

CARBENE CHEMISTRY

Second Edition

BY

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PREFACE TO THE SECOND EDITION

Active interest in carbene chemistry has been steadily growing since the first edition of this book appeared in 1964. The number of original papers dealing with various aspects of the elusive carbene species has almost tripled within the last six years. Distinct progress has been made in many areas of carbene chemistry: correlation of spectroscopic studies of isolated carbenes with quantum chemical calculations; new carbene precursors; differentiation of carbenes and carbenoids; carbene complexes of the transition metals; mechanisms of singlet and triplet carbene reactions; structure-reactivity relationships for both carbenes and their substrates; applications in synthetic organic chemistry.

In order to cover these diverse aspects within a reasonable volume, the second edition of "Carbene Chemistry" has been reorganized according to the reaction scheme: precursor $\rightarrow$ carbene (carbenoid) $\rightarrow$ product. The first part (four chapters) reviews the many reactions known to transfer a formally divalent carbon fragment from one molecule to another, with emphasis on the mechanism and a critical evaluation of the evidence for carbene intermediates. The multitude of product-forming reactions of carbenes and carbenoids with various substrates is treated in the second part (six chapters). The two parts are linked by two chapters on the spectra and structural theory of carbenes. They are supplemented by a review of Si, Ge, and Sn analogs of carbenes. The subject of carbene "analogs" outside of group IV (nitrenes, etc.) was considered to exceed the scope of the present volume.

Throughout the book, important mechanistic problems have been discussed in detail, with a supply of relevant experimental data. Much synthetic and kinetic work, on the other hand, which did not produce exceptional results has been condensed into tables which provide access to the original papers. Literature citations extend through 1969 and, more selectively, into 1970. The largely increased number of references (ca. 2500) has undoubtedly also increased the number of inadvertent omissions. As in the first edition, I have tried to augment my knowledge with the help of expert coauthors who supplied the chapters on structural theory and carbene analogs. It is a pleasure to thank Professors J. F. Harrison, P. P. Gaspar, and B. J. Herold for their valuable contributions.

Furthermore, I wish to express my gratitude to numerous colleagues who have participated in the preparation of this volume by stimulating discussions and constructive criticism. I am especially indebted to Professor B. M. Trost who read large portions of the manuscript.

WOLFGANG KIRMSE

PREFACE TO THE FIRST EDITION

Carbene chemistry has experienced a tremendous growth and wide interest in the past decade. The investigation of divalent carbon intermediates proved to be rewarding to both physical and preparative organic chemistry. Many research groups have excelled in contributing to our present knowledge of the elusive carbene species.

By now, carbene chemistry has outgrown the dimensions of review articles, and the task of providing a comprehensive monograph seemed timely. On considering the objectives of such a publication, it appears that full coverage is best achieved by a single author, whereas the most authoritative treatment may come from various experts dealing with their own fields of research. The present volume attempts to combine the advantages of both procedures. In the first ten chapters, I have tried to give an essentially complete survey of carbene chemistry. Literature citations extend through late 1963, and a few early 1964 references have been included. Scope and emphasis devoted to the various topics are undoubtedly influenced by the author's personal interests. Therefore, advance apologies are tendered to any of my colleagues who find their own work discussed inadequately, and to those whose findings I have inadvertently overlooked. Although the subject demanded a careful and critical discussion of mechanistic problems, the discussion has been kept to a minimum in the first ten chapters in anticipation of the contents of Chapters 11 and 12. In these chapters, theory is applied consistently to the interpretation of carbene reactions in those fields where it is most advanced. It is a pleasure to thank Professors H. M. Frey, P. P. Gaspar, and G. S. Hammond for their valuable contributions.

Furthermore, I wish to express my gratitude to numerous colleagues who have participated in the preparation of this volume by stimulating discussions, by constructive criticism, and by disclosure of unpublished results. I am especially indebted to Dr. Robert B. Hager who read the entire manuscript.

Marburg/Lahn
May 1964

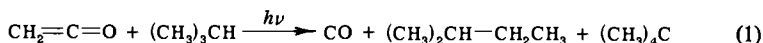
WOLFGANG KIRMSE

CHAPTER 1

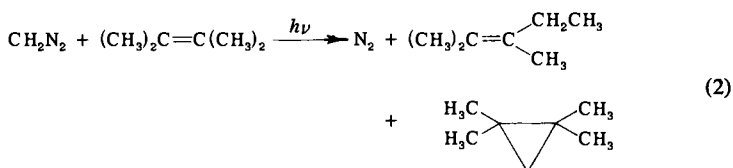
Introduction

I. EXAMPLES OF METHYLENE TRANSFER

FOR MANY YEARS, a group of organic reactions has been recognized in which a formally divalent carbon atom with two ligands is transferred between a pair of reactants. A somewhat arbitrary set of examples is presented in Eqs. (1)–(8). The term “methylene transfer” provides a purely phenomenological description, without mechanistic implications, in much the same way as we speak of “displacement,” “addition,” “elimination,” etc.

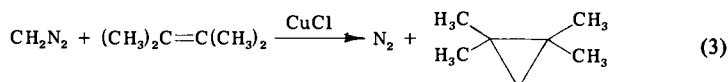


In Eq. (1), CH_2 is transferred from ketene to isobutane, under the action of light. With respect to isobutane, the process involves the “insertion” of CH_2 into the carbon–hydrogen bonds. Isopentane might also arise by insertion of CH_2 into the carbon–carbon bonds of isobutane, but the use of a suitable label would reveal that ketene furnishes C-4, rather than C-3, of 2-methylbutane. Insertion has been observed with other σ bonds such as C–Cl and C–O.

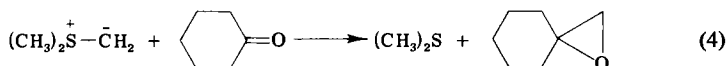


Equation (2) introduces another “methylene donor,” diazomethane. Photolysis of diazomethane in the presence of 2,3-dimethyl-2-butene affords not only the product of C–H insertion, 2,3-dimethyl-2-pentene, but also 1,1,2,2-tetramethylcyclopropane. Methylene transfer to the π bond is responsible for cyclopropane formation. With respect to the olefin,

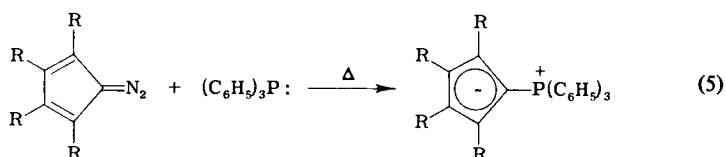
this process involves "addition" of CH_2 . (Some authors refer to the cyclopropane formation as "insertion" into π bonds, but the term addition serves better to distinguish the competing reactions and has been widely accepted.)



