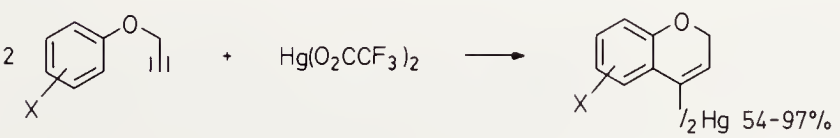
(221)

Propargylic ethers, alcohols, chlorides and amines also give organomercurial products. While phenyl propargyl ether reacts with mercuric chloride and mercuric acetate to give dimercurials (Eq. 222) [745], the analogous reac-



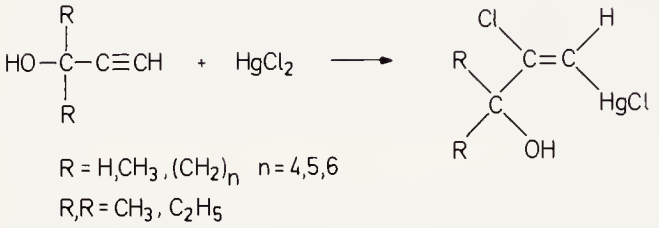
(222)

tion with mercuric trifluoroacetate reportedly affords chromenylmercurials (Eq. 223) [835]. Propargylic alcohols yield still a third type of organo-



(223)

mercurial, simple trans addition compounds (Eqs. 224, 225) [836–838]. The alcohol reactions only seem to work on highly symmetrical primary and tertiary alcohols. On the other hand, certain acetylenic diols undergo cyclization to furans and derivatives (Eq. 226) [839–846]. This reaction provides a



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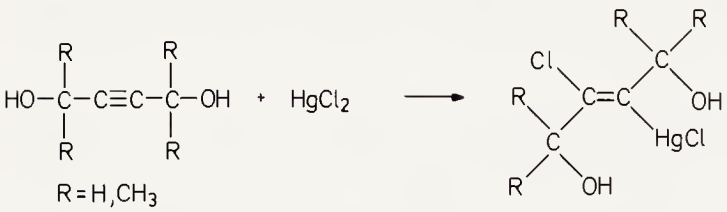

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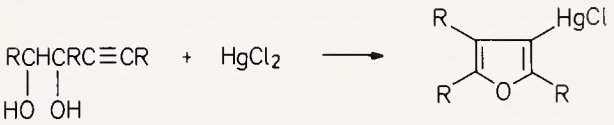
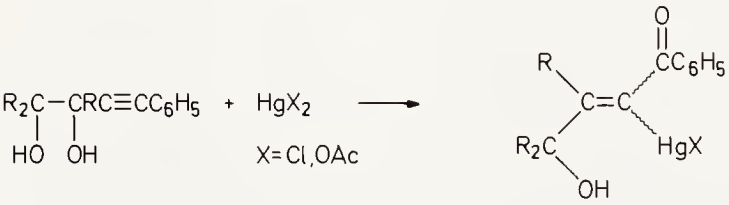


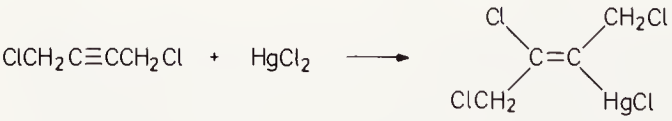
(226)

novel route to 3-chloromercuriofurans not readily available via direct mercuration of furans. Phenyl-substituted acetylenic tertiary diols afford isomerized vinylmercurials instead (Eq. 227) [847–849]. 1,4-Dichloro-2-butyne [836]



(227)

and hexafluoro-2-butyne [850] also undergo addition reactions (Eqs. 228, 229). Propargylic amines have also recently been observed to undergo facile



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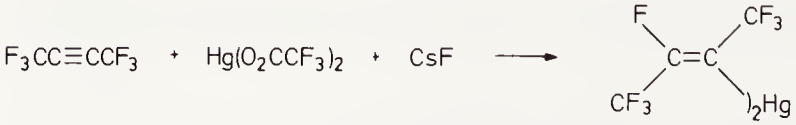
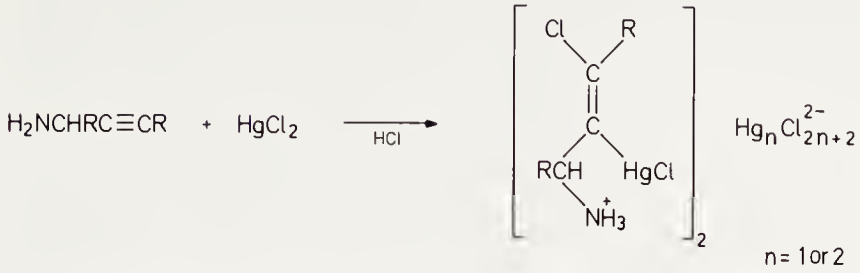


(229)

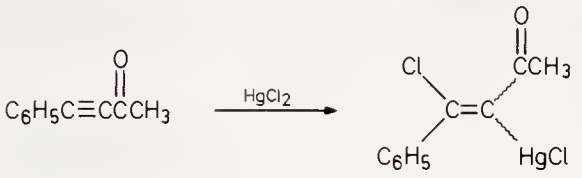
mercuration [851]. The reaction appears to involve addition of mercuric chloride in the opposite direction from that of the above reactions, pre-

sumably due to the strong electron-withdrawing effect of the ammonium group (Eq. 230).

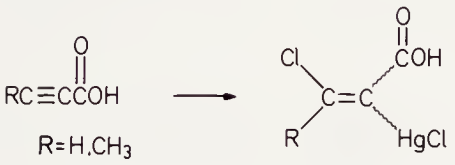


(230)

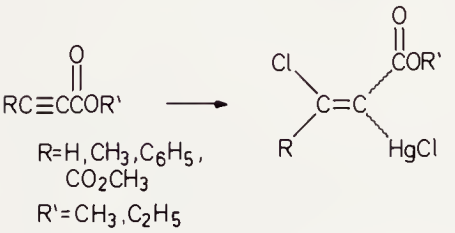
α,β-Unsaturated carbonyl compounds also readily react with mercuric chloride (Eqs. 231–233). The products appear to be trans addition compounds.



(231) [852]

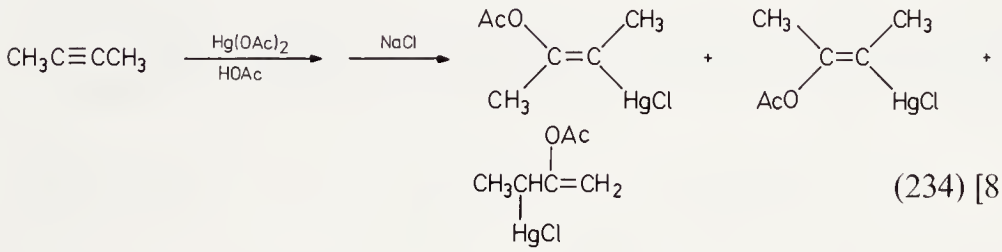


(232) [853–855]



(233) [853, 856, 857]

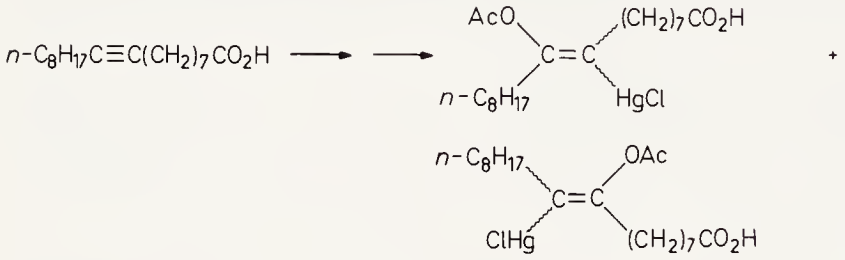
The reaction of alkynes and mercuric acetate in acetic acid is reported to give several different types of addition products. Terminal alkynes can give dialkynylmercurials [753, 782, 783]. Certain alkynes are reported to give simple addition to the triple bond (Eqs. 234–238]. With 2-butyne the major



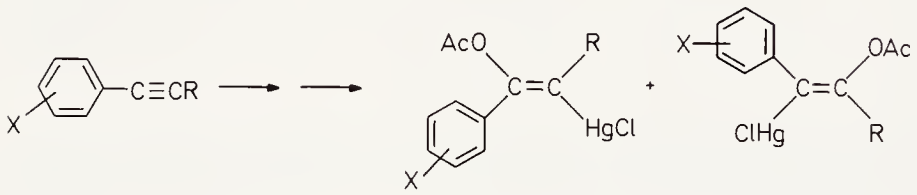
(234) [858–860]

(235) [861]

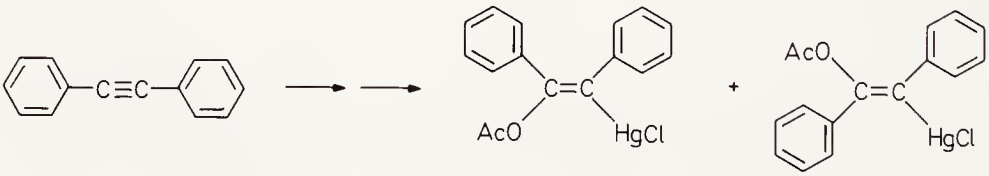
product is the trans addition compound, but procedures for the isolation of all three isomers have been published. The regio- and stereochemistry of the addition to the other dialkyl acetylenes mentioned (Eqs. 235, 236) have not been firmly established. Alkyl aryl acetylenes appear to give only trans addition, but a mixture of the two possible regioisomers is observed. The major product is always the compound with the acetoxy group next to the aromatic ring. This compound is favored by increasing the length of the alkyl chain R [782, 864] or introducing electron-donating groups into the aromatic ring [865]. If R is sterically bulky (R = *t*-Bu), no reaction occurs [782, 868]. Diphenylacetylene once again affords both cis and trans addition compounds, but in this case the former predominates and is most readily isolated.



(236) [862, 863]

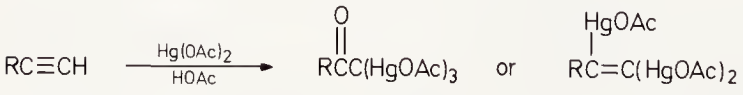


(237) [864, 865]



(238) [858, 860, 866, 867]

Much of the early work on the mercuration of alkynes was carried out on unsaturated fatty acids and esters. Entirely different types of products were reported at that time (Eqs. 239, 240) [753, 863, 869, 870]. The exact nature of



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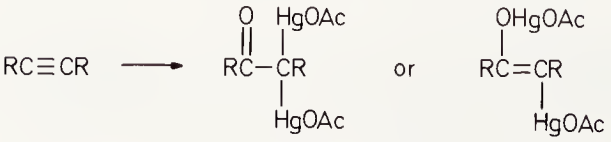
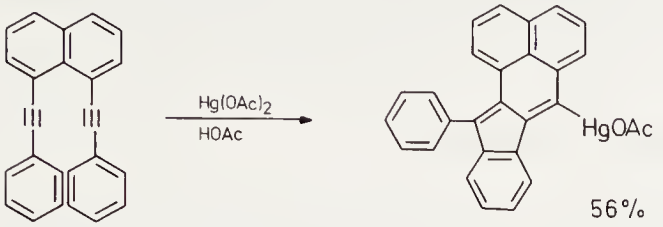


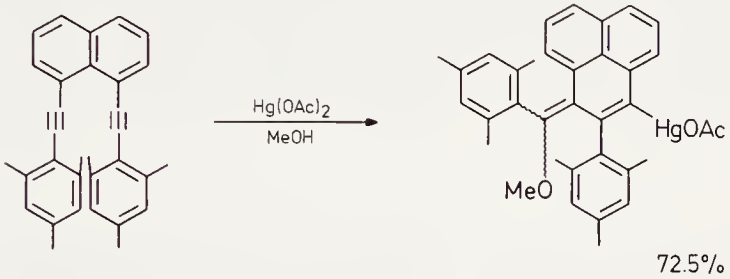
(240)

these organomercurials has yet to be determined, but the carbonyl-containing structures seem preferable.

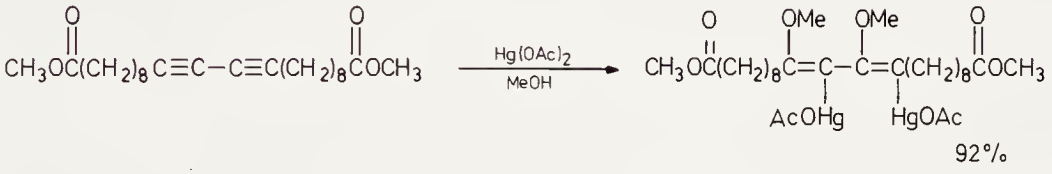
The mercuration of diynes has also been briefly examined and several different products have been reported (Eqs. 241–243).



(241) [871]

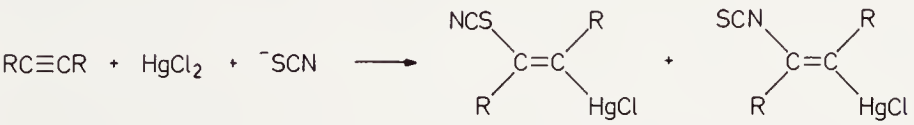


(242) [871]



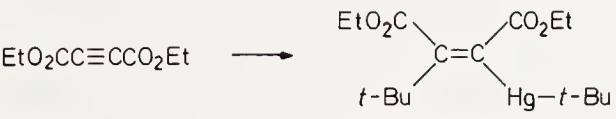
(243) [862]

Recently, mercuric chloride and thiocyanide anion have been reported to add to internal alkynes to give both sulfur- and nitrogen-bonded alkenylmercurials (Eq. 244) [872].

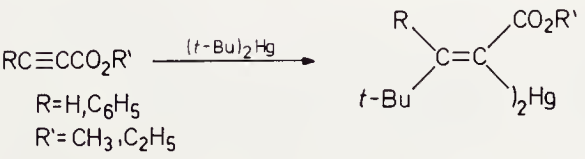


(244)

Finally, di-*t*-butylmercury has been found to add to acetylenic esters in a cis fashion to afford the corresponding vinylmercurials (Eqs. 245, 246) [873].



(245)



(246)

Unfortunately, neither diethyl- nor diphenylmercury react in this same way.

It is obvious from this brief review of the mercuration of alkynes that these reactions provide extremely important routes to a wide variety of alkynyl- and alkenylmercurials. These compounds are finding increasing utility in organic synthesis.

K. Mercuration of Aromatic Compounds

The direct electrophilic mercuration of aromatic compounds is clearly the most important method for the synthesis of aromatic organomercurials. The method is simple and direct, requiring only the arene and an electrophilic mercury salt, most commonly mercuric perchlorate, nitrate, trifluoroacetate, acetate or chloride (Eq. 247). Less reactive arenes require the former salts,

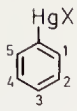
$$ArH + HgX_2 \longrightarrow ArHgX + HX \qquad (247)$$

while more reactive arenes such as phenols, anilines, furans and thiophenes react readily with mercuric acetate or mercuric chloride. The resulting arylmercurial is frequently treated on work-up with aqueous sodium chloride to obtain the more easily handled arylmercuric chloride. While the mechanism of this reaction has been studied in great detail, with special interest in the directive effects of various functional groups, emphasis here is on those organomercurials which have been prepared using this approach.

In Table 2.2 simple arylmercurials derived from benzene and substituted benzenes by direct electrophilic mercuration have been tabulated. Although the reactions of many of these substrates lead to mixtures of products, the various isomers can often be separated by simple recrystallization procedures. All compounds which have been actually isolated and at least reasonably well characterized have been included in Table 2.2. Those compounds whose structures appear impossible based on present day knowledge of these reactions have been omitted. In a few instances where a compound has been characterized, but the structural assignment appears questionable, a question mark has been placed in the column indicating the yield of the isomer. In this regard it is important to note that the structure of the vast majority of these arylmercurials has been established primarily by halogenation and comparison with known aryl halides. This approach is not without its problems in that halogenation can result in rearrangement [970]. In a few cases, the arylmercurials have been compared with those prepared by alternate methods in which the structure was more easily established, such as the use of aryldiazonium salts (Sect. L) and sulfinate elimination reactions (Sect. N).

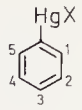
The structures have been grouped roughly according to the functional groups present in the arene starting material, beginning with benzene itself and proceeding through simple alkyl- and polyalkylbenzenes, halo- and polyhaloarenes and on to phenols, where the compounds are separated into phenol

Table 2.2. Arylmercurials Available via Mercuration of Simple Arenes



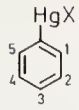
Arene	Functional groups and position of substitution					X	% Yield	Ref.
	1	2	3	4	5			
Benzene	H	H	H	H	H	Cl	92,98	874, 875
	H	H	H	H	H	OAc	80-92	875-877
	H	H	H	H	H	O_2CCF_3	99	878
	H	H	H	H	H	O_2CCCl_3	92	879
	H	H	H	H	H	$O_2C(CH_2)_{12}CH_3$	95-100	880
	H	H	H	H	H	NO_3	80	881, 882
	H	H	H	H	H	OC_6Cl_5	—	883
	H	H	H	H	H	$C(NO_2)_3$	—	496, 884
	H	H	H	H	H	O_3SCF_3	—	885
	HgOAc	H	H	H	H	OAc	—	886
	H	$HgClO_4$	H	H	H	ClO_4	—	886
	H	H	$HgClO_4$	H	H	ClO_4	—	886
Alkyl-benzenes	CH_3	H	H	H	H	Cl	—	887
	H	H	CH_3	H	H	Cl	—	887
	H	H	CH_3	H	H	OAc	61	888
	HgOAc	H	CH_3	H	H	OAc	—	889
	H	CF_3	H	H	H	Cl	—	890
	H	CF_3	H	HgCl	H	Cl	—	890
	HgCl	H	CF_3	H	H	Cl	—	890
	CH_2OH	H	H	H	H	Cl	—	891
	H	H	CH_2OH	H	H	Cl	—	891
	CH_2NHAc	H	H	H	H	Cl	—	892
	H	H	CH_2NHAc	H	H	Cl	—	892
	CH_2CH_2OH	H	H	H	H	Cl	—	892
	H	H	CH_2CH_2OH	H	H	Cl	—	892
	CH_2CO_2H	H	H	H	H	OAc	—	893

Table 2.2. (continued)



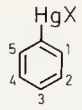
Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
	H	H	CH_2CO_2H	H	H	Cl	—	894
	H	H	$CH_2CO_2CH_3$	H	H	Cl	—	894
	H	H	$CH(CH_3)_2$	H	H	Cl	—	895
	H	$(CH_2)_3OH$	H	H	H	Cl	—	892
	H	H	$(CH_2)_3OH$	H	H	Cl	—	892
	CH_3	H	CH_3	H	H	Cl	—	330
	CH_3	H	H	CH_3	H	OAc	78	896
	CH_3	H	H	$CH(CH_3)_2$	H	Cl	—	897
	CH_3	H	H	$CH(CH_3)_2$	H	Br	—	898
	CH_3	H	H	$CH(CH_3)_2$	H	OAc	—	898
	$CH(CH_3)_2$	H	H	CH_3	H	Br	—	898
	CH_3	H	CH_3	H	CH_3	Cl	—	895
	CH_3	H	CH_3	H	CH_3	OAc	30	899
	CH_3	H	CH_3	H	CH_3	O_2CCF_3	—	900
	CH_3	HgOAc	CH_3	H	CH_3	OAc	—	895
	CH_3	H	CH_3	CH_3	H	OAc	30	899
	CH_3	CH_3	CH_3	CH_3	H	OAc	15	899
	CH_3	CH_3	CH_3	H	CH_3	OAc	60	899
	CH_3	CH_3	H	CH_3	CH_3	OAc	60	899
	CH_3	CH_3	HgCl	CH_3	CH_3	Cl	47	108
	CH_3	CH_3	HgO_2CCF_3	CH_3	CH_3	O_2CCF_3	81	900
	CH_3	CH_3	CH_3	CH_3	CH_3	OAc	80	899
	CH_3	CH_3	CH_3	CH_3	CH_3	O_2CCF_3	83	900
Aryl halides	F	H	H	H	H	Cl	11	901
	H	H	F	H	H	Cl	—	902
	F	H	F	H	F	Cl	61	903

Table 2.2. (continued)



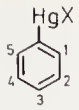
Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
	F	F	F	F	H	Cl	56	903
	F	F	F	F	H	O_2CCF_3	58	904
	HgO_2CCF_3	F	F	F	F	O_2CCF_3	89	904
	F	F	F	H	F	Ar	20	904
	F	F	F	H	F	Cl	64	903
	F	F	F	H	F	O_2CCF_3	23	904
	F	F	F	HgO_2CCF_3	F	O_2CCF_3	77	904
	F	F	H	F	F	Ar	35, 38	903, 905
	F	F	H	F	F	Cl	63	903
	F	F	H	F	F	OAc	38	905
	F	F	H	F	F	O_2CCF_3	71	905
	F	F	HgOAc	F	F	OAc	23	905
	F	F	HgO_2CCF_3	F	F	O_2CCF_3	68	905
	F	Br	F	H	F	Cl	59	903
	F	F	H	Br	F	Cl	49	903
	F	F	CH_3	F	F	Ar	76	903
	F	F	CH_3	F	F	Cl	78	903
	F	F	F	F	F	Ar	30–90	906–908
	F	F	F	F	F	Cl	60	903
	F	F	F	F	F	OAc	75	909
	F	F	F	F	F	O_2CCH_2F	71	909, 910
	F	F	F	F	F	O_2CCHF_2	69	909, 910
	F	F	F	F	F	O_2CCF_3	85	909, 910
	F	F	F	F	Br	Ar	52	903
	F	F	F	F	Br	Cl	78	903
	F	F	F	Br	F	Ar	64	903
	F	F	F	Br	F	Cl	73	903

Table 2.2. (continued)



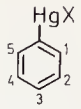
Arene	Functional groups and position of substitution					X	% Yield	Ref.
	1	2	3	4	5			
	F	F	Br	F	F	Ar	73	903
	F	F	Br	F	F	Cl	80	903
	H	H	Cl	H	H	Cl	89	875
	H	H	Cl	H	H	OAc	40,50	875, 911
	Cl	H	H	Cl	H	Ar	52	912, 913
	Cl	H	H	Cl	H	Cl	65	914
	Cl	H	H	Cl	H	OAc	50	914, 915
	H	Cl	Cl	H	H	Cl	—	895
	Cl	Cl	Cl	H	H	Ar	35	913
	Cl	H	Cl	Cl	H	Cl	60-80	916
	Cl	H	Cl	Cl	H	O_2CCF_3	70	917
	Cl	H	Cl	H	Cl	Ar	49	913
	Cl	Cl	Cl	Cl	H	Ar	30	913
	Cl	Cl	Cl	H	Cl	Ar	27	913
	Cl	Cl	H	Cl	Cl	Ar	25	913
	Cl	Cl	Cl	Cl	Cl	Ar	13-55	913, 918
	Cl	Cl	Cl	Cl	Cl	O_2CCH_2F	9	913
	Cl	Cl	Cl	Cl	Cl	O_2CCHF_2	10	913
	Cl	Cl	Cl	Cl	Cl	O_2CCF_3	91	913, 918
	Br	H	H	H	H	OAc	—	911
	H	Br	H	H	H	OAc	—	911
	H	H	Br	H	H	OAc	25	911
	Br	H	H	HgOAc	H	OAc	—	919
	H	H	I	H	H	Cl	—	902
	H	H	I	H	H	OAc	4	911
Phenols	OH	H	H	H	H	F	6	920
	OH	H	H	H	H	Cl	—,63	489-887, 920-925,
	OH	H	H	H	H	Br	21	920
	OH	H	H	H	H	I	4	920
	OH	H	H	H	H	OAc	—	926
	H	H	OH	H	H	F	3	920
	H	H	OH	H	H	Cl	—, 11, 12	489, 920-924

Table 2.2. (continued)



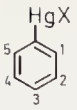
Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
	H	H	OH	H	H	Br	10	920
	H	H	OH	H	H	I	30	920
	H	H	OH	H	H	OAc	—	926
	OH	HgCl	H	HgCl	H	Cl	—	889
	OH	HgOAc	H	HgOAc	H	OAc	—	889
	OH	$HgNO_3$	H	$HgNO_3$	H	NO_3	—	889
	OH	HgCN	H	HgCN	H	CN	—	889
	OH	H	OH	H	H	Cl	—	489
	——— OHg ———		OH	HgOAc	H	OAc	— ?	927
	OH	H	OH	HgCl	H	Cl	—	489
	OH	$HgClO_4$	OH	$HgClO_4$	H	ClO_4	100	928
	OH	HgOH	OH	HgOH	OH	OH	—	929
Monoalkyl-phenols	OH	CH_3	H	H	H	OAc	16	930
	H	CH_3	OH	H	H	OAc	55	930
	OH	CH_3	H	HgOAc	H	OAc	88	930
	OH	H	CH_3	H	H	OAc	2-5	931
	CH_3	H	OH	H	H	OAc	—	888, 931
	OH	H	H	H	CH_3	OAc	— ?	888
	CH_3	HgOAc	OH	H	H	OAc	60-90	931
	OH	H	CH_3	HgOAc	H	OAc	—	931
	OH	H	H	CH_3	H	OAc	—	932-934
	OH	H	H	$C(CH_3)_3$	H	OAc	—	935
	OH	HgOAc	H	$C(CH_3)_3$	H	OAc	—	935
	OH	H	H	$(CH_2)_2CH(CH_3)_2$	H	OAc	—	935
	OH	HgOAc	H	$(CH_2)_2CH(CH_3)_2$	H	OAc	~100	935
	OH	HgOAc	H		H	OAc	—	936
	OH		H	HgOAc	H	OAc	—	936
	OH	H	H	n-C_8H_{17}	H	OAc	80	937
	OH	HgOAc	H	n-C_8H_{17}	H	OAc	90	937
	OH	H	OH	CH_2CH_3	H	OAc	—	927
	OH	HgCl	OH	CH_2CH_3	H	Cl	—	927
	OH	H	OH	n-C_6H_{13}	H	OAc	—	927
	OH	HgCl	OH	n-C_6H_{13}	H	Cl	—	927
	OH	HgOAc	H	n-C_8H_{17}	H	OAc	75	937

Table 2.2. (continued)



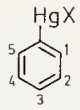
Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
Dialkyl-phenols	OH	$CH(CH_3)_2$	H	H	CH_3	Cl	—	938
	OH	$CH(CH_3)_2$	H	H	CH_3	OAc	—	939
	CH_3	H	OH	$CH(CH_3)_2$	H	Cl	—	489, 938
	CH_3	H	OH	$CH(CH_3)_2$	H	OAc	—	939
	CH_3	HgCl	OH	$CH(CH_3)_2$	H	Cl	—	489, 939
	CH_3	HgOAc	OH	$CH(CH_3)_2$	H	OAc	—	939, 940
	OH	CH_3	H	H	$CH(CH_3)_2$	Cl	—?	938
	OH	CH_3	H	H	$CH(CH_3)_2$	OAc	—?	935, 941
	$CH(CH_3)_2$	HgCl	OH	CH_3	H	Cl	—	941
	$CH(CH_3)_2$	HgOAc	OH	CH_3	H	OAc	—	935
	OH	CH_3	H	$C(CH_3)_3$	H	OAc	90	942
	OH	CH_3	H	n-C_8H_{17}	H	OAc	80	937
	H	$C(CH_3)_3$	OH	$C(CH_3)_3$	H	OAc	95	943
	4-acetoxymercurio-17 β-estradiol					OAc	38	944
Halo-phenols	OH	H	H	F	H	Cl	—	901
	F	F	OH	F	F	Ar	73	903
	F	F	OH	F	F	Cl	31	903
	OH	Cl	H	HgOAc	H	OAc	—	919
	OH	H	H	Cl	H	Cl	—	895
	OH	H	H	Cl	H	OAc	74	888, 893, 895, 945
	OH	HgOAc	H	Cl	H	OAc	99	888, 919
	OH	Cl	H	Cl	H	Cl	—	895
	OH	H	H	Br	H	OAc	—	945
	OH	H	H	Br	H	C_6H_5	—	946
	OH	HgC_6H_5	H	Br	H	C_6H_5	—	946
	OH	HgOAc	OH	Cl	H	OAc	—	934
Alkylhalo-phenols	OH	HgOAc	CH_3	Cl	H	OAc	66	888

Table 2.2. (continued)



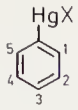
Arene	Functionol groups ond position of substitution 1	2	3	4	5	X	% Yield	Ref.
	OH	Cl	H	n-C_3H_7	H	OAc	—	947, 948
	OH	n-C_4H_9	H	Br	H	OAc	48	888
	OH	n-C_4H_9	H	Cl	OH	OAc	—	947, 949
	OH	n-C_5H_{11}	H	Cl	OH	OAc	—	947, 949
	OH	n-C_6H_{13}	H	Cl	OH	OAc	—	947, 949
	CH_3	Cl	CH_3	H	OH	OAc	—	950
	CH_3	Br	CH_3	H	OH	OAc	100	950
	OH	CH_3	H	Br	CH_3	OAc	91	950
	OH	CH_3	H	I	CH_3	OAc	80-90	950
	OH	I	CH_3	Cl	CH_3	OAc	—	950
	OH	$CH(CH_3)_2$	H	Cl	CH_3	OAc	—	947, 951
	OH	CH_3	H	Cl	$CH(CH_3)_2$	OH	—	947
	CH_3	I	OH	$CH(CH_3)_2$	H	OAc	—	952
Nitro-phenols	OH	NO_2	H	H	H	Cl, OAc	—?	938, 953
	H	NO_2	OH	H	H	Cl	—	954
	H	NO_2	OH	H	H	OAc	—	953, 955
	H	NO_2	OH	H	H	NHAc, OH	—	929
	OH	NO_2	H	HgOAc	H	OAc	—	919, 953, 955
	OH	NO_2	H	HgC_6H_5	H	C_6H_5	—	946
	OH	H	H	H	NO_2	OAc	—	919
	OH	H	H	NO_2	H	Cl	—	938, 954
	OH	H	H	NO_2	H	OAc	—	953
	OH	H	H	NO_2	H	NHAc, OH	—	929
	OH	HgOAc	H	NO_2	H	OAc	—	919, 956
	OH	HgC_6H_5	H	NO_2	H	C_6H_5	—	946, 957
	OH	NO_2	H	NO_2	H	Cl	—	954
	OH	NO_2	H	NO_2	H	OAc	—	919, 956, 958

Table 2.2. (continued)



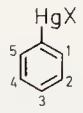
Arene	Functional groups and position of substitution						% Yield	Ref.
	1	2	3	4	5	X		
	OH	NO_2	H	H	NO_2	OAc	—	958
	NO_2	H	OH	NO_2	H	OAc	—	958
	NO_2	HgOAc	OH	NO_2	H	OAc	—	958
	H	NO_2	OH	NO_2	H	OAc	—	919, 958
	NO_2	OH	NO_2	H	NO_2	Cl	—	954
	NO_2	OH	NO_2	H	NO_2	C_6H_5	—	946
	OH	NO_2	OH	H	H	OAc	—	955
	OH	H	OH	NO_2	H	OAc	—	959
	OH	NO_2	OH	NO_2	H	OAc	—	959
Alkylnitro-phenols	OH	NO_2	H	CH_3	H	OAc	—	960
	OH	CH_3	H	NO_2	H	OAc	—	961
	OH	HgOAc	CH_3	NO_2	H	OAc	—	962
	OH	NO_2	CH_3	HgOAc	H	OAc	—	962
	OH	NO_2	H	n-C_3H_7	H	OAc	—	948
	OH	NO_2	H	n-C_3H_7	H	OH	—	947
	OH	NO_2	H	$C(CH_3)_3$	H	OAc	—	947
	OH	NO_2	H	t-C_5H_{11}	H	OAc	—	947
	CH_3	NO_2	OH	CH_3	H	OAc	—	947
	OH	$CH(CH_3)_2$	H	NO_2	CH_3	OAc	—	947
Alkoxy-phenols	OH	OCH_3	H	HgOAc	H	OAc	—	963, 964
	OH	OCH_2CH_2OH	H	H	H	Cl	—	963
	OH	H	OCH_2CH_2OH	H	H	Cl	—	963
	OH	HgCl	OCH_2CH_2OH	H	H	Cl	—	963
	OH	H	——— OCH_2O ———		H	Cl	—	965
	OH	H	H	OCH_2CH_2OH	H	Cl	—	963
	OH	HgOAc	H	OCH_2CH_2OH	H	OAc	—	963

Table 2.2. (continued)



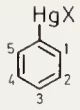
Arene	Functional groups and position of substitution						% Yield	Ref.
	1	2	3	4	5	X		
Other monosubstituted phenols	OH	H	$N(CH_3)_2$	H	H	OAc	92	966
	OH	HgOAc	H	$N(CH_3)_3OAc$	H	OAc	—	966
	OH	CH_2OAc	H	HgOAc	H	OAc	—	967
	OH	CHO	H	HgOAc	H	OAc	69	968, 969
	OH	H	H	H	CHO	OAc	—	970
	OH	HgOAc	H	CHO	H	OAc	—	968
	OH	H	H	CO_2H	H	OAc	—	945
	H	CO_2H	OH	H	H	SO_4	—	971
	OH	HgOAc	H	CO_2H	H	OAc	—	888
	OH	CO_2CH_3	H	H	H	OAc, Cl	—	972
	OH	$CO_2C_2H_5$	H	H	H	OAc	~100	972
	OH	H	H	CO_2CH_3	H	OAc	—	945
	OH	H	H	SC_6H_5	H	OAc	—	973
	OH	HgOAc	H	SC_6H_5	H	OAc	—	973
	OH	HgOAc	H	SO_3No	H	OAc	—	974
	OH	HgOAc	OH	CHO	H	OAc	—	975
Polysubstituted phenols	OH	CH_3	H	HgOAc	NHAc	OAc	—	976
	H	CH_3	OH	NHAc	H	OAc	—	976
	CH_3	HgOAc	OH	NHAc	H	OAc	—	976
	OH	HgOAc	CH_3	NHAc	H	OAc	—	976
	OH	$CH(CH_3)_2$	H	NO	CH_3	OAc	—	951
	OH	H	——— OCH_2O ———		H	Cl	—	965
	OH	OCH_3	H	H	NO_2	OAc	—	977
	OH	OCH_3	H	HgOAc	NO_2	OAc	—	977
	OH	CHO	H	$C(CH_3)_3$	H	OAc	73	935
	OH	CHO	H	$(CH_2)_2CH(CH_3)_2$	H	OAc	85	935
	OH	CH_3	H	CHO	$CH(CH_3)_2$	OAc	50	935

Table 2.2. (continued)



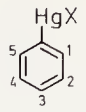
Arene	Functional groups and position of substitution						% Yield	Ref.
	1	2	3	4	5	X		
	OH	$CH(CH_3)_2$	H	CHO	CH_3	OAc	—	935
	OH	OCH_3	H	CHO	H	OH, OAc	—	893, 939, 975, 978, 979
	OH	OCH_3	H	H	CHO	OAc	—	975
	OH	CHO	H	H	OCH_3	OAc	—	975
	OH	CHO	H	OCH_3	H	Cl	—	975
	H	OCH_3	OH	CHO	H	OAc	—	975
	OCH_3	OH	OCH_3	H	CHO	Br	—	980
	OH	CHO	H	NO_2	H	OAc	—	969
	OH	HgCl	CHO	NO_2	H	Cl	—	970
	OH	NO_2	H	CHO	H	Cl, OAc	—	970
	CHO	HgX	OH	NO_2	H	Cl, O_2CH	—	970
	OH	NO_2	CHO	HgOAc	H	OAc	—	970
	H	CH_3	OH	CO_2K	H	CN	—	981
	OH	C_2H_5	H	CO_2H	OH	OH	100	982
	OH	NHAc	H	CO_2H	H	OH	—	983
	OCH_3	OH	OCH_3	H	CO_2H	Cl	—	980
	OH	CO_2H	H	NO_2	H	Cl	—	955
	OH	NH_2	H	AsO_3H_2	H	OAc	—	984
	OH	NHAc	H	AsO_3H_2	H	OH	—	983, 985
	NH_2	OH	NH_2	H	AsO_3H_2	OAc	—	984
	NHAc	OH	NHAc	H	AsO_3H_2	Cl, OAc	70	984, 985
	OH	NO_2	H	AsO_3H_2	H	OAc	—	984, 986
	NO_2	OH	NO_2	H	AsO_3H_2	OAc	—	984
Anilines	NH_2	H	H	H	H	OAc	—	987, 988
	H	H	NH_2	H	H	Cl, OAc	—, 64	987-990
	NH_2	H	H	HgOAc	H	OAc	80, 94	990-992
	NH_2	$HgHSO_4$	H	$HgHSO_4$	H	HSO_4	—	993

Table 2.2. (continued)



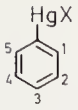
Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
	H	H	NHC_2H_5	H	H	OAc	—	989
	H	H	$NHC(CH_3)_3$	H	H	OAc	51	994
	$NHCH_2CO_2C_2H_5$	H	H	H	H	OAc	82	995
	$NHCHCH_3CO_2C_2H_5$	H	H	H	H	OAc	68?	995
	$NHCHRCO_2C_2H_5$ (R = CH_3, C_2H_5, i-C_3H_7)	H	H	HgOAc	H	OAc	80–86	995
	H	H	$N(CH_3)_2$	H	H	OAc	—, 82	987, 989, 996
	H	H	$N(CH_3)_2$	H	H	$C(NO_2)_3$	—	884
	H	H	$N(CH_3)(C_2H_5)$	H	H	OAc	85	996
	H	H	$N(C_2H_5)_2$	H	H	Cl	—	895
	H	H	$N(C_2H_5)CH_2C_6H_5$	H	H	OAc	72	996
	H	H	$N(n$-$C_3H_7)_2$	H	H	OAc	90	996
	H	H	$N(n$-$C_4H_9)_2$	H	H	OAc	91	996
Methyl-anilines	H	CH_3	NH_2	H	H	Cl, OAc	80, 100	997–1000
	NH_2	CH_3	H	H	H	OAc	72?	990
	NH_2	CH_3	H	HgOAc	H	OAc	50–100	990, 997, 999–1001
	HgOAc	CH_3	NH_2	H	H	OAc	—?	1000, 1001
	CH_3	NH_2	HgOAc	HgOAc	H	OAc	—?	1001
	$NHCH_2CO_2C_2H_5$	CH_3	H	HgOAc	H	OAc	83	997
	NH_2	H	CH_3	H	H	OAc	64?	999
	CH_3	H	NH_2	H	H	OAc	—?	1002
	CH_3	H	NH_2	HgOAc	H	OAc	—, 71	997–999, 1002
	CH_3	HgOAc	NH_2	HgOAc	H	OAc	94	997
	$NHCH_2CO_2C_2H_5$	HgOAc	CH_3	HgOAc	H	OAc	20	997
	NH_2	H	H	CH_3	H	Cl	—	998
	NH_2	H	H	CH_3	H	OAc	63, 78, 92	990, 997–999, 1003, 1004

Table 2.2. (continued)



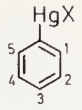
Arene	Functional groups and position of substitution						% Yield	Ref.
	1	2	3	4	5	X		
	NH_2	HgOAc	H	CH_3	H	OAc	80, 100	999, 1005
	$NHCH_2CO_2C_2H_5$	H	H	CH_3	H	OAc	80	997
	NH_2	CH_3	H	CH_3	H	OAc	99	999
	CH_3	H	NH_2	CH_3	H	OAc	64	999
	CH_3	HgOAc	NH_2	CH_3	H	OAc	87	999
	CH_3	NH_2	CH_3	H	CH_3	OAc	—	999
	CH_3	CH_3	NH_2	CH_3	CH_3	OAc	92, 100	999, 1006
Halo-anilines	F	F	NH_2	F	F	Ar	71	903
	F	F	NH_2	F	F	Cl	69	903
	H	Cl	NH_2	H	H	OAc	—, 68	990, 1000, 1007
	NH_2	Cl	H	H	H	OAc	—	1000
	NH_2	Cl	H	HgOAc	H	OAc	—	1000, 1007
	HgOAc	H	Cl	NH_2	H	OAc	—	1000
	Cl	H	NH_2	H	H	OAc	—	1008
	Cl	H	NH_2	HgOAc	H	OAc	—	1008
	Cl	HgOAc	NH_2	HgOAc	H	OAc	—	1009
	NH_2	H	H	Cl	H	OAc	—, 61	990, 998, 1002
	NH_2	Cl	H	Cl	H	OAc	—	1010
	H	Br	NH_2	H	H	OAc	—	1000, 1011
	NH_2	Br	H	HgOAc	H	OAc	—	1000
	Br	H	NH_2	H	H	OAc	—	1012
	NH_2	H	Br	HgOAc	H	OAc	—	1013
	NH_2	HgOAc	Br	HgOAc	H	OAc	—	1012
	NH_2	H	H	Br	H	OAc	—	1014
	H	I	NH_2	H	H	OAc	—	1015
	I	H	NH_2	H	H	OAc	—	1008, 1013
	I	H	NH_2	HgOAc	H	OAc	—	1013

Table 2.2. (continued)



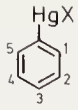
Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
	NH_2	H	HgOAc	H	I	OAc	—?	1013
	NH_2	HgOAc	I	HgOAc	H	OAc	—	1008
	NH_2	H	H	I	H	OAc	—	1015
Nitro-anilines	H	NO_2	NH_2	H	H	OAc	—,54	990, 998, 1016
	H	NO_2	$N(CH_3)_2$	H	H	OAc	—	1017
	NO_2	H	NH_2	H	H	OAc	—,67	990, 1016
	NO_2	H	NH_2	HgOAc	H	OAc	—	1016
	NO_2	H	$N(CH_3)_2$	H	H	OAc	—	1017
	NH_2	H	H	NO_2	H	OAc	—,70	990, 1016
	NH_2	HgOAc	H	NO_2	H	OAc	—	990, 1016
	$NHCH_3$	H	H	NO_2	H	OAc	—	1017
	NHC_2H_5	H	H	NO_2	H	OAc	—	1017
Other mono-substituted anilines	—— $NHC(CH_3)_2CH_2$ ——		H	HgOAc	H	OAc	—	994
	— $NHC(CH_3)_2CH_2CH(CH_3)$ —		H	HgOAc	H	OAc	—	994
	NH_2	H	H	OCH_3	H	Cl, Br, I	—	998, 1018
	NH_2	H	H	OCH_2CH_2OH	H	Cl	—	963
	OAc	H	$N(CH_3)_2$	H	H	OAc	78	966
	CO_2H	H	NH_2	H	H	OH	—	1019
	CO_2^-	H	H	NH_2	H	$-O_2C$	72	1020
	H	CO_2CH_3	NH_2	H	H	Cl	—	998
	H	CO_2CH_3	NH_2	H	H	OAc	90	998, 1021
	NH_2	CO_2CH_3	H	HgOAc	H	OAc	—	1021
	H	$CO_2C_2H_5$	NH_2	H	H	Cl, OAc	—	998
	H	CO_2CH_3	$NHCH_3$	H	H	OAc	97	1021
	H	CO_2CH_3	NHC_2H_5	H	H	OAc	100	1021
	H	CO_2CH_3	$N(CH_3)_2$	H	H	OAc	77	1021
	NH_2	H	H	$CO_2C_2H_5$	H	Cl, OAc	94,—	1022

Table 2.2. (continued)



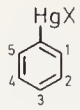
Arene	Functional groups and position of substitution						% Yield	Ref.
	1	2	3	4	5	X		
	NH_2	HgOAc	H	$CO_2C_2H_5$	H	OAc	—	1022
	NH_2	H	H	SO_2NH_2	H	Cl	—	1023
	NH_2	H	H	SO_2NH_2	H	OAc	—?	1024, 1025
	NH_2	HgCl	H	SO_2NH_2	H	Cl	—	1023
	NH_2	HgOAc	H	SO_2NH_2	H	OAc	—?	1024
	NH_2	HgCl	$N(CH_3)_3OAc$	H	H	Cl	—?	966
Polysubstituted anilines	NH_2	CH_3	H	NO_2	H	OAc	—	1026
	NO_2	H	NH_2	CH_3	H	OAc	—	1026
	NH_2	H	CH_3	NO_2	H	OAc	—?	1026
	NH_2	H	NO_2	CH_3	H	OAc	—	1026
	NH_2	Br	H	AsO_3H_2	H	OAc	—	984
Acetanilides	NHAc	H	H	HgOAc	H	OAc	—	1027
	NHAc	HgOAc	H	HgOAc	H	OAc	—	1028
	NHAc	HgOAc	HgOAc	HgOAc	H	OAc	—	1029, 1030
	NHAc	HgOAc	HgOAc	HgOAc	HgOAc	OAc	—	1030, 1031
	H	CH_3	NHAc	H	H	OAc	28	997
	NHAc	CH_3	HgOAc	HgOAc	HgOAc	OAc	—	1032
	CH_3	H	NHAc	H	H	Cl, OAc	—, 20	997
	NHAc	H	H	CH_3	H	OAc	—	997, 1033
	NHAc	H	H	OCH_3	H	OAc	—	1034
	OCH_3	HgOAc	HgOAc	NHAc	H	OAc	—	1034
	NHAc	HgOAc	HgOAc	OCH_3	HgOAc	OAc	—	1034
	NHAc	H	H	OC_2H_5	H	OAc	—	1035
	NHAc	HgOAc	HgOAc	OC_2H_5	HgOAc	OAc	—	1036
	CO_2H	H	NHAc	H	H	OH	—?	1019
	NHAc	H	H	CO_2H	H	OH	—?	1019
	H	CO_2CH_3	NHAc	H	H	Cl, OAc	—	1021

Table 2.2. (continued)



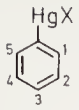
Arene	Functional groups and position of substitution						% Yield	Ref.
	1	2	3	4	5	X		
	NHAc	HgOAc	H	SO_2NHAc	H	OAc	—	1037
	NHAc	HgOAc	H	$SO_2C_3H_6N_3O$	H	OAc	—	1037
Aryl ethers	OCH_3	H	H	H	H	Cl	1	489, 1038
	H	H	OCH_3	H	H	Cl	51	1038, 1039
	H	H	OCH_3	H	H	OAc	15,37	489, 1038, 1040
	OCH_3	H	H	HgOAc	H	OAc	—	932
	OCH_3	H	H	$HgHSO_4$	H	HSO_4	—	993
	H	H	OC_2H_5	H	H	Br	—	1039
	H	H	OC_2H_5	H	H	OAc	—	489
	OC_2H_5	H	H	HgOAc	H	OAc	—	932
	H	H	$OCH_2CH{=}CH_2$	H	H	Cl	57	1041
	H	H	OCH_2CH_2OH	H	H	Cl, OAc	—	963
	H	H	$(OCH_2CH_2)_2OH$	H	H	Cl, OAc	—	963
	H	H	$OCH_2Si(OCH_3)_3$	H	H	OAc	100?	1042
	$OCH_2Si(OCH_3)_3$	H	H	HgOAc	H	OAc	100?	1042
	H	H	$OCH_2Si(C_2H_5)_3$	H	H	OAc	100?	1042
	H	H	$O(CH_2)_3Si(OCH_3)_3$	H	H	OAc	100?	1042
	$O(CH_2)_3Si(OCH_3)_3$	H	H	HgOAc	H	OAc	100	1042
	OCH_3	H	H	OCH_3	H	Cl	35	1043
	OCH_3	H	OCH_3	HgOAc	H	OAc	—	966
	OCH_2CH_2OH	H	OCH_2CH_2OH	HgOAc	H	OAc	—	963
	OCH_2CH_2OH	H	HgOAc	OCH_2CH_2OH	H	OAc	—	963
Substituted aryl ethers	OCH_3	H	H	CH_3	H	Cl	—	1039
	OR (R = C_3H_7 through C_7H_{15}, $C_{12}H_{25}$, $C_{16}H_{33}$)	H	H	CH_3	H	OAc	32-49	1044
	H	CH_3	OR (R = C_3H_7 through C_7H_{15}, $C_{12}H_{25}$, $C_{16}H_{33}$)	H	H	OAc	31-48	1044
	$OCH_2Si(OC_2H_5)_3$	H	H	CH_3	H	OAc	100	1042

Table 2.2. (continued)



Arene	Functional groups and position of substitution 1	2	3	4	5	X	% Yield	Ref.
	$O(CH_2)_nSiR_3$	H	H	R'	H	X	—	1045
	(n = 1,3; R = alkyl, aryl; R' = H, CH_3, CH_3O, halogen; X = OAc, halogen)							
	CH_3	H	H	OCH_2CH_2OH	H	Cl	—?	963
	CH_3	HgCl	H	OCH_2CH_2OH	H	Cl	—?	963
	Br	H	H	OCH_2CH_2OH	H	Cl	—?	963
	F	F	OCH_3	F	F	Ar	54, 72	903, 904
	F	F	OCH_3	F	F	Cl	72	903
	F	F	OCH_3	F	F	O_2CCF_3	71	904
	F	F	OCH_3	F	F	O_3SCF_3	40	904
	H	NO_2	OCH_3	H	H	Cl	—	895
	H	NO_2	OCH_3	H	H	OAc	50	888
	H	NO_2	OCH_3	H	H	NO_3	—	888
	OCH_3	OCH_3	OCH_3	H	CHO	OAc	80	980
	OCH_3	OCH_3	OCH_3	H	CO_2H	OAc	—	980
Nitro-arenes	NO_2	H	H	H	H	Cl	—	987, 1046
	H	NO_2	H	H	H	Cl	—	67, 895, 1047
	H	NO_2	H	H	H	Br	91	1047
	H	NO_2	H	HgCl	H	Cl	—	895
	H	NO_2	CH_3	H	H	Cl	—	1048
	NO_2	H	CH_3	H	H	Cl	—	1049
	H	NO_2	H	CH_3	H	Cl	—	1049
	NO_2	F	F	F	F	Ar	70	903
	NO_2	F	F	F	F	Cl	14	903
	NO_2	F	F	F	F	O_2CCF_3	47	904
	F	NO_2	F	F	F	Ar	70	903
	F	NO_2	F	F	F	Cl	50	903
	H	NO_2	Cl	H	H	Cl	—	895
	H	NO_2	Cl	Cl	H	Cl	—	895
	NO_2	Cl	Cl	Cl	Cl	Ar	—	1050

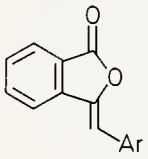
Table 2.2. (continued)



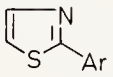
Arene	Functional groups and position of substitution					X	% Yield	Ref.
	1	2	3	4	5			
	Cl	NO_2	Cl	Cl	Cl	Ar	—	1050
	Cl	Cl	NO_2	Cl	Cl	Ar	—	1050
Other monosubstituted arenes	H	H	$NHCONH_2$	H	H	OAc	—	1051
	H	H	$NHCSNH_2$	H	H	OAc	—	1051
	H	H	SCH_3	H	H	OAc	—,37	1052, 1053
	H	CHO	H	H	H	Cl	—	895
	H	H	$N{=}C_{12}H_{11}NO_4$	H	H	OAc	—	1054
	H	CO_2H	H	H	H	Cl	—	895, 993, 1047
	CO_2CH_3	H	H	H	H	Cl	—	972
	$CONH_2$	H	H	H	H	OAc	—	894
	H	$N(CH_3)_3NO_3$	H	H	H	OAc	—	894
Other polysubstituted arenes	COCl	H	H	COCl	H	Cl	—	1055
	F	CO_2H	F	F	F	Cl	79	903
	AsO_3H_2	H	H	CO_2H	H	OAc	—	984
	SH	H	H	NO_2	H	Cl	—	1056
	H	NO_2	SH	H	H	Cl	—	1056
	CH_3	H	H	SO_3H	H	OAc	—	1057
	$NHCONH_2$	H	H	CH_3	H	OAc	—	1051
	$NHCSNH_2$	H	H	CH_3	H	OAc	—	1051
	$NHCONH_2$	H	H	Cl	H	OAc	—	1051
	Br	H	$NHCSNH_2$	H	H	OAc	—	1058
	$NHNH_2$	H	H	Br	H	OAc	—	1059
	$NHNH_2$	H	H	NO_2	H	OAc	—	1059
	$NHN{=}CHC_6H_4X$-*p* (X = H, CH_3, Cl, CH_3O, NO_2)	H	H	Br	H	OAc	20-80	1059
	$NHN{=}CHC_6H_4X$-*p* (X = CH_3, Cl, OCH_3)	H	H	NO_2	H	OAc	35-80	1059-1062
	NH_3OAc	HgOAc	HgOAc	$N(CH_3)_3OAc$	H	OAc	78	1063

and the di- and triols, monoalkyl-, dialkyl-, halo-, alkylhalo-, nitro-, alkylnitro-, alkoxy- and finally other mono- and polysubstituted phenols. The anilines are tabulated next using a similar system. Acetanilides are included separately in the section following anilines. Aryl ethers, nitroarenes, and other mono- and polysubstituted arenes close out Table 2.2. Within these latter groups alkyl-, halo- and nitro- groups have been considered simply as substituents. In cases where the arene in question undergoes di- or polymercuration, these mercurials are listed immediately following the corresponding monomercurated product. If the arylmercurial sought contains several substituents, the reader is advised to look under all possible subtitles to assure that the desired compound is found. The yields of organomercurials are also included in Table 2.2 where that data has been calculated as a percent yield in the original publication. In many instances the yields are available, but only on a weight basis and this data has not been tabulated.

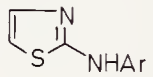
In a number of cases where more complicated substituents are involved, Table 2.2 does not afford sufficient space to adequately designate the substituent. This is particularly true of arenes substituted by the following heterocyclic systems whose references are included below.



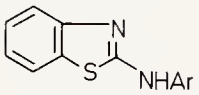
Ref. 541



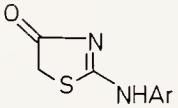
1064



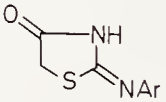
1065-1076



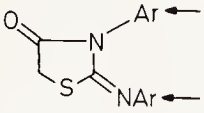
Ref. 1077



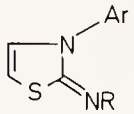
1078, 1079



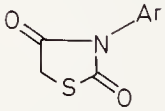
1076, 1080



Ref. 1081, 1082



1083-1085



1086-1090

In Table 2.3 all arylmercurials of known structure possessing a polynuclear carbocyclic aromatic system have been collected, starting with naphthalene and working up to compounds containing four rings. Where the structure is questionable, a question mark has been placed in front of the corresponding reference(s). Since very few yields have been reported on a percent basis, this information has been omitted. The mercuration of aromatic polymers such as polystyrene [1133–1135] and polyvinylthiophene [1134] has been omitted, although the halogenation of these compounds provides an interesting route to the corresponding halogenated polymers.

Table 2.4 contains all known examples of mercurated aromatic heterocycles starting with those of oxygen and proceeding through sulfur, selenium and nitrogen heterocycles. These compounds are listed according to in-

Table 2.3. Arylmercurials Available via Mercuration of Polynuclear Arenes

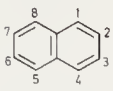
Arene	Functional Groups and Position of Substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgCl										987
	HgOAc										987, 1091
	HgOAc	Br									1092
	OH	HgCl									? 938
	OH			HgOH							? 929
	OH	HgOAc		HgOAc							1092
	HgOAc	OH									939, 1092, 1093
	HgOH	OH									929
	OH	NO_2		HgOAc							1092, 1094
	OH	HgOAc		NO_2							1092, 1094
	OH			HgOAc		NO_2					1095
	OH	NO_2		NO_2				HgOAc			? 1094
	Hg	OH	CO_2								? 1093, 1096
	OH	HgOAc		SO_3Na							1093
	HgOAc	OH				SO_3Na					1093
	OH	$N_2C_6H_5$		HgOAc							? 1097
	OH	NO_2		$N_2C_6H_5$				HgOAc			? 1097
	OH	$N_2C_6H_5$		NO_2				HgOAc			? 1097
	OH	$N_2C_6H_5$		$N_2C_6H_5$				HgOAc			? 1097
	NH_2	HgOAc		HgOAc							990, 998, 1093
	HgOAc	NH_2									990, 1093
	HgOAc	NH	(di-β-naphthylamine)								1092
	NH_2	NO_2		HgOAc							1098
	NH_2	HgOAc	NO_2								1099
	NH_2	HgOAc	NO_2	HgOAc							1099
	NH_2	HgOAc		NO_2							1100

Table 2.3. (continued)

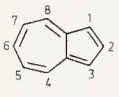
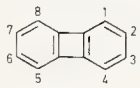
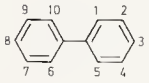
Arene	Functional Groups and Position of Substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	NH_2	HgOAc			NO_2						1101
	NH_2			HgOAc		NO_2					1102
	NO_2	NH_2	HgOAc								1103
	NH_3^+	HgOAc		HgOAc		SO_3^-					1093
	$NHCONH_2$	HgOAc		HgOAc							? 1051
	HgOAc	$NHCONH_2$	HgOAc								? 1051
	HgOAc	OCH_3									1040
	$HgNO_3$	OCH_3									1104
	HgOAc			OCH_3							1040
	HgOAc	OC_2H_5									1092
	HgOH				CO_2H						? 1105
	HgCl										1106
	HgOAc		HgOAc								1107
	HgCl		HgCl								1108
		HgOAc									1109
			HgCl								895
	F	F	HgCl	F	F	F	F	H	F	F	903
		HgOAc	OH	Br							? 1033
	OH	HgOAc		Br							1110
		HgOAc	OH	NO_2							1110
	OH	HgOAc		HgOAc				NO_2			? 1110
	OH	NO_2	HgOAc	NO_2							1110
	HgOAc	NO_2	HgOAc	NO_2	OH						1110
		HgOAc	OH				HgOAc	OH			1111, 1112
		HgOAc	OH	HgOAc			HgOAc	OH	HgOAc		1112
	OH	HgOAc		HgOAc		OH	HgOAc		HgOAc		1112

Table 2.3. (continued)

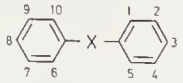
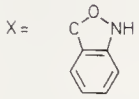
Arene	Functional Groups and Position of Substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	NH_2			HgOAc							1033
		HgOAc	NHAc								1033
											
X = CH_2	OH	HgOAc		HgOAc							936
		HgOAc	OH	HgOAc							936
		HgOAc	OH	CO_2H			HgOAc	OH	CO_2H		937
X = $C(CH_2)_5$		HgOAc	OH	HgOAc			HgOAc	OH	HgOAc		937
		HgOAc	OH	CH_3			HgOAc	OH	CH_3		937
X = 	Many examples of unknown structure, see ref. 1113										1113
X = C=O	HgCl										489, 1114
	HgBr										489
X = CH=CH	HgCl										1115
		HgCl									1115
			HgCl								1115
			HgOAc					HgOAc			1115
X = O			HgOAc								101
			HgOAc					HgOAc			101
			HgOAc					Br			101
			HgOAc					I			101
			HgOAc					$C_6H_5CO_2$			101
X = S			HgOAc								1053, 1116
X = SO_2	HgCl										1117
X = NH	HgCl		HgCl			HgCl		HgCl			? 1118
X = N=N	HgCl										1119, 1120
	HgCl				CH_3						1119, 1120
	HgOAc				CH_3						1121

Table 2.3. (continued)

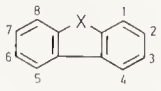
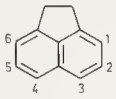
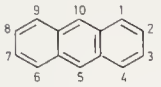
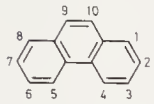
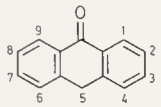
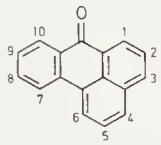
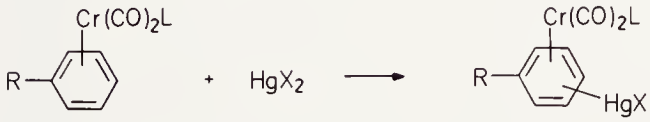
Arene	Functional Groups and Position of Substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgCl				CH_3	CH_3					1120
	HgCl				CH_3	HgCl				CH_3	1120
	HgCl		CH_3					CH_3			1122
	HgCl					CH_3				CH_3	1120
	HgCl				Cl						1120
	HgCl					Cl					1120
	HgCl				I						1119, 1120
	HgCl					I					1119, 1120
	HgCl				NO_2						1120
	HgCl					NO_2					1120
	HgCl				CN						1120
	HgCl					OCH_3					1120
	HgCl				OCH_3	OCH_3					1120
		HgCl	OH	HgCl							1123
	OH	HgOAc		CH_3							1123
		HgOAc	OH	HgOAc		Br		Br		Br	1123
		HgOAc	OH	NO_2							1123
	HgCl										1124
			HgCl								1124
	HgCl		Br								1125
	Br		HgCl								1125
		HgOAc									1126
		HgCl					HgCl				1127
			NH_2	HgOAc							1128
X = C=O	HgOAc										894

Table 2.3. (continued)

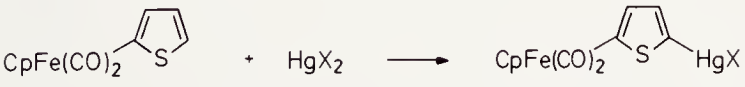
Arene	Functional Groups and Position of Substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
			HgCl								1129, 1130
					HgCl						187
	HgCl										1129, 1130
			HgCl								1129, 1130
									HgCl		1129, 1130
					Hg (dialkyl or diarylmercurial ?)						? 1131
				HgOAc							? 1132

creasing ring size and grouped according to their substituents much as before. Yields have been omitted. Question marks preceding the references indicate structures which appear questionable.

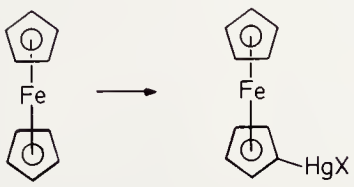
A significant number of aromatic organometallic compounds have also been mercurated. For example, π-complexed arene chromium carbonyl complexes [1283–1285] (Eq. 248) and σ-bonded iron carbonyl complexes [1106, 1286] (Eq. 249) afford organomercurials. Most extensively studied are the ferrocenes (Eq. 250) [1287–1301]. Mono-, di- and polymercurated



(248)



(249)



(250)

Table 2.4. Arylmercurials Available via Mercuration of Heterocyclic Compounds

Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgCl										1136
	HgCl			HgCl							1136
	HgOCN										1137
	HgOCN			HgOCN							1137
	HgOAc	HgOAc	HgOAc	HgOAc							1138
	HgCl	HgCl	HgCl	HgCl							1136
	HgCl			CH_3							1136
	HgOCN			CH_3							1137
	HgCl			C_2H_5							1139
	HgCl			n-C_3H_7							1139, 1140
	HgCl			i-C_3H_7							1140
	HgCl			n-C_4H_9							1140
	HgCl			i-C_4H_9							1140
	HgCl			sec-C_4H_9							1140
	HgCl			t-C_4H_9							1140
	HgCl			n-C_5H_{11}							1141
	HgCl			$CH_2C_6H_5$							1139
	CH_3	HgCl		CH_3							1142
	HgCl	CH_3		CH_3							1142, 1143
	HgCl	CH_3		n-C_3H_7							1143
	HgCl	CH_3		C_6H_5							1142, 1143
	HgCl	C_6H_5		CH_3							1142
	HgCl	CH_3	CH_3	CH_3							1142, 1143
	CH_3	HgCl	CH_3	CH_3							1142, 1143
	CH_3	HgCl	C_2H_5	CH_3							1142, 1143
	CH_3	HgCl	CH_3	C_2H_5							1142
	CH_3	HgCl	n-C_3H_7	CH_3							1142
	HgCl	CH_3	$-CH_2CH_2CH(CH_3)CH_2-$								1144
	CH_3	HgCl	$-(CH_2)_4-$								1143
	C_2H_5	HgCl	$-(CH_2)_4-$								1142, 1143

Table 2.4. (continued)

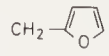
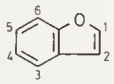
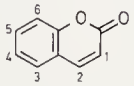
Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	C_6H_5	HgCl	———	$(CH_2)_4$ ———							1142, 1143
	HgCl			CH_2– 							1136
	HgCl			CH_2OH							1145, 1146
	HgCl			$CH_2NHCOC_6H_5$							1147
	HgOAc	HgOAc	HgOAc	$CH(OAc)_2$							?1148
	HgCl			CH_2COCH_3							1149
	HgCl			$CH_2COC_2H_5$							1149
	HgCl			$CH(CH_3)COCH_3$							1149
	HgCl			$CH(CH_3)COC_2H_5$							1149
	HgCl	I		CH_3							1136
	HgCl			I							1136
	HgCl	HgCl	HgCl	OCH_3							1150
	HgCl			SCH_3							1151
	HgCl		OCH_3	CHO							1151
	HgCl			CHO							1145, 1152, 1153
	HgOAc			CHO							1153
	HgCl			$COCH_3$							1151
	HgCl	CH_3		CO_2CH_3							1154
	Br	HgCl(OAc)		CO_2CH_3							1155
	Br	HgCl(OAc)		$CO_2C_2H_5$							1155
	CH_3	HgCl	HgCl	CH_3							1156
	HgCl										1157
				HgCl							1158
				HgCl		HgCl					1158
				HgOAc		HgOAc					1159
		CH_3		HgOAc	CH_3						1159
		CH_3		HgCl	CH_3	HgCl					1158

Table 2.4. (continued)

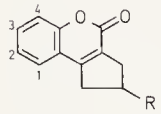
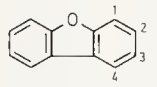
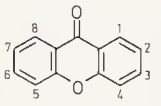
Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
		CH_3		CH_3		HgOAc					1159
		CH_3		HgOAc		CH_3					1159
		CH_3			OH	HgOAc					1160
		CH_3		HgCl	OH	HgCl					1158
		CH_3		HgOAc	OH	HgOAc					1159
		CH_3	CH_3	HgOAc	OH	HgOAc					1159
		CH_3		HgOAc	NH_2	HgOAc					1159
	$COCH_3$			HgOAc		HgOAc					1159
	COC_6H_5			HgOAc							1159
	CO_2H			HgOAc		HgOAc					1159
 R = H, CH_3		HgOAc	OH	HgOAc							1161
	OH	HgOAc	OH	HgOAc							1161
	OH	HgOAc	CH_3	HgOAc							1161
	HgOAc										1162
	HgOAc										1163
		HgOAc									1163
	HgOAc							HgOAc			1163
		HgOAc					HgOAc				1163
	HgOAc			NH_2							1163
		HgOAc	NH_2								1163
	HgOAc	NH_2	HgOAc								1163
	NH_2	HgOAc		HgOAc				HgOAc			1163
	NH_2	HgOAc		HgOAc	HgOAc		HgOAc	NH_2			1163
	HgOAc	NH_2	HgOAc			HgOAc	NH_2	HgOAc			1163
	NO_2	HgOAc			HgOAc		HgOAc	NH_2			1163
	HgOAc	NO_2				HgOAc	NH_2	HgOAc			1163
	HgOAc	NO_2									1163

Table 2.4. (continued)

Heterocycle	Functional groups and position of substitution 1	2	3	4	5	6	7	8	9	10	Ref.
	HgOAc			NO_2							1163
	NO_2	HgOAc									1163
		HgOAc	NO_2								1163
		HgBr	CH_3								1164
		HgBr	C_6H_5								1164
	CH_3	HgBr									1164
	C_6H_5	HgOAc									1165
	CH_3	HgBr	CH_3								1164
	HgOAc	C_6H_5	C_6H_5								1166
	CH_3	HgOAc	C_6H_5								1166
	C_6H_5	HgOAc	C_6H_5								1166
	C_6H_5	C_6H_5	HgOAc								1166
	HgOAc	C_6H_5									1167
	HgCl	C_6H_5									1168, 1169
	HgOAc	C_6H_5									1168
	HgCl	p-$C_6H_4OC_2H_5$									1169
	HgCl	3-C_5H_4N									1170
	HgCl										887, 1171–1173
	HgOCN										1137
	HgCl			HgCl							1171, 1172, 1174
	HgOAc			HgOAc							1174–1176
	HgOCN			HgOCN							1137
	HgX	HgX	HgX	HgX	X = Cl, Br, I, OAc						1177
alkylthiophenes	HgCl			CH_3							1171, 1173, 1178–1181
	HgOCN			CH_3							1137
	HgX	HgX	HgX	CH_3	X = Cl, OAc						1182
	HgCl	CH_3									?1171, 1183, 1184

Table 2.4. (continued)

Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgOAc		CH_3								?1174
	HgCl	CH_3		HgCl							1171, 1174, 1179, 1183
	HgOAc	CH_3		HgOAc							1174
	HgCl			C_2H_5							1173, 1185
	HgCl	C_2H_5		HgCl							1179
	HgCl			n-C_3H_7							1173, 1185
	HgCl	i-C_3H_7		HgCl							1171
	HgCl			i-C_5H_{11}							1173, 1185
	HgCl			n-$C_{10}H_{21}$							1186
	HgCl		CH_3	CH_3							1173, 1179, 1185
	HgCl	CH_3		CH_3							1173, 1185
	CH_3	HgCl		CH_3							1173, 1178, 1182, 1184
	CH_3	HgCl	HgCl	CH_3							1178
	CH_3	HgOAc	HgOAc	CH_3							1174
	HgCl		C_2H_5	CH_3							1187
	HgOAc	C_2H_5		CH_3							1188
	CH_3	HgOAc	HgOAc	C_2H_5							1189
	HgCl		CH_3	C_2H_5							1187
	HgOAc	HgOAc	CH_3	C_2H_5							1187
	C_2H_5	HgCl		C_2H_5							1190
	HgCl	C_2H_5	C_2H_5								1190, 1191
	HgCl	C_2H_5	C_2H_5	HgCl							1191
	HgCl		—— $(CH_2)_4$ ——								1192
	C_2H_5	HgCl	CH_3	C_2H_5							1190
	CH_3	HgCl	—— $(CH_2)_4$ ——								1193
	n-C_3H_7	HgCl	—— $(CH_2)_4$ ——								1193
	HgOAc	— $C(CH_3)_2(CH_2)_3$ —		CH_3							1194
	CH_3	HgCl	—— $(CH_2)_5$ ——								1186
	HgCl			$CH_2C_6H_5$							1173, 1185

Table 2.4. (continued)

Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgOAc		C_6H_5	CH_3							1195
	HgOAc	C_6H_5		CH_3							1195
	C_2H_5	HgOAc	HgOAc	1-$C_{10}H_7$							1196
	HgCl			C_6H_5							1173, 1178
	HgOAc			C_6H_5							1197
	HgCl	C_6H_5		C_6H_5							1198–1200
	HgOAc	C_6H_5		C_6H_5							1199
	HgCl			CH_2OH							1201
	HgCl			$CHOHCH_3$							1202
	HgOAc	CH_3		$\overline{C(OH)(CH_2)_4}$							1203
	HgOAc	CH_3		$\overline{C(OH)(CH_2)_5}$							1203
	HgCl			CH_2OCH_3							1204
	CH_2OCH_3	HgOAc	HgOAc	CH_2OCH_3							1204
	HgCl			CH(O-*i*-Pr)CH_3							1202
	HgOAc			$(CH_2)_2O_3POR$							1205
chlorothiophenes	HgCl			Cl							1173, 1178, 1206
	HgX	HgX	HgX	Cl	X = Cl, OAc						1206
	HgCl	Cl									1206
	HgCl	Cl		HgCl							1206
	HgCl		Cl	Cl							1206
	HgX	Cl		Cl	X = Cl, OAc						1207
	HgX	Cl	HgX	Cl	X = Cl, OAc						1206, 1207
	Cl	HgCl	HgCl	Cl							1206
	HgCl	Cl	Cl								1206
	HgCl	Cl	Cl	HgCl							1206
	HgCl	Cl	Cl	Cl							1206
	HgAr	Cl	Cl	Cl							1206
	Cl	HgAr	Cl	Cl							1206
bromothiophenes	Br	HgOAc	Cl	Cl							1206
	Br	HgAr	Cl	Cl							1206

Table 2.4. (continued)

Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgCl			Br							1173, 1178
	HgOAc			Br							1174
	HgCl	HgCl	HgCl	Br							1208
	HgCl	Br									? 1209
	HgCl		Br	Br							1209
	HgCl	HgCl	Br	Br							1208
	HgCl	Br		Br							1209
	Br	HgCl	HgCl	Br							1208
	HgCl	Br	Br								1209
	HgCl	Br	Br	HgCl							1208, 1209
	HgCl	Br	Br	Br							1208
	HgAr	Br	Br	Br							1208
	Br	HgCl	Br	Br							1208
iodothiophenes	HgCl			I							1173, 1178
	HgCl	HgCl	HgCl	I							1208
	HgCl	I									1210
	HgCl	I		HgCl							1210
	HgCl		I	I							1210
	I	HgCl	HgCl	I							1208
	HgCl	I	I								1210
	HgCl	I	I	I							1210
alkylhalothio-phenes	HgCl		Br	CH_3							1211
	HgCl	Br		CH_3							1211
	HgCl		CH_3	Br							1212
	HgCl	CH_3	Br	HgCl							1212
	HgOAc	CH_3	Br	HgOAc							1174
	HgCl	CH_3		Br							1212
	HgCl	Br	Br	CH_3							1211
	HgCl	CH_3	Br	Br							1212
	HgCl		I	CH_3							1182

Table 2.4. (continued)

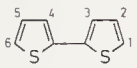
Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgCl	I		CH_3							1182
	HgCl		CH_3	I							1183
	HgX	I	CH_3	HgX	X = Cl, OAc						1183
	HgCl	CH_3		I							1183
	HgCl	I	I	CH_3							1182
	HgCl	CH_3	I	I							1183
	HgAr	CH_3	I	I							1183
	HgCl	I	CH_3	I							1183
other thiophenes	HgOAc	NO_2		HgOAc							1213
	HgOAc	NO_2	HgOAc	HgOAc							1213
	HgCl			NHAc							1214, 1215
	HgCl		HgCl	NHAc							1215
	HgCl	HgCl	HgCl	NHAc							1215
	HgCl	Br		NHAc							1215
	HgCl		Br	NHAc							1215
	HgCl			SCH_3							1216
	HgCl			SC_2H_5							1216
	HgCl	SCH_3		$CH{=}C(SCH_3)C_6H_5$							1217
	HgCl	$SCH_2C_6H_5$	HgCl	$CH{=}C(SCH_2C_6H_5)C_6H_5$							1217
	HgCl			COC_6H_5							1218
	HgOAc	HgOAc	HgOAc	COC_6H_5							1218
	HgCl			COC_6H_4I-*o*, *m*, *p*							1218
	HgOAc	HgOAc	HgOAc	$COC_6H_4CO_2H$-*o*							? 1219
	HgCl			CO_2H							1173, 1220
	HgCl					HgCl					1221, 1222
	HgCl	HgCl	HgCl	HgCl	HgCl	HgCl					1221
	HgCl					CH_3					1223
	HgCl					n-C_4H_9					1222
	CH_3	C_2H_5	HgOAc	HgOAc	C_2H_5	CH_3					1187
	HgOAc		HgOAc	HgOAc		NO_2					1213

Table 2.4. (continued)

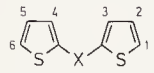
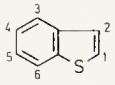
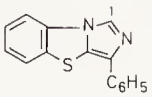
Heterocycle	Functional groups and position of substitution 1	2	3	4	5	6	7	8	9	10	Ref.
 X = –CHOCH–	HgCl					HgCl					1202
X = 	HgCl										1223
	HgCl					HgCl					1223
	HgCl					CH_3					1223
	HgOAc										1224, 1225
	HgCl	HgCl									1224
	HgOAc	HgOAc									1224, 1225
	HgOAc	CH_3									1225, 1226
	CH_3	HgOAc									1225
	HgOAc	C_6H_5									1226
	HgOAc	CH_3		CH_3							1226
	HgOAc	C_6H_5		CH_3							1226
	HgOAc	HgOAc	HgOAc								1227
	HgOAc	CH_3	CH_3								1064
	HgOAc	CH_3	C_6H_5								1064
	HgOAc	C_6H_5	C_6H_5								1228
	HgCl		NHAc								1229, 1230
	HgOAc	n-C_6H_{13}	NHAc								1231
	HgCl	p-C_6H_4X	NHAc		X = H, Cl, OCH_3, OC_2H_5						1232, 1233
	HgCl	2-$C_{10}H_7$	NHAc								1232, 1233
	HgCl	2-C_4H_3S	NHAc								1232, 1233
	HgOAc	HgOAc	$NHSO_2C_6H_4NHAc$-p								1024, 1037
	HgAr		$NHSO_2C_6H_4NHAc$-p								1037
	HgOAc										1234
	HgCl										1181, 1235
	HgOAc			HgOAc							1176

Table 2.4. (continued)

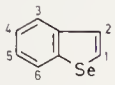
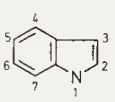
Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgCl			CH_3							1181
	HgCl	CH_3									1236
	HgCl		CH_3	CH_3							1236
	HgCl	CH_3		CH_3							1236
	HgCl	CH_3	CH_3	CH_3							1237
	HgCl	C_6H_5		C_6H_5							1198, 1238
	HgBr	C_6H_5		C_6H_5							1238
	HgCl										1239
		HgOCN			HgOCN						1137
		HgOAc	HgOAc	HgOAc	HgOAc						1138
	C_6H_5	HgOAc			HgOAc						?1240
	C_6H_5	HgOAc	HgOAc	HgOAc	HgOAc						1240
			HgCl								1241, 1242
			HgI								1243
			HgOAc	CH_3							1244
			HgCl	CH_3							?1245
		OH	HgX		HgX	X = Cl, OAc					1246
		HgX	OH			X = Cl, OAc					1246
			HgX	OH		X = Cl, OAc					?1246
			HgX	NH_2		X = Cl, OAc					1247
			HgX	NH_2	HgX	X = Cl, OAc					1247
			HgOAc			$NHSO_2C_6H_4NHAc$-*p*					1037
			HgAr			$NHSO_2C_6H_4NHAc$-*p*					1037
	O	HgOAc									1248
		HgCl									1249
	HgOAc		HgOAc								?1250
		HgOAc	HgOAc								?1251, 1252
		HgCl	HgCl								?1251

Table 2.4. (continued)

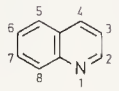
Heterocycle	Functional groups and position of substitution										Ref.
	1	2	3	4	5	6	7	8	9	10	
	HgOAc	HgOAc	HgOAc								1252
	CH_3		HgCl								1253
	CH_3	HgCl	HgCl								1253
		HgOAc	CH_3								1251
		CH_3	HgOAc								1251
	CH_3	HgCl	CH_3								1253
	CH_3	CH_3	HgCl								1253
	CH_3	CH_3	HgCl		NO_2						1253
	$COCH_3$		HgCl								1253, 1254
	$COCH_3$		HgOAc								1254
	$COCH_3$	CH_3	HgCl								1254
	$COCH_3$	HgCl	CH_3								1254
	CH_3	HgCl	$COCH_3$								1253
	CH_3	$COCH_3$	HgCl								1253
	HgOAc	HgOAc	$(CH_2)_2CO_2]_2Hg$		(mercuric carboxylate salt)						1252
			HgOAc								1245, 1255
								HgOAc			1245, 1256
						CH_3		HgCl(OAc)			1245, 1255, 1257
					HgCl(OAc)		CH_3				1245, 1255, 1257
					HgCl(OAc)			CH_3			1245, 1255, 1257
					HgOAc			OH			? 1258, 1259
							HgOAc	OH			1258, 1259
					HgOAc		HgOAc	OH			? 934, 1259
					Br		HgOAc	OH			1258
					Br	Br	HgOAc	OH			1258
					NO_2		HgOAc	$O)_2Hg$ (mercuric aryloxide)			956
		C_6H_5	HgOAc	CO_2H							1260, 1261
	O							HgCl			1262, 1263

Table 2.4. (continued)

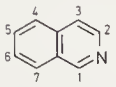
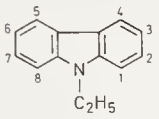
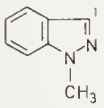
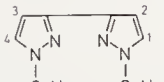
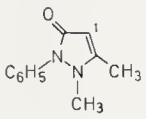
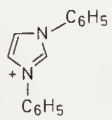
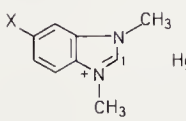
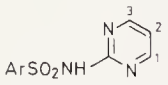
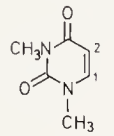
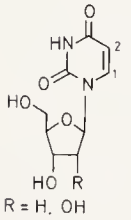
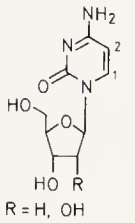
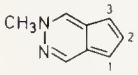
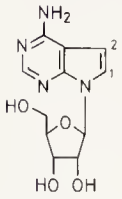
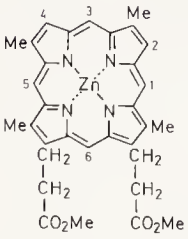
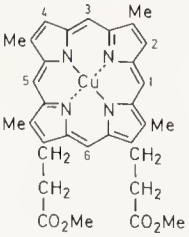
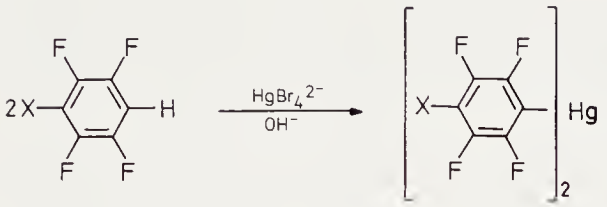
Heterocycle	Functional groups and position of substitution 1	2	3	4	5	6	7	8	9	10	Ref.
	O					CH_3		HgCl			1125
	O			HgCl				Br			1125
	O			Br				HgCl			1125
			HgCl								1245, 1255
			HgOAc								1264
	C_6H_5		HgCl								1265, 1266
	C_6H_5		HgOAc								1265
	CH_3	CH_3	HgCl	CH_3							1266
	C_2H_5	CH_3	HgCl	CH_3							1266
	C_6H_5	CH_3	HgCl	CH_3							1266
	$(CH_2)_2C_6H_5$	CH_3	HgCl	Cl							1266
	C_6H_5	CH_3	HgCl	Cl							1266
	C_6H_5	CH_3	HgOAc	Cl							1267
	HgCl										1268
	CH_3	HgOAc	HgOAc	CH_3							1269
	C_6H_5	HgOAc	HgOAc	C_6H_5							1269
	HgCl										1270
	HgCl										1271
	HgAr										1271, 1272
 X = H, CH_3, Cl, NO_2	HgCl										1273

Table 2.4. (continued)

Heterocycle	Functional groups and position of substitution 1	2	3	4	5	6	7	8	9	10	Ref.
	HgAr										1037
	HgOAc		HgOAc								1037
		HgOAc									1274, 1275
 R = H, OH		HgCl									1276–1278
		HgOAc									1279
 R = H, OH		HgCl									1276–1278
		HgOAc									1277, 1279
	HgOAc		HgOAc								1280
		HgOAc									1279
		HgCl		HgCl							1281, 1282
		$CH_2CH_2CO_2CH_3$		HgCl							1282
		HgCl		HgCl							1282
		HgCl		$COCH_3$							1282
		$COCH_3$		HgCl							1282

ferrocenes bearing a number of different substituents have been reported. Cyclopentadienyl complexes of manganese [1106, 1302–1305], rhenium [1306], cobalt [1307, 1308], and ruthenium [245, 1309] behave similarly.

Finally, it is noteworthy that certain highly fluorinated arenes can also be mercurated under basic conditions to provide diarylmercurials (Eq. 251). Mixed diarylmercurials can be obtained similarly by using an arylmercuric halide and base.



(251)

X	% Yield	Ref.
H	38	905,906
CH_3O	54	904
F	37-75	906,907

L. Mercury Substitution in Aryldiazonium Salts, Hydrazines, Hydrazones and Diazo Compounds

Primary aromatic amines can be readily diazotized and treated with mercuric halides to form complexes which can in turn be reduced in high yield to arylmercuric halides (Eqs. 252–254) [1310]. Most commonly aryldiazonium chlor-

$$ArNH_2 + NaNO_2 + 2HX \longrightarrow [ArN_2]X + NaX + 2H_2O \quad (252)$$

$$[ArN_2]X + HgX_2 \longrightarrow [ArN_2][HgX_3] \quad (253)$$

$$[ArN_2][HgX_3] + 2Cu \longrightarrow ArHgX + N_2 + 2CuX \quad (254)$$

ides and mercuric chloride are utilized. When the aryl group contains strong electron-withdrawing groups, complexes containing two diazonium moieties per mercury are obtained instead (Eq. 255) [1311], but by adding an

$$2[ArN_2]X + HgX_2 \longrightarrow [ArN_2]_2[HgX_4] \quad (255)$$

additional equivalent of mercury(II) halide during reduction, good yields of arylmercuric halide can still be obtained. Reduction is most commonly effected by using excess copper powder or copper bronze in either water or acetone, although other organic solvents have occasionally been employed. This homolytic substitution reaction on occasion affords hydrogen- or halogen-substituted arenes as side products, especially with aryl groups containing electron-withdrawing substituents. These side products can generally be avoided by using energetic stirring, slowly adding the diazonium compound to

a mixture of the copper powder and the solvent, and running the reaction at −20 °C to −10 °C [1311]. When excess copper is employed and aqueous ammonia is added prior to work-up, diarylmercurials are obtained instead (Eq. 256) [1312]. This approach to arylmercurials is especially valuable since it allows one to prepare functionally-substituted arylmercurials free of isomers common in many direct electrophilic mercuration reactions.

$$2[ArN_2][HgX_3] + 6Cu + 6NH_3 \longrightarrow Ar_2Hg + Hg + 2N_2 + 6CuX \cdot NH_3 \qquad (256)$$

The following substituted phenylmercuric chlorides have been prepared in the yields indicated using this approach: phenylmercuric chloride (51–87% yield) [1310, 1311, 1313–1318], *o,m,p*-methyl (40–68) [66, 183, 1310, 1314, 1316, 1319, 1320], 2,5-dimethyl (52) [896], *o,m,p*-chloro (25–69) [254, 1038, 1310, 1314, 1321], *m,p*-bromo (28–43) [1310, 1314, 1321], *m,p*-iodo (45–53) [1310, 1314], 2,5-dichloro (15–32) [1310, 1311, 1322], 2,6-dibromo-4-fluoro (14) [255], *o,m,p*-nitro (27–59) [1311, 1314, 1316], *o,m,p*-hydroxy (~40) [1319, 1323], *o,p*-methoxy (14–72) [1310, 1324], *o,p*-ethoxy (19–77) [1310, 1314, 1324], *o,p*-phenoxy (56–64) [1310, 1324], *o*-(*p*-tolyloxy) (57) [1325], *o,p*-methylthio (53–75) [1326], *o*-carboxy (39) [1311], *o,m,p*-carbomethoxy (37 to 56) [1310, 1320], *o,m,p*-carboethoxy (29–56) [1314, 1320], *p*-sulfo (30) [1311] and 2-methyl-4-nitro (39) [912, 915]. Phenylmercuric bromide (80) [1316, 1317] and iodide (40) [1310]; *p*-tolylmercuric bromide (72) [1317]; 2-, 3- and 4-bromomercurioanisole (40) [1038, 1327]; 2- and 4-chloromercuriobiphenyl (35) [1328–1330]; 4,4′-bis(chloromercurio)-biphenyl (32) [1329]; α- and β-naphthylmercuric chloride (20–67) [66, 1091, 1314, 1317–1319] and bromide [1319]; 4-chloromercuriostilbene (45) [1331]; 2-, 3- and 4-chloromercuriotriphenylmethane (51) [1332]; 2- and 4-chloromercuriotriphenylcarbinol (46) [1332]; 2-, 3- and 4-chloromercuriobenzophenone (40) [1333]; 4-chloromercurio-4′-methylbenzophenone (45) [1333]; 1-chloromercurio- (43 to 59) and 1,5-bis(chloromercurio)anthraquinone (27) [1334–1336]; 3-chloro-, -bromo- and -iodomercuriopyridine [1337]; 2-chloromercuriothiazole [1227]; 6-chloromercurio-2,3-dihydro-3-oxobenzoxazine [1338]; and 6-chloromercurio-2,3-dihydro-3-oxonaphthothiazine [1339] have been prepared similarly.

The addition of ~25% aqueous ammonia to these same reactions prior to work-up results in isolation of the corresponding diarylmercurials [1312]: phenyl (65% yield) [1312, 1340, 1341], *p*-tolyl (76) [1312, 1342], *p*-fluorophenyl (61) [1343], *m*-chlorophenyl (23) [1344], *p*-chlorophenyl [1345], *p*-bromophenyl [1312, 1345], *p*-iodophenyl (70) [1312, 1341], 2,4-dichlorophenyl (14) [917], 2,5-dichlorophenyl (20) [912, 1312], 2,3,5-trichlorophenyl (3) [917], 3,4,5-trichlorophenyl (9) [917], *p*-nitrophenyl (10) [1312], *o*-anisyl (60) [1312], *m*-anisyl (22) [1346], 3-iodo-4-methoxyphenyl [1347], α-naphthyl (53) [1312], β-naphthyl (45–48) [1341], 4-stilbenyl (41) [1331], 3-pyridyl [1348] and 5-bromo-3-pyridyl [1337]. With a number of alkoxyaryldiazonium salts, diarylmercurials have been observed even in the absence of ammonia [1324]. With 1- and 2-aminoanthraquinone, the diazonium salts react with mercuric sulfate at 180 °C to afford the corresponding diarylmercurials directly [1334].

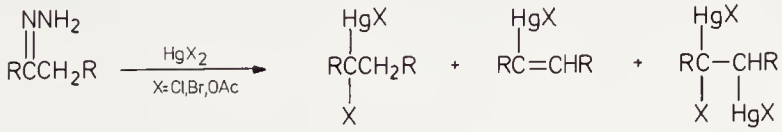
In a few instances, copper(I) chloride has been used instead of copper powder and good yields have generally been obtained: phenylmercuric chloride (77% yield) [1315, 1349], phenylmercuric bromide (80) [1349], *p*-tolylmercuric bromide (70) [1349], *p*-nitrophenylmercuric chloride (43) [1349], *p*-carboethoxyphenylmercuric chloride (40) [1350], and *p*-chloromercuriobenzenesulfonamide (33) [1350].

Even better yields of substituted phenylmercuric chlorides have recently been reported by adding an aqueous solution of the aryldiazonium salt to an acetone solution of mercuric chloride, cupric chloride and diethyl phosphite [1351]: phenylmercuric chloride (82% yield based on aniline); *o,m,p*-methyl (82–90); *o,m,p*-chloro (60–73); *o,m,p*-bromo (60–70); *p*-iodo (66); 2,4,6-tribromo (18–20); *o,m,p*-nitro (41–73); *m,p*-hydroxy (66–69); *o,m,p*-methoxy (78–92); *o,p*-ethoxy (85–90); *p*-acetyl (58); *p*-benzoyl (65); *o,m*-carboxy (66–74); *o,m,p*-carboethoxy (52–68) and α- and β-naphthylmercuric chloride.

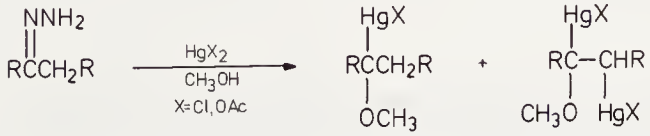
Tin(II) chloride has been used as a reducing agent in combination with aryldiazonium tetrafluoroborate salts and mercuric chloride with fair yields generally being observed [901, 1352, 1353]. Vigorous stirring with metallic mercury yields similar results [1321, 1354–1356]. Electrolytic reduction of substituted benzophenone diazonium tetrafluoroborate salts affords another route to diarylmercury compounds [1357].

The reaction of arylhydrazines and mercuric oxide [1358, 1359], or mercuric oxide plus metallic mercury [905, 1360, 1361], can be used to prepare diarylmercurials, but the yields are often low and the starting arylhydrazines are much less accessible than aryldiazonium salts. Mercuric oxide plus mercuric chloride [1359, 1361], and mercuric acetate plus small amounts of cupric acetate [1363] have also been used to convert arylhydrazines into the corresponding arylmercuric salts. Methyl hydrazine gives only a 5–10% yield of dimethylmercury upon treatment with mercuric oxide [1364].

The reaction of hydrazones and mercury salts leads to a variety of different organomercurials depending on the structure of the hydrazone, and the mercury salt and solvent employed [1365–1369]. In inert solvents such as ether or benzene, three types of products are observed: α-substituted organomercurials, vinylmercurials and/or the product of mercury salt addition to the vinylmercurial (Eq. 257). In methanol either α-methoxymercurials or dimercurials are reported (Eq. 258). While in water, vinylmercurials and

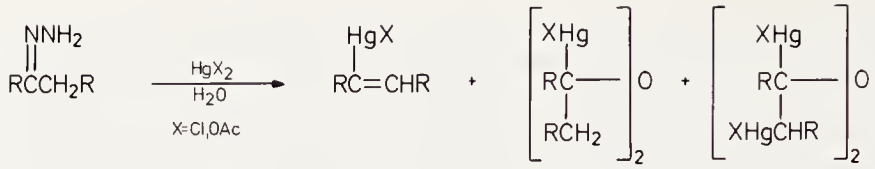


(257)



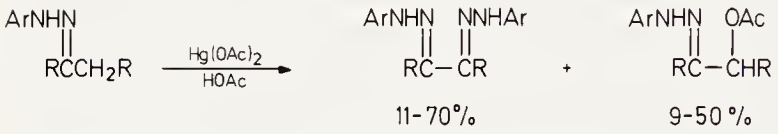
(258)

mercurated ethers are claimed (Eq. 259). It should be pointed out, however, that little structural proof has been provided for these compounds.



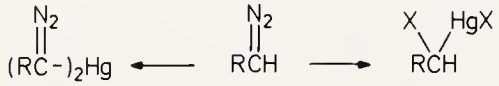
(259)

As seen earlier in Table 2.2, Sect. K, arylhydrazones usually mercurate in the ortho position of the aromatic ring. However, when the aromatic ring is deactivated by electron-withdrawing groups, the extent of aromatic mercuration diminishes and attack apparently occurs on neighboring methylene groups resulting in either bis-hydrazones or α-acetoxy hydrazones (Eq. 260) [1370].



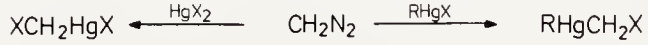
(260)

Diazo compounds react with mercury salts or organomercuric salts either with replacement of an alpha hydrogen or substitution of nitrogen (Eq. 261).



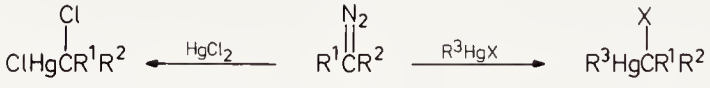
(261)

The former reaction has been discussed in Sect. II G. The latter reaction provides a useful approach to α-haloalkylmercurials which are valuable as divalent carbon transfer reagents and will be discussed in more detail in Chapter X. The majority of work in this area has been carried out on diazomethane (Eq. 262) [25, 1371–1377]. However, several other diazoalkanes



(262)

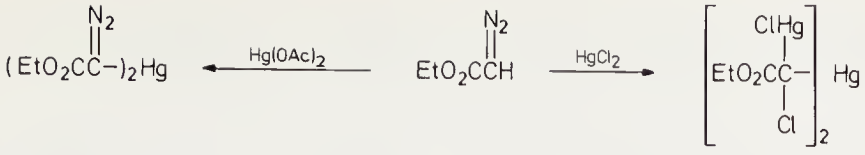
have been reported to give similar reactions and a large number of α-halodialkylmercurials have recently been prepared in this fashion (Eq. 263)



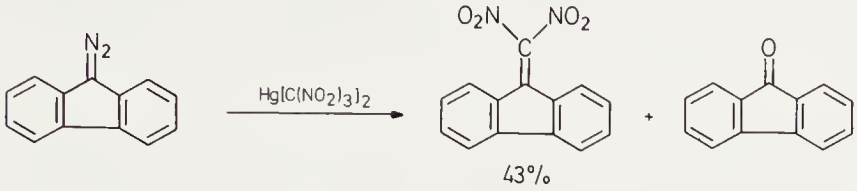
(263)

R^1	R^2	Ref.
H	CH_3	1369
H	C_2H_5	1369
H	CF_3	1371
C_6H_5	C_6H_5	1366,1369,1372
C_6H_5	$PO(OCH_3)_2$	578

[1376]. Ethyl diazoacetate undergoes both hydrogen and nitrogen substitution depending on the mercury salt employed (Eq. 264) [565, 1313, 1380, 1381]. Bis(trinitromethyl)mercury on the other hand only gives dinitro olefins and some of the corresponding ketone (Eq. 265) [1382].



(264)

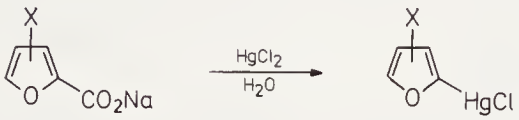


(265)

M. Decarboxylation of Mercury Carboxylates

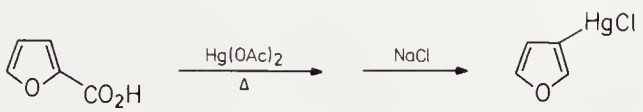
The decarboxylation of metal carboxylates is a general method for the preparation of organometallics [1383] which has proven quite useful for the synthesis of a variety of organomercurials. Decarboxylation can be effected either thermally, electrolytically, photochemically or through free radical processes.

The attempted electrophilic mercuration of certain aromatic carboxylic acids results in the formation of arylmercurials via decarboxylation. For example, a number of substituted 2-furyl carboxylate salts undergo facile decarboxylative mercuration (Eq. 266) [1136, 1147, 1154, 1384]. Yields of



(266)

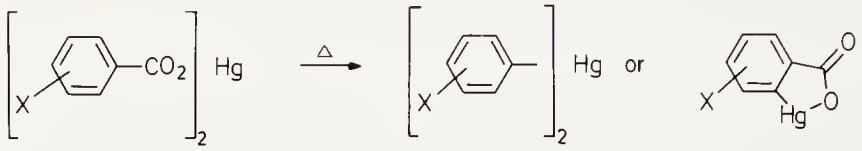
25–76% have been obtained for a number of simple 5-substituted 2-furoic acids [1136]. This reaction proceeds even when the five position is free to undergo mercuration [1154]. If 2-furoic acid and mercuric acetate are used, however, an intermediate mercury salt can be isolated which undergoes thermolysis to give 3-chloromercuriofuran upon work-up, albeit in low yield (Eq. 267) [1136, 1385]. Decarboxylative mercuration of 3-furoic acid also requires elevated temperatures and proceeds in only 12% yield [1136]. 2-Chloromercuriobenzofuran [1157] and a number of substituted chloromercuriothiophenes [1182, 1183, 1206, 1213, 1386] have also been prepared by decarboxylation of the corresponding carboxylic acids. In a number of cases polymercurated thiophenes have been obtained.



(267)

Although there are several examples of mercuration reactions of substituted benzoic acids [956, 1387, 1388] or naphthoic acids [1389] affording decarboxylated arylmercurials, the majority of work in this area has been done on the isolated mercury benzoate salts. Two different types of products are

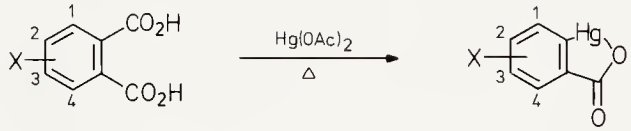
generally observed upon thermolysis of these compounds, either the diarylmercury compound or the ortho-mercurated benzoic acid (Eq. 268). The latter



(268)

compounds may not be simple cyclic monomers as commonly drawn, but actually higher polymeric species. The following substituted mercury benzoates afford diarylmercurials: *o*-nitro [1390, 1391]; 2,4,6-trinitro [1391]; perfluoro [1392, 1393]; perchloro [1394]; perbromo [1395, 1396]; and 2-methyl-, 3-methoxy-, 4-methyl-, 4-fluoro-, 4-chloro- and 4-methoxytetrabromo [1396]. Mercury salts of tetrafluoro-3- [104] and -4-pyridine [1397] carboxylic acids, 1-methyl-2-benzimidazole carboxylic acid [1269], and *o*- and *m*-carborane carboxylic acids [1398, 1399] behave similarly. Mercuric benzoate [489, 1400] and the *m*- [1390] and *p*-nitrobenzoates [1390, 1401, 1402] apparently give only ortho-mercurated compounds, while other substituted mercury benzoates have been reported to mercurate elsewhere in the ring [489, 1391].

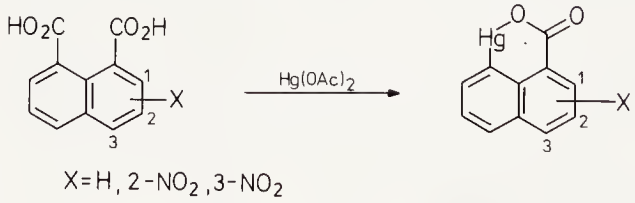
Substituted phthalic acids undergo decarboxylation to give ortho-mercurated aromatic carboxylates in which the more sterically hindered acid group is lost predominantly (Eq. 269). Naphthalene (1,2 and 1,8) [1404,



(269)

X = H [1400, 1403]; 1-CH_3 [1404]; 1-Cl [1405]; 1-Br [1405]; 1-NO_2 [1404 to 1407]; 2-NO_2 [1390]; 1-CO_2H [1408]; 1,2-$(OCH_3)_2$ [1409]; 1,2,3,4-F_4 [1410]

1411–1413], phenanthrene (1,2) [1404] and anthraquinone (1,2 and 2,3) [1414] dicarboxylic acids react similarly (Eq. 270). Mercury carboxylates derived



(270)

X=H, 2-NO_2, 3-NO_2

from perfluorophthalic acid [1410], perfluoroterephthalic acid [1415] and 2,2′-dicarboxyoctafluorobiphenyl [42, 1416], as well as phenylmercuric benzoate [1417], have been completely decarboxylated at elevated temperatures to afford oligomeric arylmercurials.

(271)

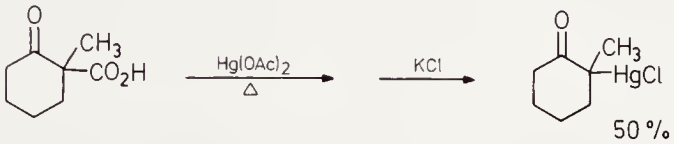
A variety of mixed diorganomercury compounds have been prepared by decarboxylating organomercury benzoates (Eq. 271) [1392–1396, 1418–1421].

The decarboxylation of mercury carboxylates derived from aliphatic carboxylic acids can be effected if strong electron-withdrawing groups are present in the acid. This approach has proven valuable for the preparation of perhaloalkylmercurials useful as divalent carbon transfer reagents and will be discussed in detail in Chapter X (Eqs. 272, 273). Mercuric hexafluoro-

$$HgCl_2 + 2NaO_2CCBr_3 \longrightarrow Hg(CBr_3)_2 \qquad (272)\ [1422]$$

$$C_6H_5HgCl + NaO_2CCCl_3 \xrightarrow{\Delta} C_6H_5HgCCl_3 \qquad (273)\ [1423]$$

isobutyrate [1424, 1425], phenylacetate [1426] and 2,4-dinitrophenylacetate [1391] have also been reported to give dialkylmercury compounds upon heating. β-Keto acids decarboxylate smoothly to afford good yields of α-keto-alkylmercurials (Eq. 274) [1427–1429].



(274)

The following miscellaneous thermal and electrolytic approaches to organomercurials have also been reported (Eqs. 275–277).

$$ArN{=}NCO_2K + HgCl_2 \longrightarrow ArHgCl \quad (31\text{–}54\ \%) \qquad (275)\ [1430]$$

$$Hg(OAc)_2 + Pb(OAc)_4 \xrightarrow[HOAc]{\Delta} CH_3HgOAc \quad (82\ \%) \qquad (276)\ [1431]$$

$$Hg(O_2CR)_2 \xrightarrow{\text{electrolysis}} RHgO_2CR \qquad (277)\ [1432, 1433]$$

R =	
Me	47%
Et	26%
n-Pr	17%

$$Hg(O_2CR)_2 \xrightarrow{h\upsilon} RHgO_2CR + CO_2 \qquad (278)$$

R = CH_3 [1434–1438], C_2H_5 [1434–1439], *n*-C_3H_7 [1434, 1438, 1440], *i*-C_3H_7 [1441], *c*-C_3H_5 [1442], *n*-C_4H_9 [1443], *i*-C_4H_9 [1441], *c*-C_4H_7 [1444, 1445], *n*-C_5H_{11} [1443], *i*-C_5H_{11} [1446], *c*-C_5H_9 [1447], *neo*-C_5H_{11} [1446], *n*-C_6H_{13} [1448], *c*-$C_5H_9CH_2$ [1449], *c*-C_6H_{11} [1447], $(CH_3)_3C(CH_2)_2$ [1446], 1-CH_3-*c*-C_6H_{10} [1450], 4-CH_3-*c*-C_6H_{10} [1450], *c*-$C_6H_{11}CH_2$ [1449], *n*-C_7H_{15} [1448], *c*-C_7H_{13} [1442], *n*-C_8H_{17} [1448], *n*-C_9H_{19} [1434, 1451], *n*-$C_{11}H_{23}$ [1452], *c*-$C_{11}H_{21}$ [1453], *c*-$C_{12}H_{23}$ [1453], *n*-$C_{15}H_{31}$ [1452], XCH_2CH_2 (X = C_6H_5 [1454], OR [1455], CO_2CH_3 [1456]), $C_6H_5(CH_2)_3$ [1454], $CH_3O_2C(CH_2)_4$ [1456], $Cl(CH_2)_5$ [1454], $CH_3O_2C(CH_2)_7$ [1456], C_6H_5 [1457, 1458], 4-$CH_3C_6H_4$ [1459], 1-$C_{10}H_7$ [1458], 2-$C_{10}H_7$ [1434].

Mercuric carboxylates can also be photochemically decarboxylated to give generally 40–70% yields of alkylmercury carboxylates depending on the organic group involved and the reaction conditions (Eq. 278). Polycyclic alkylcarboxylate salts react similarly [1460]. Aryl carboxylates give substantially lower yields [1434, 1457–1459]. Best results are generally obtained in either the corresponding carboxylic acid or, better yet, benzene as the solvent. In the latter solvent, however, phenylmercurials are occasionally isolated as side products. Mercury(I) carboxylates have also been observed as side products. In two instances, R = CH_3 and C_2H_5, dialkylmercurials have been formed directly in 66 and 68% yields respectively [1437]. This approach to alkylmercurials is most readily accounted for by the following mechanism (Scheme 2.1). The chain nature of this reaction is evident from

Scheme 2.1

$$Hg(O_2CR)_2 \xrightarrow{h\upsilon} RCO_2\cdot + \cdot HgO_2CR$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2$$

$$R\cdot + Hg(O_2CR)_2 \longrightarrow RHgO_2CR + \cdot O_2CR$$

continued CO_2 evolution after photolysis has been terminated [1440]. The following relative chain lengths and yields of alkylmercurials have been reported: cyclohexyl > cyclopentyl > cyclobutyl [1444]. The relative rates of decarboxylation reported are: n-$C_3H_7CO_2$ > $C_2H_5CO_2$ > CH_3CO_2 [1440], and $(CH_3)_3CCH_2CO_2$ > $(CH_3)_3CCH_2CH_2CO_2$ [1446]. The radical nature of the intermediates is evident from the loss of stereochemistry observed upon photolysis of mercury(II) salts of monocyclic [1450] and bicyclic [1460] alkyl carboxylates. Alkyl dimers have also been noted in the photolysis of one mercury salt (R = $CH_3O_2CCH_2CH_2$) [1456]. Mercurous acetate can also be decarboxylated photochemically, but only low yields of methylmercuric acetate are obtained (Eq. 279) [1434, 1435].

$$Hg_2(O_2CCH_3)_2 \xrightarrow{h\upsilon} CH_3HgO_2CCH_3 + Hg + CO_2 \qquad (279)$$

As one might anticipate with a free radical chain reaction, a variety of peroxides have been utilized to initiate these reactions. Yields of organomercurials are generally significantly higher using this approach. The most widely used initiators have been benzoyl peroxide, acetyl peroxide or the diacyl peroxide corresponding to the mercuric carboxylate being studied, $(RCO_2)_2$. The first two peroxides can give difficulties due to formation of phenyl- and methylmercurials and the latter is preferred although less readily available. All of the following mercury(II) carboxylates, $Hg(O_2CR)_2$, have been decarboxylated by peroxide initiators: R = CH_3 [1434, 1437, 1457, 1461–1470], C_2H_5 [1434, 1436, 1437, 1468–1471], n-C_3H_7 [1472], i-C_3H_7 [1441], c-C_3H_5 [1442], n-C_4H_9 [1443], i-C_4H_9 [1441], c-C_4H_7 [1444, 1445],

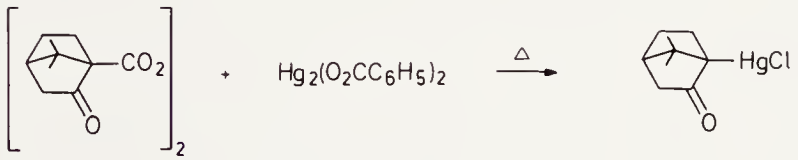
n-C_5H_{11} [1443], i-C_5H_{11} [1446], c-C_5H_9 [1447], neo-C_5H_{11} [1446], n-C_6H_{13} [1473], c-C_6H_{11} [1447, 1473, 1474], c-$C_5H_9CH_2$ [1449], $(CH_3)_3C(CH_2)_2$ [1446], 1-CH_3-c-C_6H_{10} [1450], 4-CH_3-c-C_6H_{10} [1450], c-$C_6H_{11}CH_2$ [1449], n-C_7H_{15} [1448, 1473], c-C_7H_{13} [1442], n-C_8H_{17} [1448, 1473], n-C_9H_{19} [1434, 1443, 1469, 1475], n-$C_{11}H_{23}$ [1452], c-$C_{11}H_{21}$ [1453], c-$C_{12}H_{23}$ [1453], n-$C_{15}H_{31}$ [1452], XCH_2CH_2 (X = C_6H_5 [1454], OR [1455], CO_2CH_3 [1456], $C_6H_5(CH_2)_3$ [1454], $CH_3O_2C(CH_2)_4$ [1456], $Cl(CH_2)_5$ [1454], $CH_3O_2C(CH_2)_7$ [1456], C_6H_5 [1476], X—C_6H_4 (X = o-NO_2 [1476], p-Br [1476], p-CH_3 [1434, 1459, 1476]). Good yields are once again obtained from bicyclic and tricyclic alkyl carboxylates [1460] and much improved yields of arylmercurials are obtained using the corresponding aroyl peroxides as initiators [1476]. In several instances, good yields of dialkylmercurials have been obtained from these same reactions (R = C_2H_5, n-C_9H_{19}) [1437].

Mercury(I) carboxylates have also been decarboxylated to organomercurials using peroxide initiators, but this approach is not as practical due to the limited availability of mercury(I) carboxylates and the lower yields generally observed (Eq. 280). This approach can be used, however,

$$Hg_2(O_2CR)_2 \xrightarrow[\Delta]{\text{peroxide}} RHgO_2CR \qquad (280)$$

R = CH_3 [1434, 1463, 1468, 1477], C_2H_5 [1478], n-C_3H_7 [1478], n-C_4H_9 [1479], n-C_5H_{11} [1479], C_6H_5 [1434, 1479, 1480]

to convert certain peroxides into organomercurials (Eq. 281) [1481]. Metallic mercury can also be employed in this latter reaction to produce low yields of alkyl- and arylmercurials (Eq. 282) [1482–1488].



(281)

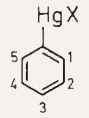
$$(RCO_2)_2 + Hg \xrightarrow{\Delta} RHgO_2CR \qquad (282)$$

N. Sulfinate and Sulfonate Elimination Reactions

Sulfinic acids or their alkali metal salts react readily with a number of mercury(II) salts to give a wide variety of organomercurials. This reaction, first reported by Peters in 1905 [1489], has been widely used for the preparation of arylmercurials. It is commonly effected by simply heating the arylsulfinic acid or salt with mercury(II) chloride, bromide, iodide or acetate in water and collecting the insoluble organomercurial (Eq. 283). The large

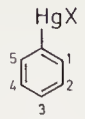
$$RSO_2H(Na) + HgX_2 \xrightarrow[H_2O]{\Delta} RHgX \qquad (283)$$

Table 2.5. Arylmercurials Available via Sulfinate Elimination Reactions



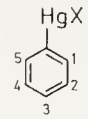
Functional groups and position of substitution							
1	2	3	4	5	X	% Yield	Ref.
H	H	H	H	H	Cl	74	1489-1492
H	H	H	H	H	SO_2Ar	28	1493
H	H	H	H	H	Ar	23-84	1493, 1494
H	HgCl	H	H	H	Cl	82	886
CH_3	H	H	H	H	Cl	42	1495
H	CH_3	H	H	H	Cl	27	1495
H	H	CH_3	H	H	Cl	51-65	1489, 1495-1499
H	H	CH_3	H	H	OAc	40	889
H	H	CH_3	H	H	SO_2Ar	32	1493
H	H	CH_3	H	H	Ar	20-35	1493, 1494
H	H	C_2H_5	H	H	Cl	65	1495
H	H	*i*-C_3H_7	H	H	Cl	62	1495
$C_6H_5CH_2$	H	H	H	H	Cl	—	1500
H	H	$C_6H_5CH{=}CH$	H	H	Cl	5	1331
α-$C_{10}H_7$	H	H	H	H	Cl	—	1501
$C_6H_5CH_2$	H	CH_3	H	H	Cl	—	1500
CH_3	H	CH_3	H	CH_3	SO_2Ar	~50	1493
CH_3	H	CH_3	H	CH_3	Ar	65	1493
p-$CH_3C_6H_4CH_2$	H	CH_3	H	CH_3	Cl	44	1502
i-C_3H_7	H	*i*-C_3H_7	H	*i*-C_3H_7	Cl	70	1503
i-C_3H_7	H	*i*-C_3H_7	H	*i*-C_3H_7	Ar	37	1493
H	H	F	H	H	Ar	90	1493
F	F	F	F	H	Cl	49	1504
F	F	F	F	HgCl	Cl	38	1504
F	F	F	F	HgBr	Br	73	1504
F	F	F	H	F	Cl	59	1504
F	F	F	H	F	Br	79	1504

Table 2.5. (continued)



Functional groups and position of substitution							
1	2	3	4	5	X	% Yield	Ref.
F	F	F	H	F	Ar	20	1504
F	F	H	F	F	Cl	47	1504
F	F	H	F	F	Br	69	1504
F	F	H	F	F	OAc	29	1504
F	F	H	F	F	Ar	78	1504
F	F	HgCl	F	F	Cl	61	1504
F	F	HgBr	F	F	Br	66	1504
F	F	HgOAc	F	F	OAc	47	1504
F	F	F	F	F	Cl	43-46	1504-1506
F	F	F	F	F	Br	49-52	1504, 1505
F	F	F	F	F	OAc	51-55	1504, 1505
F	F	F	F	F	$SO_2C_6H_5$	20	1504, 1505
F	F	F	F	F	Ar	27-66	1504, 1505
Cl	H	H	H	H	OAc	70	911
H	Cl	H	H	H	OAc	—	911
H	H	Cl	H	H	Cl	56	1492
H	H	Cl	H	H	OAc	70	911
H	H	Cl	H	H	SO_2Ar	21	1493
H	H	Cl	H	H	Ar	80	1493
Cl	H	Cl	H	H	Cl	50	1507
Cl	H	H	Cl	H	Cl	—	912, 1507
Cl	H	H	Cl	H	OAc	—	915
Cl	Cl	Cl	H	H	SO_2Ar	21	1493
Cl	Cl	Cl	H	H	Ar	53	1493
Cl	H	Cl	Cl	H	Ar	42	1493
Cl	H	Cl	H	Cl	Cl	35	1507
Cl	Cl	Cl	Cl	Cl	Cl	—	1506

Table 2.5. (continued)



Functional groups and position of substitution							
1	2	3	4	5	X	% Yield	Ref.
Br	H	H	H	H	Cl	44	1321
Br	H	H	H	H	OAc	66	911
H	Br	H	H	H	Cl	50	1321
H	Br	H	H	H	OAc	40	911
H	H	Br	H	H	Cl	60	1321
H	H	Br	H	H	OAc	60	911
H	H	Br	H	H	SO_2Ar	27	1493
H	H	Br	H	H	Ar	80	1493
H	H	I	H	H	OAc	50	911
NO_2	H	H	H	H	Cl	78	1508
H	NO_2	H	H	H	Cl	42	1508
H	H	NO_2	H	H	Cl	—	1508
NO_2	H	H	CH_3	H	Cl	—	1049
H	NO_2	CH_3	H	H	Cl	—	1048
H	NO_2	H	H	CH_3	Cl	—	912, 915, 1049
H	CH_3	NO_2	H	H	Cl	—	1048
H	H	NHAc	H	H	Ar	28	1493
ArN=N	H	H	H	H	Cl	37-57	1509, 1510
$C_6H_5N{=}N$	H	H	H	H	Br	—	1509
$C_6H_5N{=}N$	H	H	H	H	I	—	1509
ArN=N	H	Cl	H	H	Cl	42-67	1510

number of simple substituted arylmercurials which have been prepared in this fashion are summarized in Table 2.5. Mercury derivatives of the naphthalene [1318, 1493, 1495], anthraquinone [1511], coumarin [1512], pyridine [1348], quinoline [1493], dibenzofuran [1513], ferrocene [1304, 1514] and tricarbonylmanganese cyclopentadiene [1304, 1515] ring systems have also been prepared by this procedure. The reaction proceeds most readily with arylsulfinic acids containing strong electron-withdrawing groups

[1504, 1505] or sterically bulky groups [1493]. It can be used to prepare either arylmercuric salts or diarylmercurials depending on the stoichiometry employed during the reaction. Diarylmercurials are usually best obtained by heating the mercury sulfinate salts in vacuum rather than using the more common aqueous procedure [1493]. Symmetrical and unsymmetrical diarylmercurials can also be obtained by starting with an arylmercuric salt instead (Eq. 284) [1504, 1505, 1516, 1517]. As seen in

$$ArHgX + NaO_2SAr' \xrightarrow{\Delta} ArHgAr' \qquad (284)$$

Table 2.5, no difficulty is observed in preparing dimercurated aromatics from the corresponding disulfinic acids or salts. This approach to arylmercurials has the advantage that isomerically pure arylmercurials of known structure are easily obtained, generally in high yield. It suffers the disadvantage of requiring starting materials that are not readily available or easily prepared.

Alkylmercuric chlorides can also be prepared from the corresponding sulfinic acids using the Peters reaction (Eq. 285). In general, the yields are

$$RSO_2Na + HgCl_2 \xrightarrow{\Delta} RHgCl \qquad (285)$$

R = CH_3 [1518, 1519], C_2H_5 [1519], *n*-C_4H_9 [1519], $CH_2C(CH_3)_3$ [1520], *c*-C_6H_{11} [1520], *n*-C_6H_{13} [1520], $CH_2CH_2C(CH_3)_3$ [1520], *n*-$C_{12}H_{25}$ [1521], *exo*- and *endo*-norbornyl [1520], 10-camphor [1522], 3-chloro- and -bromo-10-camphor [1523]

only fair and the reaction suffers from the limited availability of the starting sulfinic acids. The mechanism of this elimination reaction has been studied [1520]. Elimination of sulfur dioxide has been found to proceed with loss of stereochemistry. Present data is inconsistent with the intermediacy of carbonium ions, free radicals or carbanions and no good mechanism has been put forth.

The thermal elimination of sulfur trioxide from fully substituted mercury(II) arenesulfonates provides another route to diarylmercurials (Eq. 286)

$$2ArSO_3H + Hg(OAc)_2 \longrightarrow (ArSO_3)_2Hg \xrightarrow{\Delta} Ar_2Hg \qquad (286)$$

[1050, 1524–1526]. The reaction appears limited to arenesulfonic acids bearing a number of electron-withdrawing groups and preferably fully substituted. The reaction is best carried out by isolating the mercury salt as its bis-pyridine complex and then heating in vacuum [1526]. If the aromatic ring contains a hydrogen on the ring, mercuration of the ring can occur [1525, 1526]. Diarylmercurials prepared in this fashion include *m*-HC_6F_4 [1525, 1526], *p*-HC_6F_4 [1525, 1526], *m*-HC_6Cl_4 [1526], *p*-HC_6Cl_4 [1525, 1526], C_6F_5 [1524–1526], C_6Cl_5 [1524–1526] and *p*-$NO_2C_6Cl_4$ [1055].

Finally, it should be mentioned that bis-perfluorophenylmercury can be prepared by sulfur or selenium extrusion from the corresponding mercury(II) sulfides or selenides (Eq. 287) [1527].

$$(C_6F_5X)_2Hg + Cu \xrightarrow[X=S,Se]{200\,^\circ C} (C_6F_5)_2Hg \qquad (287)$$

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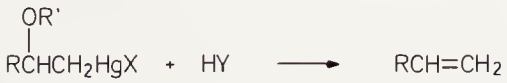
III. Hydrogen and Halogen Substitution

Hydrogen and halogen substitution in organomercury compounds have been extensively studied and a number of reviews [1–4] and one book [5] have appeared covering this topic. The primary emphasis of most of this work has been on studying the mechanism of electrophilic aliphatic substitution. Considerable kinetic and stereochemical information on these reactions is now available. The emphasis here, however, will be on possible synthetic applications of these reactions.

A. Hydrogen Substitution

The protonolysis of organomercury compounds, although extensively studied, has found relatively little synthetic utility. One instance where it might be expected to prove exceptionally valuable is in the demercuration of solvomercuration products. Unfortunately, under acidic conditions these compounds simply revert back to the starting olefin (Eq. 1), and other methods to be discussed in the monograph "Solvomercuration-Demercuration" have had to be devised to effect this important transformation.



(1)

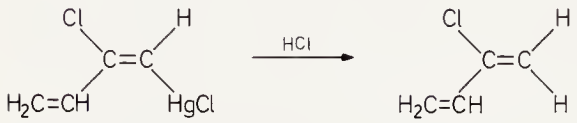
The most important synthetic application of the protonolysis reaction has been in the isotopic labelling of organic substrates. Although the deuterolysis (DCl and DOAc) of dialkylmercury compounds has been investigated from both a kinetic [6] and a stereochemical [7] standpoint, this reaction proceeds with significant racemization, apparently due to isomerization of the starting organomercurial.

The protonolysis or deuterolysis of alkenylmercurials derived from mercury salt additions to alkynes, however, provides a very nice method of preparing stereoisomerically pure alkenes (Eqs. 2–7) [8, 9]. Finally, alkenylmercurials prepared by the oxymercuration of alkylidene cyclopropanes are

(2) [10]

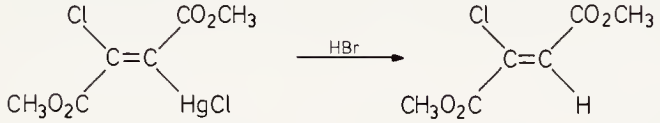
protonolyzed by hydrogen sulfide to afford high yields of enones (Eq. 8) [14].

(3) [10]

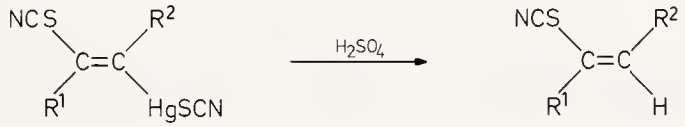


(4) [11]

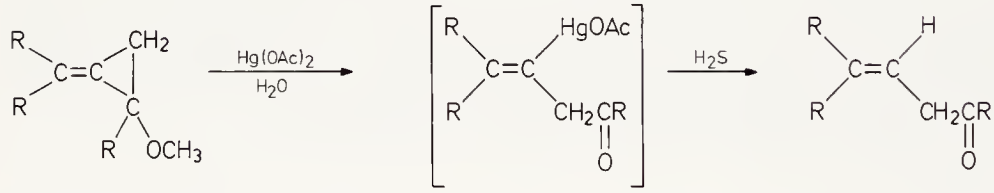
(5) [12]



(6) [12]



(7) [13]

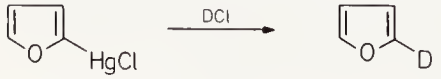


(8)

Alkynylmercurials also undergo facile deuterolysis, providing a convenient approach to labelled acetylenes (Eq. 9) [15].

(9)

Although the deuterolysis of diphenylmercury has been studied [6], the only significant synthetic applications of this type of reaction have been in the isotopic labelling of furan [16], thiophene [17, 18] and iodoferrocene [19] (Eqs. 10–15). The deuterolysis of mercurated porphyrins has been used, however, to determine the extent of mercuration [20]. The results with DCl agreed with those obtained using $NaBD_4$.



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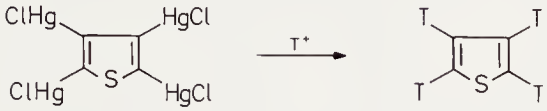

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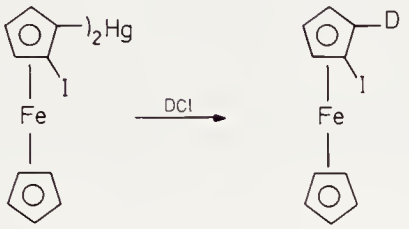
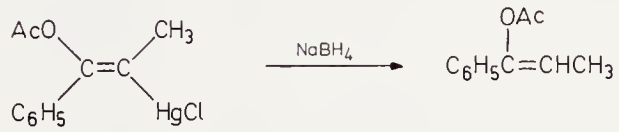


(15)

The reductive demercuration of organomercurials has also been studied extensively. While the reaction of $NaBH_4$ and organomercurials affords a number of products [21, 22], the addition of alkali results in clean substitution of mercury for hydrogen. This reaction is of great importance for the demercuration of solvomercuration products and will be covered in detail in the monograph "Solvomercuration-Demercuration". The reaction of alkylmercurials apparently involves free radicals as evidenced by the lack of stereospecificity, the presence of carbon skeleton rearrangements, and oxygen entrapment to afford alcohols [23–31]. β-Acetoxy vinylmercurials [32] and mercurated nucleotides [33] can also be demercurated in this fashion (Eqs. 16, 17).



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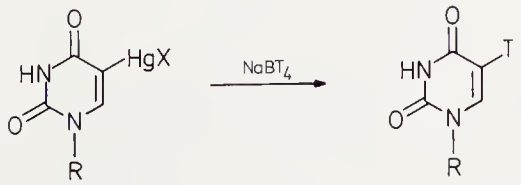


(17)

A variety of other reducing agents, including each of the following, have been employed for demercuration, but none appear to be of any particular synthetic utility: Et_2AlD [28], $LiAlH_4$ [23–25, 34, 35], $NaH_2Al(OCH_2CH_2OCH_3)_2$ [23], LiH [21, 36], n-Bu_3SnH [25, 28], DCuP $(n\text{-Bu})_3$ [28], sodium naphthalene [37], N-benzyl-1,4-dihydronicotinamide [38] and hydrazine [39].

Sodium amalgam appears to be the only reagent other than alkaline sodium borohydride which has proven truly useful for the demercuration of organomercurials [23, 24, 26, 30]. Reductions with this reagent proceed with complete retention of stereochemistry and no carbon skeleton rearrangements are observed. This approach is particularly valuable for stereospecific deuterium incorporation.

B. Halogen Substitution

The halogenation of organomercurials provides a very useful method for the preparation of a wide variety of organic halides, especially those not easily obtained by direct halogenation. This reaction has also proved extremely valuable for determining the position of mercury in an organomercurial of unknown structure. It is most commonly effected by employing the halogens themselves (Eqs. 18, 19), although a number of other reagents to be discussed

$$R_2Hg + X_2 \longrightarrow RHgX + R\text{-}X \tag{18}$$

$$RHgX + X_2 \longrightarrow HgX_2 + R\text{-}X \tag{19}$$

later can be employed. Our discussion will focus primarily on the types of organomercurials which undergo this reaction, beginning with alkylmercurials and continuing on to alkenyl-, alkynyl- and arylmercurials. A discussion of the halogenation of solvomercuration products will be largely deferred to the monograph "Solvomercuration-Demercuration", except for certain interesting stereochemical features pertinent to a discussion of the mechanism of this reaction. However, the mechanism of this widely studied [5] reaction will only be discussed in sufficient detail to aid in our understanding of the products observed upon halogenation of organomercurials.

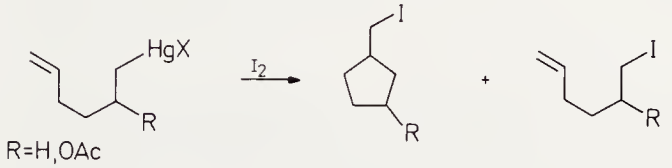
The halogenation of alkylmercurials has been extensively studied, although primarily with a view towards understanding the mechanism of this reaction. The first careful mechanistic study of the halogenation of alkylmercurials was reported by Winstein and Traylor in 1956 [40]. They and Keller [40] observed that the reaction of iodine and alkylmercuric iodides in dioxane is sensitive to light and peroxides, and greatly inhibited by oxygen. The reaction is approximately second order in iodine and independent of the organomercurial concentration, clearly implicating a free radical chain reaction (Eqs. 20–22). On the other hand, adding iodide anion and running the reaction in aqueous dioxane afforded a reaction which was first order in alkylmercuric iodide and first order in triiodide anion, suggesting a direct bi-

$$X_2 \longrightarrow 2X\cdot \tag{20}$$

$$X\cdot + RHgX \longrightarrow R\cdot + HgX_2 \tag{21}$$

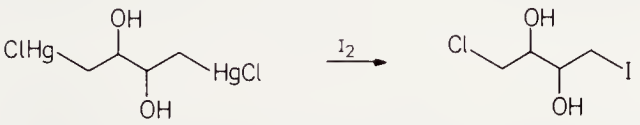
$$R\cdot + X_2 \longrightarrow R\text{-}X + X\cdot \tag{22}$$

molecular electrophilic substitution reaction. Thus, depending on the structure of the alkylmercurial, the exact reagents, the solvent and the presence or absence of air or light, one can observe either free radical or electrophilic substitution. The iodination of dialkylmercurials (methyl [41], dinitrofluoromethyl [42], ethyl [41], isopropyl [41], perfluoroisopropyl [43], *n*-butyl [41], isoamyl [41], *n*-hexyl [41] and carboranyl [44]) and alkylmercuric halides (chloromethyl [45], *n*-butyl [40], neopentyl [46], 5-hexenyl [47], 2-acetoxy-5-hexenyl [47], neophyl [40], 4-camphyl [40], 10-camphor [48], 3-chloro and -bromo-10-camphor [49], oxabicyclononyl [50–52], dioxatricyclodecyl [53] and numerous other solvomercuration products to be discussed in the monograph "Solvomercuration-Demercuration") has been shown to be quite general, and as one might expect, isomeric mixtures are often observed [50–52]. In fact, alkylmercuric iodides with substantial structural bias have been observed to undergo iodination in carbon tetrachloride primarily with inversion [51, 52]. Even aqueous triiodide anion sometimes gives isomeric mixtures [51, 53]. While a more detailed discussion of the halogenation of solvomercuration products can be found in "Solvomercuration-Demercuration", it is noteworthy that certain bicyclic intramolecular alkoxymercuration products undergo rearrangement upon iodination [50–52]. Free radical rearrangements are also evident upon iodination of 5-hexenylmercurials (Eq. 23)



(23)

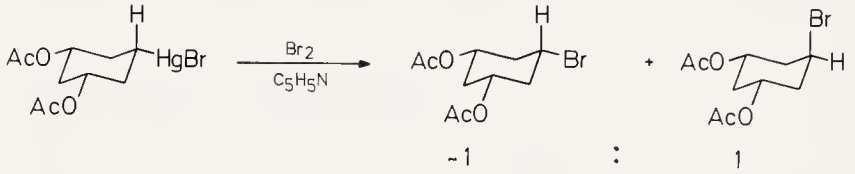
[47]. Intramolecular assistance is apparently also responsible for the introduction of a chlorine during iodination of the following organomercuric chloride (Eq. 24) [54], since other organomercuric chlorides referenced above have been iodinated without difficulty [45, 46, 48, 49].



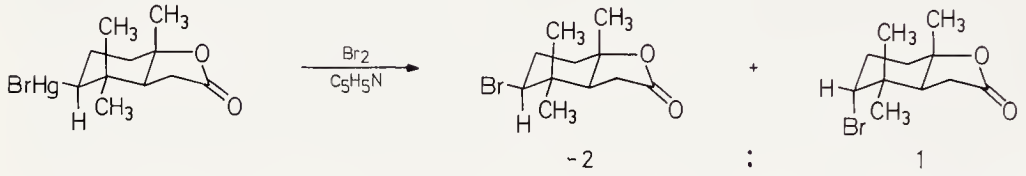
(24)

The bromination of organomercurials has received considerable attention from both a mechanistic and a synthetic viewpoint. Optically active *sec*-butylmercuric bromide has been brominated in non-polar solvents such as carbon disulfide [55] and carbon tetrachloride [56, 57] with complete loss of configuration. However, with bromine in pyridine at —65 °C, a high degree of retention is observed [55, 58]. Non-polar solvents give reactions showing overall first order kinetics and polar solvents promote second order kinetics as one would expect [56, 57], Studies on *cis*- and *trans*-4-methyl- [59, 60] and 4-*tert*-butylcyclohexylmercuric bromide [61] are consistent with this picture. Bromine in carbon tetrachloride gives approximately 50:50 mixtures from both pure isomers, while bromine in pyridine gives complete

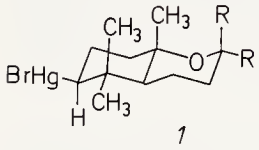
retention. This latter procedure has been suggested to hold promise as a method of preparing pure secondary bromides. Unfortunately, when applied to other cyclohexyl systems, this procedure has occasionally given mixtures of stereoisomers (Eqs. 25, 26). In the latter example, however, the product



(25) [62]

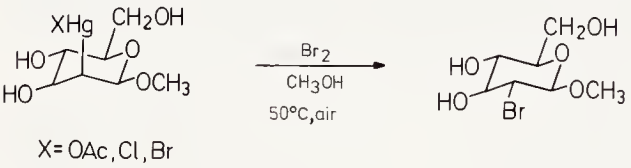


(26) [63]



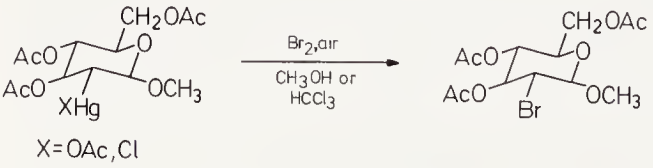
1

of retention can be obtained isomerically pure if potassium bromide and oxygen are added. Surprisingly, if the reaction is simply photolyzed, one obtains exclusively the inverted bromide. Similar results are observed on the oxadecalin system 1. A similar inversion has been reported upon bromination of mercurated methyl 2-deoxy-β-D-mannoside (Eq. 27) [64]. A related glyco-



(27)

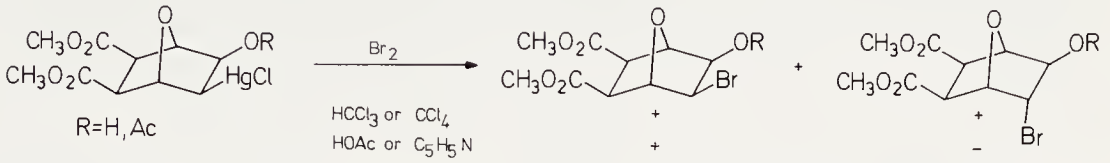
side has been shown to brominate with complete retention, even in chloroform when air is present, but when bromine in carbon tetrachloride under nitrogen is employed, a mixture of approximately equal amounts of both possible isomers is observed (Eq. 28) [64].



(28)

Other solvomercuration products behave similarly upon bromination. Diastereomerically pure peroxymercuration products have been observed to

give a single stereoisomer upon treatment with bromine in pyridine, but both possible diastereomers upon bromination in methylene chloride [65, 66]. Solvomercuration adducts of bicyclic olefins sometimes give the expected results (Eq. 29) [67–69], but not always (Eq. 30) [70]. In the latter case, acetyl hypobromite is probably formed (a known reaction of organomercury acetates and bromine [71–73]), and may initiate a radical process upon decomposition.



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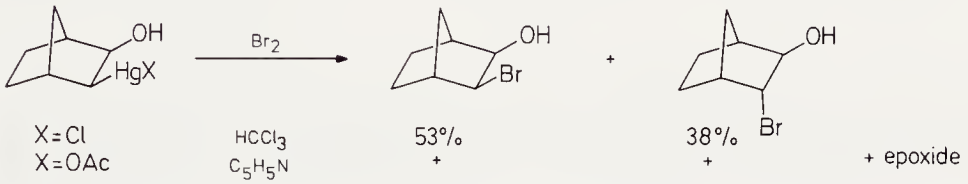
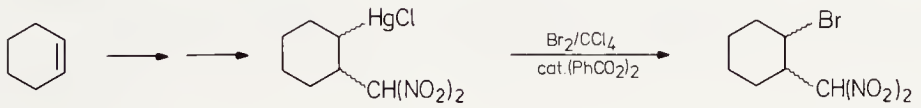


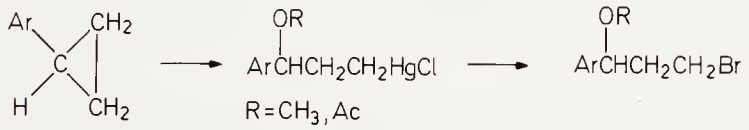
(30)

Numerous other alkylmercurials have been brominated. Dialkylmercurials [$CON(C_2H_5)_2$ [74], $CF(NO_2)_2$ [42], $CHFCO_2C_2H_5$ [75], $CF_2CO_2C_2H_5$ [75], $CFClCO_2C_2H_5$ [75], $CF(CF_3)CO_2C_2H_5$ [75], $C(CF_3)_2CO_2C_2H_5$ [75], $CF(CF_3)_2$ [43], $C(CF_3)_3$ [43], $CH_2C(CH_3)_2C(NO_2)_3$ [74]] generally give good yields, although temperatures of 200–300 °C are required for the polyfluorinated compounds. A variety of other simple alkylmercuric chlorides [$CH_2C(CH_3)_3$ [46], 10-camphor [48], 3-chloro- and -bromo-10-camphor [49]] undergo facile bromination, although it has been reported that organomercurials such as 3-acetoxy-2-chloromercurio-1,1,1-trifluoropropane cannot be brominated [77]. A number of γ-bromodinitroalkanes have been prepared by bromination of the corresponding alkylmercuric chlorides under free radical conditions (Eq. 31) [78]. These compounds are apparently unreactive



(31)

towards electrophilic substitution. Alkylmercurials derived from cyclopropanes by either ring opening [79, 80] or direct hydrogen substitution [81, 82] are easily brominated (Eqs. 32, 33).



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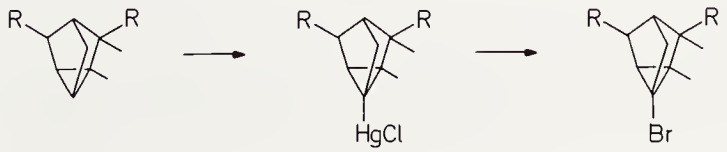


(33)

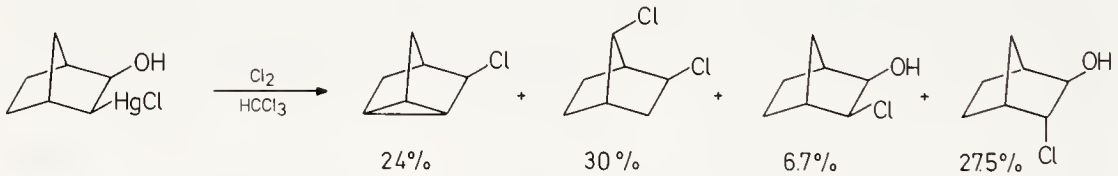
The hydroboration-mercuration of terminal olefins and subsequent in situ bromination affords a convenient method for the anti-Markovnikov hydrobromination of olefins (Eq. 34) [83]. Internal olefins give greatly reduced

$$RCH{=}CH_2 \xrightarrow{1/3\ BH_3} \xrightarrow{Hg(OAc)_2} \xrightarrow{Br_2} RCH_2CH_2Br \quad 71\text{-}86\% \tag{34}$$

yields. Although direct iodination produces alkyl acetates (see Chap. IV), if one adds methanol prior to iodination or uses dicyclohexylborane instead of diborane, one can obtain excellent yields of primary alkyl iodides by this same sequence (Eq. 35) [84]. Other equally convenient procedures now exist for the direct bromination or iodination of organoboranes however.

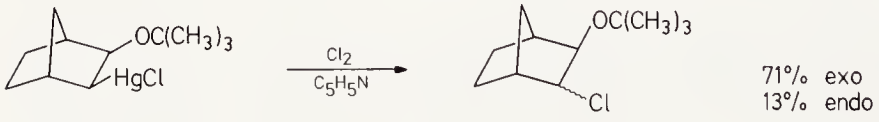
$$RCH{=}CH_2 \xrightarrow{(C_6H_{11})_2BH} \xrightarrow{Hg(OAc)_2} \xrightarrow{I_2} RCH_2CH_2I \tag{35}$$

The reaction of alkylmercurials and chlorine has received little attention, presumably due to the difficulty in handling this reagent. While *cis,cis*-3,5-diacetoxycyclohexylmercuric chloride reacts with chlorine in pyridine with complete retention [62], *trans*-4-*tert*-butylcyclohexylmercuric chloride reacts with chlorine in carbon disulfide to give only the rearranged tertiary alkyl chloride [61]. Similarly, $Hg[CF(NO_2)_2]_2$ [42] in ether and α-keto-β-peroxyalkylmercuric chlorides in methanol chlorinate normally, but α-keto-β-peroxyalkylmercuric *bromides* reportedly react with chlorine in methylene chloride to give a mixture of the corresponding alkyl chloride and bromide [73]. In methanol the alkyl bromide is the only product. Difficulties are encountered in the chlorination of other solvomercuration products also. Chlorination of the hydroxymercurial of norbornene gives a variety of side products in chloroform (Eq. 36) [70]. In pyridine, the major product is norbornene oxide. The



(36)

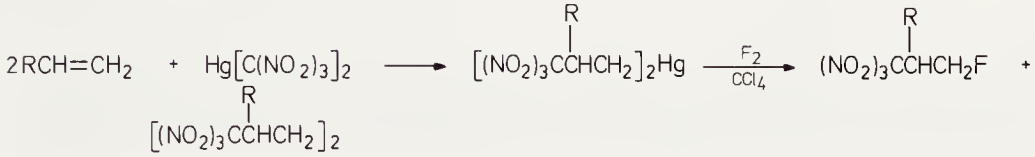
corresponding *tert*-butoxymercurial reacts more cleanly, but again an *exo-endo* mixture results (Eq. 37).



(37)

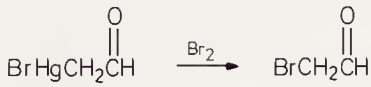
Fluorination studies have been limited to the adducts derived from olefins and *bis*-(trinitromethyl) mercury. Alkyl fluorides are obtained in modest yield along with dimers presumed to be formed by a free radical process (Eq. 38) [85, 86].

The halogenation of benzylic mercurials has received considerable mechanistic attention. The bromination of benzylmercuric chloride [87–89], and the iodination of benzylmercuric chloride [90–93], bromide [94] and iodide [91, 95], as well as dibenzylmercury [41], ring-substituted benzylmercuric halides [96] and ethyl α-bromomercuriophenylacetate [94] and its ring-substituted derivatives [97] have all been studied. The effect on the kinetics of added halide reagents and solvent polarity has been closely examined. Both first and second order kinetics are observed indicating that both free radical and electrophilic processes can occur under the appropriate reaction conditions.



(38)

α-Mercurated carbonyl-containing compounds halogenate readily. Thus, mercurated acetaldehyde [98] and its corresponding acylal [99] and acetal [100] derivatives all undergo facile bromination (Eqs. 39–41). The organo-



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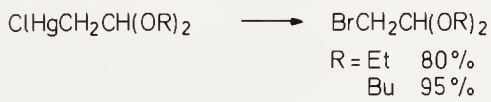
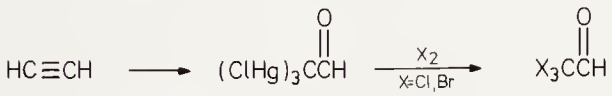


(41)

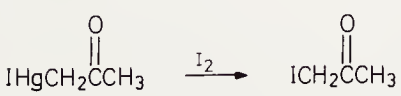
mercurial derived from the aqueous mercuration of acetylene has been suggested to be tri(chloromercurio)-acetaldehyde based on the fact that it affords halogenated acetaldehydes upon chlorination and bromination (Eq. 42)



(42)

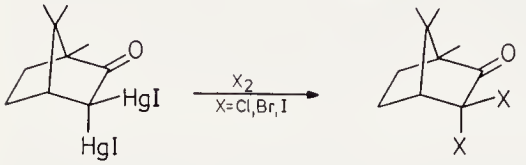
[101]. Iodination in base produces iodoform. α-Keto-alkylmercuric halides have also been halogenated (Eqs. 43–45), as have simple monomercurated

(43) [102]

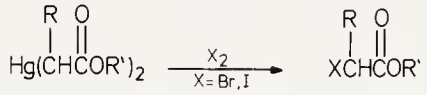


(44) [103]

carboxylic acids [106] and esters [41, 106] (Eq. 46). Bromination of the dimercurated and trimercurated compounds obtained from treating conjugated

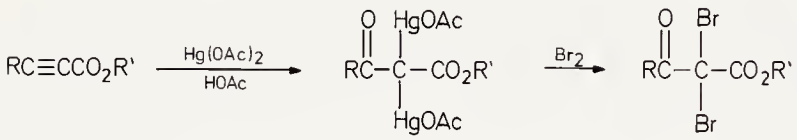


(45) [104, 105]

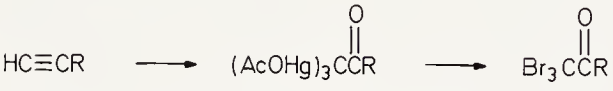


(46)

alkynoic acids and esters or terminal acetylenes with mercuric acetate in acetic acid gives dibromoketo acids and esters or tribromomethylketones respectively (Eqs. 47, 48) [107]. Non-conjugated alkynoic acids give organo-

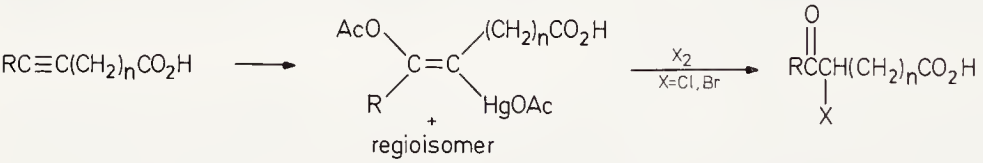


(47)

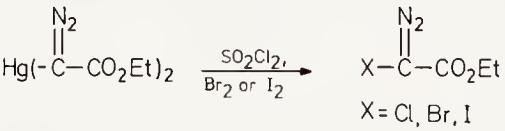


(48)

mercurials (presumably mercuric acetate trans addition compounds) which chlorinate or brominate to give quantitative yields of monohaloketones (Eq. 49) [107]. While conditions have been published for the monohalogena-

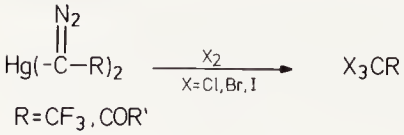


(49)



(50)

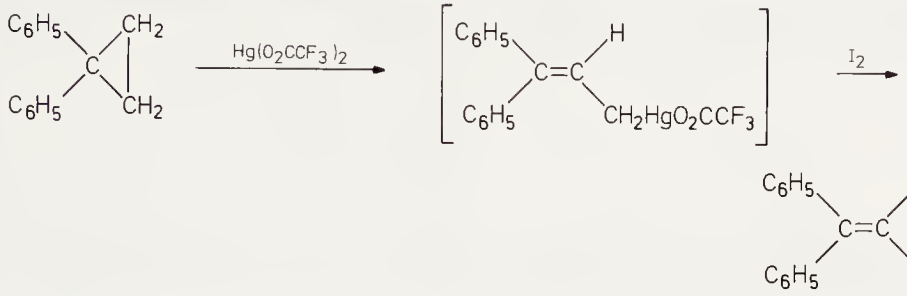
tion of mercurated diazo esters (Eq. 50) [108–110], the halogenation of other mercurated diazo compounds reportedly gives trihalomethyl compounds (Eq. 51) [111, 112]. Iodine monochloride in this latter reaction affords the corresponding unstable chlorodiiodomethyl ketone [113]. These reactions appear to have some real preparative significance since certain ketones, such



(51)

as adamantyl methyl ketone, apparently cannot be fully halogenated using halogen alone.

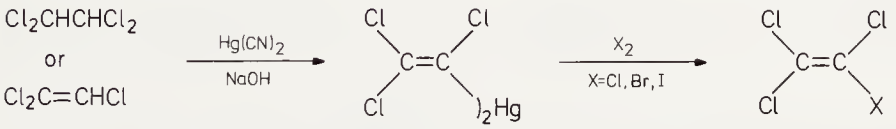
Few examples of the halogenation of allylic mercurials appear to exist in the literature. An allylic iodide has been obtained in unspecified yield upon mercuration-iodination of 1,1-diphenylcyclopropane (Eq. 52) [114].



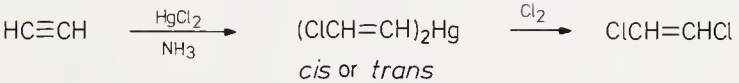
(52)

The attempted low temperature bromination of dicyclopentadienylmercury afforded a 93% yield of a compound with molecular formula $C_5H_5Br_3$ [115]. No structure was offered for this compound. Under basic conditions bromination of dicyclopentadienylmercury apparently produces hexabromocyclopentadiene (61% yield).

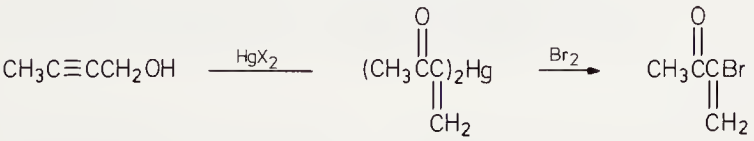
The halogenation of alkenylmercurials provides a useful route to a wide variety of alkenyl halides. The chlorination [116, 117], bromination [118–121] and iodination [121] of dialkenylmercurials have been reported. Where the stereochemical outcome makes a difference and the results have been reported, halogenation has been indicated to proceed with complete retention [118, 119]. Besides *cis*- and *trans*-distilbenylmercurials prepared from the corresponding alkenyl lithium reagents, the dialkenylmercurials which have been reported to undergo halogenation have been prepared directly from either alkanes or alkenes (Eq. 53), and alkynes (Eqs. 54–56). This approach



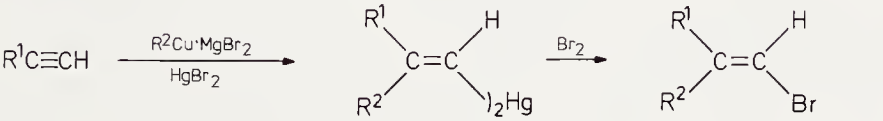
(53) [116, 121]



(54) [117]



(55) [120]

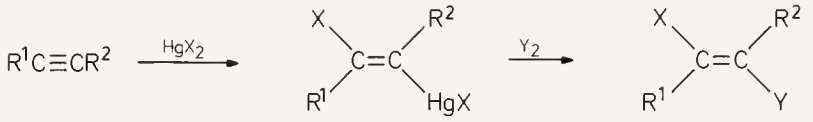


(56) [119]

R^1	R^2	% Yield
CH_3	C_2H_5	77
H	C_7H_{15}	71
C_4H_9	C_4H_9	74
C_4H_9	C_2H_5	68

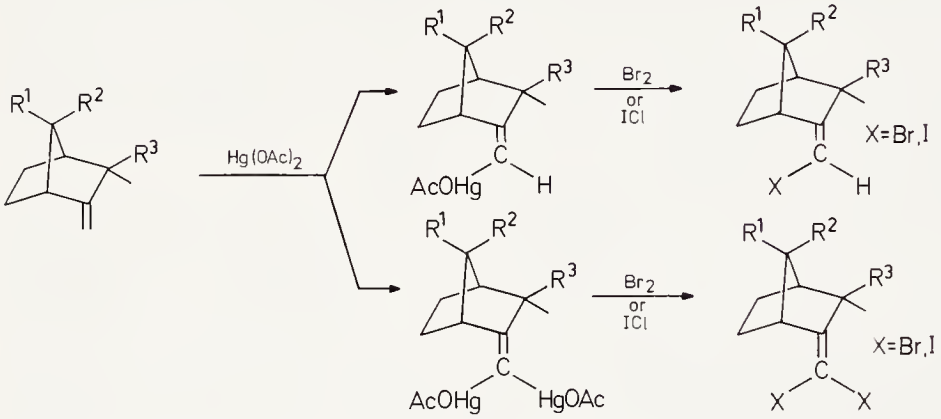
therefore provides an especially short and convenient route to these alkenyl halides.

A substantial number of alkenylmercuric halides have also been either brominated or iodinated (Eqs. 57–59). Note that all of these alkenyl

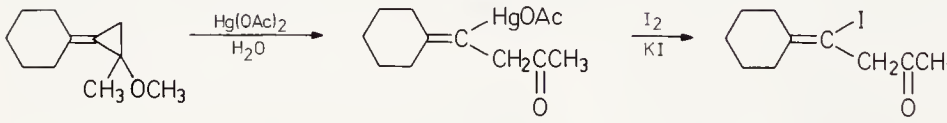


(57)

R^1	R^2	X	Y	Ref.
H	H	Cl	I	122-127
CH_3	H	Cl	I	11
CH_2OH	CH_2OH	Cl	Br, I	128
C_6H_5	CH_3	OAc	Br, I	32
R	R	SCN	Br, I	13



(58) [129]

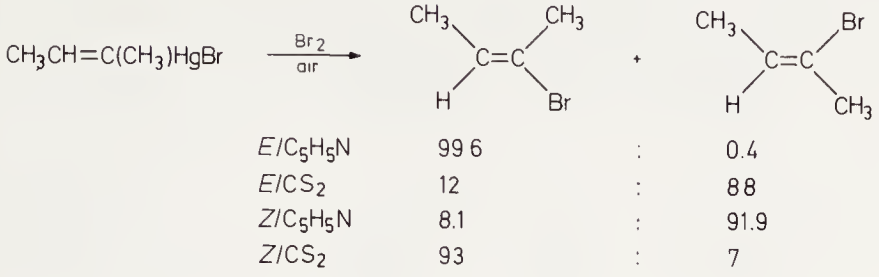


(59) [14]

halides have been prepared from alkynes or alkenes in only two steps. The stereochemical outcome of these reactions has not always been reported, however. Less readily available alkenylmercurials such as *cis*-β-chlorovinylmercuric chloride [124, 125, 127, 130] and *cis*- and *trans*-stilbenylmercuric halides [118] have also been iodinated and brominated respectively, apparently with retention of configuration.

Only in a few cases has the stereochemistry of these halogenation reactions been closely examined. Thus, while *cis*- and *trans*-β-chlorovinylmercuric chloride react with iodine in polar solvents with complete retention [124, 126, 127], in benzene and carbon tetrachloride each isomer gives approximately an equal mixture of the corresponding cis and trans iodides [126, 131]. Identical results have been obtained upon bromination of *cis*- and *trans*-styrylmercuric bromides [126, 132]. In both cases, a free radical intermediate was assumed responsible for isomerization. More recently, however, it has been observed that while alkenylmercuric bromides react

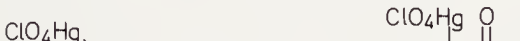
with bromine in pyridine in the presence of air with almost complete retention, bromine in carbon disulfide in the presence of air gives predominant inversion (Eq. 60) [133]. A mechanism involving trans addition of bromine to the



E/C_5H_5N	99.6	:	0.4
E/CS_2	12	:	88
Z/C_5H_5N	8.1	:	91.9
Z/CS_2	93	:	7

(60)

carbon—carbon double bond, followed by trans elimination of mercuric bromide was suggested. Consistent with this picture are three examples of the addition of bromine to the double bond of alkenylmercurials (Eqs. 61–63).



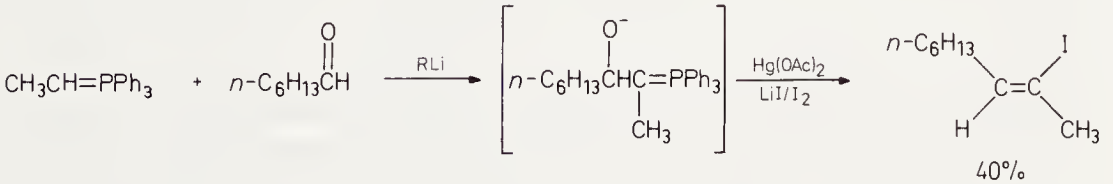
(61) [134]

(62) [135]

(63) [135]

This ability to control the stereochemistry in the bromination of alkenylmercurials makes this a particularly attractive route to alkenyl bromides, especially in view of the ease with which these compounds can now be prepared directly from alkynes via hydroboration-mercuration.

Finally, a totally different approach to alkenyl iodides, involving an organomercurial intermediate should be mentioned. Readily available β-oxido ylids react with mercuric acetate, followed by lithium iodide and iodine, to provide a convenient stereospecific route to alkenyl iodides (Eq. 64) [136]. Iodine alone cannot be used.



40%

(64)

The halogenation of alkynylmercurials provides a very simple method for the preparation of alkynyl halides (Eqs. 65–67). In one instance, however, the

alkyne initially formed apparently undergoes further halogenation (Eq. 68) [116].

$$HC{\equiv}CH \longrightarrow [C_2Hg] \xrightarrow{I_2} IC{\equiv}CI \qquad (65)\ [137]$$

$$(CH_3)_3SiC{\equiv}CH \longrightarrow (CH_3)_3SiC{\equiv}CHgX \xrightarrow{I_2} (CH_3)_3SiC{\equiv}CI \qquad (66)\ [138]$$

X=OAc, I

$$RC{\equiv}CH \longrightarrow (RC{\equiv}C)_2Hg \xrightarrow{X_2} RC{\equiv}CX \qquad (67)$$

R	X	Ref.
CF_3	I	139
C_6H_5	I	140
C_6H_5	Br	141
C_6H_{13}	Br	141
$H_2C{=}CH$	Br	142
$H_2C{=}CH$	Cl	142

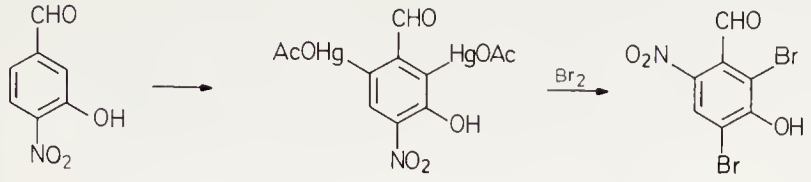
$$(ClC{\equiv}C)_2Hg \xrightarrow{I_2} \begin{matrix} Cl & & I \\ & C{=}C & \\ I & & I \end{matrix} \qquad (68)$$

The halogenation of aromatic organomercurials has been a widely employed reaction. It has been used as an analytical tool, studied mechanistically, employed in the structure determination of many an arylmercurial, and utilized to synthesize a wide variety of aromatic halides. Analytically, iodine titration can be used to determine the ratio of arylmercuric iodide to diarylmercurial in a mixture [143].

Both the bromination [144, 145] and iodination [41, 144–147] of diarylmercurials and arylmercuric halides have been studied mechanistically by Russian workers. The reaction is generally bimolecular even in non-polar solvents [41, 147], unless photolysis is employed [144].

The halogenation of arylmercurials has proven invaluable in determining the position of mercury within a new compound or for establishing the ratio of isomers of an inseparable mixture of arylmercurials such as one might obtain during electrophilic mercuration. For example, the mercuration of nitrobenzene [148–150], benzoic acid [149, 150] and benzenesulfonic acid [149] clearly gives a mixture of all three possible mercuration products. Under certain conditions specific isomers have been isolated (see Chap. II, Sect. K). The ratio of isomers in each of these mercuration reactions has been determined by analyzing the bromination products. In this way it has been observed that each of these compounds gives an unusually high percentage of ortho mercuration, presumably due to coordination of the mercury reagent to the functional group and subsequent intramolecular delivery of the electrophilic species. One should be aware of the fact that during bromination, rearrangements have been observed (Eqs. 69, 70) [151]. Iodination of these same arylmercurials apparently proceeds without rearrangement. While

these appear to be the only two examples of rearrangement during halogenation, one should be alert to this possibility.



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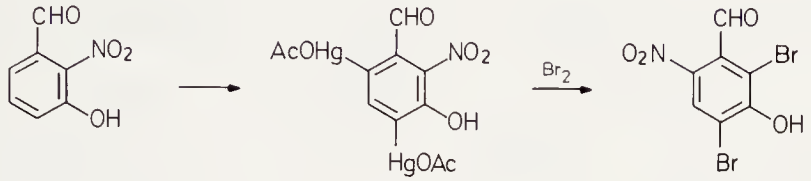
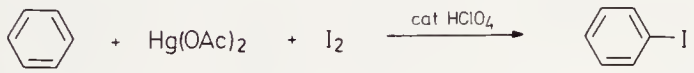


(70)

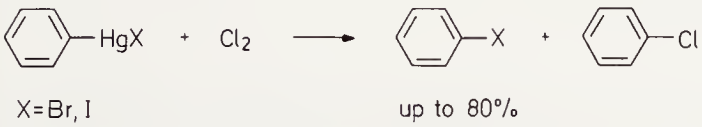
In general, the halogenation of arylmercurials is a very valuable approach to aryl halides and has been frequently employed. No attempt will be made to completely list the large number of aryl halides prepared in this manner. Only selected examples will be cited to illustrate the synthetic possibilities. If a specific aryl halide is being sought, the reader should refer to the appropriate sections in Chap. II to ascertain whether the desired arylmercurial has been previously reported. If so, the reader should check the original reference for possible halogenation results.

To date, almost all arylmercurial halogenation studies have been limited to iodination or bromination, both of which proceed readily. In fact, iodination can be effected by simply mixing the arene, mercury reagent and iodine (Eq. 71) [152]. This reaction apparently proceeds through an inter-



(71)

mediate arylmercurial. Bromination, as will be seen by subsequent examples, proceeds readily with a wide variety of aromatic mercurials. Chlorination, on the other hand, has received little attention and appears limited to diarylmercurials and only certain arylmercuric salts. The chlorination of arylmercuric iodides or bromides can result in halogen exchange (Eq. 72) [153]. Quite



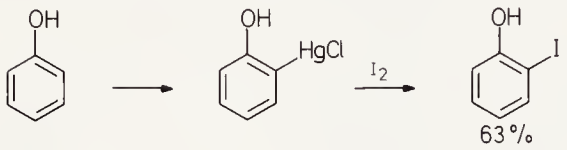
(72)

recently, arylmercurials have been employed for the first time in the synthesis of astatine compounds (Eq. 73) [154]. High yields are obtained.

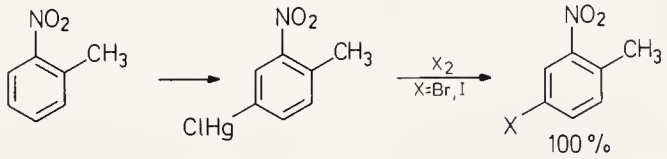
(73)

A number of major synthetic advantages are offered by the halogenation of aromatic mercurials as opposed to other approaches to these compounds.

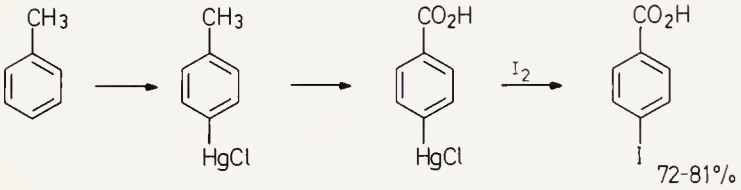
Where direct halogenation may result in isomeric mixtures, one can frequently isolate directly or by simple recrystallization procedures isomerically pure arylmercurials which can be subsequently halogenated to afford isomerically pure aryl halides. The following literature examples nicely illustrate this point (Eqs. 74–77). The synthesis of *p*-iodobenzoic acid is an interesting example of functional group interconversion on an organomercurial.



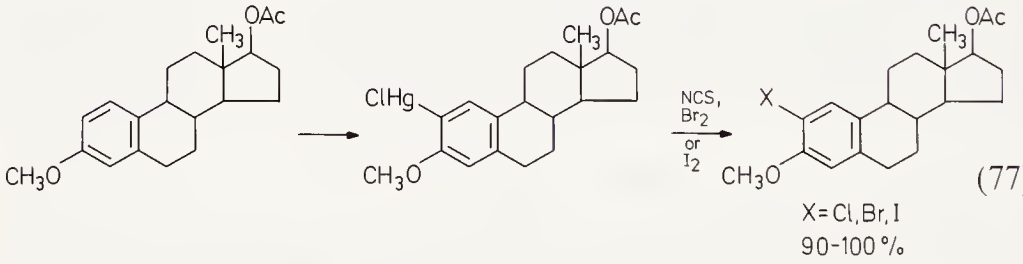
(74) [155, 156]



(75) [157]

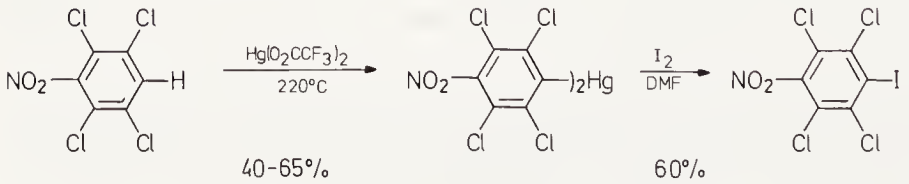


(76) [158]



(77) [159]

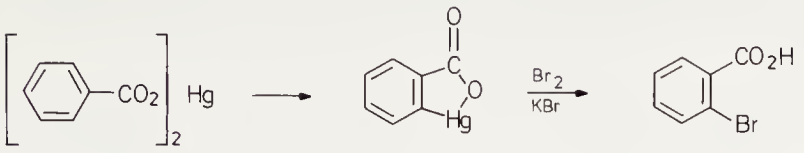
A further advantage of arylmercurial halogenation is that many arenes can be mercurated which will not undergo direct halogenation. In this manner, highly electron-deficient aryl halides are easily prepared as illustrated by the following example (Eq. 78) [160, 161].



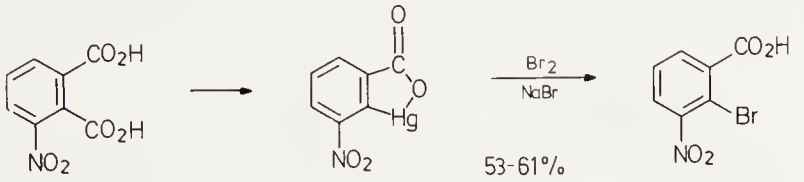
(78) [162]

One can also take advantage of the wide variety of methods available for the synthesis of arylmercurials. For example, intramolecular substitution or decarboxylation of aryl carboxylic acids, and subsequent halogenation affords a convenient regiospecific approach to aryl halides (Eqs. 79–81). Sulfur dioxide

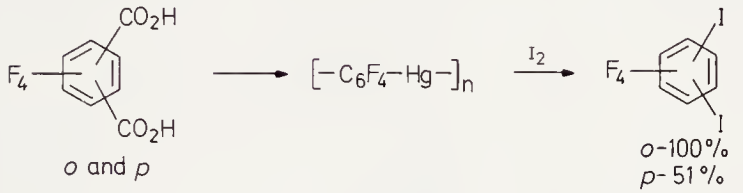
[167, 168] and trioxide elmination from arylsulfinic and -sulfonic acids and subsequent halogenation also offers certain possibilities (Eqs. 82–85).



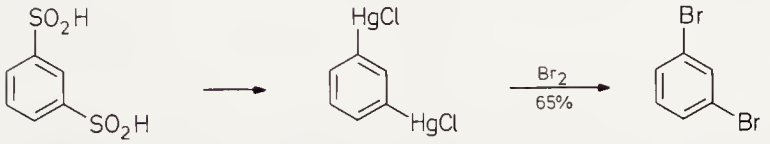
(79) [163]



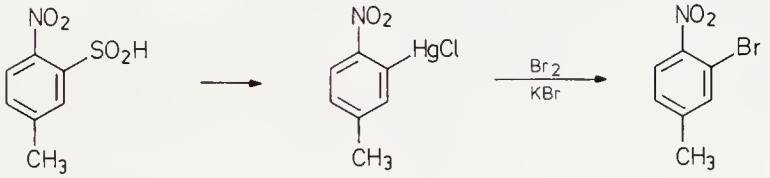
(80) [164]



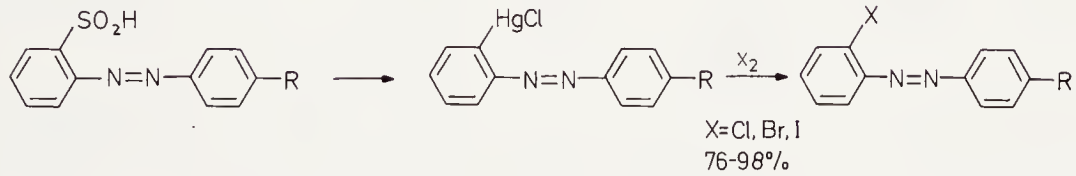
(81) [165, 166]



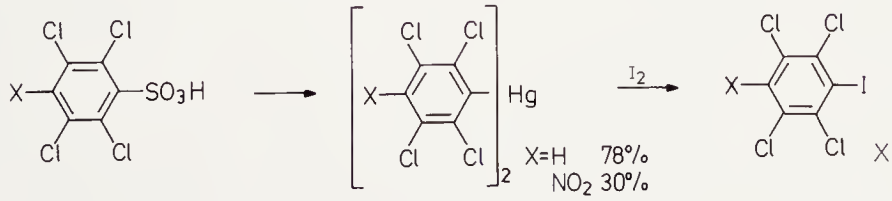
(82) [148]



(83) [169]



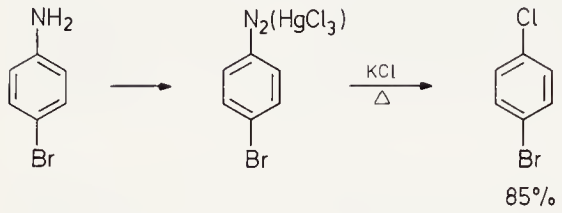
(84) [170]



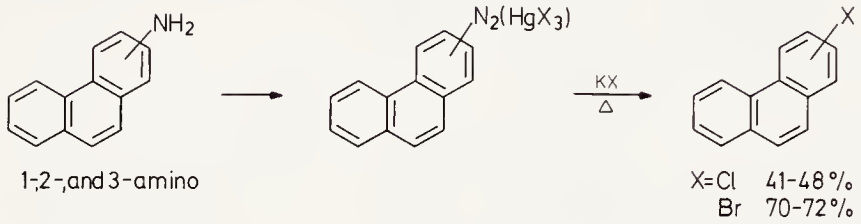
(85)

At first glance, the preparation of aryl halides via mercuration-halogenation of diazonium salts appears unnecessarily lengthy in view of the vast utility of the more direct Sandmeyer approach. However, there are occasions when the Sandmeyer reaction fails. In those cases, simple thermolysis of the

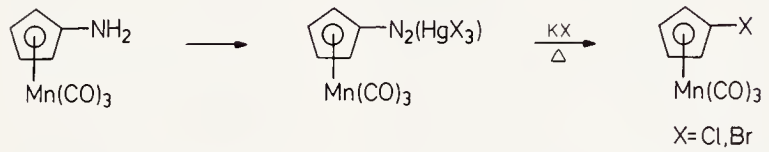
aryldiazonium-mercury halide complexes previously discussed as intermediates in the synthesis of arylmercurials (Chap. II, Sect. L) provides good yields of aryl halides directly (Eqs. 86–88). The following aryl halides, some



(86) [172]



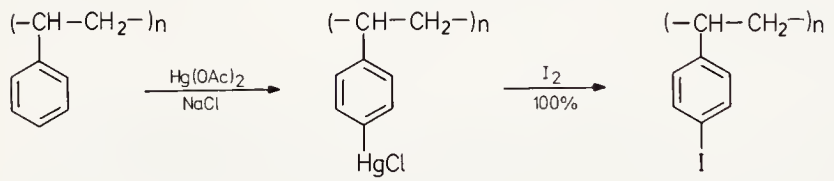
(87) [173]



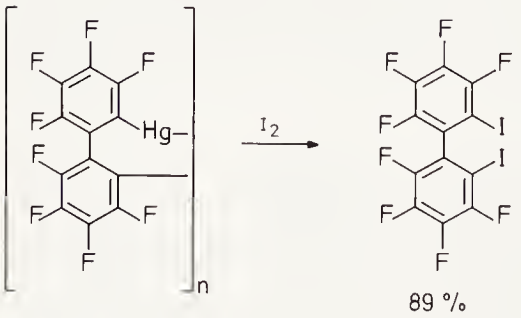
(88) [174]

of which are difficult to prepare by the Sandmeyer reaction, have also been prepared by this procedure: *o,o'*- and *p,p'*-dichlorobiphenyl (>80%), *o,o'*-dibromobiphenyl (>80%), and 2-bromonaphthalene (65%).

The iodination of organomercury polymers has proven useful both synthetically and in the determination of their structure (Eqs. 89, 90) [175].



(89) [176]

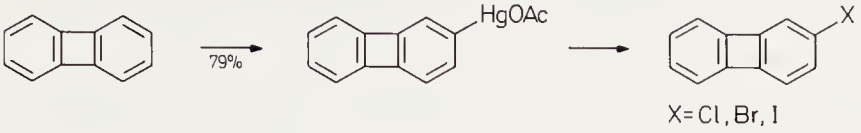


(90) [177]

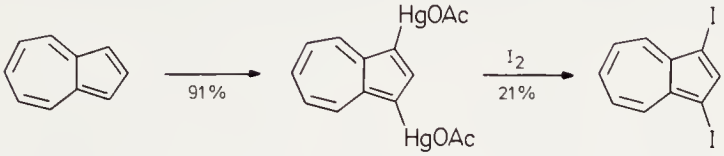
The mercuration-halogenation of polycyclic aromatic hydrocarbons can also be useful synthetically (Eqs. 91, 92).

The halogenation of a wide variety of heterocyclic mercurials, including furans [180–182], benzofuran [183], dibenzofurans [184, 185], numerous

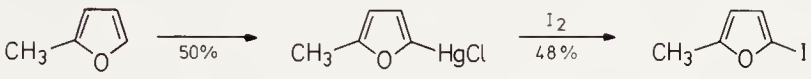
thiophenes [41, 186–188], 1-phenylpyrazole [189], pyridine *N*-oxide [190–192], quinoline *N*-oxide [191, 193], and mercurated mono- and polynucleotides [33] and nucleosides [194] has been affected. As seen by the following examples, these reactions hold considerable synthetic utility (Eqs. 93–99).



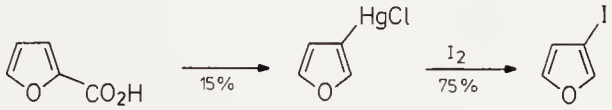
(91) [178]



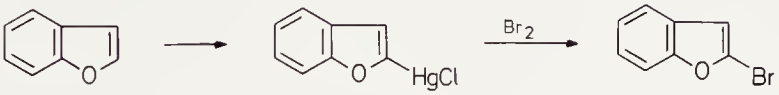
(92) [179]



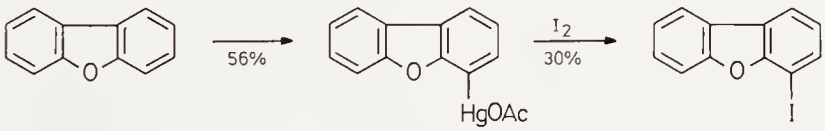
(93) [180]



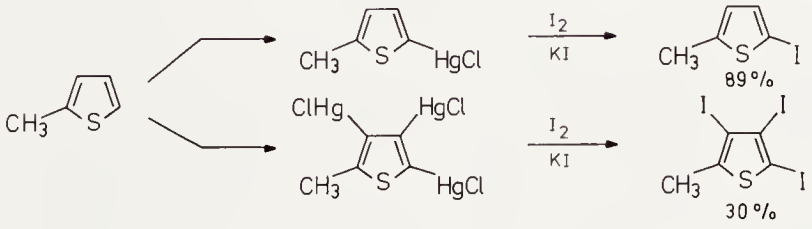
(94) [182]



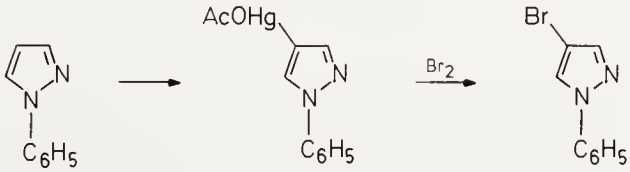
(95) [183]



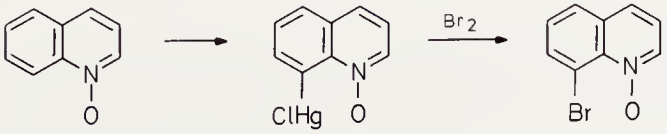
(96) [184]



(97) [186]



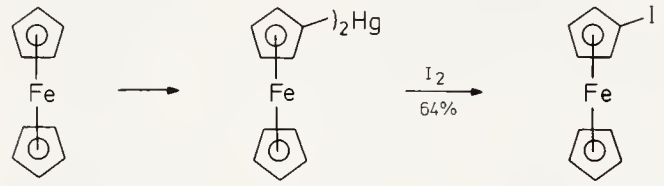
(98) [189]



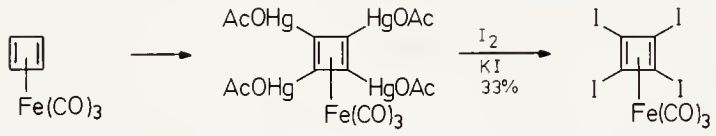
(99) [191, 193]

It should be noted that the bromination of furan mercurials gives only very low yields of the corresponding bromides however [180, 182].

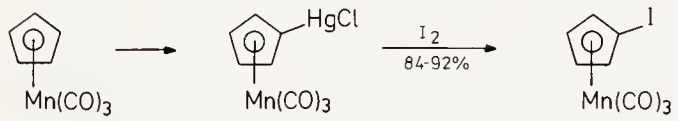
The mercuration-iodination of certain organometallics, such as ferrocenes (Eq. 100) [19, 195–199], cyclobutadiene iron tricarbonyl (Eq. 101) [200], cymantrene (Eq. 102) [201–203], and cyclopentadienyl(tetraphenylcyclobutadiene)cobalt (Eq. (103) [204] has provided a valuable method for the functionalization of these organometallics. Attempted bromination of mercurated ferrocenes [197] and cymantrene [203] has failed, indicating the sensitivity of these organometallics. It is noteworthy that attempted direct halogenation of cyclobutadiene iron tricarbonyl also failed [200].



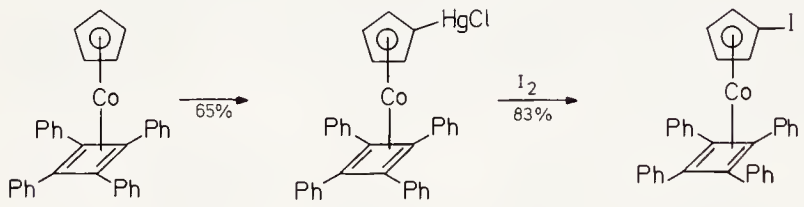
(100) [197]



(101) [200]

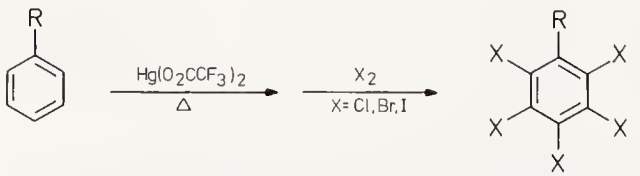


(102) [201, 202]



(103) [204]

The polyhalogenation of aromatics can also be conveniently effected using a mercuration-halogenation sequence, as several of the above examples have illustrated. By employing a highly electrophilic mercury salt such as mercuric trifluoroacetate and elevated temperatures, one can conveniently prepare a wide variety of polyhalobenzenes this way (Eq. 104) [205–210]. Polyfunctional



(104)

R=H, NH_2, NHAc, CH_3O, CH_3, CF_3, F, Cl, Br, NO_2, CO_2H, CO_2Na, $CONH_2$

benzenes have also been employed in this reaction. When phenylmercuric chloride is employed as a starting material, penta- and hexamercurated ben-

zene derivatives can be obtained, as evidenced by the formation of pentabromo- and hexabromobenzene upon bromination. When carboxylic acids are mercurated, products of decarboxylation are frequently observed [208]. By analogous procedures octachloronaphthalene [209], tetraiodofuran [211], a number of polyiodothiophenes [186–188], and tetraiodopyrrole [211] have also been prepared. Quite clearly, the mercuration-halogenation approach is one of the most convenient routes to polyhalo aromatic compounds, a class of compounds often not readily accessible by any other procedure.

Not all halogenation reactions of organomercurials have been effected by using the elements themselves. On occasions, for example, a more polar iodinating agent is desired and IBr [105] or more commonly ICl have been employed. Simple alkyl [212], α-keto- and α-diazoalkyl- [113], cyclopropyl- [82], alkenyl- [129] and arylmercurials [213, 214] have been iodinated in this fashion. It has been noted, however, that β-phenethylmercuric chloride gives approximately equal amounts of the corresponding alkyl chloride and iodide when treated with ICl. In this case, the alkyl iodide was shown to react with ICl to produce the alkyl chloride.

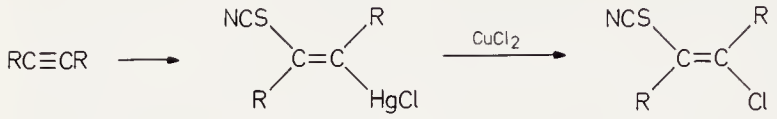
N-Iodosuccinimide appears to only have been employed twice for the iodination of mercurated ferrocenes [215], but *N*-bromosuccinimide (NBS) has been widely used as a brominating agent. Dialkyl- [216, 217], dialkenyl- [218], dialkynyl- [219], and diarylmercurials [216, 217, 220] are all readily brominated by this reagent. However, it appears that only one of the two organic groups reacts, at least in non-polar solvents [219], thus greatly limiting the synthetic utility of this reaction. Bromination by NBS is much more valuable for the synthesis of bromoferrocenes, since bromine cannot be employed here [215, 221–223]. Brominated mono- and polynucleotides can also be obtained in nearly quantitative yield by employing NBS [33]. *N*-Bromophthalimide and *N*-bromoacetamide have also been employed once each for the bromination of organomercurials [215, 218]. *N*-Chlorosuccinimide has also been successfully utilized once for the chlorination of an arylmercurial [159].

The halogenation of a wide variety of organomercurials has been effected by simply stirring with cupric chloride or bromide in a polar solvent, usually DMF or acetonitrile (Eq. 105). Modest to excellent yields of organic halides

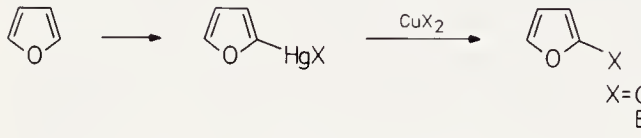
$$RHgX \xrightarrow[X=Cl,Br]{CuX_2} R-X \qquad (105)$$

have been obtained in this fashion from simple alkylmercuric halides [224 to 226] and dialkylmercurials [224, 225]; polyhalodialkylmercurials [224, 225]; bicyclic alkylmercuric chlorides [226]; α-ketodialkylmercurials [224, 225]; benzylic mercurials [224, 225, 227, 228]; alkenylmercuric halides derived from mercury salt additions to acetylenes [11, 13, 229]; dialkynylmercurials [225]; arylmercurials [224, 225, 230]; polynuclear aromatic mercurials [231]; heterocyclic mercurials [231]; ferrocene-derived mercurials [195, 196, 232, 233]; mercurated manganese- [203, 231, 234], rheniúm- [234] and chromium [235] tricarbonyl organometallics; and carbomethoxymercuric acetate [236].

A few examples should suffice to illustrate the synthetic utility of this reaction (Eqs. 106–108). Recall that furan cannot be directly brominated, nor

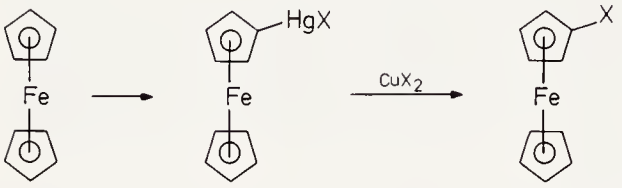


(106) [13]



X=Cl 75%
Br 51%

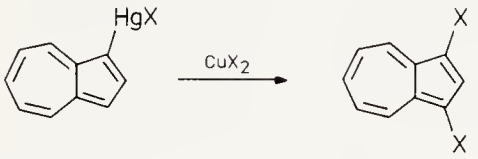
(107) [231]



X=Cl 58%
Br 69%

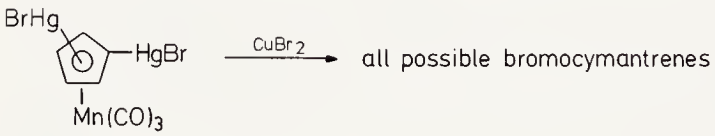
(108) [233]

can mercurated furans be brominated using Br_2. Thus, the use of cupric bromide appears to provide the simplest route to bromofurans. Similarly, cuprous chloride provides the most convenient approach to chlorofurans and chloroferrocenes. Difficulties have been encountered in attempting to employ this procedure for the preparation of chloro- and bromoazulenes (Eq. 109) [231] and dichloro- and dibromocymantrenes (Eq. 110) [203]. Di- and



X=Cl 99%
Br 100%

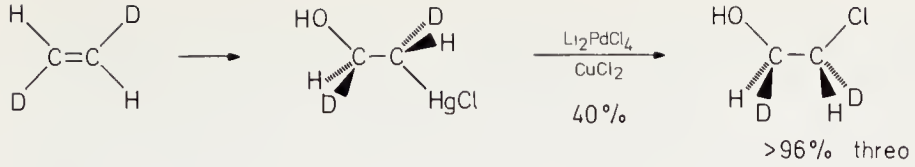
(109)



(110)

polyhalogenation products were observed instead. It has also been reported that alkylmercuric chlorides react with cupric bromide to give substantial amounts of the corresponding alkyl chloride [226]. Primary and secondary bicyclic alkylmercuric chlorides are brominated with predominant loss of stereochemistry, presumably due to free radical intermediates [226].

The combination of cupric chloride and catalytic amounts of palladium chloride has also been utilized to chlorinate organomercurials [237, 238]. Here predominant inversion is observed, except where phenonium ion intermediates are possible (Eqs. 111, 112). Ferric chloride reportedly chlorinates dibenzylmercury [227].



(111)

$$(CH_3)_3CCHDCHDHgCl \xrightarrow[CuCl_2]{Li_2PdCl_4} (CH_3)_3CCHDCHDCl \qquad (112)$$

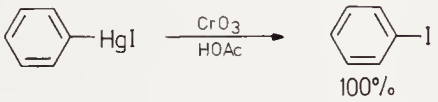
threo >85% erythro

Several other unique methods exist for halogen substitution in organomercurials. Alkylmercuric salts react with sodium borohydride in carbon tetrachloride or bromotrichloromethane to produce the corresponding alkyl chloride or bromide respectively [239–241]. Free radicals are involved here and this approach has been employed to study the selectivity of various radicals as a function of temperature. The pyrolysis of secondary alkylmercuric chlorides also affords the corresponding alkyl chlorides in moderate yield (Eq. 113) [242, 243]. This pyrolysis approach fails with phenylmercuric salts

$$CH_3CH_2\underset{|}{\overset{HgCl}{C}}HCH_3 + HgCl_2 \xrightarrow[2\,hr.]{260°C} CH_3CH_2\underset{|}{\overset{Cl}{C}}HCH_3 \qquad (113)$$

64%

other than phenylmercuric cyanide. However, phenylmercuric iodide can reportedly be quantitatively oxidized to iodobenzene upon treatment with chromium trioxide (Eq. 114) [244]. Free radicals are apparently involved in all these reactions.