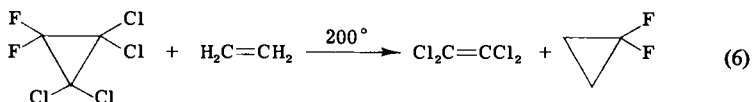
Equation (3) utilizes the same reactants as Eq. (2). Methylene transfer is effected, however, by CuCl catalysis rather than by irradiation. As a consequence, exclusive transfer of CH_2 to the π bond is observed and insertion into $\text{C}-\text{H}$ bonds does not take place. Obviously the two reactions, Eqs. (2) and (3), proceed by different mechanisms.



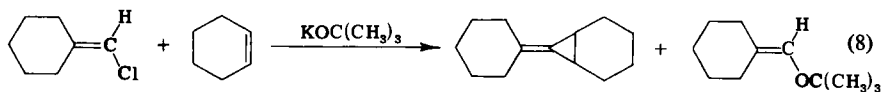
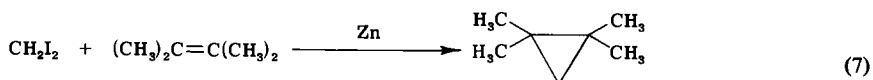
In contrast to the nonpolar $\text{C}=\text{C}$ bonds mentioned so far, Eq. (4) features the polar carbonyl group as a methylene acceptor. Dimethylsulfonium methylene acts as a methylene donor.



An ylide is the reaction "product" in Eq. (5), arising from transfer of a rather complex substituted methylene to the lone electron pair on the phosphorus of triphenylphosphine.



CX_2 transfer from polyhalocyclopropanes to olefins takes place at elevated temperatures in the gas phase. Significantly, only the CF_2 group is transferred in Eq. (6).

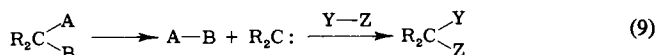


Reactions (1)–(6) proceed thermally or photochemically. The last two examples of methylene transfer, Eqs. (7) and (8), involve additional reagents which take over parts of the methylene donor [$\text{Zn} \rightarrow \text{ZnI}_2$; $\text{KOC}(\text{CH}_3)_3 \rightarrow \text{KCl} + \text{HOC}(\text{CH}_3)_3$]. Otherwise, reaction (7) is comparable to reaction (3): Addition of CH_2 to 2,3-dimethyl-2-butene proceeds without competing insertion. Reaction (8) affords two products: Transfer of an unsaturated methylene to the double bond of cyclohexene is accompanied by insertion into the O—H bond of *t*-butyl alcohol.

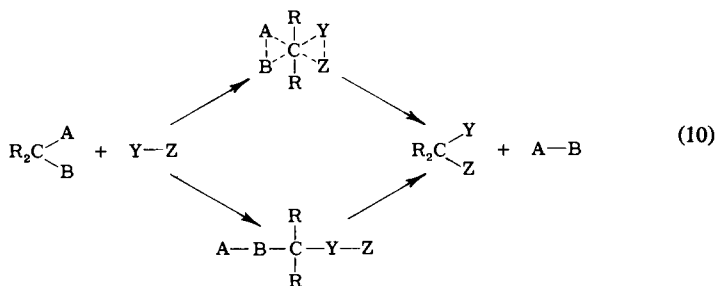
II. MECHANISMS OF METHYLENE TRANSFER

A simple and attractive way of explaining methylene transfer reactions is the assumption of a divalent carbon "intermediate," generally referred to as a "carbene." Methylene transfer is thought to proceed in two steps, (i) dissociation of the methylene donor to produce a carbene, and (ii) reaction of the carbene with the methylene acceptor.

The long-lasting fascination of the carbene concept for organic chemists appears to have emotional rather than empirical grounds. The desire to prepare compounds of divalent carbon can be traced back to the early nineteenth century, when the quadrivalency of carbon was not yet established. Thereafter a sort of *recherche du temps perdu*, the search has been continued on the more sophisticated level of divalent carbon intermediates. As is shown below, the unequivocal identification of transient carbenes is a difficult problem which, in many cases, still awaits final resolution. Oversimplification in favor of Eq. (9) has been a source of many pitfalls and, more importantly, a strong incentive to research.

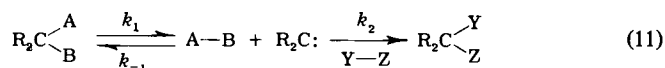


The other mechanistic extreme is a bimolecular reaction between methylene donor and methylene acceptor which leads to a concerted or successive displacement of the groups A, B by the groups Y, Z.



In order to distinguish between mechanisms (9) and (10) one has to determine at what stage in the overall reaction the groups A and B are detached from the methylene donor. The problem resembles that of distinguishing between the unimolecular and bimolecular mechanisms of substitution at a saturated carbon atom, and the general procedures employed are indeed quite similar.

a. Kinetics. If mechanism (9) operates, the rate of disappearance of the methylene donor R_2CAB should be independent of the concentration of the methylene acceptor $Y-Z$. This criterion is based on the premise that carbenes are highly reactive, i.e., their subsequent reactions are fast compared to the rate of formation. The kinetic criterion would be clearly invalid in case of an equilibrium, Eq. (11), with $k_{-1} \gg k_2$.



b. Partitioning between Competing Reaction Paths, e.g., insertion and addition; cf. Eq. (2). For a series of methylene donors R_2CAB , $R_2CA'B'$, ..., the relative reactivity should be independent of the nature of the groups A and B if the methylene transfer involves a common carbene intermediate, $R_2C:$. Variation of the groups A and B should lead to different product patterns in the bimolecular mechanism, Eq. (10). Thus, if reaction (2) possibly proceeds via free CH_2 , reactions (3) and (7) clearly do not.

c. Identification of Carbenes by Spectroscopic Methods. Although such physical evidence is most conclusive, it is rarely, if ever, obtained under the conditions of chemical transformation. Some doubt remains whether the spectroscopically observed species has any significance in methylene transfer reactions.