(114)

A number of other reagents have been employed to halogenate organomercurials, but none of these seem to have any real synthetic utility: $ClN(CF_3)_2$ [245], $BrN(CF_3)_2$ [245], ClN_3 [246, 247], HOCl [248], HOBr [60], $[C_5H_5NH]Br_3$ [60, 215], $C_6H_5SO_2NBr_2$ [60], RCO_2Br [217], $HClO_3$ [178], SO_2Cl_2 [61, 110], $TeCl_2$ [249], $C_6H_5ICl_2$ [250] and 2,4,4,6-tetrabromo-2,5-cyclohexadienone [219].

Before concluding this chapter, it is perhaps worth noting a halogen substitution reaction employing mercury salts which, while not actually involving organomercurials as intermediates, is nevertheless a very useful route to alkyl halides. This is the mercury version of the classical Hunsdiecker reaction. In a review of the Hunsdiecker reaction in 1956, a number of references to the use of mercurous and mercuric salts were given, but it was stated that those reactions generally give lower yields than the reactions with silver salts [251]. In 1961 Cristol and Firth reported a procedure using mercuric oxide and either bromine or iodine, which is more convenient than the Hunsdiecker reaction and generally gives at least comparable, if not better, yields (Eq. 115) [252].

$$RCO_2H + HgO + X_2 \longrightarrow R{-}X \qquad (115)$$

The reaction conditions have since been optimized [253] and a number of simple, as well as small ring [254–256] and bicyclic [257, 258] alkyl halides have been prepared using this reaction. The reaction with bromine as commonly run in carbon tetrachloride has been observed, however, to give substantial amounts of alkyl chloride when bicyclo[2.2.2]octane carboxylic acid was employed [259]. This problem was overcome by using bromotrichloromethane as a solvent plus excess bromine, or more conveniently by employing 1,2-dibromoethane as the solvent. Iodination of this same system afforded predominately the corresponding ester. More recently it has been reported that photolysis during reaction can result in substantially higher yields, particularly with aromatic carboxylic acids [260].

The mechanism of this reaction has been studied [261–263]. The reaction apparently involves intermediate acyl hypohalites and free radicals. As anticipated, free radical rearrangements are observed [258, 264]. In one case, however, the halodecarboxylation of pyridine carboxylic acids has been suggested to involve halogenation of the corresponding heterocyclic mercurial [265]. In general, this reaction is quite convenient and gives excellent yields. It does not seem to have received the attention it deserves.

More recently, the halogenation of mercurous carboxylates in carbon tetrachloride has been examined [266]. Bromination affords good to excellent yields of alkyl bromides, while iodination gives comparable yields of the corresponding esters (Eqs. 116, 117). No alkyl chloride is observed in the former reaction and only trace amounts of alkyl iodide are evident in the latter reaction.

$$Hg_2(O_2CR)_2 + 3Br_2 \longrightarrow 2RBr + 2CO_2 + 2HgBr_2 \quad (116)$$

$$Hg_2(O_2CR)_2 + 2I_2 \longrightarrow RCO_2R + CO_2 + 2HgI_2 \quad (117)$$

In conclusion, virtually every type of alkyl-, alkenyl-, alkynyl-, aryl-, heterocyclic or organometallic halide can be obtained from the corresponding organomercurial using direct halogenation with chlorine, bromine or iodine. Where these reagents fail, NBS or cupric halides often work quite well. With the many unique methods now available for the preparation of organomercurials, one can expect to see increasing application of this approach to the synthesis of difficult to obtain organic halides in the years ahead.

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IV. Synthesis of Heteroatom-Containing Compounds

A. Introduction

A wide variety of heteroatom-containing compounds can be conveniently prepared via organomercury intermediates. A number of the more synthetically interesting of these transformations will be covered in this chapter, starting first with some methods of forming oxygen-containing compounds. Subsequent sections will deal with the synthesis of organic compounds of some of the Group VIb (sulfur, selenium and tellurium) and Vb (nitrogen and phosphorus) elements, followed by a very brief discussion of the synthesis of some organosilicon compounds which might be of interest to the organic chemist. The synthesis of organic compounds of other elements of the periodic table is beyond the scope of this monograph and will not be covered.

B. Oxygen Compounds

The vast majority of organomercury compounds are inert to oxygen, this being one of the characteristics which makes these compounds attractive as synthetic intermediates. Secondary and tertiary alkylmercurials are, however, slowly oxidized by air and can be cleaved under free radical conditions or elevated temperatures. Organomercuric salts also react rapidly with sodium borohydride to generate free radicals which can be oxidized by air to the corresponding alcohols (Eqs. 1, 2) [1–4]. As indicated, free radical rearrange-

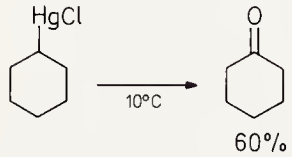
$$(C_6H_5)_3CCH_2HgCl \xrightarrow[\substack{NaOH\\air}]{NaBH_4} \underset{6\%}{(C_6H_5)_3CCH_3} + \underset{\displaystyle OH}{\underset{|}{(C_6H_5)_2CCH_2C_6H_5}} \quad \underset{70\%}{} \qquad (1)\ [1]$$

$$H_2C{=}CH(CH_2)_4HgBr \xrightarrow[O_2]{NaBH_4} \underset{68\%}{H_2C{=}CH(CH_2)_4OH} \qquad (2)\ [2, 3]$$

ments can occur reducing the synthetic utility of this reaction. Nevertheless, solvomercuration and subsequent sodium borohydride — induced oxidation has recently proved quite useful in the synthesis of hydroxy-tetrahydrofurans [5, 6], -carbohydrates [7] and -prostaglandins [8. 9], as well as aphidicolin [10]. These reactions will be discussed in more detail in the monograph "Solvomercuration-Demercuration".

On the other hand, ozone reacts rapidly with alkylmercurials even at low temperatures (Eqs. 3–5) [11–13]. At —76 °C primary dialkylmercury com-

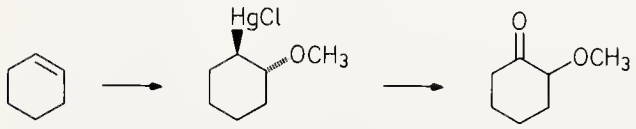
$$(n\text{-}C_6H_{13})_2Hg \xrightarrow[-76\,^\circ C]{O_3} \underset{80\%}{2n\text{-}C_5H_{11}CO_2H} \tag{3}$$



(4)

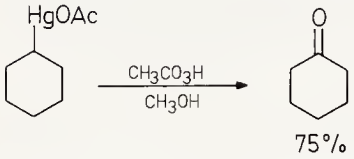
$$(CH_3)_3CHgCl \xrightarrow{10\,^\circ C} \underset{50\%}{(CH_3)_3COH} + \underset{22\%}{CH_3\overset{O}{\overset{\|}{C}}CH_3} + \underset{28\%}{HCO_2H} \tag{5}$$

pounds give good yields of the corresponding carboxylic acids. However, at 10 °C both primary dialkylmercurials and alkylmercuric bromides give a mixture of all possible carboxylic acids of shorter chain length. Secondary alkylmercuric chlorides give good yields of ketones. This particular reaction appears quite useful for the synthesis of α-substituted ketones via solvomercuration-oxidation (Eq. 6). The oxidation of tertiary alkylmercurials to tertiary alcohols by ozone appears less useful, since these organomercurials are relatively inaccessible.



(6)

Secondary alkylmercurials can also be oxidized to ketones by peracids (Eq. 7) [14]. The oxidation of diphenylmercury by chromium trioxide in



(7)

acetic acid/acetic anhydride has also been observed, but no yield was reported (Eq. 8) [15]. Analogous oxidation of phenylmercuric iodide produces phenyl iodide in quantitative yield, while benzylmercuric chloride undergoes oxidation primarily to benzaldehyde.

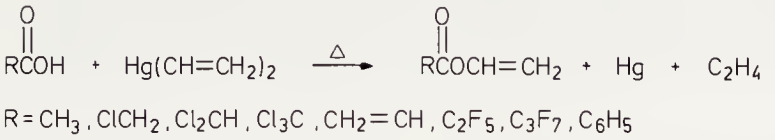
$$(C_6H_5)_2Hg \xrightarrow[HOAc/Ac_2O]{CrO_3} C_6H_5OAc \tag{8}$$

The thermal decomposition of organomercuric acetates has been briefly examined (Eq. 9) [16–18]. While aryl and simple alkylmercurials give only

$$RHgOAc \xrightarrow{\Delta} ROAc + Hg^\circ$$

$$R = C_6H_5\,(0\%),\ n\text{-}C_4H_9\,(5\text{-}10\%),\ C_6H_5CH_2\,(0.2\text{-}18\%),\ H_2C{=}CHCH_2\,(56\%),\ H_2C{=}CH\,(95\%) \tag{9}$$

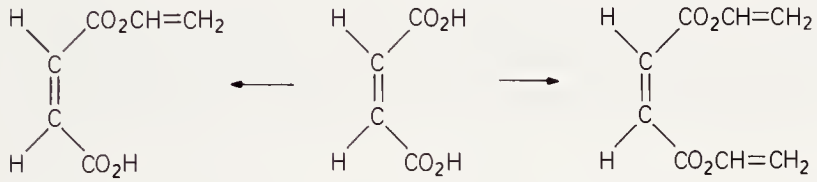
low yields of the corresponding acetates, allyl acetate is formed in good yield and vinyl acetate in near quantitative yield. The facile thermal decomposition of alkenylmercuric carboxylates has proven quite general and provides a very simple method for the vinylation of a wide variety of carboxylic acids (Eq. 10)



$$RCOH + Hg(CH{=}CH_2)_2 \xrightarrow{\Delta} RCOCH{=}CH_2 + Hg + C_2H_4 \qquad (10)$$

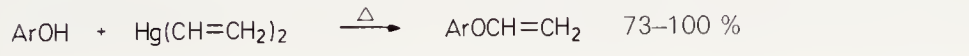
$R = CH_3, ClCH_2, Cl_2CH, Cl_3C, CH_2{=}CH, C_2F_5, C_3F_7, C_6H_5$

[17–20]. The more acidic the carboxylic acid, the more readily thermal decomposition of the intermediate vinylmercuric carboxylate takes place. This reaction has been used to mono- and divinylate fumaric, maleic, adipic and isophthalic acids (Eq. 11) [17, 19]. Unfortunately, this reaction is not stereospecific. Thermolysis of both *cis*- and *trans*-1-propenylmercuric acetates gives approximately a 2 to 1 mixture of *cis*- and *trans*-1-propenyl acetates [18].



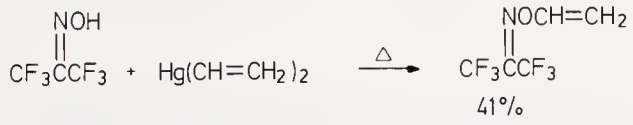
(11)

This type of reaction is also applicable to the synthesis of aryl vinyl ethers (Eq. 12) [17, 21]. Even the oxime from hexafluoroacetone is a sufficiently strong acid to undergo vinylation (Eq. 13) [20]. Analogous reactions between perfluorodivinylmercury and fluorosulfonic acid and phosphorus-containing acids gave only rearranged products [20], but a variety of vinylsulfur and phosphorus-containing compounds can be prepared in this manner as will be discussed later.



$$ArOH + Hg(CH{=}CH_2)_2 \xrightarrow{\Delta} ArOCH{=}CH_2 \quad 73\text{–}100\ \% \qquad (12)$$

$Ar = C_6H_5; p\text{-}CH_3C_6H_4; 2,4\text{-}Cl_2C_6H_3; 2,6\text{-}Cl_2C_6H_3; 2,4,6\text{-}Cl_3C_6H_2; Cl_5C_6; 2,4\text{-}(NO_2)_2C_6H_3$



$$CF_3CCF_3 + Hg(CH{=}CH_2)_2 \xrightarrow{\Delta} CF_3CCF_3 \quad (41\%) \qquad (13)$$

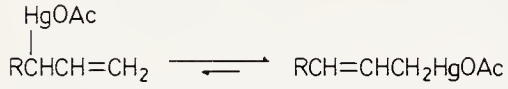
The majority of other synthetically useful oxidation reactions involving organomercurials have been performed more or less under solvolytic conditions. The solvolysis of alkylmercuric salts has been studied for some twenty years now (Eq. 14) [14, 22–35]. While this reaction provides a convenient

$$XHgR \longrightarrow X^- + {}^+HgR \longrightarrow Hg^\circ + R^+ \qquad (14)$$

method for generating carbonium ions bearing a very large positive charge relative to the ground state and less susceptible to nucleophilic attack on

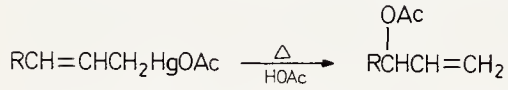
carbon than other methods, like most carbonium ion reactions, it often results in a variety of products and is generally of little synthetic utility.

While the solvolysis of benzylic mercurials has not proved synthetically useful [36, 37], the solvolysis of allylic mercurials has been of considerable mechanistic and synthetic interest. Although allylic mercurials exist in equilibrium, that equilibrium lies far towards the primary organomercurial (Eq. 15) [38, 39]. Nevertheless, solvolysis of these compounds gives almost



(15)

exclusive formation of the less thermodynamically stable secondary allylic acetate (Eq. 16) [38–42]. The addition of mercuric acetate tends to increase

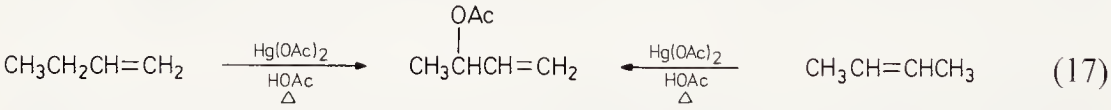


(16)

still further the amount of secondary acetate [41]. Cyclic mechanisms of the following types have generally been favored for these reactions, although a certain amount of carbonium ion character is also evident, at least when

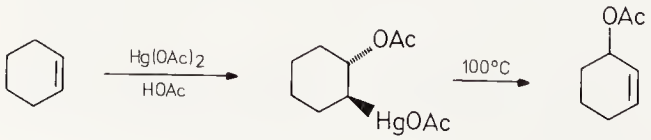
$R = C_6H_5$ [40, 42]. Under the usual solvolysis conditions or in the presence of excess mercuric acetate, the initially formed secondary acetate can isomerize to the more stable primary acetate and mixtures can sometimes occur.

Synthetically, the demercuration of allylmercurials is quite valuable. The direct reaction of olefins and mercuric acetate provides a convenient method for allylic acetoxylation (Eq. 17) [43, 44]. This reaction, first reported in 1948



(17)

by Treibs [45], apparently proceeds via initial rate determining allylmercuric acetate formation, followed by demercuration of the allylmercurial [39, 41]. Although addition compounds are readily formed upon reacting olefins with mercuric acetate (see the monograph "Solvomercuration-Demercuration") and these compounds have been shown to thermally decompose to allylic acetates (Eq. 18) [46–48], it appears that adduct formation is only a side



(18)

Table 4.1. Allylic Acyloxylation of Olefins

Olefin	Product	% Yield	Ref.
$CH_3CH_2CH=CH_2$	$CH_3\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (94%) + $CH_3CH=CHCH_2OAc$ (6%)	50	39, 41
trans-$CH_3CH=CHCH_3$	$CH_3\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (90-94%) + $CH_3CH=CHCH_2OAc$ (10-6%)	—	39, 41
cis-$CH_3CH=CHCH_3$	$CH_3\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (92%) + $CH_3CH=CHCH_2OAc$ (8%)	35	39, 41
n-$C_3H_7CH=CH_2$	$C_2H_5\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (99%) + $C_2H_5CH=CHCH_2OAc$ (1%)	86	39, 41
cis-$C_2H_5CH=CHCH_3$	$CH_3\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CHCH_3$ (~19%) + $C_2H_5\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (~79%) + $C_2H_5CH=CHCH_2OAc$ (~2%)	52	39, 41
n-$C_4H_9CH=CH_2$	*n*-$C_3H_7\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (97.5%) + *n*-$C_3H_7CH=CHCH_2OAc$ (2.5%)	90	39, 41, 47
n-$C_3H_7CH=CHCH_3$	primary and secondary allylic acetates	—	47
n-$C_5H_{11}CH=CH_2$	*n*-$C_4H_9\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (92%) + *n*-$C_4H_9CH=CHCH_2OAc$ (8%)	95	39, 41
n-$C_6H_{13}CH=CH_2$	*n*-$C_5H_{11}\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (98.5%) + *n*-$C_5H_{11}CH=CHCH_2OAc$ (1.5%)	100	39, 41, 47, 49
n-$C_5H_{11}CH=CHCH_3$ *cis* and *trans*	primary and secondary allylic acetates	—	41, 47, 49
$(CH_3)_2CH(CH_2)_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CHCH_3$ + $(CH_3)_2CHCH_2CH=\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH_2CH_3$	four acetates	—	50

Table 4.1. (continued)

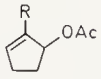
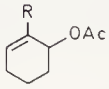
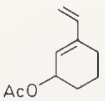
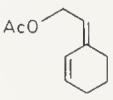
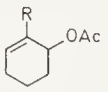
Olefin	Product	% Yield	Ref.
$C_6H_5CH_2CH=CH_2$	$C_6H_5\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (1%) + $C_6H_5CH=CHCH_2OAc$ (99%)	72	39-41, 46, 47
trans-$C_6H_5CH=CHCH_3$	$C_6H_5\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ (22%) + $C_6H_5CH=CHCH_2OAc$ (78%)	low	41
$C_6H_5(CH_2)_2CH=CHCH_3$	four acetates	—	41
trans-$CH_3O_2C(CH_2)_6CH=CHCH_3$	*trans*-$CH_3O_2C(CH_2)_6CH=CHCH_2OAc$	85	51
$CH_3O_2C(CH_2)_8CH=CH_2$	$CH_3O_2C(CH_2)_7\underset{\displaystyle OAc}{\underset{\vert}{C}}HCH=CH_2$ + $CH_3O_2C(CH_2)_7CH=CHCH_2OAc$	—	51
$CH_3O_2C(CH_2)_7CH=CH(CH_2)_7CH_3$	methyl 8-acetoxy-9-, 9-acetoxy-10-, 10-acetoxy-8-, and 11-acetoxy-9-octodecenoates	60-78	48, 53-55
$CH_3O_2C(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$	methyl 9-acetoxy-10, 12-; 10-acetoxy-8, 12-; 12-acetoxy-9, 13-; and 13-acetoxy-9, 11-octodienoate plus diacetates	—	56
			
R = $H_2C=CH$		25-35	57
R = C_6H_5		54	58
			
R = H		19, 52	45, 47, 59-62
R = CH_3		21	45, 61
R = $H_2C=CH$		25-30	57
		35-40	
		~5	
R = 		48	58
R = 		40	58

Table 4.1. (continued)

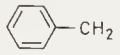
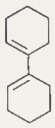
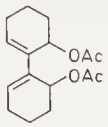
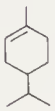
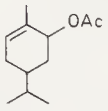
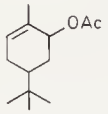
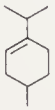
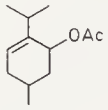
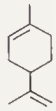
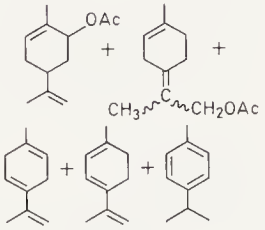
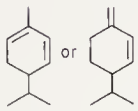
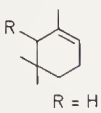
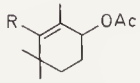
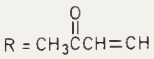
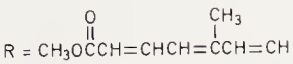
Olefin	Product	% Yield	Ref.
R = 		71	57, 58
R = 		45	58
		31	58
 optically active	 racemic cis/trans = 72:28	80	50, 59, 61, 63
 OH	 OH (OAc)	—	50
 optically active	 racemic	80	45, 59, 63
		—	45, 59, 64
	product unknown	—	59
 R = H		24	65
		5	66
		very low	67

Table 4.1. (continued)

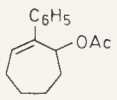
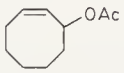
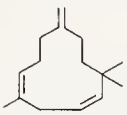
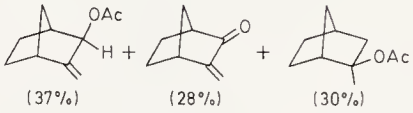
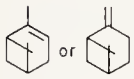
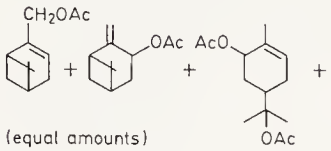
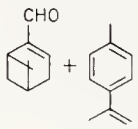
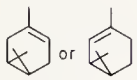
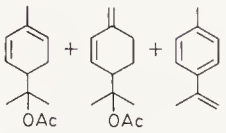
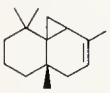
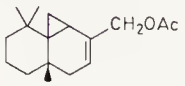
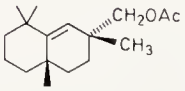
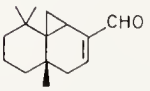
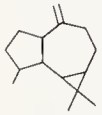
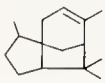
Olefin	Product	% Yield	Ref.
		54	58
		34	47, 68, 69
	product unknown	—	59
	 (37%) (28%) (30%)	9	70
	 (equal amounts) 	—	50, 61, 71
		—	72, 73
	 +  + 	14.4 5.4 11.1	74
	product unknown	—	45, 59
	product unknown	—	45, 59

Table 4.1. (continued)

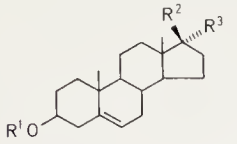
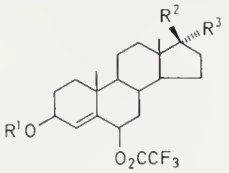
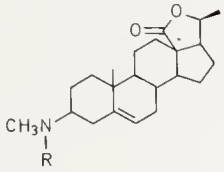
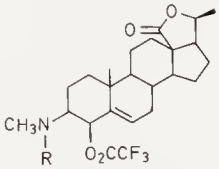
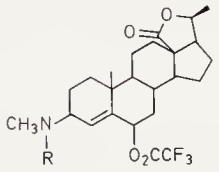
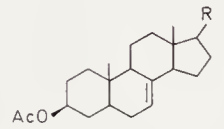
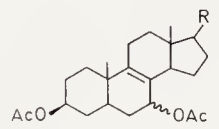
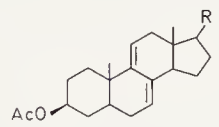
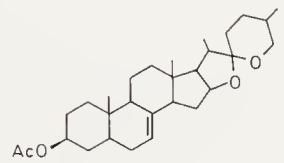
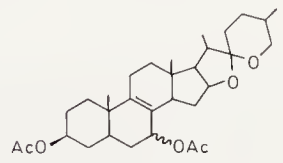
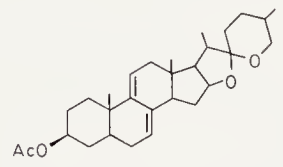
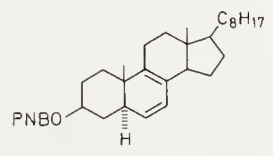
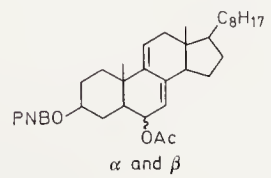
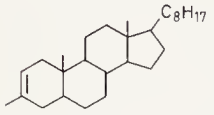
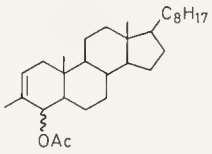
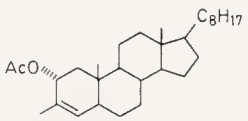
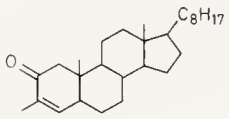
Olefin	Product		% Yield	Ref.
				
R^1 R^2 R^3				
Ac =O			40	75
Ac C_8H_{17} H			45	
CF_3CO C_8H_{17} H			70	
		R = H	30	75
		CH_3	12	
		Ac	18	
		CF_3CO	26	
	+			
		R = H	32	
		CH_3	18	
		Ac	30	
		CF_3CO	46	
		R = $COCH_3$	—	76
		$CH(CH_3)CO_2CH_3$	—	
		C_9H_{17}	—	
	+			
				
			—	76
	+			
				
			—	77
	α and β			

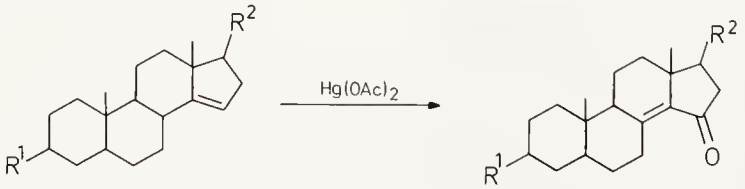
Table 4.1. (continued)

Olefin	Product	% Yield	Ref.
	 +  + 	α -17 β -35 8 10	78

reaction and decomposition to the allylic acetate involves olefin regeneration. Synthetically, the Treibs reaction has found considerable utility for the preparation of allylic acetates (see Table 4.1) due to the ease with which the reaction can be run, the convenient separation of the inorganic products, and the few side products observed in these reactions. On the other hand, a considerable amount of starting material sometimes remains after reaction and the yields in those cases are not very high. Unsymmetrical olefins can also lead to four possible allylic isomers, not counting possible stereoisomers (Eq. 19).

$$RCH_2CH{=}CHCH_3 \longrightarrow RCH_2CH{=}CHCH_2OAc + RCH_2\underset{\displaystyle OAc}{\underset{|}{C}}HCH{=}CH_2 + R\underset{\displaystyle OAc}{\underset{|}{C}}HCH{=}CHCH_3 + RCH{=}CH\underset{\displaystyle OAc}{\underset{|}{C}}HCH_3 \qquad (19)$$

As seen in Table 4.1, two side reactions are evident during the Treibs reaction. In certain cases the initially formed allylic acetate is apparently oxidized further to an unsaturated carbonyl compound. Enones are in fact the only products observed upon treating certain steroids with mercuric acetate (Eqs. 20, 21) [79].

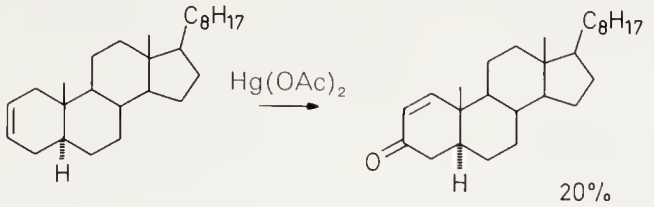


(20)

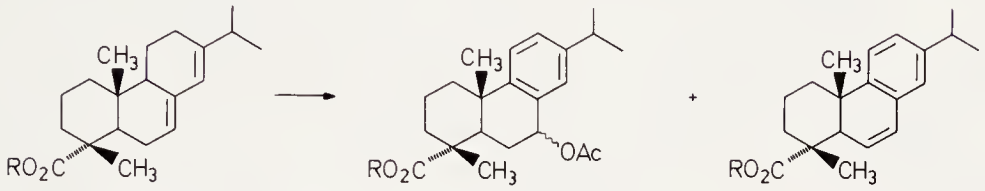
R^1	R^2
H	C_9H_{19}
OAc	C_9H_{19}
OAc	C_8H_{17}

~10%

Dehydrogenation is also commonly observed under Treibs conditions. For example, abietic acid and its methyl ester afford the corresponding acetoxy and olefinic dehydroabietic acid derivatives (Eq. 22) [80–83]. A number

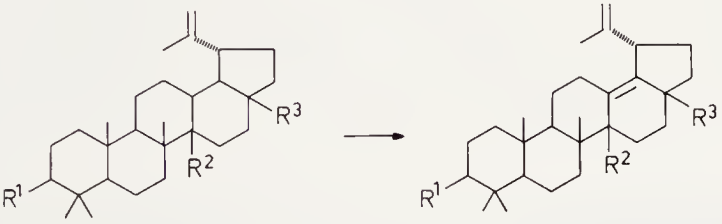


(21)



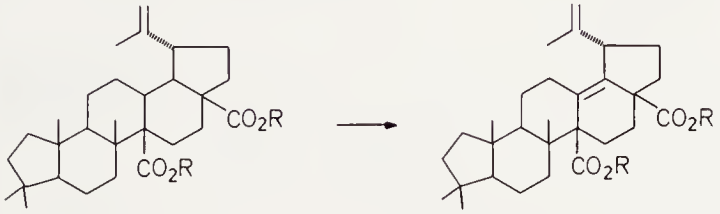
(22)

of pentacyclic triterpenes have been similarly dehydrogenated under Treibs conditions (Eqs. 23, 24). In fact, treatment with mercuric carboxylate salts



(23) [84–88]

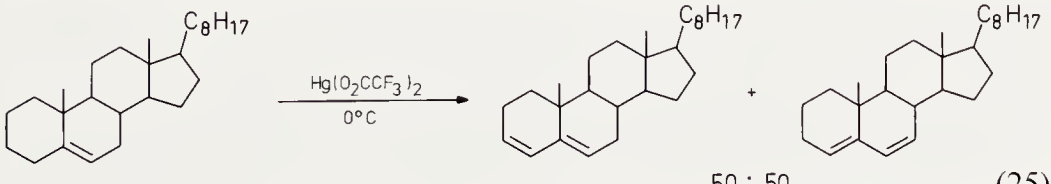
R^1 = H, OH, OAc, OBz, =O
R^2 = CH_3, CH_2OAc, CO_2Me
R^3 = CH_3, CO_2Me



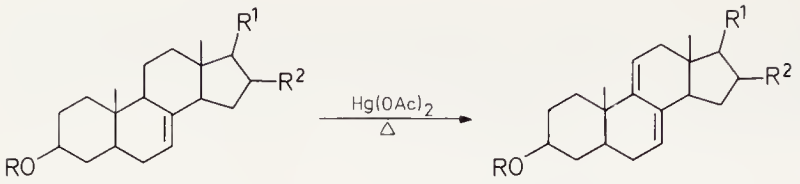
(24) [89, 90]

R = H, Me

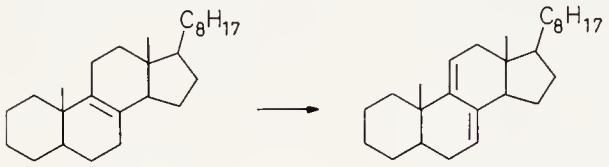
has proven quite useful in the dehydrogenation of a wide variety of steroids. Each of the following dehydrogenation patterns has been reported (Eqs. 25 to 29).



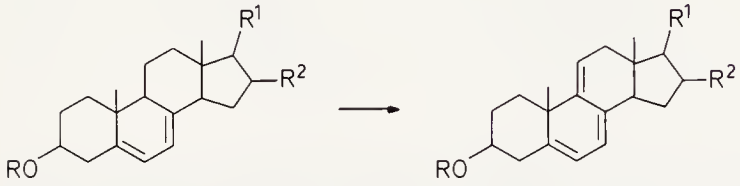
(25) [75]



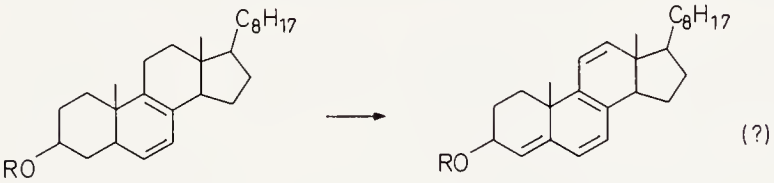
(26) [76, 91–98]



(27) [99]

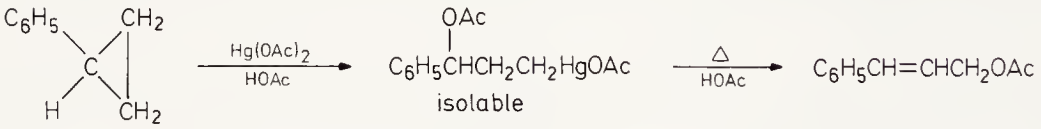


(28) [93, 95–97, 100, 101]

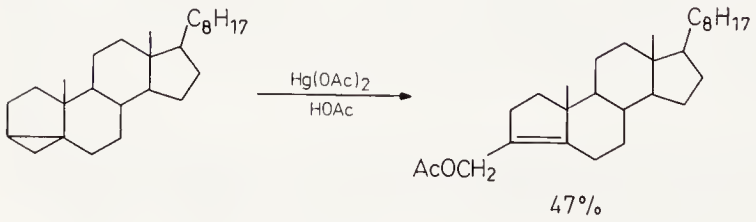


(29) [102]

The treatment of cyclopropanes under Treibs' reaction conditions can also lead to allylic acetates (Eqs. 30, 31).



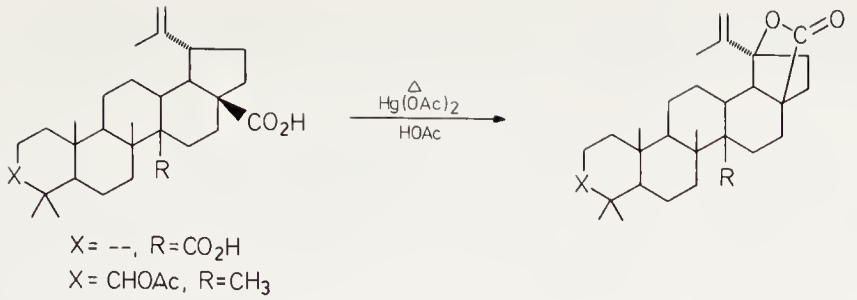
(30) [103]



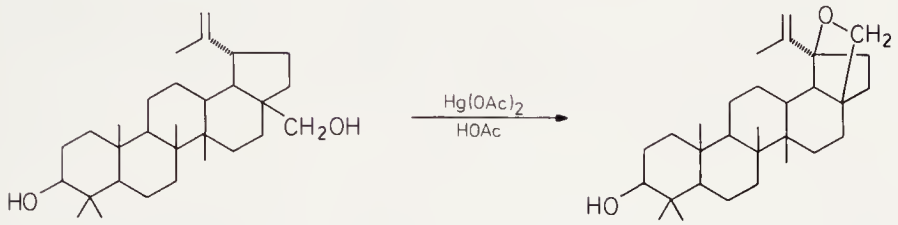
(31) [104]

The literature also contains several interesting examples where reactions of olefins with mercuric acetate apparently result in allylmercurial formation followed by intramolecular substitution or elimination (Eqs. 32–35).

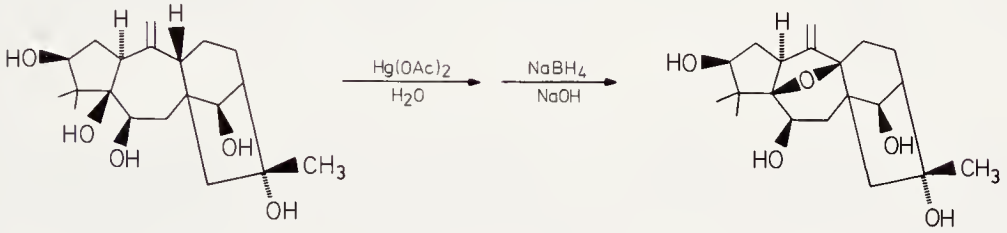
As noted earlier, the Treibs' reaction of olefins sometimes gives rise to α,β-unsaturated carbonyl compounds. In heating olefins and a variety of mercuric and mercurous salts under aqueous acid conditions, excellent



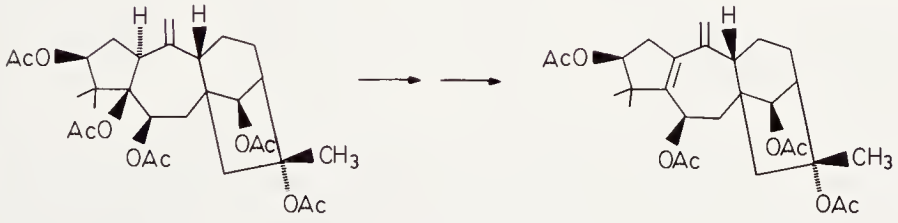
(32) [84, 87, 105]



(33) [84, 106]

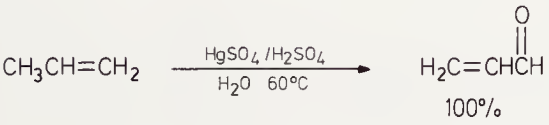


(34) [107]



(35) [107]

yields of α,β-unsaturated carbonyl compounds can be obtained [43]. The quantitative oxidation of propene to acrolein has been extensively studied, especially in industry, and numerous patents have been issued on this process (Eq. 36) [108–122]. This reaction, first reported by Deniges in 1898 [108, 109],



(36) [112]

has never achieved industrial prominence due to difficulties in economically reoxidizing the mercury salts. Once again, this reaction appears to proceed via solvolysis of an intermediate allylmercurial to allyl alcohol, which in turn is rapidly oxidized further [43, 119]. Using similar procedures 1-butene [115, 118, 119, 122–126], 1-pentene [124], 1-hexene [123], 1-octene [123, 124], isobutylene [113, 118, 119, 122, 126, 127], 2-methyl-2-butene [119] and cyclo-

hexene [113] have all been oxidized to α,β-unsaturated carbonyl compounds often in excellent yield (Eqs. 37–40).

(37)

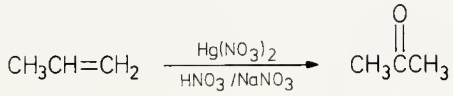
$R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_5H_{11}$

(38)

(39)

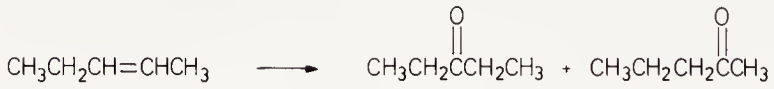
(40)

Reaction conditions have also been reported for the oxidation of olefins to saturated carbonyl compounds. For example, at high concentrations of mercuric nitrate the oxidation of 1-propene gives acetone as the sole product (Eq. 41) [128]. Under these conditions, 1- and 2-butene give 2-butanone and



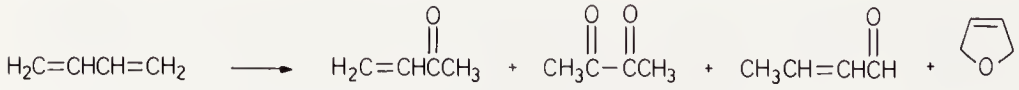
(41)

isobutylene affords *tert*-butanol. Similar results are reported using other mercury(II) salts [123, 126] or mercuric nitrate in the presence of nitrous acid [129]. Unsymmetrical internal olefins give both possible ketones (Eq. 42) [123]. The oxidation of 1,3-butadiene has been examined by several groups



(42)

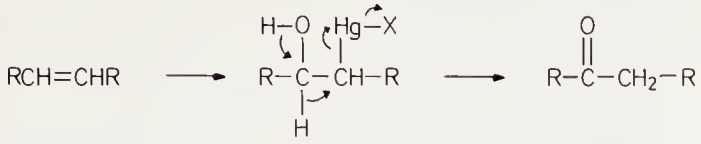
[123, 125, 130, 131]. Four major products have been reported in varying amounts depending on the procedure followed (Eq. 43). Vinyl acetylene apparently affords primarily biacetyl [130]. These saturated carbonyl products



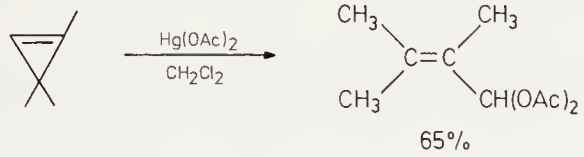
(43)

apparently arise via solvolytic rearrangement of initially formed oxymercuration products (Eq. 44) [43, 126].

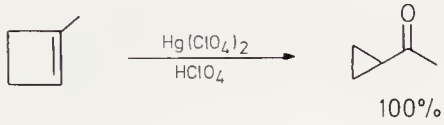
In a number of cases, the solvomercuration of olefins results in unstable organomercurials which undergo further reaction to afford oxidation products (Eq. 45–53).



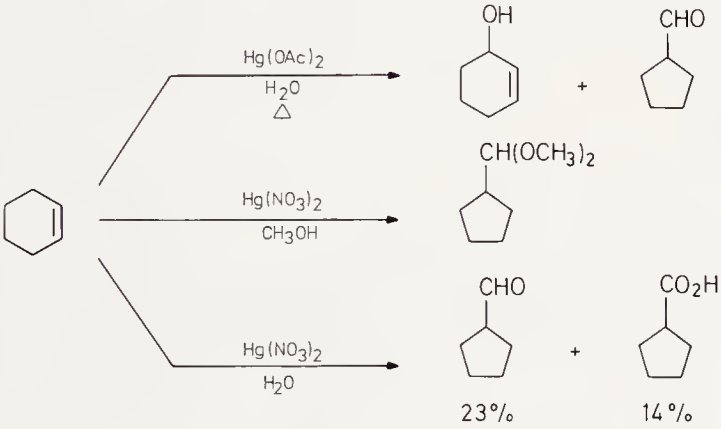
(44)



(45) [132, 133]



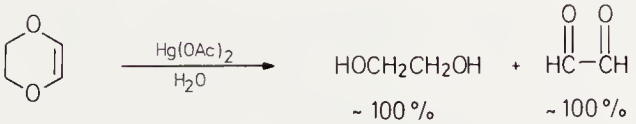
(46) [134]



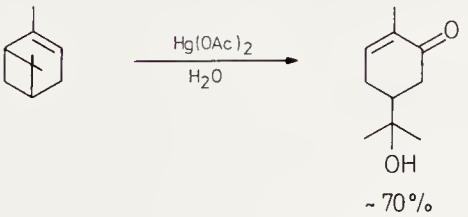
(47) [62]

(48) [135]

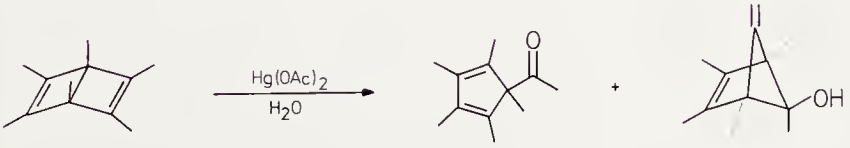
(49) [135]



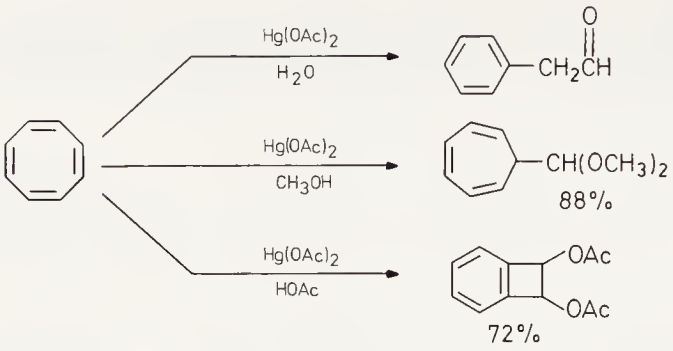
(50) [136]



(51) [137, 138]

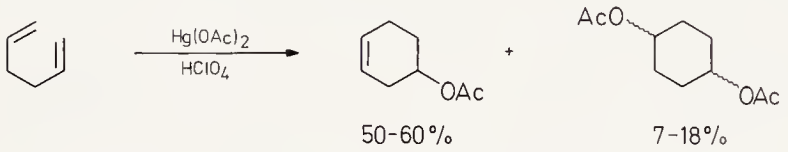


(52) [139, 140]

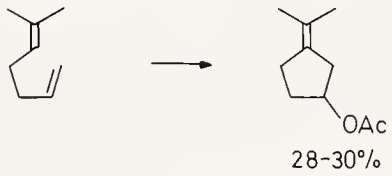


(53) [141]

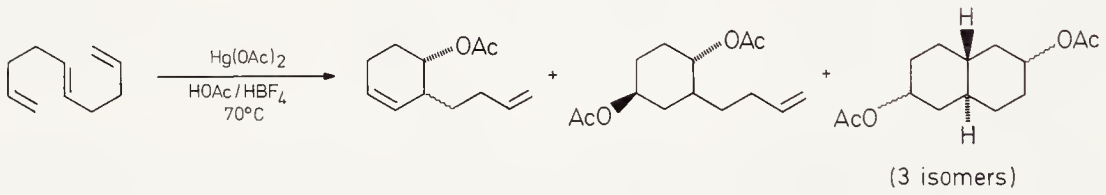
With highly electrophilic mercury salts, dienes and trienes undergo cyclic carbomercuration followed by solvolysis [Eq. 54–56].



(54) [142, 143]

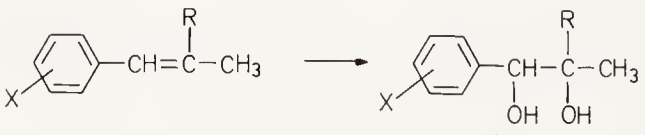


(55) [142, 143]



(56) [144]

The oxymercuration or methoxymercuration of styrene or stilbene derivatives with highly electrophilic mercury salts results in direct diol or dimethyl ether formation (Eqs. 57, 58) [14, 135–138, 145, 146]. These reactions have been utilized to distinguish natural products containing the 1-propenylbenzene moiety from those bearing an allylbenzene group, since the



(57)

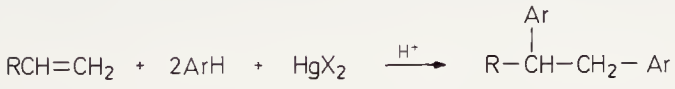
X	R	% Yield	Ref.
H	CH_3	70	135
2-OCH_3	H	<50	136
4-OCH_3	H	66	136
3,4-$(OCH_3)_2$	H	—	138
3,4-OCH_2O	H	—	137, 138
2,3-$(OCH_3)_2$-4,5-OCH_2O	H	—	138

latter compounds give stable solvomercuration adducts while the former produce metallic mercury [144]. It is not clear if the products are formed via solvolysis of benzylic mercurials or β-phenethylmercurials since both are known to solvolyze readily [23, 30, 147].

(58)

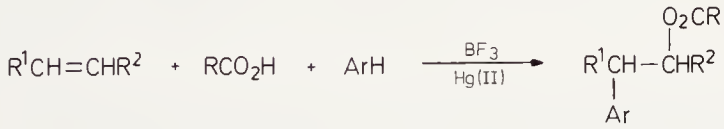
X	R^1	R^2	%Yield	Ref.
H	H	H	50	146
H	H	C_6H_5	~20	135
H	CH_3	CH_3	31-54	14,135
4-OCH_3	H	H	40	146

β-Phenethylmercurials are definitely intermediates in the following carbomercuration-solvolysis reactions however (Eqs. 59–63). These reactions apparently proceed via either initial mercury-olefin complexation, followed



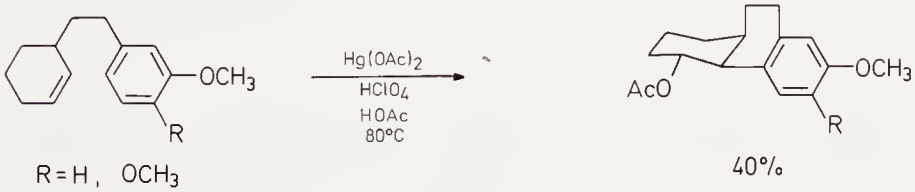
(59) [147–149]

R=H, C_6H_5 Ar = C_6H_5, p-$CH_3OC_6H_4$



(60)

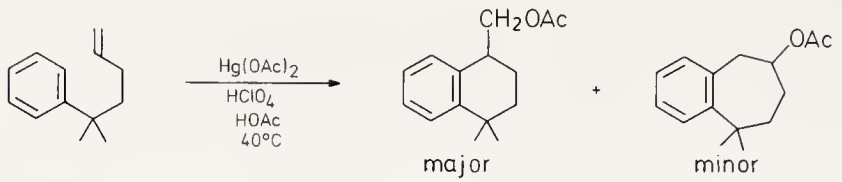
R^1	R^2	R	ArH	%Yield	Ref.
H	H	CH_3	C_6H_6	–	147
H	H	CH_3	$C_6H_5CH_3$	–	147
H	H	CH_3	o-$C_6H_4(CH_3)_2$	–	147
H	H	CH_3	C_6H_5Cl	–	147
H	H	CH_3	$C_{10}H_8$	–	147
H	H	CH_3	$C_6H_5OCH_3$	70	147
H	H	H	$C_6H_5OCH_3$	46	147
H	H	C_2H_5	$C_6H_5OCH_3$	42	147
H	H	C_5H_{11}	$C_6H_5OCH_3$	27	147
H	H	CH_3	o-$C_6H_4(OCH_3)_2$	60	150
H	H	CH_3	m-$C_6H_4(OCH_3)_2$	~60	150
H	H	CH_3	p-$C_6H_4(OCH_3)_2$	~60	150
H	CH_3	CH_3	$C_6H_5OCH_3$	45-67	149,150
H	CH_3	CH_3	o-$C_6H_4(OCH_3)_2$	65	150
H	CH_3	CH_3	m-$C_6H_4(OCH_3)_2$	~60	150
H	CH_3	CH_3	p-$C_6H_4(OCH_3)_2$	~60	150
CH_3	CH_3	CH_3	$C_6H_5OCH_3$	40	149



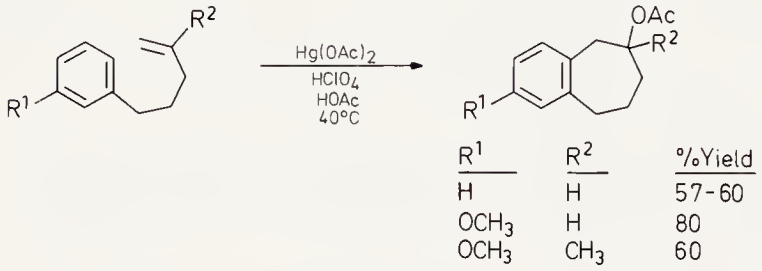
(61) [151]

R=H, OCH_3

40%



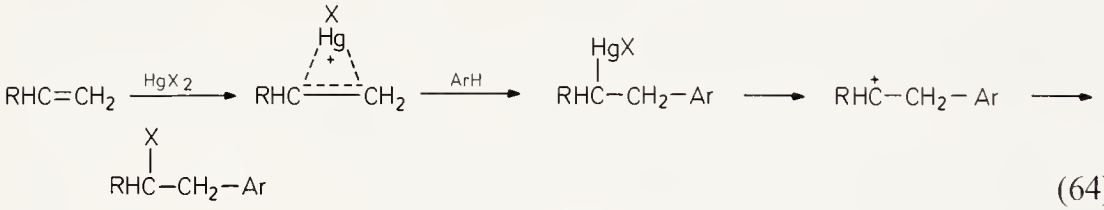
(62) [151]



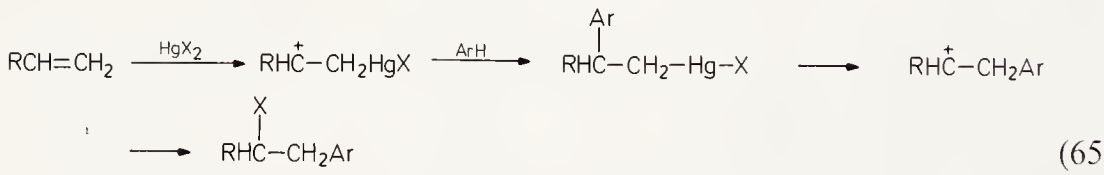
R^1	R^2	%Yield
H	H	57-60
OCH_3	H	80
OCH_3	CH_3	60

(63) [142, 151]

by nucleophilic attack of the arene and subsequent solvolysis of the resulting β-phenethylmercurial (Eq. 64), or electrophilic attack of a mercury-stabilized cation on the arene, followed by aryl migration during solvolysis (Eq. 65).

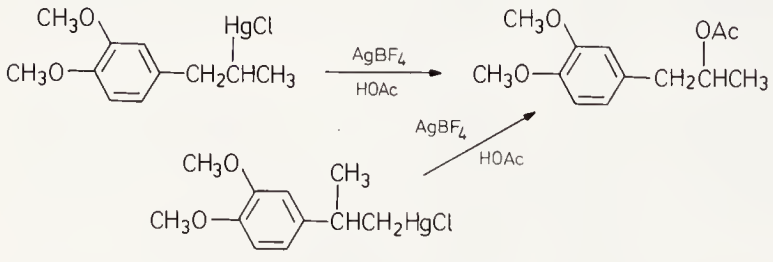


(64)

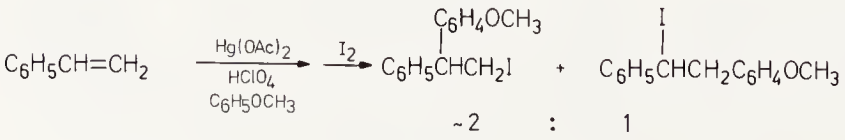


(65)

The solvolysis of isolated β-phenethylmercurials supports the latter course (Eq. 66) [152], while the iodination of intermediate mercurials in the diarylation of styrene suggests that both pathways may occur (Eq. 67) [149].

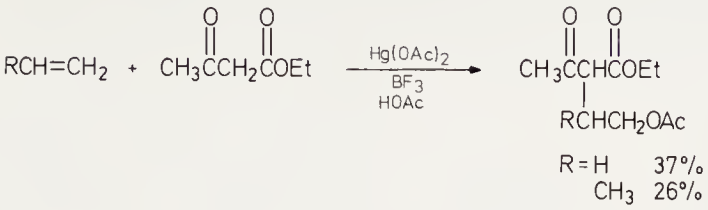


(66)



(67)

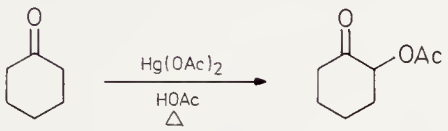
The carbomercuration-solvolysis of olefins and ethyl acetoacetate is consistent with the attack of a mercury-stabilized cation on the enol (Eq. 68) [153].



(68)

Intermediate organomercurials have been isolated [147, 152, 153] or intercepted [149, 151, 152] in several of these reactions. These carbomercuration reactions will be discussed in more detail in the monograph "Solvomercuration-Demercuration".

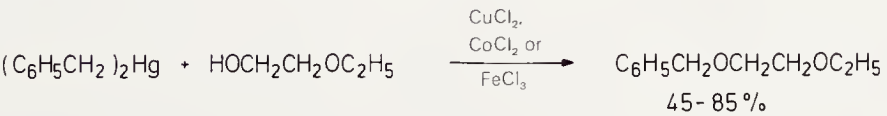
In his original publications on the reaction of olefins and mercuric acetate, Treibs also reported that ketones readily undergo α-acetoxylation upon heating with mercuric acetate in acetic acid (Eq. 69) [44, 45, 59]. Presumably,



(69)

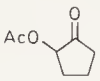
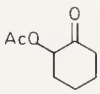
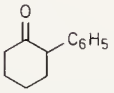
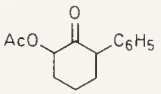
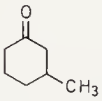
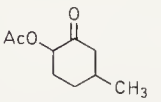
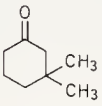
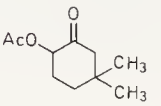
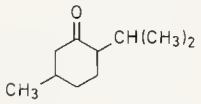
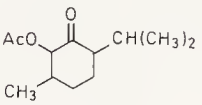
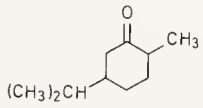
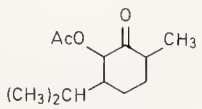
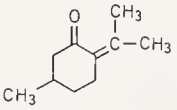
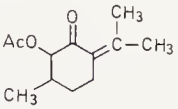
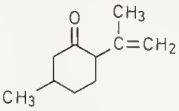
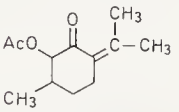
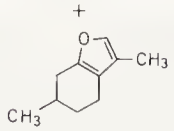
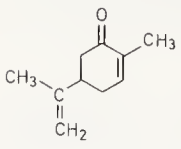
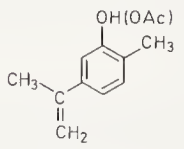
this reaction proceeds via thermal decomposition of intermediate α-acetoxymercurioketones. Table 4.2 summarizes the successes reported to date. No reaction was evident with α-indanone, α-tetralone, α-benzsuberon and 2-phenylcycloheptanone, and only tars were obtained from 2-phenylcyclopentanone [58]. So the reaction appears somewhat limited in scope and the yields are frequently low. The reaction does appear to be quite regioselective however. Thus, α-substituted ketones give only α′-acetoxyketones, and 3-methyl- and 3,3-dimethylcyclohexanone substitute only in the 6 position. In general, cis-trans mixtures arise, although menthone gives only the product with the methyl and acetoxy groups trans to each other [156]. Both menthone and isomenthone give 2-acetoxymenthone [156]. Optically active menthone gives an optically active product [59]. Both pulegone and isopulegone give 2-acetoxypulegone [158].

Organomercurials are also readily oxidized by a variety of metal salts. For example, benzylmercurials react with copper(II), cobalt(II) or iron(III) chlorides in β-ethoxyethanol to give good yields of the corresponding ether (Eq. 70) [159]. However, the reaction of cupric acetate with dibenzylmercury



(70)

Table 4.2. α-Acetoxylation of Ketones

Ketone	Product	% Yield	Ref.
		—	45
		19	45, 59
		68	58
		33	45, 59
		14	154
 menthone (trans) isomenthone (cis)		62 - 87[a]	45, 59, 154 - 156
 carvomenthon		76[a]	45, 59
 pulegone	 *cis* and *trans*	44	45, 59, 157, 158
 isopulegone	 *cis* and *trans* + 	—	63, 158
		60 - 65	63

[a] Yield based on reacted ketone.

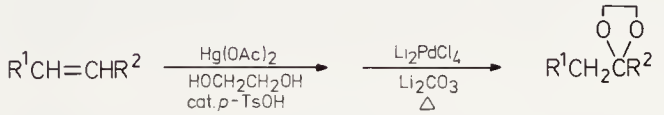
[160, 161], diphenylmercury [161] or ferrocenylmercuric bromide [162] has not proven synthetically useful.

Palladium salts do react with a variety of organomercurials to afford useful oxidation processes. The solvomercuration-palladation of olefins in fact provides a very convenient method for the oxidation of olefins to carbonyl compounds (Eq. 71) [163, 164]. The reaction is catalytic in palla-

(71)

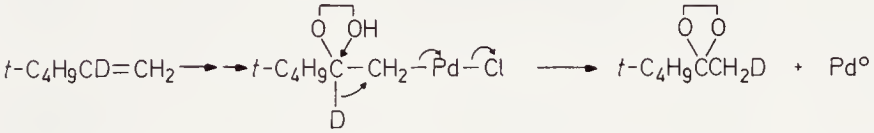
R^1	R^2	% Yield
H	H	94
H	n-C_4H_9	100
H	t-C_4H_9	90
H	C_6H_5	90
H	n-C_9H_{19}	89
n-C_3H_7	n-C_3H_7	82

dium when cupric chloride is added [164]. When ethylene glycol is employed as the solvent, the corresponding ethylene ketals can be prepared in 40–95% yields (Eq. 72) [165]. Better results are obtained here using stoichiometric



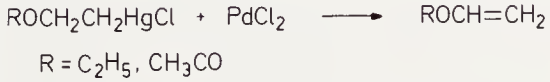
(72)

amounts of palladium chloride. Deuterium labeling studies are consistent with the following mechanism (Eq. 73). Other β-substituted alkylmercurials



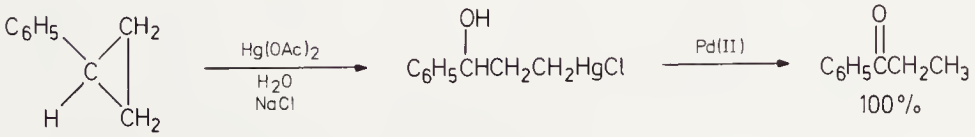
(73)

react with palladium chloride to afford simple β-hydride elimination products (Eq. 74) [163]. On the other hand, the oxymercuration-palladation of cyclo-



(74)

propanes once again provides the saturated ketone and not the allylic alcohol (Eq. 75) [166].



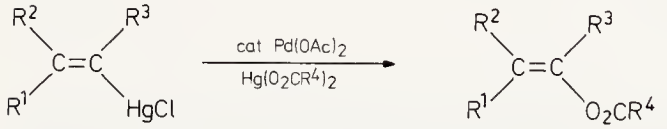
(75)

The treatment of allylmercuric acetates with palladium acetate, thallic acetate or lead tetraacetate results in rapid demercuration to the corresponding allylic acetates (Eq. 76) [42]. Both the thallium and lead salts increase the rate of reaction over that of mercuric acetate, and lead tetraacetate is seen to give a large amount of the cis primary acetate.

(76)

R	Metal Acetate	% Yield Acetates	Ratio of Allylic Acetates *cis*	*trans*	
CH_3	—	84	0	0	100
CH_3	$Pd(OAc)_2$	—	2	8	90
CH_3	$Tl(OAc)_3$	75	14	32	54
CH_3	$Pb(OAc)_4$	92	51	4	45
C_6H_5	—	95	−60−		40
C_6H_5	$Tl(OAc)_3$	95	−43−		57
C_6H_5	$Pb(OAc)_4$	90	−19−		81

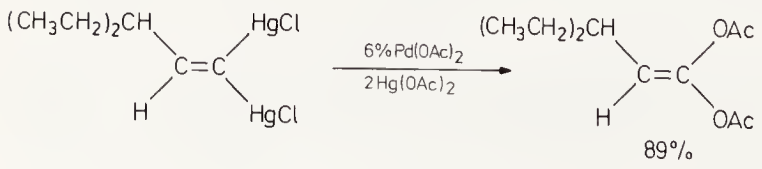
As discussed earlier in this chapter, alkenylmercuric acetates non-stereospecifically decompose at elevated temperatures to give good yields of the corresponding enol esters. Upon adding palladium acetate to alkenylmercuric chlorides, one can effect this same reaction at room temperature stereospecifically (Eq. 77) [167]. Furthermore, this reaction can be carried



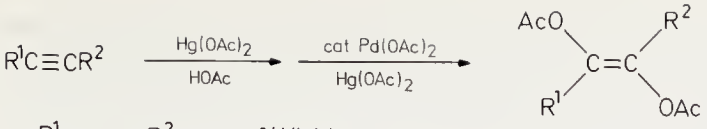
(77)

R^1	R^2	R^3	R^4	$\%Pd(OAc)_2$	%Yield
H	t-C_4H_9	H	CH_3	0.5	77
H	t-C_4H_9	H	C_6H_5	22	71
H	C_6H_5	H	CH_3	1	100
H	C_6H_5	H	n-C_3H_7	13	72
H	t-C_4H_9	CH_3	CH_3	5	97
H	C_6H_5	C_6H_5	CH_3	1	87
t-C_4H_9	H	c-C_6H_{11}	CH_3	15	68

out using only catalytic amounts of the palladium salt, if one equivalent of mercuric acetate is added to the reaction. By employing other mercury(II) carboxylate salts, one can prepare a variety of other enol esters as well. Olefinic diacetates can also be obtained using this procedure (Eqs. 78, 79). This latter transformation can be effected in one pot directly from the acetylene. How-



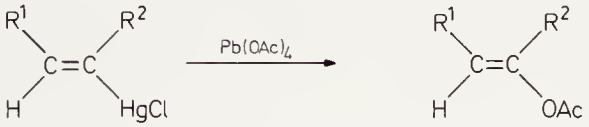
(78)



(79)

R^1	R^2	%Yield
CH_3	CH_3	60
CH_3	i-C_3H_7	40-45
CH_3	t-C_4H_9	7
CH_3	C_6H_5	87
C_2H_5	C_2H_5	80-86
C_6H_5	C_6H_5	5-8

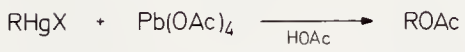
ever, steric hindrance sharply reduces the yield of diacetate. These esterification reactions can also be effected using lead tetraacetate, but the yields are lower (Eq. 80).



(80)

R^1	R^2	%Yield
C_6H_5	H	80
t-C_4H_9	CH_3	<37

Lead(IV) carboxylates will also oxidize alkyl- and arylmercurials (Eqs. 81–83). While good yields of alkyl acetates can be obtained occasionally,

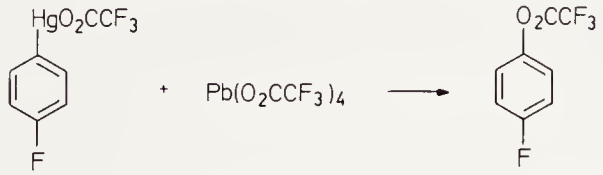


(81) [168]

R	X	%Yield
n-C_3H_7	Cl	<65
i-C_4H_9	OAc	<10
$C_6H_5CH_2$	OAc	82

(82) [169]

R = n-C_4H_9(69%), $(CH_3)_3CCH_2$, $C_6H_5CH_2$ (75%), $C_6H_5CH_2CH_2$ (72%), $C_6H_5C(CH_3)_2CH_2$



(83) [170]

this reaction is prone to undergo carbonium ion-like rearrangements [168, 169].

Finally, there are two organoborane-mediated oxidation procedures which have proven useful in organic synthesis. One involves the treatment of arylmercurials with borane-THF, followed by alkaline oxidation (Eq. 84) [171]. This sequence provides good to excellent yields of phenols from

(84)

Ar = C_6H_5 (72-98%); m-$CH_3C_6H_4$ (99%); p-$CH_3C_6H_4$ (99%); 2,4,6-$(CH_3)_3C_6H_2$ (16%); p-$CH_3OC_6H_4$ (65%); p-ClC_6H_4 (77%)

either arylmercuric halides or diarylmercurials, but apparently cannot be used with carboxylic acid- or amine-containing arylmercurials. Recently, an aromatic steroid has been oxidized in this fashion [172]. The reaction proceeds through intermediate arylboranes.

As briefly mentioned in Chap. III, primary trialkylboranes derived from terminal olefins via hydroboration react readily with mercuric carboxylates of weak acids, followed by iodine, to give excellent yields of alkyl esters (Eq. 85) [173]. More highly substituted olefins give sharply reduced yields.

$$RCH{=}CH_2 \xrightarrow{1/3\ BH_3} \xrightarrow{Hg(O_2CR')_2} \xrightarrow{I_2} RCH_2CH_2O\overset{\overset{O}{\|}}{C}R' \qquad (85)$$

R	R'	%Yield
H	CH_3	92
H	CF_3	17
H	n-C_3H_7	97
H	C_6H_5	86
C_2H_5	CH_3	93
C_2H_5	n-C_3H_7	84
i-C_3H_7	CH_3	88
t-C_4H_9	CH_3	73
n-C_8H_{17}	CH_3	89

This reaction has been shown to proceed through intermediate alkylmercurials to iodides, which are in turn rapidly esterified under the reaction conditions. In fact, mercuric carboxylates in the presence of catalytic amounts of boron carboxylates provide a useful method for esterifying certain alkyl halides (Eq. 86) [174].

$$R{-}X + Hg(O_2CR')_2 \xrightarrow{\text{cat. } B(O_2CR')_3} ROC\overset{\overset{O}{\|}}{R}' \qquad (86)$$

The iodination of mercurous carboxylates also affords excellent yields of symmetrical alkyl esters (Eq. 87) [175].

$$Hg_2(O_2CR)_2 + I_2 \longrightarrow ROC\overset{\overset{O}{\|}}{R} \quad 56-98\ \% \qquad (87)$$

R = C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, n-C_5H_{11}, c-C_6H_{11}, n-C_7H_{15}, $C_6H_5CH_2$, 1-adamantyl

C. Sulfur, Selenium and Tellurium Compounds

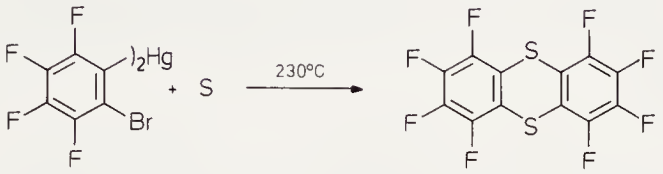
A wide variety of organosulfur compounds have been synthesized via organomercurial intermediates. The direct reaction of diphenylmercury and sulfur

was first reported in 1869 to give thiophenol and diphenylsulfide (Eq. 88) [176, 177]. At somewhat lower temperatures than originally used, the small amount of thiophenol can be eliminated and this reaction provides a useful, general approach to diarylsulfides (Eqs. 89, 90). At still lower temperatures, very good yields of diaryl- as well as dialkyl disulfides can be obtained from

$$(C_6H_5)_2Hg + S \longrightarrow C_6H_5SH + (C_6H_5)_2S \quad (88)$$

$$Ar_2Hg + S \xrightarrow{220\text{-}250^\circ C} (Ar)_2S \quad (89)$$

Ar = C_6H_5 (>66 %) [178], *o*-$CH_3C_6H_4$ [179], *o*-C_6HF_4 [180], C_6F_5 [82 %) [181, 182]



(90) [183]

organomercuric chlorides (Eq. 91) [184]. Results by others with perfluorophenylmercuric chloride [182] and diferrocenylmercury [185] have been much less successful.

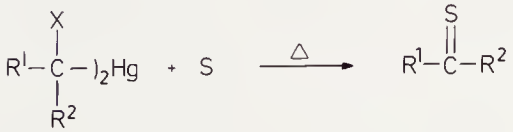
$$RHgCl + S \xrightarrow[140\text{-}180^\circ C]{} \underset{60\text{-}75\%}{R\text{-}S\text{-}S\text{-}R} \quad (91)$$

R = C_6H_5; 2,4,6-$(CH_3)_3C_6H_2$; *o*-FC_6H_4; *o*-$CH_3OC_6H_4$; 2,6-$Cl_2C_6H_3$; α-$C_{10}H_7$; *n*-$C_{12}H_{25}$

Polyfluorinated dialkylmercury compounds give di- and polysulfides at lower temperatures and perfluorothiocarbonyl compounds at elevated temperatures (Eqs. 92, 93). In the presence of potassium or cesium fluoride,

$$R_2Hg + S \xrightarrow{200\text{-}250^\circ C} R\text{-}S_n\text{-}R \quad (92)\ [186\text{–}188]$$

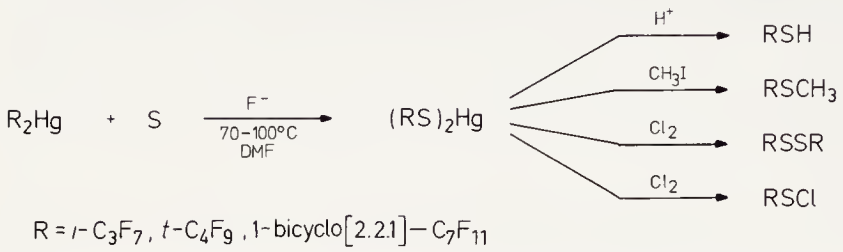
R = C_2F_5, *i*-C_3F_7, 1-bicyclo[2.2.1]-C_7F_{11} n = 2,3,4



(93)

R^1	R^2	X	%Yield	Ref.
F	CF_3	F	–	186
F	CF_3	Cl	67,80	186,189
Cl	CF_3	Cl	37	186
CF_3	CF_3	F	60	186,189,190
CF_3	CF_2CF_2H	F	30	186,190
CF_3	CF_2CF_2Cl	F	–	186,190
CF_3	*n*-C_6F_{13}	F	–	190
CF_3	*n*-C_7F_{15}	F	–	190

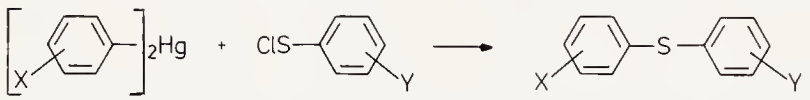
sulfur reacts at much lower temperatures with these same compounds to provide mercury(II) mercaptides, easily converted into the corresponding mercaptans, methyl sulfides, disulfides or sulfenyl chlorides (Eq. 94) [188, 191, 192].



(94)

R = *i*-C_3F_7, *t*-C_4F_9, 1-bicyclo[2.2.1]-C_7F_{11}

There appears to be only one report of the reaction of sulfenyl chlorides and organomercurials (Eq. 95) [193]. The reaction proceeds at room temperature in carbon tetrachloride.

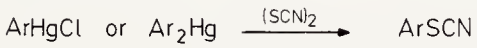


(95)

X = H; *o,m,p*-CH_3; *o,m,p*-Cl

Y = H; *o,p*-CH_3; *o,m,p*-Cl; *o,p*-NO_2

Thiocyanogen also reacts readily with both aryl- and allylic mercurials to afford the corresponding thiocyanates (Eqs. 96, 97). Diphenylmercury

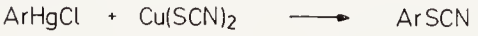


(96)

(97)

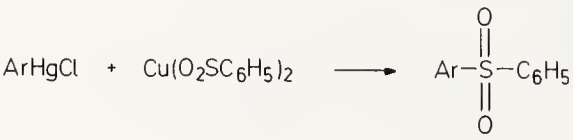
reacts quantitatively [194, 195], but low yields are reported for diferrocenylmercury [196], 4-chloromercurio-1-phenylpyrazole [197] and 3-chloromercurio-furan [198] (which affords primarily the 2-substituted furan). As noted above, crotylmercuric bromide undergoes substitution with complete allylic rearrangement [199].

Copper salts can also be utilized to prepare organic sulfur compounds. For example, cupric thiocyanate reacts with ferrocenyl- [162, 200, 201], cymantrenyl- [201] and azulenylmercurials [201] to afford the corresponding thiocyanates (Eq. 98). Similarly, phenyl sulfones can be prepared from cupric



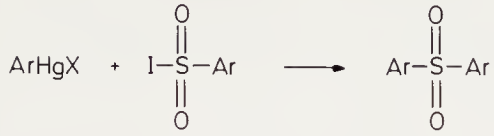
(98)

benzenesulfinate and organomercuric salts of ferrocene [200, 201], 3-phenylsydnone [201] and thiophene [201] (Eq. 99). None of these sulfones can be prepared by reacting the arene directly with benzenesulfonyl chloride and aluminum chloride.

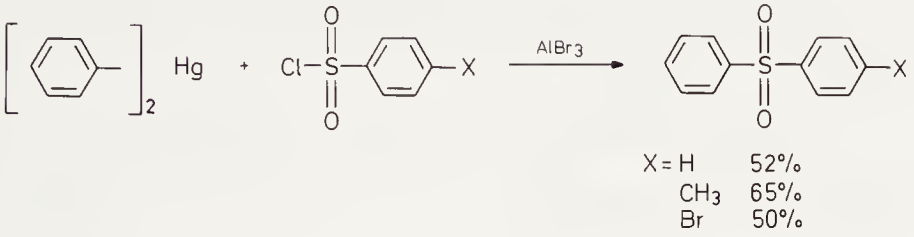


(99)

Although arylsulfonyl chlorides react poorly with arylmercurials [196, 202, 203], arylsulfonyl iodides give somewhat better yields of the corresponding sulfones (Eq. 100) [196, 203, 204]. Still better results are obtained however by adding aluminum bromide to the reaction (Eq. 101) [205].



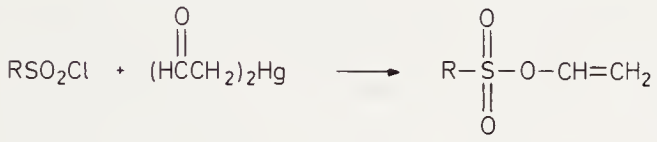
(100)



(101)

X = H 52%
CH3 65%
Br 50%

Alkenylsulfur compounds can be prepared from organomercurials by a variety of methods. For example, mercurated acetaldehyde reacts with sulfur halides to afford vinyl acid derivatives (Eqs. 102, 103) [206]. The addition of mercuric thiocyanate to alkynes, followed by protonolysis, can be used to



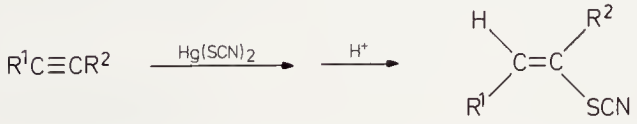
(102)

R = CH_3 (45%), C_2H_5 (42%), C_6H_5 (70%), p-$CH_3C_6H_4$ (75%)

(103)

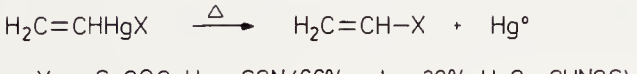
45%

prepare alkenyl thiocyanates (Eq. 104) [207]. The thermal decomposition of vinylmercuric salts bearing sulfur-containing anions appears to be a very



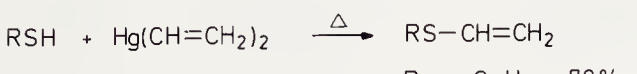
(104)

general route to thiocyanates and a variety of other vinylsulfur derivatives (Eqs. 105–107). Alkenylsulfides and -sulfones can also be prepared in excellent



(105) [208]

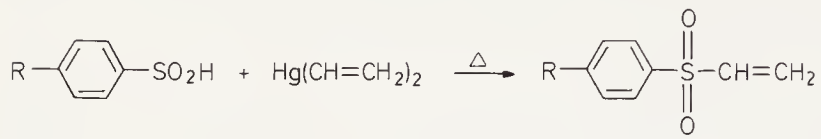
X = $S_2COC_2H_5$, SCN (66%, plus 30% $H_2C{=}CHNCS$)



(106) [17, 18, 209]

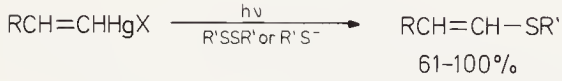
R = n-$C_{12}H_{25}$ 70%
C_6H_5 76–90%

yields by the photoinitiated reaction of alkenylmercurials with disulfides, mercaptides, benzenesulfonyl chloride and sulfinate salts (Eq. 108, 109) [211, 212]. The reactions of the first three reagents apparently proceed by a



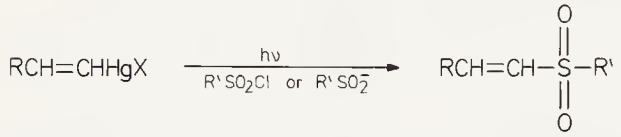
(107) [17, 210]

R = H, CH_3 (75%)



(108)

61–100%

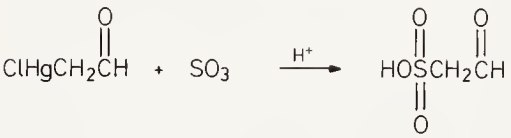


(109)

31–85%

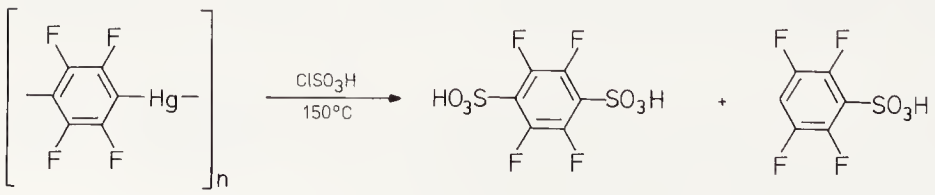
free radical chain addition elimination mechanism. This results in the products being cis-trans mixtures, except where R is quite bulky. An $S_{RN}1$ mechanism has been suggested for the sulfinate reaction [212].

The reaction of organometallic compounds with sulfur dioxide and sulfur trioxide has received considerable attention in recent years [213, 214]. Alkyl- [215, 216], allyl- [217], benzyl- [216, 217] and arylmercurials [216, 218–223] have been shown to react readily with sulfur dioxide and considerable effort has been expended on determining the nature of the bonding (O-Hg or S-Hg) in the resulting products. However, hydrolysis to the corresponding sulfinic acids has never been achieved. In the one attempt reported, sulfur dioxide was evolved [223]. With sulfur trioxide, insertion into the carbon-mercury bond of dialkyl- and diarylmercurials, as well as chloromercurioacetaldehyde, occurs readily and the corresponding sulfonic acids have been isolated as their barium salts (Eq. 110) [220, 224–226]. In one instance,



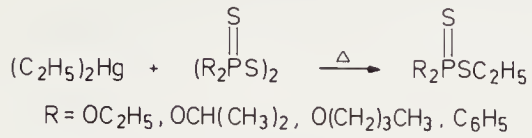
(110) [224]

chlorosulfonic acid has been employed to convert an arylmercurial into the corresponding arylsulfonic acid (Eq. 111) [227].



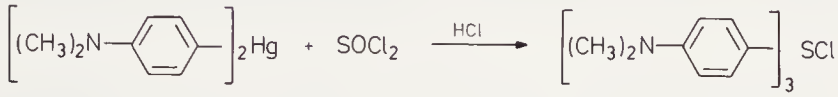
(111)

Finally, a variety of other sulfur-containing compounds have been prepared via miscellaneous organomercury reactions (Eqs. 112–118).

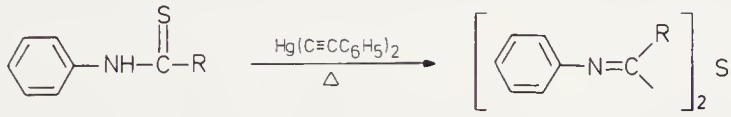


(112) [228]

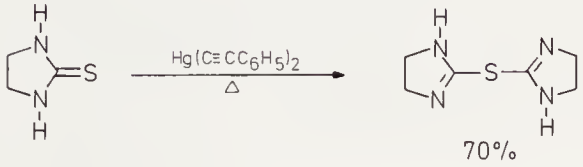
(113) [229]



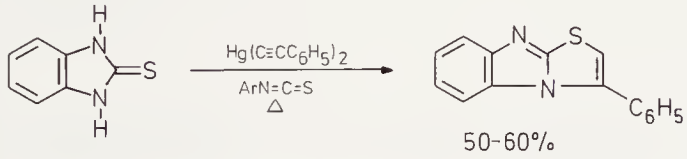
(114) [230]



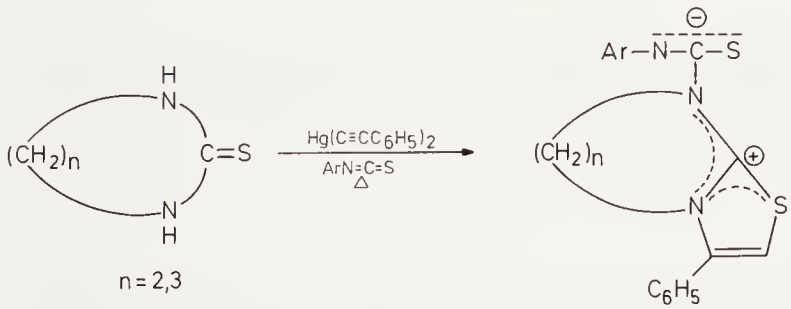
(115) [231]



(116) [232]

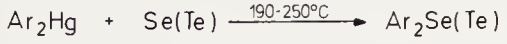


(117) [232]



(118) [232, 233]

Many of the methods employed in the preparation of organosulfur compounds are applicable to the synthesis of organoselenium and -tellurium compounds as well. For example, heating arylmercurials with elemental selenium or tellerium affords a convenient route to the corresponding diarylselenides and -tellurides (Eq. 119) [178, 179, 181–183, 234]. Diethyl-



(119)

mercury also reacts with tellurium to give diethyltelluride [179]. Arylselenyl halides react readily with diarylmercurials or styrylmercuric chloride to provide a valuable route to unsymmetrical selenides (Eqs. 120, 121).

$$Ar_2Hg + Ar'SeBr \longrightarrow ArSeAr' \quad (120)\ [235]$$

$$C_6H_5CH{=}CHHgCl + C_6H_5SeCl \longrightarrow C_6H_5CH{=}CHSeC_6H_5 \quad (121)\ [236]$$

The reactions of selenium dioxide [237] with dialkylmercurials, and selenium tetrabromide [196, 238] or diarylselenium dihalides with diarylmercurials also produce the corresponding selenides (Eq. 122). The last combination of reagents can also lead to organoselenium(IV) halides (Eq. 123) [239, 240].

$$R_2Hg \xrightarrow[SeBr_4\ R_2SeBr_2]{SeO_2} R_2Se \quad (122)$$

$$Ar_2Hg + Ar_2SeCl_2 \longrightarrow Ar_3SeCl \quad (123)$$

Dialkylmercurials and alkenylmercuric chlorides also react with organic diselenides or ditellurides to afford good yields of the corresponding mixed selenides or tellurides (Eqs. 124, 125). The latter reaction again appears to proceed by a free radical addition-elimination mechanism. Diphenylmercury fails to react with diphenyl diselenide upon heating [241].

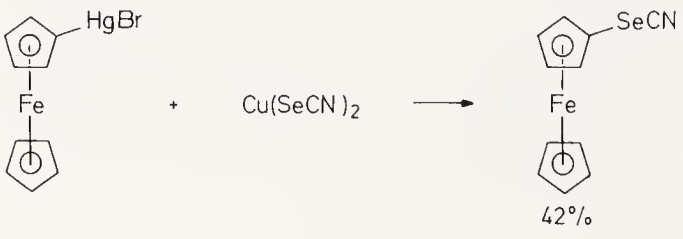
$$R_2Hg + \begin{matrix}(R'Se)_2\\ \text{or}\\ (R'Te)_2\end{matrix} \xrightarrow{\Delta} \begin{matrix}RSeR'\ (45\text{-}80\%)\\ \text{or}\\ RTeR'\ (75\text{-}79\%)\end{matrix} \quad (124)\ [241]$$

$$RCH{=}CHHgCl + \begin{matrix}(R'Se)_2\\ \text{or}\\ (R'Te)_2\end{matrix} \xrightarrow{h\nu} \begin{matrix}RCH{=}CHSeR'\ (90\text{-}95\%)\\ \text{or}\\ RCH{=}CHTeR'\ (89\%)\end{matrix} \quad (125)\ [211]$$

Finally, several methods are available for the preparation of selenocyanates from organomercurials (Eqs. 126–128).

$$(C_6H_5)_2Hg + Se(CN)_2 \longrightarrow \underset{78\%}{C_6H_5SeCN} \quad (126)\ [242]$$

$$R_2Hg + Se(SeCN)_2 \xrightarrow{\Delta} \underset{\begin{matrix}R=CH_3\ 28\%\\ C_6H_5\ 90\%\end{matrix}}{RSeCN} \quad (127)\ [242]$$



42%

(128) [243]

D. Nitrogen Compounds

The preparation of a variety of nitrogen-containing compounds has been effected using organomercurials. However, most of the work in this area has involved the synthesis of nitroso, nitro and diazonium compounds.

Polyhalogenated alkyl, as well as simple alkynyl and aryl nitroso compounds have been prepared by reacting the corresponding organomercurials with nitrosyl halides (Eqs. 129–132). Nitrosyl tetrafluoroborate reacts similarly (Eq. 133) [249].

$$R_2Hg + NOCl \xrightarrow[DMF]{} R{-}NO \qquad (129)\ [244]$$

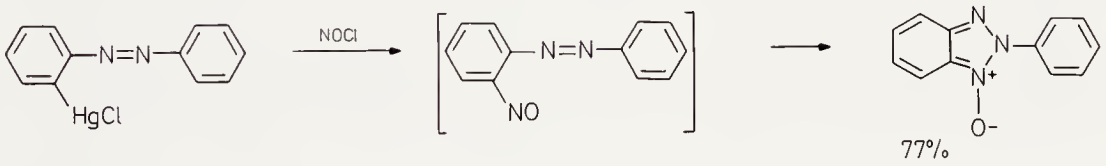
$R = CF_3CFCl,\ CF_3CCl_2,\ (CF_3)_2CF$

$$(RC{\equiv}C)_2Hg + NOCl \xrightarrow{-40°C} RC{\equiv}CNO \xrightarrow{25°C} RC(=O)CN \qquad (130)\ [245]$$

$R = n\text{-}$ and $t\text{-}C_4H_9$

$$Ar_2Hg \text{ or } ArHgOAc \xrightarrow[\text{or } NOBr]{NOCl} Ar{-}NO \qquad (131)\ [246, 247]$$

Ar = C_6H_5; 2,4,5-$(CH_3)_3C_6H_2$ (68 %); 2,4,6-$(CH_3)_3C_6H_2$ (90 %); 2,3,4,5-$(CH_3)_4C_6H$ (70 %); 2,3,4,6-$(CH_3)_4C_6H$ (61 %); 2,3,5,6-$(CH_3)_4C_6H$ (81 %); $(CH_3)_5C_6$ (80 %); $C_{10}H_7$ (α or β?)



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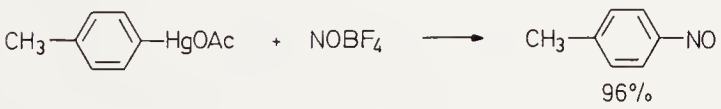
(132) [248]



96%

(133)

Nitrogen oxides reportedly give nitroso compounds, as well as aryldiazonium salts. Thus, early work with diarylmercurials and N_2O_4 indicates that nitroso arenes are formed along with the corresponding arylmercuric nitrate (Eq. 134) [250, 251]. On the other hand, N_2O_3 was reported to

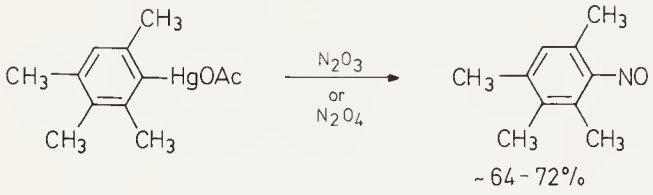
$$Ar_2Hg \xrightarrow{N_2O_4} ArNO + ArHgNO_3 \qquad (134)$$

afford primarily an aryldiazonium salt, plus arylmercuric nitrate (Eq. 135) [250–252]. The diazonium salt is apparently formed by rapid oxidation

$$Ar_2Hg \xrightarrow{N_2O_3} ArN_2^+NO_3^- + ArHgNO_3 \qquad (135)$$

of the initially formed nitroso compound by NO [247, 252]. Good yields of both types of products have been obtained. Consistent with this picture is the report that the arylmercuric acetate derived from isodurene gives only the nitroso product upon reaction with either N_2O_3 or N_2O_4 (Eq.

136) [247]. The latter compound is apparently less susceptible to further oxidation. The reaction of alkylmercurials and nitrogen oxides affords mixtures of products and no synthetic utility is evident [253, 254].



(136)

Aryldiazonium salts are also obtained upon reacting arylmercurials with nitrosylsulfuric acid, or nitric acid plus sodium nitrite or NO (Eqs. 137, 138). Once again nitroso compounds are clearly implicated as intermediates

$$(C_6H_5Hg)_2SO_4 + NOSO_3H \xrightarrow[H_2SO_4]{0°C} (C_6H_5N_2)_2SO_4 \qquad (137)\ [255]$$

$$ArHgX + HNO_3 \xrightarrow[\text{or NO}]{NaNO_2} (ArN_2)NO_3 \qquad (138)\ [256, 257]$$

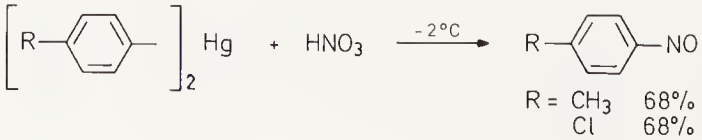
Ar = C_6H_5 (100%), *o*-ClC_6H_4, *m*-ClC_6H_4 (78%)

in these reactions since they have been isolated from these or closely related reactions.

Aromatic nitro compounds are readily available via treatment of arylmercurials with nitric acid (Eq. 139). Each of the following compounds has been prepared in this manner: $C_6H_5NO_2$ [176, 177]; 2,3,4,6-$(CH_3)_4$-

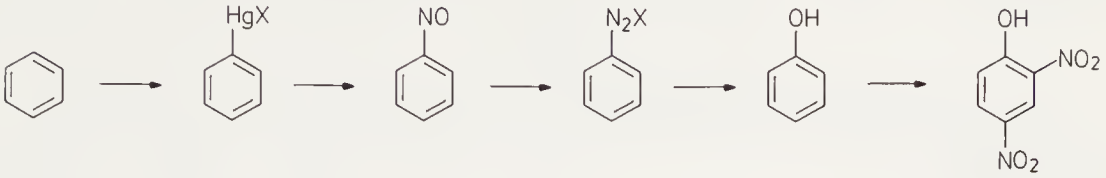
$$ArHgX + HNO_3 \longrightarrow ArNO_2 \qquad (139)$$

C_6HNO_2 (82%) [247]; 2,3,5,6-$(CH_3)_4C_6HNO_2$ (40%) [247]; *o*- and *p*-$ClC_6H_4NO_2$ [258]; *o*- and *p*-$BrC_6H_4NO_2$ [258]; 2,5-$Cl_2C_6H_3NO_2$ [259]; *o*-$(NO_2)_2C_6H_4$ [260]; 2-CH_3-4,6-$(NO_2)_2C_6H_2OH$ [261]; 4-(*t*-C_4H_9)-2,6-$(NO_2)_2C_6H_2OH$ [262]; 2-(CH_3O)-4,6-$(NO_2)_2C_6H_2OH$ [263]. All of these reactions proceed by direct mercury substitution and not a demercuration-nitration mechanism. Because of the regioselectivity of this reaction, it would appear to have synthetic utility in those cases where the desired arylmercurial is readily available. These reactions, plus the mercury(II) catalyzed nitration of arenes, have all been suggested to proceed through intermediate nitrosoarenes [247, 260, 264–266]. In fact, under certain conditions such compounds can be isolated, sometimes in high yield (Eq. 140) [257, 267]. Under other conditions, aryldiazonium salts [257] or nitrophenols can be isolated [256, 257, 260, 267–271].



(140) [257]

The conversion of arenes or arylmercurials to nitrophenols has received considerable mechanistic and synthetic attention. This reaction evidently proceeds through mercuration of the arene, nitrosation, oxidation to the diazonium salt, hydrolysis and subsequent nitration (Eq. 141) [256]. A variety of substituted di- and tri-nitrophenols have been prepared by this reaction.



(141)

The reaction of arylmercurials and nitronium tetrafluoroborate produces a complex mixture of products (Eq. 142) [15, 249, 272]. Similar products are obtained using nitric acid in acetic anhydride [15, 273]. These reagents

$$ArHgX \xrightarrow{NO_2BF_4} ArH + ArNO_2 + ArX + NO_2{-}ArHgX \qquad (142)$$

also react with alkylmercurials to produce a mixture of products [15, 272]. These reactions which have been suggested to proceed through radical intermediates are of little synthetic utility at present.

The reaction of aryldiazonium salts and organomercurials has been examined [274–276]. Simple alkyl- or arylmercurials either fail to react or they dimerize the diazonium salt to the corresponding biaryl [274]. α-Halomercuriocarbonyl compounds react more readily to afford low to reasonable yields of the corresponding monoarylhydrazones (Eqs. 143, 144). However, these reactions do not appear to be very general and side products are prevalent. The reaction of mercurated phenols and aryldiazonium salts proceeds via hydrogen not mercury substitution as one would anticipate from the above discussion.