Variation of the groups A and B imparts much flexibility to the transition state of the bimolecular reaction (10). Weak bonding of A and B to carbon in the transition state minimizes the difference between mechanisms (9) and (10). The epithet "carbenoid" has been suggested to classify such borderline cases of methylene transfer. Again, the analogy with solvolytic displacement reactions is obvious. In both fields, however, the "first approximation" provided by the unimolecular and bimolecular mechanisms has proved to be extremely useful.

Additional problems arise from the fact that many methylene donors are themselves transient intermediates. For instance, diazomethane does not react with 2,3-dimethyl-2-butene at moderate temperatures unless

light, Eq. (2), or catalysts, Eq. (3), are admitted. In the photochemical reaction the effective methylene donor may be an electronically excited state of diazomethane, or a vibrationally excited ground state formed in the deexcitation process. Even if we succeed in determining the electronic state of the effective methylene donor, application of kinetic criteria will be extremely difficult. Similar considerations apply to the elusive diazomethane-CuCl complex, which probably intervenes in the catalytic reaction, Eq. (3).

One purpose of this section is to justify the scrutiny of methylene transfer mechanism to which much of the discussion in the following chapters is devoted. Another purpose is to restrain the reader's expectation of definitive answers.

III. CARBENES AND CARBENOIDS

Carbenes have been classified as divalent carbon intermediates. More precisely, the carbene carbon is linked to two adjacent groups by covalent bonds, and it possesses two nonbonding electrons which may have anti-parallel spins (singlet state) or parallel spins (triplet state). The nature of the ground state depends on the relative energies of the two nonbonding orbitals. If the two orbitals are equivalent, according to Hund's rules the electrons should be assigned to different orbitals with parallel spins. On the other hand, if the two available orbitals are not degenerate, the two electrons would probably occupy the lower of the two orbitals with consequent spin pairing. Regardless of the nature of the ground state, singlet carbenes are expected from most carbene precursors as a consequence of spin conservation. Intersystem crossing may or may not occur before the individual carbene reacts with a suitable acceptor.

The formal relationship of carbenes to other simple intermediates is presented in Table I. Triplet carbenes may be considered as diradicals, although the interaction of two unpaired electrons in orbitals of the same carbon atom gives rise to some peculiarities. Singlet carbenes are electron-deficient species comparable to carbonium ions; on the other hand, they possess a nonbonding pair of electrons comparable to that of carbanions. The electrophilic or nucleophilic character of singlet carbenes depends, therefore, strongly on the ability of adjacent groups to withdraw electrons from, or supply electrons to, the carbene carbon.

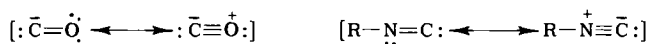
With most of the intermediates mentioned in Table I, the existence of moderately stable species (e.g., triarylmethyl derivatives) has provided a

TABLE I

Simple Intermediates in the Chemistry of Carbon Compounds

Intermediates		Number of covalent bonds	Number of valence electrons
Carbanions	—C:	3	8
Radicals	$\text{—C}\cdot$	3	7
Carbonium ions	—C^+	3	6
Carbenes	C:	2	6

basis for the investigation of transient analogs. In contrast, little useful information is provided by stable compounds with formally "divalent" carbon. In carbon monoxide, isocyanides, and fulminic acid derivatives, resonance stabilization of the "divalent" carbon by neighboring groups is extremely strong. Atomic distances, dipole moments, etc., have clearly revealed that triply bonded structures make a major contribution to the resonance hybrid.



The challenge of preparing compounds having properties intermediate between those of the transient carbenes and the strongly resonance-stabilized structures has not been met successfully. Substitution of the carbene carbon with two donor groups, such as NR_2 , SR , and OR , exerts a strong influence on the reactivity. Such carbenes behave like nucleophiles, in contrast to the electrophilic behavior of many other divalent carbon intermediates. None of these species, however, has been detected *in solution* by spectroscopic methods.

The term "carbenoid" has been suggested for the description of intermediates which exhibit reactions qualitatively similar to those of carbenes without necessarily being free divalent carbon species as studied by Closs and Moss in 1964. Although the carbene is structurally well defined, the carbenoid usually is not. The term "carbenoid" may, therefore, be objectionable to the purist. Nevertheless it is very useful in the discussion of many methylene transfer reactions where the precise constitution of the reactive species has not been delineated.

Several systems of nomenclature have been applied to carbenes and carbenoids. As the generic term, "carbene" is generally preferred to "methylene." The parent species, :CH_2 , is almost unanimously called methylene (rather than carbene). Particular structures have been designated as:

- (i) derivatives of methylene ($\text{CH}_3\text{CH:} = \text{methylmethylene}$);
- (ii) carbenes, using the carbinol convention ($\text{CH}_3\text{CH:} = \text{methyl-carbene}$); and
- (iii) radicals, according to the IUPAC rules ($\text{CH}_3\text{CH:} = \text{ethylidene}$).

The carbene nomenclature has much to recommend it and it is used in this monograph. In particular, it can be easily adapted to structures in which the divalent carbon is located in a ring by using the prefix "carbena" in a fashion similar to the use of "oxa," "aza," etc., in heterocyclic chemistry. The only inconsistency in the carbene nomenclature is the parent species, methylene. "Methylene" is also used in a different sense ("methylene transfer"), implying a structural unit, R_2C , rather than an intermediate.