$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2HgBr + ArN_2BF_4 \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}CH{=}NNHAr \quad \text{up to } 41\% \qquad (143)$$

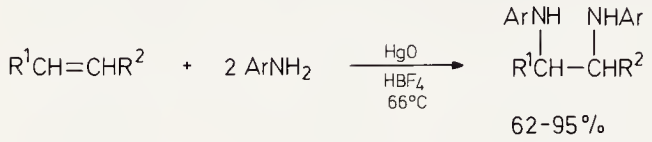
$$C_6H_5\underset{HgBr}{\underset{|}{C}}HCO_2C_2H_5 + ArN_2BF_4 \longrightarrow C_6H_5\overset{NNHAr}{\overset{\|}{C}}CO_2C_2H_5 \quad 43\text{-}77\% \qquad (144)$$

In a rather unique reaction, arylhydrazones of simple ketones react with mercuric acetate in acetic acid to generate bis-hydrazones, plus smaller amounts of acetoxyhydrazones (Eq. 145) [277].

$$R^1CH_2\overset{NNHAr}{\overset{\|}{C}}R^2 \xrightarrow[HOAc]{Hg(OAc)_2} ArHNN\underset{\|}{\overset{\|}{C}}NNHAr + AcO\underset{\|}{\overset{|}{C}}NNHAr \qquad (145)$$

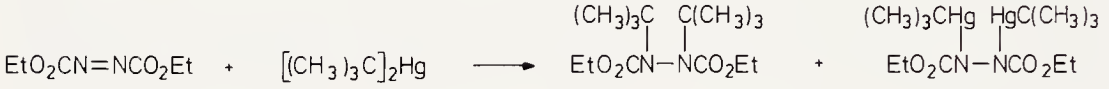
$R^1C{-}CR^2$ (10-70%) + R^1CHCR^2 (9-50%)

Simple vicinal arylamines can be prepared conveniently by treating olefins with mercuric tetrafluoroborate and the corresponding amine (Eq. 146) [278].



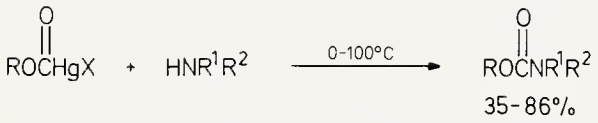
(146)

Carbon addition across the nitrogen—nitrogen double bond has also been observed (Eq. 147) [279, 280]. A radical process has been proposed for this reaction.



(147)

The reaction of carboalkoxymercurials and amines affords good yields of urethanes (Eq. 148) [281].



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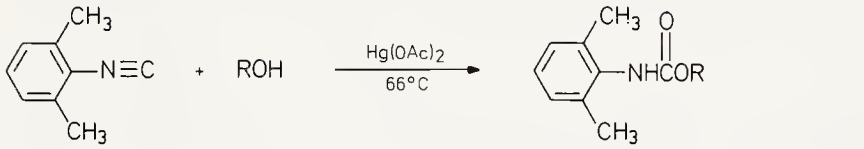
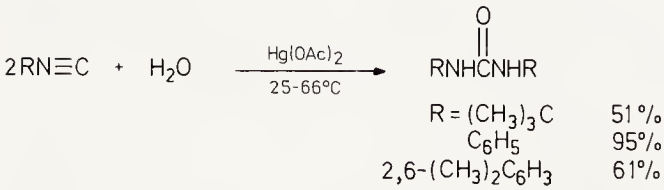
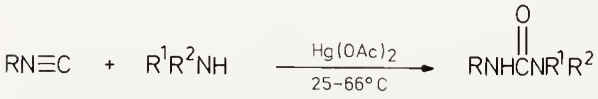


(149) [282]



(150) [282, 283]

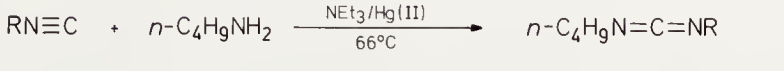


(151) [282, 284]

R	R^1	R^2	%Yield
$(CH_3)_3C$	H	n-C_4H_9	64
$(CH_3)_3C$	H	C_6H_5	42
2,6-$(CH_3)_2C_6H_3$	H	n-C_4H_9	91
2,6-$(CH_3)_2C_6H_3$	CH_3	C_6H_5	40
2,6-$(CH_3)_2C_6H_3$	C_2H_5	C_2H_5	80*

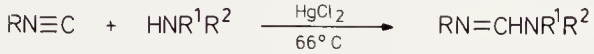
* using $HgCl_2$

A variety of nitrogen-containing compounds have been obtained, generally in good yield, from the reactions of mercury(II) salts and isonitriles. These include urethanes, symmetrical and unsymmetrical ureas, carbodiimides, formamidines, guanidinium salts and heterocyclic compounds (Eqs. 149–155).



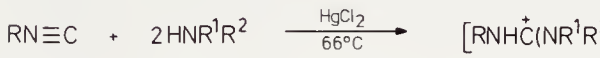
(152) [284]

R	% Yield
$(CH_3)_3C$	39%
$2,6\text{-}(CH_3)_2C_6H_3$	77%



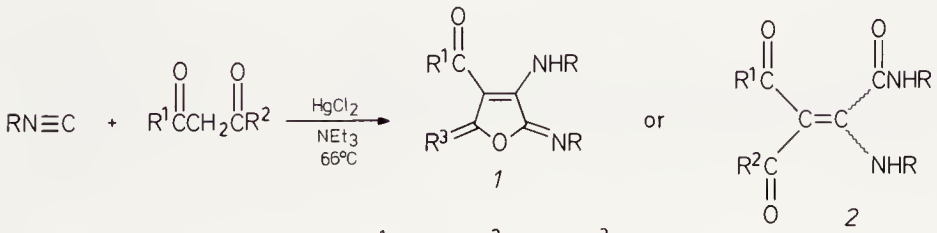
(153) [284]

R	R^1	R^2	% Yield
$(CH_3)_3C$	C_2H_5	C_2H_5	<30
$2,6\text{-}(CH_3)_2C_6H_3$	CH_3	C_6H_5	~100



(154) [282, 284]

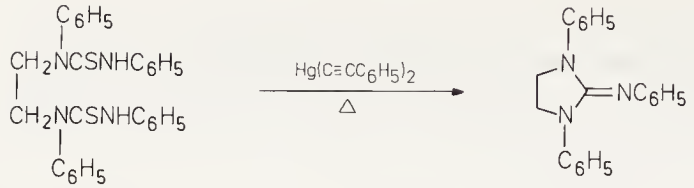
R	R^1	R^2	% Yield
$(CH_3)_3C$	H	$n\text{-}C_4H_9$	39
$(CH_3)_3C$	H	C_6H_5	47
$(CH_3)_3C$	C_2H_5	C_2H_5	70
$C_6H_5CH_2$	H	$n\text{-}C_4H_9$	90
C_6H_5	H	$n\text{-}C_4H_9$	98
C_6H_5	H	$c\text{-}C_6H_{11}$	95
C_6H_5	H	C_6H_5	42
$2,6\text{-}(CH_3)_2C_6H_3$	H	$n\text{-}C_4H_9$	97
$2,6\text{-}(CH_3)_2C_6H_3$	H	$c\text{-}C_6H_{13}$	48
$2,6\text{-}(CH_3)_2C_6H_3$	H	C_6H_5	41
$2,6\text{-}(CH_3)_2C_6H_3$	CH_3	C_6H_5	high
$2,6\text{-}(CH_3)_2C_6H_3$	C_6H_5	C_6H_5	77



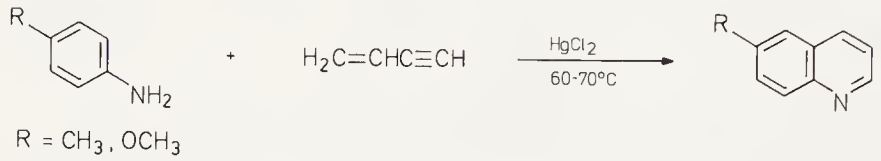
(155) [285]

Product	R	R^1	R^2	R^3	% Yield
1	C_6H_5	CH_3	CH_3	CH_2	56
1	$2,6\text{-}(CH_3)_2C_6H_3$	CH_3	CH_3	CH_2	62
2	$c\text{-}C_6H_{11}$	CH_3	CH_3	—	—
2	$2,6\text{-}(CH_3)_2C_6H_3$	CH_3	C_6H_5	—	55
1	$2,6\text{-}(CH_3)_2C_6H_3$	C_2H_5O	CH_3	CH_2	53
2	$2,6\text{-}(CH_3)_2C_6H_3$	C_2H_5O	C_6H_5	—	54
1	$2,6\text{-}(CH_3)_2C_6H_3$	C_2H_5O	C_2H_5O	O	28
1	C_6H_5	C_2H_5O	C_2H_5O	O	29
2	$c\text{-}C_6H_{11}$	C_2H_5O	C_2H_5O	—	18

Other nitrogen heterocycles have also been obtained via organomercury promoted cyclizations (Eqs. 156, 157).



(156) [231]

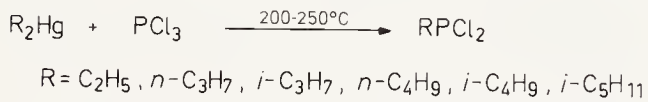


(157) [286]

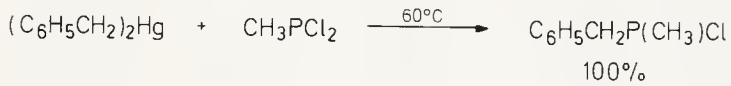
E. Phosphorus Compounds

Organomercurials proved quite useful early on in the synthesis of many organophosphorus compounds. More recently other methods have supplanted the use of organomercurials, except perhaps for the synthesis of alkenyl-containing phosphorus compounds.

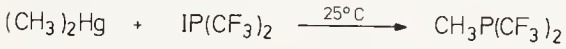
A number of alkylphosphines have been obtained upon heating dialkylmercurials with phosphorus(III) halides (Eqs. 158–160). As indicated, mono-,



(158) [287–289]

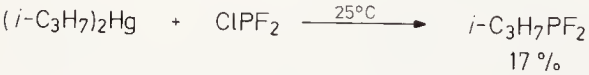


(159) [290]

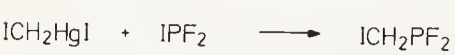


(160) [291]

di- and trialkylphosphines can be obtained in this manner. Alkylphosphorus halides, as well as mixed phosphorus halides (Eqs. 161, 162) can be employed. As the last example indicates, all alkyl groups attached to mercury can be utilized.



(161) [292]



(162) [293]

Vinylphosphorus dihalides can be prepared in like manner (Eq. 163) [294–297]. Attempts with excess divinylmercury to attach a second vinyl group

(163)

to phosphorus have failed [295]. However, alkynylmercurials will fully substitute phosphorus triiodide (Eq. 164) [298].

$$(RC{\equiv}CC{\equiv}C)_2Hg + PI_3 \longrightarrow (RC{\equiv}CC{\equiv}C)_3P \quad (164)$$

R = CH_3 73%
C_2H_5 62%
C_6H_5 28%

The reaction of arylmercurials and phosphorus trichloride, first reported in 1870 by Dreher and Otto [177, 299], was subsequently used to prepare a number of aryldichlorophosphines (Eq. 165). This approach proved es-

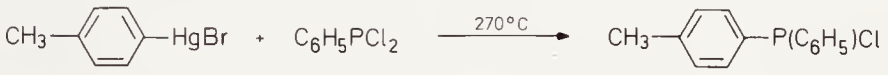
$$Ar_2Hg + PCl_3 \xrightarrow{\Delta} ArPCl_2 \quad (165)$$

Ar = C_6H_5 [300–303]; *o*-$CH_3C_6H_4$ [304, 305]; *m*-$CH_3C_6H_4$ [305]; *p*-$CH_3C_6H_4$ [304]; 2,4-$(CH_3)_2C_6H_3$ [305]; 2,4,5-$(CH_3)_3C_6H_2$ [306]; *m*-ClC_6H_4 [307]; *p*-$(CH_3)_2NHC_6H_4$ [308]; $C_{10}H_7$ (α or β?) [309]

pecially useful for the preparation of arylphosphines not readily available by Friedel-Crafts procedures, particularly the above-mentioned ortho or meta substituted compounds. Diarylchlorophosphines can also be obtained in this same manner (Eqs. 166, 167). As indicated, complete utilization of the aryl groups attached to mercury can be achieved. This reaction has proved quite useful for the synthesis of diarylchlorophosphines, since over-arylation is not a problem.

$$Ar_2Hg + Ar'PCl_2 \xrightarrow{\Delta} ArP(Ar')Cl \quad (166)\ [310\text{–}314]$$

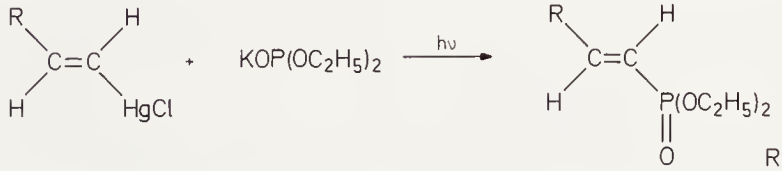
Ar = C_6H_5, *p*-$CH_3C_6H_4$, *m*-$CH_3OC_6H_4$
Ar′ = C_6H_5; *p*-$CH_3C_6H_4$; 2,4,5-$(CH_3)_3C_6H_2$



(167) [302]

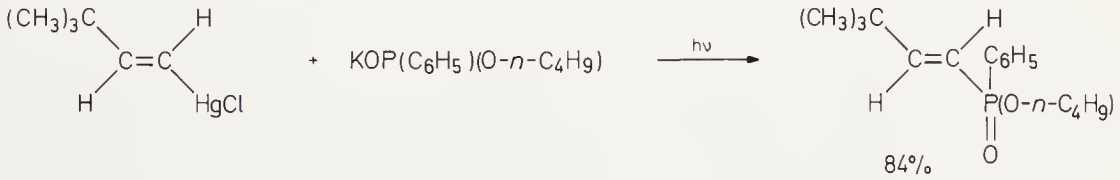
64%

A wide variety of alkenyl-containing phosphorus compounds have recently become available via organomercurial procedures. For example, the photo-initiated reaction of alkenylmercuric halides and phosphorus-containing anions provides a convenient route to alkenylphosphorus esters (Eqs. 168, 169) [211]. Unfortunately, some loss of stereochemistry is observed in these



(168)

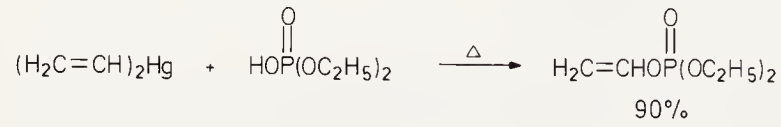
R = *n*-C_3H_7 56%
$(CH_3)_3C$ 76%



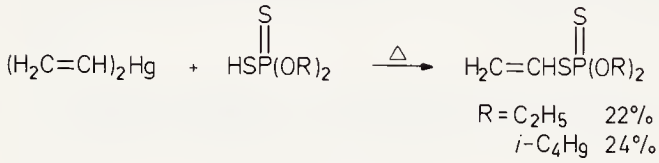
84%

(169)

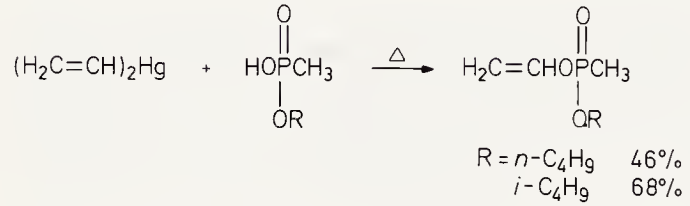
reactions. Oxygen- or sulfur-substituted vinyl phosphonates and phosphates can also be obtained by heating the appropriate acid with divinylmercury, a type of reaction we have seen earlier in the synthesis of oxygen and sulfur compounds (Eqs. 170–172) [315].



(170)

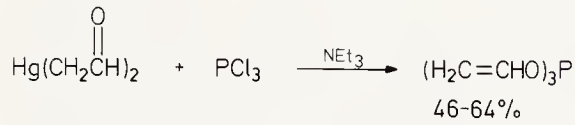


(171)



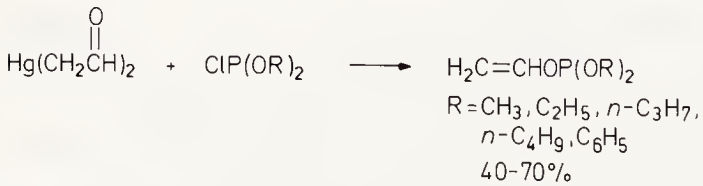
(172)

The reaction of α-halomercuriocarbonyl compounds and a number of different phosphorus compounds results in attack at oxygen and the formation of a variety of alkenyloxy phosphorus derivatives (Eqs. 173–175) [316].

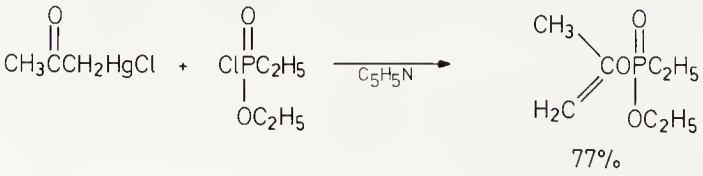


(173)

(174)

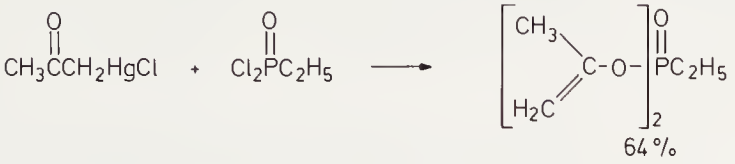


(175)



(176)

Mercurated ketones work equally well in all of these reactions [317] and this approach can be extended to the synthesis of alkenylphosphonates and -phosphates of all types (Eqs. 176–179) [318]. Trialkylphosphites can also be employed in place of phosphorus halides (Eq. 180) [319, 320].

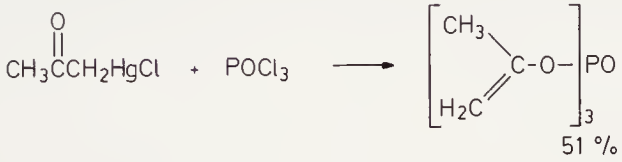


64 %

(177)

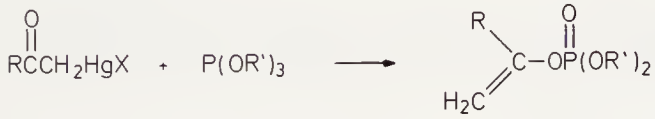
R=CH_3 39%
n-C_4H_9 51%

(178)

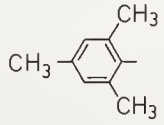


51 %

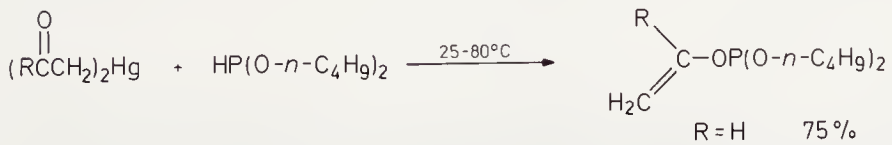
(179)



(180)

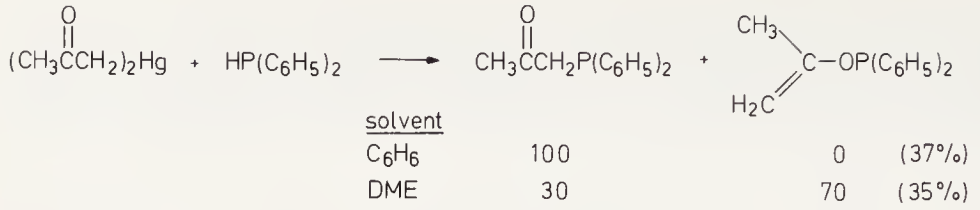
R	X	R'	%Yield
H	Cl	C_2H_5	60
CH_3	Br	C_2H_5	72
$(CH_3)_3C$	Cl	CH_3	65
	Cl	CH_3	70

Phosphorus(III) compounds containing either phosphorus-hydrogen or phosphorus-metal bonds also undergo similar reactions (Eqs. 181–183). In the reactions involving phosphorus-hydrogen compounds, dialkylmercurials apparently must be employed and one of the two groups is lost as the aldehyde or ketone. With diphenylphosphine the direction of bonding (0 versus C) is highly solvent dependent. With potassium diphenylphosphide only phosphorus-oxygen bonding is observed and alkylmercuric chlorides

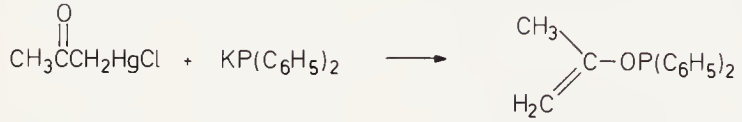


R=H 75%
CH_3 70%
CH_3O 84%

(181) [321]



(182) [322, 323]

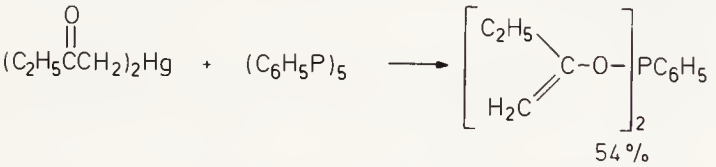


(183) [322, 323]

can be employed, thus making more effective use of the organic groups attached to mercury. When methyl- or phenylphosphine react with dibenzylmercury or α-mercurated carbonyl compounds, cyclic organophosphines are formed in high yield (Eq. 184) [290, 324]. This provides one of the most

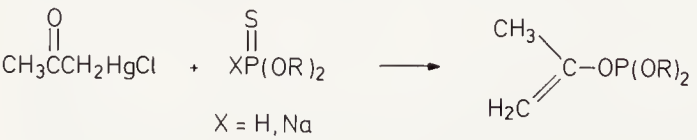
(184)

convenient syntheses of these compounds which have been observed to react further with mercurated ketones to form the corresponding alkenyloxy derivatives (Eq. 185) [324].



(185)

Finally, similar reactions of higher-valent phosphorus compounds containing a phosphorus-sulfur bond are observed to occur with reduction of phosphorus and removal of sulfur (Eqs. 186, 187) [325]. Note that ester-



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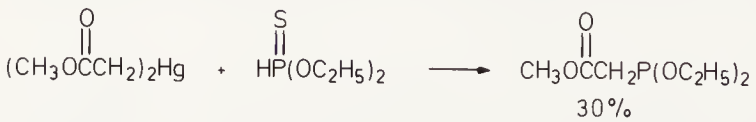
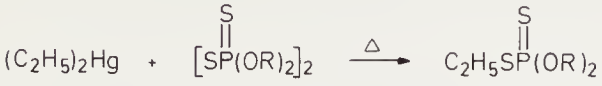


(187)

containing mercurials react with carbon-phosphorus bond formation here, while oxygen-phosphorus coupling was observed in the analogous reaction with $HP(OR)_2$ (Eq. 181). Recall also from the section on sulfur compounds

that the following reaction occurs without eliminating sulfur (Eq. 188) [228].



$$(C_2H_5)_2Hg + [SP(OR)_2]_2 \xrightarrow{\Delta} C_2H_5SP(OR)_2 \qquad (188)$$

F. Silicon Compounds

Organosilicon compounds have found increasing use in organic synthesis in recent years. It therefore seems appropriate to mention some of the more important methods by which they may be prepared from organomercurials.

Silyl halides react with certain organomercurials to form organosilanes (Eqs. 189–191). However, the reaction with α-mercurated carbonyl com-

$$(C_6H_5)_2Hg + Si_nH_{2n+1}I \longrightarrow Si_nH_{2n+1}C_6H_5 \qquad (189)\ [326]$$

$n = 2,3$

$$(C_2H_5OC{-}\overset{O}{\overset{\|}{C}}{-}\overset{N_2}{\overset{\|}{}})_2Hg + 2R_3SiI \longrightarrow 2C_2H_5OC{-}\overset{O}{\overset{\|}{C}}{-}\overset{N_2}{\overset{\|}{}}{-}SiR_3 \qquad (190)\ [327]$$

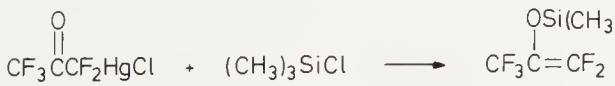
$R = CH_3, C_2H_5, C_6H_5$

80–90 %

$$(o\text{-}RCB_{10}H_{10}C)_2Hg + (CH_3)_3SiCl \xrightarrow{(n\text{-}Bu)_4NI} o\text{-}RCB_{10}H_{10}CSi(CH_3)_3 \qquad (191)\ [328]$$

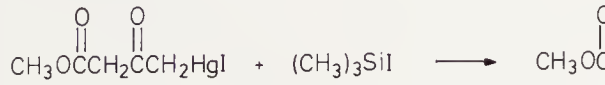
$R = CH_3, C_6H_5$

pounds once again involves attack on oxygen and formation of enol silanes (Eqs. 192–194). With α-mercurated esters both silicon-oxygen and silicon-



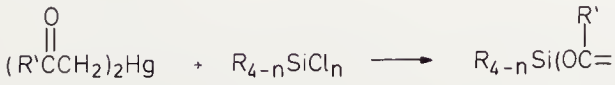
$$CF_3C(=O)CF_2HgCl + (CH_3)_3SiCl \longrightarrow CF_3C(OSi(CH_3)_3)=CF_2 \qquad (192)\ [329, 330]$$

71 %



$$CH_3OC(=O)CH_2C(=O)CH_2HgI + (CH_3)_3SiI \longrightarrow CH_3OC(=O)CH_2C(OSi(CH_3)_3)=CH_2 \qquad (193)\ [331]$$

88 %

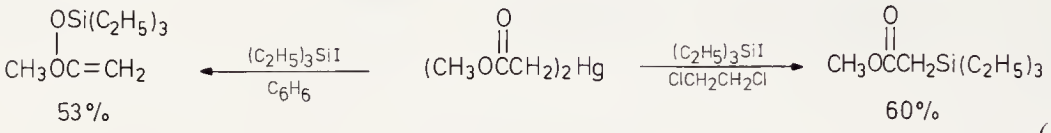


$$(R'C(=O)CH_2)_2Hg + R_{4-n}SiCl_n \longrightarrow R_{4-n}Si(OC(R')=CH_2)_n \qquad (194)\ [332, 333]$$

45–89 %

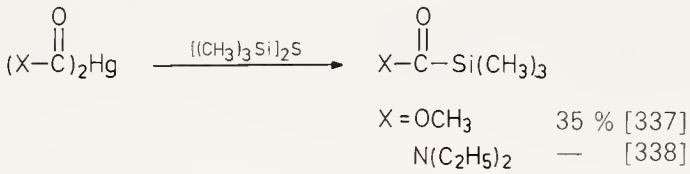
$R' = H, CH_3, C_6H_5$; $R = CH_3, ClCH_2, C_2H_5, C_6H_5, OC_2H_5$; $n = 1\text{–}4$

carbon coupling products have been observed depending on the solvent employed (Eq. 195) [334–336]. The enol silane can be converted into the ester upon heating with a catalytic amount of mercuric iodide [336].



(195)

Trialkylsilyl sulfides can also be utilized to effect many of these same reactions (Eqs. 196–198). Note that an enol silane is formed from the mercurated ester in this case.



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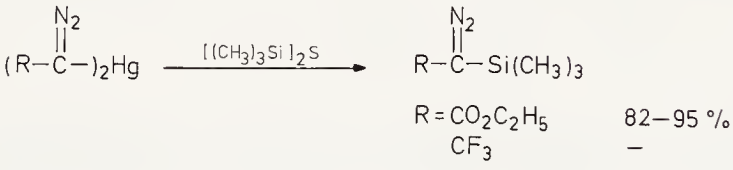
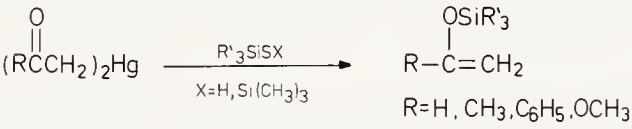
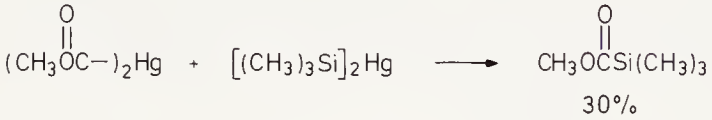


(197) [339, 340]

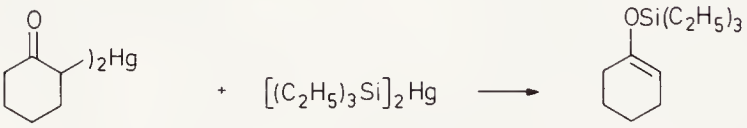


(198) [333, 341, 342]

Trialkylsilylmercurials undergo similar reactions with certain organomercurials (Eqs. 199, 200).



(199) [337]



(200) [343]

G. Conclusion

It should be evident from having read this chapter that organomercurials can be utilized in a number of ways to prepare a wide variety of heteroatom-containing compounds. Thus, the thermal or solvolytic decomposition of intermediate organomercurials provides a convenient route to allyl esters,

vinyl esters and ethers, α-acctoxy ketones, saturated ketones and enones, and β-phenethyl esters and arenes. Organometallic procedures employing palladium and boron are effective in the synthesis of enol esters, ketones, phenols and primary alkyl esters. Aryl and alkenyl sulfides, sulfones and isothiocyanates, as well as perfluorothiocarbonyl compounds, are directly available via organomercurial procedures, as are aryl and alkenyl selenides, selenocyanates and diaryltellurides. Alkyl, alkynyl and aryl nitroso compounds, and aryl nitro and diazonium compounds, can be conveniently prepared using organomercury reagents. Isonitriles and mercury salts provide an easy entry into urethanes, ureas, carbodiimides, formamidines and guanidinium salts. Organomercurials have proven valuable in the synthesis of a wide variety of alkyl, alkenyl, alkynyl and aryl phosphines and numerous phosphorus esters containing alkenyl groups. Finally, simple alkyl and arylsilanes, plus a number of different enol silanes have been synthesized by organomercury intermediates. In the future one can anticipate increasing utilization of these reactions and the development of still further practical applications of organomercurials in the synthesis of heteroatom-containing compounds.

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V. Dimerization

The dimerization of organomercurials provides a convenient route to 1,3-dienes and biaryls. It is less useful for the synthesis of alkanes. These reactions can be effected thermally, photolytically or more commonly by employing transition metal reagents. The scope of these reactions will be detailed in this chapter. Methods for unsymmetrical carbon—carbon bond formation via organomercurials will be covered in the following two chapters.

Methods for the symmetrical dimerization of alkylmercurials are very limited. Dialkylmercurials derived from propionic acid and derivatives can be photolytically dimerized in good yield (Eq. 1). Similar results have been reported for α-chloromercurioethanol (Eq. 2) and 1,7-dioxa-4,10-dimercuriocyclododecane (Eq. 3) [3]. However, photolysis of other simple alkylmercurials leads to free radicals and yields of dimers are generally very poor.

$$(XCH_2CH_2)_2Hg \xrightarrow{h\upsilon} XCH_2CH_2CH_2CH_2X \quad (1)$$

X = CO_2H 24 % [1]
CO_2CH_3 >90 % [1]
CN 90 % [2]

$$HOCH_2CH_2HgCl \xrightarrow{h\upsilon} HOCH_2CH_2CH_2CH_2OH \quad (2)$$

40%

25% (3)

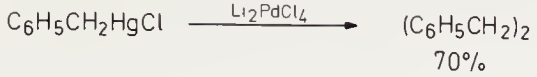
Benzylic mercurials are more readily dimerized. For example, thermolysis [4–6] or photolysis [7] of dibenzylmercury affords bibenzyl in excellent yield (Eq. 4). A number of transition metals also catalyze this reaction: Pd >

$$(C_6H_5CH_2)_2Hg \longrightarrow (C_6H_5CH_2)_2 + Hg \quad (4)$$

△ 73-96%
hυ 80 %

> Pt > Ag > Au > Cu > Ni > Fe > Co [8–10]. The reaction with palladium or platinum proceeds at room temperature. In a similar fashion, dilithium tetrachloropalladate will dimerize benzylmercuric chloride [11],

as well as allylmercuric iodide [11] and carbomethoxymercuric acetate [12] (Eqs. 5–7). Unfortunately, these latter reactions require stoichiometric

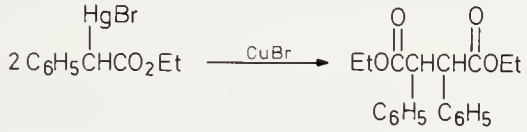


(5)

(6)

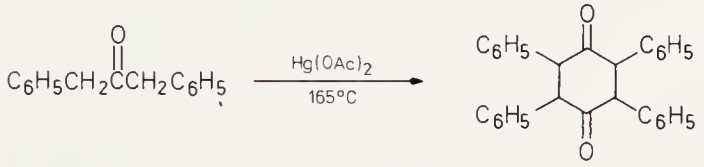
(7)

amounts of the expensive palladium salt. Ethyl α-bromomercuriophenylacetate has also been dimerized using cuprous bromide in DMF (Eq. 8) [13].



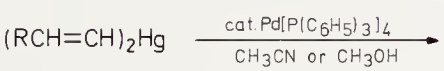
(8)

This transformation is also evident as a side reaction when diphenyliodonium salts are used to phenylate this same mercurial (see Chap. VI) [14]. Finally, in an unusual example of oxidative dimerization, it is reported that 1,3-diphenylacetone when heated with mercuric acetate dimerizes to the corresponding 1,4-cyclohexanedione (Eq. 9) [15].



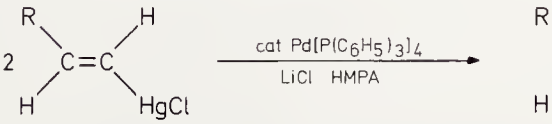
(9)

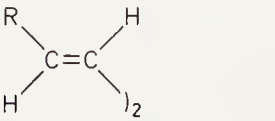
1,3-Dienes are readily available by palladium or rhodium promoted dimerization of alkenylmercurials. Tetrakis(triphenylphosphine)palladium(0) effectively catalyzes this reaction (Eq. 10). Yields based on *cis*- and *trans*-



R = *cis*- and *trans*-CH_3 [16], $(CH_3)_3Si$ (95 %) [17] (10)

di-1-propenylmercury were not reported, but the catalyst turnover is high (485 to 1300). Unfortunately, 4–12% loss of stereospecificity is observed. Similar results are reported for alkenylmercuric chlorides in a variation of this original procedure (Eq. 11) [11].





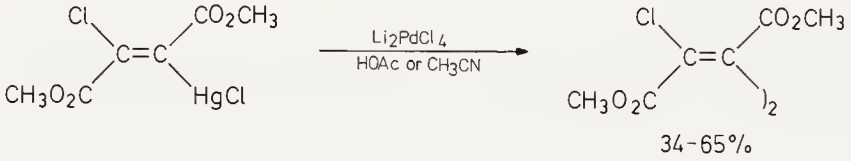
(11)

R = *n*-C_4H_9 59%
C_6H_5 80%

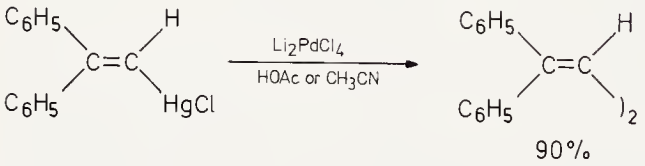
Initial reports on the reactions of alkenylmercurials and palladium(II) salts indicated that good yields of dienes can be obtained, but where the stereochemical outcome was reported, considerable isomerization was observed (Eqs. 12–15). Note the predominant inversion in this latter reaction. The

$(CH_3CH{=}CH)_2Hg \xrightarrow{(1,5\text{-COD})PdCl_2} (CH_3CH{=}CH)_2$ (12) [16, 18]

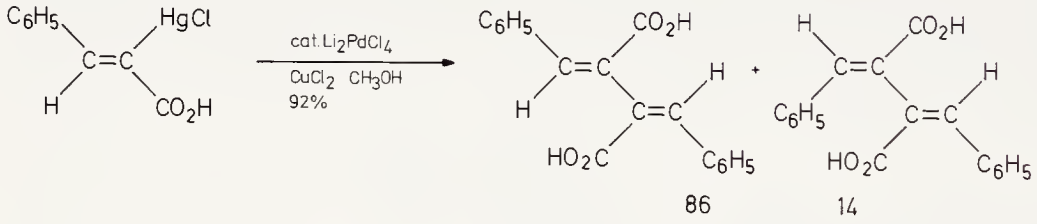
		cis-cis	cis-trans	trans-trans
cis	76% (CH_3OH)	35	24	41
trans	92% (CH_3CN)	0	65	35



(13) [19]

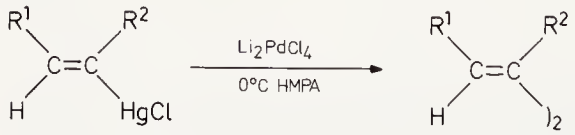


(14) [19]



(15) [20]

yield and stereoselectivity of these reactions has been found to be highly solvent dependent. By adding excess lithium chloride and employing a very polar solvent such as HMPA, one can obtain highly stereoselectively excellent yields of 1,3-dienes (Eq. 16) [11]. As indicated, this reaction is applicable



(16)

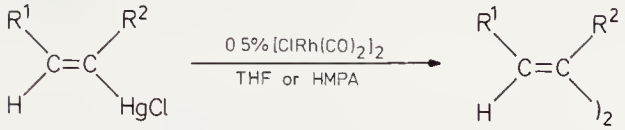
R^1	R^2	% Yield
n-C_3H_7	H	98
n-C_4H_9	H	100
t-C_4H_9	H	96
$CH_3O_2C(CH_2)_8$	H	94
C_6H_5	H	100
C_2H_5	C_2H_5	75
C_6H_5	C_6H_5	100
OAc	CH_3	82
$H_2C{=}C(CH_3)$	H	95
CH_3	$CH_3C{\equiv}C$	92

to the synthesis of 1,4-diacetoxy-1,3-butadienes, diene-diynes and tetraenes. Unlike the example of Eq. 15, this approach cannot be made catalytic in palladium by adding cupric chloride to reoxidize the palladium.

The reaction of β-chlorovinylmercuric chloride and palladium chloride produces not only the corresponding butadiene, but also higher oligomers (Eq. 17) [21]. This reaction is catalytic in palladium when ferric chloride or

$$ClCH{=}CHHgCl \xrightarrow{PdCl_2} Cl(CH{=}CH)_nCl \quad n = 2\text{-}6 \tag{17}$$

benzoquinone are added. 1,4-Dichloro-1,3-butadiene is also observed upon reacting this mercurial with $AuCl_3$, $PtCl_4$, $RhCl_3$ or $[ClRh(CO)_2]_2$. The two rhodium reagents, in fact, very nicely catalyze the stereospecific dimerization of alkenylmercurials overcoming many of the difficulties encountered in the earlier Li_2PdCl_4-HMPA procedure (Eq. 18) [22]. Slightly better results are

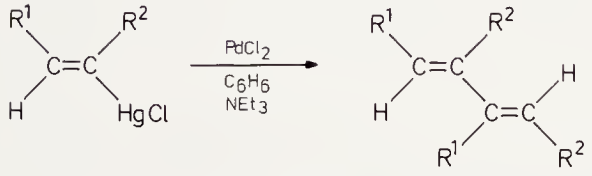


(18)

R^1	R^2	%Yield
n-C_4H_9	H	100
t-C_4H_9	H	100
c-C_6H_{11}	H	97
	H	92
C_6H_5	H	100
C_2H_5	C_2H_5	35

obtained with the rhodium(I) reagent, but low yields are observed for more hindered alkenylmercurials.

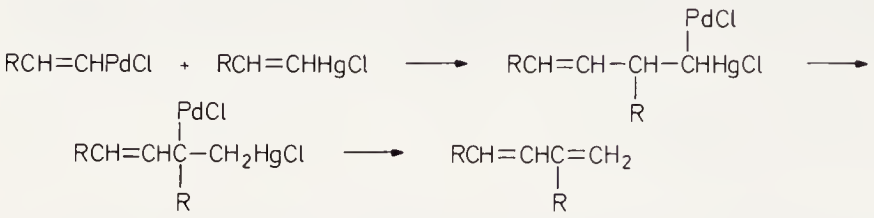
As noted earlier, the palladium promoted dimerizations are highly solvent dependent, a highly polar solvent being required to obtained high yields of symmetrical 1,3-dienes and high stereoselectivity. It has subsequently been reported that this same reaction affords unsymmetrical 1,3-butadienes via "head-to-tail" coupling when a non-polar solvent such as benzene is employed (Eq. 19) [23]. No more than 2–6% of the symmetrical diene is generally



(19)

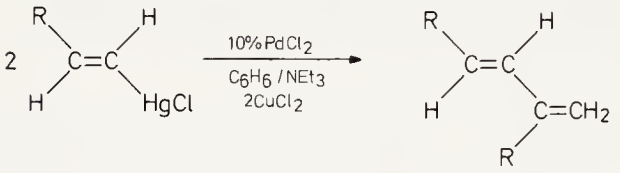
R^1	R^2	%Yield
n-C_4H_9	H	98
t-C_4H_9	H	91
c-C_6H_{11}	H	91
n-C_8H_{17}	H	88
t-C_4H_9	CH_3	62

observed under these conditions. The reaction appears to proceed by alkenylpalladium addition to the alkenylmercurial, subsequent palladium hydride rearrangement and finally mercury-palladium elimination (Eq. 20). Contrary



(20)

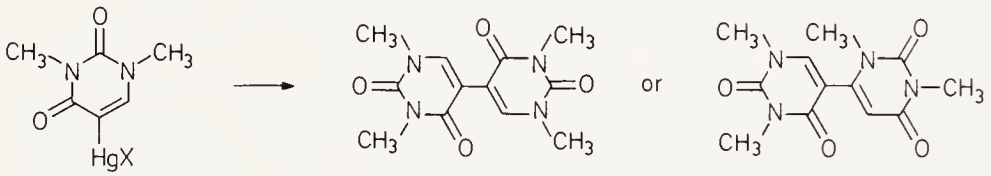
to the reaction in HMPA, this reaction can be made catalytic in palladium by adding two equivalents of cupric chloride (Eq. 21).



(21)

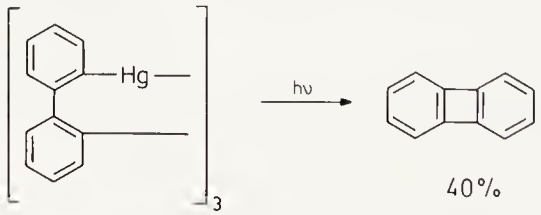
R = *n*-C_4H_9 89%
c-C_6H_{11} 98%

Similar symmetrical and unsymmetrical dimerizations have been effected using pyrimidinylmercuric salts by varying the anions present in the reaction mixture (Eq. 22) [24].

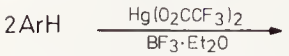


(22)

Arylmercurials can also be efficiently dimerized to biaryls using a variety of procedures. Although thermolysis of diphenylmercury gives only low yields of biphenyl [25], intramolecular dimerization has been achieved by photolysis (Eq. 23) [26]. Certain electron-rich arenes can also be dimerized by mercuric trifluoroacetate plus boron trifluoride etherate (Eq. 24) [27].



(23)



(24)

This reaction probably does not involve intermediate arylmercurials, but electron transfer processes. The yields are generally low and much better results

are obtained using thallium trifluoroacetate, lead tetraacetate or cobalt trifluoride.

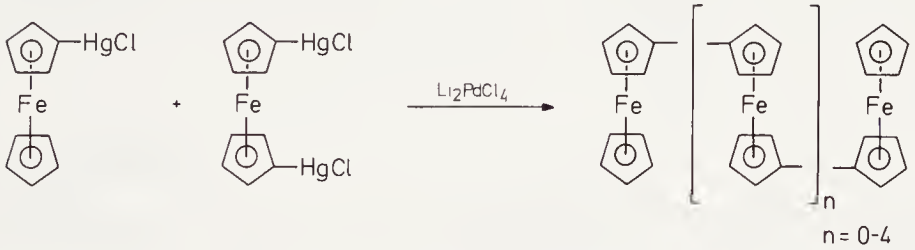
Once again a variety of transition metals have been reported to dimerize diphenylmercury: Pd > Pt > Ag > Au > Co > Cu > Fe > Ni [8–10, 25, 28]. More recently $Pd[P(C_6H_5)_3]_4$, $Cl_2Ru[P(C_6H_5)_3]_4$ and $ClRh[P(C_6H_5)_3]_3$ have been examined as catalysts for the dimerization of diphenylmercury [29]. The rhodium reagent in HMPA was found to be the most effective catalyst (100% yield of biphenyl). Simultaneously but independently, it was reported that $[ClRh(CO)_2]_2$ every efficiently dimerizes arylmercuric chlorides under conditions almost identical to those used in the dimerization of alkenylmercuric chlorides (Eq. 25) [22].

$$2\,ArHgCl \xrightarrow[4\,LiCl \quad HMPA]{0.5\%\,[ClRh(CO)_2]_2} Ar{-}Ar \qquad (25)$$

80°C 24 hr.

Ar = C_6H_5 (81%), *p*-$CH_3C_6H_4$ (92%), *p*-$CH_3OC_6H_4$ (88%), *p*-HOC_6H_4 (88%), *m*-$NO_2C_6H_4$ (53%), *p*-$C_6H_5C_6H_4$ (40%), 2-$C_{10}H_7$ (94%), 2-furyl (70%), 2-thienyl (96%)

A number of publications have examined the utility of palladium reagents for the dimerization of arylmercurials. The reaction of *m*-phenylenemercury polymer [30] and of diferrocenylmercury [31] with palladium black gives biaryls, but other palladium reagents look more promising. Excellent yields of biphenyl can be obtained from phenylmercuric chloride (87%) and diphenylmercury (95%) when Li_2PdCl_4 in HMPA is employed [11]. A similar reaction has been used to cross-couple ferrocenylmercurials to ferrocene-containing polymers (Eq. 26) [32]. This type of reaction becomes



(26)

catalytic in palladium when either cupric chloride or copper powder are added to the reaction (Eqs. 27, 28). While the Ullman reaction fails in the

$$2\,CH_3{-}C_6H_4{-}HgCl \xrightarrow[LiCl \quad CuCl_2]{cat.\,PdCl_2} (CH_3{-}C_6H_4{-})_2 \qquad (27)\ [33]$$

73%

$$2\,ArHgX \xrightarrow[C_5H_5N \quad 115°C]{cat\,PdCl_2/Cu} Ar{-}Ar \qquad (28)\ [34]$$

Ar = C_6H_5 (86%), *p*-ClC_6H_4 (62%), *o*-$CH_3OC_6H_4$ (84%), *p*-$CH_3OC_6H_4$ (90%), *p*-$H_2NC_6H_4$ (76%), *p*-$AcNHC_6H_4$ (69%), 1-$C_{10}H_7$ (47%), 2-furyl (86%), 2-thienyl (95%)

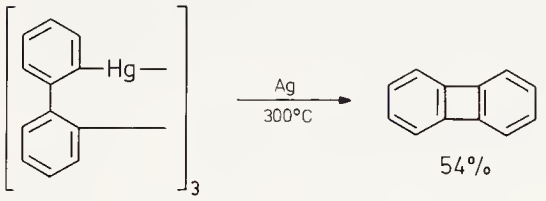
synthesis of amine-containing biaryls, this latter procedure works well. However, sterically hindered arylmercurials or those containing OH or

CO_2H groups fail. Fortunately, the $CuCl_2$ procedure apparently accommodates the CO_2H group, while the earlier mentioned $[ClRh(CO)_2]_2$ procedure works well with phenols. In a related reaction, the palladium chloride promoted dimerization of arylsulfinate salts to biaryls is catalyzed by mercuric chloride (Eq. 29) [35]. Addition of cupric chloride allows one to employ only catalytic amounts of palladium as well.

$$2\,ArSO_2Na \xrightarrow[CuCl_2]{HgCl_2\ Na_2PdCl_4} Ar{-}Ar \qquad (29)$$

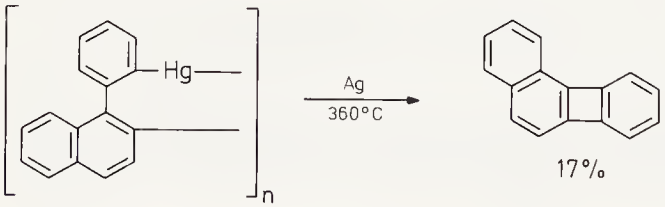
The reaction of *p*-tolylmercuric acetate and di-*p*-tolylmercury with palladium acetate has been briefly examined [36]. The former mercurial reacts only slowly at room temperature. Similarly, only one of the two aryl groups of the latter compound apparently takes part in the reaction with palladium acetate to give a near quantitative yield of bitolyl. The direct reaction of toluene and mercuric acetate, plus palladium acetate or chloroplatinic acid has also been examined. Mixtures of five of the six possible isomeric bitolyls are observed. The addition of $K_2Cr_2O_7$ to the reaction of phenylmercuric acetate, lithium acetate and palladium acetate gives only a 12% yield of biphenyl, plus 5% of phenyl acetate [37].

Silver at elevated temperatures has also been frequently employed to dimerize arylmercurials. For example, di- and triphenylene derivatives can be prepared in this manner (Eqs. 30–33). Even organometallic compounds withstand these rather severe conditions (Eqs. 34–36).



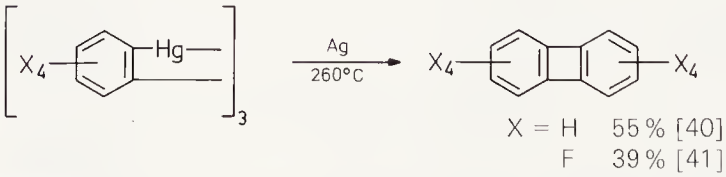
54%

(30) [38]



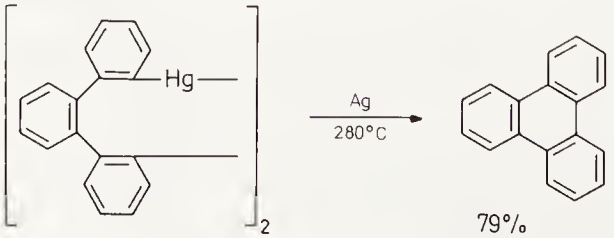
17%

(31) [39]



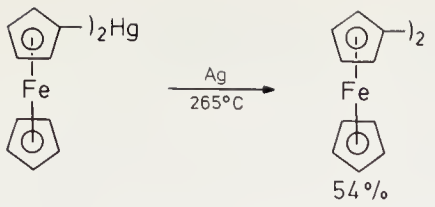
X = H 55% [40]
F 39% [41]

(32)

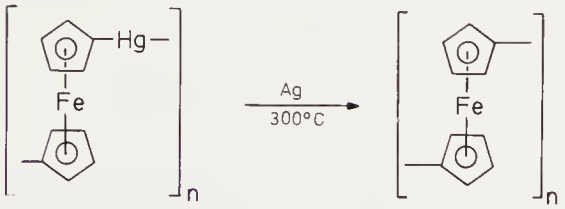


79%

(33) [42]



(34) [43]



(35) [44]

(36) [45]

From this short discussion, it should be evident that alkenyl- and arylmercurials are readily dimerized to 1,3-dienes and biaryls respectively. Although no work has been published on the dimerization of dialkynylmercurials, we have observed that palladium chloride produces high yields of conjugated diynes upon reaction with dialkynylmercurials (Eq. 37) [46]. At present no general method exists for the dimerization of simple alkyl groups attached to mercury.

$$(RC{\equiv}C)_2Hg \xrightarrow{Li_2PdCl_4} RC{\equiv}C{-}C{\equiv}CR \qquad (37)$$

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VI. Alkylation

Carbon—carbon bond formation via alkylation of organomercurials is a reaction of considerable synthetic potential. Unfortunately, to date there are few general methods to effect this transformation, success having been limited to relatively few examples of alkylation with organic halides and the use of certain organometallic reagents.

The most obvious approach to the alkylation of organomercurials is the cross-coupling of organic halides and organomercurials (Eq. 1). While some success along these lines has been achieved as evident in Table 6.1,

$$R_2Hg + R'X \longrightarrow R{-}R' \qquad (1)$$

the literature abounds with examples where this approach fails completely [1–9]. To date, with only one exception (see entry 22), the successful alkylation of alkyl-, benzyl-, aryl-, alkenyl-, alkynyl- and α-carbonyl-containing organomercurials has been limited to benzylic and allylic halides or α-halo ethers. Dialkylmercurials bearing a number of strong electron-withdrawing groups are more reactive, however, and can be alkylated by simple alkyl halides. In the reactions of triphenylmethyl bromide, there is increasing evidence for radical intermediates. Chemically induced dynamic nuclear polarization (CIDNP) has been observed during certain reactions [12, 14, 24], and triphenylmethyl peroxide is a frequent by-product [11, 15, 16].

The reactions of alpha mercurated carbonyl compounds are quite interesting. Alkylation occurs either on carbon or on oxygen depending on the electronic nature of the organic halide (compare entries 29 and 30), the solvent (entries 36 and 37) and the substituents present in the organomercurial (entries 38, 39 and 40). Mono- and dialkylation at a remote site have also been observed (entries 41 and 42). The delicate balance in reactivity is particularly evident in the reactions of ethyl α-bromomercurio-phenyl acetate. In nitromethane, triphenylmethyl bromide gives O-alkylation. In 1,2-dichloroethane, exclusive C-alkylation is observed [13, 29]. Electron-donating substituents on the aromatic ring of the mercurial accelerate the reaction [29, 36]. As expected, introducing electron-donating methyl groups into the para position of triphenylmethyl bromide slows the rate of reaction. Quite unexpectedly, however, para nitro groups in the same position completely inhibit reaction. This phenomena is observed in reactions of other organomercurials as well [13, 29]. No reaction is observed with triphenylmethyl perchlorate, or tin tetrachloride plus triphenylmethyl bromide. Evidently,

Table 6.1. Alkylation of Organomercurials

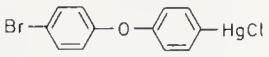
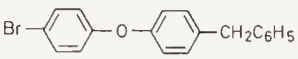
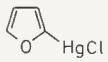
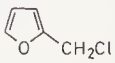
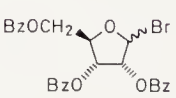
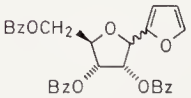
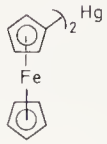
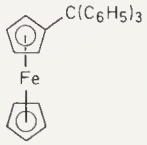
Entry	Organomercurial	Alkylating agent	Product	% Yield	Ref.
1	$(CH_3)_2Hg$	$(C_6H_5)_3CClO_4$	$CH_3C(C_6H_5)_3$	—	10
2	$(C_2H_5)_2Hg$	$(C_6H_5)_3CBr$	$C_2H_5C(C_6H_5)_3$	19	11
3	$(n\text{-}C_4H_9)_2Hg$	$(C_6H_5)_3CX$ X = Cl, Br, ClO_4	$n\text{-}C_4H_9C(C_6H_5)_3$	—	12
4		$(C_6H_5)_2CHBr$	$n\text{-}C_4H_9CH(C_6H_5)_2$	35	3
5	$(sec\text{-}C_4H_9)_2Hg$	$(C_6H_5)_3CX$ X = Cl, Br, ClO_4	$sec\text{-}C_4H_9C(C_6H_5)_3$	13 (X=Br)	11,12
6	$sec\text{-}C_4H_9HgBr$	$(C_6H_5)_3CBr$	$sec\text{-}C_4H_9C(C_6H_5)_3$?	—	13
7	$(C_6H_5CH_2)_2Hg$	$(C_6H_5)_3CBr$	$C_6H_5CH_2C(C_6H_5)_3$	—	14
8	$C_6H_5CH_2HgBr$	$(C_6H_5)_3CBr$	$C_6H_5CH_2C(C_6H_5)_3$	—	14
9	$p\text{-}CH_3C_6H_4CH_2HgBr$	$(C_6H_5)_3CBr$	$p\text{-}CH_3C_6H_4CH_2C(C_6H_5)_3$	~100	14,15
10	$(C_6H_5)_2Hg$	$(C_6H_5)_3CBr$	$(C_6H_5)_4C$	—	15,16
11		$(C_6H_5)_2CHBr$	$(C_6H_5)_3CH$	90	3
12		$C_6H_5CHCl_2$	$(C_6H_5)_3CH$	—	17
13	C_6H_5HgBr	$(C_6H_5)_3CBr$	$(C_6H_5)_4C$	100	15,18
14		$(C_6H_5)_3CClO_4$	$(C_6H_5)_4C$?	—	13
15	$(p\text{-}CH_3C_6H_4)_2Hg$	$(C_6H_5)_2CHBr$	$p\text{-}CH_3C_6H_4CH(C_6H_5)_2$	80	3
16	$(p\text{-}ClC_6H_4)_2Hg$	$(C_6H_5)_3CBr$	$p\text{-}ClC_6H_4C(C_6H_5)_3$	—	15,16
17	$p\text{-}C_6H_5OC_6H_4HgCl$	$C_6H_5CH_2Cl$	$p\text{-}C_6H_5OC_6H_4CH_2C_6H_5$ + $(p\text{-}C_6H_5CH_2C_6H_4)_2O$	22 23	19
18		$C_6H_5CH_2Cl$		—	19
19				9.5	20
20				α - 53 β - 5	21
21		$(C_6H_5)_3CCl$		18	22

Table 6.1. (continued)

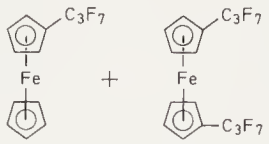
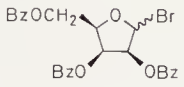
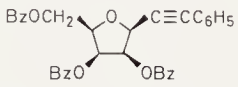
Entry	Organomercurial	Alkylating agent	Product	% Yield	Ref.
22		n-C_3F_7I		—	23
23	$(H_2C{=}CH)_2Hg$	$(C_6H_5)_3CBr$	$H_2C{=}CHC(C_6H_5)_3$	—	15,24
24	$H_2C{=}CHHgX$ (X=?)			—	15
25	$(C_6H_5C{\equiv}C)_2Hg$			—	25
26	$HCCH_2HgCl$	$(C_6H_5)_3CCl$	$HCCH_2C(C_6H_5)_3$	65	26,27
27		$(C_6H_5)_2CClCH_3$	$HCCH_2C(CH_3)(C_6H_5)_3$	7.5	27
28		p-$CH_3OC_6H_4CHClC_6H_5$	$HCCH_2CHC_6H_4OCH_3$-p	70	27
29	$HCCH_2HgBr$	$(C_6H_5)_3CBr$	$HCCH_2C(C_6H_5)_3$	—	4
30		$(p$-$NO_2C_6H_4)_3CBr$	$H_2C{=}CHOC(C_6H_4NO_2$-$p)_3$	40	4
31	$HCCHHgCl$ (CH₃)	$(C_6H_5)_3CCl$	$HCCHC(C_6H_5)_3$ (CH₃)	32	27
32	$HCCHHgCl$ (C_2H_5)		$HCCHC(C_6H_5)_3$ (C_2H_5)	20	27
33	CH_3CCH_2HgCl		$CH_3CCH_2C(C_6H_5)_3$	40	26
34	$C_6H_5CCH_2HgCl$		$C_6H_5CCH_2C(C_6H_5)_3$	38	26
35	CF_3CCF_2HgCl	CH_3OCH_2Cl	$CF_3C(OCH_2OCH_3){=}CF_2$	—	1
36	$C_2H_5OCCHHgBr$ (C_6H_5)	$(C_6H_5)_3CBr/ClCH_2CH_2Cl$	$C_2H_5OCCHC(C_6H_5)_3$ (C_6H_5)	80	13, 28,29
37		$(C_6H_5)_3CBr/CH_3NO_2$	$C_2H_5OC(OC(C_6H_5)_3){=}CHC_6H_5$	—	13, 28,29

Table 6.1. (continued)

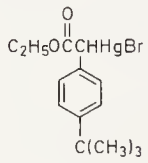
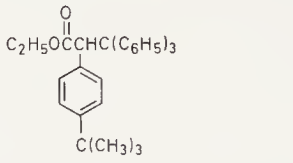
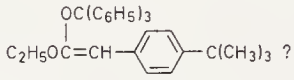
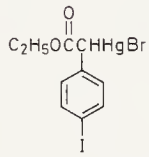
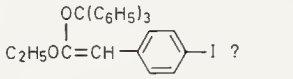
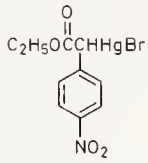
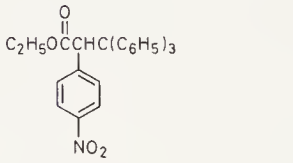
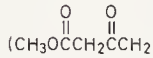
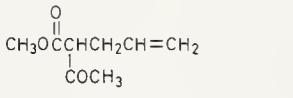
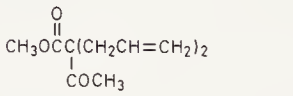
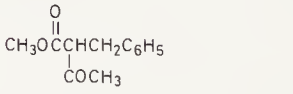
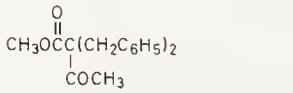
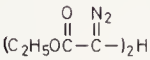
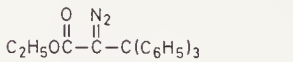
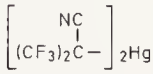
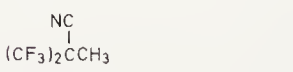
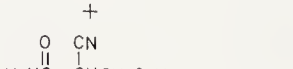
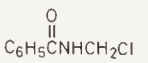
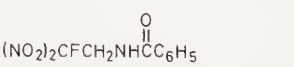
Entry	Organomercurial	Alkylating agent	Product	% Yield	Ref.
38		$(C_6H_5)_3CBr$	 +  ?	— —	28
39			 ?	—	28
40				—	28
41		$H_2C{=}CHCH_2I$	 + 	10 33	5,30
42		$C_6H_5CH_2I$	 + 	— —	5
43		$(C_6H_5)_3CBr$		55	31
44		CH_3I		70	32
45	$[(NC)_3C]_2Hg$	$C_6H_5CH_2Cl$	$(NC)_2CHCH_2C_6H_5$ + 	— —	33
46	$[(NO_2)_2CF]_2Hg$			100	34

Table 6.1. (continued)

Entry	Organomercurial	Alkylating agent	Product	% Yield	Ref.
47	$[(NO_2)_3C]_2Hg$	CH_3I	$(NO_2)_3CCH_3$	71	35
48		C_2H_5I	$(NO_2)_3CC_2H_5$	25	35
49		$n\text{-}C_3H_7I$	$(NO_2)_3C(CH_2)_2CH_3$	30	35
50		$H_2C{=}CHCH_2I$	$(NO_2)_3CCH_2CH{=}CH_2$	60	35
51		$n\text{-}C_5H_{11}I$	$(NO_2)_3C(CH_2)_4CH_3$	32	35
52		$CH_3O\overset{O}{\overset{\|}{C}}CH_2CH_2I$	$(NO_2)_3CCH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3$	6	35

the organic halide must contain a sufficiently electrophilic carbon and the possibility of nucleophilic assistance by the halide moiety.

The nature of the alkylating agent is extremely important in these reactions. While triphenylmethyl perchlorate fails to react with the above-mentioned mercurated ester, successful alkylations have been reported with dimethylmercury (entry 1) and phenylmercuric bromide (entry 14). With dialkylmercurials bearing β-hydrogens, dehydromercuration becomes the dominant reaction (Eq. 2) [10, 11, 37, 38]. Diphenyliodonium salts can also be employed for the alkylation of organomercurials although side products are observed (Eq. 3) [39].

$$(CH_3\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_2)_2Hg + (C_6H_5)_3CX \longrightarrow CH_3\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_2HgX + (CH_3)_2C{=}CH_2 + (C_6H_5)_3CH \qquad X = Br,\ ClO_4,\ BF_4 \tag{2}$$

$$C_2H_5O\overset{O}{\overset{\|}{C}}\underset{\displaystyle C_6H_5}{\overset{\displaystyle HgBr}{\overset{|}{\underset{|}{CH}}}} + (C_6H_5)_2IBF_4 \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}CH(C_6H_5)_2 \tag{3}$$

The addition of a Lewis acid to these reactions has on occasion been observed to promote alkylation, although inhibition of reaction has also been reported. For example, the alkylation of ethyl α-bromomercuriophenyl acetate by triphenylmethyl bromide is curtailed by addition of tin tetrachloride, while the reaction of α-chloromercurioacetaldehyde and benzhydryl chloride occurs only in its presence (Eq. 4) [27]. The addition of tin tetrachloride fails

$$H\overset{O}{\overset{\|}{C}}CH_2HgCl + ClCH(C_6H_5)_2 \xrightarrow{SnCl_4} H\overset{O}{\overset{\|}{C}}CH_2CH(C_6H_5)_2 \quad 37\% \tag{4}$$

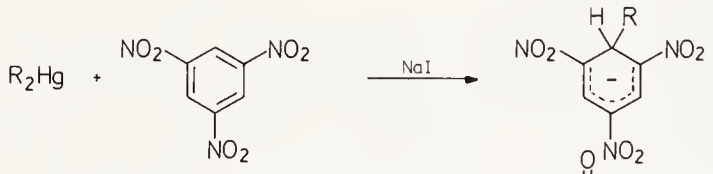
to improve the yield of alkylation product in the reaction of α-chloromercurioacetaldehyde and 1-chloro-1,1-diphenylethane (entry 27 in Table 6.1). The addition of zinc chloride to the reaction of di-*sec*-butylmercury and triphenylmethyl bromide favors dehydromercuration over alkylation [11]. In the alkylation of 4-chloromercuriodiphenyl ether by benzyl chloride, the mercuric chloride produced is apparently a sufficiently strong Lewis acid to effect alkylation, as well as dialkylation (entry 17). In a number of cases aluminium bromide addition has promoted alkylation, but the yields are too low to be synthetically useful (Eq. 5) [40]. An analogous reaction between

$$R_2Hg + R'X \xrightarrow[CH_2Cl_2]{AlBr_3} R-R' \qquad (5)$$

R	R'	X	%Yield
C_6H_5	C_2H_5	Br	35
C_6H_5	$C_6H_5CH_2$	Br	41
C_6H_5	p-$NO_2C_6H_4CH_2$	Br	36
C_6H_5	$(C_6H_5)_2CH$	Br	40
C_6H_5	CH_3OCH_2	Cl	60
$C_6H_5CH_2$	CH_3	I	20

trans-1-hexenylmercuric chloride, allyl chloride and a number of Lewis acids failed to provide any of the desired 1,4-diene [41].

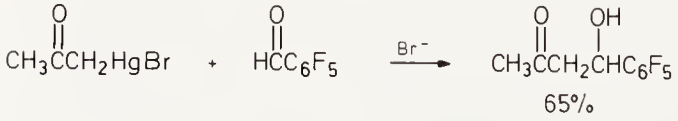
An alternate approach to the alkylation of organomercurials takes advantage of the increased nucleophilicity of the organic groups attached to mercury when halide anions are present. Thus, 1,3,5-trinitrobenzene can be alkylated by organomercurials bearing strong electron-withdrawing groups if sodium iodide is added (Eq. 6) [15, 42, 43]. The observation of CIDNP suggests that an electron transfer process is occurring.



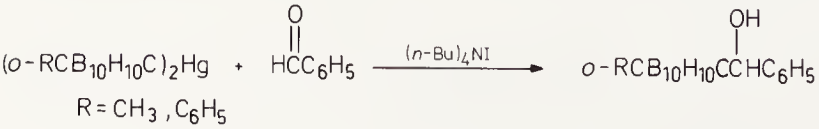
(6)

R = CN, CCl_3, $CH(CF_3)_2$, C_6F_5, $C{\equiv}CC_6H_5$, CH_2CCH_3, $C_2H_5O_2CCHC_6H_5$, *o*-carboranyl

Organomercurials bearing anion-stabilizing groups will also add to aldehydes in the presence of halide anions (Eqs. 7, 8). Apparently the halide is not always necessary in this type of reaction, since similar reactions

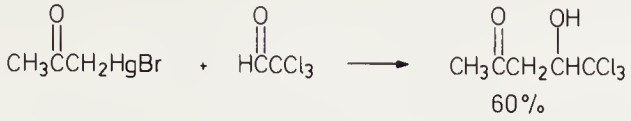


(7) [44]

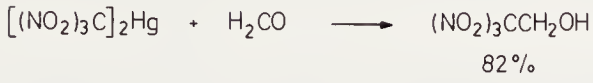


(8) [45]

have been reported to proceed in the absence of halides with highly reactive aldehydes (Eqs. 9, 10). Mercurated ketones react with simple aldehydes

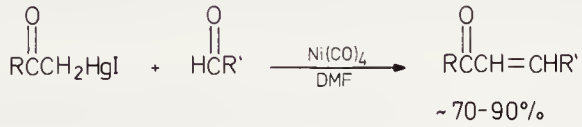


(9) [44]



(10) [46]

or ketones in the presence of nickel tetracarbonyl to afford the products of a directed aldol condensation in generally quite good yield (Eq. 11) [47].



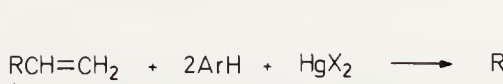
(11)

Carboxamidomercurials can also be added to carbonyl compounds if first treated with *n*-butyl lithium at −75 °C (Eq. 12) [48]. In a similar manner,

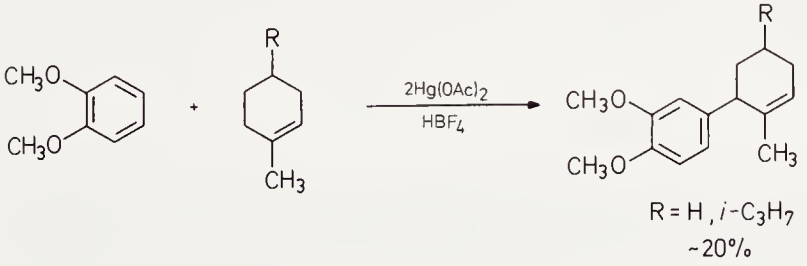
(12)

methyl iodide, benzoyl chloride and ethyl benzoate react with this reagent to afford the corresponding products Et_2NCOCH_3 (23%) and $Et_2NCOCOC_6H_5$ (65% and 31%) respectively. This carboxamido lithium equivalent should prove valuable in organic synthesis.

In all of the above alkylation reactions, the organic moiety in the organomercurial has functioned as a nucleophile. There are several examples in the literature in which the organomercurial behaves as an electrophile in carbon—carbon bond forming reactions. One of these reactions was discussed briefly in Chap. IV, namely the diarylation of olefins, which appears to proceed via carbomercuration, solvolysis, and subsequent electrophilic aromatic substitution by the resulting carbocation (Eq. 13) [49–51]. Under similar conditions allylic cations can apparently also be generated from olefins as

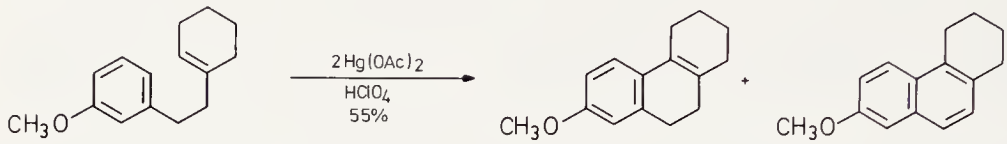


(13)

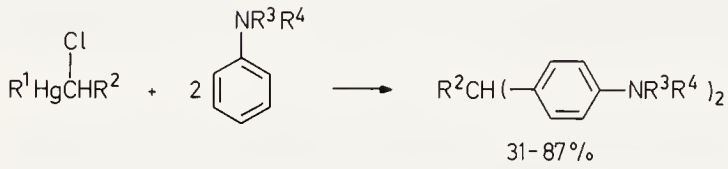


(14)

illustrated by the following examples (Eqs. 14, 15) [52]. α-Haloorganomercurials can also alkylate substituted anilines (Eq. 16) [53, 54]. Since the

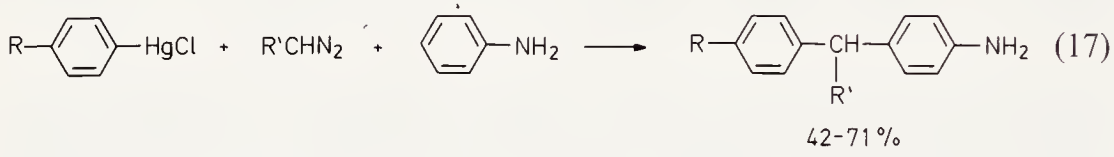


(15)



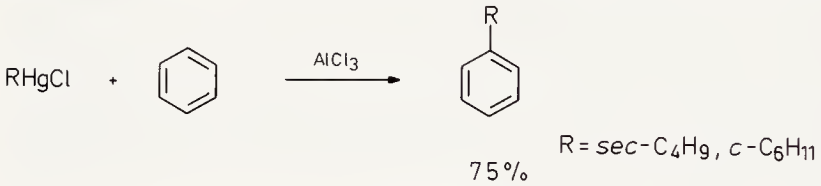
(16)

mercurials themselves are prepared from diazoalkanes, the following arylation becomes possible (Eq. 17) [53].



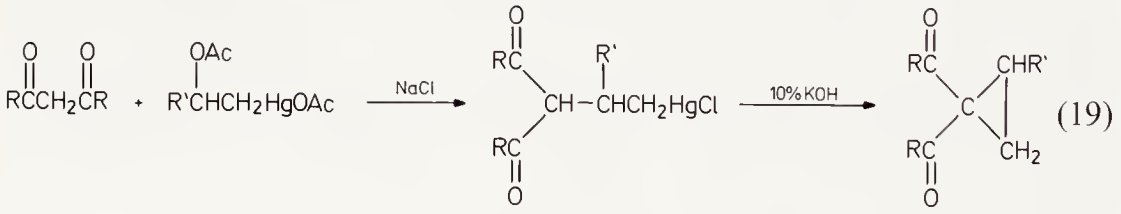
(17)

Organomercurials can also be employed as electrophilic reagents in Friedel-Crafts type aromatic substitution reactions (Eq. 18) [55, 56].



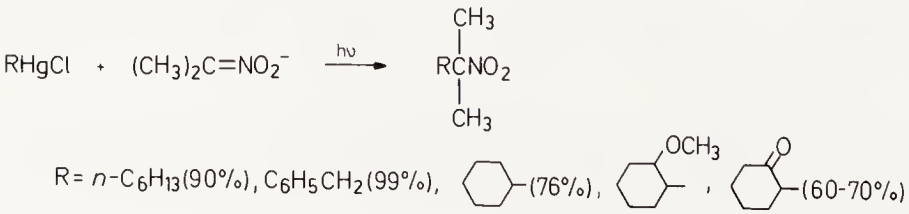
(18)

In a few cases, nucleophiles have been shown to directly displace the mercury moiety in organomercurials. For example, the carbomercuration of olefins by β-diketones affords organomercurials readily cyclized to cyclopropyl diketones (Eq. 19) [57, 58]. Recently nitronate anions have been shown



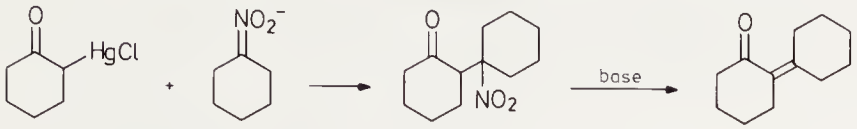
(19)

to alkylate a variety of primary, secondary and benzylic organomercurials photochemically (Eq. 20) [59]. The use of α-halomercurio-ketones affords a



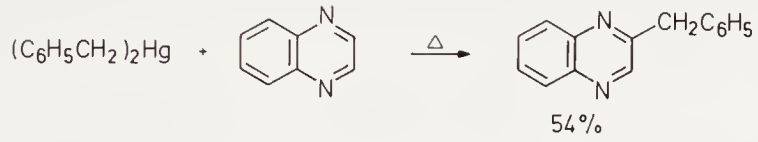
(20)

novel approach to enones by subsequent elimination (Eq. 21). Aryl- and alkenylmercurials fail to undergo this reaction. A photostimulated free radical chain process ($S_{RN}1$) has been suggested for these reactions.

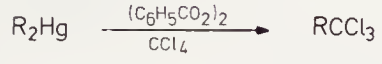


(21)

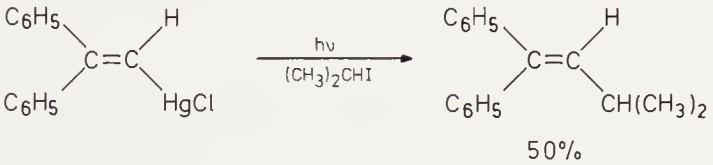
Free radical reactions have been employed to effect several other alkylation processes (Eqs. 22–24).



(22) [60]

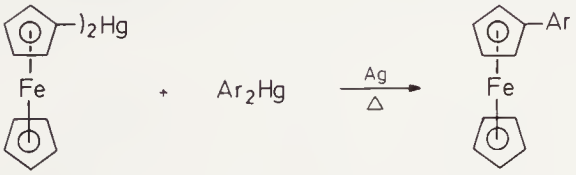


(23) [61–63]



(24) [64]

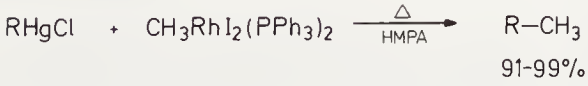
Several organometallic procedures have been reported which provide fairly general methods for the alkylation of a wide variety of organomercurials. The silver promoted dimerization of organomercurials discussed in the previous chapter has been used to effect the cross-coupling of organomercurials as well (Eq. 25) [65].



(25)

Ar = C_6H_5 (45%), *o*-$C_6H_4C_6H_5$ (6%), *m*-$C_6H_4C_6H_5$ (22%), *p*-$C_6H_4C_6H_5$ (20%)

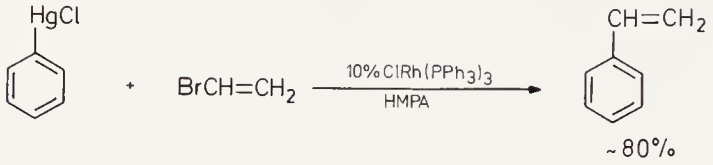
Organorhodium intermediates can be employed to effect the methylation of alkenyl-, alkynyl- and arylmercurials (Eq. 26) [66]. Unfortunately, this procedure fails with alkylmercurials, and other organorhodium(III) com-



(26)

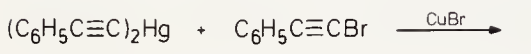
pounds have generally given only low yields of cross-coupled product. While this reaction requires stoichiometric amounts of expensive rhodium,

it appears that rhodium(I) catalysts can be employed to effect the cross-coupling of certain organomercurials and organic halides (Eq. 27).



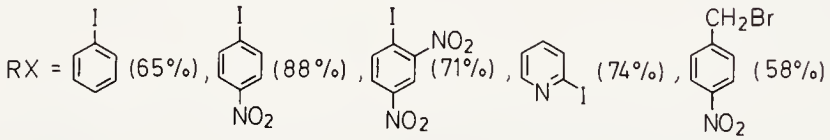
(27)

Copper reagents appear to be more useful for the alkylation of a wide variety of organomercurials. For example, the following reactions have recently been reported (Eqs. 28, 29). Secondary alkylmercuric bromides

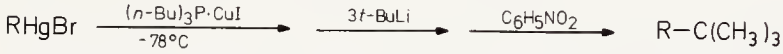


(28) [67]

(29) [68]



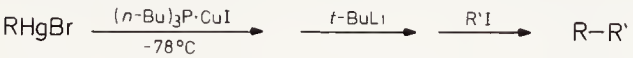
can be cross-coupled with *tert*-butyl lithium by adding $(n\text{-Bu})_3P \cdot CuI$ and oxidizing with nitrobenzene (Eq. 30) [69]. The complex organometallic inter-



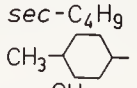
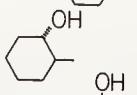
R = 2-norbornyl and 4-methylcyclohexyl — 40–75%

(30)

mediate suggested for these reactions will also react with primary alkyl iodides to give cross-coupled products (Eq. 31). These reactions generally

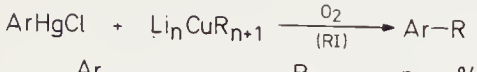


(31)

R	R'	%Yield
2-norbornyl	CH_3	~70
sec-C_4H_9	n-C_6H_{13}	15–25
	CH_3	45–48
	CH_3	41
n-$C_6H_{13}CHCH_2$ (OH)	n-C_3H_7	21

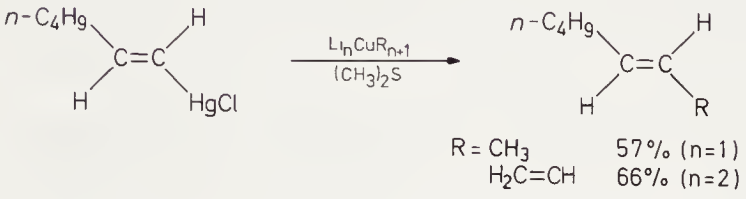
proceed with predominant retention of the organomercurial stereochemistry. This type of cross-coupling reaction can be carried out in good yield using a wide variety of organocuprate reagents and organomercurials (Eqs. 32–34) [70, 71]. At present this approach appears to be the most general method for the alkylation of a wide variety of organomercurials.

The alkylation of aromatic lead compounds, now readily available from diarylmercurials [72] via transmetallation, is also noteworthy (Eq. 35).



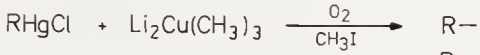
(32)

Ar	R	n	%Yield
C_6H_5	CH_3	2	92
p-$CH_3OC_6H_4$	CH_3	2	65
m-$CH_3O_2CC_6H_4$	CH_3	2	82
2,4,6-$(CH_3)_3C_6H_2$	CH_3	2	75
C_6H_5	n-C_4H_9	1	42
C_6H_5	sec-C_4H_9	1	35
C_6H_5	$H_2C{=}CH$	1	59



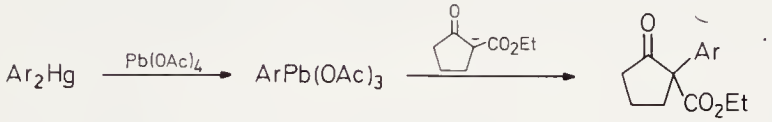
(33)

R = CH_3 57% (n=1)
$H_2C{=}CH$ 66% (n=2)



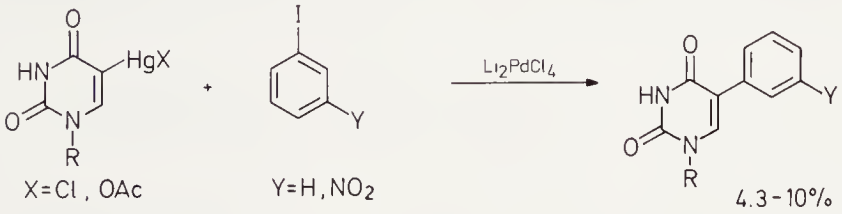
(34)

R = n-C_6H_{13} 62%
n-$C_4H_9CHOHCH_2$ 51%



(35)

Finally, it should be mentioned that the reaction of mercurated pyrimidines and aryl iodides in the presence of Li_2PdCl_4 leads to low yields of cross-coupled products (Eq. 36) [73]. A number of much more useful palladium-promoted carbon—carbon bond forming reactions will be discussed in the next chapter.



X=Cl, OAc Y=H, NO_2 4.3-10%

(36)

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VII. Alkene and Alkyne Addition and Substitution Reactions

The organic moiety in organomercurials can be made to add to carbon—carbon double or triple bonds or to substitute olefinic or acetylenic hydrogens thereby greatly expanding the limited number of approaches described in the previous chapter for the alkylation of organomercurials. While few organomercurials will add directly to carbon—carbon multiple bonds, such reactions can be effected via generation of free radical or organopalladium intermediates readily available from organomercurials. These synthetically valuable reactions will be discussed in detail in this chapter.

The direct addition of organomercurials to carbon—carbon multiple bonds appears limited to double or triple bonds containing strong electron-withdrawing groups. For example, tetracyanoethylene (TCNE) readily inserts into benzylmercuric chloride [1] and a number of simple dialkylmercurials [2, 3] (Eq. 1). The relative rates of reaction are R = *i*-C_3H_7 > C_2H_5 > CH_3 and for $(p\text{-}XC_6H_4CH_2)_2Hg$, X = CH_3 > H > CF_3 (no

$$R_2Hg + (NC)_2C{=}C(CN)_2 \longrightarrow R{-}\overset{CN\ CN}{\underset{CN\ CN}{C{-}C}}{-}HgR \qquad (1)$$

R=CH_3, C_2H_5, *i*-C_3H_7, $C_6H_5CH_2$ (73%), *p*-$CH_3C_6H_4CH_2$ (60%)

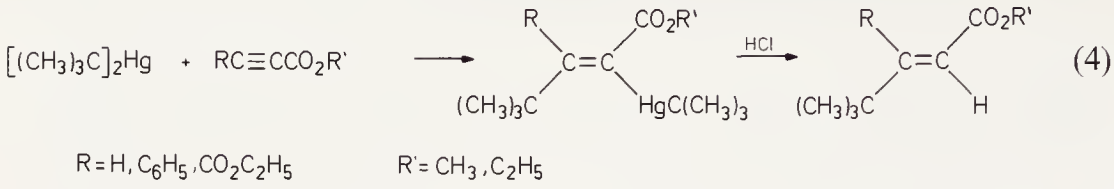
reaction). The benzyl adduct thermally eliminates benzylmercuric cyanide (97% in 24 hours at 20 °C) or it can be protonated (Eq. 2) [3]. Di-*tert*-butylmercury will add readily to a wide variety of olefins, acetylenes and azo

$$C_6H_5CH_2\overset{CN}{\underset{}{C}}{=}C(CN)_2 \xleftarrow{?} C_6H_5CH_2{-}\overset{CN\ CN}{\underset{CN\ CN}{C{-}C}}{-}HgCH_2C_6H_5 \xrightarrow{HCl} C_6H_5CH_2{-}\overset{CN\ CN}{\underset{CN\ CN}{C{-}CH}} \qquad (2)$$

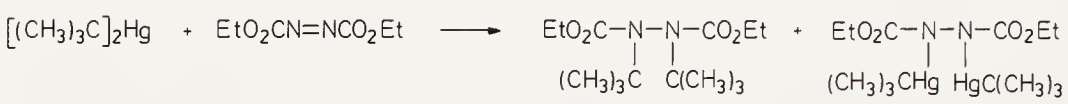
$$[(CH_3)_3C]_2Hg + \begin{matrix} R^2 & & R^3 \\ & C{=}C & \\ R^1 & & R^4 \end{matrix} \longrightarrow (CH_3)_3C{-}\overset{R^2\ R^3}{\underset{R^1\ R^4}{C{-}C}}{-}HgC(CH_3)_3 \qquad (3)$$

R^1	R^2	R^3	R^4	%Yield
H	C_6H_5	CN	CN	75
H	*p*-$CH_3C_6H_4$	CN	CN	45
H	*p*-ClC_6H_4	CN	CN	65
CH_3	CH_3	CN	CN	40
CH_3	CH_3	CN	$CO_2C_2H_5$	35-40

compounds bearing strong electron-withdrawing groups (Eqs. 3–5) [4, 5]. As noted, the addition to acetylenes proceeds stereo- and regioselectively,



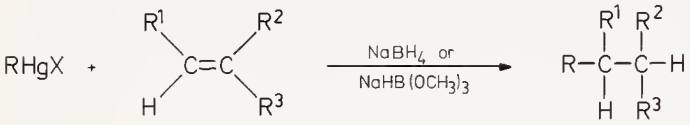
(4)



(5)

and the resulting alkenylmercurials are readily protonated affording a useful stereospecific olefin synthesis. The azo reaction proceeds with disproportionation and apparently works with diethylmercury as well.

In a recent development of considerable synthetic utility, electron-deficient olefins can be readily alkylated by free radicals generated by treating organomercurials with $NaBH_4$ or $NaHB(OCH_3)_3$ (Eq. 6) [6–22]. The results reported to date using this approach are summarized in Table 7.1.



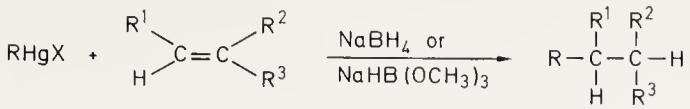
(6)

Several variations in experimental procedure have been employed. As solvents, ethanol, chloroform, methylene chloride and the olefin itself have been used. In the reactions of benzylmercuric acetate, best results were obtained using pyridine as a solvent and adding di-2-pyridylamine [10]. The olefin is generally added in excess and the yields reported are based on the organomercurial. Both $NaBH_4$ and $NaHB(OCH_3)_3$ have been utilized interchangeably, although the former reagent apparently gives better results with mercurials derived from cyclopropanes via methoxymercuration [14]. In one case, $NaBH_3CN$ has also been employed quite successfully [19].

The reaction appears quite general for a wide variety of organomercurials, including primary, secondary, and tertiary alkyl and benzylic mercurials, as well as those derived from olefins [11, 12], cyclopropanes [13, 14] and conjugated dienes [15] via methoxymercuration. The nature of the alkyl group seems to be relatively unimportant as far as yields are concerned, although some variation has been observed with the methoxymercurials derived from olefins. Methoxymercurials derived from olefins of the type $H_2C{=}CH_2$, $RCH{=}CH_2$ and $RCH{=}CHR$ give 48–65% yields of addition product with methyl acrylate, while methoxymercurials from $R_2C{=}CH_2$ and $R_2C{=}CHR$ fail completely [11].

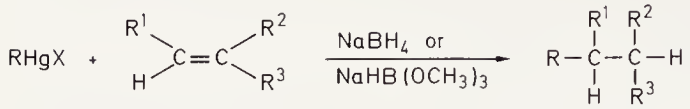
Recently, the successful borohydride-induced alkylation of β-hydroxymercurials derived from olefins has been reported [16]. With acrylonitrile

Table 7.1. Alkyl Addition to Alkenes



R	X	R^1	R^2	R^3	% Yield	Ref.
n-C_6H_{13}	OAc	H	H	CO_2CH_3	64	8
				$COCH_3$	51	8
				C_6H_5	20	8
			CH_3	CO_2CH_3	31	8
		CH_3	H	CO_2CH_3	49	8
		$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$		CH_3	50–60	9
c-C_6H_{11}	OAc	H	H	CN	61	8
				CO_2CH_3	62	8
				$CO_2C_2H_5$	62	8
				$COCH_3$	70	8
				CHO	27	8
				C_6H_5	45	8
			CH_3	CN	50	8
				CO_2CH_3	84	8
			Cl	Cl	27	8
		CH_3	H	CN	53	8
				CO_2CH_3	24	8
		CO_2CH_3		CO_2CH_3	34	8
		H	H	n-C_6H_{13}	2	8
				OC_2H_5	< 2	8
		$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$		CH_3	50–60	9
t-C_4H_9	Cl	H	H	CO_2CH_3	83	8
				$COCH_3$	69	8
				C_6H_5	15	8
			CH_3	CO_2CH_3	83	8
		CH_3	H	CO_2CH_3	< 1	8

Table 7.1. (continued)



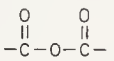
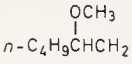
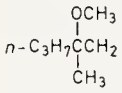
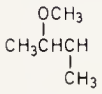
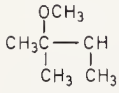
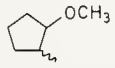
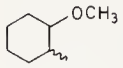
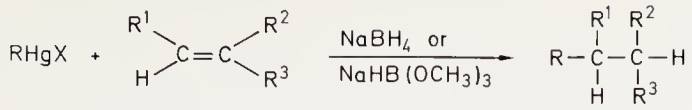
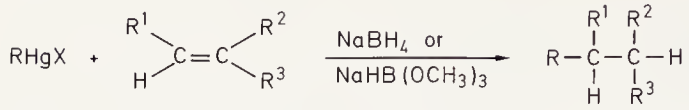
R	X	R^1	R^2	R^3	% Yield	Ref.
				CH_3	50–60	9
$C_6H_5CH_2$	OAc	H	H	$CO_2C_2H_5$	59	10
				C_6H_5	20	10
				$CH_2C_6H_5$	47	10
$CH_3OCH_2CH_2$	OAc			CO_2CH_3	50	11
					48	11
					30	11
					53	11
					32	11
					65	11
					58	11
	Cl			CN	77	12
				C_6H_5	22	12
			CH_3	CN	47	12
				CO_2CH_3	38	12
			Cl	CN	65	12
				Cl	25	12
		CN	H	CN	61	12
		$CO_2C_2H_5$		$CO_2C_2H_5$	53	12
			$CO_2C_2H_5$	H	30	12

Table 7.1. (continued)



R	X	R^1	R^2	R^3	% Yield	Ref.
		CH_3	H	CN	8	12
		$CO_2C_2H_5$	CH_3	$CO_2C_2H_5$	31	12
$C_6H_5CH(OCH_3)CH_2$	OAc	H	H	CO_2CH_3	50	11
	Cl				44	12
				CN	60	12
				C_6H_5	10	12
			CH_3	CN	43	12
				CO_2CH_3	36	12
			Cl	CN	65	12
		CN	H		34	12
		$CO_2C_2H_5$		$CO_2C_2H_5$	38	12
			$CO_2C_2H_5$	H	21	12
		CH_3	H	CN	6	12
		$CO_2C_2H_5$	CH_3	$CO_2C_2H_5$	22	12
$n\text{-}C_6H_{13}CH(OCH_3)CH_2CH_2$	OAc	H	H	CN	50	13
$C_2H_5C(OCH_3)(C_2H_5)CH_2CH_2$					87	13
$CH_3CH(OCH_3)CH(CH_3)CH(CH_3)$					93	13
$CH_3C(OCH_3)(CH_3)CHCH_2$					81	13
$CH_3O(CH_3)CH_3C-C(CH_3)CH_2$					56	13
$C_6H_5CH(OCH_3)CH_2CH_2$					87	13

Table 7.1. (continued)



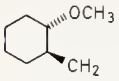
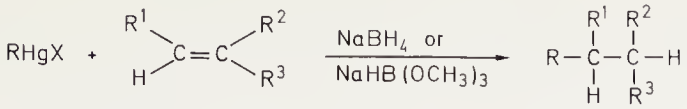
R	X	R^1	R^2	R^3	% Yield	Ref.
	Cl				90	14
				CO_2CH_3	77	14
				C_6H_5	38	14
			CH_3	CN	70	14
				CO_2CH_3	67	14
			Cl	CN	87	14
				Cl	51	14
		CN	H	CN	90	14
		$CO_2C_2H_5$		$CO_2C_2H_5$	95	14
			$CO_2C_2H_5$	H	42	14
		CH_3	H	CN	21	14
				$CO_2C_2H_5$	12	14
		$CO_2C_2H_5$	CH_3		67	14
	OAc	H	H	CN	82	13
	Cl				80	14
				CO_2CH_3	76	14
				C_6H_5	34	14
			CH_3	CN	80	14
				CO_2CH_3	68	14
			Cl	CN	76	14
				Cl	44	14
		CN	H	CN	84	14
		$CO_2C_2H_5$		$CO_2C_2H_5$	35	14
			$CO_2C_2H_5$	H	35	14
		CH_3	H	CN	22	14
				$CO_2C_2H_5$	13	14

Table 7.1. (continued)



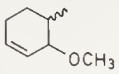
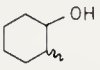
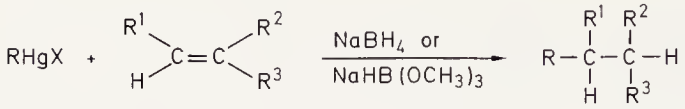
R	X	R^1	R^2	R^3	% Yield	Ref.
		$CO_2C_2H_5$	CH_3	$CO_2C_2H_5$	60	14
$H_2C{=}CHCH(OCH_3)CH_2$	OAc	H	H	CN	47	15
				CO_2CH_3	34	15
				$COCH_3$	22	15
			CH_3	CN	24	15
			Cl	CN	60	15
$CH_3CH{=}CHCH(OCH_3)CH_2$					59	15
$H_2C{=}C(CH_3)C(CH_3)(OCH_3)CH_2$					24	15
					27	15
$n\text{-}C_6H_{13}CH(OH)CH_2$	Cl		H	CN	60	16
				CO_2CH_3	50	16
$(CH_3)_2CC(OH)H(C_2H_5)$				CN	70	16
				CO_2CH_3	43	16
$C_6H_5CH(OH)CH_2$				CN	72	16
				CO_2CH_3	37	16
$C_6H_5CH_2OCH_2CH(OH)CH_2$				CN	94	16
				CO_2CH_3	50	16
				CN	74	16
				CO_2CH_3	78	16
$n\text{-}C_9H_{19}C(OH)CH_2OCH_2THP$	Br		CH_3	CN	49	16

Table 7.1. (continued)



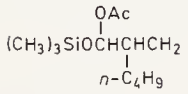
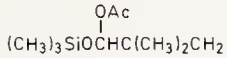
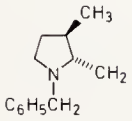
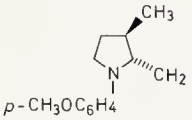
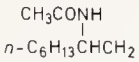
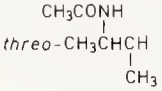
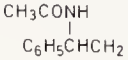
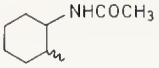
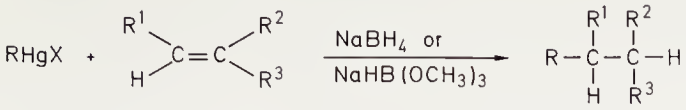
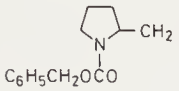
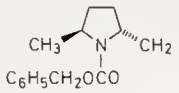
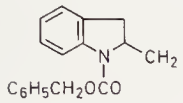
R	X	R^1	R^2	R^3	% Yield	Ref.
	OAc				40	17
			Cl		65	17
			H		60	17
				CO_2CH_3	52	17
				$COCH_3$	61	17
		$CO_2C_2H_5$		$CO_2C_2H_5$	60	17
					45	17
		H	CH_3	CN	30	17
			Cl		51	17
			H		51	17
				CO_2CH_3	49	17
	Cl		Cl	CN	26	18
				Cl	43	18
					18	18
				CN	45	18
			H		67	18
				CO_2CH_3	40	18
					26	18
				CN	74	18
					67	18
				CO_2CH_3	22	18
					15	18
				CN	78	18

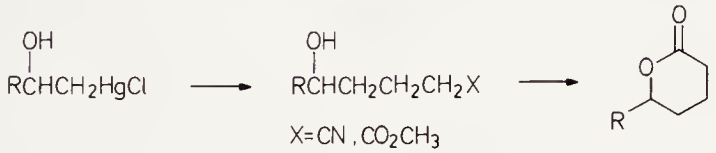
Table 7.1. (continued)



R	X	R^1	R^2	R^3	% Yield	Ref.
	OAc			CO_2CH_3	64	19
					41	19
				CN	79[a]	19

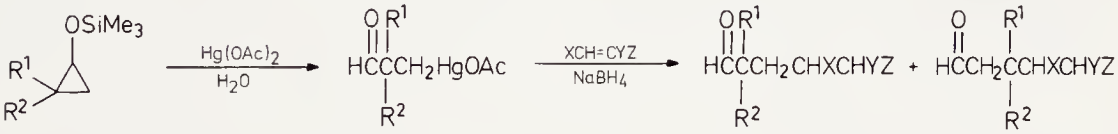
[a] $NaBH_3CN$ used as the reducing agent.

and methyl acrylate, the resulting products are readily lactonized (Eq. 7). This approach has provided a simple synthesis of the antibiotic lactone malyngolide.



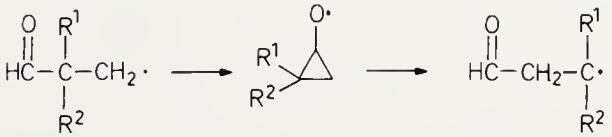
(7)

The alkylation of β-mercurated aldehydes derived from hydroxymercuration of trimethylsilyloxycyclopropanes has also been examined (Eq. 8) [17]. This reaction apparently proceeds via rapid rearrangement of the initial free



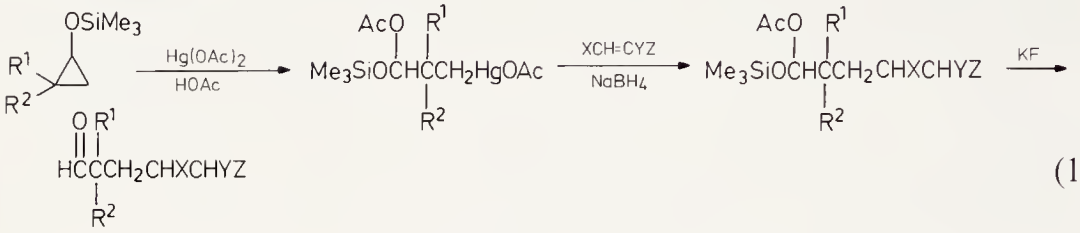
(8)

radical such that a mixture of alkylated aldehydes results (Eq. 9). This difficulty is circumvented by using the corresponding acetoxymercuration products and desilylating later with KF (Eq. 10).

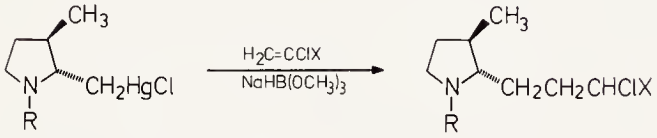


(9)

Efforts to employ solvomercuration products bearing nitrogen functionality in these alkylation reactions have also proven successful. While β-nitro- and β-azidomercurials apparently revert back to olefins under the usual reaction conditions, cyclic aminomercuration products can be alkylated (Eq. 11) [18].



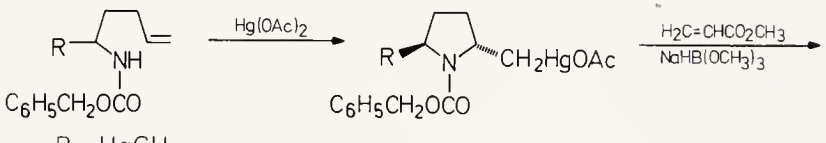
(10)



(11)

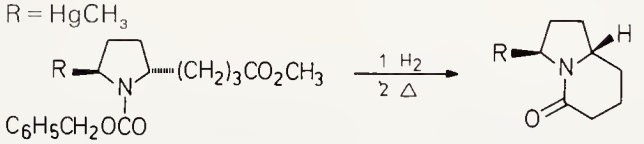
$R = C_6H_5CH_2, p\text{-}CH_3OC_6H_4$ $X = Cl, CN$

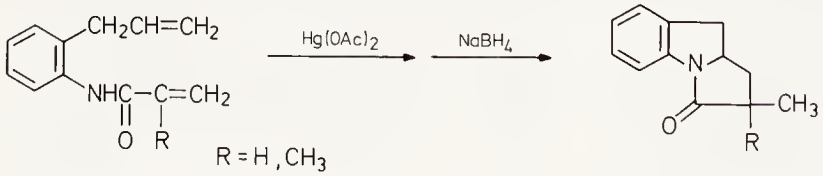
Considerable success has also been achieved using amidomercuration products [18]. For example, cyclic ureidomercuration, alkylation and subsequent deprotection provides a useful new approach to bicyclic lactams (Eq. 12) [19]. Intramolecular alkylation has also been reported (Eq. 13) [20].



(12)

$R = HgCH_3$

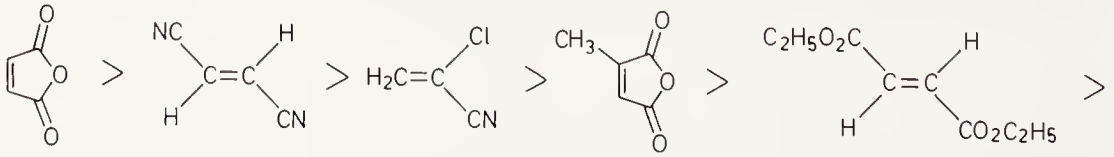




(13)

$R = H, CH_3$

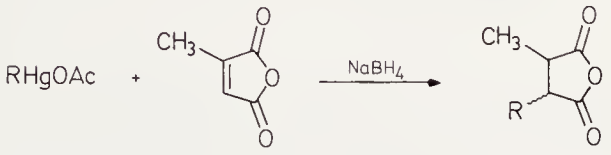
The nature of the alkene appears to be a much more important factor in determining the outcome of these addition reactions. The following relative reactivities have been determined for these radical addition reactions [21]:



$H_2C{=}CHCN > H_2C{=}CHCO_2C_2H_5$.

However, the yield of alkyl addition product does not always parallel this sequence. In general, the stronger the electron-withdrawing group is, the better the yield: $CN > CO_2R > Cl > C_6H_5 > R$. Steric effects are also quite important. The less hindered the double bond is, the higher the yield. Yields decrease slightly in going from olefins of the type $H_2C{=}CHR$ to $H_2C{=}C(CH_3)R$ and a substantial decrease is observed with olefins of the type $CH_3CH{=}CHR$. Diethyl fumarate pretty consistantly gives higher yields than its cis isomer diethyl maleate.

The regio- and stereochemistry of the resulting products has been closely examined in the case of methyl maleic anhydride. Addition to the less hindered end of the double bond occurs to the extent of >97% (Eq. 14) [22]. Cis/trans mixtures are obtained, with the proportion of cis isomer increasing as the



(14)

steric bulk of the alkyl group is increased [R (% cis): CH_3 (43), n-C_6H_{13} (62), c-C_6H_{11} (89), t-C_4H_9 (92)] [9].

These reactions appear to proceed by the following free radical chain mechanism (Scheme 7.1). The most serious side reaction is generally reduction of the alkylmercurial to the corresponding alkane.

Scheme 7.1

$$RHgX + NaBH_4 \longrightarrow RHgH$$

$$RHgH \longrightarrow R\cdot + Hg + H\cdot$$

$$R\cdot + H_2C{=}CHX \longrightarrow RCH_2\dot{C}HX$$

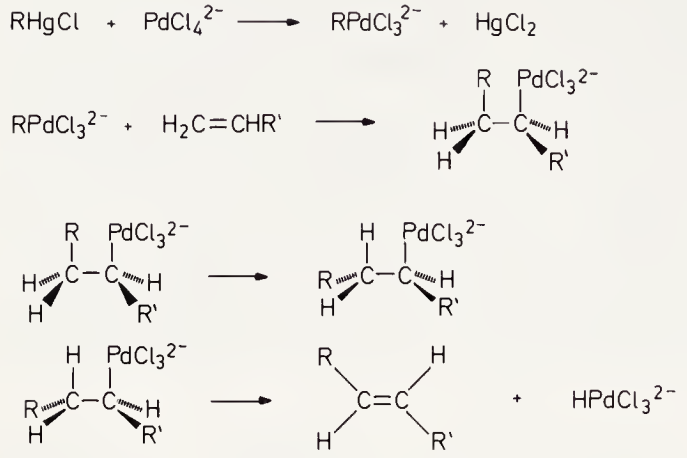
$$RCH_2\dot{C}HX + RHgH \longrightarrow RCH_2CH_2X + Hg + R\cdot$$

Nicely complementing these alkene addition reactions is a reaction first reported in 1968 by R. F. Heck. Heck observed that organopalladium compounds prepared by transmetallation of organomercurials react with alkenes to afford vinyl hydrogen substitution products (Eq. 15) [23]. Table 7.2 summarizes the large number of examples of this reaction reported to date.

$$RHgCl + H_2C{=}CHR' \xrightarrow{Li_2PdCl_4} RCH{=}CHR' \qquad (15)$$

The Heck reaction apparently proceeds as follows (Scheme 7.2). Organomercurials readily undergo transmetallation with a variety of palladium(II) salts. Palladium acetate, and palladium chloride plus lithium chloride (to help solubilize the polymeric palladium chloride) are the most widely used salts. Although more expensive, palladium acetate is perhaps to be preferred, since it generally gives slightly higher yields and is less prone to give rearranged products (compare entries 32 and 41 in Table 7.2). Evidence for the intermediacy of organopalladium compounds has been obtained by actually iso-

Scheme 7.2



lating such compounds in certain cases or by isolating their carbonylation products (see Chap. VIII). Dimerization is also a common side reaction typical of organopalladium compounds. These same organopalladium compounds can also be prepared by oxidative addition of organic halides to zerovalent palladium, thus providing a useful alternative approach to the Heck reaction. Though often more convenient, this approach requires much higher temperatures which can be a disadvantage at times. Organomercurials bearing β-hydrogens cannot be employed in these reactions, because of the ease with which the corresponding alkylpalladium compounds readily undergo cis β-hydride elimination.

The intermediate organopalladium compound generated in the initial transmetallation step then adds in a cis manner to the olefin double bond. Cis adducts can actually be isolated in certain systems to be discussed later. Addition occurs primarily so as to place the organic moiety on the less hindered end of the double bond, although significant amounts of products from internal addition to terminal double bonds are sometimes observed (see Table 7.2, entries 37–39, 76, 88, 89 and 130). Methyl palladium acetate has been found to be more selective for the less hindered end of a terminal double bond than phenylpalladium acetate [25]. In fact, Heck reactions with the former reagent are limited to terminal monosubstituted olefins. In the case of unsymmetrical internal olefins bearing ester, acetoxy and aryl groups, addition occurs predominantly to the olefinic carbon further removed from the functional group (entries 16, 17, 36, 56–60, 91, 157, 165). With internal vinyl ethers and benzofurans, the organic moiety adds primarily to the carbon bearing the oxygen.

Once the initial organopalladium species has added to the olefin, a new organopalladium intermediate containing β-hydrogens is generated. As noted earlier, such compounds are quite unstable and undergo facile cis β-hydride elimination. In the reactions of terminal olefins, both cis and trans products can ensue. In general, the more stable trans isomer is obtained, but mixtures are common (entries 27, 37, 45, 49, 50, 54, 72, 76, 78, 130). In those intermediate addition compounds in which β-hydride elimination

Table 7.2. Organopalladium Substitution Reactions of Alkenes

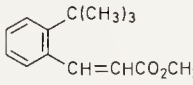
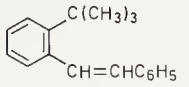
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
1	CH_3HgCl	$H_2C{=}CHCO_2CH_3$	*trans*-$CH_3CH{=}CHCO_2CH_3$	16	23
2		$H_2C{=}CHC_6H_5$	*trans*-$CH_3CH{=}CHC_6H_5$	75	23
3	CH_3HgOAc	$H_2C{=}CHCO_2CH_3$	*trans*-$CH_3CH{=}CHCO_2CH_3$	84	24
4		$H_2C{=}CHC_6H_5$	*trans*-$CH_3CH{=}CHC_6H_5$	39	25
5		$H_2C{=}C(CH_3)C_6H_5$	$CH_3CH_2\overset{CH_2}{\overset{\|\|}{C}}C_6H_5$	78	24
6	$(CH_3)_3CCH_2HgOAc$	$H_2C{=}CHCO_2CH_3$	*trans*-$(CH_3)_3CCH_2CH{=}CHCO_2CH_3$	94	24
7	$C_6H_5\overset{CH_3}{\overset{\|}{\underset{CH_3}{\underset{\|}{C}}}}CH_2HgOAc$		*trans*-$C_6H_5\overset{CH_3}{\overset{\|}{\underset{CH_3}{\underset{\|}{C}}}}CH_2CH{=}CHCO_2CH_3$	41	24
			+		
			trans 	19	
8		$H_2C{=}CHC_6H_5$	*trans* 	50	24
			+		
			$AcOCH{=}CHC_6H_5$	46	
9	$C_6H_5CH_2HgOAc$	$H_2C{=}CHCO_2CH_3$	*trans*-$C_6H_5CH_2CH{=}CHCO_2CH_3$	60	24
			+		
			$C_6H_5CH_2OAc$	10	
10	CH_3O_2CHgCl	$H_2C{=}CH_2$	$CH_3O_2CCH{=}CH_2$	50	23
11		$H_2C{=}CHCH_3$	*trans*-$CH_3O_2CCH{=}CHCH_3$	16	23
12	$CH_3O_2CHgOAc$	$H_2C{=}CHC_6H_5$	*trans*-$CH_3O_2CCH{=}CHC_6H_5$	33	23
13		$H_2C{=}CH(CH_2)_3CH_3$	*trans*-$CH_3O_2CCH{=}CH(CH_2)_3CH_3$	30	25
			+		
			$CH_3O_2CCH_2CH{=}CH(CH_2)_2CH_3$	43	
14		$H_2C{=}CHOAc$	*trans*-$CH_3O_2CCH{=}CHOAc$	10	26
15		$H_2C{=}C(CH_3)C_6H_5$	$CH_3O_2CCH_2\overset{CH_2}{\overset{\|\|}{C}}C_6H_5$	83	25
16		*trans*-$CH_3CH{=}CHC_6H_5$	*E*-$CH_3O_2C\overset{CH_3}{\overset{\|}{C}}{=}CHC_6H_5$	80	25
17		*cis*-$CH_3CH{=}CHC_6H_5$	*Z*-$CH_3O_2C\overset{CH_3}{\overset{\|}{C}}{=}CHC_6H_5$	44	25

Table 7.2. (continued)

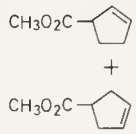
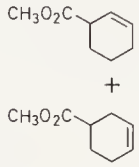
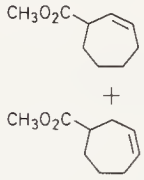
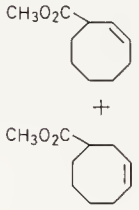
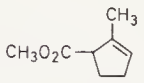
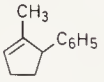
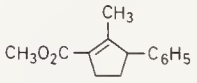
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
18				53 25	27
19				8 7	27
20				48 15	27
21				24 29	27
22				76	27
23				20	27
24	$C_2H_5O_2CHgOAc$	$H_2C{=}CH_2$	$C_2H_5O_2CCH{=}CH_2$	50	23
25		$H_2C{=}CHC_6H_5$	*trans*-$C_2H_5O_2CCH{=}CHC_6H_5$	13	23
26	$(C_6H_5)_2Hg$	$H_2C{=}CH_2$	$C_6H_5CH{=}CH_2$	63	23
27		$H_2C{=}CHCH_3$	*trans*-$C_6H_5CH{=}CHCH_3$ + *cis*-$C_6H_5CH{=}CHCH_3$	49 10	23
28		$H_2C{=}CHCHO$	*trans*-$C_6H_5CH{=}CHCHO$	60	23
29		$H_2C{=}CHCOCH_3$	*trans*-$C_6H_5CH{=}CHCOCH_3$	64	23
30		$H_2C{=}CHCO_2CH_3$	*trans*-$C_6H_5CH{=}CHCO_2CH_3$	88	23
31	C_6H_5HgCl	$H_2C{=}CH(CH_2)_2Cl$	*trans*-$C_6H_5CH{=}CH(CH_2)_2Cl$	36	27

Table 7.2. (continued)

Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
32		$H_2C{=}CHCH_2C_6H_5$	$C_6H_5CH{=}CHCH_2C_6H_5$ + $C_6H_5\overset{CH_3}{\overset{\vert}{C}}{=}CHC_6H_5$	7 20	23
33		$H_2C{=}CHCO_2CH_3$	*trans*-$C_6H_5CH{=}CHCO_2CH_3$	53	23
34		$H_2C{=}CHCO_2C_2H_5$	*trans*-$C_6H_5CH{=}CHCO_2C_2H_5$	30	23
35		$H_2C{=}\overset{OH}{\overset{\vert}{C}}HC(CH_3)_2$	$C_6H_5CH{=}\overset{OH}{\overset{\vert}{C}}HC(CH_3)_2$	83	28
36		$CH_3CH{=}CHC_6H_5$	$C_6H_5\overset{CH_3}{\overset{\vert}{C}}{=}CHC_6H_5$	21	23
37	C_6H_5HgOAc	$H_2C{=}CHCH_3$ (in CH_3CN)	*trans*-$C_6H_5CH{=}CHCH_3$ + *cis*-$C_6H_5CH{=}CHCH_3$ + $C_6H_5CH_2CH{=}CH_2$ + $H_2C{=}\overset{C_6H_5}{\overset{\vert}{C}}CH_3$	57 5 12 26	27
38		$H_2C{=}CH(CH_2)_3CH_3$	$C_6H_5CH{=}CH(CH_2)_3CH_3$ + $C_6H_5CH_2CH{=}CH(CH_2)_2CH_3$ + $H_2C{=}\overset{C_6H_5}{\overset{\vert}{C}}(CH_2)_3CH_3$	47 7 18	27
39		$H_2C{=}CH(CH_2)_3OH$	$C_6H_5CH{=}CH(CH_2)_3OH$ + $H_2C{=}\overset{C_6H_5}{\overset{\vert}{C}}(CH_2)_3OH$	28 18	27
40		$H_2C{=}CHCH_2\overset{OH}{\overset{\vert}{C}}HCH_3$	$C_6H_5CH{=}CHCH_2\overset{OH}{\overset{\vert}{C}}HCH_3$	59	27
41		$H_2C{=}CHCH_2C_6H_5$	$C_6H_5CH{=}CHCH_2C_6H_5$	73	23
42		$H_2C{=}CHCH_2CO_2CH_3$	$C_6H_5CH{=}CHCH_2CO_2CH_3$	54	27
43		$H_2C{=}CHCH_2CN$	$C_6H_5CH{=}CHCH_2CN$ + $AcOCH{=}CHCN$	45 55	27
44		$H_2C{=}CHCH_2OAc$	$C_6H_5CH{=}CHCH_2OAc$	63	23
45		$H_2C{=}CHCH(OAc)_2$	*trans*-$C_6H_5CH{=}CHCH(OAc)_2$ + *cis*-$C_6H_5CH{=}CHCH(OAc)_2$	46 6	26

Table 7.2. (continued)

Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
46		$H_2C{=}CHC_6H_5$	*trans*-$C_6H_5CH{=}CHC_6H_5$	78	23
47		$H_2C{=}CHCO_2CH_3$	*trans*-$C_6H_5CH{=}CHCO_2CH_3$	84	27
48		$H_2C{=}CHCHO$	*trans*-$C_6H_5CH{=}CHCHO$	85	27
49		$H_2C{=}CHCN$	*trans*-$C_6H_5CH{=}CHCN$	26	27
			+		
			cis-$C_6H_5CH{=}CHCN$	17	
50		$H_2C{=}CHOAc$	*trans*-$C_6H_5CH{=}CHOAc$	74	26
			+		
			cis-$C_6H_5CH{=}CHOAc$	17	
			+		
			$C_6H_5CH{=}CH_2$	5	
51		$H_2C{=}CHO_2CC_2H_5$	$C_6H_5CH{=}CHO_2CC_2H_5$	60	26
52		$H_2C{=}C(CH_3)CO_2CH_3$	$C_6H_5CH_2C(=CH_2)CO_2CH_3$	72	25
			+		
			E-$C_6H_5CH{=}C(CH_3)CO_2CH_3$	28	
53		$H_2C{=}C(CH_3)C_6H_5$	*E*-$C_6H_5CH{=}C(CH_3)C_6H_5$	55	25
			+		
			$C_6H_5CH_2C(=CH_2)C_6H_5$	41	
54		$H_2C{=}C(OAc)CH_3$	*trans*-$C_6H_5CH{=}C(OAc)CH_3$	40	26
			+		
			cis-$C_6H_5CH{=}C(OAc)CH_3$	11	
			+		
			$C_6H_5CH_2C(OAc){=}CH_2$	40	
55		*trans*-$C_2H_5CH{=}CHC_2H_5$	$C_2H_5CH(C_6H_5)CH{=}CHCH_3$	48	27
			+		
			$C_2H_5C(C_6H_5){=}CHC_2H_5$	30	
56		*trans*-$CH_3CH{=}CHCO_2CH_3$	*E*-$C_6H_5C(CH_3){=}CHCO_2CH_3$	95	25
57		*trans*-$CH_3CH{=}CHC_6H_5$	*E*-$C_6H_5C(CH_3){=}CHC_6H_5$	98	25

Table 7.2. (continued)

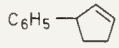
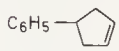
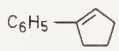
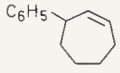
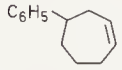
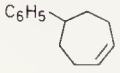
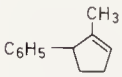
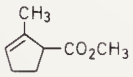
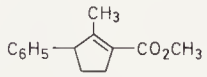
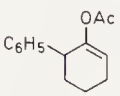
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
58		*cis*-$CH_3CH{=}CHC_6H_5$	*Z*-$C_6H_5C(CH_3){=}CHC_6H_5$	55	25
			+		
			E-$C_6H_5C(CH_3){=}CHC_6H_5$	19	
			+		
			$H_2C{=}CCH_2C_6H_5$ (C_6H_5)	9	
59		70% *cis*-$CH_3CH{=}CHOAc$	*cis*-$C_6H_5C(CH_3){=}CHOAc$	40	26
			+		
			trans-$C_6H_5C(CH_3){=}CHOAc$	19	
60		85% *trans*-$CH_3CH{=}CHOAc$	*trans*-$C_6H_5C(CH_3){=}CHOAc$	36	26
			+		
			cis-$C_6H_5C(CH_3){=}CHOAc$	9	
61		86% *trans*-$C_6H_5CH{=}CHOAc$	*trans*-$C_6H_5CH{=}CHC_6H_5$	22	26
62				47	27
			+		
				29	
			+		
				5	
63				29	27
			+		
				21	
			+		
				10	
64				83	27
65				62	27
66				64	26

Table 7.2. (continued)

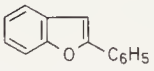
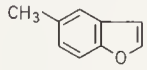
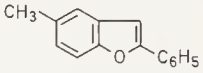
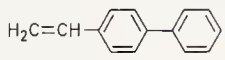
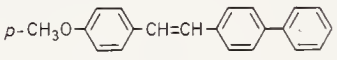
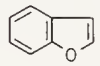
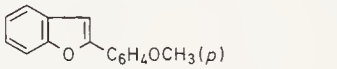
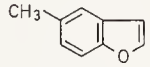
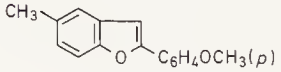
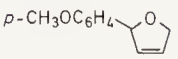
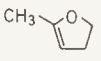
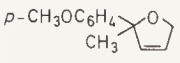
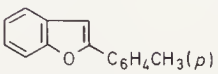
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
67				77	29
68				75	29
69	*p*-$(C_2H_5)_2NC_6H_4HgCl$	$H_2C{=}CHCO_2CH_3$	*trans*-*p*-$(C_2H_5)_2NC_6H_4CH{=}CHCO_2CH_3$	22	23
70	*p*-$AcNHC_6H_4HgCl$		*trans*-*p*-$AcNHC_6H_4CH{=}CHCO_2CH_3$	10	23
71	*o*-HOC_6H_4HgCl		*trans*-*o*-$HOC_6H_4CH{=}CHCO_2CH_3$	4	23
72	*p*-$CH_3OC_6H_4HgCl$	$H_2C{=}CHCH_3$	*trans*-*p*-$CH_3OC_6H_4CH{=}CHCH_3$ + *cis*-*p*-$CH_3OC_6H_4CH{=}CHCH_3$	26 6	23
73				11	23
74				71	29
75				66	29
76	*p*-$CH_3OC_6H_4HgOAc$	$H_2C{=}CHCH_3$	*trans*-*p*-$CH_3OC_6H_4CH{=}CHCH_3$ + *cis*-*p*-$CH_3OC_6H_4CH{=}CHCH_3$ + $H_2C{=}C(C_6H_4OCH_3(p))-CH_3$ + *p*-$CH_3OC_6H_4CH_2CH{=}CH_2$	31 10 18 7	25
77		$H_2C{=}CHCH(OAc)_2$	*p*-$CH_3OC_6H_4CH{=}CHCH(OAc)_2$	6	26
78		$H_2C{=}CHOAc$	*trans*-$CH_3OC_6H_4CH{=}CHOAc$ + *cis*-$CH_3OC_6H_4CH{=}CHOAc$	54 13	26
79				80	30
80				55	30
81	*p*-$CH_3C_6H_4HgCl$	$H_2C{=}CHC_6H_5$	*p*-$CH_3C_6H_4CH{=}CHC_6H_5$	48	23
82				79	29

Table 7.2. (continued)

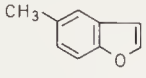
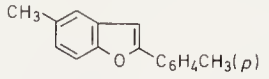
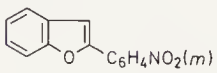
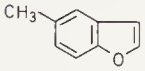
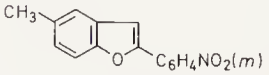
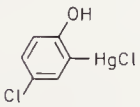
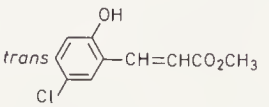
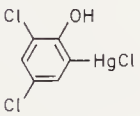
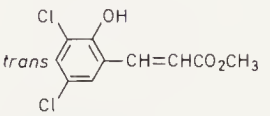
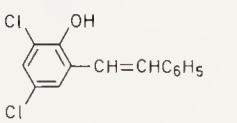
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
83				72	29
84	p-$(CH_3)_2CHC_6H_4HgCl$	$H_2C{=}CHC_6H_5$	p-$(CH_3)_2CHC_6H_4CH{=}CHC_6H_5$	42	23
85	m-$OCHC_6H_4HgCl$		m-$OCHC_6H_4CH{=}CHC_6H_5$	38	23
86	m-$HO_2CC_6H_4HgCl$	$H_2C{=}CHCO_2CH_3$ (in CH_3OH)	*trans*-m-$CH_3O_2CC_6H_4CH{=}CHCO_2CH_3$	54	23
87	p-$HO_2CC_6H_4HgCl$	$H_2C{=}CHC_6H_5$ (in CH_3OH)	p-$CH_3O_2CC_6H_4CH{=}CHC_6H_5$	26	23
88	p-$CH_3O_2CC_6H_4HgCl$	$H_2C{=}CHCH_3$	*trans*-p-$CH_3O_2CC_6H_4CH{=}CHCH_3$ + $H_2C{=}C(C_6H_4CO_2CH_3(p))CH_3$	81 18	27
89	p-$CH_3O_2CC_6H_4HgOAc$		*trans*-p-$CH_3O_2CC_6H_4CH{=}CHCH_3$ + $H_2C{=}C(C_6H_4CO_2CH_3(p))CH_3$	55 22	27
90	m-$NO_2C_6H_4HgCl$	$H_2C{=}CHCO_2CH_3$	*trans*-m-$NO_2C_6H_4CH{=}CHCO_2CH_3$	24	23
91		*trans*-p-$CH_3CH{=}CHC_6H_4OCH_3$	$CH_3C(C_6H_4NO_2(m)){=}CHC_6H_4OCH_3(p)$	7	23
92				70	29
93				60	29
94	2,4,6-$(CH_3)_3C_6H_2HgOAc$	$H_2C{=}CHC_6H_5$	*trans*-2,4,6-$(CH_3)_3C_6H_2CH{=}CHC_6H_5$	40	25
95	$(CH_3)_5C_6HgCl$		$(CH_3)_5C_6CH{=}CHC_6H_5$	42	23
96	3,4-$Cl_2C_6H_3HgCl$	$H_2C{=}CHCO_2CH_3$	*trans*-3,4-$Cl_2C_6H_3CH{=}CHCO_2CH_3$	45	23
97				13	23
98				11	23
99		$H_2C{=}CHC_6H_5$		15	23

Table 7.2. (continued)

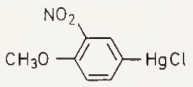
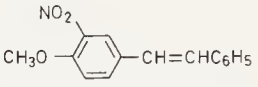
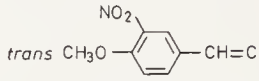
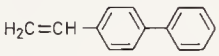
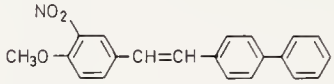
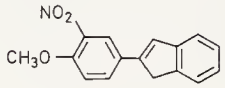
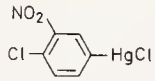
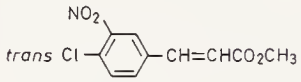
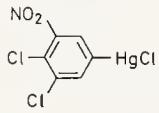
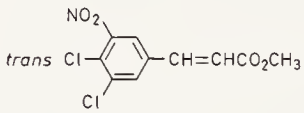
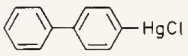
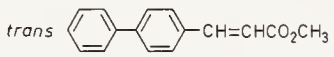
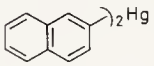
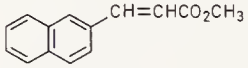
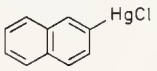
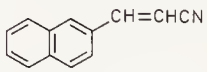
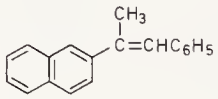
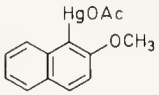
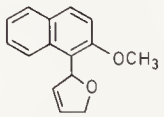
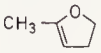
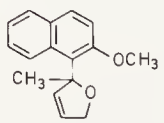
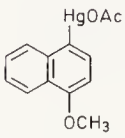
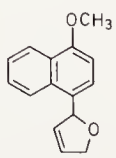
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
100				18	23
101		$H_2C{=}CHCO_2CH_3$		40	23
102				17	23
103				10	23
104		$H_2C{=}CHCO_2CH_3$		3	23
105				19	23
106				2	23
107				35	23
108		$H_2C{=}CHCN$		30	23
109		$H_2C{=}CHCH_2C_6H_5$		18	23
110				77	30
111				27	30
112				90	30

Table 7.2. (continued)

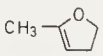
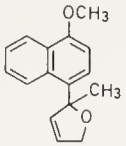
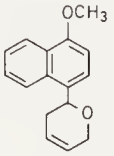
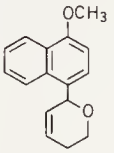
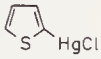
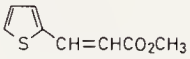
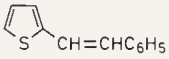
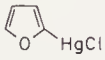
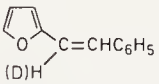
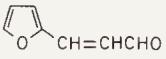
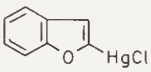
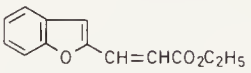
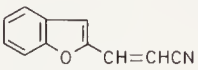
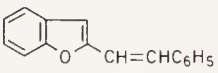
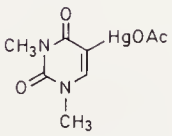
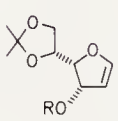
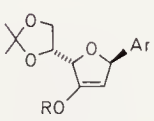
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
113				54	30
114			 + 	75 15	30
115		$H_2C{=}CHCO_2CH_3$		36	23
116		$H_2C{=}CHC_6H_5$		16	23
117		$(D_2)H_2C{=}CHC_6H_5$		—	31
118		$H_2C{=}CHCHO$		—	31
119		$H_2C{=}CHCO_2C_2H_5$		—	32
120		$H_2C{=}CHCN$		—	32
121		$H_2C{=}CHC_6H_5$		—	32
122	 (ArHgOAc)	 	 	86	30
123		$R = CH_3OCH_2O$		56	33

Table 7.2. (continued)

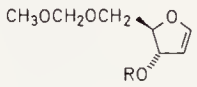
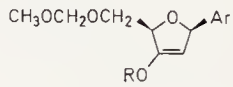
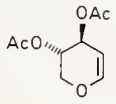
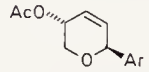
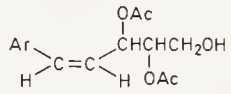
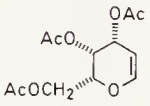
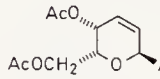
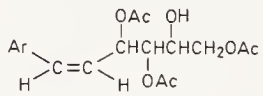
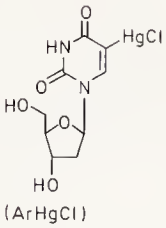
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
124		R = (*i*-Pr)$_3$Si		88	33
					
125		R = CH_3OCH_2		71	33
126		R = (*i*-Pr)$_3$Si		92	33
127			 + 	66 24	34, 35
128			 + 	20 32	34
129			 + 	20 73	34
130	 (ArHgCl)	$H_2C{=}CHCH_3$ (in CH_3OH)	*trans*-$ArCH{=}CHCH_3$ + *cis*-$ArCH{=}CHCH_3$ + $ArC(CH_3){=}CH_2$ + $ArCH(OCH_3)CH_2CH_3$ + $ArC(CH_3)_2(OCH_3)$	11 — — — —	36
131		$H_2C{=}CHCF_3$ (in CH_3OH)	$ArCH{=}CHCF_3$	17	37
132		$H_2C{=}CHC_6H_5$	*trans*-$ArCH{=}CHC_6H_5$	55,57	38, 39

Table 7.2. (continued)

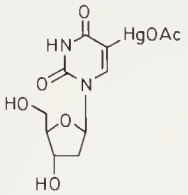
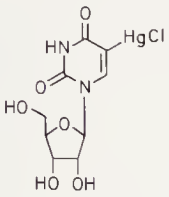
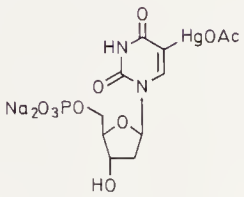
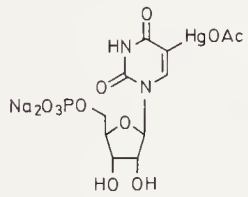
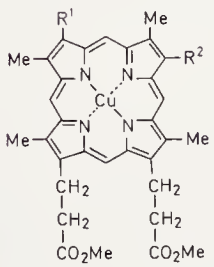
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
133		$H_2C{=}CHC_6H_4NO_2(m)$	*trans*-$ArCH{=}CHC_6H_4NO_2(m)$	45,50	38,39
134	 (ArHgOAc)	$H_2C{=}CHC_6H_5$	$ArCH{=}CHC_6H_5$	50	38
135		$H_2C{=}CHC_6H_4NH_2(m)$	$ArCH{=}CHC_6H_4NH_2(m)$	30	39
136		$H_2C{=}CHC_6H_4NO_2(m)$	$ArCH{=}CHC_6H_4NO_2(m)$	61,62	38,39
137		$H_2C{=}CHC_6H_4NO_2(p)$	$ArCH{=}CHC_6H_4NO_2(p)$	8,11	38,39
138	 (ArHgCl)	$H_2C{=}CH_2$ (in CH_3OH)	$ArCH(OCH_3)CH_3$ + $ArCH{=}CH_2$	39 —	36, 40
139		$H_2C{=}CHCO_2CH_3$	*trans*-$ArCH{=}CHCO_2CH_3$	48,57	36, 40
140		$H_2C{=}CHC_6H_5$	*trans*-$ArCH{=}CHC_6H_5$	39	36
141	 (ArHgOAc)		*trans*-$ArCH{=}CHC_6H_5$	50	39
142		$H_2C{=}CHC_6H_4N_3(m)$	*trans*-$ArCH{=}CHC_6H_4N_3(m)$	25	39
143		$H_2C{=}CHC_6H_4NO_2(m)$	*trans*-$ArCH{=}CHC_6H_4NO_2(m)$	66,69	38,39
144		$H_2C{=}CHC_6H_4NO_2(p)$	*trans*-$ArCH{=}CHC_6H_4NO_2(p)$	59	39
145	 (ArHgOAc)	$H_2C{=}CHC_6H_4NO_2(m)$	*trans*-$ArCH{=}CHC_6H_4NO_2(m)$	75,82	38, 39
146	 (ArHgCl) $R^1 = COCH_3$ $R^2 = HgCl$ $R^1 = HgCl$ $R^2 = COCH_3$	$H_2C{=}CHCO_2CH_3$	$ArCH{=}CHCO_2CH_3$ (mixture of both compounds)	76	41, 42

Table 7.2. (continued)

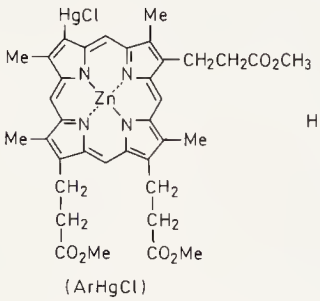
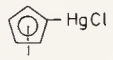
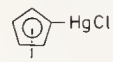
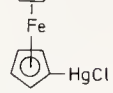
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
147	 (ArHgCl)	$H_2C{=}CHCO_2CH_3$	$ArCH{=}CHCO_2CH_3$	—	42
148		$H_2C{=}CH_2$	$Fer{-}CH{=}CH_2$	45	43
149		$H_2C{=}CHC_6H_5$	$Fer{-}CH{=}CHC_6H_5$	52	43
150	(Fer-HgCl)	$H_2C{=}CHCO_2C_2H_5$	$Fer{-}CH{=}CHCO_2C_2H_5$	58	43
151		$H_2C{=}CHCN$	$Fer{-}CH{=}CHCN$	49	43
152		$H_2C{=}CHCHO$	$Fer{-}CH{=}CHCHO$	45	43
153		$H_2C{=}CHCOCH_3$	$Fer{-}CH{=}CHCOCH_3$	46	43
154		$H_2C{=}CHCOC_6H_5$	$Fer{-}CH{=}CHCOC_6H_5$	45	43
155		$H_2C{=}C(CH_3)CO_2CH_3$	$Fer{-}CH{=}C(CH_3)CO_2CH_3$	48	43
156		$H_2C{=}C(CH_3)CH_2Cl$	$Fer{-}CH{=}C(CH_3)CH_2Cl$	21	44
157		$CH_3CH{=}CHCO_2C_2H_5$	$Fer{-}C(CH_3){=}CHCO_2C_2H_5$	52	45
158		$H_2C{=}CHC_6H_5$	$Fer(CH{=}CHC_6H_5)_2$	37	43
159		$H_2C{=}CHCO_2C_2H_5$	$Fer(CH{=}CHCO_2C_2H_5)_2$	28	43
160	$[Fer(HgCl)_2]$	$H_2C{=}CHCN$	$Fer(CH{=}CHCN)_2$	28	43
161		$H_2C{=}CHCHO$	$Fer(CH{=}CHCHO)_2$	22	43
162		$H_2C{=}CHCOCH_3$	$Fer(CH{=}CHCOCH_3)_2$	27	43
163		$H_2C{=}CHCOC_6H_5$	$Fer(CH{=}CHCOC_6H_5)_2$	25	43
164		$H_2C{=}C(CH_3)CO_2CH_3$	$Fer(CH{=}C(CH_3)CO_2CH_3)_2$	31	43
165		$CH_3CH{=}CHCO_2C_2H_5$	$Fer(C(CH_3){=}CHCO_2C_2H_5)_2$	25	43

Table 7.2. (continued)

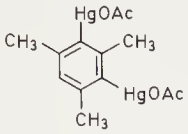
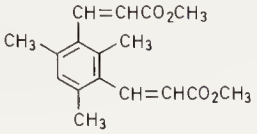
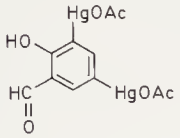
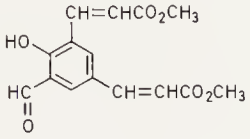
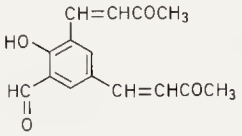
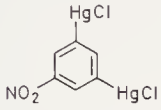
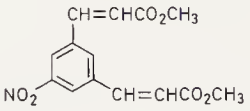
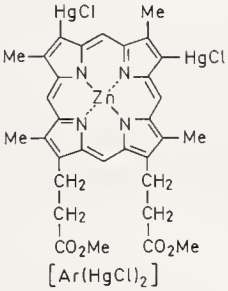
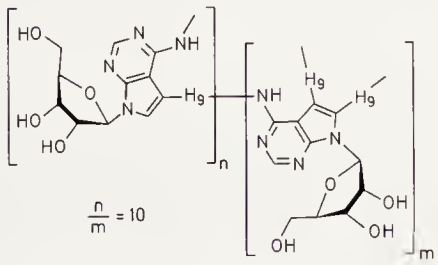
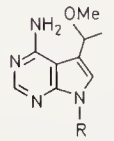
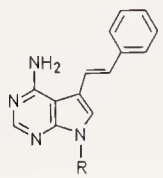
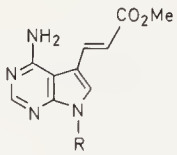
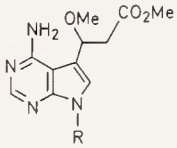
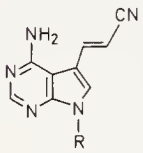
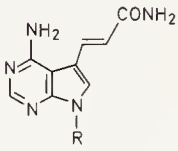
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
166		$H_2C{=}CHCO_2CH_3$		17	23
167				13	23
168		$H_2C{=}CHCOCH_3$		1	23
169		$H_2C{=}CHCO_2CH_3$		18	23
170		$H_2C{=}CH_2$	$Ar(CH{=}CH_2)_2$	low	41, 42
171		$H_2C{=}CHCO_2CH_3$	$Ar(CH{=}CHCO_2CH_3)_2$	31, 37	41, 42
172		$H_2C{=}CH_2$ (in CH_3OH)		73	46
173		$H_2C{=}CHC_6H_5$		25	46

Table 7.2. (continued)

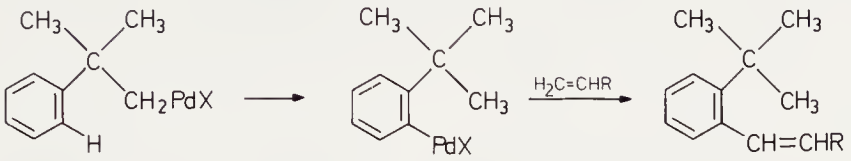
Entry	Organomercurial	Alkene	Major product(s)	% Yield	Ref.
174		$H_2C{=}CHCO_2CH_3$	 + 	57 9	46
175		$H_2C{=}CHCN$		22	46
176		$H_2C{=}CHCONH_2$		7	46

in more than one direction is possible, mixtures of products are generally observed (entries 5, 13, 15, 37, 38, 52–55, 76). In the reactions of cyclic olefins, cis elimination of the original vinyl hydrogen is impossible and products from remote β-hydride elimination predominate (entries 18–22, 62–66, 79, 80, 110–114, 122–129). The stereospecific nature of these addition and elimination reactions is best seen by comparing entries 16 and 17, and 57 and 58.

In the elimination step a palladium hydride species is apparently generated. This species can readd to the newly formed double bond in the opposite direction to form a new organopalladium species which can undergo elimination in other directions affording isomeric mixtures. Palladium hydrides or possibly the initial palladium salt itself may also be responsible for products which appear to arise by rearrangement of the initial olefin prior to vinylic hydrogen substitution (entries 32 and 109).

A number of generalities about the Heck reaction can be made. It can be run at room temperature in air in a number of different solvents, including benzene, methylene chloride, glyme, diglyme, THF, acetone, acetic acid, ethanol, methanol and acetonitrile. The latter two solvents have been most widely employed. Acetonitrile has the disadvantage of giving rise to increased amounts of addition of the organic group to the internal carbon of terminal olefins.

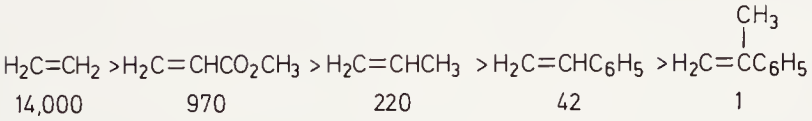
Organomercurials which can be employed include benzyl, carboalkoxy, simple aryl, polynuclear aromatic, heterocyclic, organometallic, nucleoside- and nucleotide-containing organomercurials and certain alkylmercurials. However, neither alkylmercurials containing β-hydrogens nor vinylmercurials can be employed. Dimercurials react, but tend to give low yields. In one case, rearrangement of the intermediate organopalladium species has been observed (entries 7 and 8) (Eq. 16) [24]. Benzylic mercuric acetates are

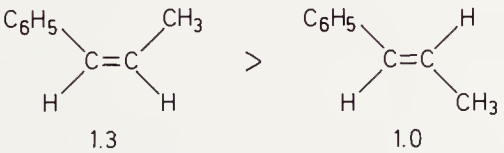


(16)

apparently easily oxidized by palladium acetate to the corresponding benzylic acetates [24]. Although steric constraints in the organomercurial appear minimal, electronic effects can be important. Electron-donating groups in arylmercurials significantly lower the yield of substitution product [23]. *p*-Anisylmercuric acetate gives more addition to the internal carbon of terminal olefins than phenylmercuric acetate, and larger amounts of cis product are also observed [25, 27]. On the other hand, carboalkoxymercurials give addition only to the terminal carbon [27]. Finally, it should be noted that a wide range of functional groups can be accommodated in the organomercurial.

The nature of the olefin is of paramount importance. Steric effects seem to outweigh electronic effects, although both are important. The less hindered the double bond is, the more reactive it will be. Electron-withdrawing groups increase both the rate of reaction, as well as the amount of addition of the organic group to the opposite end of the double bond. The following relative rates of arylation have been reported [23, 25]:





The olefins $H_2C{=}CHCN$, $H_2C{=}CHCO_2CH_3$, $H_2C{=}CHCHO$, $H_2C{=}CHC_6H_5$, $H_2C{=}CHOAc$ and $H_2C{=}CHCH_2Cl$ give practically exclusive addition of the organic moiety to the terminal carbon, while $H_2C{=}CHCH_3$, $H_2C{=}CHC_4H_9$, $H_2C{=}CHCH_2OH$ and $H_2C{=}CHCH_2OAc$ give appreciable amounts of internal addition. With allylic alcohols chelation can also become important. As seen in Table 7.2, olefins containing a wide variety of functional groups are readily accommodated in these reactions. As we will

soon see, however, allylic alcohols, esters and halides, as well as enol esters, can give rise to entirely different products.

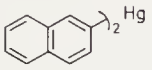
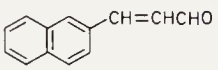
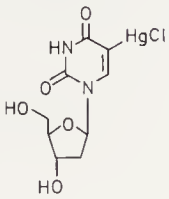
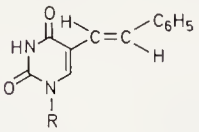
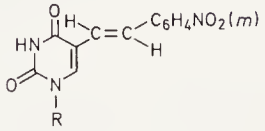
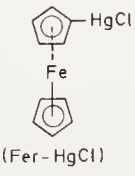
Although the Heck reaction provides a synthetic transformation unique in organic chemistry, it suffers one major disadvantage, the palladium(II) reagent is reduced to palladium metal requiring that stoichiometric amounts of the expensive palladium salt be employed. This difficulty can be circumvented by adding reagents capable of reoxidizing palladium. However, the yields are generally quite a bit lower. Table 7.3 summarizes all attempts reported to date to catalyze these vinylic hydrogen substitution reactions of organomercurials. Cupric chloride appears to be the most successful reoxidant. It is important to realize, however, that when one employs organic halides as alkylating agents in these reactions, only catalytic amounts of palladium need be used, thus realizing a major advantage over the organomercurial approach. Note in the examples cited that vinyl halides, ethers and acetates often proceed with displacement of the functional group and that enol acetates also give rise to carbonyl compounds under catalytic conditions.

The Heck reaction also provides a convenient method for the alkylation of organomercurials when the initial products are directly treated with $NaBH_4$ and hydrogen. This reaction has proven particularly valuable for the synthesis of C-5 alkylated nucleosides and nucleotides where undesired methyl

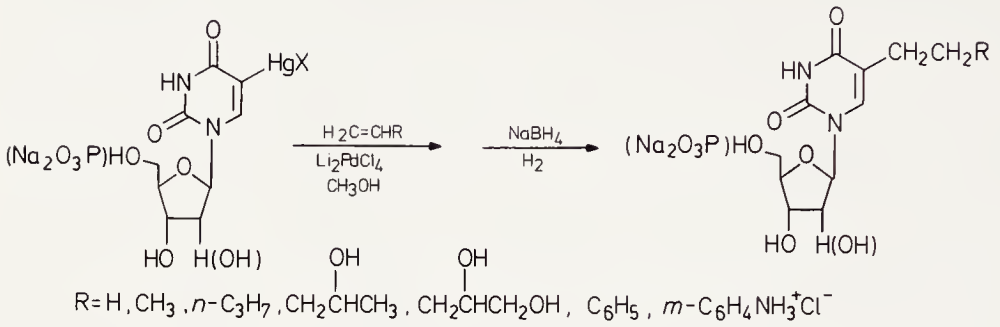
Table 7.3. Catalytic Vinylic Hydrogen Substitution of Alkenes

Organomercurial	Alkene	Catalyst	Reoxidant	Product (s)	% Yield	Ref.
$(C_6H_5)_2Hg$	$H_2C{=}CHCO_2CH_3$	$Pd(NO_3)_2$	$Fe(NO_3)_3$	*trans*-$C_6H_5CH{=}CHCO_2CH_3$	37	23
			$Hg(NO_3)_2$		37	23
C_6H_5HgCl		Li_2PdCl_4	$CuCl_2, O_2$, NaCl, HCl		60	23
			$CuCl_2$		57	23
	$H_2C{=}C(CH_3)CO_2CH_3$			$C_6H_5CH{=}C(CH_3)CO_2CH_3$	35	23
	$CH_3CH{=}CHCO_2CH_3$			$C_6H_5C(CH_3){=}CHCO_2CH_3$	24	23
	$CH_3CH{=}CHCH_2OAc$	$LiPdCl_3$		$C_6H_5C(CH_3){=}CHCH_2OAc$	15	23
	$H_2C{=}CHOC_4H_9$			*trans*-$C_6H_5CH{=}CHC_6H_5$	11	44
	$H_2C{=}CHCl$	Li_2PdCl_4			35	44
	$H_2C{=}CHOAc$			*trans*-$C_6H_5CH{=}CHC_6H_5$	34	44
				+		
				$C_6H_5CH_2CHO$	33	
				+		
				$C_6H_5CH{=}CHOAc$	30	

Table 7.3. (continued)

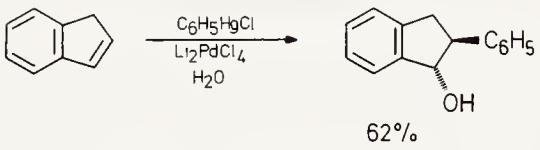
Organo-mercurial	Alkene	Catalyst	Reoxidant	Product (s)	% Yield	Ref.
	$H_2C{=}C(OAc)CH_3$			$C_6H_5CH_2COCH_3$	50	44
	$H_2C{=}C(O_2CC_6H_5)C_6H_5$			$C_6H_5CH_2C(=O)C_6H_5$	40	44
	$CH_3CH{=}CHOAc$			$C_6H_5CH{=}C(C_6H_5)CH_3$ + $CH_3CH(C_6H_5)CHO$	66 21	44
C_6H_5HgOAc	$H_2C{=}CHCH_2C_6H_5$	$Pd(OAc)_2$	$Hg(OAc)_2$	*trans*-$C_6H_5CH{=}CHCH_2C_6H_5$	8	23
	$H_2C{=}CHCH_2OC_2H_5$			$C_6H_5CH{=}CHCH_2OC_2H_5$	42	23
p-$CH_3OC_6H_4HgOAc$	$H_2C{=}CHCO_2CH_3$			*trans*-*p*-$CH_3OC_6H_4CH{=}CHCO_2CH_3$	27	23
p-$HO_2CC_6H_4HgCl$		Li_2PdCl_4	$CuCl_2$	*trans*-*p*-$HO_2CC_6H_4CH{=}CHCO_2CH_3$	20	23
	$H_2C{=}CHCHO$				8	23
	$H_2C{=}CHC_6H_5$				47	38,39
	$H_2C{=}CHC_6H_4NO_2(m)$				43,49	38,39
	$H_2C{=}CHC_6H_5$			Fer–CH=CHC_6H_5	44	43
	$H_2C{=}CHCO_2C_2H_5$			Fer–CH=CH$CO_2C_2H_5$	41	43
	$H_2C{=}C(CH_3)CO_2CH_3$			Fer–CH=C(CH_3)CO_2CH_3	38	43
	$CH_3CH{=}CHCO_2C_2H_5$			Fer–C(CH_3)=CH$CO_2C_2H_5$	36	43
	$H_2C{=}CHCOCH_3$			Fer–CH=CH$COCH_3$	31	43
	$H_2C{=}CHCOC_6H_5$			Fer–CH=CHCOC_6H_5	37	43
	$H_2C{=}CHCN$			Fer–CH=CHCN	33	43

ether side products are converted to product by hydrogenolysis (Eq. 17) [36, 39, 40].

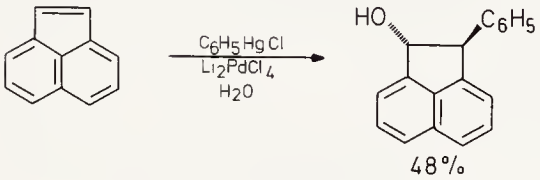


(17)

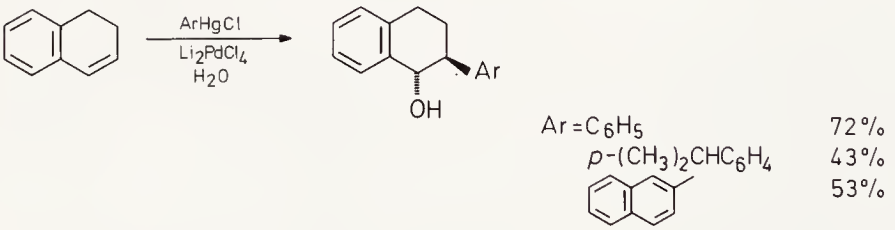
When the arylation of aromatic olefins is carried out under aqueous conditions, solvolysis products similar to the nucleoside methyl ethers are observed. While the oxyarylation of methyl styrenes tends to give a variety of organic products [45], the reaction of cyclic aryl olefins can be synthetically useful (Eqs. 18–20) [47, 48]. In fact, these reactions have recently afforded



(18)

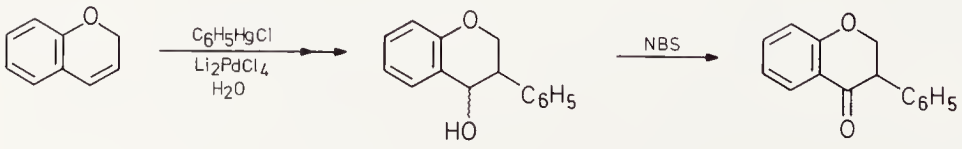


(19)

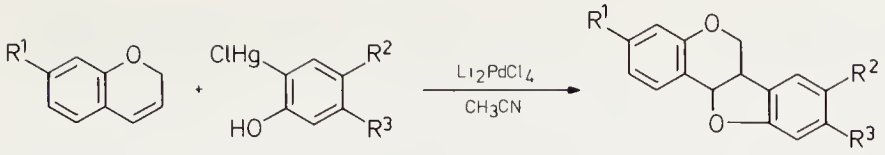


(20)

novel syntheses of ring systems common to a number of natural products (Eqs. 21–23).

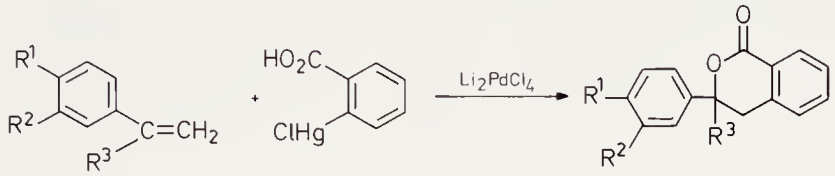


(21) [49]



(22)

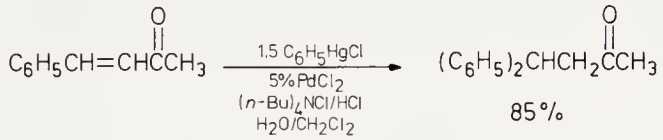
R^1	R^2	R^3	%Yield	Ref.
H	H	H	85	50
H	$-OCH_2O-$		36	50
CH_3O	H	H	54	50
CH_3O	$-OCH_2O-$		58	50
$C_6H_5CH_2O$	$-OCH_2O-$		–	51



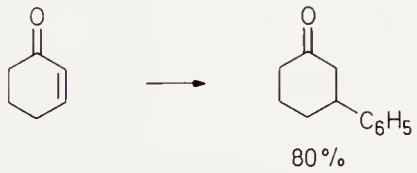
(23) [52]

R^1	R^2	R^3	%Yield
H	H	CH_3	83
CH_3O	AcO	H	60
CH_3O	CH_3O	H	50
$-OCH_2O-$		H	58

Under strongly acidic phase transfer conditions, organopalladium reactions can also be used to effect conjugate addition to enones (Eqs. 24, 25) [53]. Note that this reaction is catalytic in palladium. As one might expect,

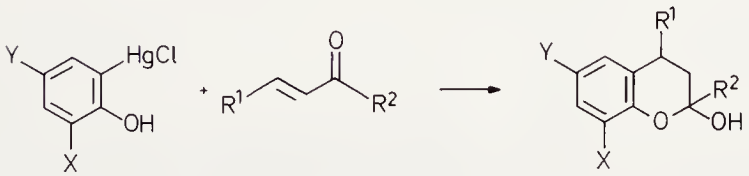


(24)



(25)

the reaction fails with β-disubstituted enones. By employing *o*-mercurated phenols in this reaction, 2-chromanols and 2-chromenes can be prepared (Eq. 26) [54].



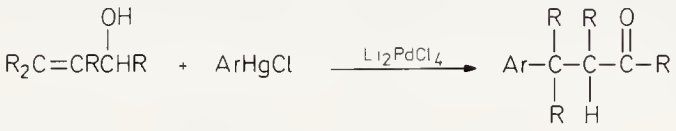
(26)

Although a wide variety of functional groups are readily tolerated in the above reactions, certain groups substantially alter the course of the reac-

tion. While the phenylation of 3-methyl-1-buten-3-ol proceeds normally (Eq. 27) [28], the arylation of primary and secondary allylic alcohols affords

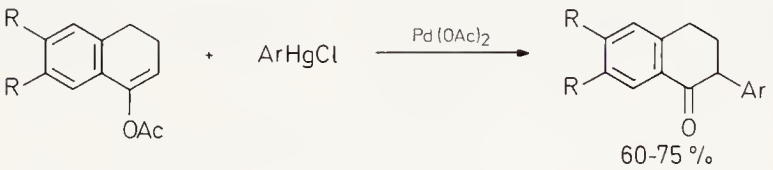
(27)

primarily β-substituted aryl carbonyl compounds (Eq. 28) [28]. This reaction has been examined on a wide variety of allylic alcohols using simple arylmercurials [28], pyrimidinylmercurials [33] and chloromercurioferrocene [43]. Unfortunately, the yields are generally too low to interest most synthetic organic chemists (10–35% are common). It appears that chelation may play an important role in this organopalladium addition reaction [27]. Obviously, palladium hydride elimination from the initial adduct is being directed preferentially towards the alcohol group, generating an enol which tautomerizes to the final carbonyl product.



(28)

While there are a number of examples where the arylation of enol esters using stoichiometric amounts of palladium proceeds as expected (see Table 7.2; entries 14, 50, 51, 54, 59, 60, 78), there are two notable exceptions. One of these has proven quite useful for the synthesis of isoflavanones (Eq. 29)

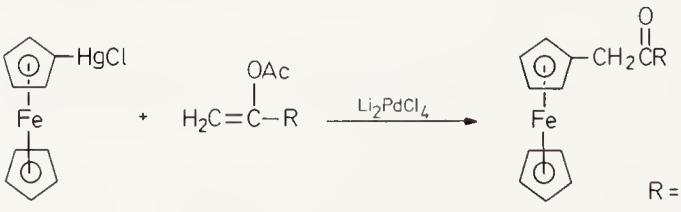


(29)

R = H, OCH_3

Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$C_6H_5C_6H_4$, p-ClC_6H_4, m-$NO_2C_6H_4$

[55]. In this reaction the isoflavanones are produced directly in the reaction and not on hydrolysis. The reaction of chloromercurioferrocene and enol esters also affords carbonyl compounds though in much lower yield (Eq. 30)

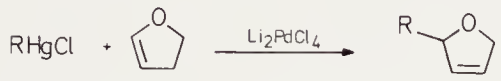


(30)

[43]. Attempts to catalyze the arylation of enol esters have generally afforded only low yields of mixtures of olefinic and carbonyl products [44] as seen

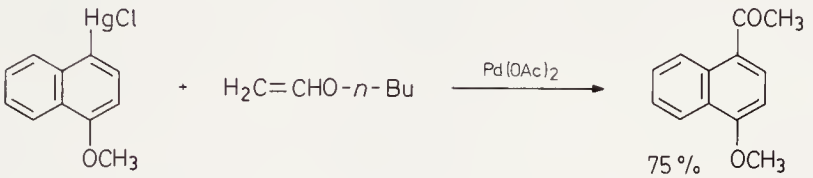
in the few examples summarized in Table 7.3. Much lower yields were reported for a number of other examples not included in that table.

The Heck reaction of vinyl ethers has received little attention. However, benzofurans undergo facile arylation [29] in the two position and cyclic vinyl ethers undergo regiospecific alpha substitution with migration of the double bond (Eq. 31) [30, 33–35]. The only stoichiometric reaction of an acyclic



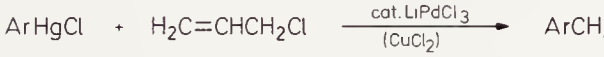
(31)

vinyl ether so far reported is the following (Eq. 32) [30]. This reaction appears to have potential as a method for acylation of organomercurials. Attempts to catalyze this type of coupling have led to a low yield of a mixture of products [44].

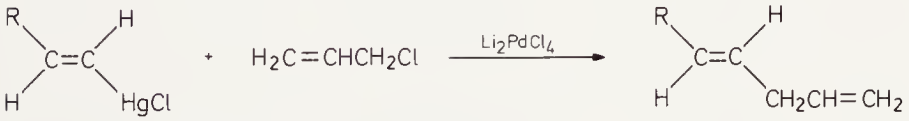


(32)

While the reaction of arylmercurials, allylic acetates and halides, and the corresponding palladium(II) salts occasionally gives vinyl hydrogen substitution products (see Table 7.2, entries 44, 75, 77, 156), aryl- and vinylmercurials more commonly afford allylation products in such reactions (Eqs. 33, 34). Table 7.4 summarizes the literature results reported on these reactions. Allylation apparently proceeds as follows (Scheme 7.3). As the

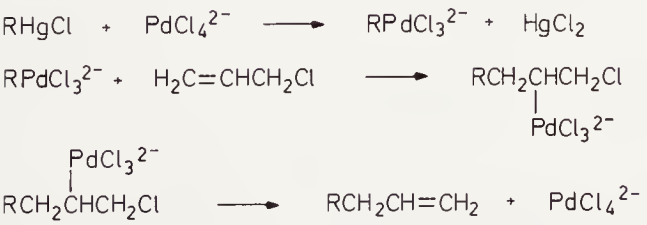


(33) [56]



(34) [57]

Scheme 7.3



mechanism suggests, substitution occurs in an S_N2' fashion and the reactions have been found to be catalytic in the palladium(II) reagent. However, 10–30% palladium was required in the arylation reactions or else 10–30% $CuCl_2$ was added to reoxidize the palladium. In the reactions of vinyl-

Table 7.4. Allylation of Organomercurials

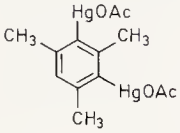
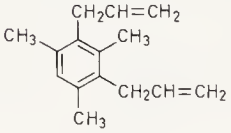
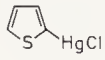
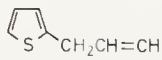
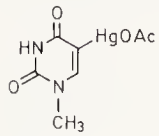
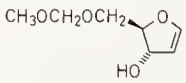
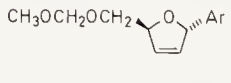
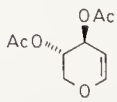
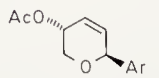
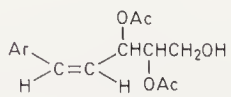
Organomercurial	Allylic substrate	Product(s)	% Yield	Ref.
C_6H_5HgCl	$H_2C{=}CHCH_2Cl$	$C_6H_5CH_2CH{=}CH_2$	61	56
	$H_2C{=}CHCHClCH_3$	$C_6H_5CH_2CH{=}CHCH_3$	50	56
	$H_2C{=}C(CH_3)CH_2Cl$	$C_6H_5CH_2C(CH_3){=}CH_2$	74	56
	$H_2C{=}CClCH_2Cl$	$C_6H_5CH_2CCl{=}CH_2$	68	56
	$CH_3CH{=}CHCH_2Cl$	$C_6H_5C(CH_3){=}CHCH_3$ + $C_6H_5CH{=}CHCH_2CH_3$ + $C_6H_5CH_2CH{=}CHCH_3$	34 29 15	56
$4\text{-}(C_2H_5)_2NC_6H_4HgCl$	$H_2C{=}CHCH_2Cl$	$4\text{-}(C_2H_5)_2NC_6H_4CH_2CH{=}CH_2$	33	56
$4\text{-}CH_3OC_6H_4HgCl$		$4\text{-}CH_3OC_6H_4CH_2CH{=}CH_2$	47	56
	$H_2C{=}C(CH_3)CH_2Cl$	$4\text{-}CH_3OC_6H_4CH_2C(CH_3){=}CH_2$	35	56
$3,4\text{-}Cl_2C_6H_3HgCl$	$H_2C{=}CHCH_2Cl$	$3,4\text{-}Cl_2C_6H_3CH_2CH{=}CH_2$	28	56
			49	44
$3\text{-}OCHC_6H_4HgCl$		$3\text{-}OCHC_6H_4CH_2CH{=}CH_2$	43	56
$3\text{-}NO_2C_6H_4HgCl$	$H_2C{=}CClCH_2Cl$	$3\text{-}NO_2C_6H_4CH_2CCl{=}CH_2$	87	56
	$H_2C{=}CHCH_2Cl$		12	56
 (ArHgOAc)			78	33
		 + 	20 32	34

Table 7.4. (continued)

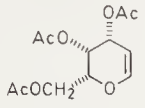
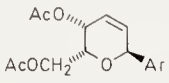
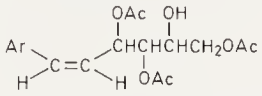
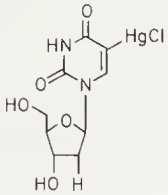
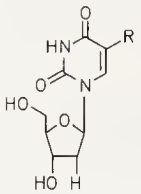
Organomercurial	Allylic substrate	Product(s)	% Yield	Ref.
		 + 	20 73	34
	$H_2C{=}CHCH_2Cl$	 R= $CH_2CH{=}CH_2$	64-92	58,59
	$H_2C{=}CHCH_2OH$	$CH_2CH{=}CH_2$	64-92	58
	$H_2C{=}C(CH_3)CH_2Cl$	$CH_2C(CH_3){=}CH_2$	—	58
	$H_2C{=}CHCH(Cl)CH_3$	*trans*-$CH_2CH{=}CHCH_3$ + *cis*-$CH_2CH{=}CHCH_3$ + $CH(CH_3)CH{=}CH_2$	43 21 7	58
	$H_2C{=}CHCH(OAc)CH_3$	*cis*- + *trans*-$CH_2CH{=}CHCH_3$	24	58
	$H_2C{=}CHC(OH)(CH_3)_2$	$CH(OCH_3)CH_2C(OH)(CH_3)_2$ + $CH_2CH{=}C(CH_3)_2$	16 5	58
	$H_2C{=}CHC(OAc)(CH_3)_2$	$CH_2CH{=}C(CH_3)_2$ + $CH_2CH_2C(OH)(CH_3)_2$	15 10	58
	$H_2C{=}CHCH(Cl)CH_2CH_3$	*trans*-$CH_2CH{=}CHCH_2CH_3$	50	58
	$H_2C{=}CHCH(Cl)CH(CH_3)_2$	*trans*-$CH_2CH{=}CHCH(CH_3)_2$	—	58
	$H_2C{=}CHCH(OH)CH(CH_3)_2$	$CH_2CH_2COCH(CH_3)_2$ + *trans*-$CH_2CH{=}CHCH(CH_3)_2$	24 18	58

Table 7.4. (continued)

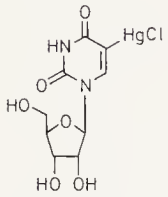
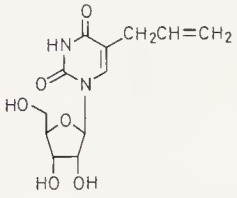
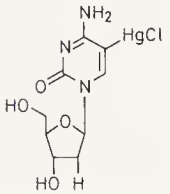
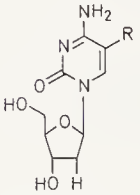
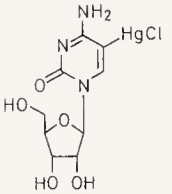
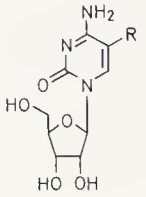
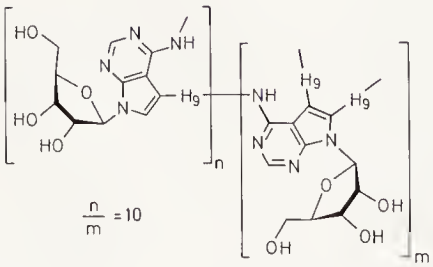
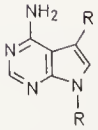
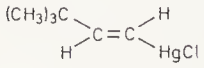
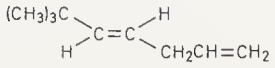
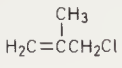
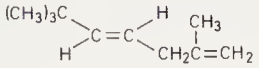
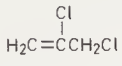
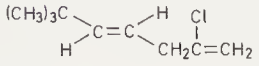
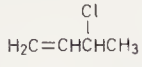
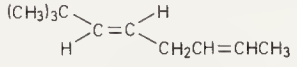
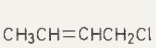
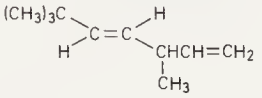
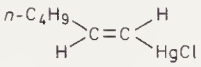
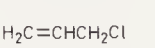
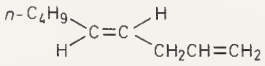
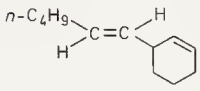
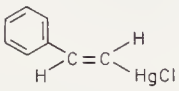
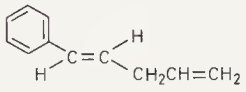
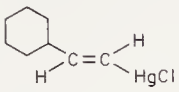
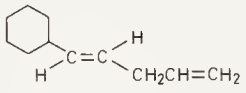
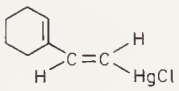
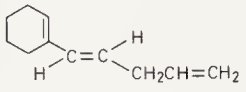
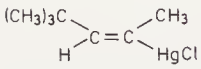
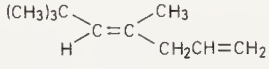
Organomercurial	Allylic substrate	Product(s)	% Yield	Ref.
	$H_2C{=}CHCH(OAc)CH(CH_3)_2$	*trans*-$CH{=}CHCH{=}C(CH_3)_2$ + *trans*-$CH_2CH{=}CHCH(CH_3)_2$	13 5	58
	$H_2C{=}CHCH(Cl)CH_2CH_2CN$	*cis*- + *trans*-$CH_2CH{=}CHCH_2CH_2CN$	38	58
	$H_2C{=}CHCH(OAc)CH_2CH_2CN$	*cis*- + *trans*-$CH_2CH{=}CHCH_2CH_2CN$	16	58
	$H_2C{=}CHCH_2Cl$		78-84	40,59
	$H_2C{=}CHCH_2Cl$	 R= $CH_2CH{=}CH_2$	65-80	59
	$H_2C{=}CHCH(Cl)CH_2CH_3$	*trans*-$CH_2CH{=}CHCH_2CH_3$	44	58
	$H_2C{=}CHCH_2Cl$	 R= $CH_2CH{=}CH_2$	70	58,59
	$H_2C{=}CHCH(Cl)CH_3$	*cis*-+*trans*-$CH_2CH{=}CHCH_3$ + $CH(CH_3)CH{=}CH_2$	72 4.5	58
				
	$H_2C{=}CHCH_2Cl$	 R= $CH_2CH{=}CH_2$	low	46
	$H_2C{=}CHCH(Cl)CH_3$	$CH_2CH{=}CHCH_3$	20	46
	$H_2C{=}CHCH_2Cl$		96	57

Table 7.4. (continued)

Organomercurial	Allylic substrate	Product(s)	% Yield	Ref.
			46	57
			28	57
			49	57
			32	57
			71	57
			39	57
			80	57
			73	57
			100	57
			99	57

mercurials, the reaction is again catalytic in palladium, but a full equivalent was often necessary to obtain satisfactory yields. As seen in earlier organopalladium reactions, the yields drop off sharply when the olefin becomes more hindered. In such cases isomerization of the allylic halide becomes an important side reaction and mixtures of products can arise.

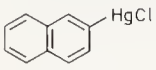
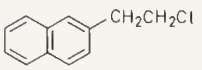
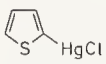
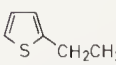
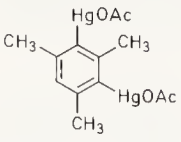
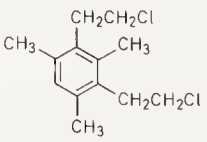
In the reaction of phenylmercuric chloride, $LiPdCl_3$ and substituted acrylyl chlorides, it appears that addition-elimination generates a ketene (Eq. 35) [60]. However, the yields of ketene-derived products are too low to make this a useful synthetic procedure.

$$C_6H_5HgCl + RCH{=}C(R)C(=O)Cl \xrightarrow{LiPdCl_3} C_6H_5CH(R)C(R){=}C{=}O \qquad (35)$$

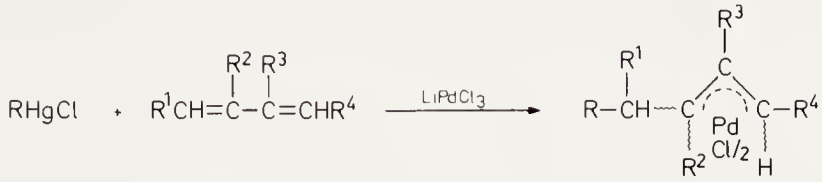
In many of the above reactions, it has been pointed out that cupric chloride can be added as a reoxidant for palladium, making the reactions catalytic in palladium. At high cupric chloride concentrations, however, chlorination takes place (Eq. 36). In fact, this reaction provides a useful route for the chloroarylation of alkenes (Table 7.5) [61]. Note that α-chloroaldehydes and ketones, but not esters, can be prepared in this manner. One cannot use cupric bromide in this reaction since aryl bromides become the major product. Phenonium ions have been suggested as intermediates in these reactions in order to explain the stereochemistry of chlorination [62].

$$ArHgCl + H_2C{=}CHR \xrightarrow[CuCl_2 \quad LiCl \\ H_2O \quad HOAc]{cat.\ Li_2PdCl_4} ArCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HR \tag{36}$$

Table 7.5. Chloroarylation of Alkenes

Arylmercurial	Alkene	Product	% Yield
C_6H_5HgCl	$H_2C{=}CH_2$	$C_6H_5CH_2CH_2Cl$	76
	$H_2C{=}CHCH_3$	$C_6H_5CH_2CHClCH_3$	50
	$H_2C{=}CHCHO$	$C_6H_5CH_2CHClCHO$	63
	$H_2C{=}CHCOCH_3$	$C_6H_5CH_2CHClCOCH_3$	~80
	$H_2C{=}CHCO_2CH_3$	$C_6H_5CH_2CHClCO_2CH_3$	10
	$CH_3CH{=}CHCHO$	$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCHClCHO$	22
$4\text{-}(C_2H_5)_2NC_6H_4HgCl$	$H_2C{=}CH_2$	$4\text{-}(C_2H_5)_2NC_6H_4CH_2CH_2Cl$	20
$3\text{-}NO_2C_6H_4HgCl$		$3\text{-}NO_2C_6H_4CH_2CH_2Cl$	47
$4\text{-}HO_2CC_6H_4HgCl$		$4\text{-}HO_2CC_6H_4CH_2CH_2Cl$	72
	$H_2C{=}CHCOCH_3$	$4\text{-}HO_2CC_6H_4CH_2CHClCOCH_3$	5
$1,3,5\text{-}(CH_3)_3C_6H_2HgCl$	$H_2C{=}CH_2$	$1,3,5\text{-}(CH_3)_3C_6H_2CH_2CH_2Cl$	2
			30
			13
			0.2

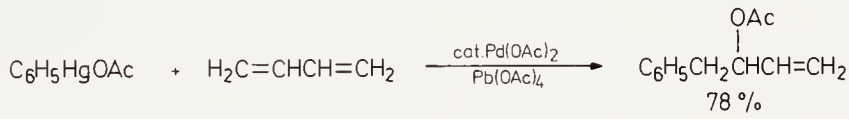
In all of the above reactions, highly reactive organopalladium compounds have been suggested as intermediates. In certain reactions one can actually isolate organopalladium compounds as the major product of the reaction. For example, the addition of methyl, benzyl, aryl or ferrocenylmercurials to $LiPdCl_3$ and 1,3-dienes affords low yields of π-allylpalladium chloride dimers (Eq. 37) [63, 64]. If one employs only catalytic amounts of palladium



(37)

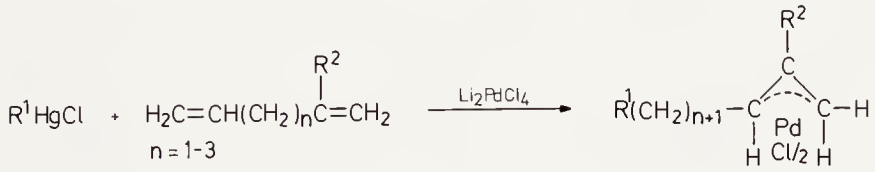
R	R^1	R^2	R^3	R^4	%Yield
CH_3	H	H	H	H	30
$C_6H_5CH_2$	H	H	CH_3	H	1
1-$C_{10}H_7CH_2$	H	H	H	H	—
C_6H_5	H	H	H	H	48
C_6H_5	H	H	CH_3	H	56
C_6H_5	H	H	H	CH_3	20
p-$CH_3OC_6H_4$	H	H	H	H	10
ferrocenyl	H	H	H	H	35
ferrocenyl	H	H	CH_3	H	24
ferrocenyl	H	CH_3	CH_3	H	29
ferrocenyl	CH_3	H	H	CO_2CH_3	28

acetate and one equivalent of lead tetraacetate in this reaction, an allylic acetate can be obtained (Eq. 38) [63].



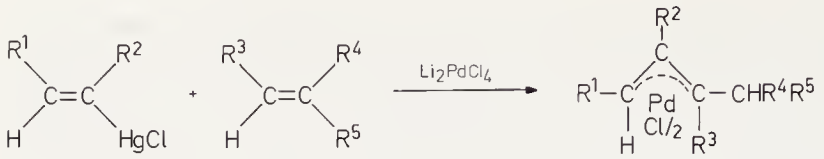
(38)

The reaction of non-conjugated dienes, organomercurials and Li_2PdCl_4 also yields π-allylpalladium compounds by regiospecific addition to the less substituted double bond and palladium migration (Eq. 39) [65].



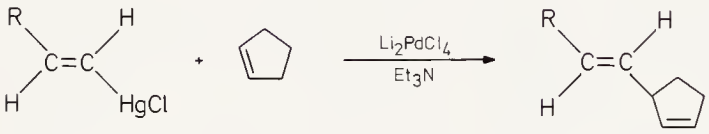
(39)

The reaction of vinylmercuric chlorides, Li_2PdCl_4 and alkenes similarly affords π-allylpalladium compounds and not the anticipated 1,3-diene (Eq. 40) [66, 67]. The following mechanism involving a palladium hydride rearrangement has been suggested (Scheme 7.4). Cyclic olefins similarly afford π-allylpalladium compounds, but the addition of triethylamine to the reaction results in high yields of allylation products (Eq. 41) [68].



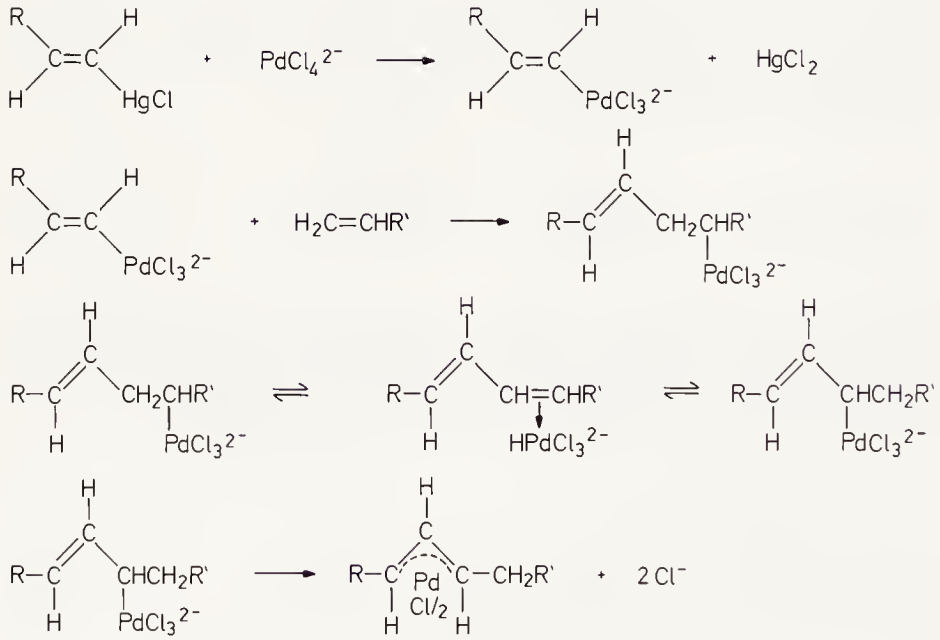
(40)

R^1	R^2	R^3	R^4	R^5	%Yield
n-C_4H_9	H	H	H	$CO_2C_2H_5$	66
C_6H_5	H	H	H	$CO_2C_2H_5$	100
t-C_4H_9	CH_3	H	H	$CO_2C_2H_5$	97
t-C_4H_9	H	H	H	$CO_2C_2H_5$	90
t-C_4H_9	H	H	H	CN	87
t-C_4H_9	H	H	H	$COCH_3$	100
t-C_4H_9	H	H	CH_3	CO_2CH_3	29
t-C_4H_9	H	H	H	H	92
t-C_4H_9	H	H	H	n-C_4H_9	—
t-C_4H_9	H	H	CH_3	CH_3	41
t-C_4H_9	H	CH_3	CH_3	H	—
t-C_4H_9	H	CH_3	CH_3	CH_3	—



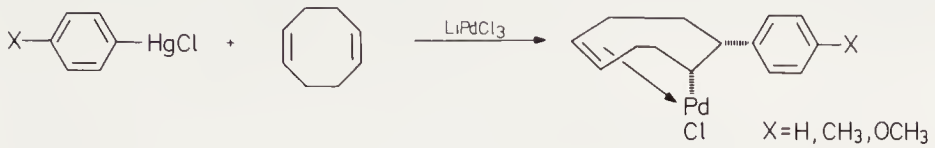
(41)

Scheme 7.4

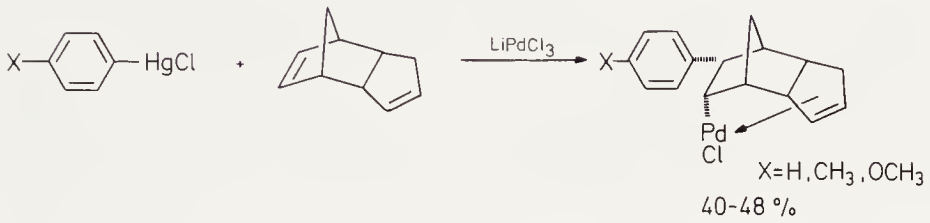


Arylmercurials can also be added to certain non-conjugated dienes to produce organopalladium compounds stabilized by coordination to the remaining double bond (Eqs. 42, 43) [69]. Treatment of these complexes with sodium borohydride gives the corresponding completely saturated hydrocarbons. Aryl- and vinylpalladation of norbornadiene and norbornene give

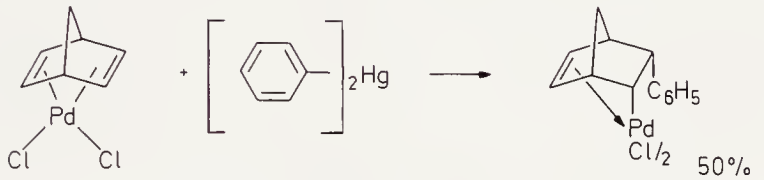
analogous complexes (Eqs. 44–49). These complexes presumably derive their stability from coordination to the neighboring sulfur or π system and from the fact that there is no cis β-hydrogen to eliminate. The thienyl- and



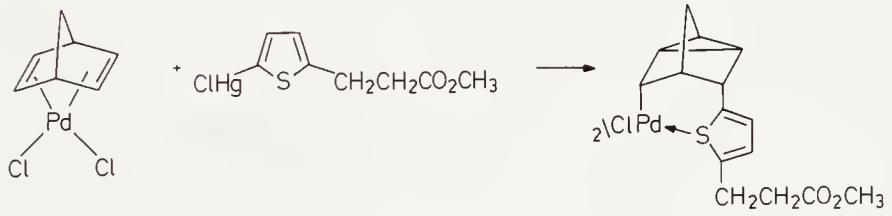
(42)



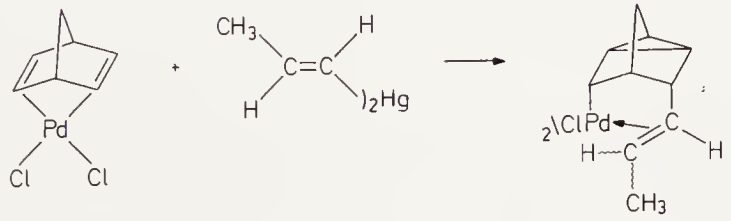
(43)



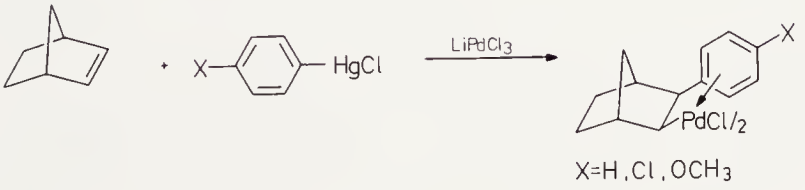
(44) [70, 71]



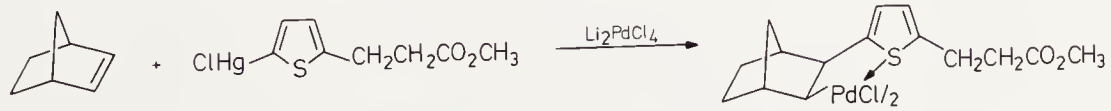
(45) [72]



(46) [73, 74]

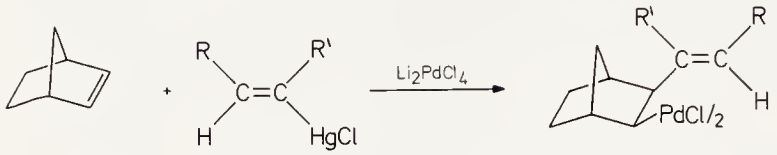


(47) [75]

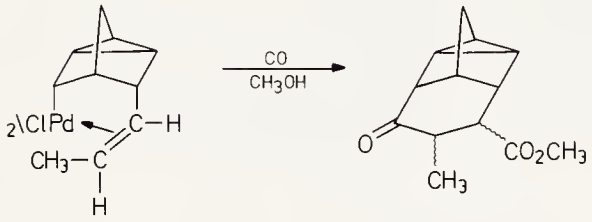


(48) [72]

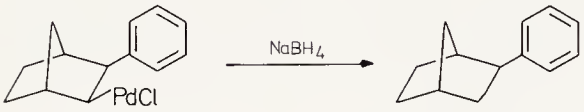
vinylpalladation products of norbornadiene apparently exist in the cyclized nortricycyl form. Carbonylation of the latter product forms a tetracyclic keto ester (Eq. 50) [74]. The adducts from norbornene undergo a number of useful synthetic conversions (Eqs. 51, 52 and Scheme 7.5). These reactions have proven useful for the synthesis of prostaglandin endoperoxide analogs.