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CHAPTER 2

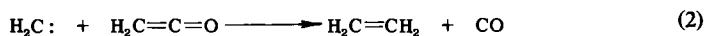
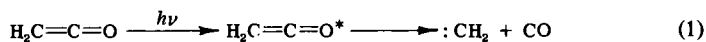
Photochemical and Thermal Methylene Transfer Reactions

I. PHOTOLYSIS OF KETENE

THE FIRST ABSORPTION REGION of ketene is at 3700–2600 Å, $\lambda_{\max}$ 3300 Å, $\epsilon = 12$. A strong transition, with ϵ as high as 3000, is observed below 2400 Å. Photolysis of ketene yields ethylene and carbon monoxide as major products, together with small amounts of cyclopropane, propylene, ethane, and acetylene. The ratio of carbon monoxide to ethylene is always a little greater than 2 (~ 2.2). Some polymer formation is observed and accounts for part of the deficiency of ethylene. The production of ethane and acetylene is completely suppressed in the presence of small quantities of oxygen and is probably due to radical side reactions (1). If ketene is photolyzed by flashes of high intensity, acetylene and hydrogen become major products (2). The differences in products, compared to those yielded at lower intensities, are probably due to the adiabatic nature of the process, which leads to very high temperatures.

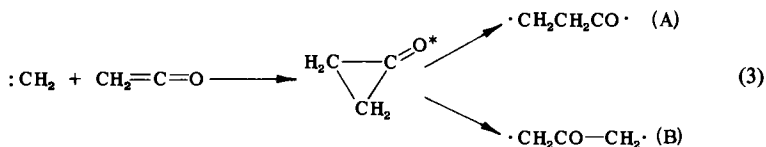
The work of Noyes (1, 3, 4) and Porter (5, 6) has indicated a marked difference in the photolytic behavior of ketene at wavelengths around 2700 Å from that at wavelengths around 3700 Å. At 2700 Å the quantum yield of CO is 2 within experimental error. After a small initial decrease, the ethylene yield is not dependent on oxygen pressure. At 3700 Å the quantum yield of CO is both pressure- and temperature-dependent. Addition of O₂ reduces the ethylene yield to less than one-third of its oxygen-free value. The data obtained at 3200 Å are intermediate between the two cases.

The behavior at 2700 Å suggests that one molecule of ketene dissociates per photon absorbed, and that methylene reacts with a second molecule of ketene to produce ethylene and carbon monoxide.



The alternative assumption, reaction of a photoexcited state of ketene with a second molecule of ketene, is clearly incompatible with the invariance of the quantum yield with pressure. When methylene is diverted to other reaction paths, the quantum yield should decrease and finally approach unity. Kistiakowsky and Sauer (7) photolyzed mixtures of ethylene and ketene, and of an inert gas and ketene, under identical conditions. In the cell containing the large excess of ethylene, intervening methylene was trapped by addition to ethylene, and reaction (2) was eliminated. Although the ratio of carbon monoxide formation in the two cells was slightly smaller than 2, no change was observed over a wide range of light intensities. Without noticeable effect the same amount of light energy was administered either as constant radiation or as a series of flashes. This result excludes a significant contribution of the dimerization reaction $2 \text{:CH}_2 \rightarrow \text{H}_2\text{C}=\text{CH}_2$.

The mechanism of reaction (2) has not yet been completely established. The intervention of an excited molecule of cyclopropanone has been suggested (7) which might break to give the radicals (A) and (B). Radical



(A) is thought to give ethylene and carbon monoxide very rapidly, whereas (B) may be somewhat longer lived. There are several indications of a comparatively stable intermediate in ketene photolysis. The quantitative application of the Paneth technique (removal of tellurium mirrors in a flow system) yields an apparent half-life of the order of 0.1 sec (8, 9). More information was obtained by a combination of flash photolysis and mass spectrometry (10). No increase of mass 14 (CH_2) was observed, but a peak of mass 55 ($\text{C}_3\text{H}_4\text{O}$) formed and disappeared gradually. Both observations may be due to the presence of the radical (B).

The photolysis of ketene by radiation of 2139 Å gives results which differ but slightly from those obtained at 2700 Å (11). The increased production of ethane and acetylene is not surprising in view of the fact

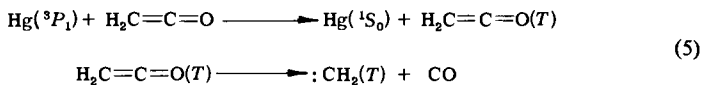
The photolytic behavior of ketene at longer wavelengths indicates that excited ketene molecules react not only by dissociation, Eq. (1), but also by collisional deactivation. It is now important to ascertain whether or not the first excited state of ketene passes over to the triplet state and then dissociates. The intervention of a triplet state of ketene is indicated by quenching experiments with biacetyl (1) and, more conclusively, *cis*-2-butene (12). Addition of *cis*-2-butene to the photolysis of ketene causes a reduction in the rate of formation of carbon monoxide. Ethylene production diminishes more rapidly and is approaching zero, whereas the yield of carbon monoxide is still finite. The decline in production of ethylene and CO is accompanied by a steady increase in isomerization of *cis*-2-butene to the trans isomer. This behavior is ascribed to the dual effect of *cis*-2-butene in quenching the excited ketene molecules and in removing $\cdot\text{CH}_2$. Yields of addition products of methylene with *cis*-2-butene pass through a maximum and decrease at higher pressures of added olefin. The isomerization of *cis*-2-butene most probably arises from an energy transfer involving triplet-state ketene molecules.

[illegible]
$$\frac{2}{\phi_{CO}} = \frac{k_2 + k_3 + k_4 (M)}{k_2 + k_3 k_5 / (k_5 + k_6)}$$

The identification of excited singlet and triplet states in the photolysis of ketene suggests that singlet and triplet methylenes are formed by

dissociation of $\text{CH}_2=\text{C}=\text{O}$ (S)* and $\text{CH}_2=\text{C}=\text{O}$ (T), respectively. The determination of singlet and triplet methylene fractions rests on specific assumptions concerning the relative reactivity of both species toward $\text{C}=\text{C}$ and $\text{C}-\text{H}$ bonds (cf. Chapter 8, Section I). The validity of these assumptions has been questioned, and additional complications arise from the fact that singlet methylene may be collisionally deactivated to its triplet ground state before reacting with the added hydrocarbons. With these reservations, the following fractions of triplet methylene have been reported: 26–32% at 2139 Å (11), 15–20% at 2800 Å (14–16), 20–30% at 3130 Å (17, 18), and 60–75% at 3660 Å (4, 15, 16).

Triplet methylene predominates in the mercury-photosensitized decomposition of ketene (19). Transfer of excitation from mercury triplets produces triplet ketene which decomposes with direct formation of triplet methylene.



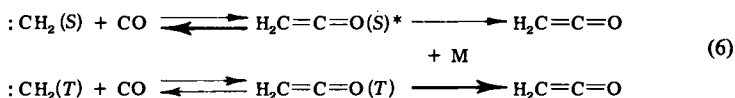
The amount of light absorbed directly by ketene at 2537 Å (mercury resonance line) remains relatively small up to appreciable ketene pressures (2% at 50 mm Hg, 5% at 100 mm Hg, 9–10% at 200 mm Hg) (20). The mercury-sensitized photolysis of ketene has therefore been interpreted as a source of triplet methylene uncontaminated by the presence of the singlet species. Recent studies, however, have confirmed the existence of an appreciable concentration of singlet methylene in the photolysis of mercury–ketene systems (21, 22). The hydrocarbons added as methylene acceptors reduce the yield of photosensitization of ketene itself and increase the fraction of direct photolysis beyond the values reported above (21). The direct (spin-forbidden) formation of singlet methylene in reaction (5) as a consequence of appreciable mixing of states in the mercury atom has also been considered (22).

Unlike singlet methylene, the triplet species appears to be rather long-lived. Combination of two triplet methylene molecules to give “hot” ethylene has been suggested as a source of acetylene and other secondary products in the mercury-photosensitized decomposition of ketene (22a).



The kinetic evidence presented above in favor of the intermediacy of methylene may be supplemented by further arguments. Photolysis of

ketene in the presence of ^{13}C -labeled carbon monoxide led to incorporation of ^{13}C in the recovered ketene (23, 24). In the recombination of methylene with carbon monoxide, triplet methylene reacts more readily than does singlet methylene ($\sim 20:1$ at 50°) (25). Evidence that it is the triplet that reacts preferentially with carbon monoxide is provided by the selective suppression of probable products of triplet reactions. Oxygen has no effect on the ethylene quantum yields at sufficiently high concentrations of CO. Triplet methylene reacts twice as fast with CO as with *cis*-2-butene (26). The unexpectedly high reactivity of triplet methylene toward CO is probably due to the relatively long lifetime and efficient deactivation of triplet ketene. The lesser stability of the excited singlet ketene, on the other hand, leads to an apparently slow reaction of singlet methylene with carbon monoxide.



In a recent study, triplet methylene generated by the flash photolysis of ketene was directly observed and monitored by kinetic spectroscopy at $1415 \text{ \AA}$ (26a). The growth of the triplet absorption as a function of inert gas pressure indicated that singlet methylene was the major primary product. Various inert additives quenched the singlet to the triplet state, while reactive additives were able to intercept the singlet before quenching occurred (cf. Chapter 8, Section I).

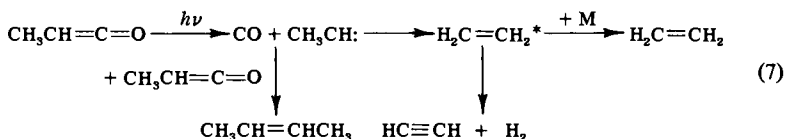
TABLE I
Reactivity of Methylene toward C—H Bonds

Alkane	: CH_2 source	Relative rates of insertion "per bond"			
		Prim.	Sec.	Tert.	Ref.
Propane	Ketene, $3130 \text{ \AA}$	1.00	1.29		(29)
	CH_2N_2 , $4358 \text{ \AA}$	1.00	1.20		(30)
Butane	Ketene, $3130 \text{ \AA}$	1.00	1.32		(29)
	CH_2N_2 , $3660 + 4358 \text{ \AA}$	1.00	1.35		(31)
Isopentane	Ketene, unfilt.	1.00	1.22	1.42	(32)
	CH_2N_2 , unfilt.	1.00	1.22	1.39	(32)

In the early work on the gas-phase interaction of methylene with carbon-hydrogen bonds, methylene from diazomethane was found to be less selective than methylene from ketene (27, 28). Part of the reported selectivity, however, must be attributed to triplet methylene effects. On the basis of recent work with added radical scavengers (Table I) (29-32) it appears that there is no real difference in the reactivity of singlet methylene from diazomethane and that from ketene. These results strongly support a true carbene intermediate the reactivity of which should be independent of its genesis.

II. PHOTOLYSIS OF ALKYL- AND ARYLKETENES

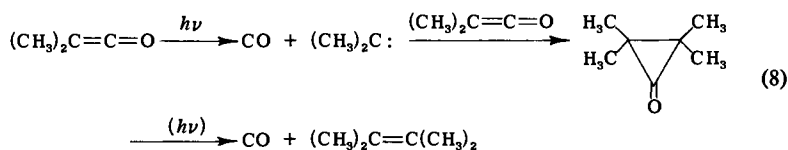
The photochemical behavior of methylketene (33, 34) and dimethylketene (35) in the vapor phase is similar in many respects to that of ketene. The major reaction of the presumed alkylcarbenes is rearrangement to give ethylene and propene, respectively. These intramolecular reactions are fast compared to the bimolecular reaction with the alkylketene. Consequently, 2-butene (from methylketene) and 2,3-dimethyl-2-butene (from dimethylketene) are only minor products, and the quantum yield of carbon monoxide in the 2700 Å region is close to unity. At 3660 Å the quantum yields are well below unity and decrease with increasing alkylketene concentration.



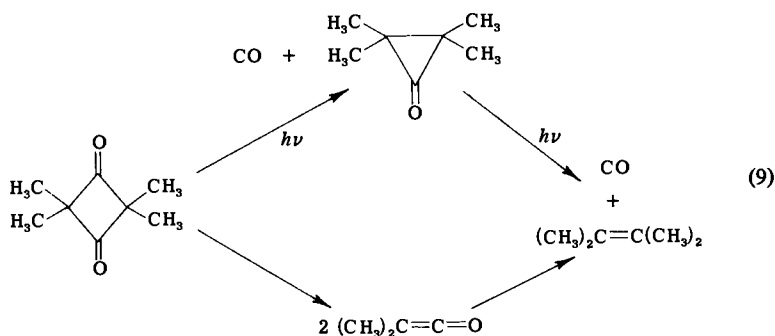
A significant feature of the photolysis of methylketene is the production of acetylene, which increases rapidly with increasing energy of the photons. One expects ethylene to be formed with some excitation energy carried over from the photodissociative process. The "hot" ethylene either decomposes to acetylene and hydrogen or is stabilized by collisional deactivation. The incomplete dissipation of excess energy is a serious objection in the comparison with other sources of methylcarbene. The photolysis of diazoethane does, in fact, produce different ratios of ethylene and acetylene under otherwise identical conditions (36). Strictly speaking,

the results obtained in the photolysis of methylketene do not require the intermediacy of methylcarbene, and could be explained by direct reactions of excited methylketene.