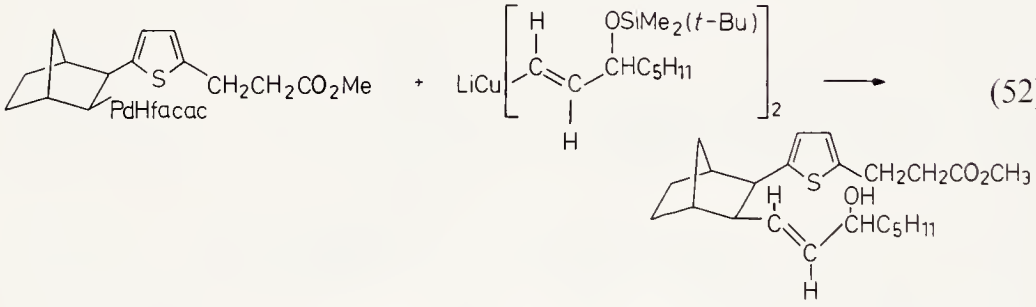
(49) [68]



(50)

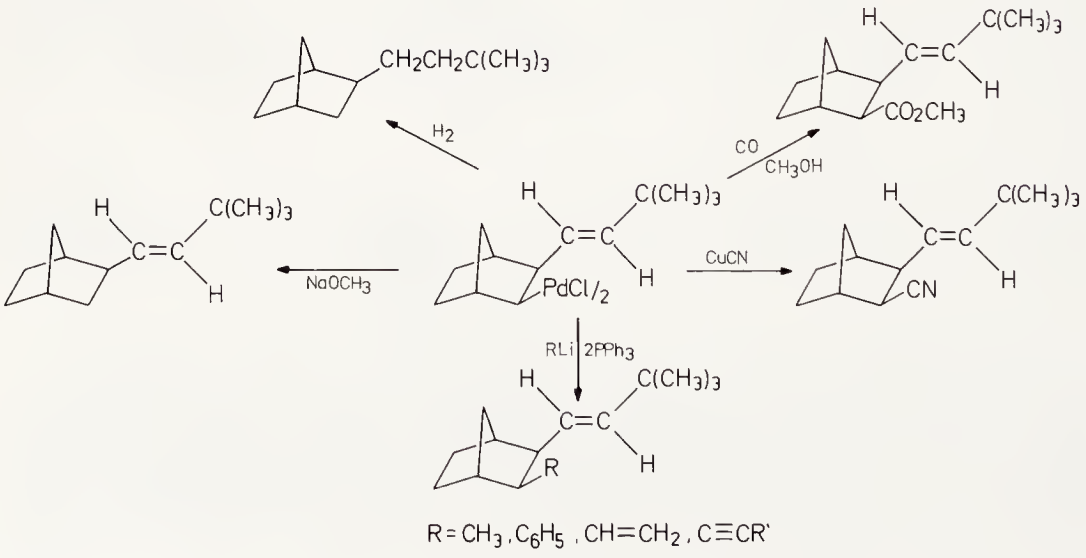


(51) [75]



(52) [72]

Scheme 7.5 [68]

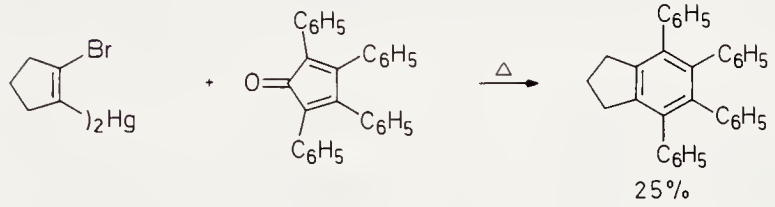


To this point nothing has been said about the reaction of organopalladium compounds and alkynes. The following reaction summarizes what little has been reported along these lines using organomercurials (Eq. 53) [76].

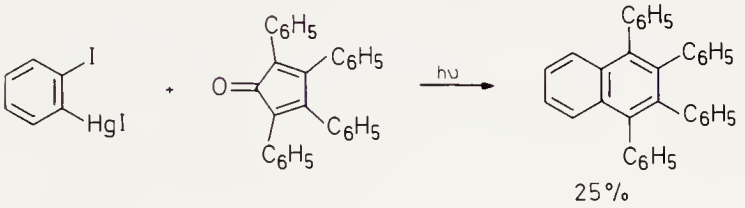
$$RHgOAc + C_6H_5C{\equiv}CH \xrightarrow{Pd(OAc)_2} RC{\equiv}CC_6H_5 \quad (53)$$

R = CH_3 26%
C_6H_5 77%
CO_2CH_3 41%, 82%

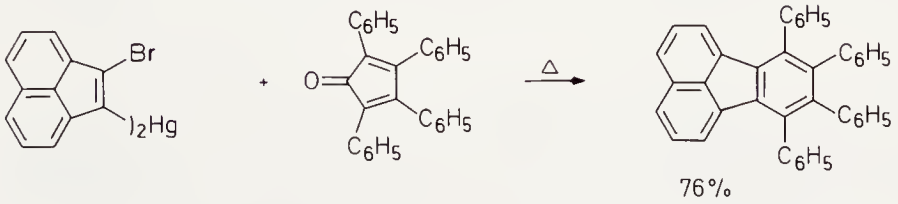
Finally, changing directions completely, organomercurials have been examined as possible precursors for the generation of a number of highly reactive intermediates including small ring cycloalkynes and arynes (Eqs. 54–56). Tetraphenylcyclopentadienone has been widely used as a trap for these intermediates. Although tetraphenylbenzene derivatives have been isolated in most of these reactions, this is not conclusive proof for the inter-



(54) [77]

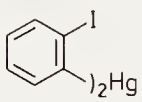


(55) [78, 79]

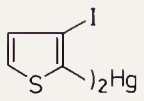


(56) [80]

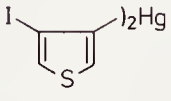
Also



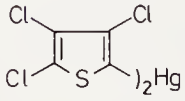
[81]



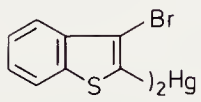
[82, 83]



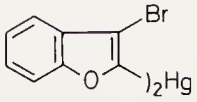
[83]



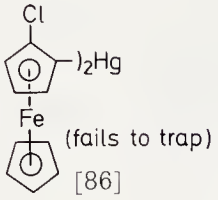
[84]



[83]

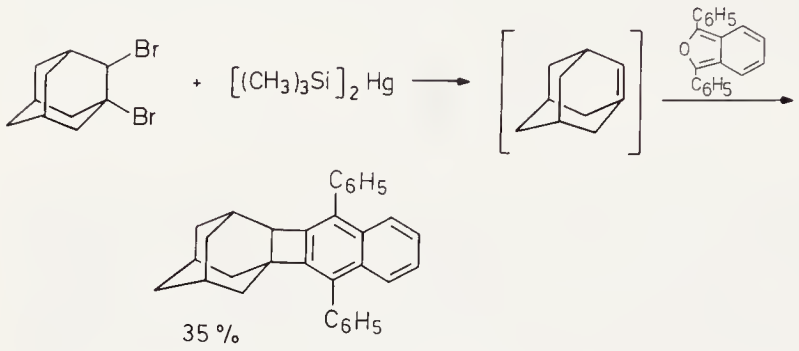


[85]



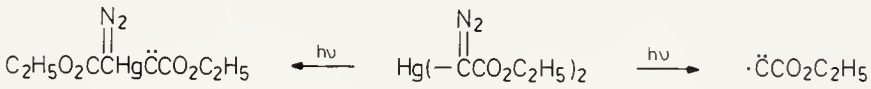
[86]

mediacy of an aryne, since Diels-Alder addition followed by elimination of mercuric halide and carbon monoxide will give the same products. Mercury reagents also appear useful for the generation of strained bridgehead double bonds (Eq. 57) [87]. The photolysis of mercurated diazoesters and ketones has



(57)

been examined as a possible route to carbynes and mercurated carbenes (Eq. 58) [88–93]. Both species can apparently be generated in this fashion as judged by the products of their reaction with alkenes.



(58)

In conclusion, while few organomercurials will add directly to alkenes, they provide a valuable source of free radicals or organopalladium compounds which will readily undergo addition or substitution reactions with alkenes. These reactions accommodate a wide variety of functional groups and should prove quite useful in organic synthesis. Organomercurials have also proven valuable as starting materials for the preparation of highly reactive organic intermediates of interest to the physical organic chemist.

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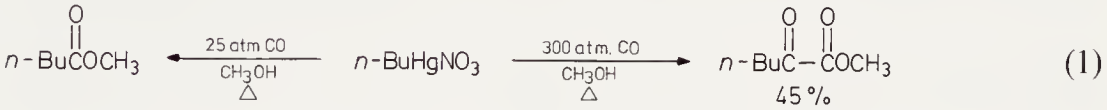
VIII. Carbonylation

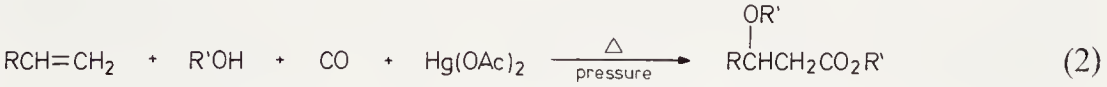
The direct carbonylation of organomercurials occurs only with great difficulty. However, a number of transition metal reagents promote carbonylation under mild conditions. These reactions can be used to prepare a host of carbonyl-containing products, including carboxylic acids and esters, carbonates, urethanes, ureas and ketones. These reactions are the subject of this chapter.

The direct reaction of organomercurials and carbon monoxide requires high pressures and elevated temperatures, and generally affords only low yields of the corresponding carboxylic acids, esters or anhydrides. Phenyl- [1, 2] and naphthylmercurials [3] have been converted to the corresponding carboxylic acids and derivatives in this manner. Carbonylation of simple alkylmercuric salts apparently gives either simple carboxylic acid derivatives [4, 5] or α-keto carboxylic acids [6] depending on the carbon monoxide pressure (Eq. 1). Yields up to 50% have been achieved. Best results are



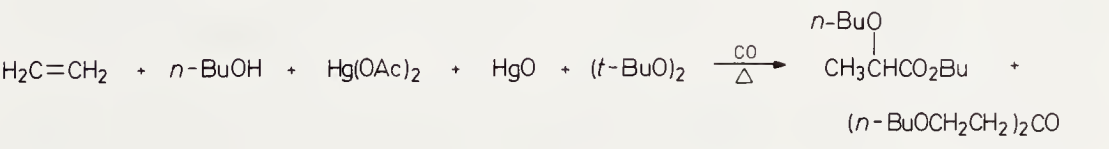
(1)

observed using the more ionic alkylmercuric salts. β-Alkoxy carboxylic esters can be obtained via alkoxymercuration and carbonylation (Eq. 2) [4, 7–10].



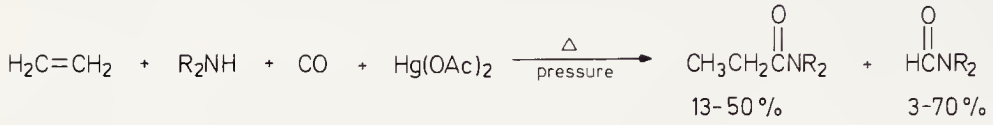
(2)

Highest yields (~80% based on reacted olefin) are achieved using a two step sequence in which the olefin is added last [9]. Organomercurials of the type $RCH(OR')CH_2HgCO_2R'$ have been suggested as intermediates [10]. Under similar reaction conditions, but with added di-*t*-butylperoxide, the major products become α-alkoxy esters and β-alkoxy ketones (Eq. 3) [11].



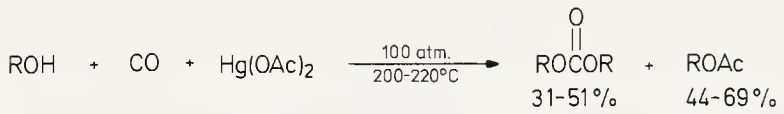
(3)

When amines are employed in these reactions, one obtains modest yields of simple amides and formamides (Eq. 4) [12].



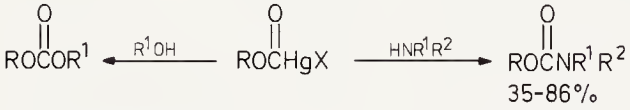
(4)

In Chap. IV the synthesis of urethanes and ureas from isonitriles and mercury salts was discussed. The carbonylation of alcohols and amines in the presence of mercuric acetate provides an alternate approach to carbonates, urethanes and ureas. The reaction of alcohols affords reasonable yields of carbonates alongside major amounts of the corresponding acetate (Eq. 5)



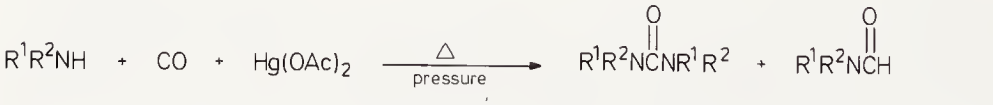
(5) [14]

[13–15]. The mercuric acetate is reduced to metallic mercury in this reaction. Efforts to reoxidize the mercury by adding copper or lead salts only lowered the yield of carbonate [15]. The use of two different alcohols in either a one or two step approach affords only mixtures of carbonates [16]. Reactions with glycols [13] or allyl alcohol [17] produce polycarbonates. The reaction between carboalkoxymercurials and alcohols or amines provides the corresponding unsymmetrical carbonates [18, 19] or urethanes [18] respectively (Eq. 6), while the direct carbonylation of amines yields ureas and/or



(6)

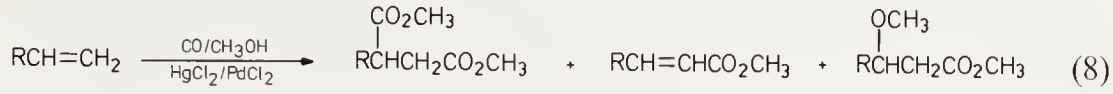
formamides depending on the amine employed and the reaction conditions (Eq. 7) [20–26]. Anilines apparently give only the urea, while primary and secondary aliphatic amines give mixtures and primary amino alcohols afford predominantly formamides. Using two different amines one can prepare unsymmetrical ureas [22].



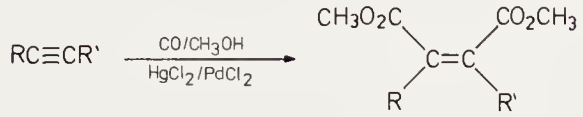
(7)

Organomercurials are much more easily carbonylated by employing transition metal reagents. Palladium has been the metal most effectively utilized. We have already seen in Chap. VII the use of carboalkoxymercurials in the Heck reaction as a means of preparing unsaturated carboxylic esters. The in situ reaction of olefins, palladium chloride, mercuric chloride and carbon monoxide in methanol affords substituted succinate esters, although substantial amounts of the corresponding α,β-unsaturated or β-methoxy esters

are also frequently observed (Eq. 8) [27]. Alkynes react catalytically in palladium under these same conditions to generate substituted maleates (Eq. 9).

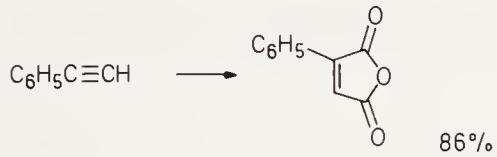


(8)



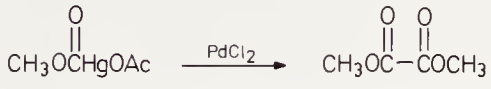
(9)

β-Chloroacrylate esters are a common side product in these reactions. The reaction of phenyl acetylene in water gives a high yield of phenyl maleic anhydride (Eq. 10). Finally, dimethyl oxalate can be obtained in low yield



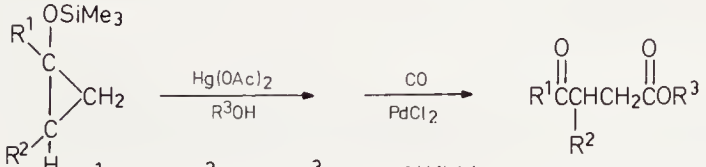
(10)

when carbomethoxymercuric acetate is simply treated with palladium chloride (Eq. 11) [28].



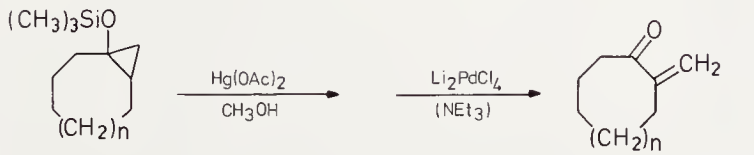
(11)

The palladium-promoted carbonylation of simple alkyl- [29] and cyclic alkylmercurials [30] has been studied, and in the latter case has been shown to proceed with predominant retention of configuration in the transmetallation step and complete retention during carbonylation. Unfortunately, the yields are generally not very high. Nonetheless, the reaction of cyclopropyl trimethylsilyl ethers with mercuric acetate in methanol, followed by palladium-promoted carbonylation, provides a unique approach to γ-keto esters (Eq. 12)



R^1	R^2	R^3	%Yield
t-C_4H_9	H	CH_3	52
C_6H_5	CH_3	CH_3	48
$-(CH_2)_4-$		C_2H_5	46

(12)

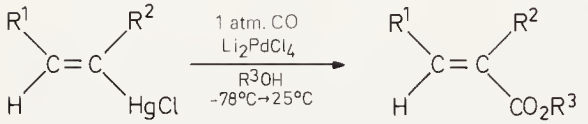


n	
1	80%
2	97%
6	80%

(13)

[31]. In the absence of carbon monoxide, excellent yields of α-methylene ketones are obtained by β-hydride elimination (Eq. 13).

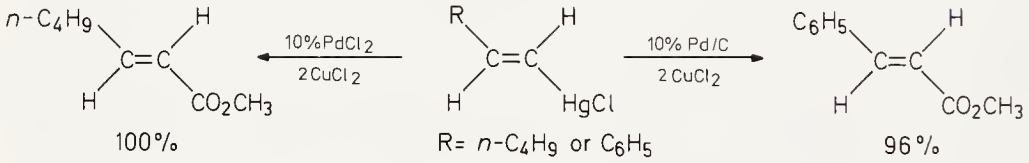
Vinylmercurials are readily carbonylated in excellent yield with essentially complete retention of configuration when using Li_2PdCl_4 in alcohol solvents at low temperatures and pressures (Eq. 14) [32]. These reactions become catalytic



(14)

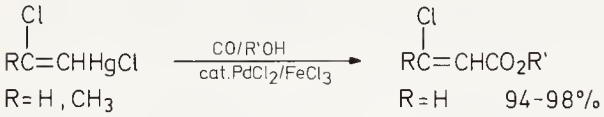
R^1	R^2	R^3	%Yield
C_6H_5	H	CH_3	100
n-C_4H_9	H	CH_3	98
t-C_4H_9	H	C_2H_5	90
c-C_6H_{11}	H	CH_3	96
$NC(CH_2)_3$	H	CH_3	98
$H_2C{=}CCH_3$	H	C_2H_5	93
C_2H_5	C_2H_5	C_2H_5	85
C_6H_5	C_6H_5	CH_3	99

in palladium when cupric chloride is added, and either palladium chloride or palladium on charcoal is employed as the catalyst (Eq. 15). Ferric chloride



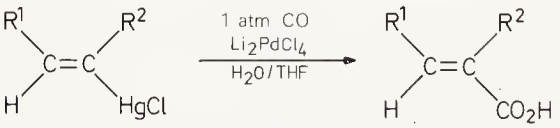
(15)

has also been effectively employed as a reoxidant in the carbonylation of β-chlorovinylmercurials (Eq. 16) [33, 34]. At higher temperatures and pressures $PdCl_2(PPh_3)_2$ alone serves to catalyze these carbonylation reactions, but low yields are generally obtained [35].



(16)

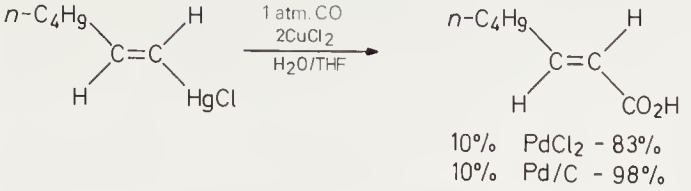
When 2–5% aqueous THF is employed as the solvent for the carbonylation of vinylmercurials, α,β-unsaturated carboxylic acids are obtained instead



(17)

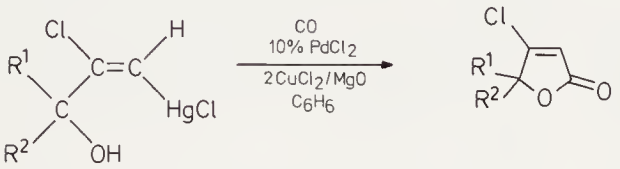
R^1	R^2	%Yield
n-C_4H_9	H	99
t-C_4H_9	H	98
c-C_6H_{11}	H	90
C_6H_5	H	80
$NC(CH_2)_3$	H	72
	H	72
C_2H_5	C_2H_5	85

(Eq. 17) [32]. Once again palladium chloride or palladium on charcoal catalyze carbonylation when cupric chloride is added (Eq. 18).



(18)

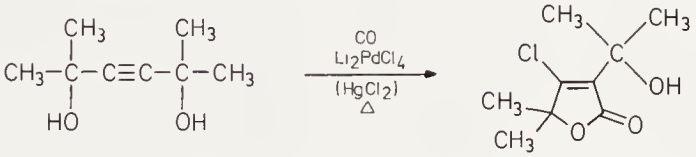
These carbonylation reactions provide a novel approach to butenolides when applied to vinylmercurials derived from propargylic alcohols (Eq. 19)



R^1	R^2	%Yield
H	H	78
CH_3	CH_3	96
CH_3	C_2H_5	100
$-(CH_2)_4-$		93
$-(CH_2)_5-$		81

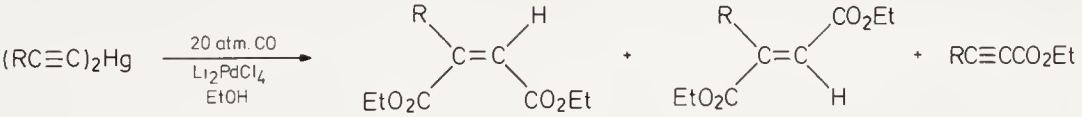
(19)

[32, 36, 37]. In fact, one can react 2,5-dimethyl-3-hexyn-2,5-diol directly with carbon monoxide, lithium chloride and palladium chloride, with or without mercuric chloride, and obtain the corresponding butenolide in 92% or 70% yields respectively (Eq. 20).



(20)

The carbonylation of dialkynylmercurials affords little of the expected acetylenic ester, but produces maleate esters instead, contaminated with small amounts of the corresponding fumarate ester (Eq. 21) [38].

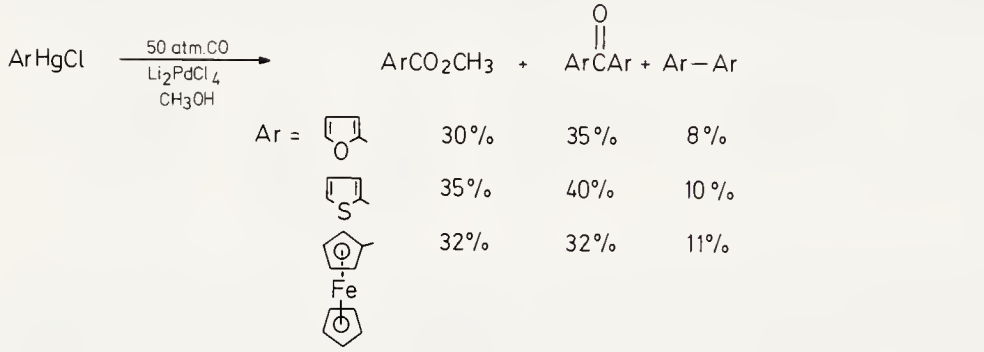


$R = C_6H_5$	62%	6%	5%
C_2H_5	40%	10%	6%

(21)

The carbonylation of arylmercurials has not proven particularly successful. Although simple arylmercurials afford carboxylic acids, acid chlorides and esters when treated with palladium chloride and carbon monoxide under the right conditions, the yields reported are generally much less than 50% [29]. In fact, one can obtain a higher yield of benzoic acid (60%) simply by heating phenylmercuric acetate with palladium acetate and excess sodium acetate in acetic acid plus acetic anhydride [39]. Nevertheless, the palladium-promoted

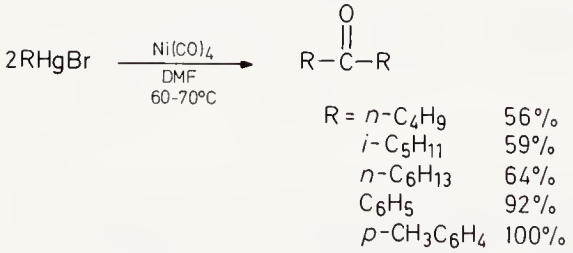
carbonylation of 5-mercuriotubercidin has recently provided a convenient synthesis of the nucleoside 5-carbomethoxytubercidin [40]. With mercurials derived from furan [41], thiophene [41], benzofuran [42] and ferrocene [43], the desired esters are contaminated with comparable amounts of the corresponding symmetrical ketones, plus small amounts of the corresponding biaryl (Eq. 22). In a similar manner, 1,1′-bis(chloromercurio)ferrocene gives the corresponding cyclic analogs (Eq. 23) [43]. The carbonylation of arylmercurials becomes catalytic in palladium when palladium reagents such as $PdCl_2(PPh_3)_2$ are employed at elevated temperatures and pressures [35]. Yields of 10–99% are achieved.



(22)

(23)

A number of transition metals other than palladium have also proven useful in the carbonylation of organomercurials. For example, primary alkyl- and arylmercuric bromides react with nickel tetracarbonyl in DMF to give good to excellent yields of the corresponding symmetrical ketones (Eq. 24)



(24)

[44]. Both the halide present in the mercurial and the solvent are critical. For instance, phenylmercuric chloride in polar solvents such as DMF, DMSO and acetonitrile gives benzophenone in 95–97% yield, but primarily diphenylmercury in less polar solvents such as THF and benzene. While *p*-tolylmercuric bromide gives a 99% yield of ketone in THF, *p*-tolylmercuric

chloride gives a 90% yield of the corresponding diarylmercurial in this same solvent. Phenylmercuric acetate gives a 91% yield of diphenylmercury even in DMF. The carbonylation reaction with $Ni(CO)_4$ affords unsymmetrical ketones in high yield when one reacts arylmercuric chlorides or bromides with aryl iodides in benzene (Eq. 25) [44, 45].

$$ArHgX + Ar'I \xrightarrow[C_6H_6,\ 60\text{-}70^\circ C]{Ni(CO)_4} ArC(=O)Ar' \quad 60\text{-}92\% \qquad (25)$$

ArHgX = *p*-$CH_3C_6H_4HgCl$, *p*-ClC_6H_4HgCl, C_6H_5HgBr
Ar'I = C_6H_5I, *p*-$CH_3C_6H_4I$, *p*-$NH_2C_6H_4I$

Dicobalt octacarbonyl can be employed in a manner similar to nickel tetracarbonyl for the preparation of dialkyl and diaryl ketones (Eq. 26) [46–49]. However, in this reaction note that either an organomercuric halide

$$RHgX \text{ or } R_2Hg \xrightarrow{Co_2(CO)_8} R-C(=O)-R \qquad (26)$$

R = C_2H_5 (60%), *n*-C_4H_9 (42%), *c*-C_3H_5 (66%), $C_6H_5CH_2$ (51%), C_6H_5 (83%), *p*-$CH_3C_6H_4$ (86%), *p*-$CH_3OC_6H_4$ (84%), *p*-ClC_6H_4 (89%), *p*-FC_6H_4 (93%), π-$(CO)_3CrC_6H_5$ (43%), π-$(CO)_3Cr$-*p*-$CH_3C_6H_4$ (66%)

or a diorganomercurial may be utilized as the starting material, contrary to the $Ni(CO)_4$ reaction. It has been observed, however, that hindered arylmercuric bromides produce diarylmercurials as a major side product and primary alkylmercurials, such as *n*-butylmercuric bromide, afford branched chain by-products in significant amounts, a problem not encountered with $Ni(CO)_4$. Using diarylmercurials and carbon monoxide, moreover, it has been reported that ketone formation can be catalyzed by either $Co_2(CO)_8$ or $Hg[Co(CO)_4]_2$ (Eq. 27) [49, 50].

$$(X\text{-}C_6H_4\text{-})_2Hg \xrightarrow{CO/h\nu} X\text{-}C_6H_4\text{-}C(=O)\text{-}C_6H_4\text{-}X \qquad (27)$$

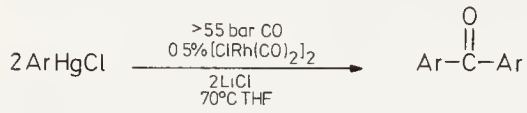
catalyst	X = CH_3O	CH_3	H	Cl	F
$Co_2(CO)_8$	—	—	91%	85%	87%
$Hg[Co(CO)_4]_2$	64%	62%	88%	59%	68%

Although having received relatively little attention, rhodium(I) reagents appear effective as catalysts for the carbonylation of organomercurials. At elevated temperatures and pressures Wilkinson's catalyst efficiently catalyzes the carbonylation of alkyl- [35, 51] and arylmercuric salts [35, 52] to the

$$RHgOAc \xrightarrow[CH_3OH]{CO,\ cat\ ClRh(PPh_3)_3} RCO_2CH_3 + RCO_2H \qquad (28)$$

R = C_2H_5	66%	—
C_6H_5	38%	50%

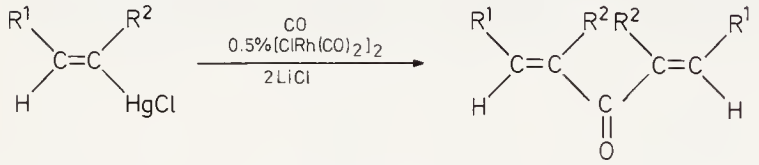
corresponding carboxylic esters and/or acids (Eq. 28). While both $RhCl_3 \cdot 3\,H_2O$ and $ClRhCO(PR_3)_2$ catalyze the carbonylation of arylmercuric chlorides to the corresponding diaryl ketones [53], $[ClRh(CO)_2]_2$ appears to be a much more efficient catalyst (Eq. 29) [54]. This same catalyst also



(29)

Ar = C_6H_5 (80%), *m*-$NO_2C_6H_4$ (60%), 2-naphthyl (100%), 2-thienyl (89%)

very effectively converts vinylmercuric chlorides to divinyl ketones at room temperature and atmospheric pressure (Eq. 30) [54]. The latter conversion can also be effected in high yield using $RhCl_3 \cdot 3\,H_2O$.



(30)

R^1	R^2	%Yield
H	H	89
Cl	H	—
n-C_4H_9	H	94
t-C_4H_9	H	96
C_6H_5	H	99
$H_2C{=}\overset{|}{C}CH_3$	H	—
	H	100
t-C_4H_9	CH_3	64

Once again in this chapter we have seen that while organomercurials themselves are not very reactive towards carbon monoxide, a number of useful synthetic transformations can be effected using transition metal reagents particularly those of palladium. This chapter has described a variety of useful carbonyl syntheses which have become feasible using such reagents. The following chapter takes a look at the preparation of carbonyl compounds via acylation of organomercurials.

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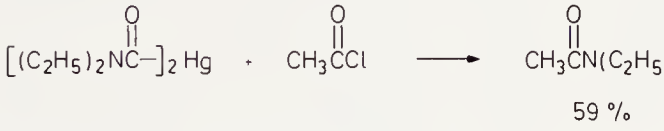
IX. Acylation

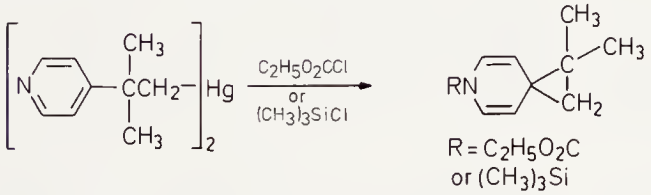
Although the reaction of organomercurials and alkyl halides is severely limited, the reaction with acyl halides is more general and can afford a useful route to ketones, as well as enol esters. The addition of a palladium(0) catalyst or aluminum halides often affords ketones in high yield under mild conditions. These routes to carbonyl compounds will be surveyed in this chapter on the acylation of organomercurials.

A wide variety of functionally substituted organomercurials have been acylated without effecting the mercury moiety. For example, mercurated anilines are smoothly converted to the corresponding acetanilides upon treatment with acetic anhydride [1–4]. Although a number of mercurated alcohols [5, 6] and phenols [7, 8] have been acylated by acid chlorides, β-alkoxymercurials revert to olefins upon reaction with acid chlorides [9–11]. The acylation of carboxamidomercurials proceeds by attack on nitrogen (Eq. 1) [12], as does the following interesting reaction (Eq. 2) [13].



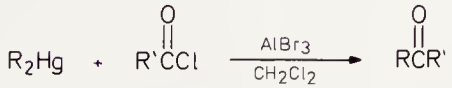
59 %

(1)



$R = C_2H_5O_2C$ or $(CH_3)_3Si$

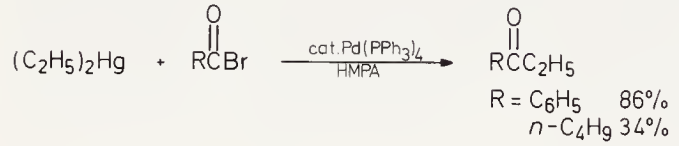
(2)



(3)

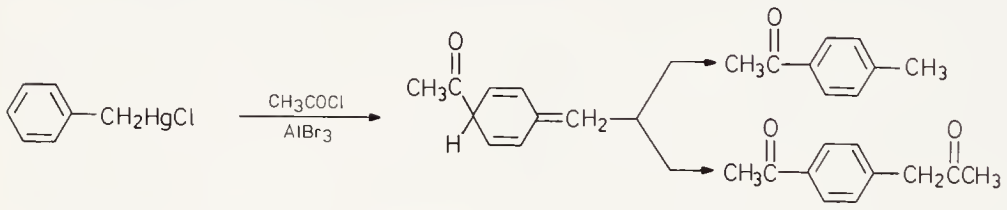
R	R'	%Yield
C_2H_5	CH_3	100
C_2H_5	n-C_3H_7	83
n-C_4H_9	CH_3	85
n-C_4H_9	n-C_3H_7	75
n-C_4H_9	n-C_4H_9	80
n-C_4H_9	C_6H_5	73
n-C_4H_9	p-$NO_2C_6H_5$	70
n-C_6H_{13}	CH_3	79

Simple alkylmercurials can be acylated under the appropriate conditions to give good yields of ketones. Although diethylmercury reacts directly with acid chlorides under forcing conditions to give low yields of ketones and the corresponding alkylmercuric chloride [14], the addition of aluminum bromide gives high yields at room temperature (Eq. 3) [15]. It is unclear whether one or both organic groups on mercury can be utilized in this reaction. Catalytic amounts of $Pd(PPh_3)_4$ in HMPA also promote the acylation of diethylmercury (Eq. 4) [16]. Unfortunately, lower yields are obtained when aliphatic acid bromides are employed in this reaction and organomercuric chlorides apparently fail to react.



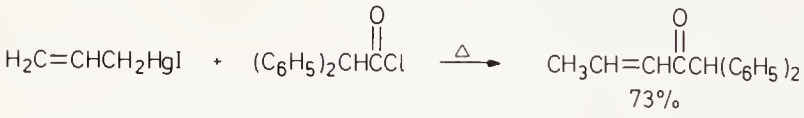
(4)

The reaction of benzylmercuric chloride, acetyl chloride and aluminum bromide affords two totally unexpected products (Eq. 5) [17, 18]. Both products appear to arise via initial acylation in the para position to produce a cyclohexadiene which can either rearrange to give the minor product or undergo further acylation to produce the major product observed, the diketone.

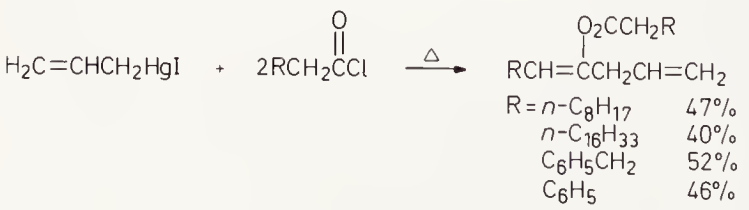


(5)

The direct reaction of allylmercuric iodide and acid chlorides also provides unexpected products (Eqs. 6, 7) [19]. The latter product appears to



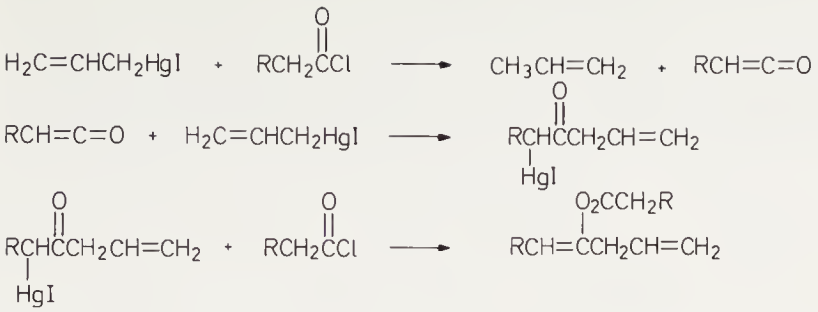
(6)



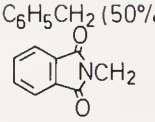
(7)

arise via ketene formation and insertion into the allylmercurial, followed by acylation of the resulting α-mercurated ketone (Scheme 9.1).

Scheme 9.1

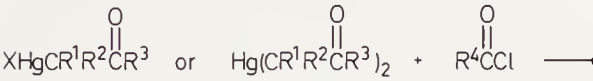


(8) [20–22]

R = CH_3 (48%), $ClCH_2$ (58%), Cl_3C (53%), F_3C (32%), $C_6H_5CH_2$ (50%), $(C_6H_5)_3C$ (48%), C_6H_5 (65%), *p*-NCC_6H_4 (50%), *p*-$NO_2C_6H_4$ (55%),  (40%)

(9) [23]

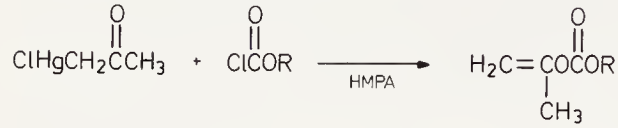
R = H (62%), CH_3



(10)

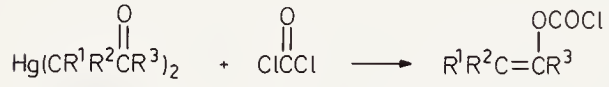
R^1	R^2	R^3	R^4	%Yield	Ref.
H	H	CH_3	C_6H_5	63	20
H	H	$CH(OC_2H_5)_2$	CH_3	10	24
H	H	$CH_2CO_2CH_3$	CH_3	64,80	25,26
H	H	$CH_2CO_2CH_3$	CCl_3	87	26
H	H	$CH_2CO_2CH_3$	C_2H_5	84	25,26
H	H	$CH_2CO_2CH_3$	C_6H_5	--	25,26
H	H	C_6H_5	CH_3	82	27
H	*n*-C_3H_7	*n*-C_4H_9	*t*-C_4H_9	39	28
H	*n*-C_3H_7	*n*-C_4H_9	C_6H_5	62	28
H	C_6H_5	CH_3	CH_3	99	27
H	$-(CH_2)_4-$		CH_3	57,88	20,27
H	$-(CH_2)_4-$		*t*-C_4H_9	73	28
H	$-(CH_2)_4-$		C_6H_5	63	20,28
H	$(CH_3)_2CHCO$	$(CH_3)_2CH$	C_6H_5	--	29
H	$(CH_3)_2CHCO$	$(CH_3)_2CH$	*p*-$NO_2C_6H_4$	--	29
H	$(CH_3)_3CCO$	$(CH_3)_3C$	C_6H_5	--	29
H	$(CH_3)_3CCO$	$(CH_3)_3C$	*p*-$NO_2C_6H_4$	--	29
H	$(C_6H_5)_3P^+$	CH_3	C_6H_5	--	30,31
H	$(C_6H_5)_3P^+$	C_6H_5	CH_3	--	30,31
H	$(C_6H_5)_3As^+$	C_6H_5	CH_3	--	32
F	F	CF_3	CH_3	80	33,34
CH_3	CH_3	CH_3	CH_3	60	35
CH_3	CH_3	CH_3	C_6H_5	53	35
CH_3	C_2H_5	CH_3	CH_3	60	35
C_2H_5	C_2H_5	CH_3	CH_3	--	35
CH_3	$-(CH_2)_4-$		CH_3	55	35
CH_3	$-(CH_2)_4-$		C_6H_5	55	35

In fact, the acylation of α-mercurated carbonyl compounds affords a very convenient route to a wide variety of enol esters (Eqs. 8–10). In this latter summation, note the versatility of this approach. In fact, this type of acylation affords the most convenient route to enol carbonates [36] and chloroformates [37] (Eqs. 11, 12). It appears that even the mercurial derived from 1-phenyl-1-



(11)

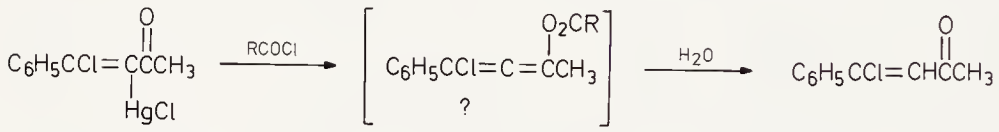
R = CH_3(48%), C_2H_5(78%), $H_2C{=}CHCH_2$(72%), $C_6H_5CH_2$(56%), C_6H_5(76%)



(12)

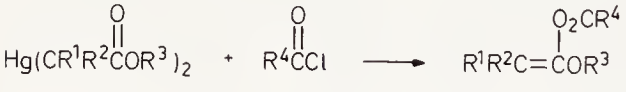
R^1	R^2	R^3	%Yield
H	H	H	--
H	H	CH_3	86
H	H	*c*-C_3H_5	--
H	H	*t*-C_4H_9	38
H	H	C_6H_5	45
H	$-(CH_2)_4-$		64

butyn-3-one by mercuric chloride addition undergoes this type of acylation since demercuration is observed upon treatment with acid halides (Eq. 13)



(13)

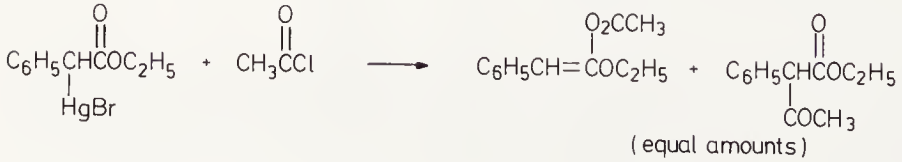
[38]. The acylation of mercurated esters affords a simple route to alkoxy substituted enol esters including carbonates (Eq. 14). As noted, carbon acylation has also been observed to occur in some of these reactions (Eq. 15)



(14)

R^1	R^2	R^3	R^4	%Yield	Ref.
H	H	CH_3	CH_3	35	39
H	H	CH_3	C_6H_5	48	39
H	H	CH_3	CH_3O	36	40
H	H	CH_3	C_2H_5O	43-54	40
H	H	CH_3	C_6H_5O	18	40
H	H	*i*-C_4H_9	CH_3	~43*	39
H	H	*i*-C_4H_9	*i*-C_4H_9	43	39
H	F	C_2H_5	C_6H_5	52	41

* 24% C-acylation also observed

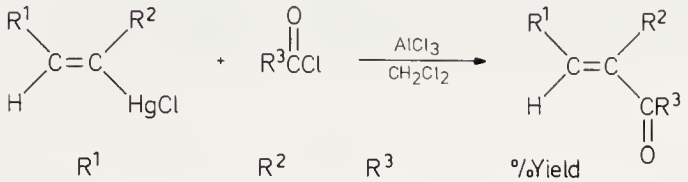


(15)

(equal amounts)

[42]. You will recall that analogous oxygen and carbon substitution reactions of α-mercurated carbonyl compounds are observed when one uses sulfur, phosphorus and silicon halides (see Chap. IV).

While vinylmercurials do not react directly with acid chlorides, addition of an equivalent of aluminum chloride promotes rapid acylation and affords excellent yields of α,β-unsaturated ketones (Eq. 16) [43, 44]. A number of

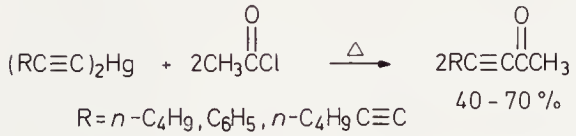


(16)

R^1	R^2	R^3	%Yield
n-C_3H_7	H	$CH_3CH{=}CH$	97
n-C_4H_9	H	CH_3	97
n-C_4H_9	H	C_6H_5	64
t-C_4H_9	H	CH_3	95
c-C_6H_{11}	H	n-C_3H_7	96
n-C_8H_{17}	H	i-C_3H_7	97
$CH_3O_2C(CH_2)_8$	H	CH_3	100
C_2H_5	C_2H_5	$CHCl_2$	89
t-C_4H_9	CH_3	CH_3	99
C_6H_5	C_6H_5	n-C_3H_7	72

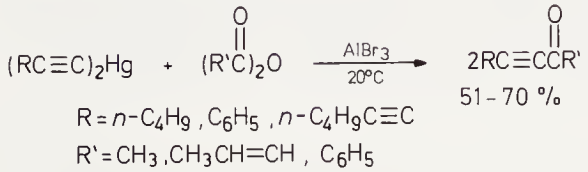
other reagents [Al, $AlBr_3$, $TiCl_4$, $[ClRh(CO)_2]_2$ and $Pd(PPh_3)_4$] also facilitate acylation, but the yields are generally lower and mixtures of stereoisomers are common. Several observations during the course of this work suggest that these reactions may be proceeding by addition of the acid chloride across the carbon—carbon double bond, followed by mercuric chloride elimination.

Dialkynylmercurials are sufficiently reactive towards aliphatic acid halides that both groups are transferred in refluxing heptane (Eq. 17) [45].



(17)

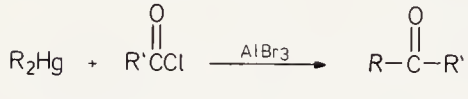
Acid anhydrides can also be employed in these reactions if aluminum bromide is added (Eq. 18).



(18)

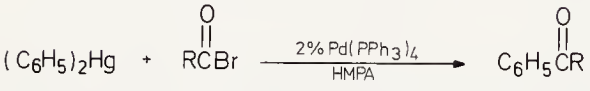
Although simple arylmercuric halides and diarylmercurials will react at high temperatures with acid halides [46–48], better yields of ketones are obtained by adding aluminum halides [15, 49, 50] or by using $Pd(PPh_3)_4$ catalysis [16] (Eqs. 19, 20). In the former reaction, it is unclear whether one

or both organic groups on mercury can be utilized. Using palladium catalysis, organomercuric chlorides apparently fail to react. The literature also contains a number of examples of heteroatom-containing arylmercurials which react directly with acid halides. These include organomercurials derived from diphenyl ether [51], furans [52–54], benzofuran [55], thiophenes [56–59], benzothiophene [60] and selenophene [61]. Yields vary substantially from compound to compound, but the acylation of these arylmercurials can prove synthetically useful. Finally 1,3-bis(acetoxymercurioazulene reacts with acetic anhydride upon heating, but only 1-acetylazulene could be isolated in 34% yield [62].



(19) [15]

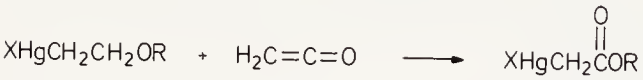
R	R'	%Yield
C_6H_5	n-C_4H_9	92
C_6H_5	p-$NO_2C_6H_4$	88
p-$CH_3C_6H_4$	CH_3	100
p-ClC_6H_4	CH_3	95



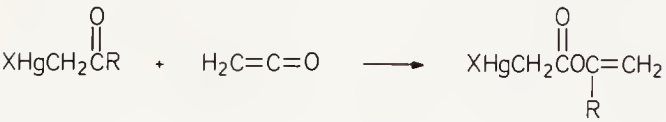
(20)

R = CH_3 66%
C_6H_5 68%

As indicated earlier, ketenes will also acylate organomercurials, but this approach is rather restricted due to the limited availability of ketenes. Nevertheless, phenyl- and furylmercurials have been acylated by ketene in 14–50% yield [63, 64]. From β-alkoxymercurials or α-mercurated ketones, mercurated esters are obtained (Eqs. 21, 22).



(21) [65]



(22) [25, 65]

As this chapter has shown, certain organomercurials will react directly with acid halides to afford ketones and enol esters. However, with most organomercurials better results are obtained if aluminum halides are added. Under these conditions a wide variety of ketones become readily available via organomercurials.

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X. Divalent Carbon Transfer Reactions

A. Introduction

The use of α-haloorganomercury compounds as divalent carbon transfer reagents is an important recent development in organic synthesis. Since the first reported reaction of this type in 1962 by Seyferth and co-workers [1], a large number of these compounds have been prepared and their application in organic synthesis explored. Their unique properties have made them particularly valuable as reagents in cyclopropane formation, ring expansion reactions, and the synthesis of organometallic and heteroatom-containing compounds. These topics have been the subject of earlier reviews [2–5], but they will be discussed in greater detail here.

B. Preparation of the Reagents

A variety of methods exist for the preparation of α-haloorganomercury compounds. The most widely used method involves the reaction of an organomercuric halide, commonly phenylmercuric chloride, with a polyhaloalkane and potassium *tert*-butoxide (Eq. 1). Sodium methoxide in methanol is

$$RHgX + HCXYZ + KO\text{-}t\text{-}Bu \longrightarrow RHgCXYZ \quad (1)$$

also occasionally employed as a base. Benzene, ether and THF are the most common solvents and the reaction is usually run at temperatures ranging from −75 °C to 5 °C, depending on the solvent system, the solubility of the reactants, and the stability of the product. Best results are usually obtained at lower temperatures. High speed stirring is also sometimes required. In some cases the products are not particularly stable or they are difficult to separate from the diarylmercury by-products occasionally observed in these reactions. However, such impurities do not generally seem to interfere with subsequent synthetic applications. The wide variety of α-haloorganomercurials prepared in this manner is summarized in Table 10.1, along with the reaction conditions employed and the yield obtained. A thorough study of the reaction conditions has indicated that in general the simple phenyltrihalomethylmercury compounds are best prepared using 1.4 equivalents of potassium *tert*-butoxide/*tert*-butanol monosolvate in THF at −25 °C [8]. This procedure eliminates the need for high speed stirring and a large excess of the trihalomethane, and allows one to use commercially available potassium *tert*-butoxide. It is evident from the large number of α-halo-

Table 10.1. Synthesis of α-Haloorganomercurials via Organomercuric Chlorides

$RHgCl + HCXYZ + MOR' \longrightarrow RHgCXYZ$

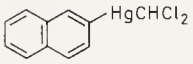
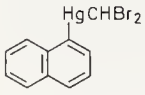
Organomercurial prepared (RHgCXYZ)	Base	Solvent	Temp. (°C)	% Isolated yield	Ref.
$C_6H_5HgCHCl_2$	KO-*t*-Bu	$C_6H_5CH_3$	5	38[a]	6
				45	6
		C_6H_6	–	70[b]	7
p-$CH_3OC_6H_4HgCHCl_2$			–	65[b]	7
			–	77[b]	7
$C_6H_5HgCHClBr$		$C_6H_5CH_3$	5	63	6
$C_6H_5HgCHClI$				35 (crude)	6
$C_6H_5HgCHBr_2$		C_6H_6	–	20[a,b]	7
		$C_6H_5CH_3$	5	65	6
		THF			8
		—	–	70–80[c]	9
p-$CH_3OC_6H_4HgCHBr_2$		C_6H_6	25	30[a,b]	7
			–	17[a,b]	7
$C_6H_5HgCHBrI$		$C_6H_5CH_3$	5	62	6
$C_6H_5HgCHI_2$				65	6
$C_6H_5HgCFCl_2$		Et_2O	-20	35[b]	10,11
	NaOMe	THF/MeOH	-40	85–90[b]	12
$C_6H_5HgCFClCO_2Me$	KO-*t*-Bu	THF	-50	44	13
$C_6H_5HgCFBr_2$			-55	35	14
	NaOMe	THF/MeOH	-22	55	14
$C_6H_5HgCFBrCF_3$			-35	64	15,16
$C_6H_5HgCFBrCF_2OEt$	KO-*t*-Bu	THF	0	25	16
$C_6H_5HgCFBrCO_2Et$			-50	8	13
$ClHgCCl_3$		C_6H_6	25	2	17,18
	pyridine	$HCCl_3$		74[d]	19

Table 10.1. (continued)

$RHgCl + HCXYZ + MOR' \longrightarrow RHgCXYZ$

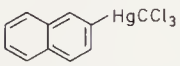
Organomercurial prepared ($RHgCXYZ$)	Base	Solvent	Temp. (°C)	% Isolated yield	Ref.
trans-$ClCH{=}CHHgCCl_3$	KO-*t*-Bu	C_6H_6	5	53	17, 18
cis-$ClCH{=}CHHgCCl_3$			–	10.5	18
$C_6H_5HgCCl_3$			0	51[a]	20
			–	52	17, 18
			10	66[a]	21
	NaOH/KF	$HCCl_3$	25	72[e]	22
p-$NO_2C_6H_4HgCCl_3$	KO-*t*-Bu	dioxane		31	18
p-$CH_3OC_6H_4HgCCl_3$			–	85	18
p-$(CH_3)_2NC_6H_4HgCCl_3$		C_6H_6	–	49	18
		THF	-55	40	23, 24
$C_6H_5CH_2HgCCl_3$			-50	35	24
$C_6H_5CH_2CH_2HgCCl_3$			-40	74	24
2,4,6-$(CH_3)_3C_6H_2HgCCl_3$			0	42	24
		dioxane	–	57	18
$C_6H_5HgCCl_2Br$		Et_2O	-20	–[c]	25
		C_6H_6	10	59[a]	21
	NaOH/KF	CH_2Cl_2	25	64[e]	22
	KO-*t*-Bu	THF	-25	72	8
		C_6H_6	10	81 (crude)	21
p-$FC_6H_4HgCCl_2Br$		Et_2O	-20	77	26
p-$ClC_6H_4HgCCl_2Br$		C_6H_6	–	50	26
p-$CH_3C_6H_4HgCCl_2Br$				75	26
p-$CH_3OC_6H_4HgCCl_2Br$				77	26
		THF/Me_2O	-60	83	23, 24
$C_6H_5CH_2CH_2HgCCl_2Br$		THF	-45	53	24
$C_6H_5HgCCl_2I$		THF/Et_2O	-55	58[f]	27, 28

Table 10.1. (continued)

$RHgCl + HCXYZ + MOR' \longrightarrow RHgCXYZ$

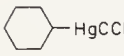
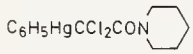
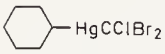
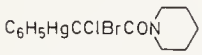
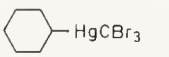
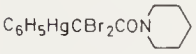
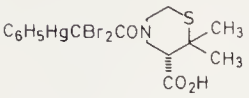
Organomercurial prepared ($RHgCXYZ$)	Base	Solvent	Temp. (°C)	% Isalated yield	Ref.
$C_6H_5HgCCl_2CF_3$		THF	0	75	29, 30
$C_6H_5HgCCl_2CO_2Me$			-50		29, 31
			-65	57	32
$C_6H_5CH_2CH_2HgCCl_2CO_2Me$				71	32
$C_6H_5HgCCl_2CO_2CH_2CH{=}CH_2$			-45	61	31
$C_6H_5HgCCl_2CO_2$-*t*-Bu			-60	64	31
$C_6H_5HgCCl_2CONMe_2$				35	32
			-20	60	33
$C_6H_5HgCCl_2SO_2C_6H_5$			-60	65	32
$C_6H_5HgCClBr_2$		THF/*t*-BuOH	10	66 (crude)[a]	21
		THF	-25	75	8
			-60	60	23, 24
$C_6H_5HgCClBrI$		THF/Et_2O	-65	76	28, 34
$C_6H_5HgCClBrCF_3$		THF	0	86	29, 30
$C_6H_5HgCClBrCO_2Me$			-64	85	31
			-75	48	35
$C_6H_5HgCClICO_2Me$			-60	54	32
$C_6H_5HgCBr_3$	—	—	–	41	18
	NaOH/KF	$HCBr_3$	15	54[e]	22
	KO-*t*-Bu	THF	-25	73	8
		C_6H_6	10	90[a]	21
		THF	-60	60	23, 24
$C_6H_5CH_2CH_2HgCBr_3$				65	24
$C_6H_5HgCBr_2I$		THF/Et_2O		49	28
$C_6H_5HgCBr_2CO_2Me$		THF		55	29, 31

Table 10.1. (continued)

$RHgCl + HCXYZ + MOR' \longrightarrow RHgCXYZ$

Organomercurial prepared (RHgCXYZ)	Base	Solvent	Temp. (°C)	% Isolated yield	Ref.
$C_6H_5HgCBr_2CON$ 		C_6H_6	5	50	36
		THF	-20	80	33
$C_6H_5HgCBr_2CON$ 			low	good	37
$C_6H_5HgCBr_2SO_2C_6H_5$			-60	63	32

[a] Arylmercuric bromide starting material.
[b] Contaminated with diarylmercury.
[c] Arylmercuric chloride or bromide starting material.
[d] Photolysis, 30 hr., not enolytically pure.
[e] Phase transfer catalysis.
[f] Unstable, difficult to purify.

organomercurials prepared by these base-promoted displacement reactions that this approach is not only quite versatile, but the method of choice.

Ethyl trichloroacetate has also been employed as a trichloromethyl source in this type of reaction (Eq. 2) [38]. However, this approach has not been extended to the synthesis of other organomercurials.

$$C_6H_5HgBr + NaOMe + Cl_3CCOEt \longrightarrow \underset{62\%}{C_6H_5HgCCl_3} \qquad (2)$$

The mechanism of these displacement reactions has been the subject of some dispute. Several early publications on the preparation of these reagents suggested that they were formed by carbene insertion into the mercury-halogen bond (Scheme 10.1) [7, 17, 19]. However, syntheses of the following type

Scheme 10.1

$$HCX_3 \longrightarrow :CX_2$$
$$ArHgY + :CX_2 \longrightarrow ArHgCX_2Y$$

clearly implicate the trihalomethyl anion and rule out carbene insertions (Eqs. 3–5). Appropriate blank reactions have been run in each of these cases to eliminate the possibility of carbene insertion, followed by halogen exchange.

$$C_6H_5HgBr + H_2CCl_2 \xrightarrow{KO\text{-}t\text{-}Bu} C_6H_5HgCHCl_2 \qquad (3)\ [6]$$

$$C_6H_5HgBr + HCCl_3 \xrightarrow{KO\text{-}t\text{-}Bu} C_6H_5HgCCl_3 \qquad (4)\ [20, 21]$$

$$C_6H_5HgCl + HCCl_2Br \xrightarrow{KO\text{-}t\text{-}Bu} C_6H_5HgCCl_2Br \qquad (5)\ [20, 21]$$

Preformed organomercury alkoxides, amides, hydroxides and oxides have also been employed in the preparation of α-haloorganomercurials under much the same conditions as described above (Eq. 6). The organomercury alkoxides and amides are prepared as follows (Eqs. 7–11), the first

$$RHgOR' + HCXYZ \longrightarrow RHgCXYZ \quad (6)$$

$$RHgX + MOR' \longrightarrow RHgOR' \quad (7)\ [39, 40]$$

$$RHgOH + HOR' \longrightarrow RHgOR' \quad (8)\ [39, 41]$$

$$RHgOH + R'OCOR' \longrightarrow RHgOR' \quad (9)\ [41]$$

$$(RHg)_2O + R'OCOR' \longrightarrow RHgOR' \quad (10)\ [39, 41]$$

$$RHgOR' + HNR'_2 \longrightarrow RHgNR'_2 \quad (11)\ [42]$$

method being the one most commonly employed. Although subsequent reactions with polyhalomethanes generally give good to excellent yields of α-haloorganomercurials (Table 10.2), this approach appears to offer no advantage over the more direct route mentioned earlier.

Mercuric halides and phenylmercuric chloride have also been treated with a variety of α-haloorganometallic compounds to generate new organomercurials (Eqs. 12, 13). Organolithium, magnesium, -zinc and -chromium

$$HgX_2 \xrightarrow{RCX_2M} XHgCX_2R \xrightarrow{RCX_2M} Hg(CX_2R)_2 \quad (12)$$

$$C_6H_5HgCl \xrightarrow{RCX_2M} C_6H_5HgCX_2R \quad (13)$$

reagents have proven most useful here. The organolithium reagents are best prepared by low temperature metallation of the corresponding alkane or alkyl halide by butyl lithium. For silicon-containing organomercurials, this approach has proven superior to the more direct potassium *tert*-butoxide procedure detailed above [46]. α-Haloorganomagnesium compounds react similarly [47]. For simple haloalkylmercurials the corresponding organozinc compounds are generally most convenient. They can be readily prepared from the corresponding dihaloalkane by either of two procedures (Eqs. 14, 15).

$$CH_2I_2 + Zn \longrightarrow ICH_2ZnI \quad (14)\ [48]$$

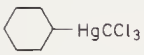
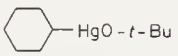
$$CH_3CHI_2 + EtZnI \longrightarrow CH_3CHIZnI \quad (15)\ [49]$$

Similar organochromium compounds can also be prepared by chromium(II) reduction of chloroform and bromoform and subsequent mercuration (Eq. 16). This approach appears less useful, however, for the preparation of

$$Cr(ClO_4)_2 + HCX_3 \longrightarrow CrCH_2X^{2+} \xrightarrow[NaY]{Hg(NO_3)_2} YHgCH_2X \quad (16)$$

Table 10.2. Synthesis of α-Haloorganomercurials via Organomercury Bases

$RHgW + HCXYZ \longrightarrow RHgCXYZ$

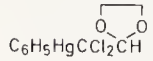
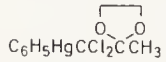
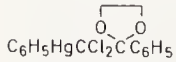
RHgCXYZ	RHgW	% Yield	Ref.
n-PrHgCHCl$_2$	*n*-PrHgO-*t*-Bu	—	43
C$_6$H$_5$HgCHCl$_2$	C$_6$H$_5$HgO-*t*-Bu	50	43
	C$_6$H$_5$HgNEt$_2$	0	42
n-PrHgCCl$_3$	*n*-PrHgO-*t*-Bu	100	44
C$_6$H$_5$HgCCl$_3$	C$_6$H$_5$HgOMe	—	41
	C$_6$H$_5$HgO-*t*-Bu	—	44
	C$_6$H$_5$HgOR[a]	—	39
	C$_6$H$_5$HgOH	—	41
	(C$_6$H$_5$Hg)$_2$O	—	41
	C$_6$H$_5$HgNEt$_2$	75	42
		100	44
C$_6$H$_5$CH$_2$HgCCl$_3$	C$_6$H$_5$CH$_2$HgO-*t*-Bu	—	44
n-PrHgCCl$_2$Br	*n*-PrHgO-*t*-Bu	—	45
C$_6$H$_5$HgCCl$_2$Br	C$_6$H$_5$HgOMe	—	40
	C$_6$H$_5$HgOR[a]	—	39
C$_6$H$_5$HgCClBr$_2$		—	39
C$_6$H$_5$HgCBr$_3$		—	39

[a] R = Me, Et, *n*-Pr, *n*-Bu and *t*-Bu; organomercury alkoxides probably impure, see reference 41.

Table 10.3. Synthesis of α-Haloorganomercurials via α-Haloorganometallics

Organomercurial	Organometallic	Mercuric halide	% Yield	Ref.
ClHgCH$_2$Cl	ClCH$_2$Cr^{2+}	Hg(NO$_3$)$_2$/NaCl	45	50
BrHgCH$_2$Cl		Hg(NO$_3$)$_2$/NaBr	50	50
ClHgCH$_2$Br	BrCH$_2$Cr^{2+}	Hg(NO$_3$)$_2$/NaCl	57	50
BrHgCH$_2$Br		Hg(NO$_3$)$_2$/NaBr	37	50

Table 10.3. (continued)

Organomercurial	Organometallic	Mercuric halide	% Yield	Ref.
$Hg(CH_2Br)_2$	$BrZnCH_2Br$	—	43	51
		$HgBr_2$	59	48
$Hg(CH_2I)_2$	$IZnCH_2I$	$HgCl_2$	67	49
		HgI_2	78	51
		—	86	48
$Hg(CD_2I)_2$	$IZnCD_2I$	HgI_2	76	48
$Hg(CHICH_3)_2$	$IZnCHICH_3$	$HgCl_2$	60	49
$Hg(CHBrSiMe_3)_2$	$LiCHBrSiMe_3$	$HgBr_2$	44	47
$Hg(CHISiMe_3)_2$	$IZnCHISiMe_3$	$HgCl_2$	44	49
$Hg[CH(SiMe_3)_2]_2$	$LiCH(SiMe_3)_2$	$HgBr_2$	16	47
$BrHgCCl_2SiMe_3$	$LiCCl_2SiMe_3$		—	52
$Hg(CCl_2SiMe_3)_2$			34–35	46,52
$Hg[CCl(SiMe_3)_2]_2$	$LiCCl(SiMe_3)_2$	$HgCl_2$	28,58	46
		C_6H_5HgCl	37	46
$Hg(CBr_2SiMe_3)_2$	$LiCBr_2SiMe_3$	—	10	47
	$ClMgCBr_2SiMe_3$	$HgCl_2$	25	47
$Hg(CCl{=}CH_2)_2$	$LiCCl{=}CH_2$		63	53
$Hg(CBr{=}CMe_2)_2$	$LiCBr{=}CMe_2$		75	54
$C_6H_5HgCCl_2CH_3$	$LiCCl_2CH_3$	C_6H_5HgCl	67	55
$C_6H_5HgCCl_2C_6H_5$	$LiCCl_2C_6H_5$		61	56
$C_6H_5HgCCl_2CH(OEt)_2$	$LiCCl_2CH(OEt)_2$		52	57
			30	57
			42	57
			64	57
$C_6H_5HgCCl_2Pb(C_6H_5)_3$	$LiCCl_2Pb(C_6H_5)_3$		—	58

simple halomethylmercurials than use of the zinc reagents. Representative yields for all these organometallic procedures are tabulated in Table 10.3.

As indicated in Chap. II, Sect. B, a number of polyhaloalkanes react directly with mercury or mercury amalgams to give the corresponding α-haloorganomercurials. However, it appears that only the following reactions afford compounds useful as divalent carbon transfer reagents (Eq. 17–20).

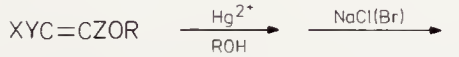
(17) [59]

(18) [60, 61]

(19) [62, 63]

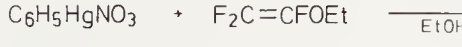
(20) [64]

The mercuration of alkenes is an especially valuable route to organomercurials. A number of examples of this reaction have been discussed earlier in Chap. II, Sect. I, and the tremendous synthetic utility of these reactions will be covered in a separate monograph. There are several applications of this reaction, however, which are pertinent to a discussion of divalent carbon transfer reactions and they deserve attention here. α-Halomercurated esters can be prepared using potassium *tert*-butoxide displacement reactions, but the yields are sometimes low. In those instances the mercuration of vinyl halides, particularly halovinyl ethers, in alcohol solvent provides a useful alternative (Eq. 21) (Table 10.4). In several instances symmetrization to the



(21)

corresponding dialkylmercurial is observed. In those cases treatment with diphenylmercury provides a simple direct route to the corresponding phenylmercurials. Direct mercuration with phenylmercuric nitrate has also been examined, but only the dialkylmercurial was formed (Eq. 22) [66].



(22)

The decarboxylation of mercury carboxylates is another important route to organomercurials (Chap. II, Sect. M). It has proven especially valuable in the synthesis of trihalomethylmercurials, reagents useful in divalent carbon transfer reactions. For example, mercuric trifluoroacetate undergoes thermal decarboxylation to provide either the mono- [70–72] or dialkylmercurial [73, 74] depending upon the reaction conditions employed (Eq. 23). Tri-

(23)

fluoromethylmercuric trifluoroacetate is in turn readily converted to the corresponding bromide [72] or iodide [71] (Eq. 24). The latter compound is a

(24)

Table 10.4. Synthesis of α-Mercurated α-Halocarbonyl Compounds via Mercuration of Vinyl Halides

$$XYC{=}CZOR \xrightarrow{Hg^{2+}} \xrightarrow[\text{or NaBr}]{NaCl} ClHgCXYCO_2R\ (Br)$$

Organomercurial	Vinyl halide	Mercury salt	% Yield	Ref.
$ClHgCHFCO_2Me$	$FHC{=}CF_2$	$Hg(NO_3)_2$	83[a]	65
$ClHgCHClCO_2Et$	$ClHC{=}CClOEt$	$Hg(OAc)_2$	66	32
$ClHgCF_2CO_2Et$	$F_2C{=}CFOEt$	$HgCl_2$	84	66
		$Hg(NO_3)_2$	93	66
$BrHgCF_2CO_2Et$		$Hg(OAc)_2$	64	66
		$HgBr_2$	low	66
$ClHgCFClCO_2Et$	$FClC{=}CFOEt$	$Hg(NO_3)_2$	26[b]	67
$ClHgCFCF_3CO_2Et$[b,c]	$CF_3FC{=}CFOEt$	$Hg(OAc)_2$	65	67
$Hg(CHClCO-C_6H_5)_2$	$ClHC{=}C(OSiMe_3)-C_6H_5$	$Hg(OAc)_2/HgO$	28	68
$Hg(CF_2CO_2Et)_2$	$F_2C{=}CFOEt$	$C_6H_5HgNO_3$	—	65
$Hg(CCl_2CO_2Me)_2$	$Cl_2C{=}CClOMe$	$Hg(OAc)_2$	91	32
$C_6H_5HgCFClCO_2Et$[c]	$FClC{=}CFOEt$	$Hg(NO_3)_2$	67[d]	13,69
$C_6H_5HgCFBrCO_2Et$[c]	$FBrC{=}CFOEt$		49[d]	13

[a] Isolated as the alkylmercuric nitrate.
[b] Partial symmetrization occurs; mercuric chloride added during work-up.
[c] Obtained as a 1:1 sodium chloride adduct.
[d] Partial symmetrization occurs; diphenylmercury added during work-up.

useful difluorocarbon transfer reagent, and both compounds are valuable intermediates in the preparation of $C_6H_5HgCF_3$. Other mercury polyfluorocarboxylates have likewise been decarboxylated to provide the corresponding mono- [70] or dialkylmercury [73] compounds. However, conflicting reports exist on the ability to thermally decarboxylate arylmercury trifluoroacetates to the corresponding aryltrifluoromethylmercury compounds [72, 74, 75].

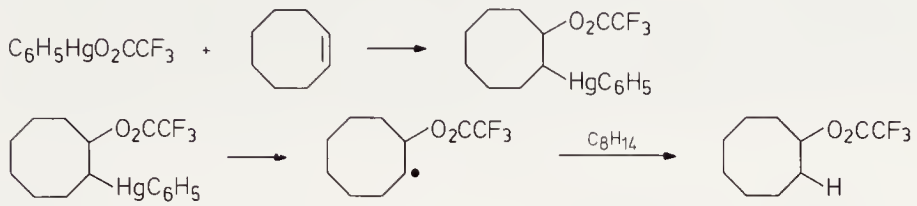
Attempted reactions involving in situ sequential decarboxylation and difluorocarbon transfer employing cyclooctene and phenylmercuric trifluoroacetate or chlorodifluoroacetate provided only the corresponding cyclooctyl esters in high yield and none of the desired difluorocyclopropane (Eq. 25)

$$C_6H_5HgO_2CCF_2X + \bigcirc \xrightarrow{\Delta} \bigcirc\!-\!O_2CCF_2X \qquad (25)$$

X = F 83%
Cl 86%

[76]. It has been suggested that this reaction proceeds as follows (Scheme 10.2). Such reactions may have some advantages over direct HO_2CCF_2X additions to olefins which are frequently accompanied by carbonium ion rearrangements [77].

Scheme 10.2



Although no organomercurial is apparently formed upon reaction of mercuric oxide and trichloroacetic acid in water [78], sodium trichloroacetate reacts with mercuric salts in refluxing DME to give good yields of either trichloromethylmercuric chloride or bromide, or *bis*(trichloromethyl)mercury (Eqs. 26, 27). The direct thermolysis of mercuric trichloroacetate also affords

$$HgX_2 + NaO_2CCCl_3 \longrightarrow XHgCCl_3 \quad (X = Cl\ 76\%,\ Br\ 44\%) \qquad (26)\ [79, 80]$$

$$HgX_2 + 2\,NaO_2CCCl_3 \longrightarrow Hg(CCl_3)_2 \quad (X = Cl\ 71\%,\ OAc\ 54\%) \qquad (27)\ [80]$$

low yields of trichloromethylmercuric chloride [81]. Despite an early report that phenylmercuric trichloroacetate gives only phenylmercuric chloride upon photolysis and thermolysis [60], recent reports indicate that the reactions of arylmercuric salts and metal trichloroacetates [82], particularly phenylmercuric chloride and sodium trichloroacetate [79, 80, 83], give good yields of the corresponding aryltrichloromethylmercurials (Eq. 28). Tribromomethylmercurials can be prepared in similar fashion (Eqs. 29, 30) [84], although analogous reactions of phenylmercuric salts and sodium bromodichloroacetate, dibromochloroacetate and tribromoacetate apparently fail [39].

$$C_6H_5HgCl + NaO_2CCCl_3 \xrightarrow[DME]{\triangle} C_6H_5HgCCl_3 \quad (65\%) \qquad (28)\ [83]$$

$$HgCl_2 + NaO_2CCBr_3 \longrightarrow BrHgCBr_3 + Hg(CBr_3)_2 \qquad (29)$$

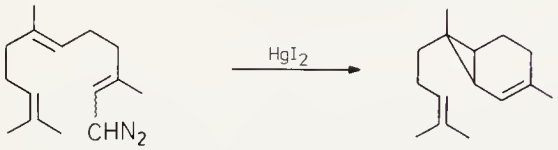
$$HgX_2 + 2NaO_2CCBr_3 \xrightarrow[H_2O]{5\text{-}10^\circ C} Hg(CBr_3)_2 \quad (X = Cl, OAc;\ 85\text{-}90\%) \qquad (30)$$

As indicated in Chap. II, the reaction of diazoalkanes and mercury salts provides a useful route to organomercurials. Depending upon the stoichio-

metry of the reaction, diazomethane reacts with mercuric chloride [85] or bromide [86] to give either the monoalkyl- or dialkylmercurial (Eq. 31).

$$HgX_2 \xrightarrow{CH_2N_2} XHgCH_2X \xrightarrow{CH_2N_2} Hg(CH_2X)_2 \quad (31)$$

Using similar conditions with mercuric iodide, one apparently obtains only low yields of $Hg(CH_2I)_2$. Corey has reported that the analogous reaction of mercuric iodide and unsaturated diazoalkane *1* leads directly to cyclopropane *2* (Eq. 32) [87]. Several other examples of successful diazoalkane insertions into mercury halide bonds are known (Eqs. 33–36). The preparation



1 *2* (32)

$$HgCl_2 + N_2CHCF_3 \longrightarrow Hg(CHClCF_3)_2 \quad (33)\ [88]$$

$$HgCl_2 + N_2C(C_6H_5)_2 \longrightarrow ClHgC(Cl)(C_6H_5)_2 \quad (34)\ [85, 89]$$

$$Cl_3CHgBr + CH_2N_2 \longrightarrow Cl_3CHgCH_2Br \quad (35)\ [90]$$

$$C_6H_5CH_2HgX + CH_2N_2 \longrightarrow C_6H_5CH_2HgCH_2X \quad (36)$$
X = Cl [85], I [91]

of benzyl(iodomethyl)mercury in this fashion is significant, as this organomercurial has proven to be a very valuable methylene transfer reagent. Analogous reactions of arylmercuric chlorides and diazomethane afford insertion products, but are accompanied by disproportionation (Eq. 37) [85].

$$2ArHgCl + 2CH_2N_2 \longrightarrow Ar_2Hg + Hg(CH_2Cl)_2 \quad (37)$$

Dichlorocarbene can be inserted into the carbon-mercury bond of dialkylmercurials to provide an alternate route to α-haloorganomercurials (Eq. 38) [55, 92–94], but diarylmercurials apparently do not undergo this

$$R_2Hg \xrightarrow[NaOMe]{Cl_3CCO_2Et} RCCl_2HgR \quad (38)$$

reaction [94]. Increasing amounts of carbon-hydrogen insertion products occur as the β-hydrogen is changed from primary to tertiary (Eq. 39)

$$(RCH(R')CH_2)_2Hg \longrightarrow RCH(R')CH_2HgCH_2CR(R')(CCl_2H) \quad (39)$$

[93–96]. This reaction occurs with some retention of configuration. Unfortunately, these α-halo compounds have not yet proven useful as divalent carbon transfer reagents.

A number of useful organomercurial divalent carbon transfer reagents have been prepared through chemical modification of phenyl(halomethyl)-mercurials. For example, iodide displacement processes have provided useful syntheses of phenyl(chloroiodomethyl)mercury and phenyl(diiodomethyl)-mercury (Eqs. 40, 41) [6]. The former preparation is apparently superior to

$$C_6H_5HgCHClBr + NaI \longrightarrow C_6H_5HgCHClI \quad (40)$$

$$C_6H_5HgCHX_2 + 2NaI \longrightarrow C_6H_5HgCHI_2 \quad (41)$$
$$X = Cl, Br$$

that involving potassium *tert*-butoxide, chloroiodomethane and phenylmercuric chloride. One cannot, however, obtain pure $C_6H_5HgCHBrI$ by analogous iodide displacement on $C_6H_5HgCHBr_2$.

Similar fluorine displacement reactions have been achieved using a hydrofluoric acid adduct of phenylmercuric fluoride (Eqs. 42, 43) [97, 98].

$$C_6H_5HgCCl_2Br \xrightarrow{C_6H_5HgF\cdot HF} C_6H_5HgCCl_2F \quad (42)$$

$$C_6H_5HgCX_3 \xrightarrow[\substack{X=Cl\ 53\text{-}55\% \\ Br\ 60\text{-}75\%}]{C_6H_5HgF\cdot HF} C_6H_5HgCF_3 \quad (43)$$

Attempted partial fluorination of $C_6H_5HgCBr_3$, $C_6H_5HgCClBr_2$ and $C_6H_5HgCFBr_2$ were unsuccessful however, as $C_6H_5HgCF_3$ was always obtained as the major product. The partially fluorinated compounds are apparently more reactive than the starting materials. On the other hand, $C_6H_5HgCHClBr$ and $C_6H_5HgCHBr_2$ proved unreactive. Mechanistically, mercury-assisted nucleophilic substitution at carbon has been suggested. The relative reactivity of the organomercurials evidently parallel their ease of divalent carbon extrusion [34, 99]: $C_6H_5HgCF_2Br > C_6H_5HgCFBr_2 > C_6H_5HgCBr_3 > C_6H_5HgCCl_3 > C_6H_5HgCHBr_2$, $C_6H_5HgCHClBr$. These fluorination procedures unfortunately tend to be somewhat tedious and alternate routes to the above compounds have generally proven more convenient.

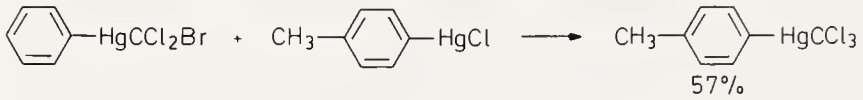
Several analogous chlorination reactions using phenylmercuric chloride have also been reported (Eqs. 44–46). In these reactions, however, it appears

$$C_6H_5HgCHClBr \xrightarrow{C_6H_5HgCl} \underset{79\%}{C_6H_5HgCHCl_2} \quad (44)\ [100, 101]$$

$$C_6H_5HgCCl_2Br \xrightarrow{C_6H_5HgCl} \underset{62\ \%}{C_6H_5HgCCl_3} \quad (45)\ [100, 101]$$

$$C_6H_5HgCFBrCO_2Et \xrightarrow{C_6H_5HgCl} \underset{55\ \%}{C_6H_5HgCFClCO_2Et} \quad (46)\ [13]$$

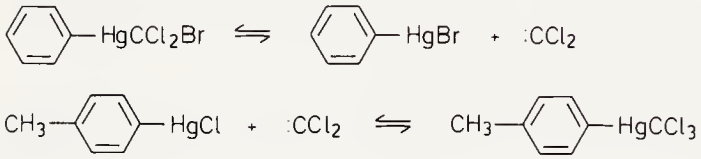
that a divalent carbon species is being transferred between organomercurials, rather than the organomercurials undergoing simple halogen exchange. This is clearly demonstrated by the following experiment (Eq. 47) [100, 101]. The



(47)

fact that these reactions generally occur only at temperatures at which phenyl(halomethyl)mercurials cyclopropanate olefins, strongly suggests that reversible carbene transfer processes are responsible for these reactions (Scheme 10.3). Insertion of the divalent carbon species into the mercury-

Scheme 10.3



halogen bond appears to be competitive with addition to carbon-carbon double bonds. While a carbene mechanism is consistent with all of the facts, bimolecular carbon transfer reactions between organomercurials cannot be entirely ruled out in the above chlorination reactions.

Phenyltrihalomethylmercurials can also be reduced to the corresponding dihalomethyl compounds, but the yields are generally not very good and these compounds are best prepared other ways (Eqs. 48–50) [102, 103]. These

$$C_6H_5HgCBr_3 \xrightarrow[\sim 20\%]{(n\text{-}Bu)_3SnH} C_6H_5HgCHBr_2 \qquad (48)$$

$$C_6H_5HgCClBr_2 \xrightarrow[\sim 20\%]{(n\text{-}Bu)_3SnH} C_6H_5HgCHClBr \qquad (49)$$

$$C_6H_5HgCCl_2Br \xrightarrow[40\text{-}85\%]{(n\text{-}Bu)_3SnH} C_6H_5HgCHCl_2 \qquad (50)$$

results are in sharp contrast to the corresponding reactions of germanes and silanes in which a divalent carbon species is inserted into the metal-hydrogen bond. This subject will be discussed in greater detail later in this chapter.

Finally, the preparation of phosphonate-containing organomercurials via reaction of phenyl(halomethyl)mercurials and trialkylphosphites deserves mention (Eqs. 51, 52) [104]. Unfortunately, these reagents have not proved useful as divalent carbon transfer reagents.

$$C_6H_5HgCCl_2Br + P(OR)_3 \longrightarrow C_6H_5HgCCl_2\overset{O}{\overset{\|}{P}}(OR)_2 \qquad (51)$$

$$C_6H_5HgCHClBr + P(OR)_3 \longrightarrow C_6H_5HgCHCl\overset{O}{\overset{\|}{P}}(OR)_2 \qquad (52)$$

Halomethylmercuric halides are often readily available via the simple procedures outlined earlier. Unfortunately, these compounds have not always proved as useful as divalent carbon transfer reagents as the analogous phenyl(halomethyl)mercurials. It is therefore desirable to convert these simple halomercurials to the corresponding phenylmercurials. This has been accomplished using phenylmagnesium [60, 61], -tin [60] and -boron [7] compounds (Eqs. 53–55). More commonly, however, diphenylmercury and related compounds are employed (Eqs. 56–60). In the first example (Eq. 56),

$$C_6H_5MgBr + BrHgCCl_3 \longrightarrow C_6H_5HgCCl_3 \quad (53)$$

$$(C_6H_5)_2SnCl_2 + BrHgCCl_3 \longrightarrow C_6H_5HgCCl_3 \quad (54)$$

$$C_6H_5B(OH)_2 + ClHgCHCl_2 \longrightarrow C_6H_5HgCHCl_2 \quad (55)$$

$$XHgCF_3 \xrightarrow{(C_6H_5)_2Hg} C_6H_5HgCF_3 \quad (56)$$

X = Br [72], I [71]

$$ClHgCFCl_2 \xrightarrow{(C_6H_5)_2Hg} C_6H_5HgCFCl_2 \quad (57)\ [11]$$

$$ClHgCHClCO_2Et \xrightarrow{(C_6H_5)_2Hg} C_6H_5HgCHClCO_2Et \quad (58)\ [32]$$

$$BrHgCCl{=}CCl_2 \xrightarrow{(C_6H_5)_2Hg} C_6H_5HgCCl{=}CCl_2 \quad (59)\ [105]$$

$$(C_6H_5CH_2CH_2)_2Hg + Hg(CCl_2CO_2Me)_2 \longrightarrow 2C_6H_5CH_2CH_2HgCCl_2CO_2Me \quad (60)\ [32]$$

this reaction constitutes the last step in the recommended procedure for the preparation of phenyl(trifluoromethyl)mercury. The second reaction (Eq. 57) illustrates a useful, though round-about way of purifying phenyl(dichlorofluoromethyl)mercury. This compound is obtained contaminated with diphenylmercury when using the potassium *tert*-butoxide/trihalomethane procedure. It can be purified best by cleavage to the organomercuric chloride, which is isolated and then treated with diphenylmercury to regenerate the organomercurial (Eq. 61).

$$C_6H_5HgCFCl_2 \xrightarrow{HCl} ClHgCFCl_2 \xrightarrow{(C_6H_5)_2Hg} C_6H_5HgCFCl_2 \quad (61)$$

C. Synthesis of Cyclopropanes

The most important synthetic application of α-haloorganomercurials has been in the synthesis of cyclopropanes. Under relatively mild, neutral reaction conditions these compounds transfer a divalent carbon species stereospecifically to olefins to provide good yields of cyclopropanes (Eq. 62). Although Nes-

$$C_6H_5HgCX_3 + \text{cyclohexene} \xrightarrow{\Delta} \text{bicyclo[4.1.0]heptane, 7,7-dihalo} + C_6H_5HgX \quad (62)$$

Table 10.5. Cyclopropanation of Cyclohexene

Transfer species	Organomercurial employed	Reaction temp., °C	Reaction time[a]	% Yield of bicycloheptane[b,c]	Ref.
CH_2	$IHgCH_2I$	80	8d	24	106,107
	$Hg(CH_2Br)_2$		8d	74	106,107
	$Hg(CH_2I)_2$	85	6h	(98)	108
	$C_6H_5CH_2HgCH_2I$	90	4h	80	91
CHCl	$C_6H_5HgCHCl_2$	140	60h	57	99
	$C_6H_5HgCHClBr$	84	6d	63	99
		130	10h	95	9
CHBr	$C_6H_5HgCHBr_2$	132	11h	86	9
CFCl	$C_6H_5HgCFCl_2$	80	20h	84	12
			48h	86	10,11
CFBr	$C_6H_5HgCFBr_2$	25	3d	90	14,34
		80	20m	88	14,34
$CFCF_3$	$C_6H_5HgCFBrCF_3$	155	24h	87	15,16
$CFCO_2Me$	$C_6H_5HgCFClCO_2Me$	135	60h	47	13
			48h	(85-88)	13
$CFCO_2Et$	$C_6H_5HgCFClCO_2Et$	132	24h	69	13
	$C_6H_5HgCFBrCO_2Et$	125	20h	59	13
CCl_2	$ClHgCCl_3$	250	15m	36	80
	$Hg(CCl_3)_3$			25	80
	n-$PrHgCCl_3$	80	8h	82	45
	i-$PrHgCCl_3$		3h	71	109
	$C_6H_5HgCCl_3$		36-48h	89	110
			27.5	99	24
			6.5h	92	23, 24
	$C_6H_5CH_2CH_2HgCCl_3$		14h	65	24
	2,4,6-$(CH_3)_3C_6H_2HgCCl_3$		36h	(75)	24
	n-$PrHgCCl_2Br$	25	3d	70	45
		40	5h	85	45

Table 10.5. (continued)

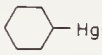
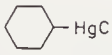
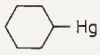
Transfer species	Organomercurial employed	Reaction temp., °C	Reaction time[a]	% Yield of bicycloheptane[b,c]	Ref.
	$C_6H_5HgCCl_2Br$	25	18 d	72	111
		80	2 h	89	110
		25	49 h	95	23, 24
		80	6 m	96	23, 24
	$C_6H_5CH_2CH_2HgCCl_2Br$		15 m	77	24
	$C_6H_5HCCl_2I$	0	8 d	71	27, 28
		24	24 h	89	27, 28
		80	< 1 m	85	27, 28
$CClBr$	$C_6H_5HgCClBr_2$	25	16 d	71	111
		80	—	84	110, 112
		25	3 d	87	23, 24
		80	7 m	85	23, 24
	$C_6H_5HgCClBrI$	25	4 d	75	28
		80	< 10 m	81	28
$CClCF_3$	$C_6H_5HgCClBrCF_3$	140	9 d	41	30
		138	5.5 d	(74)	29, 30
$CClCO_2Me$	$C_6H_5HgCCl_2CO_2Me$	110 - 135	7 d	42	31
		130	11 d	(73)	29
			57 h	(78)	32
	$C_6H_5CH_2CH_2HgCCl_2CO_2Me$	140	44 h	(26)	32
	$C_6H_5HgCClBrCO_2Me$	101	8 h	44	29, 31
		127	24 h	(67)	31
	$C_6H_5HgCClICO_2Me$	80	8 h	(10)	32
		135	4 h	(10)	32
$CClC_6H_5$	$C_6H_5HgCCl_2C_6H_5$	60 - 80	15 - 48	—[d]	56
$CClSiMe_3$	$Hg(CCl_2SiMe_3)_2$	120	6 d	24	113
$CClSO_2C_6H_5$	$C_6H_5HgCCl_2SO_2C_6H_5$	140	8 d	(49)	32

Table 10.5. (continued)

Transfer species	Organomercurial employed	Reaction temp., °C	Reaction time[a]	% Yield of bicycloheptane[b,c]	Ref.
CBr_2	$C_6H_5HgCBr_3$	25	15d	69	111
		80	2h	88	1,110
		25	48h	50	23, 24
		80	10m	40	23, 24
	$C_6H_5CH_2CH_2HgCBr_3$	25	96h	10	24
		80	20m	24	24
	$C_6H_5HgCBr_2I$	25	7d	65	28
$CBrCO_2Me$	$C_6H_5HgCBr_2CO_2Me$	101	24h	12	31
		130	43h	(50)	29, 31
$CBrSO_2C_6H_5$	$C_6H_5HgCBr_2SO_2C_6H_5$	135	48h	(20)	32
$C{=}CCl_2$	$C_6H_5HgCCl{=}CCl_2$	25	—	20[e]	105

[a] d = days, h = hours, m = minutes.
[b] Yield based on transfer of one carbon group from the organomercurial.
[c] Yields in parentheses refer to synthesis of bicyclononanes from cyclooctene.
[d] Pertinent yields not available; 24–67 % yields reported for other simple olefins.
[e] Reaction carried out photochemically.

meyanov and co-workers in 1957 first reported that the thermal decomposition of phenyl(trichloromethyl)mercury results in elimination of the dichlorocarbon moiety [60], it was not until 1962 with the report of Seyferth that the synthetic utility of these reagents for cyclopropane formation was first appreciated [1]. Since that time a tremendous number of examples of this reaction have been reported, and the synthetic utility of this reaction has been extensively examined by Seyferth and co-workers. Table 10.5 indicates the vast number of these reagents which have been examined, the reaction conditions required to effect cyclopropanation, and some representative yields using cyclohexene as an example. A comparison of these results will give the reader a good feel for the relative merits of each of the reagents.

In general, these reactions are run in a hydrocarbon solvent, most commonly benzene, at temperatures from 25 to 130 °C (sealed tube) depending on the organomercurial reagent employed. In one instance photolysis proved useful when the organomercurial turned out to be too thermally stable [105]. Although in many cases the olefin is used in excess and yields are reported based on starting organomercurial, an equal molar ratio of olefin and organomercurial can be employed with success. The rate of reaction can be conveniently followed by watching the disappearance of the organomercurial reagent by TLC, monitoring the precipitation of the mercury halide product, or analyzing the cyclopropane product by gas chromatography. The cyclo-

propane is readily isolated by filtering off the insoluble organomercuric halide and evaporating the solvent. When phenyl(halomethyl)mercury compounds are employed, the recovered phenylmercuric halide can be reused in the preparation of further reagent.

The real value of this reaction arises from its ability to accommodate a wide range of olefins. Numerous simple mono-, di-, tri- and tetrasubstituted olefins have been shown to undergo facile cyclopropanation using these reagents. With simple sterically unhindered olefins the following relative reactivities towards $C_6H_5HgCCl_2Br$ have been observed [114]: $R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CH_2 > CH_2{=}CH_2$. The selectivity of $C_6H_5HgCX_3$ (X = F, Cl, Br) towards a mixture of isobutylene and 2-methyl-2-butene as a function of temperature has also been studied [115].

Though among the least reactive of the simple olefins, ethylene still gives good results upon cyclopropanation (Eq. 63) [110, 116]. These results are significant, because it has been reported that the chloroform-potassium *tert*-butoxide approach to 1,1-dichlorocyclopropane fails to give any of the desired product [117].

$$H_2C{=}CH_2 \xrightarrow{C_6H_5HgCX_2Br} \underset{\substack{X=Cl \quad 65\% \\ Br \quad 53\%}}{H_2C\!\!<\!\!\begin{matrix}CX_2\\ \\ CH_2\end{matrix}} \qquad (63)$$

From the above-mentioned relative reactivities, steric effects would appear to be minimal. However, substantial steric crowding about the double bond results in decreased rates of reaction as indicated by the following relative reactivities [118]. However, even in sterically crowded systems good yields can still be obtained. For example, 3,3-dimethyl-1-butene, which gives only a

$CH_3CH_2CH_2CH_2CH_2CH{=}CH_2$	$CH_3CH_2C(CH_3)_2CH{=}CH_2$	$CH_3CH_2C(CH_3)_2CH{=}CH_2$
1.00	0.78	0.043

7% yield of the corresponding dibromocyclopropane when using bromoform and potassium *tert*-butoxide, reacts with $C_6H_5HgCBr_3$ to give a 45% yield of the desired dibromocyclopropane (Eq. 64) [119]. Even more highly hindered 3,3-dimethyl-1-pentene gives good yields (Eq. 65) [120]. Sterically

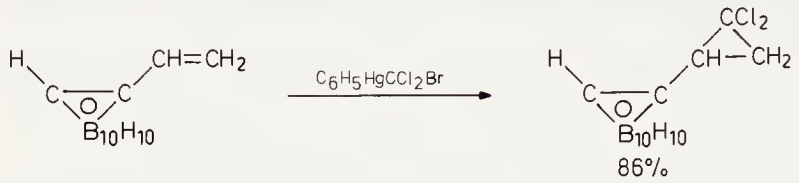
$$CH_3{-}C(CH_3)_2{-}CH{=}CH_2 \xrightarrow{C_6H_5HgCBr_3} CH_3{-}C(CH_3)(CBr_2){-}CH{-}CH_2 \qquad (64)$$

45%

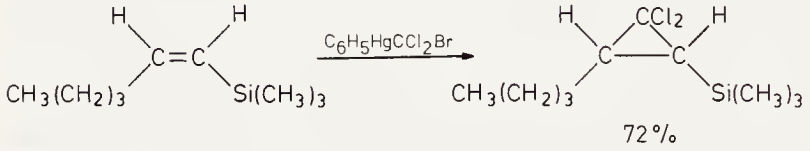
$$CH_3CH_2{-}C(CH_3)_2{-}CH{=}CH_2 \xrightarrow{C_6H_5HgCX_2Br} CH_3CH_2{-}C(CH_3)(CX_2){-}CH{-}CH_2 \qquad (65)$$

X = Cl 66%
Br 44%

crowded vinylcarboranes [121] and -silanes [120, 122] also undergo smooth reactions (Eqs. 66, 67). The carborane transformation is especially interest-

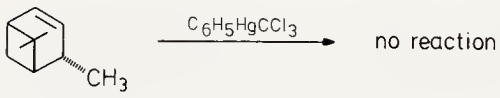


(66) [121]



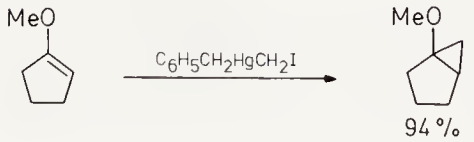
(67) [122]

ing when one considers that the carborane group also has an electron-withdrawing inductive effect, further decreasing the reactivity of the double bond towards the electrophilic reagent. In the vinylsilane example, it should be noted that chloroform and sodium hydroxide under phase transfer conditions [123] give an equally high yield of cyclopropane [122]. On the other hand, *trans*-δ-pinene is so highly hindered that cyclopropanation apparently fails completely even with the organomercurial reagents (Eq. 68) [124].