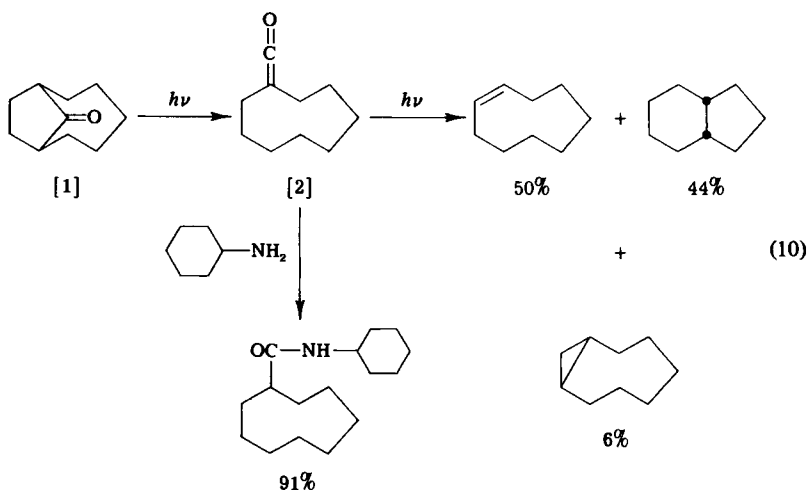
In contrast to the gas-phase reaction, photolysis of dimethylketene in cyclohexane at 2537 Å gave carbon monoxide and 2,3-dimethyl-2-butene as products (37). An IR absorption of the solution at 1840 cm⁻¹ was attributable only to the presence of tetramethylcyclopropanone, which is probably an intermediate in the formation of 2,3-dimethyl-2-butene.



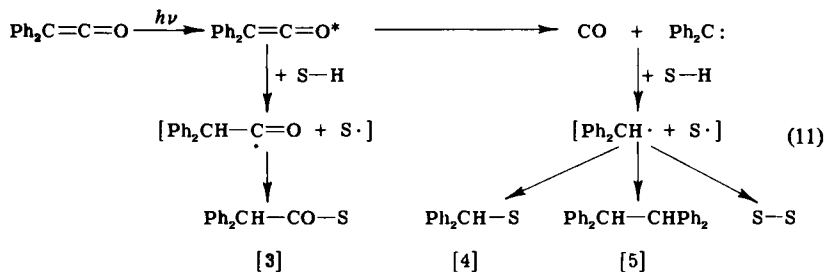
Some cases of *in situ* formation and photolysis of alkylketenes have been reported. In the photolysis of tetramethyl-1,3-cyclobutanedione, a fraction of at least 20% of the excited molecules decompose to give two molecules of dimethylketene (37). The photolysis of dimethylketene, Eq. (8), contributes to the formation of 2,3-dimethyl-2-butene from tetramethyl-1,3-cyclobutanedione.



The photolysis of bicyclo[5.2.1]decan-10-one [1] affords a mixture of C₉H₁₆ hydrocarbons (38). The hydrocarbons appear to be secondary products from the photolysis of octamethyleneketene [2]. The presence of [2] in the reaction mixture was established by IR and chemical trapping. The photolysis of [2] and the pyrolysis of diazocyclononane gave qualitatively the same products.



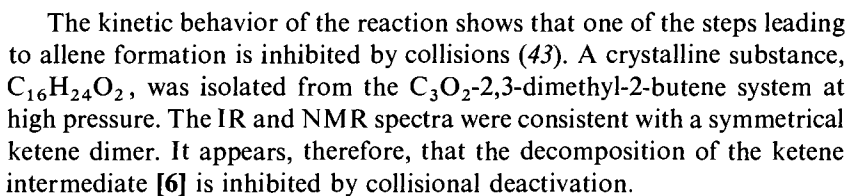
The photolytic behavior of diphenylketene cannot be satisfactorily interpreted by assuming the intermediacy of diphenylcarbene alone (39). Some of the reaction products, [4] and [5], undoubtedly originate from abstraction of hydrogen by diphenylcarbene, but the formation of the acylation products [3] must be attributed to photochemically excited ketene molecules.



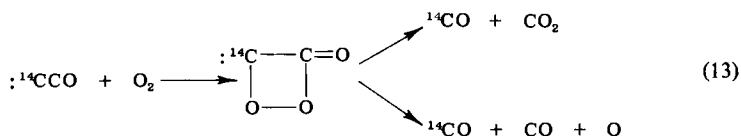
III. PHOTOLYSIS OF CARBON SUBOXIDE

Carbon suboxide, C_3O_2 , undergoes a simple photochemical reaction with olefins (40). A single carbon atom is inserted into the carbon-carbon double bond, giving an allene and two molecules of CO. Smaller amounts of acetylenes are also formed. The percentage of acetylene isomers decreases with pressure and with increasing molecular weight of the olefin (41). The newly inserted carbon atom derives from the center position of the

The available evidence favors C_2O as the intermediate in the photolysis of C_3O_2 . The recently determined heat of formation of C_3O_2 eliminates the possibility that the reactive intermediate could be a carbon atom; the dissociation of C_3O_2 to give $C(^3P) + 2 CO$ would be endothermic by 141.5 kcal/mole (43). The C_2O molecule has been identified in a low-temperature matrix by its IR spectrum (44). Its electronic absorption spectrum may have been observed in the gas phase during flash photolysis of carbon suboxide (45, 46). It remains to be established, however, whether free carbon atoms intervene in the photolysis of C_3O_2 at 1470 Å (47), where their production would be energetically feasible.

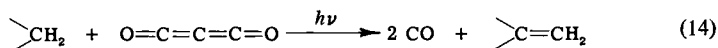


The photolysis of carbon suboxide at 3000 Å and at 2500 Å produces two different intermediates which are thought to be the triplet ground state and first excited singlet state of C₂O (48). At wavelengths >2900 Å, a few percent of oxygen strongly inhibit the formation of allenes. CO and CO₂ were produced in an 8 : 1 ratio (43, 48). Labeled ¹⁴C:CCO produced very little ¹⁴CO₂, and a four-center complex has been invoked to explain these results (49).



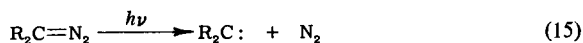
At 2500 Å large amounts of oxygen have little effect on the photochemical formation of allenes. Moreover, it has been shown that the intermediate produced at 2500 Å reacts quite indiscriminately with a wide variety of olefins (48). In contrast, the 3000 Å intermediate is rather selective; a relative rate of 250 has been measured for 2,3-dimethyl-2-butene compared to 1.0 for ethylene (48).

C₂O appears to be capable of C—H insertion, although this reaction is slow compared to the addition to olefins (49, 50). The products of the photolysis of C₃O₂ in the presence of methane, ethane, propane, and neopentane are ethylene, propene, isobutene, and 3,3-dimethyl-1-butene, respectively. No cyclopropanes were found, and the intervention of alkylcarbenes is questionable.

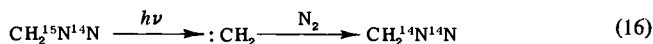


IV. PHOTOLYSIS OF DIAZO COMPOUNDS

Diazo compounds show a weak absorption in the visible region, which has been assigned as a forbidden $n \rightarrow \pi^*$ transition (51), and a somewhat stronger absorption at shorter wavelengths. The photolysis of diazo compounds both in the gas phase and in solution initiates methylene transfer reactions. Spectroscopic investigations have shown that carbenes can be generated by irradiation of diazoalkanes. The electronic spectrum of methylene produced in the gas phase by flash photolysis of diazomethane was recorded by Herzberg and Shoosmith (52). ESR spectra of various aryl- and fluoroalkylcarbenes in their triplet states were observed after photolysis of the corresponding diazoalkanes in a solid matrix at low temperatures (Chapter 6, Section II).



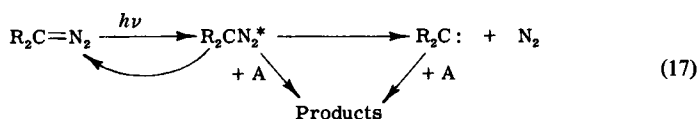
Isotopic labeling experiments revealed that the photolysis of diazomethane isolated in solid nitrogen produces methylene which subsequently reacts with neighboring nitrogen molecules to form diazomethane (53).



Russian workers have observed noticeable amounts of CH₂¹⁵N₂ after partial decomposition of diazomethane in an atmosphere of ¹⁵N₂ (54).

In view of so much supporting evidence, the intermediacy of free carbenes in the photolysis of diazo compounds has been widely accepted.

It should be remembered, however, that the electronic absorption spectra of simple diazoalkanes show definite fine structure (55). This implies that the photoexcited state is bonding (51) and consequently may be sufficiently long-lived to react directly with another molecule rather than decompose unimolecularly to give a carbene. If photoexcited states of diazo compounds actually participate in product formation, the quantum yield of the photolysis should depend on the nature and concentration of the reactant(s). The fraction of excited molecules returning to the ground state will be lowered by diverting them to other reaction paths, as indicated in Eq. (17). This argument applies regardless of whether $R_2CN_2^*$ represents an electronically excited state or a vibrationally excited ground state.



The quantum yield of the photolysis of diazomethane is not precisely known; the reported value $\phi_{N_2} \sim 4$ (gas phase) may be in error because of the ϵ used (56, 57). The initial rates of photolysis were found to be identical, however, in cyclohexane and cyclohexene (58). Methylcyclohexane is the only product obtained from cyclohexane, whereas cyclohexene produces a mixture of norcarane and methylcyclohexenes. Similarly, the photolysis of diphenyldiazomethane ($\phi_{N_2} = 0.78$ in methanol at $\lambda_{\max} = 2880 \text{ \AA}$) proceeded with identical initial rates in a variety of solvents which give rise to entirely different products (59).

The quantum yields of the photolysis of diazocarbonyl compounds are solvent-dependent (Tables II and III). These data do not necessarily imply solvent participation in the photodissociative step. The variation of solvent produces spectral shifts which can be explained as substantially

TABLE II
Quantum Yields (ϕ_{N_2}) of Ethyl Diazoacetate Photolysis (60)

Solvent	2600 Å	2804 Å	3130 Å	3650 Å	4200 Å
Heptane	1.11	1.02	0.54	0.31	0.20
Ethanol	1.35	1.1	0.34	0.15	0.12
Methanol	1.42	1.1	0.37	0.14	0.12
Water	2.8	—	0.36	0.12	—

TABLE III

Quantum Yields of the Photolysis of Substituted Diazoacetophenones, $p\text{-X-C}_6\text{H}_4\text{COCHN}_2$ (61, 62)

χ	<i>n</i> -Hexane		Methanol		Ethanol-water (20:80)	
	$\lambda_{\max}$	ϕ_{N_2}	$\lambda_{\max}$	ϕ_{N_2}	$\lambda_{\max}$	ϕ_{N_2}
H	277	0.55	294	0.46	298	0.40
CH ₃	286	0.62	296	0.41	301	0.30
CH ₃ O	283	0.50	304	0.34	—	—
Cl	287	0.62	299	0.41	—	—
NO ₂	299	0.31	307	0.18	—	—

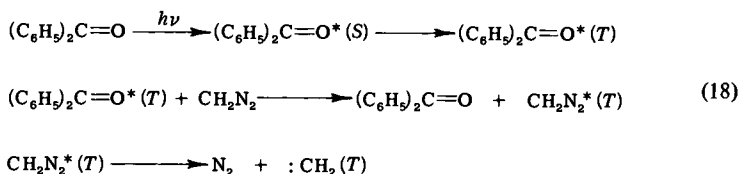
due to mesomeric effects. Varying extents of conjugative phenomena in the photoexcited state may cause an excitation energy redistribution more or less favorable for dissociation.