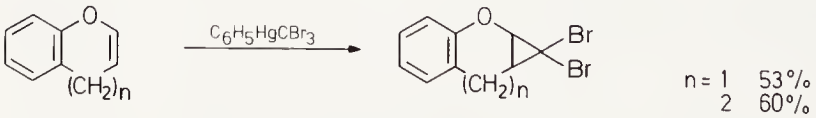


(68)

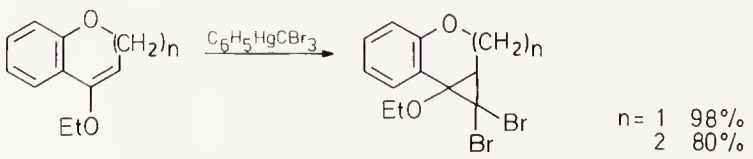
A large number of functionally substituted olefins have been shown to undergo facile cyclopropane formation using organomercurial reagents. As with most other reagents which generate electrophilic carbene intermediates, the organomercurial reagents are quite effective on electron-rich olefins. Thus, a variety of vinyl ethers have been converted to cyclopropanes in this manner (Eqs. 69–71) [91, 125, 126]. Tetramethoxyethylene also reacts, but sub-



(69) [91]

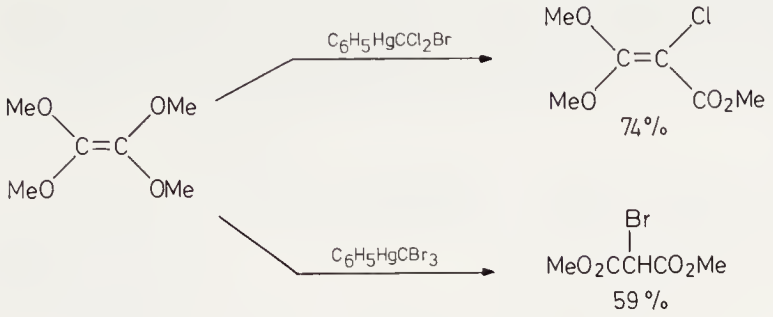


(70) [125]



(71) [125]

sequent rearrangements result in acyclic products (Eqs. 72, 73) [127]. The vinyl chloride is readily hydrolyzed to dimethyl chloromalonate, suggesting the intermediacy of the analogous vinyl bromide in the latter transformation.

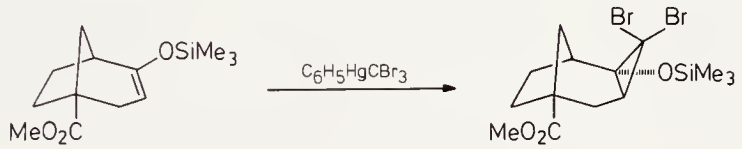


(72)

(73)

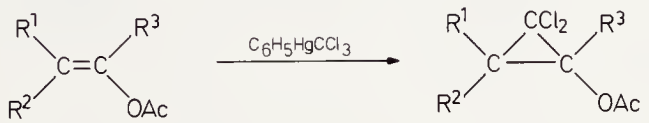
The desired 1,1-dichloro-2,2,3,3-tetramethoxycyclopropane is best prepared using chloroform and potassium *tert*-butoxide at −10 °C [127]. At 110 °C it rearranges in 91 % yield to the vinyl chloride observed in Eq. 72.

Silyl enol ethers undergo divalent carbon transfer reactions also (Eq. 74) [128]. Dibromocyclopropanes of this type are useful intermediates for ring expansion as will be described in a latter section in this chapter.



(74)

The cyclopropanation of enol acetates has been studied extensively. Numerous examples of this reaction are known and the products are valuable intermediates in ring expansion sequences and heterocyclic synthesis. Some simple examples will be presented here and further applications will be taken up in appropriate sections later in this chapter. Vinyl acetate itself has been converted into a number of different dihalocyclopropanes using each of the following organomercurials: $C_6H_5HgCCl_2Br$ (85%) [110], $HgCCl_2Br$ (81%) [24], $C_6H_5HgCCl_2I$ (38%) [28], $C_6H_5HgCFCl_2$ (86%) [11], $C_6H_5HgCFBr_2$ (95%) [14], $C_6H_5HgCClBr_2$ (74%) [112]. The high yields of cyclopropanes from this base-sensitive olefin point out the preparative value of this approach. The basic conditions inherent to most other procedures simply would not allow this transformation. A number



(75)

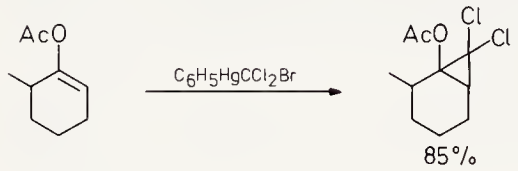
R^1	R^2	R^3	%Yield	Ref.
H	H	CH_3	78	129
H	H	C_6H_5	70	130
CH_3	H	CH_3	72	131
H	C_6H_5	C_6H_5	74	129

of other acyclic enol acetates have been similarly converted to cyclopropanes as indicated by the following examples (Eq. 75). The resulting cyclopropanes are useful intermediates in pyrazole and pyrimidine syntheses.

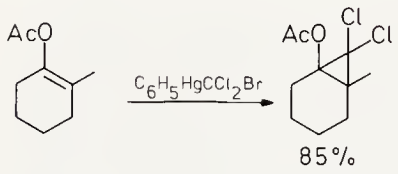
Cyclic enol acetates are also readily cyclopropanated to give products useful in ring expansion procedures (Eqs. 76–85). It is noteworthy that 1-cyclohexenyl acetate gives a 75% yield of dichlorocyclopropane upon treatment with $C_6H_5HgCCl_3$, but only 18% when NaO_2CCCl_3 is employed [131].

(76)

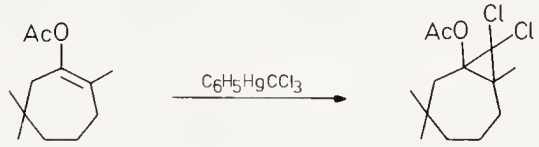
			Ref.
$C_6H_5HgCCl_3$	n=6	75%	131
	8	80%	131
	12	57%	129
$C_6H_5HgCCl_2Br$	n=5	—	132
	6	85%	132
	7	72%	132



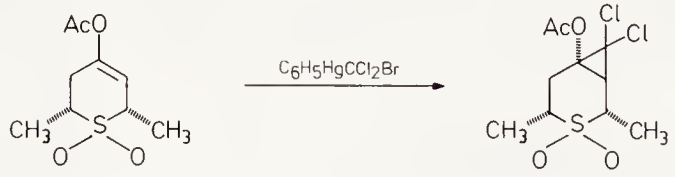
(77) [132]



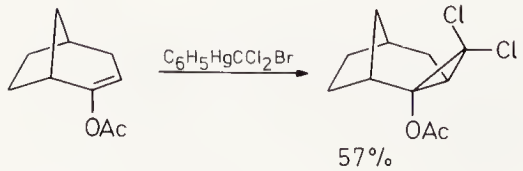
(78) [132]



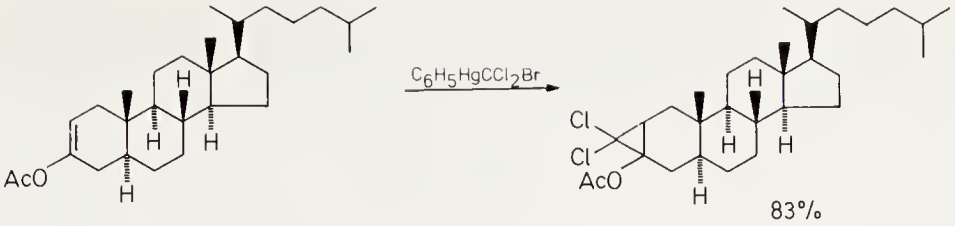
(79) [133]



(80) [134]

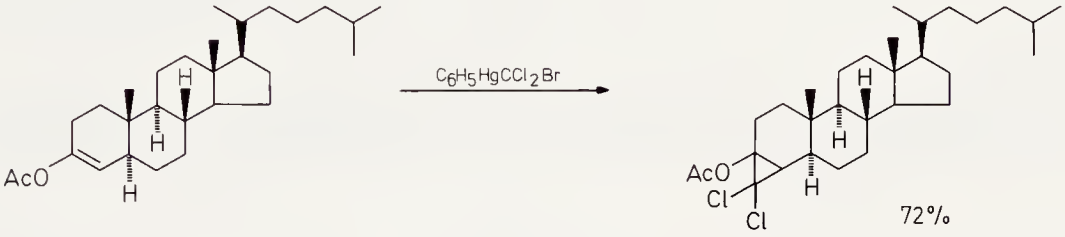


(81) [135]

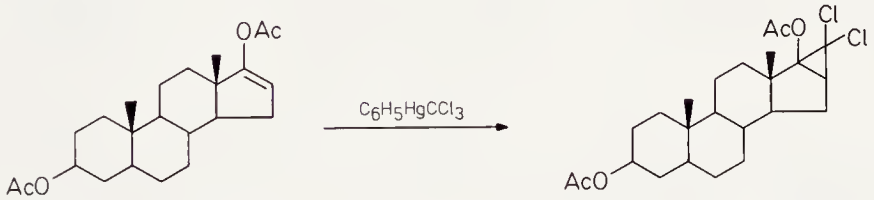


(82) [132]

(83) [136]

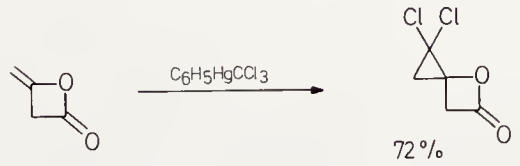


(84) [132]

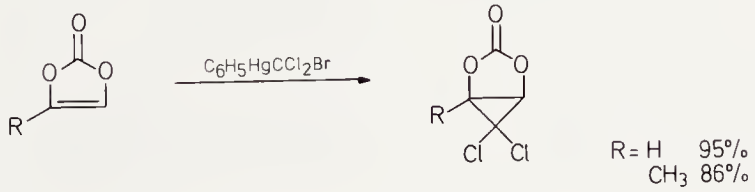


(85) [136]

There are other examples of cyclic unsaturated esters undergoing analogous cyclopropane formation (Eqs. 86, 87).



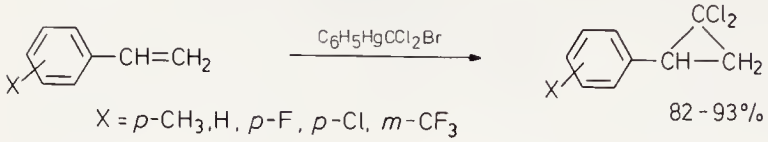
(86) [137]



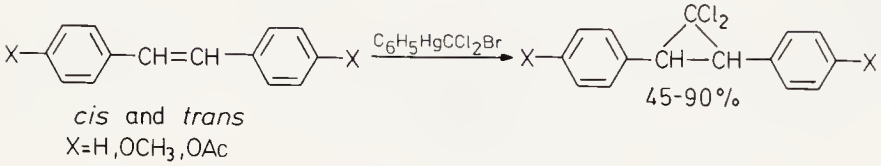
(87) [138]

While many of the other common reagents for converting olefins to cyclopropanes fail with electron-poor olefins, the organomercurial reagents often give excellent yields. Thus, a number of substituted styrenes, stilbenes and other aromatic olefins have been converted to the corresponding

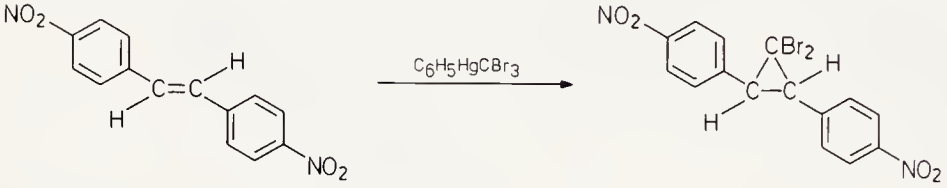
dihalocyclopropanes in high yields (Eqs. 88–92). In the second example (Eq. 89), a phase transfer approach was also used except where solubility



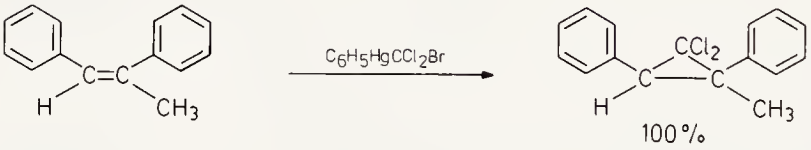
(88) [26]



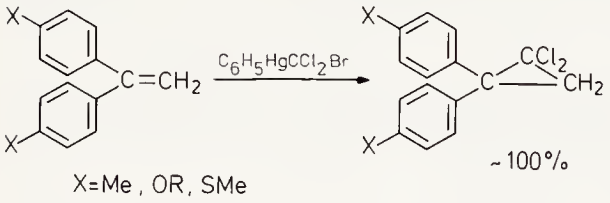
(89) [110, 116, 139]



(90) [140]

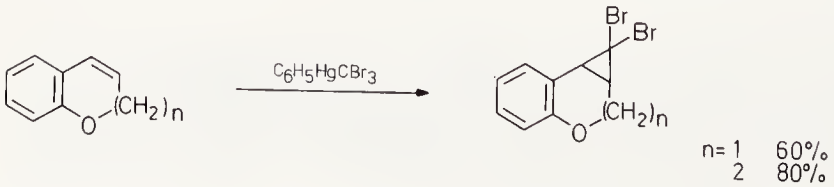


(91) [141]



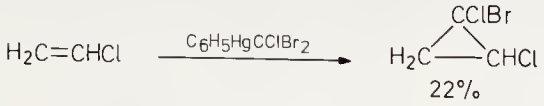
(92) [142]

in chloroform and reaction with strong base prevented it [139]. The usual chloroform/KO-*t*-Bu procedure fails completely with *trans*-stilbene [143]. Methylene transfer using $C_6H_5CH_2HgCH_2I$ also fails [91]. The dichlorocyclopropanes derived from the substituted 1,1-diarylethylenes (Eq. 92) were of interest for their possible insecticidal activity [142], while the cyclopropanes obtained by simple halide reduction of the products of Eq. 89 were of interest for their possible estrogenic and/or anticancer activity [139]. Cyclic aryl olefins also undergo facile cyclopropane formation (Eq. 93) [125].

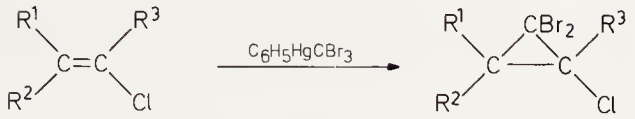


(93)

Although vinyl halides are often quite unreactive towards most electrophilic carbene reagents, the organomercurial reagents have proven most effective in their conversion to cyclopropanes. A number of simple vinyl chlorides have been cyclopropanated in this fashion (Eqs. 94, 95).

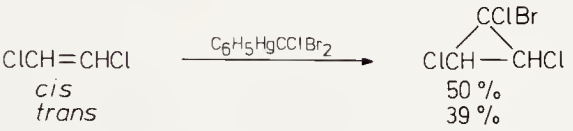


(94) [144]



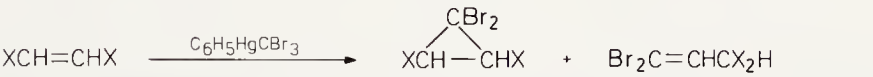
R^1	R^2	R^3	%Yield	Ref.
H	H	$CH(CH_3)_2$	71	145
H	H	$c\text{-}C_3H_5$	65	146
CH_3	CH_3	H	--	147

Polybrominated and -chlorinated olefins are even less reactive, but still give fair yields of cyclopropanes (Eqs. 96–99). In the examples in Eq. 97



cis 50 %
trans 39 %

(96) [112]



(97)

		%Yield	%Yield	Ref.
X = Cl	*cis*	--	--	147
	trans	41	59	148,149
Br	*cis*	29	71	148,149
	trans	31	69	148,149

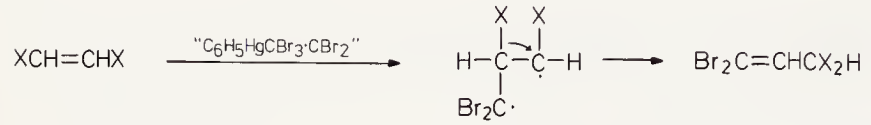
(98)

	X	Y	%Yield	Ref.
$C_6H_5HgCFBr_2$	F	Br	58	14
$C_6H_5HgCCl_3$	Cl	Cl	63	110
$C_6H_5HgCCl_2Br$	Cl	Cl	89	110

(99)

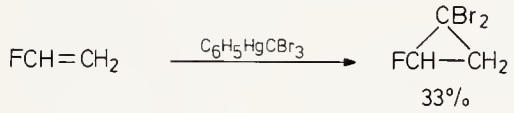
	X	Y	%Yield	Ref.
$C_6H_5HgCCl_3$	Cl	Cl	74	110
$C_6H_5HgCCl_2Br$	Cl	Cl	83	110
$C_6H_5HgCClBr_2$	Cl	Br	48	110,116
$C_6H_5HgCBr_3$	Br	Br	30	110

it has been suggested that the cyclopropanes are formed stereospecifically by singlet dibromocarbene addition, but that the carbene is in equilibrium with an organomercurial-dibromocarbene adduct which gives the rearrangement products as follows (Eq. 100) [149]. Previous attempts to add CCl_2 to tetrachloroethylene using a variety of the standard reagents gave only a 10% yield [150–153]. This nicely illustrates the advantages of the organomercurial reagents.

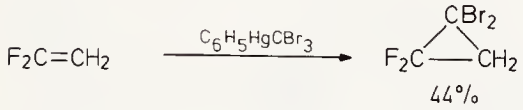


(100)

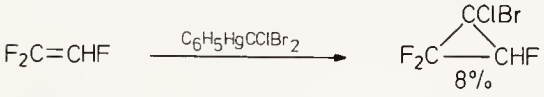
Even vinyl fluorides react, although in low yield, as indicated by the following selected examples (Eqs. 101–104) [144, 154, 155]. The dibromodifluorocyclopropane (Eq. 102) is claimed to be an inhalation anesthetic [155], while the analogous chlorobromodifluoro compound is reportedly an effective pesticide and fumigant [154]. Perfluorocyclohexene is apparently unreactive towards $C_6H_5HgCCl_2Br$ [110].



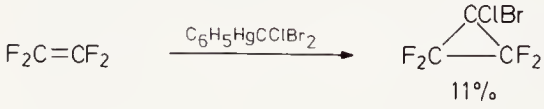
(101) [144]



(102) [144, 155]

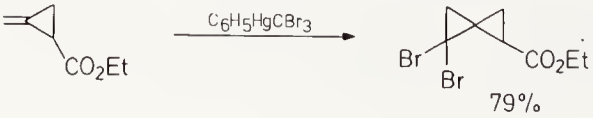


(103) [144]

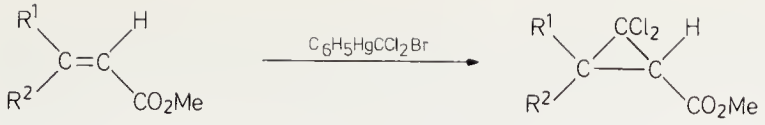


(104) [144]

A large number of other electron-deficient olefins have been converted to cyclopropanes using organomercurial reagents. Numerous examples of the cyclopropanation of unsaturated esters are known (Eqs. 105–109) [156–158]. It should be pointed out that basic reagents cannot be used with these esters.

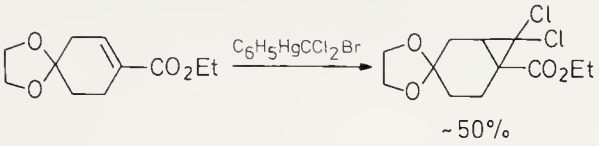


(105) [159]

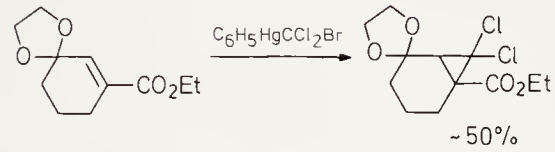


(106)

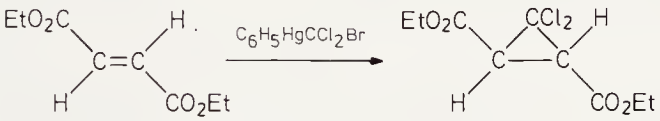
R^1	R^2	%Yield	Ref.
H	H	48	110
H	CH_3	62	110
H	$(CH_3)_3Si$	37	160
CH_3	H	76	110
C_6H_5	H	66	161
$(CH_3)_3Si$	H	35	160
CH_3	CH_3	38	161



(107) [162]

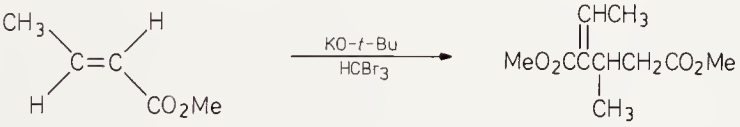


(108) [162]

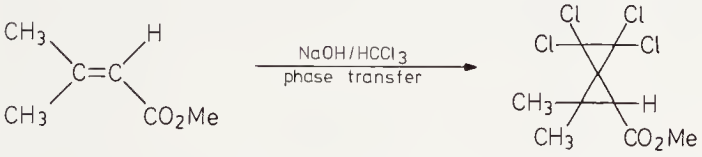


(109) [163, 164]

Where they have been employed, entirely different products are observed (Eqs. 110, 111). While the above dihalocarbon transfer reagents work well on unsaturated esters, $C_6H_5CH_2HgCH_2I$ fails [91].

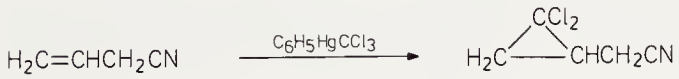


(110) [156]

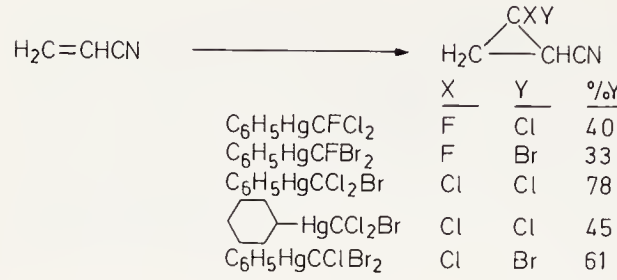


(111) [161]

Unsaturated nitriles also undergo facile cyclopropane formation using organomercurial reagents (Eqs. 112, 113). The dichlorocyclopropane derived from allyl cyanide is claimed to be a useful intermediate in the synthesis of coccidiostats. Once again these highly base-sensitive olefins are converted in high yields to cyclopropanes.



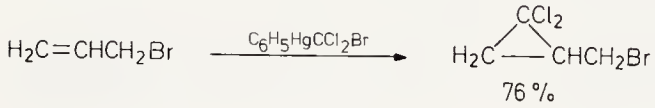
(112) [165]



	X	Y	%Yield	Ref.
$C_6H_5HgCFCl_2$	F	Cl	40	10,11
$C_6H_5HgCFBr_2$	F	Br	33	14
$C_6H_5HgCCl_2Br$	Cl	Cl	78	110
	Cl	Cl	45	24
$C_6H_5HgCClBr_2$	Cl	Br	61	112

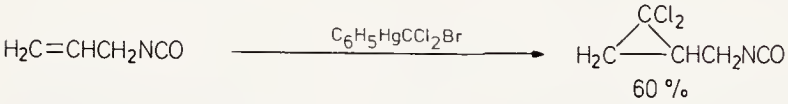
(113)

A variety of other functionally-substituted olefins react readily with organomercurials to give cyclopropanes (Eqs. 114–118) [157]. In the last two examples the products did not appear to be stable under the reaction conditions. Although the yield of cyclopropylsulfone was not high, the organomercurial procedure is apparently the only successful method to effect this transformation.



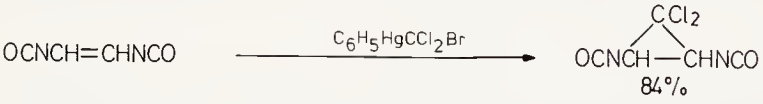
76 %

(114) [110]



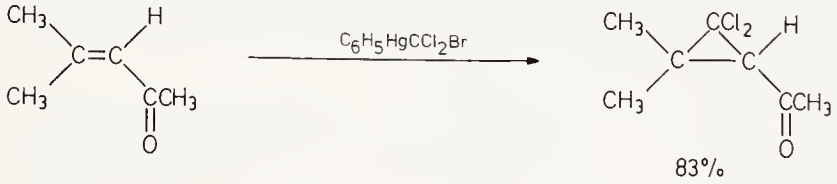
60 %

(115) [110]



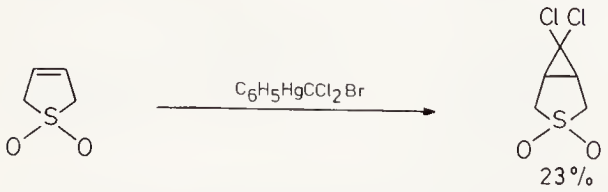
84 %

(116) [166]



83 %

(117) [110]

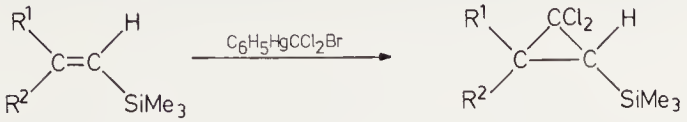


23 %

(118) [167]

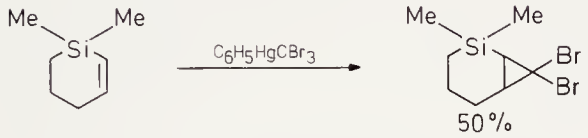
As noted earlier, a number of unsaturated silanes have been reacted with the organomercurial reagents to effect cyclopropane formation. For example, sterically hindered trimethylvinylsilane reacts with each of the following organomercurials to give the expected cyclopropylsilane in the yields indicated: $C_6H_5HgCFCl_2$ (95%) [11], $C_6H_5HgCFBr_2$ (55%) [14], $C_6H_5HgCCl_2Br$ (53% [112], 67% [116], 78% [110, 120]), $C_6H_5HgCBr_3$ (57%) [110, 116, 120]. The high yields of dichlorocyclopropylsilane are even more impressive when one realizes that $HCCl_3$ and KO-*t*-Bu give only a

0.2% yield [168]. Other simple trialkylvinylsilanes react similarly (Eqs. 119–121) [120]. The products of these reactions are useful starting materials in the synthesis of highly reactive cyclopropenyl chlorides (Eqs. 122, 123) [170].

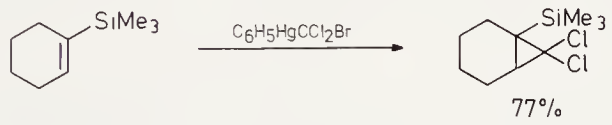


(119)

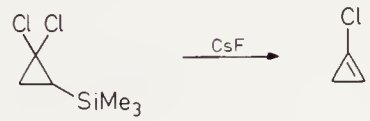
R^1	R^2	%Yield	Ref.
CH_3	H	73	110
H	CH_3	78	110
H	n-C_4H_9	72	122



(120) [169]



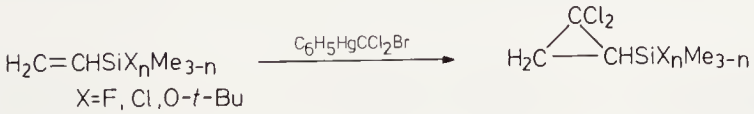
(121) [170]



(122)

(123)

Fluoro- [171], chloro- [110, 116, 120, 172] and *tert*-butoxy- [173] vinylsilanes have similarly been treated with $C_6H_5HgCCl_2Br$ to obtain the corresponding dichlorocyclopropanes (Eq. 124). Quite obviously the usual basic cyclopropane-forming reagents cannot be employed in these reactions. The relative rates of these reactions have been studied in the hopes of learning more about the nature of the silicon-vinyl bond [171–173].

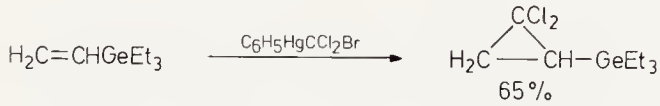


(124)

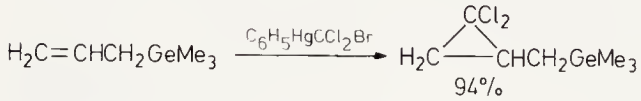
Allyltrimethylsilane has also been reacted with a wide variety of organomercurial reagents to obtain the corresponding cyclopropanes: $C_6H_5HgCHClBr$ (62%) [99], $C_6H_5HgCFClCO_2Et$ (44%) [69], $C_6H_5HgCFBr_2$ (70%) [14], $C_6H_5HgCFBrCF_3$ (93%) [15], $C_6H_5HgCCl_2Br$ (97%) [120], $C_6H_5HgCCl_2I$ (95%) [27, 28], $C_6H_5HgCCl_2CO_2Me$ (71% [32], 73% [31]),  $HgCCl_2CO_2Me$ (48%) [32], $C_6H_5HgCCl_2SO_2C_6H_5$ (47%) [32], C_6H_5Hg-

$CClBr_2$ (84%) [112], $C_6H_5HgCClBrI$ (70%) [34], $C_6H_5HgClBrCF_3$ (9%) [30], $C_6H_5HgCClBrCO_2Me$ (64%) [31], $C_6H_5HgCBr_2CO_2Me$ (62%) [31]. Other allylic silanes also react with these reagents [120, 174].

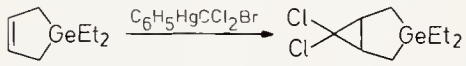
Allylic and vinylgermanes [118, 120, 174], vinylstannanes [120], and vinylboranes [175] also undergo cyclopropane formation (Eqs. 125–129). The last reaction proceeds in only 4% yield when sodium trichloroacetate is used as the reagent.



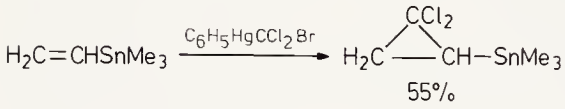
(125) [120]



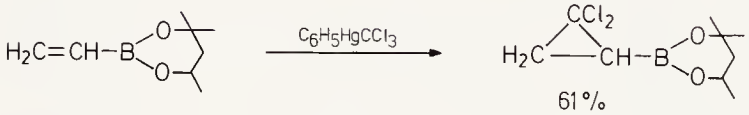
(126) [120]



(127) [174]

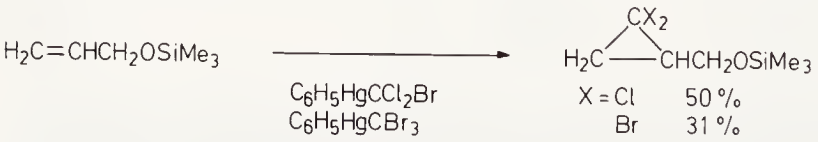


(128) [120]



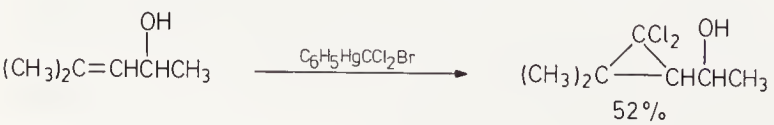
(129) [175]

It is obvious from the many examples given so far that the organomercury divalent carbon transfer reagents are tolerant of a wide range of important organic functionality. However, several important functional groups, namely alcohols, amines, carboxylic acids and ethers, can react with these reagents to give products other than cyclopropanes. The reactions of allylic alcohols are especially interesting [176]. Allyl alcohol itself reacts primarily at the alcohol group, not the double bond [177]. In this case the alcohol is best protected as its trimethylsilyl ether which reacts as desired (Eq. 130). On the other hand, 4-methyl-3-penten-2-ol gives a reasonable



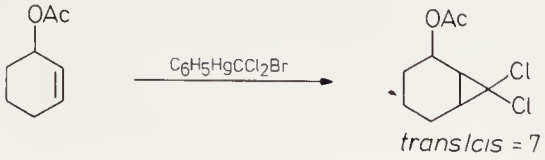
(130)

yield of cyclopropane without protection, probably due to the increased nucleophilicity of the double bond (Eq. 131) [176]. 3-Cyclohexenol gives



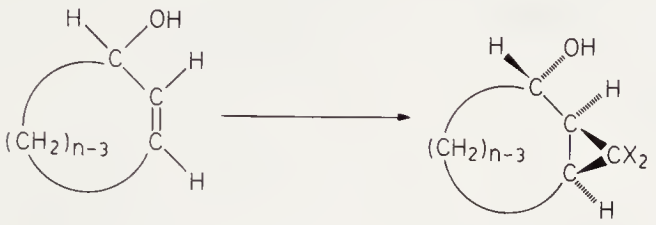
(131)

none of the desired cyclopropane and must be protected as its acetate (Eq. 132) [176], while cyclic 7, 8 and 9 membered ring allylic alcohols give



84 % (132)

varying yields of cyclopropanes (Eq. 133). The trans products were the only cyclopropyl alcohol products in each case. However, numerous side

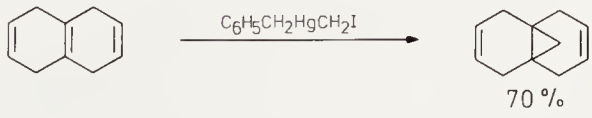


(133)

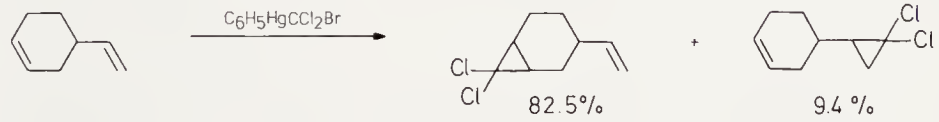
	X	n	%Yield	Ref.
$C_6H_5HgCCl_2Br$	Cl	7	31	176
		8	70	176
		9	28	176
$C_6H_5HgCBr_3$	Br	9	88	178

products were observed. In general, better results were obtained using the corresponding acetates. The exact nature of the alcohol, amine, carboxylic acid and ether reactions will be taken up in later sections in this chapter.

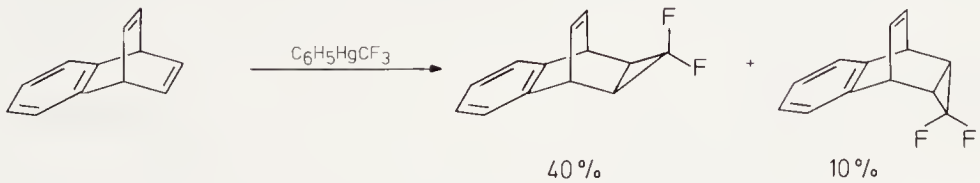
The reaction of polyenes presents no unusual difficulties and the reaction can often be controlled to give unsaturated cyclopropanes in high yield as evidenced by the following examples (Eqs. 134–142). The vinylcyclopropanes



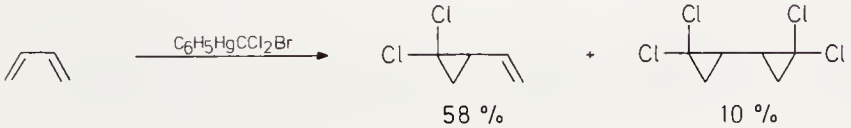
70 % (134) [91]



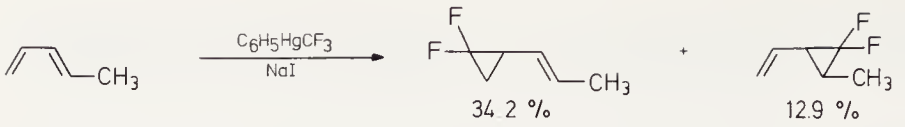
82.5% 9.4 % (135) [110]



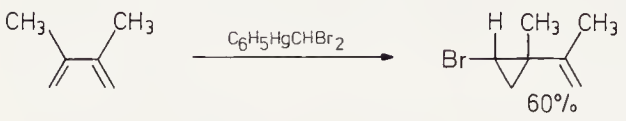
40 % 10 % (136) [179]



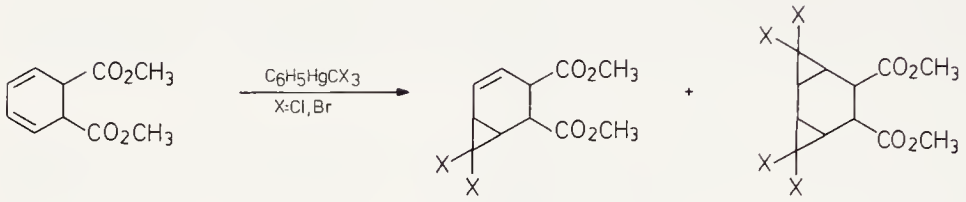
58 % 10 % (137) [110]



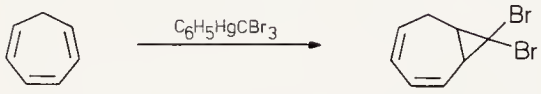
(138) [180]



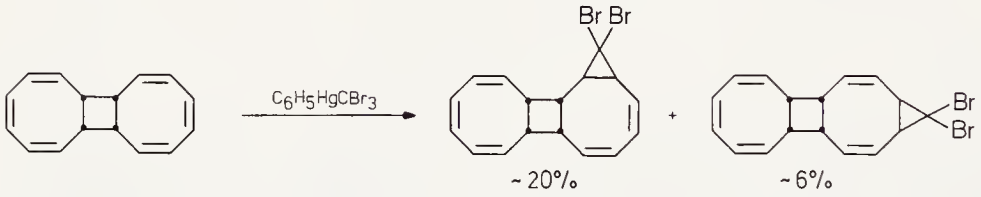
(139) [181]



(140) [182]

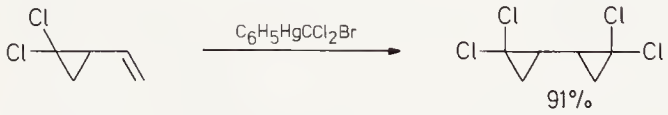


(141) [183]

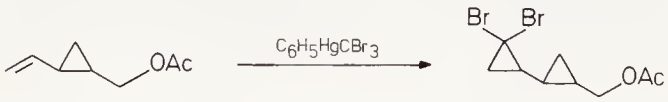


(142) [184]

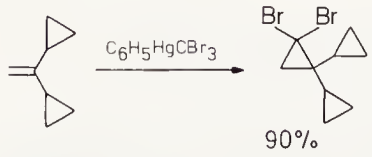
obtained from conjugated polyenes can be further cyclopropanated (Eqs. 143–146). In similar fashion, allenes can be converted to alkylidene cyclopropanes, which can in turn be further cyclopropanated (Eqs. 147–150).



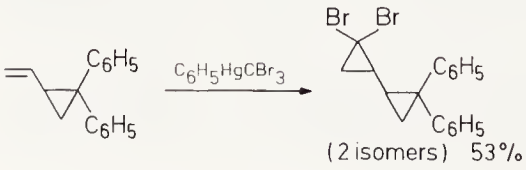
(143) [110]



(144) [185]

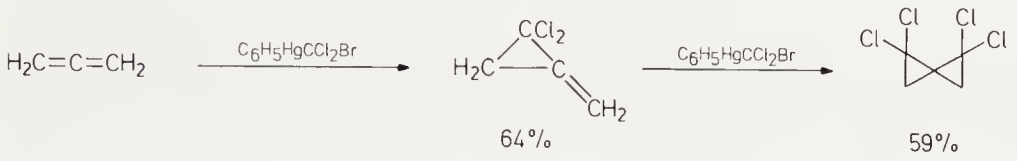


(145) [186]

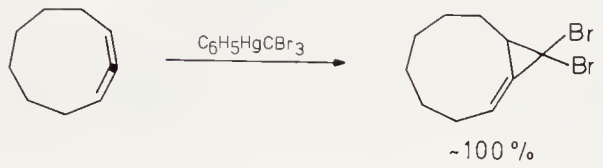


(146) [187]

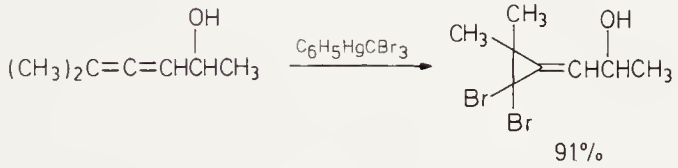
The complete cyclopropanation of carbon—carbon double bonds present in polybutadiene, polyisoprene and polychloroprene has also been effected using the reagents $C_6H_5HgCCl_2Br$ and $C_6H_5HgCClBr_2$ [191, 192]. The first two polymers gave only low conversions using base and chloroform, while the last polymer was inert. The resulting cyclopropanes should prove useful in further structural modifications of these polymers.



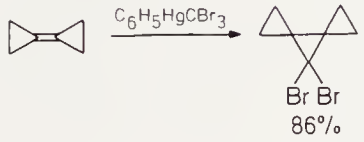
(147) [110]



(148) [188]

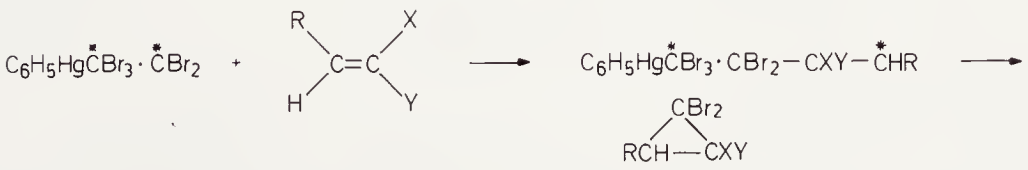


(149) [189]



(150) [190]

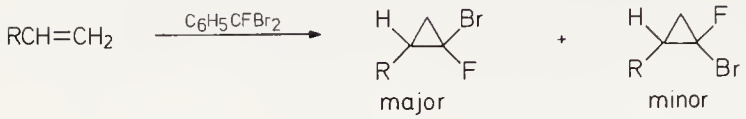
At this time it seems appropriate that we turn our attention to the stereochemistry of these cyclopropane-forming reactions. In practically all examples of this reaction reported to date, the olefin has undergone cyclopropanation with complete retention of configuration [11, 14, 30, 99, 110]. The only exceptions appear to be the reactions of $C_6H_5HgCBr_3$ and *cis*-2-deuterostyrene or fumaronitrile [193]. The loss of stereospecificity is ascribed to the reaction of a carbene-complexed mercurial and the olefin to form a diradical-like intermediate which closes nonstereospecifically (Eq. 151).



(151)

When unsymmetrical carbon species CXY are transferred to olefins such as cyclohexene, syn/anti mixtures can arise and almost always do. For example, the reaction of $C_6H_5HgCFBr_2$ and terminal olefins affords a

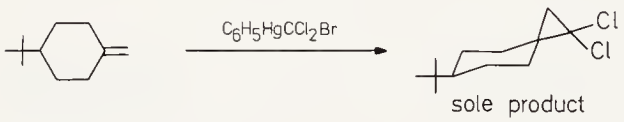
syn/anti mixture in which the bromine prefers to be trans to the R group (Eq. 152) [194]. In these isomeric mixtures it is not always obvious as to



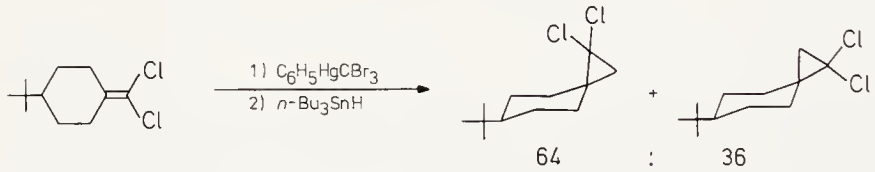
(152)

which of the two products will predominate. One might have assumed that the more bulky of the two groups would prefer the exo position, but this apparently is not always true [14, 99]. Only the chlorotrimethylsilyl carbon species is reported to give only one of the two isomers (probably with the silicon exo), but the products are not real stable under the reaction conditions and one of the isomers may have been selectively destroyed [113].

The stereochemistry of addition to cyclic systems has also been closely examined. Additions to conformationally rigid 4-*tert*-butylmethylenecyclohexane systems gives predominant equatorial attack (Eqs. 153, 154) [195].

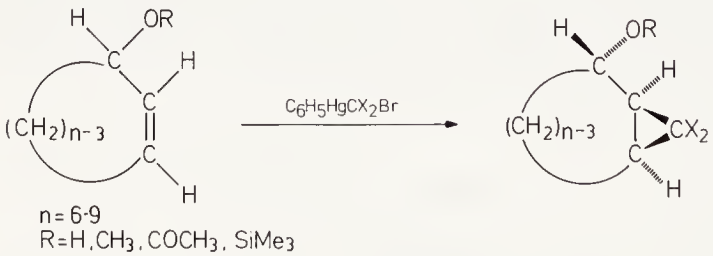


(153)



(154)

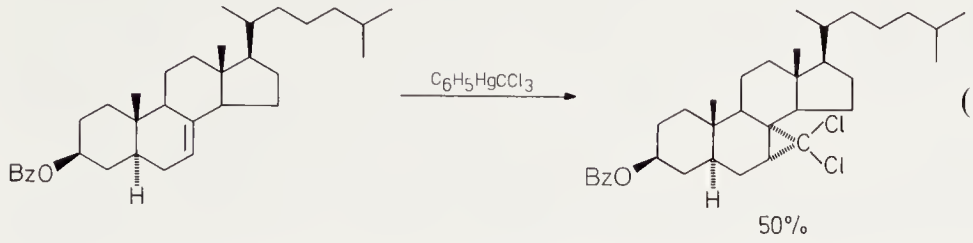
As mentioned earlier, additions to 6, 7, 8 and 9 membered ring cyclic allylic alcohols, ethers and acetates give almost exclusive trans addition (Eq. 155) [176]. These results suggest that no prior coordination of the organomercurial



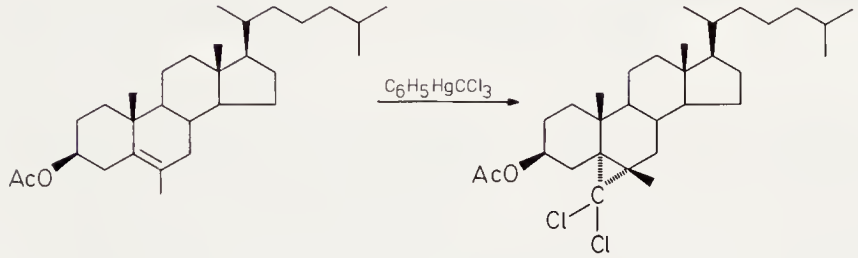
(155)

to the oxygen atom occurs, but rather that addition occurs from the less hindered side of the carbon—carbon double bond. These results are just the opposite of those observed in the Simmons-Smith reaction where prior coordination of ICH_2ZnI seems evident. Additions to steroids also appear

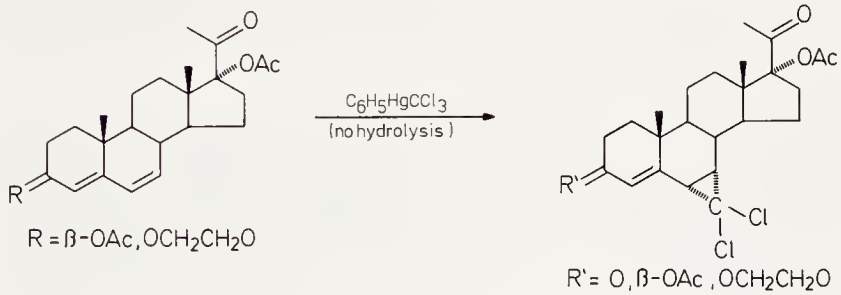
to occur primarily from the less hindered alpha face although mixtures commonly occur (Eqs. 156–160).



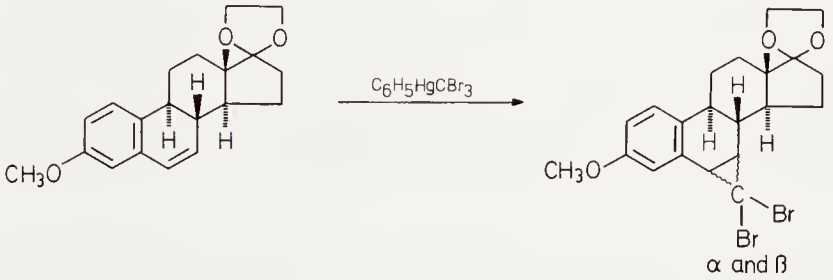
(156) [196]



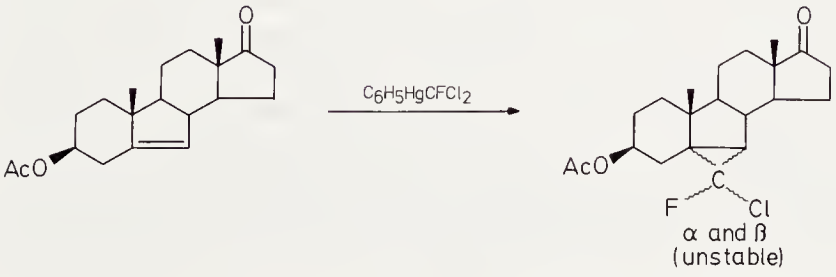
(157) [196]



(158) [197]



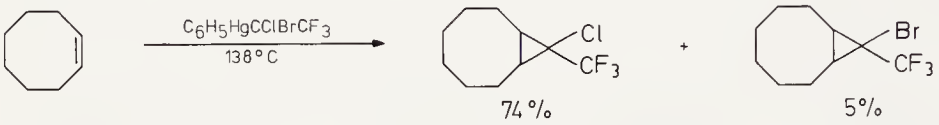
(159) [198, 199]



(160) [200]

D. Organomercurial Reactivity

Up to this time we have focussed our attention on the olefinic substrates undergoing cyclopropane formation. It now seems appropriate to shift our attention to the organomercurials and examine the ease with which they undergo reaction. It is evident from a close perusal of Table 10.5 that the preference for phenylmercuric halide elimination from the organomercurial reagents is I > Br > Cl > F. This order is rigorously obeyed in all reagents but one (Eq. 161) [29, 30]. The diminished specificity in this case is attributed to the high temperatures required to effect reaction. This usual preference



(161)

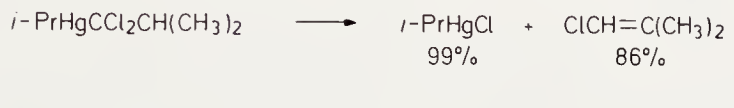
for elimination manifests itself in an increased overall rate of reaction and a decrease in the temperature necessary to effect reaction. The following relative rates of reaction of a variety of organomercurials have been observed: $C_6H_5HgCBr_2I > C_6H_5HgCBr_3$ [28], $C_6H_5HgCClBrI > C_6H_5HgCClBr_2$ [28], $C_6H_5HgCCl_2I > C_6H_5HgCCl_2Br$ [28], $C_6H_5HgCCl_2Br > C_6H_5HgCCl_3$ [20], $C_6H_5HgCClBrCO_2Me > C_6H_5HgCCl_2CO_2Me$ [30, 31]. The first three reagents cited above are sufficiently unstable at room temperature that they are difficult to purify [28].

The nature of the divalent carbon species being transferred is equally as important as the halide being eliminated as evidenced by the following relative rates of reaction: $C_6H_5HgCFBr_2 > C_6H_5HgCBr_3$ [14, 34, 201], $C_6H_5HgCBr_3 > C_6H_5HgCClBr_2 > C_6H_5HgCCl_2Br$ [111], $C_6H_5HgCCl_2$-$C_6H_5 > C_6H_5HgCCl_2R$ [56] (R = F, Cl, H, CH_3, CF_3, CO_2Me), $C_6H_5HgCFCl_2 > C_6H_5HgCCl_3$ [12, 26], $C_6H_5HgCFBrCF_3 > C_6H_5HgCClBrCF_3$ [15, 16], $C_6H_5HgCFClCO_2Me > C_6H_5HgCCl_2CO_2Me$ [13]. It is quite evident from this data that a fluorine has a greater stabilizing effect on the group being transferred than does a chlorine. A few other relative rates have been reported in the literature: $C_6H_5HgCBr_2SO_2C_6H_5 > C_6H_5HgCCl_2SO_2C_6H_5$ [32], $C_6H_5HgCCl_nBr_{3-n} > C_6H_5HgCFBrCF_3$ [16], $C_6H_5HgCFCl_2 > C_6H_5HgCFBrCF_3$ [16], $C_6H_5HgCClBrCF_3 > C_6H_5HgCClBrCO_2Me$ [31].

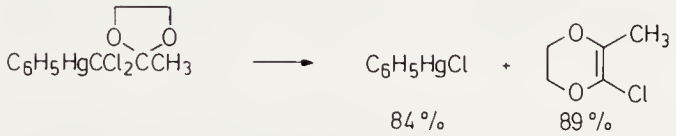
When the phenyl group in the above compounds is replaced by an alkyl group a significant increase in reactivity is observed. The alkyl groups studied to date include *n*-propyl [45], isopropyl [45], cyclohexyl [23, 24], benzyl [91] and *β*-phenethyl [24]. Some of the cyclohexyl compounds have proven to be useful reagents even at room temperature. Unfortunately, they also have the disadvantage that they are more difficult to isolate and store, and they are subject to autoxidation and induced decomposition in certain solvents. The preparation of a number of other alkylmercurial reagents has been attempted, but oils have generally been obtained [24]. In general, there appear to be few advantages in working with the alkylmercurial reagents in spite of their increased reactivity.

Some organomercurial reagents seem to react readily, but only low yields of cyclopropanes are obtained. Among these reagents are $C_6H_5HgCClICO_2Me$ [32],  -$HgCBr_3$ [23, 24] and $C_6H_5CH_2CH_2HgCBr_3$ [24]. The difficulties here are not obvious. The compound $C_6H_5HgCFBrCF_2OEt$ also reacts, but gives no cyclopropanes, perhaps due to beta rather than alpha elimination of a halide [16].

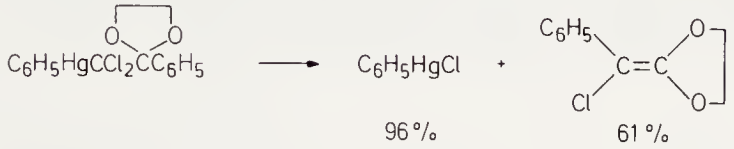
Other organomercurial reagents appear to generate carbenes which rearrange before they can undergo addition to olefins (Eqs. 162–164) [55, 57, 202]. Analogous acetal-containing organomercurials give similar rearrangement products, although not as cleanly. Concerted rearrangements cannot be ruled out in these reactions. A similar rearrangement probably accounts for the failure of the reaction of phenyl(1,1-dichloroethyl)mercury and cyclooctene to produce any cyclopropane, although allyltrimethylsilane affords the desired cyclopropane in low yield (Eq. 165) [55].



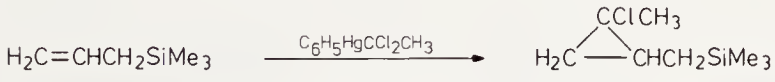
(162) [55]



(163) [57]



(164) [57]

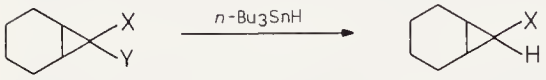


(165)

A number of organomercurial reagents which have been prepared have simply proved too thermally stable to be of use as divalent carbon transfer reagents under any sort of reasonable reaction conditions. Among these compounds are $BrHgCH_2Br$ [106, 107], $Hg(CHClCO-$  $)_2$ [68], $C_6H_5HgCHClCO_2Et$ [32], $Hg(CHBrSiMe_3)_2$ [47], $Hg(CHISiMe_3)_2$ [49], $C_6H_5HgCCl_2CF_3$ [29], $C_6H_5HgCCl_2CONMe_2$ [32], $Hg(CCl_2SiMe_3)_2$ [52] and $Hg(CBr_2SiMe_3)_2$ [47]. While $C_6H_5HgCCl{=}CCl_2$ also proved quite thermally stable, photolysis could be employed to effect cyclopropane formation [105].

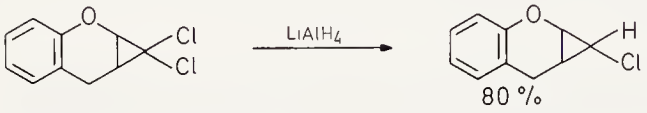
In comparing the relative reactivity of the various organomercurial reagents, it becomes obvious that it is significantly more difficult to transfer a divalent carbon species bearing one or two hydrogens than one containing only halogens. This means that the synthesis of the corresponding hydrogen-containing cyclopropanes using the organomercurial route is limited by the high temperatures or long reaction times required to effect reaction. For-

tunately, however, many dihalocyclopropanes can be selectively reduced in high yield to the corresponding monohalocyclopropanes using tin hydrides, as illustrated by the following simple examples (Eq. 166). Lithium aluminium hydride can also be employed in these reductions (Eq. 167). Complete



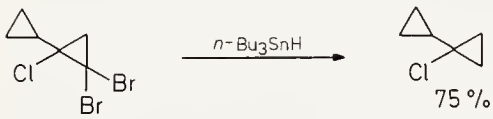
(166)

X	Y	°C	%Yield	Ref.
Br	Br	<40	82	203
Cl	Br	0	97	203
Cl	Cl	140	83	203
F	Cl	140	78	204

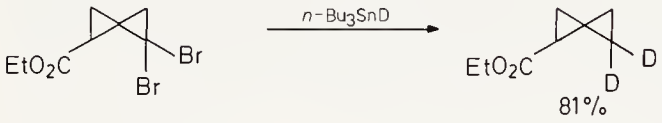


(167) [125, 126]

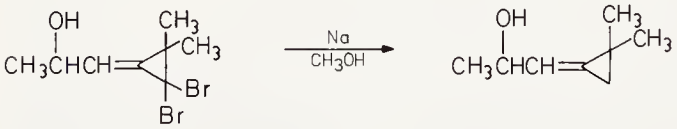
reduction can also be effected using either tin hydrides or sodium in methanol (Eqs. 168–171). These reductions obviously greatly enhance the synthetic utility of the organomercury divalent carbon transfer reactions.



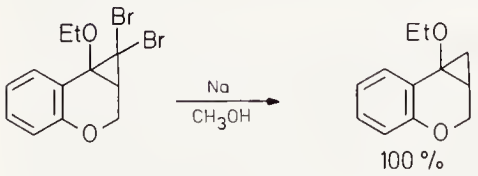
(168) [145]



(169) [159]



(170) [188]



(171) [126]

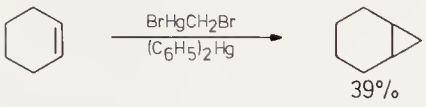
Some of the organomercurials mentioned earlier as being insufficiently reactive to be useful, can in fact be activated by the addition of diphenylmercury to the reaction mixture. It appears that diphenylmercury either causes disproportionation to occur (Eq. 172) or generates new, more reactive

(172) [107]

phenylmercurial reagents (Eqs. 173, 174). What actually occurs is not clear. Thus, $BrHgCH_2Br$ which is totally unreactive by itself, reacts in the presence of diphenylmercury (Eq. 175) [106]. Similarly, by adding diphenylmercury

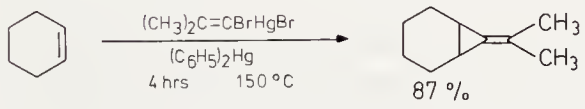
$$BrHgCH_2Br + (C_6H_5)_2Hg \longrightarrow C_6H_5HgCH_2Br + C_6H_5HgBr \quad (173)\ [106]$$

$$Hg(CH_2Br)_2 + (C_6H_5)_2Hg \longrightarrow 2\,C_6H_5HgCH_2Br \quad (174)\ [107]$$



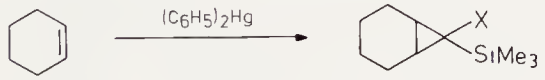
(175)

to ICH_2HgI, the yield of norcarane can be improved from 24% to 64% [106, 107]. Addition of dibenzylmercury also works well [108]. While $Hg(CH_2Br)_2$ and $Hg(CH_2I)_2$ both give reasonable yields of cyclopropanes based on transfer of one CH_2 group, addition of diphenyl- or dibenzylmercury allows transfer of both CH_2 groups in good yield [107, 108]. The use of the Simmons-Smith reaction is probably still preferable in these cases however. Alkenylidene species can also be transferred to olefins using this technique (Eq. 176) [54]. A number of previously unreactive silicon-con-



(176)

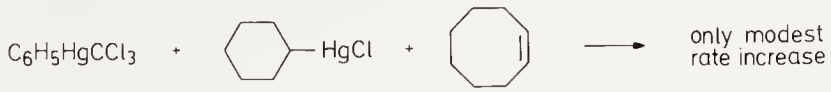
taining organomercurials can also be made to undergo transfer reactions upon addition of diphenylmercury (Eq. 177). However, attempts to take



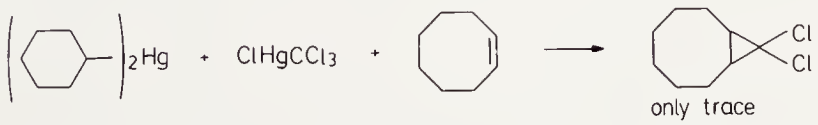
(177)

$ClHgCCl_2SiMe_3$	X = Cl	46% [113]
$Hg(CCl_2SiMe_3)_2$		62% [52, 113]
$Hg(CBr_2SiMe_3)_2$	X = Br	51% [113]

advantage of the increased reactivity of cyclohexyltrichloromethylmercury in the following reactions were quite disappointing (Eqs. 178, 179) [24].



(178)



(179)

An alternate technique which has proven exceptionally valuable in lowering the temperatures at which certain organomercurials react, simply involves the addition of anhydrous sodium iodide to the reaction mixture.

Table 10.6. Cyclopropane Synthesis Using the NaI Procedure

Transfer species	Organomercurial employed	Reaction temp., °C	Reaction time, hrs	% Yield of bicycloheptane[a]	Ref.
CF_2	$IHgCF_3$	80	15-20	88(0)	71, 205
	$Hg(CF_3)_2$		—	35(0)	74
	$C_6H_5HgCF_3$		15-19	83(0)	97, 205
CFCl	$C_6H_5HgCFCl_2$	25	48	85(0)	11
		85	3-5	70-79	10, 11
			3	89	97
CCl_2	$C_6H_5HgCCl_3$	30-35	48	66-72(0)	206, 207
		80	4	72(16)	206
		85	3	78(15)	207
	$C_6H_5HgCCl_2Br$	30	4	75(1.5)	206, 207

[a] Anticipated or observed yields in the absence of NaI .

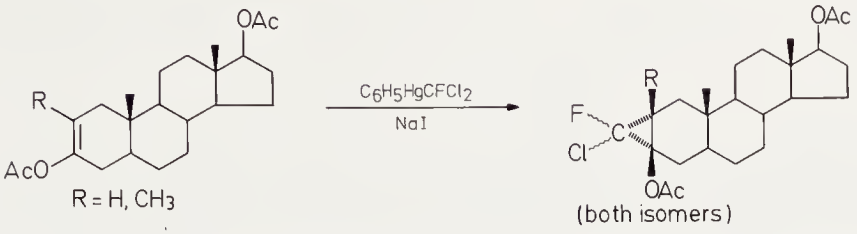
This approach has been especially useful in transfer of the groups CF_2, CFCl and CCl_2 as indicated in Table 10.6 where some representative yields employing cyclohexene are tabulated. The observed or anticipated yields of bicyclo[4.1.0]heptane in the absence of sodium iodide are also included in parentheses for comparison purposes. The tremendous activating effect of sodium iodide is obvious. For example, $C_6H_5HgCF_3$, which fails to react at all after ten days of refluxing in benzene, gives an 83% yield of difluoronorcarane after 15 hours in the presence of sodium iodide [205].

Most of these reactions proceed in good yield with all of the same types of olefins discussed earlier. For example, the most important CF_2 transfer reagent, $C_6H_5HgCF_3$/NaI, gives good yields with 1-heptene (70%), allyltrimethylsilane (99%), trimethylvinylsilane (53%) and trichloroethylene (72%) [97, 205]. These reactions are stereospecific with respect to the olefin [205]. Equally important, the CF_2 and CFCl transfer reagents also react with vinyl acetates to give good yields of the corresponding cyclopropanes (Eqs. 180, 181). The yields with acrylonitrile are much lower (Eq. 182). In none of these reactions are any halomethyl anion conjugate addition products observed. Unfortunately, the CCl_2 transfer reagents give only low

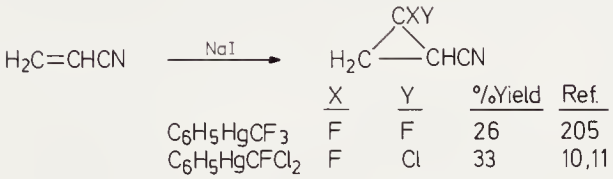
(180)

	R	X	Y	%Yield	Ref.
$C_6H_5HgCF_3$	H	F	F	84	205
$C_6H_5HgCFCl_2$	H	F	Cl	70	10, 11
$Hg(CF_3)_2$	CH_3	F	F	35	74

yields with polyhaloethylenes [207, 208], vinyl acetate and acrylonitrile [206, 207]. With the latter two olefins significant amounts of products apparently formed by conjugate addition of $^{\ominus}CCl_3$ and $^{\ominus}CCl_2Br$ are observed.



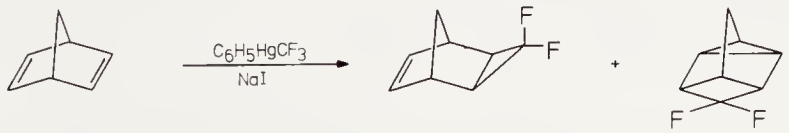
(181) [136]



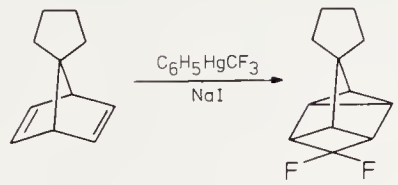
	X	Y	%Yield	Ref.
$C_6H_5HgCF_3$	F	F	26	205
$C_6H_5HgCFCl_2$	F	Cl	33	10,11

(182)

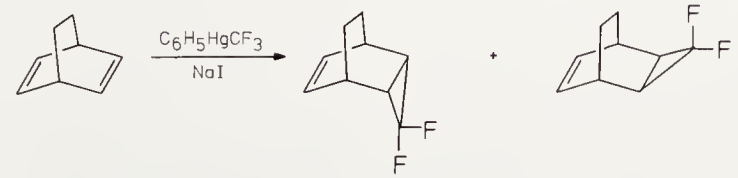
The relative reactivity and stereoselectivity of various olefins towards these reagents has been examined. The relative reactivity of $C_6H_5HgCF_3$/NaI towards a number of substituted styrenes [209], and a wide variety of acyclic, cyclic and bicyclic olefins has been examined [210], as has the stereoselectivity of addition to bicyclic and steroidal olefins [211]. The mode of addition to bicyclic dienes has been the subject of several publications. Additions to either one or both double bonds are observed (Eqs. 183–185). The combination $C_6H_5HgCCl_3$ and NaI shows exactly the same relative reactivity towards olefins as does $C_6H_5HgCCl_3$: $R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CH_2$ [204].



(183) [212–214]



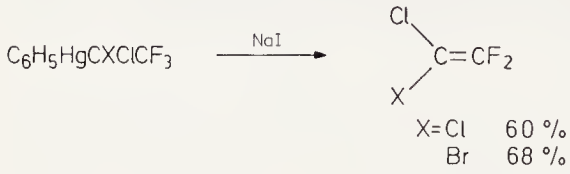
(184) [215]



(185) [216]

The sodium iodide technique has failed in several instances. Neither $C_6H_5HgCCl_2CO_2Me$ [29] not $C_6H_5HgCXClCF_3$ (X = Cl, Br) [30] gave any

cyclopropanes upon addition of sodium iodide. The latter reagents were observed to decompose to olefins instead (Eq. 186) [29, 30]. It should



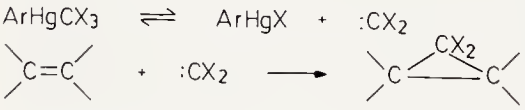
(186)

also be remembered that certain phenylmercurial reagents undergo halide substitution by iodide under these conditions providing new organomercurial reagents.

E. Mechanism of Cyclopropane Formation

Three different mechanisms appear to exist for these divalent carbon transfer reactions. The most common mechanism appears to involve reversible alpha elimination of a mercury halide from the organomercurial reagent to generate a carbene, which rapidly adds to the olefin (Scheme 10.4). Direct divalent

Scheme 10.4

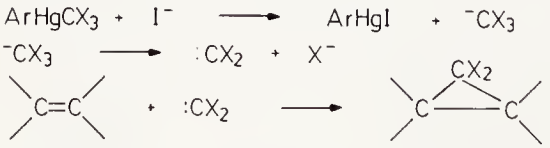


carbon transfer to the olefin by the organomercurial also appears to occur with some reagents (Eq. 187). Finally, the sodium iodide promoted reactions

(187)

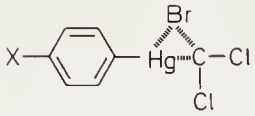
appear to involve displacement of a trihalomethyl anion from the organomercurial reagent, followed by rapid carbene formation and cyclopropanation (Scheme 10.5). Evidence for each of these mechanisms will be presented in the order outlined above.

Scheme 10.5



The mechanism which appears to account for the vast majority of the cyclopropanation reactions is the first one mentioned above, namely generation of a free carbene and subsequent addition to the olefin. The first step, reversible alpha elimination of a carbene, has been suggested to occur through a concerted cyclic elimination involving nucleophilic attack of one of the

alpha halides on the mercury, presumably through a transition state of the following type [26, 201]. The observed preference for elimination of the



more weakly bonded and more nucleophilic halide (I > Br > Cl > F) is consistent with this picture. A kinetic study of the relative rates of reaction of a variety of para substituted phenylbromodichloromethylmercury compounds (X = H, F, Cl, Me, OMe) demonstrated that little polar character is developed in the transition state of the elimination reaction [26]. As pointed out earlier, not only the type of halide undergoing elimination, but also the nature of the divalent carbon species being generated, has a major effect on the overall rate of reaction. The presence of a fluorine in the resulting carbon species dramatically enhances the overall rate of reaction. This is explained by the greater ability of fluorine to donate electron density to the empty p orbital of the resulting carbene through $p\pi$-$p\pi$ dative bonding [11, 14].

What evidence exists for the reversible generation of a free carbene, as opposed to the direct transfer of a carbenoid species? First, the initial kinetics of the reaction of $C_6H_5HgCCl_2Br$ and several olefins has clearly established that the reaction is first order in organomercurial and independent of olefin concentration [201]. The free energy, enthalpy and entropy of cyclopropane formation have been determined and appear to preclude any significant ionic character in the transition state. On the other hand, the reactions of organomercurials of the type $C_6H_5HgCCl_2R$ [R = CH_3, CF_3, C_6H_5, CO_2Me, $C(OR)_2R$] have been suggested to develop at least some positive charge on the carbene carbon in the transition state, thus explaining why the phenyl compound (R = C_6H_5) is substantially more reactive than the others [56]. Evidence for the reversibility of carbene formation is based on kinetics [201] and observation of exchange reactions of the following type (Eq. 188) [32].

$$C_6H_5HgCClBrCO_2Me + C_6H_5HgCl \longrightarrow \underset{72\%}{C_6H_5HgCCl_2CO_2Me} + C_6H_5HgBr \qquad (188)$$

Unfavorable reversible carbene formation and reinsertion have been argued to account for the very long reaction times required for transfer of this particular carbene (Eq. 189) [32].

$$C_6H_5HgCX_2CO_2R \rightleftharpoons C_6H_5HgX + :CXCO_2R \qquad (189)$$

Important evidence for the presence of carbenes comes from the direct spectroscopic observation of such species in a rare gas matrix after gas phase pyrolysis of some of the more common organomercurial reagents (Eq. 190) [217–221]. Free radicals are also observed in most of these reactions.

$$RHgCCl_2X \xrightarrow{200\text{-}600^\circ C} :CCl_2 \qquad (190)$$

R = Cl, CCl_3, C_6H_5
X = Cl, Br

The majority of the evidence for the intermediacy of a free carbene comes from a comparison of the reactivity of the organomercurial reagents with a number of other reagents known to generate free carbenes. For example, the relative reactivity of a variety of olefins towards $C_6H_5HgCCl_2Br$ is the same as that of the reagents KO-*t*-Bu/$HCCl_3$ and NaO_2CCCl_3, both known dichlorocarbene sources, and differs significantly in many respects from the Simmons-Smith reaction, known to involve a zinc carbenoid, and the oxymercuration reaction to be discussed in detail in the monograph "Solvomercuration-Demercuration" [114, 201]. As with other dihalocarbene reactions, the organomercurial reagents generally transfer CX_2 stereospecifically to olefins. The failure of these reagents to polymerize dienes, styrenes, vinylcyclopropanes, vinyl acetate and acrylonitrile has been used as evidence against free radical intermediates [110].

Similarly, carbanions are ruled out by the facile cyclopropanation of highly base-sensitive olefins such as enones, acrylate esters, vinyl acetate and acrylonitrile [110]. In fact, kinetic evidence from the reaction of C_6H_5-$HgCCl_2Br$ and substituted styrenes suggests a concerted electrophilic attack with only slight polar character to the transition state and small steric factors [26, 114]. This is in accord with the known behavior of dichlorocarbene. It has also been observed that neither solvent polarity [114, 201, 222], nor the presence of various oxygen-containing functional groups (ketals [158, 162], esters [158, 162], alcohols [176], ethers [176] or acetates [76]) in the olefin significantly alters the reactivity or stereoselectivity of these reagents. Once again this is contrary to observations made in the Simmons-Smith reaction in which sterically-demanding, oxygen-coordinating, electrophilic zinc carbenoid intermediates are involved. Thus, all evidence suggests the presence of free carbenes and not complexed carbenes as intermediates in at least the reactions of $C_6H_5HgCCl_2Br$, and probably a large number of the other organomercurial reactions.

It has generally been assumed that singlet carbenes are involved in these reactions, thus accounting for the high stereospecificity of olefin addition. However, as noted earlier in the reactions of $C_6H_5HgCBr_3$ and *cis*- and *trans*-1,2-dibromoethylene and *trans*-1,2-dichloroethylene, rearrangement products have been observed that were originally suggested to arise via triplet dibromocarbene [148]. More recent observations suggest that a carbene-mercurial complex may be formed which reacts directly with the olefin to give a diradical-like intermediate, which results in rearranged products or loss of stereospecificity [193]. This phenomenon may be more common than generally assumed.

The reactions of olefins and $Hg(CH_2Br)_2$, $IHgCH_2I$ and related reagents appear to take a different mechanistic course than that described above [107]. Once again the reactions are stereospecific, but the nature of the olefin has a larger effect on the rate of reaction. Unlike the reactions of $C_6H_5HgCCl_2Br$, electron-withdrawal or steric hindrance substantially retard the methylene transfer reactions. Electronic factors appear to be the more important, and the effects of steric hindrance are not so important as in the Simmons-Smith $IZnCH_2I$ reactions. Kinetically, the rate of product formation is rate

determining and dependent on olefin concentration. Thus, $Hg(CH_2Br)_2$ is stable in refluxing benzene for 20 days in the absence of olefin, but gives high yields of cyclopropane in significantly less time in the presence of olefins. Finally, no C—H insertion products expected of a free methylene, $:CH_2$, are observed in any of the reactions. All of the evidence speaks in favor of a direct transfer of CH_2 from organomercurial to olefin and not a carbene mechanism. The reactivity of $C_6H_5HgCHClBr$ is similar in the fact that no reaction occurs in the absence of an olefin trap, thus ruling out a carbene mechanism [99]. It would appear, therefore, that organomercurial reagents which would lead to less stable carbenes undergo cyclopropanation reactions by direct divalent carbon transfer to olefins.

The sodium iodide promoted reactions appear to proceed by still a third type of mechanism, namely trihalomethyl anion displacement, carbene formation, and cyclopropanation (Scheme 10.5). Consistent with this mechanism is the following evidence. The relative reactivity of a variety of olefins towards $C_6H_5HgCCl_3/NaI$ is the same as that of $C_6H_5HgCCl_2Br$, NaO_2CCCl_3 and KO-*t*-Bu/$HCCl_3$, suggesting the intermediacy of dichlorocarbene [207]. The response to olefin steric effects and electronic factors is also quite similar. Thus, electron-deficient olefins show low reactivity, and carbanion addition products begin to appear (Eqs. 191, 192) [206, 207]. In

$$H_2C=CHOAc \xrightarrow[NaI]{C_6H_5HgCCl_3} H_3C\overset{CCl_3}{\underset{|}{C}}HOAc \quad 10\% \tag{191}$$

$$H_2C=CHCN \xrightarrow[NaI]{C_6H_5HgCCl_3} \underset{22\%}{HCCl_3} + \underset{15\%}{Cl_3CCH_2CH_2CN} \tag{192}$$

neat acrylonitrile substantial polymer formation occurs. In acetone these same reagents also give carbonyl addition products (Eq. 193) [206, 207].

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[NaI]{C_6H_5HgCCl_3} CH_3\overset{OH}{\underset{|}{\overset{|}{C}}}CH_3 \quad \underset{CCl_3}{|} \quad 26\% \tag{193}$$

The reagent $C_6H_5HgCCl_2Br/NaI$ shows analogous behavior. However, the reactions of vinyl acetate and acrylonitrile with $C_6H_5HgCF_3/NaI$ [205] and $C_6H_5HgCFCl_2/NaI$ [10] show none of the anticipated addition products and cyclopropanes are formed in modest yield (Eqs. 194, 195). All of the

$$H_2C=CHX \xrightarrow[NaI]{C_6H_5HgCF_3} \underset{X=OAc \quad 84\%}{\underset{CN \quad 26\%}{H_2C\overset{CF_2}{\diagup\diagdown}CHX}} \tag{194}$$

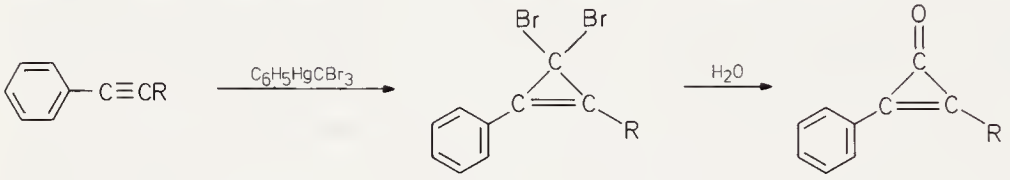
$$H_2C=CHX \xrightarrow[NaI]{C_6H_5HgCFCl_2} \underset{X=OAc \quad 33\%}{\underset{CN \quad 70\%}{H_2C\overset{CFCl}{\diagup\diagdown}CHX}} \tag{195}$$

above evidence is consistent with a mechanism involving free trihalomethyl anions, with the proviso in the last two examples that decomposition of the anion to the fluorine stabilized carbenes :CF_2 and :CFCl is quite rapid, precluding formation of carbanion addition products (Eq. 196).

$$^-CF_3 \xrightarrow{\text{fast}} :CF_2 + F^- \qquad (196)$$

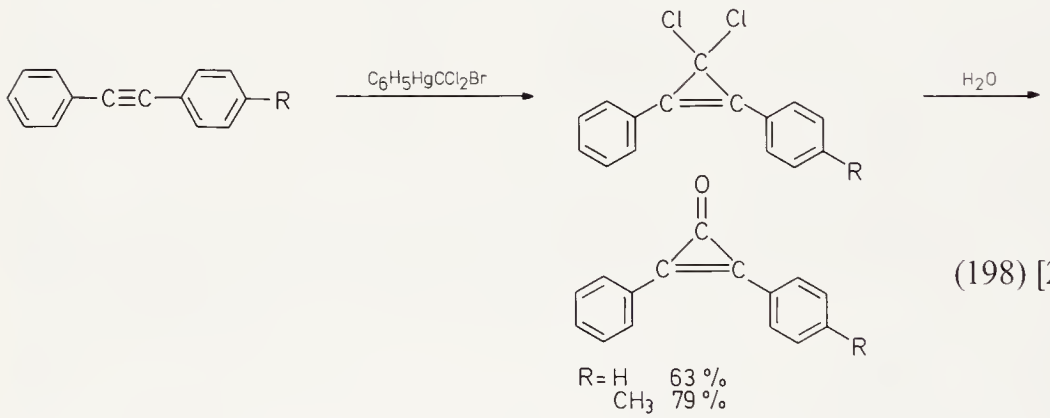
F. Synthesis of Cyclopropenones

The divalent transfer reactions of organomercurial reagents can be extended to alkylarylacetylenes and diarylacetylenes to provide dihalocyclopropenes, useful intermediates in the synthesis of cyclopropenones (Eqs. 197, 198).



R=C_2H_5,C_6H_5 (15%), CH=CHC_6H_5, C≡CC_6H_5

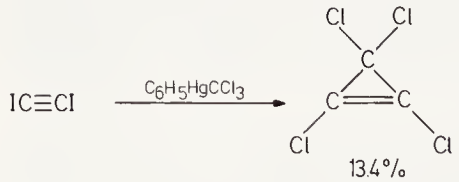
(197) [223]



R=H 63%
CH_3 79%

(198) [224]

Unfortunately, this approach is not applicable to dialkylacetylenes [223], and diiodoacetylene gives a mixture of products upon attempted reaction with $C_6H_5HgCCl_3$ (Eq. 199) [225].

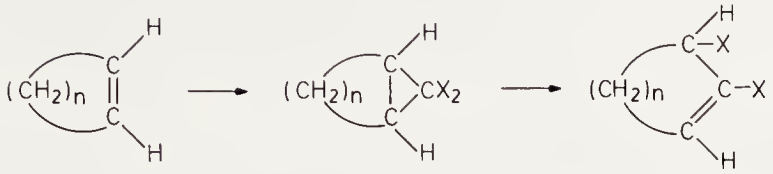


13.4% + IC≡$CCCl_3$ 12.9% + C_6H_5I 4.2% + Cl_2C=CCl_2 1.9% (199)

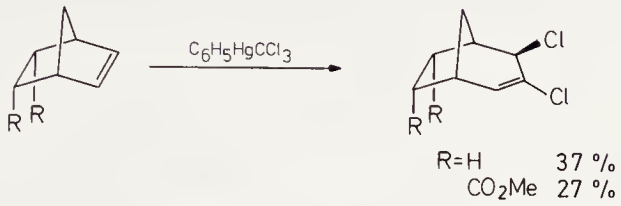
G. Ring Expansion Reactions

The cyclopropanes formed in organomercurial divalent carbon transfer reactions are valuable intermediates in a number of ring expansion proce-

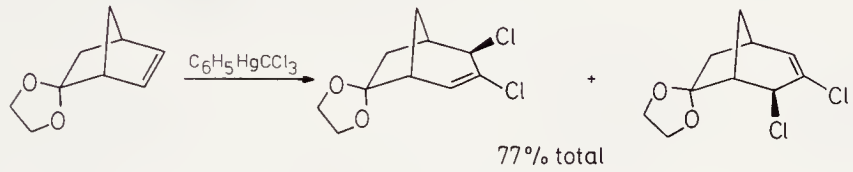
dures. In fact, in a number of cases the dihalocyclopropanes cannot even be isolated, but undergo immediate thermal isomerization to the corresponding ring expanded allylic halides (Eq. 200). In general, strained bicyclic olefins give the best yields (Eqs. 201–205). Note the remarkable regioselectivity of



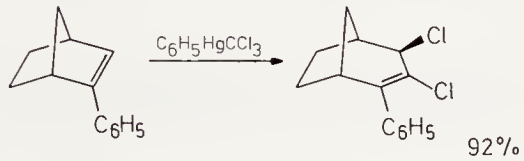
(200)



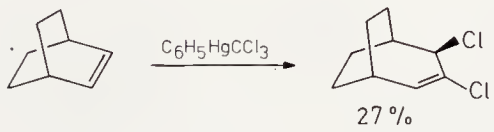
(201) [226]



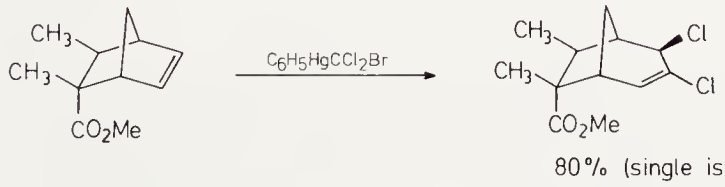
(202) [226]



(203) [226]



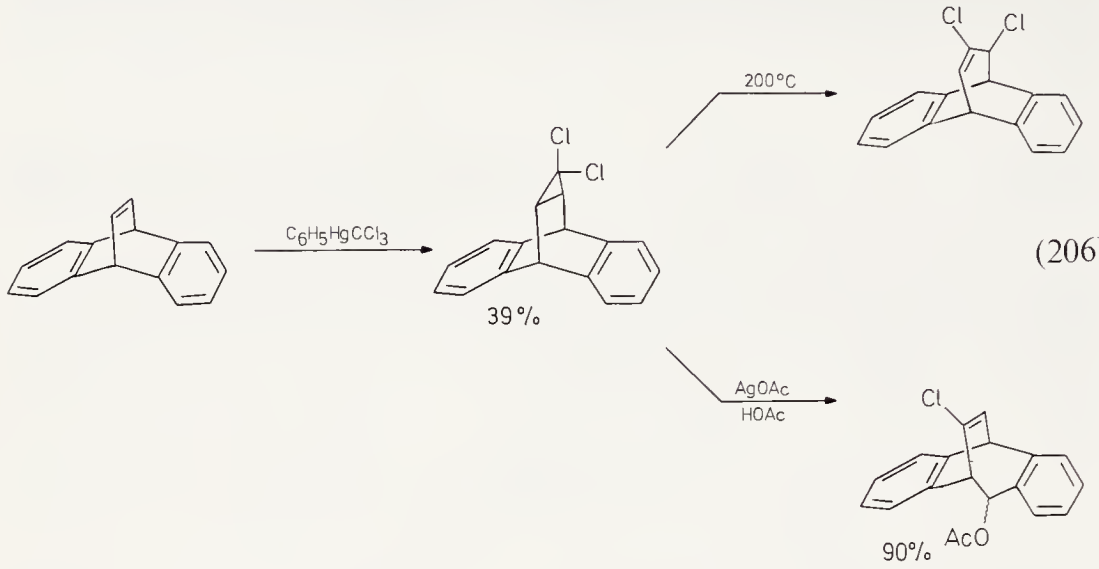
(204) [226]



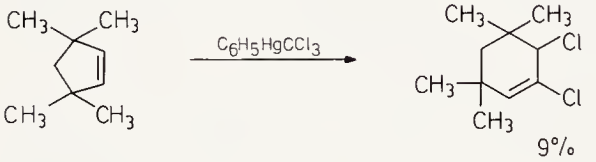
(205) [227]

this last example. Highly hindered bornylene proved unreactive toward addition [226], while reaction of norbornene and $C_6H_5HgCFCl_2/NaI$ led to a multitude of addition and rearrangement products [214]. The dichlorocyclopropane adduct of dibenzobicyclo[2.2.2]octatriene, which could only be prepared using $C_6H_5HgCCl_3$, proved to be more stable, but can be rearranged using higher temperatures or silver acetate in acetic acid (Eq. 206) [228, 229]. Simple unstrained cyclic olefins usually give stable addition compounds, but occasional rearrangement reactions have been reported (Eqs. 207–209).

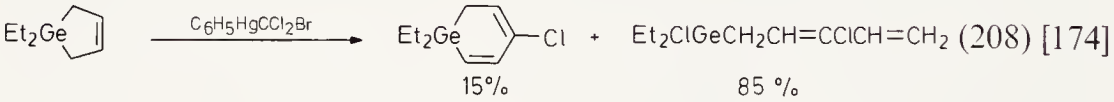
The organogermanium reaction presumably proceeds through rearrangement to the allylic chloride and subsequent H—Cl and Ge—Cl eliminations.



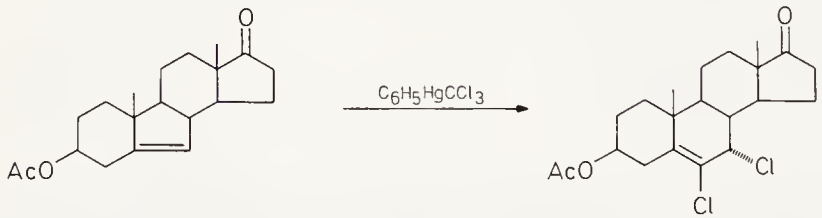
(206)



(207) [226]

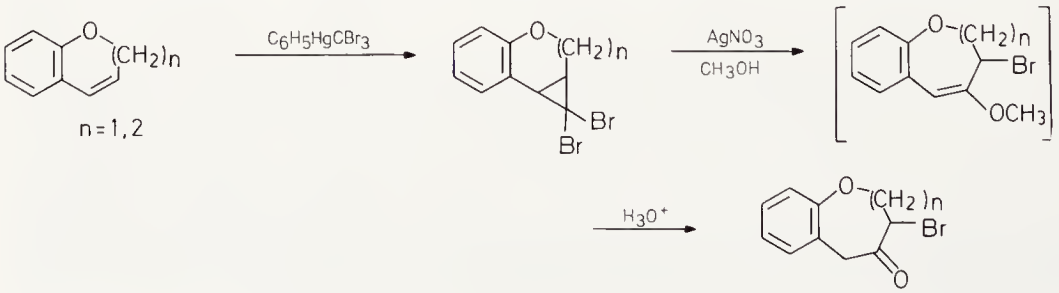


(208) [174]



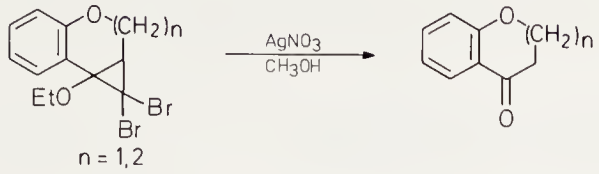
(209) [200]

Cyclopropanes derived from cyclic aryl olefins are much more prone to rearrangement. Some of these reactions are useful in ring expansion sequences, as illustrated by the following example (Eq. 210) [125]. Dibromocyclo-



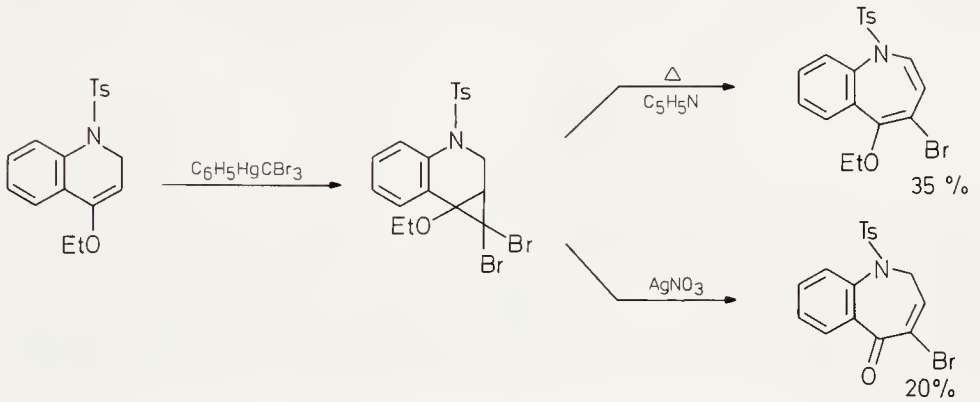
(210)

propanes derived from the isomeric vinyl ethers fail to rearrange, while ethoxy analogs of the above compounds eliminate the cyclopropane carbon (Eq. 211). On the other hand, ring expansion products are observed from



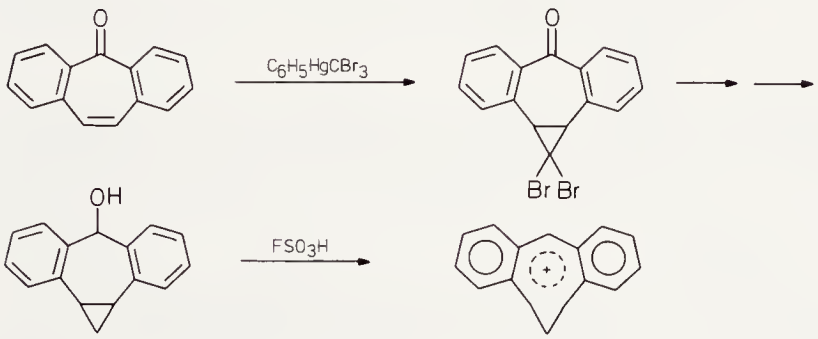
(211)

analogous nitrogen heterocycles providing a new azepine and azepinone synthesis (Eq. 212) [230].



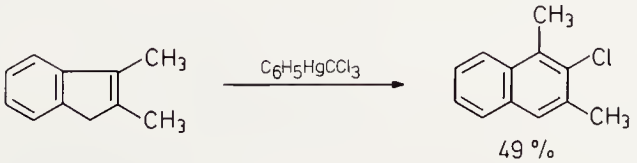
(212)

Ring expansion reactions have also been used in a synthesis of the dibenzohomotropylium ion (Eq. 213) [231, 232].

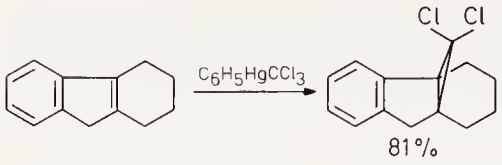


(213)

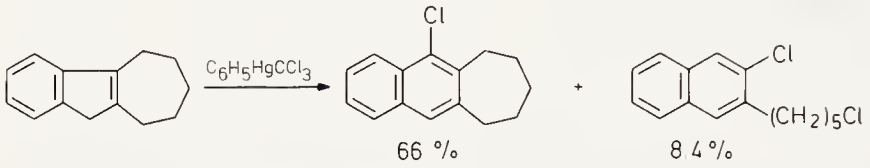
Substituted indenes can be ring expanded to halonaphthalenes using organomercurial reagents. Although the reaction is dependent upon the ring size involved, this approach provides a novel synthesis of 1,3-bridged naphthalenes (Eqs. 214–217) [233, 234]. The naphthalene products apparently arise



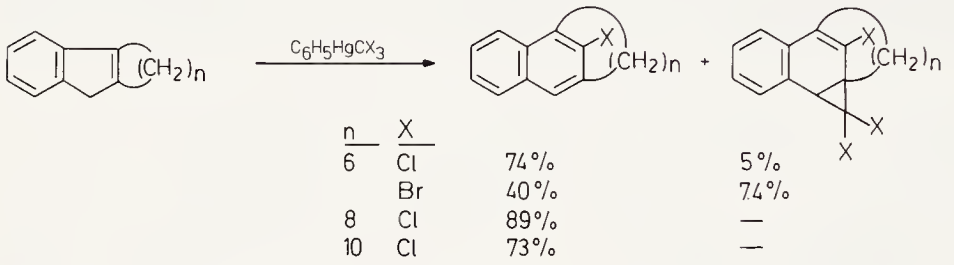
(214)



(215)



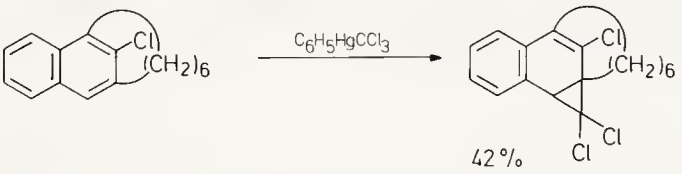
(216)



n	X		
6	Cl	74%	5%
	Br	40%	7.4%
8	Cl	89%	—
10	Cl	73%	—

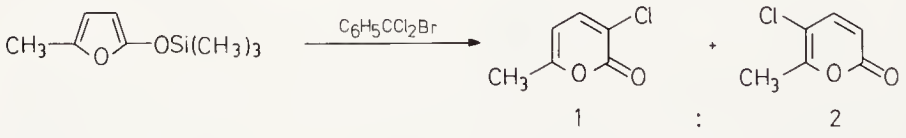
(217)

by elimination of HCl from the anticipated allylic chloride. In the third example (Eq. 216), the major product is explained by invoking phenyl migration in an intermediate cyclopropyl cation. When the bridged naphthalene products become sufficiently strained (n = 6), products of further addition are observed. Additional organomercurial reagent can provide these polycyclic products in reasonable yield (Eq. 218).

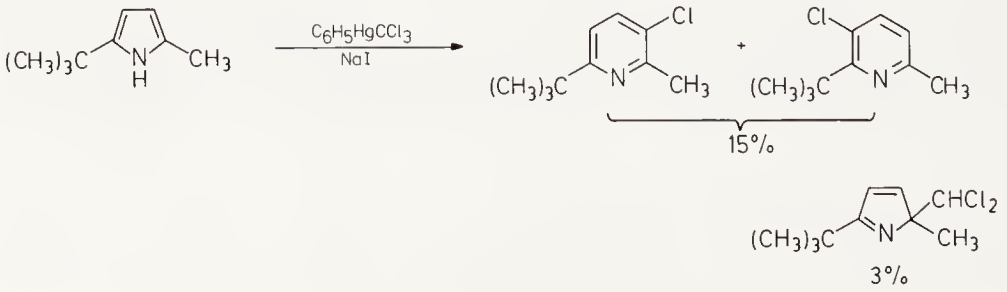


(218)

Similar ring expansions can be effected using heterocyclic compounds (Eqs. 219–221). In the last reaction (Eq. 221) with n = 5, the isomeric 4-chloro-

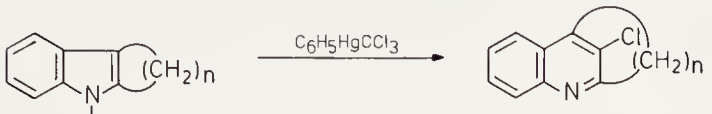


(219) [235]



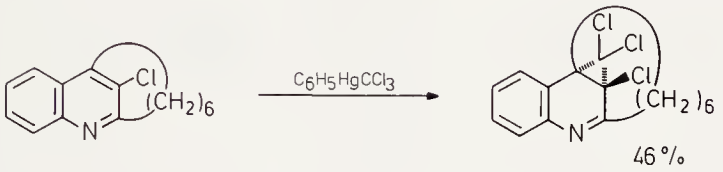
(220) [236]

quinoline is the major product (11.6% yield) analogous to the corresponding indene reaction. These bridged quinolines can also undergo further addition reactions, the products of which are dependent upon the length of the bridge in the starting material (Eqs. 222, 223) [238]. Arsenic heterocycles also rearrange when sufficient strain is present in the cyclopropane (Eqs. 224, 225) [239].

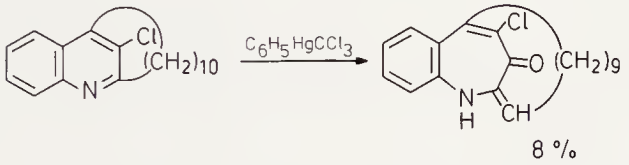


n	X	%Yield
5	H	0
6	H	48.6
8	H	53.5
10	H	69
10	Ac	76

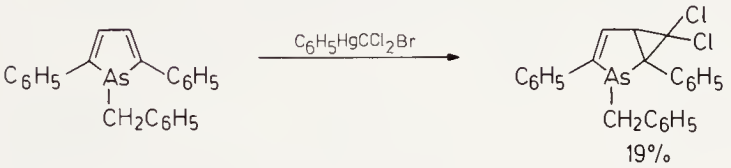
(221) [237]



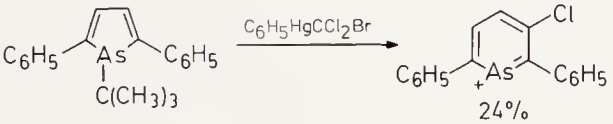
(222)



(223)

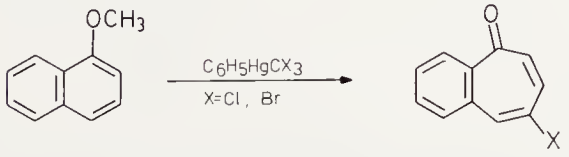


(224)

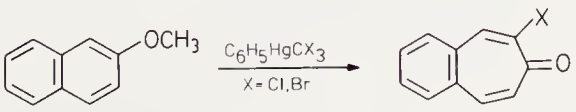


(225)

α- and β-Naphthyl ethers also undergo ring expansion reactions upon reaction with organomercurial reagents to provide a highly convenient synthesis of benzotropones (Eqs. 226, 227) [240–242]. The structures of the

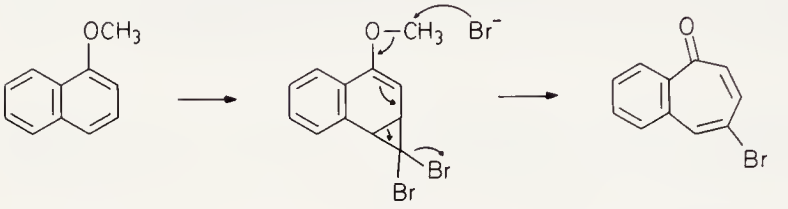


(226)



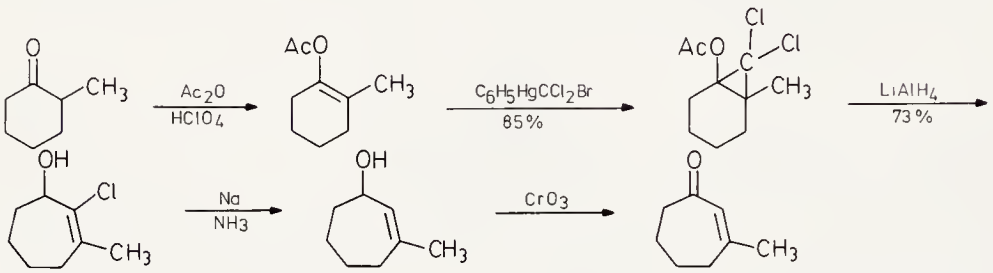
(227)

α-naphthyl products were originally misassigned [242]. The tropones presumably arise as follows (Eq. 228). Anisole gives a host of products, but no tropone [240].

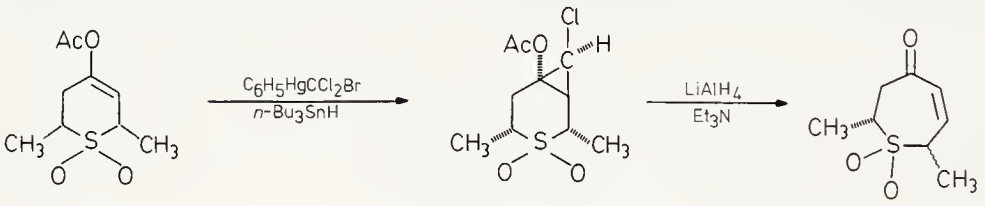


(228)

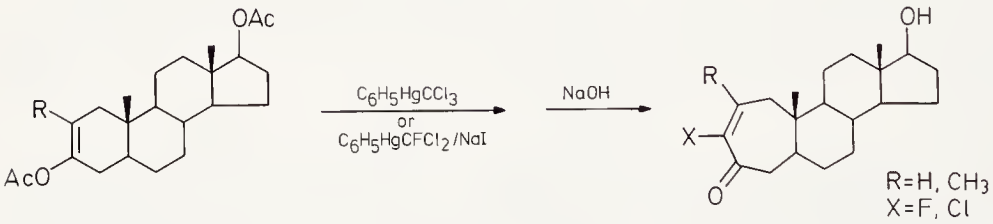
The treatment of dihalocyclopropanes derived from enol acetates with bases affords a valuable method for ring expanding ketones (Eqs. 229–233).



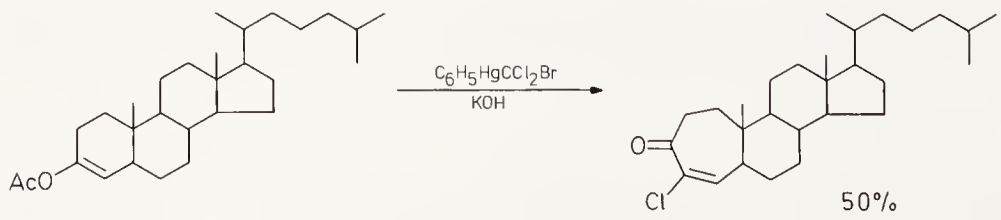
(229) [132, 243]



(230) [134]

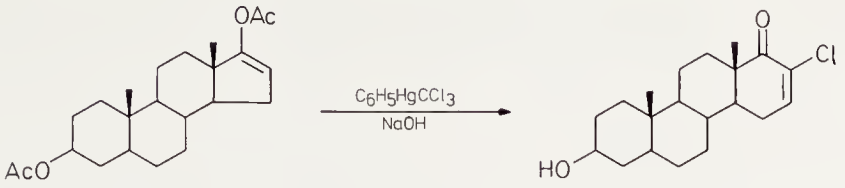


(231) [136]

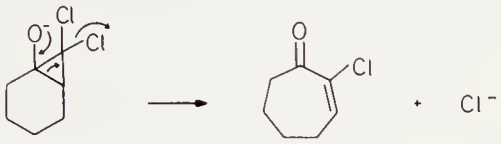


(232) [132]

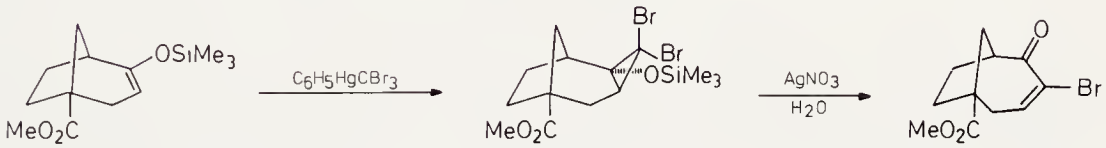
These ring expansions presumably proceed through an intermediate alkoxide as follows (Eq. 234). Analogous ring expansion has been accomplished by solvolysis of a cyclopropyl silyl ether (Eq. 235) [128].



(233) [136]

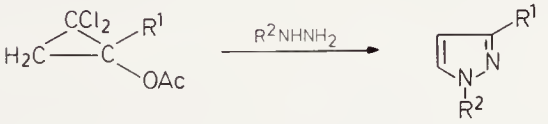


(234)



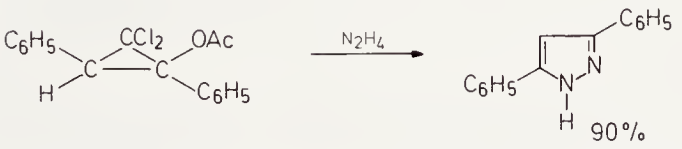
(235)

Dichlorocyclopropyl acetates are also very useful intermediates in the synthesis of heterocyclic compounds. For example, treatment with hydrazines affords pyrazoles (Eqs. 236, 237). Cyclic enol acetates lead to mixtures of



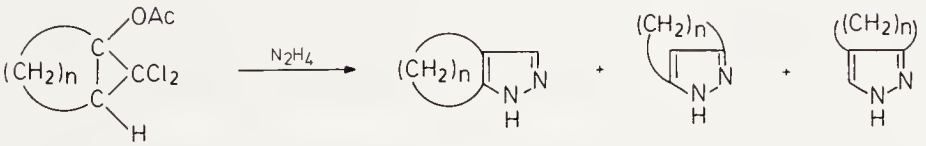
R^1	R^2	%Yield
CH_3	H	78
CH_3	C_6H_5	43
C_6H_5	H	100
C_6H_5	C_6H_5	35

(236) [129, 130]



(237) [129]

pyrazoles whose structures have not been convincingly established (Eq. 238) [129, 131]. Dual pathways are apparently followed by these reactions

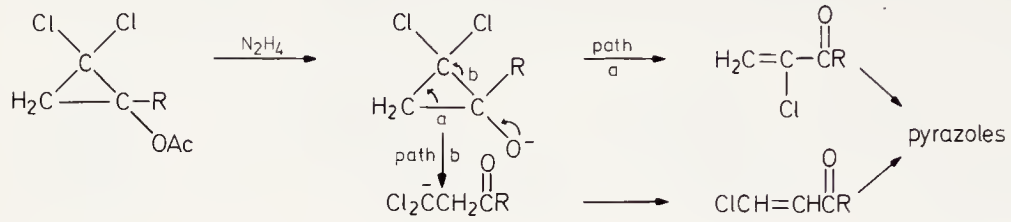


(238)

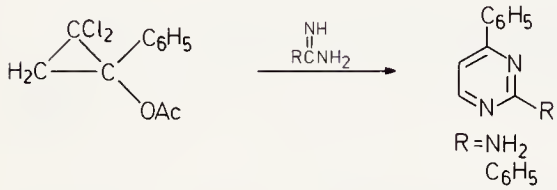
(Eq. 239). If guanidine or benzamidine are used instead of hydrazines, pyrimidines are formed (Eqs. 240, 241) [130].

Before concluding this section, it seems appropriate to point out that dihalocyclopropanes react with alkyl lithium reagents to provide allenes.

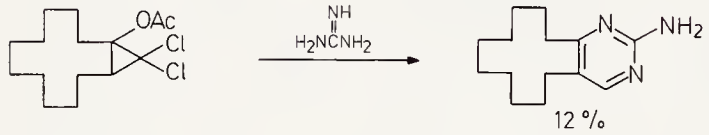
These reactions can also be extended to cyclic olefins to afford ring expanded products (Eqs. 242, 243).



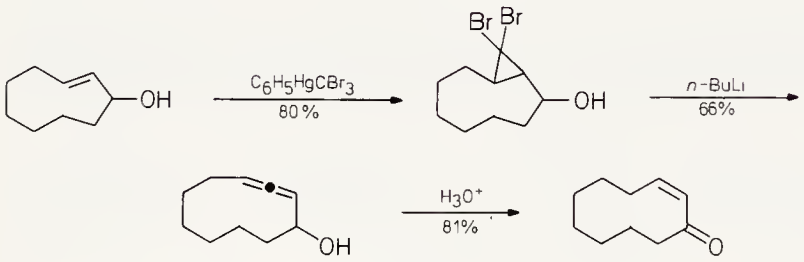
(239)



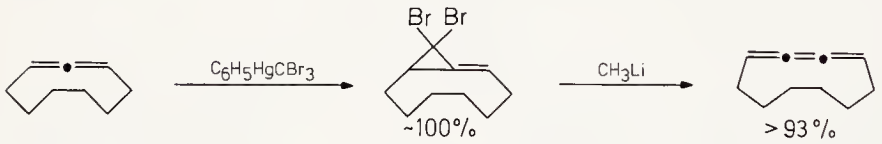
(240)



(241)



(242) [178]



(243) [188]

H. Reactions with Oxygen, Nitrogen and Sulfur Compounds

Although organomercurial divalent transfer reactions are tolerant of a wide range of important organic functionality, a number of functional groups can react with these reagents in the presence or absence of an olefinic double bond. The nature of these reactions and their possible synthetic utility is the subject of this section.

Alcohols can react with the organomercurial reagents. As noted earlier, the alcohol group in allylic alcohols can effectively compete with the carbon—carbon double bond for the organomercurial reagent [176]. Low yields of cyclopropanes are common, and it is best to protect the alcohol as either an acetate or a silyl ether in order to obtain high yields of cyclopropyl alcohols.

The reaction with alcohols has been more closely examined and a variety of products have been reported (Eq. 244) [177]. The products appear to arise as follows (Scheme 10.6). The less nucleophilic alcohols CF_3CH_2OH and

$$ROH \xrightarrow{C_6H_5HgCCl_2Br} RCl + ROCH(=O) + C_6H_6 + HCCl_3 \qquad (244)$$

Scheme 10.6

$$ROH + :CCl_2 \longrightarrow ROCCl_2H$$
$$ROCCl_2H + ROH \longrightarrow (RO)_2CHCl + HCl$$
$$(RO)_2CHCl \longrightarrow RCl + ROCH(=O)$$
$$C_6H_5HgCCl_2Br + HCl \longrightarrow C_6H_6 + ClHgCCl_2Br$$
$$:CCl_2 + HCl \longrightarrow HCCl_3$$

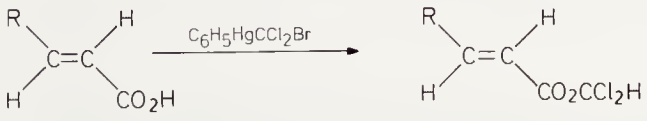
$CF_3CF_2CH_2OH$ do not react, but give substantial yields of $Cl_2C{=}CCl_2$, while more sterically hindered *tert*-butanol gives *tert*-butyl chloride and $Cl_2C{=}CCl_2$ as major products. The latter compound presumably arises from dichlorocarbene insertion into the organomercurial and elimination of the olefin and phenylmercuric bromide. In general, these reactions do not appear to have any preparative utility.

The reaction of carboxylic acids with $C_6H_5HgCCl_2Br$ provides an excellent general preparative route to the corresponding dichloromethyl esters (Eq. 245) [25, 110, 244, 245]. It is expecially valuable when direct chlorination

$$RC(=O)OH \xrightarrow{C_6H_5HgCCl_2Br} RC(=O)OCCl_2H \qquad (245)$$

R = CH_3 (92%), CH_3CH_2 (87%), $(CH_3)_3C$ (84%), C_6H_5 (95%), CH_3OCH_2 (84%), $ClCH_2$ (86%), $BrCH_2$ (92%), CH_3CHBr (88%), Cl_2CH (76%), Cl_3C (59%)

cannot be used as in the synthesis of unsaturated esters (Eqs. 246, 247) [110, 245]. As indicated by these examples, the organomercurials react pre-



R=H 83%
CH_3 87% (246)

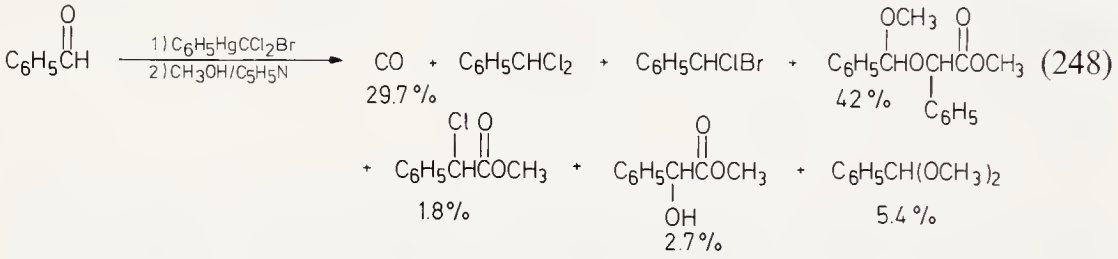
$$H_2C{=}CHCH_2CO_2H \xrightarrow{C_6H_5HgCCl_2Br} H_2C{=}CHCH_2CO_2CCl_2H \quad 76\% \qquad (247)$$

ferentially with the carboxylic acid moiety. Competition studies between cyclohexene and acetic acid indicate a preference of approximately 2 to 1 in favor of the acid [244, 245]. Kinetic studies indicate that the reaction is first order in organomercurial and zero order in carboxylic acid, suggesting the

intermediacy of dichlorocarbene [245]. Unfortunately, reactions with $C_6H_5HgCClBr_2$ and $C_6H_5HgCBr_3$ do not provide the corresponding bromomethyl esters.

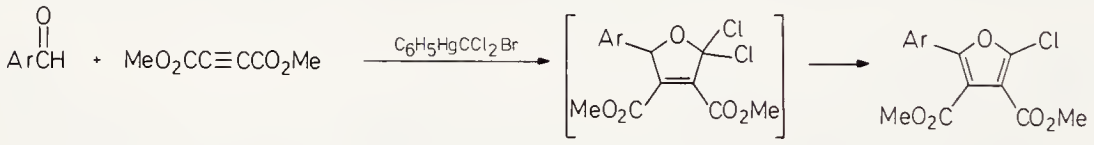
Simple aldehydes and ketones do not react with the organomercurial reagents and do not interfere with the usual cyclopropanation reactions [246]. However, carbonyl compounds do react with these reagents in the absence of olefinic double bonds. Thus, simple aldehydes and ketones react with formation of carbon monoxide [247].

Benzaldehyde gives a large variety of products (Eq. 248) [248, 249]. Analogous products are obtained from substituted benzaldehydes [249], but the

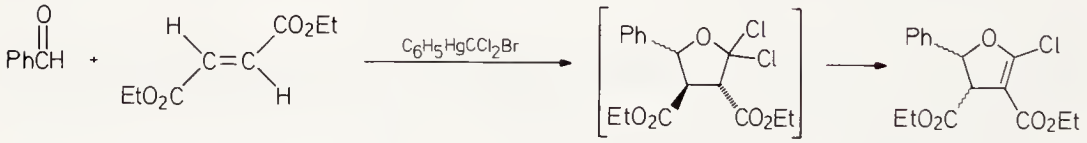


(248)

reaction of benzaldehyde and $C_6H_5HgCBr_3$ gives CO and $C_6H_5CHBr_2$ as the only observed products. On the presence of dimethyl acetylenedicarboxylate (Eq. 249) and diethyl fumarate (Eq. 250), substituted benzaldehydes react with $C_6H_5HgCCl_2Br$ to afford furans and dihydrofurans respectively [250, 251].

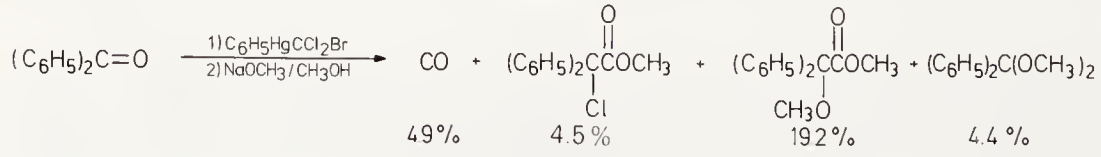


(249)



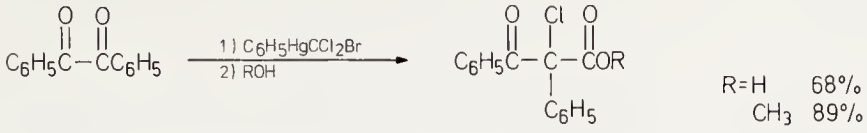
(250)

Benzophenone also reacts with these mercurials to give numerous products (Eq. 251). No intermediates could be trapped by adding dimethyl



(251)

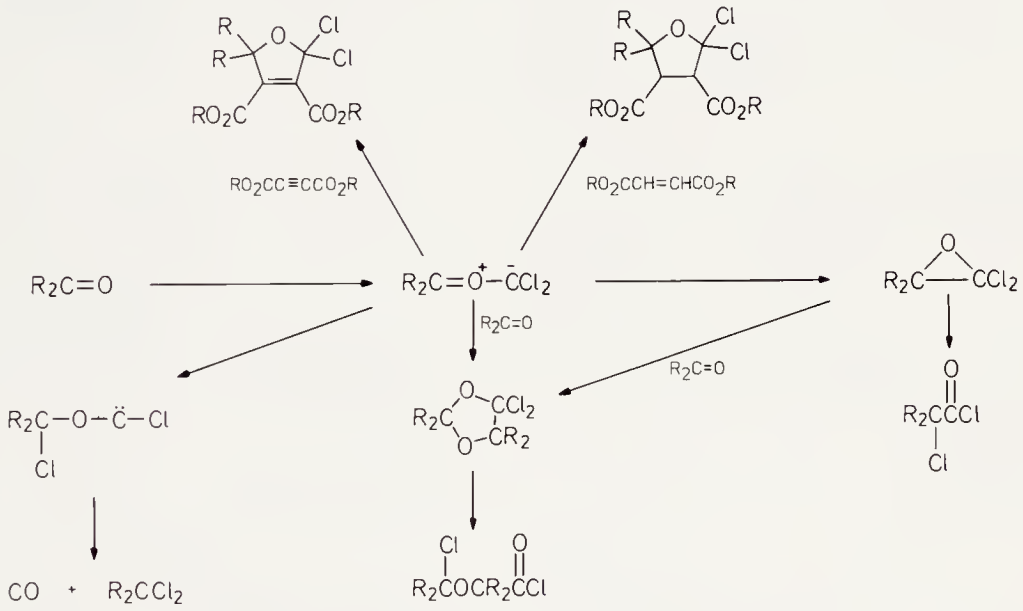
acetylenedicarboxylate [252]. Benzil gives analogous products, but in much better yield (Eq. 252) [253, 254].



(252)

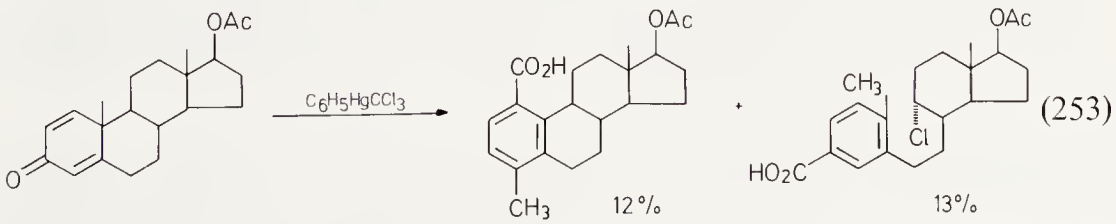
The following mechanistic pathways have been suggested for these reactions (Scheme 10.7) [248–252, 255]. It is known that both benzaldehyde and benzophenone form complexes with $C_6H_5HgCCl_2Br$ as seen by a shift in the

Scheme 10.7



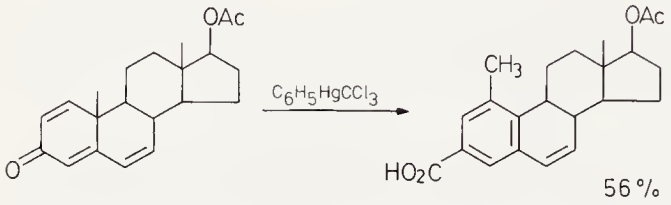
carbonyl absorption in the infrared [249]. Benzaldehyde also enhances the rate of organomercurial decomposition, but the relative reactivity of olefins towards the organomercurial under these conditions is unchanged and only dichlorocyclopropanes are formed. Apparently the dichlorocarbene formed remains uncomplexed during addition to the olefin. It appears that free dichlorocarbene must not be present in the above carbonyl reactions, however, since the reaction occurs under conditions in which $C_6H_5HgCCl_2Br$ does not react with olefins.

Unsaturated steroidal ketones react with $C_6H_5HgCCl_3$ to give aromatic products (Eqs. 253, 254) [197]. Once again these reactions appear to proceed



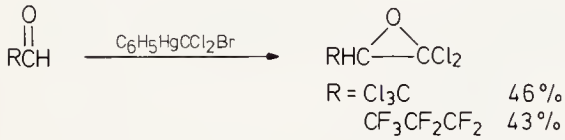
(253)

through carbonyl ylids or oxiranes followed by a complicated series of rearrangements.

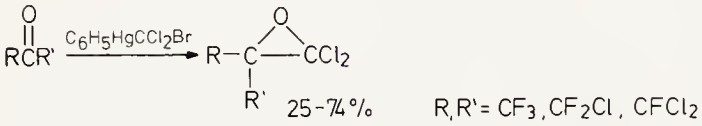


(254)

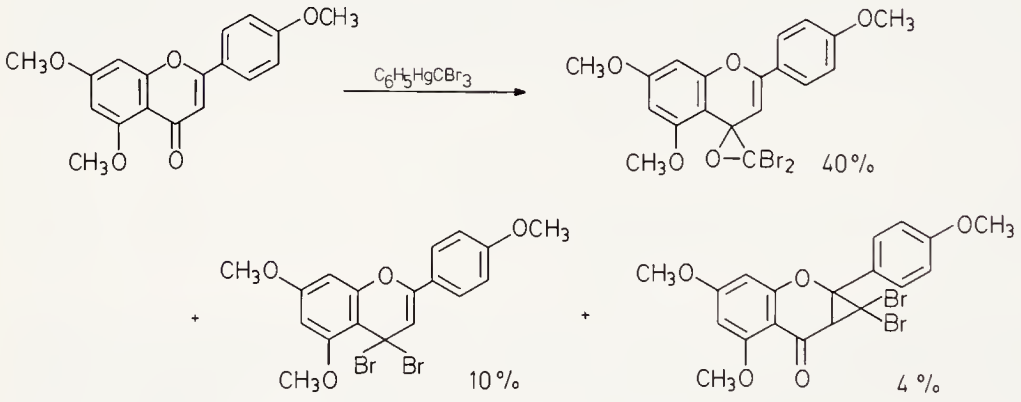
With highly halogenated aldehydes and ketones or 5,7,4′-trimethoxyflavone, one can actually isolate the anticipated oxiranes (Eqs. 255–257).



(255) [253]



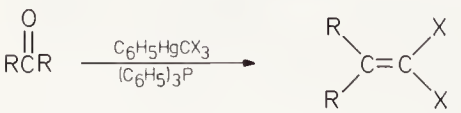
(256) [246, 254]



(257) [256]

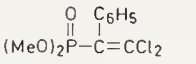
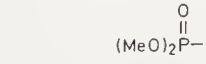
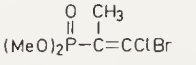
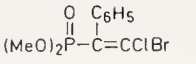
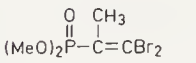
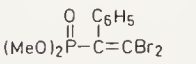
Hexachloroacetone gives only octachloro-2-butanone in low yield, presumably via the oxirane [254]. Other organomercurials also afford the corresponding oxiranes ($C_6H_5HgCFBr_2$ [14], $C_6H_5HgCClBr_2$ [246, 254], $C_6H_5HgCBr_3$ [246, 254]), but $C_6H_5HgCF_3$/NaI fails [205].

In the presence of triphenylphosphine, the reaction of organomercurials and aldehydes and ketones takes an entirely different course. A Wittig-like reaction ensues and excellent yields of olefins are obtained (Eq. 258). Some representative yields are included in Table 10.7. These reactions are much



(258)

Table 10.7. Synthesis of Vinyl Halides from Carbonyl and Diazo Compounds

Organomercurial	Substrate	Vinyl halide	% Yield	Ref.
$C_6H_5HgCHClBr$	$CH_3(CH_2)_5CHO$	$CH_3(CH_2)_5CH{=}CHCl$	82	257
	C_6H_5CHO	$C_6H_5CH{=}CHCl$	73	
			77	
$C_6H_5HgCHBr_2$	$CH_3(CH_2)_5CHO$	$CH_3(CH_2)_5CH{=}CHBr$	53	
	C_6H_5CHO	$C_6H_5CH{=}CHBr$	55	
			52	
$C_6H_5HgCCl_2Br$	C_6H_5CHO	$C_6H_5CH{=}CCl_2$	65	
			65	
			80	258
			57	
$C_6H_5HgCClBr_2$			68	
			58	
$C_6H_5HgCBr_3$	C_6H_5CHO	$C_6H_5CH{=}CBr_2$	53	257
			74	258
			51	
$C_6H_5HgCCl_2CH_3$	C_6H_5CHO	$C_6H_5CH{=}CClCH_3$	0	55
$C_6H_5HgCClBrCF_3$	C_6H_5CHO	$C_6H_5CH{=}CClCF_3$	38	30

more rapid than cyclopropane formation from olefins, indicating that a free carbene is probably not involved. The following mechanism is favored (Scheme 10.8). It should be pointed out that two alternate and generally more convenient routes to these same olefins exist (Eqs. 259, 260).

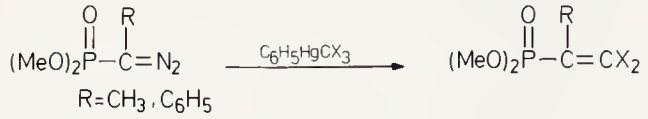
Scheme 10.8

$$C_6H_5HgCX_3 + P(C_6H_5)_3 \longrightarrow C_6H_5HgCX_2\overset{+}{P}(C_6H_5)_3\ X^-$$
$$C_6H_5HgCX_2\overset{+}{P}(C_6H_5)_3\ X^- \longrightarrow C_6H_5HgX + X_2C{=}P(C_6H_5)_3$$
$$R_2C{=}O + X_2C{=}P(C_6H_5)_3 \longrightarrow R_2C{=}CX_2 + OP(C_6H_5)_3$$

$$R_2C{=}O + (C_6H_5)_3P + CX_4 \longrightarrow R_2C{=}CX_2 \qquad (259)$$

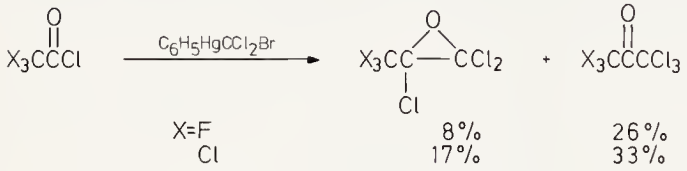
$$R_2C{=}O + (C_6H_5)_3P + NaO_2CCX_3 \longrightarrow R_2C{=}CX_2 \qquad (260)$$

Similar olefination reactions have been accomplished using phosphonate-stabilized diazo compounds (Table 10.7) (Eq. 261) [258].

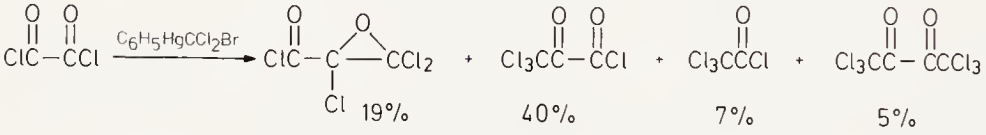


(261)

Highly halogenated acid halides also react with the organomercurial reagents to give oxiranes and ketones (Eqs. 262, 263) [253, 254]. The ketones

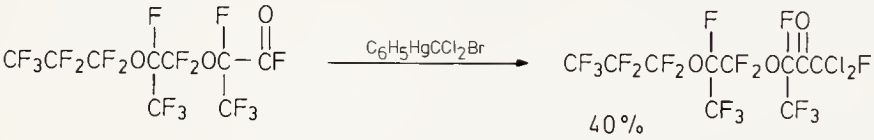


(262)



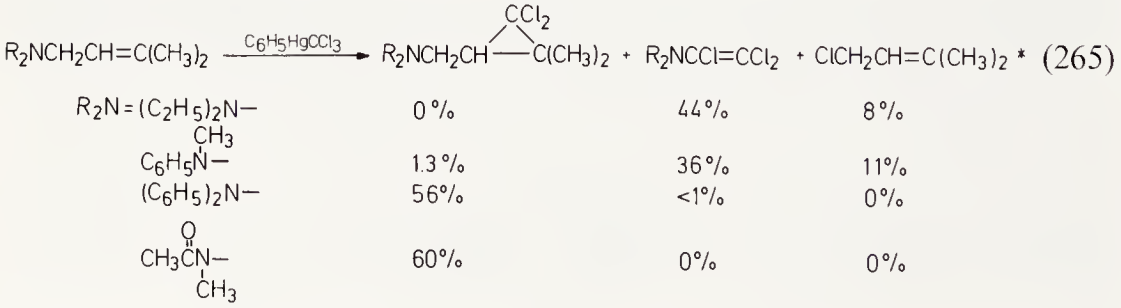
(263)

appear to arise by direct carbon-chlorine insertion and not rearrangement of the oxiranes. Neither phosgene [246, 253] nor perfluorobenzoyl fluoride [254] react, but one other acid fluoride has been converted to the corresponding ketone (Eq. 264) [254].



(264)

A large number of different nitrogen-containing functional groups have been shown to react with the organomercurial reagents. Tertiary amines give a variety of products. For example, allylic tertiary amines react with $C_6H_5HgCCl_3$ to give cyclopropanes or enamines depending on the basicity of the amine (Eq. 265) [259].

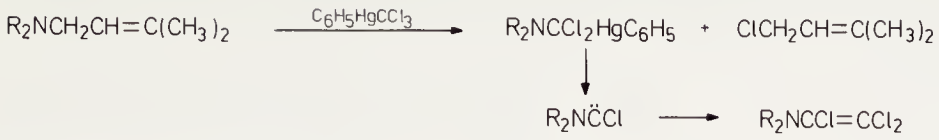


(265)

(* Identified by gas chromatography as isoprene)

The following mechanism has been suggested, although a number of other possibilities exist (Scheme 10.9). Triethyl- and tri-*n*-butylamine also give

Scheme 10.9

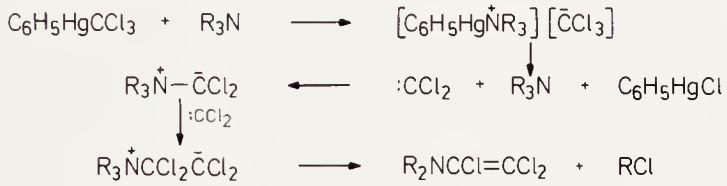


trichlorovinylamines as the major products, although in only low yield (Eq. 266) [260]. Higher yields of these products can be obtained using alternate

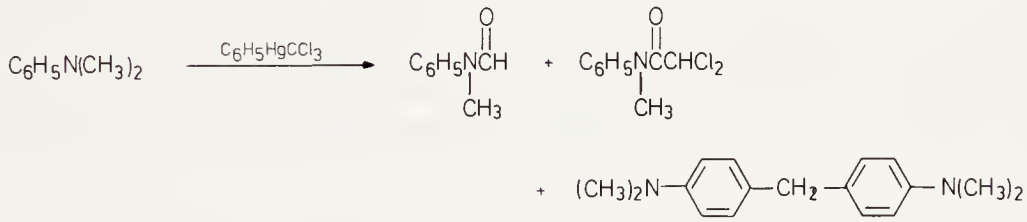
(266)

procedures. These reactions occur at temperatures lower than normally required to thermally generate dichlorocarbene from the organomercurials, suggesting a displacement mechanism (Scheme 10.10). A similar mechanism

Scheme 10.10

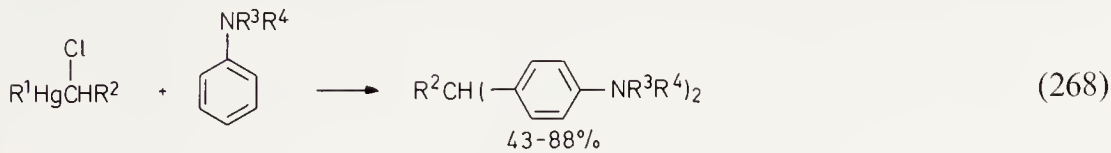


can be invoked to explain some of the products obtained from *N,N*-dimethylaniline (Eq. 267) [261]. The acetamide is assumed to arise from the cor-

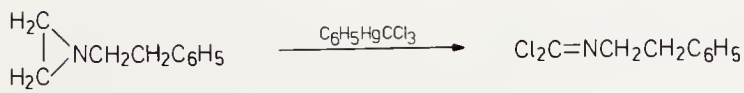


(267)

responding trichlorovinylamine, the formamide from the corresponding dichloromethyl compound, and the diamine through electrophilic substitution on the starting aniline followed by a rearrangement. This latter type of product turns out to be available from the reaction of a wide variety of α-haloorganomercurials and primary, secondary and tertiary aromatic amines as noted in Chap. VI (Eq. 268) [262, 263]. Still a different type of product is observed in the reaction of β-phenethylaziridine (Eq. 269) [264]. An aziridinium ylid intermediate is assumed.



(268)

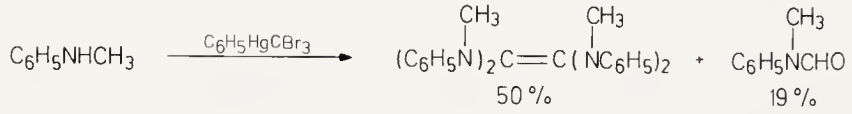


(269)

Secondary amines also form enamine products (Eqs. 270, 271). Mechanistically, it is known that the diamino product does not arise by substitution

R	R`		
C_2H_5	C_2H_5	4%	42%
CH_3	C_6H_5	14.5%	84%
C_6H_5	C_6H_5	45%	0%

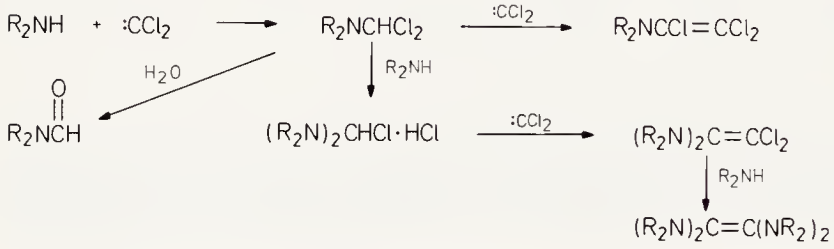
(270) [265]



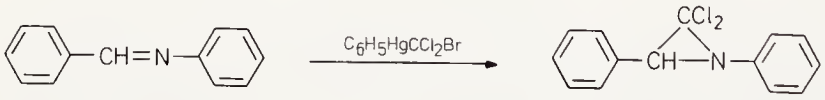
(271) [266]

of the monoamine, and the following vague general scheme has been suggested (Scheme 10.11).

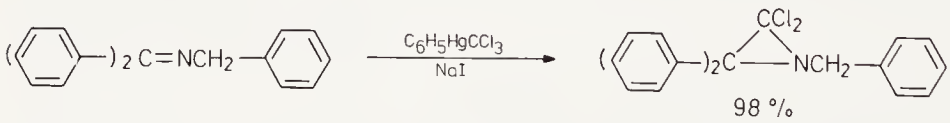
Scheme 10.11



In general, simple imines do not react cleanly with halomethylmercurials to give aziridines [267–270]. However, there are isolated examples of this reaction (Eqs. 272, 273). This reaction is generally best carried out using

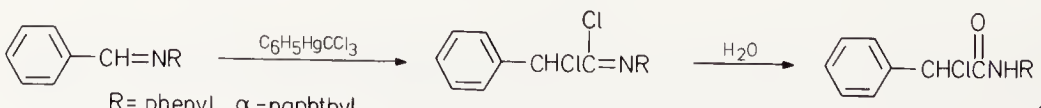


(272) [269, 270]



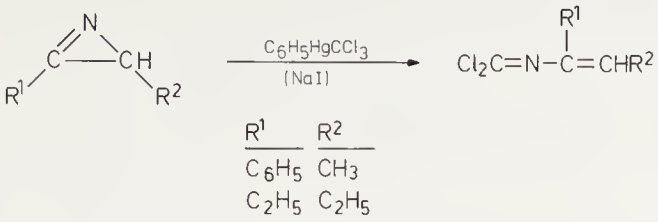
(273) [270]

chloroform and base under phase transfer conditions [270]. With higher temperatures and longer reaction times, rearranged products are observed and the corresponding amides are obtained in good yield after hydrolysis (Eq. 274) [270]. Although the anticipated aziridines are thermally stable, the difficulty lies in the fact that they are easily rearranged in the presence of



(274)

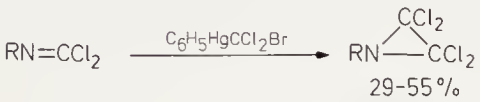
phenylmercuric halides. Azirines also give rearranged products as might be anticipated (Eq. 275) [271, 272]. Aziridine products are much more easily



(275)

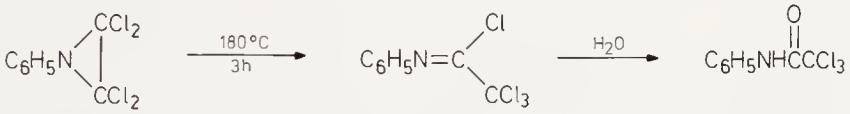
R^1	R^2
C_6H_5	CH_3
C_2H_5	C_2H_5

obtained from less basic dichloromethylene imines (Eq. 276) [268, 269]. The organomercurials $C_6H_5CFBrCO_2Et$ [13] R = isopropyl, cyclohexyl, phenyl,

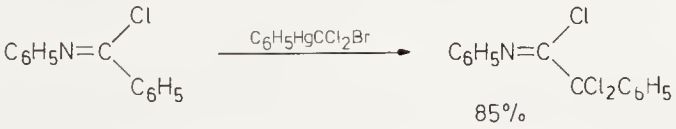


(276)

4-chlorophenyl, *p*-tolyl and $C_6H_5HgCFCl_2$ [12], with and without NaI, also afford the corresponding aziridines, but $C_6H_5HgCF_3$/NaI fails to react [205]. The resulting highly halogenated aziridines, although reasonably thermally stable, do rearrange at higher temperatures (Eq. 277) [269]. An analogous rearrangement is observed during the reaction of $C_6H_5N{=}CClC_6H_5$ (Eq. 278). The compound $C_6H_5N{=}CClCCl_3$ fails to react.

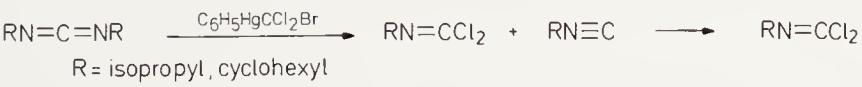


(277)



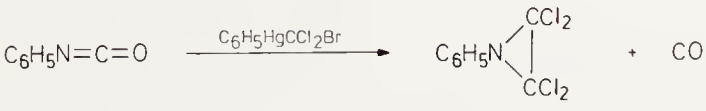
(278)

Carbodiimides react readily with $C_6H_5HgCCl_2Br$ to initially give dichloromethylene imines and isonitriles, which react with further reagent to give more dichloromethylene imine (Eq. 279) [166, 273]. Although high yields are obtained, this reaction appears to have little preparative utility. The reaction



(279)

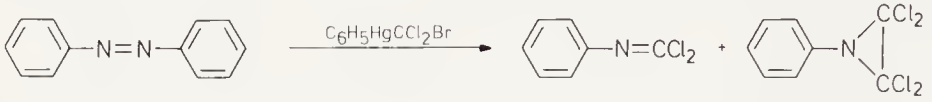
of phenylisocycanate proceeds one step further to the aziridine (Eq. 280) [166], while isothiocyanates give primarily carbon-sulfur bond cleavage (Eq. 281).



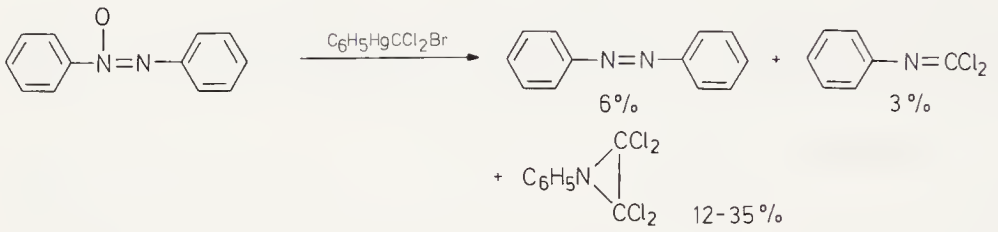
(280)

(281)

The nitrogen—nitrogen double bond also reacts with the phenylmercurial reagents. Azoarenes give cleavage products identical to those of the above reactions (Eq. 282) [269, 273, 274]. Phenyl azide behaves similarly [275], as does azoxybenzene (Eq. 283) [269]. A similar deoxygenation of pyridine

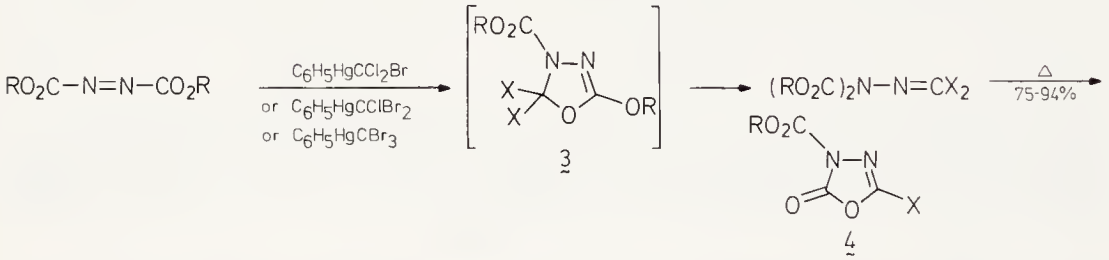


(282)



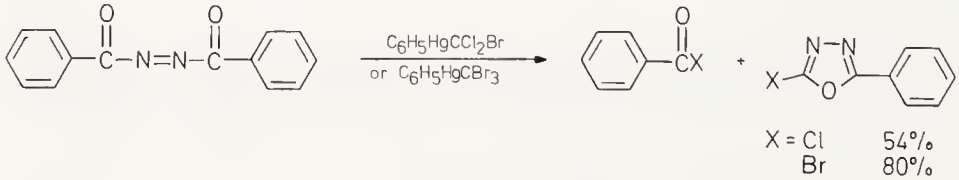
(283)

N-oxide has also been reported [276]. The reaction of dialkyl azodicarboxylates and all three bromochloromethylmercurials gives rearranged hydrazones and not cleavage products (Eq. 284) [164, 274, 277]. The combination $C_6H_5HgCF_3$/NaI fails to react, but identical products are obtained from

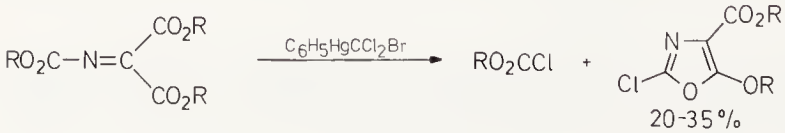


(284)

NaO_2CCCl_3. Intermediates of the type 3 have been observed and isolated, and shown to thermally rearrange to the expected hydrazones [274, 277]. Further heating of the hydrazones affords *4* in good yield [164, 274, 277]. Analogous reactions are observed with related compounds (Eqs. 285, 286)

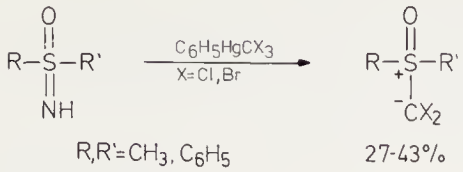


(285)



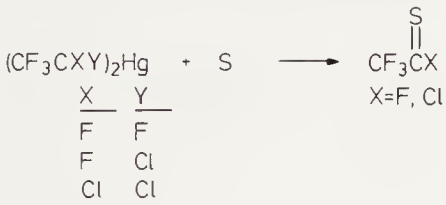
(286)

[164, 288]. Finally, sulfoximines react to produce modest yields of the corresponding sulfur ylids (Eq. 287) [279].

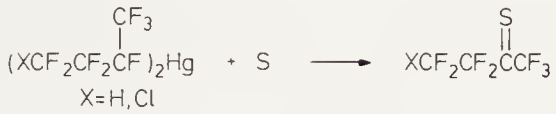


(287)

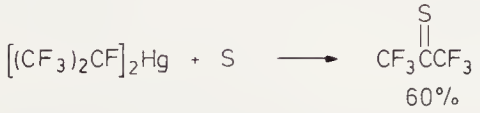
A number of other reactions of sulfur compounds and α-haloorganomercurials have been reported. For example, the vapors of elemental sulfur react with polyhalogenated organomercurials to give thiocarbonyl compounds (Eqs. 288–290) [280–282]. The last compound has been shown to be



(288)



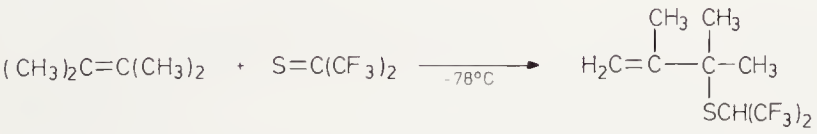
(289)



(290)

highly reactive even at −78 °C in Diels-Alder and ene reactions (Eqs. 291, 292) [280]. At lower temperatures the reaction of the same organomercurials and sulfur gives polysulfides instead (Eq. 293) [282].

(291)

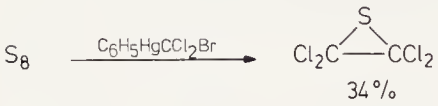


(292)

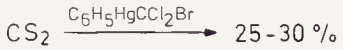
(293)

The organomercurial $C_6H_5HgCCl_2Br$ reacts with sulfur and carbon disulfide to give tetrachlorothiirane, presumably via thiophosgene, which is

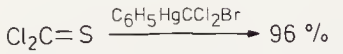
known to react in this fashion (Eqs. 294–296). The analogous thiirane can be obtained from thiobenzophenone and $C_6H_5HgCCl_2Br$, but $C_6H_5HgCFCl_2$-



(294) [283, 284]

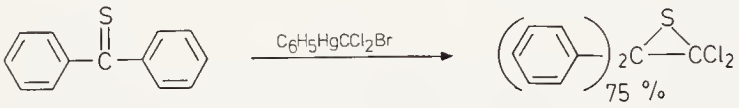


(295) [166]



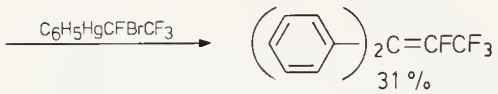
(296) [283, 284]

(NaI) and $C_6H_5HgCFBrCF_3$ give olefins instead (Eqs. 297–299). The combination $C_6H_5HgCF_3$/NaI fails to react.



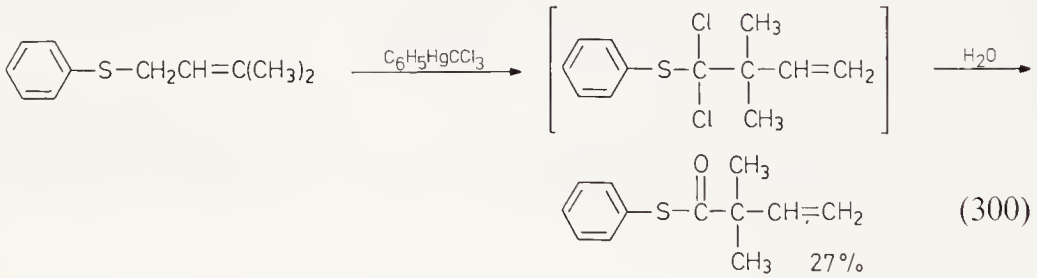
(297) [283–285]

(298) [12]

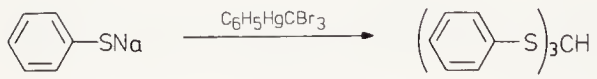


(299) [16]

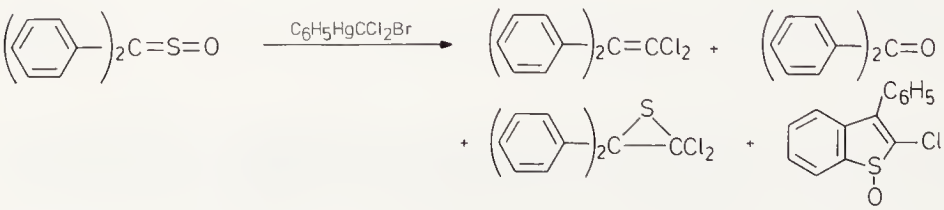
Several other miscellaneous sulfur reactions have been reported (Eqs. 300–303). A number of other sulfur oxides have been reported not to react



(300) [259]

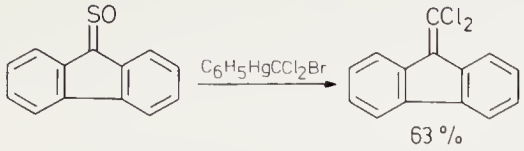


(301) [286]



(302) [285]

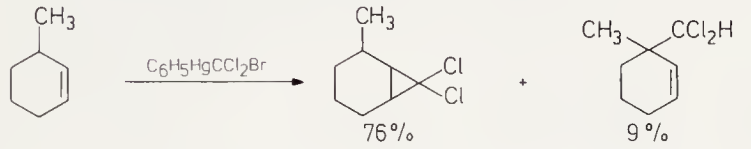
with $C_6H_5HgCCl_2Br$ [285], while analogous reactions of disulfides, diselenides and ditellurides gave no clear-cut products [288].



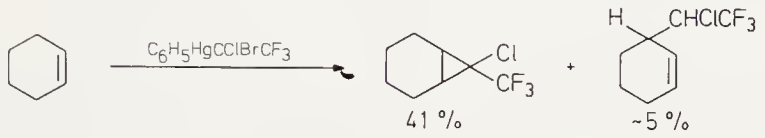
(303) [287]

I. C—H and Si—H Insertion Reactions

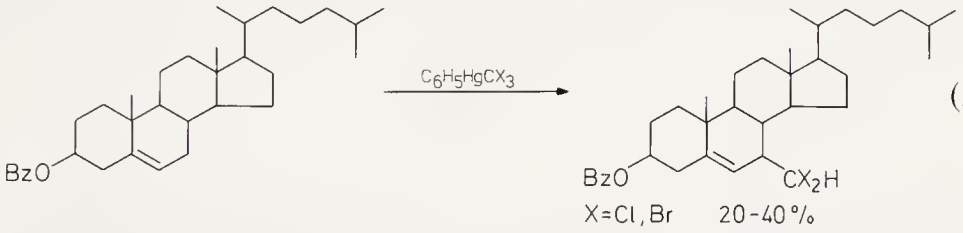
In all of the reported reactions of simple alkenes and α-haloorganomercury compounds, there are precious few examples of competitive C—H insertion occurring (Eqs. 304–307). However, simple cyclic alkanes can undergo C—H



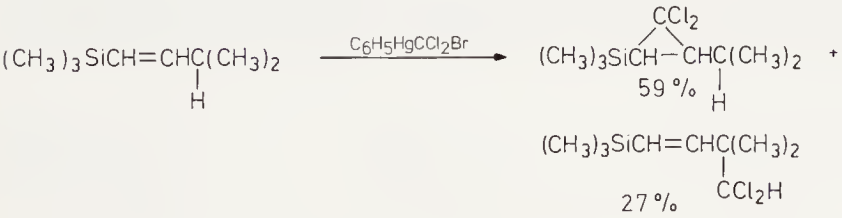
(304) [289]



(305) [30]

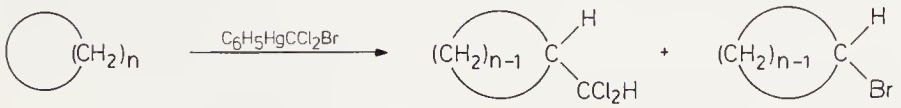


(306) [196]



(307) [289]

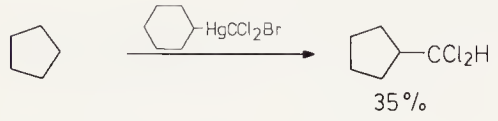
insertion in high yield in the absence of carbon—carbon double bonds (Eqs. 308–310). To obtain good yields, however, one must use the alkane in large



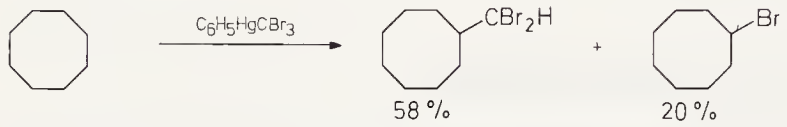
(308) [290]

n	%	%
5	57	22
6	32	22
7	48	low
8	83	low
10	64	—

excess, preferably as the solvent. The preference for C—H insertion has been observed to be CH > CH_2 > CH_3 [289].



(309) [24]



(310) [283]

Benzylic insertion is particularly facile and a number of examples exist (Eqs. 311, 312). In the last example, *n*-Bu_3SnH reduction without isolation

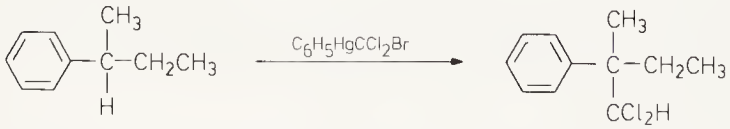
(311) [289, 291]

$C_6H_5HgCCl_2Br$	X = Cl	35%
$C_6H_5HgCBr_3$	Br	6.5%

(312)

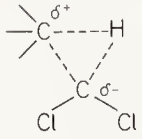
	X	Y	%Yield	Ref.
n-$PrHgCCl_3$	Cl	Cl	36	45
$C_6H_5HgCCl_2Br$	Cl	Cl	58	289,291
$C_6H_5HgCClBr_2$	Cl	Br	21	112

gave a 53% yield of $C_6H_5C(CH_3)_2CH_2Cl$. In general, the yields of insertion products are twice those obtained using NaO_2CCCl_3 [289, 291]. The mechanism of insertion has been studied on optically active 2-phenylbutane (Eq. 313). An initial report indicated that the product was optically inactive [292],

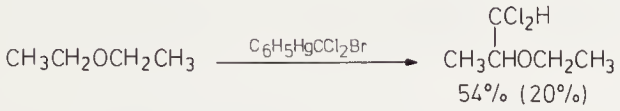


(313)

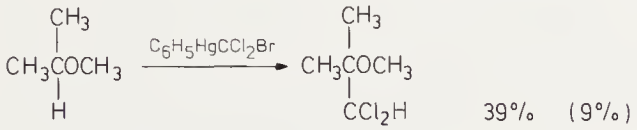
but subsequent studies have indicated that the reaction proceeds with greater than 90% retention of configuration [293, 294]. The kinetic deuterium isotope effect (k_H/k_D) has been reported as both 1.8 [292] and 2.5 [294]. Kinetic studies on ring substituted cumenes correlate equally well with $\sigma = -1.19$ and $\sigma^+ = -.894$, and a three-centered transition state of the following type has been postulated [294].



Hydrogens alpha to an ether oxygen also undergo relatively facile insertion. A detailed study of this reaction has been undertaken and the following conclusions can be drawn [295]. This approach is a substantial improvement over the use of NaO_2CCCl_3 as evidenced by the following yields (yields using NaO_2CCCl_3 are in parentheses) (Eqs. 314, 315). Best yields are ob-

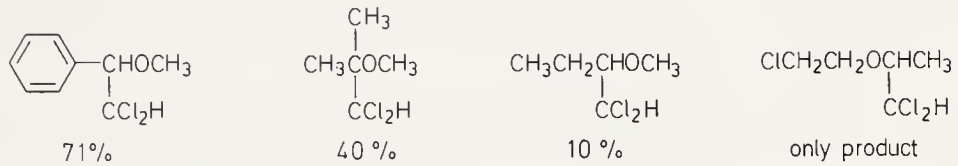


(314)

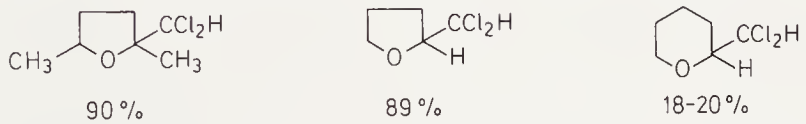


(315)

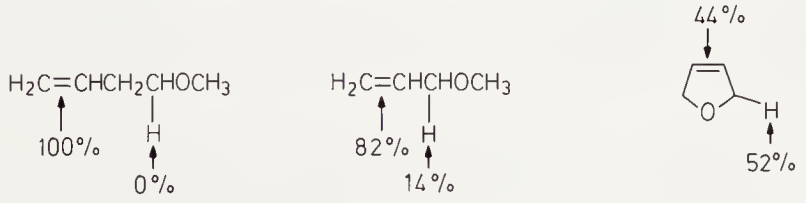
tained from those ethers which contain a carbon best able to bear a positive charge. Compare the following results:

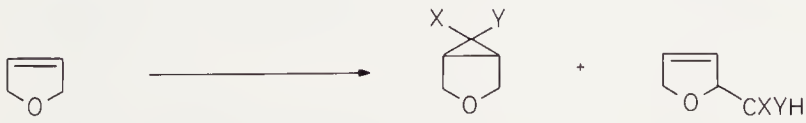


No insertion into the methyl group of methyl ethers is observed. Steric hindrance is very important as indicated by the 3% yield from methyl neopentyl ether. Cyclic five membered ring ethers are more reactive than their six membered ring counterparts. Carbon—carbon double bonds are still substantially

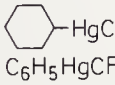


more reactive than the C—H group unless the hydrogen is also allylic. The chemoselectivity of several different organomercurials towards dihydrofuran

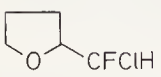




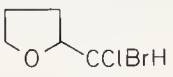
(316)

	only product		Ref.
$C_6H_5HgCF_3$	–	–	205
$C_6H_5HgCFCl_2$	9	1	10, 11
$C_6H_5HgCClBr_2$	1	1	112
$C_6H_5HgCCl_2Br$	0.85	1	110
	0.78	1	24
$C_6H_5HgCFBrCO_2Et$	0.77	1	13

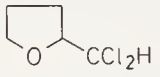
has been studied with the results indicated (Eq. 316). Clearly, the selectivity in favor of olefin addition follows the order $CF_2 > CFCl > CClBr \simeq CCl_2 \simeq CFCO_2Et$. The yields of tetrahydrofuran insertion products substantiate this trend. These mechanistic studies suggest the presence of a free carbene



0% [11]



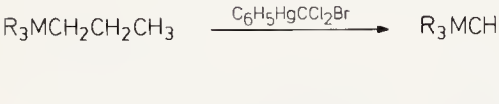
39% [112]



67% [110]

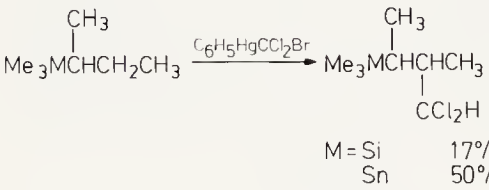
in these reactions with no need to invoke an oxygen-carbene ylid prior to insertion.

Hydrogens beta to a silicon, germanium or tin atom are also significantly activated towards C—H insertion as indicated by the following examples (Eqs. 317–319). In all cases, the yields are substantially higher than those



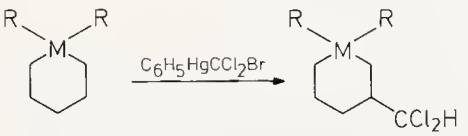
(317)

R_3M	%Yield	Ref.
Me_3Si	15 (41% neat)	278,296,297
Et_3Ge	41	298
Me_3Sn	70	296,297



(318) [299]

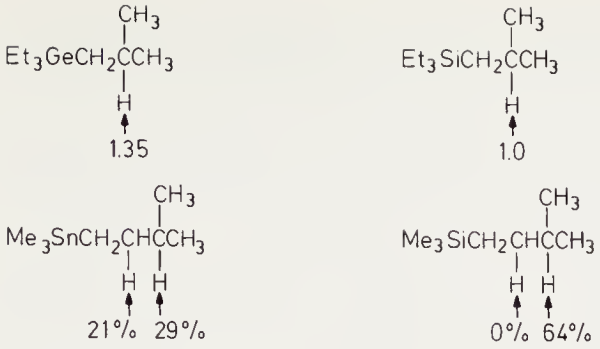
M = Si 17%
Sn 50%



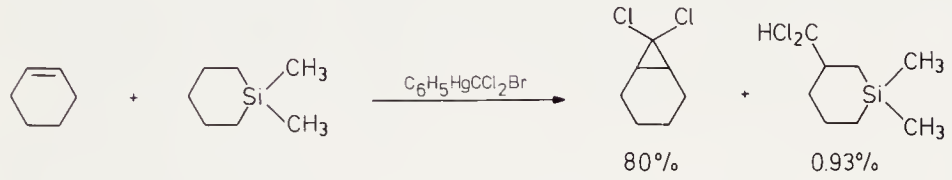
(319)

R_2M	%Yield	Ref.
Me_2Si	68	296,297
Et_2Ge	71	298
Me_2Sn	50	296,297

obtained from the corresponding alkanes. In strained silacyclobutanes Si—C insertions become competitive and reduce the yields. Detailed studies of these reactions allow the following generalities to be made [296]. C—H insertion beta to the metal is preferred and follows the order $3° > 2° > 1°$. Both tin and germanium are more effective than silicon as illustrated by the following reported relative reactivities [296, 298]. The hydrogens next to the metal are generally inert, perhaps due to steric hindrance which is known to be important in these reactions. Conformational effects also play a significant role. Carbon-carbon double bonds are still an order of magnitude more reactive as indicated by the following yields reported from a competition experiment (Eq. 320) [296, 297]. Once again the more selective fluorine-containing transfer species, such as $C_6H_5HgCFCl_2$ [10], fail to undergo insertion.

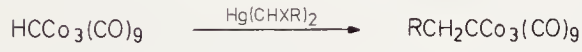


Mechanistic studies speak against a metallacyclopropenium ion intermediate and in favor of σ,π-stabilization of the transition state by metal-carbon bond hyperconjugation [299].



(320)

The only reported C—H insertion alpha to a metal appears to be the following (Eq. 321) [300, 301]. The mechanism of this reaction remains obscure.

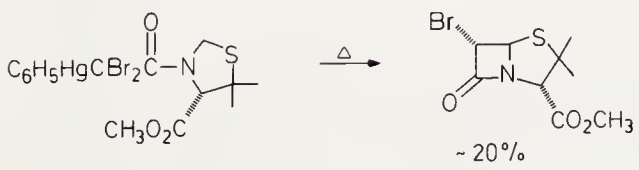


(321)

A number of the organomercurial reagents fail to give any insertion products. These include $C_6H_5CH_2HgCH_2I$ [91], $C_6H_5HgCF_3/NaI$ [205], $C_6H_5HgCFClCO_2Me$ [13], and $C_6H_5HgCFBrCO_2Et$ [13]. In the first case, this merely reflects the fact that this reagent does not appear to generate free methylene. In the other examples, the high selectivity of fluorine-containing carbenes is once again demonstrated. The last two examples are particularly interesting since related amide-containing organomercurials are reported to undergo facile intramolecular C—H insertions to provide a novel route to β-lactams (Eq. 322). This approach affords (+)-methyl 6-bromopenicillinate in ~20% yield (Eq. 323) [37]. Amine displacement with

(322)

Ref.	X	Y	%Yield	%Yield
33	Cl	Cl	45	8
35	Cl	Br	~51	≤3
36	Br	Br	47	14



(323)

inversion should give penicillin derivatives with the correct configuration. Intramolecular C—H insertions would appear to provide a potentially valuable synthetic route to a variety of cyclic products.

The Si—H bond is even more reactive towards insertion reactions than the C—H bond and numerous examples of this reaction are known [2]. For instance, each of the following reagents has been shown to insert the anticipated divalent carbon species into the Si—H bond of triethylsilane: $Hg(CH_2Br)_2$ (89%) [302], $Hg(CH_2Br)_2/(C_6H_5)_2Hg$ (68%) [302], $IHgCH_2I/(C_6H_5)_2Hg$ (83%) [102, 302], $Hg(CH_2I)_2/(C_6H_5)_2Hg$ (72%) [48], $C_6H_5HgCHClBr$ (72%; 7% bromide apparently due to the high reaction temperatures required) [303], $BrHgCHBr_2/(C_6H_5)_2Hg$ (85%) [303], $C_6H_5HgCHBr_2$ (61% [303], 72% [9]), $C_6H_5HgCFCl_2$ (80% [12], 83% [10, 11]), $C_6H_5HgCFClCO_2Me$ (72%) [13], $C_6H_5HgCFClCO_2Et$ (71%) [13, 69], $C_6H_5HgCFBr_2$ [87% [14], 92% [34]), $C_6H_5HgCFBrCF_3$ (53%) [15, 16], $C_6H_5HgCFBrCO_2Et$ (74%) [13], *n*-$PrHgCCl_3$ (48%) [45],  $HgCCl_3$ (88%) [23, 24], $C_6H_5HgCCl_2Br$ (79% [291], 83% [103]),  $HgCCl_2Br$ (80%) [23, 24], $C_6H_5CH_2CH_2HgCCl_2Br$ (73%) [24], $C_6H_5HgCCl_2I$ (83%) [27, 28], $C_6H_5HgCCl_2CH_3$ (35%) [55], $C_6H_5HgCCl_2C_6H_5$ (83%) [56], $C_6H_5HgCCl_2CO_2Me$ (47%) [31], $(Me_3SiCCl_2)_2Hg/(C_6H_5)_2Hg$ (42%) [52, 113], $C_6H_5HgCClBr_2$ (70% [23], 81% [304]),  $HgCClBr_2$ (70%) [54], $C_6H_5HgCClBrI$ (60% [34], 64% [28]), $C_6H_5HgCClBrCF_3$ (51%, 4% bromide) [29], $C_6H_5HgCClBrCO_2Me$ (40%) [31], $C_6H_5HgCBr_3$ (65%) [103], $C_6H_5HgCBr_2CO_2Me$ (35%) [31], $(CH_3)_2C{=}{=}CBrHgBr/(C_6H_5)_2Hg$ (91%) [54]. Excellent yields are also generally obtained from other alkyl- [48, 303–305] and arylsilanes [103, 291, 302, 304, 306], although the latter compounds do occasionally present difficulties [303].

It is especially noteworthy that some of the organomercurial reagents which are included in the above compilation are reagents which do not react particularly well with even some simple olefins. In fact, the Si—H bond in triethylsilane is about 0.8 times as reactive towards $C_6H_5HgCCl_2Br$ as cyclohexene [103, 291], and substantially more reactive towards $Hg(CH_2Br)_2$ than even 3-ethyl-2-pentene (which is four times more reactive than cyclohexene) (Eq. 324) [302]. As anticipated, the Si—H bond in simple silanes is far more reactive than the double bond in vinylsilanes (Eqs. 325, 326).

$$Et_3SiH + Et_2C{=}CHMe \xrightarrow{Hg(CH_2Br)_2} \underset{82\%}{Et_3SiCH_3} + \underset{7\%}{Et_2C\overset{CH_2}{\diagup\diagdown}CHMe} \qquad (324)$$

$$Et_3SiH + Et_3SiCH{=}CH_2 \xrightarrow{C_6H_5HgCCl_2Br} \underset{\text{only product}}{Et_3SiCCl_2H} \qquad (325)\ [291]$$

(326) [103]

$Hg(CH_2Br)_2/(C_6H_5)_2Hg$ X = H 83%
$C_6H_5HgCCl_2Br$ Cl 82%

Even highly hindered silanes give good yields (Eq. 327). It is significant that the combination potassium *tert*-butoxide/chloroform does not work in these reactions [307].

$$R_3SiH \xrightarrow{C_6H_5HgCXYZ} R_3SiCXYH \qquad (327)$$

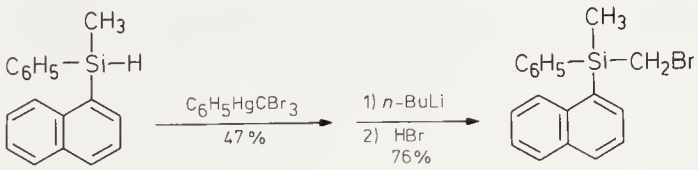
R	X	Y	%Yield	Ref.
i-Pr	Cl	Cl	53	307
	Cl	Cl	53	307
t-Bu	H	Br	41	308
	Cl	Cl	53	309,310
	Br	Br	54	309,310

While most of the silane insertion reactions go well, some difficulties have been encountered, particularly with arylsilanes, while attempting to introduce the CHCl or CHBr groups due to the high temperatures required in these reactions. It has sometimes proven advantageous instead to prepare the corresponding dihalo compounds and reduce them (Eqs. 328–330).

$$R_3SiH \xrightarrow[\text{or } C_6H_5HgCBr_3]{C_6H_5HgCClBr_2} \xrightarrow{n\text{-}Bu_3SnH} R_3SiCH_2X \qquad (328)\ [304]$$

R	X	%Yield
Et	Cl	74
	Br	79
C_6H_5	Cl	81
	Br	76

$$(C_6H_5)_3SiH \xrightarrow[65\%]{C_6H_5HgCBr_3} \xrightarrow[2)\ HBr,\ 83\%]{1)\ n\text{-}BuLi} (C_6H_5)_3SiCH_2Br \qquad (329)\ [311]$$



(330) [311]

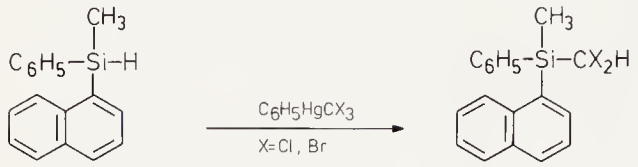
Two different mechanisms appear operative for these insertion reactions depending on the reagent employed. The reactions of $C_6H_5HgCCl_2Br$ have been most closely studied. The reaction with triethylsilane has been found to be first order in organomercurial and zero order in silane, suggesting a carbene mechanism (Scheme 10.12) [103, 306]. The kinetic isotope effect

Scheme 10.12

$$C_6H_5HgCX_3 \rightleftharpoons C_6H_5HgX + :CX_2$$
$$R_3SiH + :CX_2 \longrightarrow R_3SiCX_2H$$

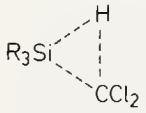
(k_H/k_D) for tri-*n*-butylsilane is 1.23, which is very similar to values determined for a number of other reactions of this compound [305]. Kinetic data from the reaction of ring substituted dimethylsilylbenzenes correlate best with σ and afford a value of $\varrho = -0.632 \pm 0.032$, indicating that electro-

philic attack by $:CCl_2$ occurs with little charge separation in the transition state [306]. Insertion into optically active silanes proceeds with ~93% retention of configuration (Eq. 331) [312–314]. A three-center transition state of



(331)

the following type is preferred [314]. A reduction-alkylation mechanism of



the following type (Scheme 10.13) can be ruled out by the failure of the second reaction to proceed under the usual reaction conditions required for insertion [102, 103].

Scheme 10.13

$$Et_3SiH + C_6H_5HgCCl_2Br \longrightarrow Et_3SiBr + C_6H_5HgCHCl_2$$

$$Et_3SiBr + C_6H_5HgCHCl_2 \longrightarrow Et_3SiCHCl_2 + C_6H_5HgBr$$

On the other hand, the reactions involving CH_2 insertion probably do not involve a free carbene. Thus, $Hg(CH_2Br)_2$ is thermally stable at temperatures at which it transfers CH_2. With substituted dimethylsilylbenzenes, σ° values give the best correlation with $\varrho = -1.31 \pm 0.04$, indicating a more polar transition state than with $C_6H_5HgCCl_2Br$. The electrophilic CH_2 transfer species is thus more selective than the CCl_2 transfer species, which rules out free $:CH_2$ which is known to be less selective than $:CCl_2$. A reduction-alkylation sequence for the following reactions (Eqs. 332, 333) can once again be

$$Et_3SiH + Hg(CH_2Br)_2 \longrightarrow Et_3SiCH_3 + BrHgCH_2Br \quad (332)\ [302]$$

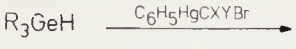
$$Et_3SiH + IHgCH_2I + (C_6H_5)_2Hg \longrightarrow Et_3SiCH_3 + 2C_6H_5HgI \quad (333)\ [102]$$

excluded by the failure of methylmercuric iodide and triethylsilyl iodide to react under the required reaction conditions. An alkylation-reduction sequence can also be ruled out on the basis of the following results (Eq. 334) [48].

$$Et_3SiD + n\text{-}Bu_3SiH \xrightarrow[(C_6H_5)_2Hg]{Hg(CH_2I)_2} Et_3SiCH_2D + n\text{-}Bu_3SiCH_3 \quad (334)$$

Alkyl- and arylgermanium compounds also undergo Ge—H insertion when treated with halomethylmercurial reagents (Eq. 335) [2]. The more difficult to prepare arylhalomethylgermanes are once again best prepared by insertion of a dihalo species and subsequent reduction (Eqs. 336, 337). Optic-

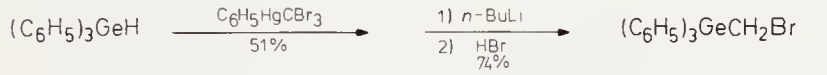
ally active germanes proceed with virtually complete retention of configuration [313] and can be further reduced as well (Eq. 338) [311]. The relative reactivity of Et_3GeH versus Et_3SiH has been determined to be 4.5 [103].



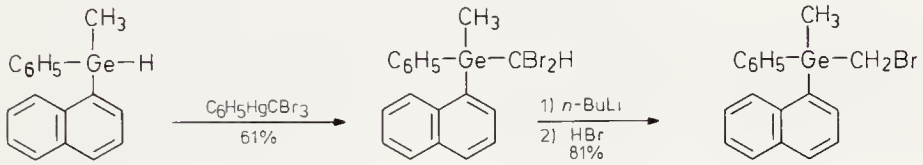
(335)

R	X	Y	%Yield	Ref.
Et	H	H	40	302
	H	Br	70	303
	Cl	Br	73	304
C_6H_5	Cl	Cl	88	291
	Cl	Br	73	304
	Br	Br	51	311

(336) [304]



(337) [311]

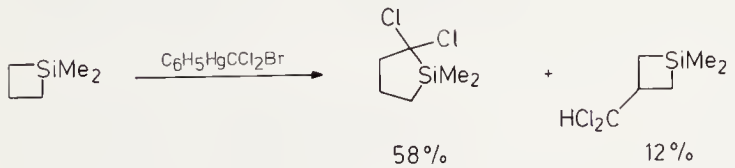


(338)

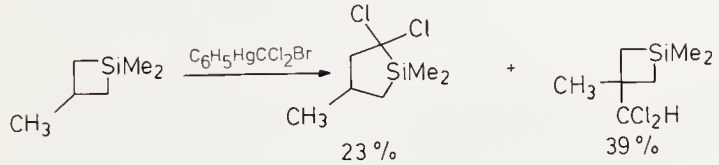
As reported earlier, tin hydrides do not generally undergo insertion reactions of the sort described above. They tend to reduce halogens off of the organomercurials instead [103]. Unfortunately, the yields are generally not sufficiently high to be of real synthetic utility.

J. Insertion Reactions in Metal—Carbon, Metal—Halide and Metal—Metal Bonds

Organomercurial insertion reactions into metal-carbon, metal-halide and metal-metal bonds have been reviewed [2]. There appear to be very few examples of divalent carbon insertions into metal-carbon bonds using organomercurial reagents. The more common pathway discussed earlier appears to be beta C—H insertion. In organosilicon chemistry only the highly strained silacyclobutane ring system undergoes competitive Si—C insertions (Eqs. 339, 340). These reactions, C—H and Si—C insertions, both appear to proceed

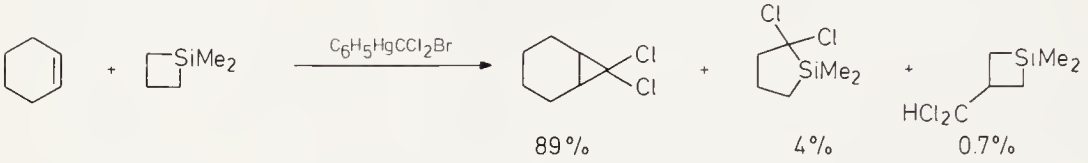


(339) [278, 315]

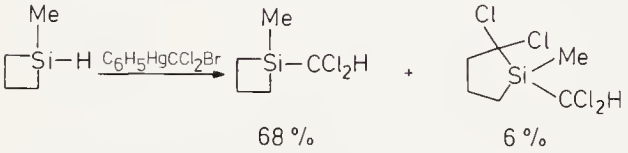


(340) [278, 315]

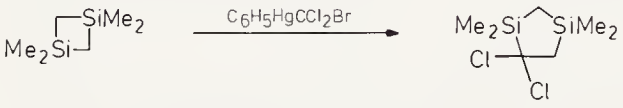
with retention of configuration [316]. Olefins and Si—H bonds are substantially more reactive than even these strained ring systems however (Eqs. 341, 342). When competitive C—H insertion no longer becomes possible as in 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the major product arises via Si—C insertion (Eq. 343) [278].



(341) [278]

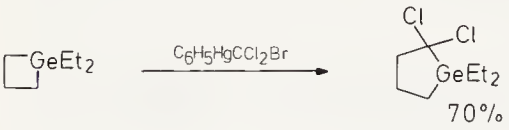


(342) [278, 315]

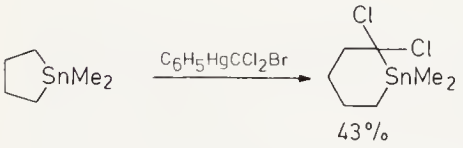


(343)

Germacyclobutanes and stannacyclopentanes also undergo metal-carbon insertion reactions analogous to those described above (Eqs. 344, 345).

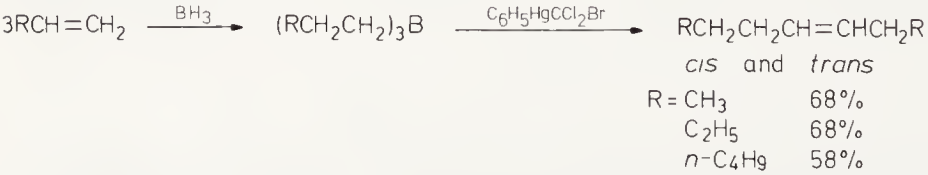


(344) [317]

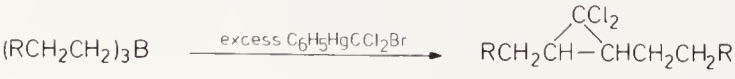


(345) [318]

Organoboranes react with $C_6H_5HgCCl_2Br$ to provide olefins in what appears to be the only other reported example of metal-carbon insertion (Eq. 346) [319]. When excess organomercurial reagent is employed, the anticipated cyclopropanes can also be obtained (Eq. 347). The suggested



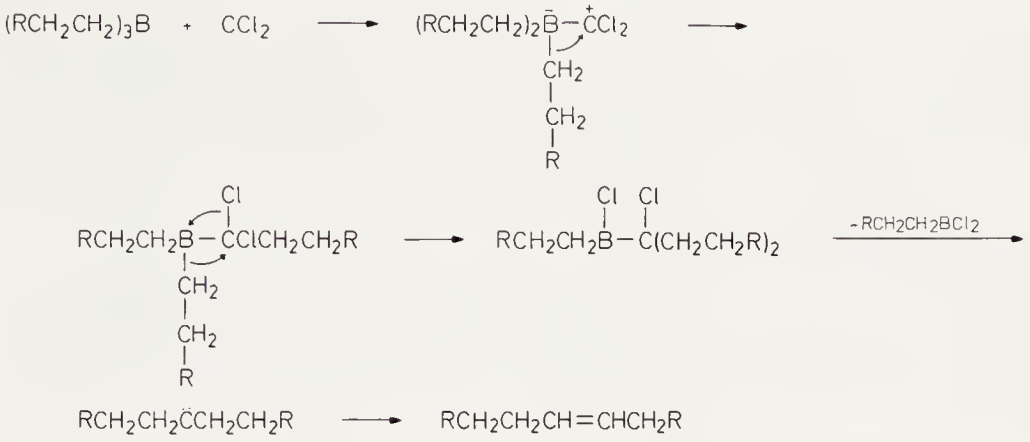
(346)



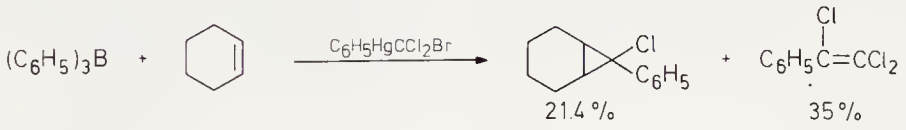
(347)

mechanism involves rearrangements of a sort well known in organoboron chemistry, followed by an α-elimination leading to a carbene (Scheme 10.14).

Scheme 10.14

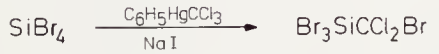


When intramolecular C—H insertion in the carbene is impossible as in the reaction of triphenylborane, transfer products typical of a carbene are observed (Eq. 348).

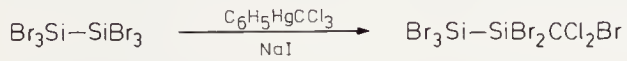


(348)

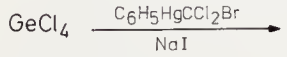
As suggested by our earlier discussion of the mechanism of cyclopropanation, carbenes appear to readily insert into mercury-halogen bonds. Analogous reactions are also possible with silicon, germanium and tin halides (Eqs. 349–354). In the fifth example, it is assumed that the initial insertion product Br_3SnCCl_2Br is simply undergoing further halogen exchange with the tin tetrabromide. In the last example, it is not immediately clear if the reaction



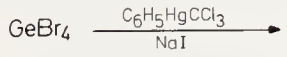
(349) [320, 321]



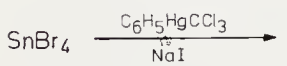
(350) [321]



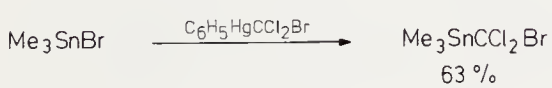
(351) [321]



(352) [320, 321]



(353) [320]



(354) [322, 323]

follows an insertion mechanism or proceeds by carbon-halogen exchange. The following experiment clearly implicates both pathways (Eq. 355) [322, 323].

$$Me_3SnCl \xrightarrow[16\%]{C_6H_5HgCCl_2Br} Me_3SnCCl_3 + Me_3SnCCl_2Br \quad (355)$$
$$1.5 : 1.0$$

There are very few examples of metal-metal insertion reactions using organomercurial reagents. The reactions of silyl- and germylmercurials (Eq.

$$(R_3M)_2Hg \xrightarrow{C_6H_5HgCCl_2Br} R_3MCCl{=}CCl_2 + R_3MCl + Hg \quad (356)$$
$$R_3M = Me_3Si, Et_3Si, Me_3Ge, n\text{-}Bu_3Ge$$

356) appear to proceed via two consecutive insertion reactions followed by mercury halide β-elimination (Scheme 10.15) [324, 325]. Silicon-silicon and

Scheme 10.15

$$(R_3M)_2Hg \longrightarrow R_3MCCl_2HgMR_3 \longrightarrow R_3MCCl_2CCl_2HgMR_3 \longrightarrow$$
$$R_3MCCl{=}CCl_2 + ClHgMR_3 \longrightarrow Hg + ClMR_3$$

tin-tin bonds also undergo facile insertion as illustrated by the following examples (Eqs. 357, 358). Other distannanes undergo the same reactions [327]. Insertion into the germanium-phosphorus bond has also been observed [328].

$$Cl_3Si{-}SiCl_3 \xrightarrow[X=Cl, Br \\ NaI]{C_6H_5HgCCl_2X} Cl_3SiCCl_2SiCl_3 \quad (357)\ [321]$$

$$Me_3Sn{-}SnMe_3 \longrightarrow Me_3Sn{-}\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{C}}{-}SnMe_3 \quad (358)$$

	X	Y	%Yield	Ref
$C_6H_5HgCFCl_2$	F	Cl	36	10,11
n-$PrHgCCl_3$	Cl	Cl	40	45
$C_6H_5HgCCl_2Br$	Cl	Cl	60	326,327
$C_6H_5HgCClBr_2$	Cl	Br	41	326,327
$C_6H_5HgCBr_3$	Br	Br	37	327

Although there are relatively few examples of divalent carbon insertion reactions into metal-carbon, metal-halogen and metal-metal bonds this route to new organometallics appears quite promising and will no doubt receive further attention in the future.

It seems appropriate to conclude this chapter with some general comments. The use of organomercurials as divalent carbon transfer reagents is a relatively new application of mercury in organic synthesis. A large number of these reagents are now available either commercially or through relatively easy laboratory preparations. The mild reaction conditions required to effect a wide variety of often unique synthetic transformations makes them increasingly

useful to the synthetic chemist. Their wide use in cyclopropane formation has clearly demonstrated their versatility and one can anticipate ever increasing use of these reagents in the years to come.

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Subject Index