Photolysis of diazomethane in the gas phase (4358 Å) produces 15–20% of triplet methylene (15, 63). Addition of a few percent of oxygen removes triplet methylene (or its reaction products). No triplet methylene appears to be generated by the photolysis of diazomethane in the liquid phase. The product pattern resulting from the photolysis of diazomethane in isopentane solution is identical with that obtained in the gas phase with added oxygen (15). Triplet states of other carbenes, however, have been observed in the liquid-phase photolysis of the corresponding diazoalkanes. Phenylcarbene (64), diphenylcarbene (65), and ethynylcarbene (66) afforded triplet-derived products in 3–13% yield.

The mode or modes of formation of the triplet carbenes are not yet clear. The ground states of the carbenes mentioned in the preceding paragraph are triplet, and collisionally induced spin inversion can occur. It is also possible that triplet carbenes result from triplet precursors. In contrast to ketene, no independent evidence for the intervention of triplet diazomethane (or other diazoalkanes) in the direct photolysis is yet available.

Benzophenone is an efficient photosensitizer for the decomposition of diazomethane. Excitation of benzophenone in solution is followed by quantitative intersystem crossing to the triplet state (67, 68). Transfer of energy from benzophenone triplets to diazomethane will excite the

latter to a triplet state which decomposes with formation of triplet methylene (69).



The benzophenone sensitization technique has been applied to dimethyl diazomalonate (70, 71). The stereochemistry of bis(carbomethoxy) carbene addition to olefins is strongly affected by the sensitizer, and dramatic changes in rate occur when the olefin is a diene. These observations indicate that the carbene formed in the direct photolysis of dimethyl diazomalonate is predominantly singlet.

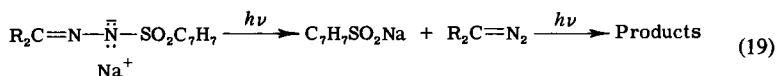
Direct irradiation of diazoacetophenone in cyclohexene yields much the same product distribution as that obtained through the intermediacy of triplet sensitizers, indicating that the reactant benzoylcarbene is most likely a triplet (72). In alcohol solvents, however, sensitized and direct photolyses give very different product distributions (73). The major reaction path of the direct photolysis is Wolff rearrangement (Chapter 12, Section V), whereas the sensitized photolysis produces mostly acetophenone. Reduction of the diazo group may also occur by way of a radical chain, initiated by $\text{Ph}_2\dot{\text{C}}-\text{OH}$, rather than by triplet benzoylcarbene (74).

Irradiation of azibenzil (diazo- α -phenylacetophenone) in glassy methyltetrahydrofuran at 77°K produces a triplet carbene, as evidenced by its ESR spectrum (75). Warming this solution does not afford diphenylketene. In contrast, direct irradiation of the diazo compound at room temperature produces at least 90% diphenylketene. An investigation of the sensitized photolysis of 2-diazocyclohexanone and diazoacetone (76) confirms that triplet ketocarbenes do not undergo the Wolff rearrangement.

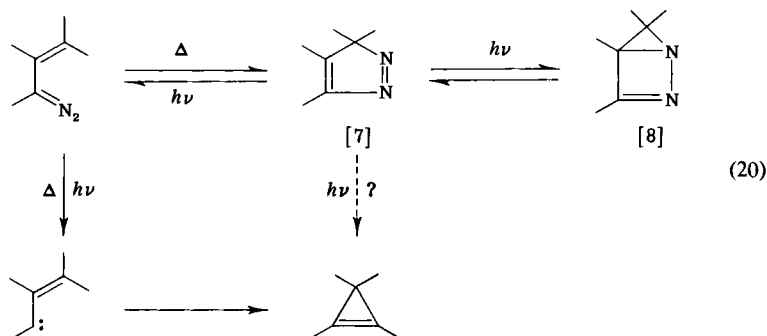
The photolytic behavior of diethyl diazomalonate is also strongly affected by the presence of thiobenzophenone (77). The nature of this effect, whether sensitization or formation of an unstable adduct, is not yet clear.

In concluding this section, it must be stated that some reactions, in which diazo compounds are generated and subsequently destroyed by irradiation, deserve comment. Photolysis of the sodium salts of *p*-toluenesulfonylhydrazones (tosylhydrazones) in aprotic solvents yields the same

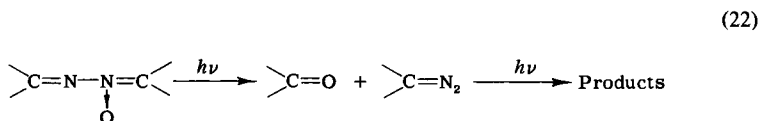
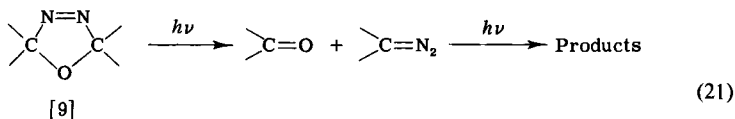
products as does the direct photolysis of diazoalkanes. Transient coloration supports the intermediacy of diazoalkanes (78) (cf. Section VI).



Pyrazolenines (3*H*-pyrazoles) [7] are converted photochemically into cyclopropenes (79–82). Evidence suggesting the intermediacy of diazoalkenes was obtained when suitable pyrazolenines were irradiated using a filter eliminating both the visible and the UV light below 3200 Å. This procedure led to the isolation of diazoalkenes in better than 50% yield (81). The diazo compounds have also been trapped by acetic acid as the corresponding esters (80). Thermally, the diazoalkenes revert to pyrazolenines. In the case of fully alkylated pyrazolenines, the photolytic reaction is further complicated by the valence isomerization [7] ⇌ [8] (83).

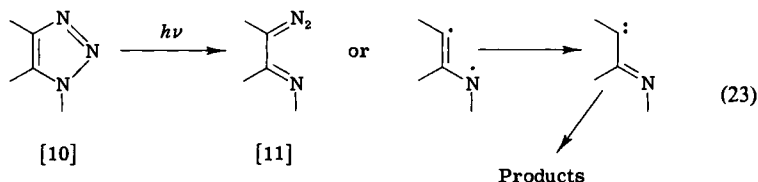


Irradiation of 1,3,4-oxdiazolines [9] results in the formation of diazoalkanes and carbonyl compounds (84, 85), Eq. (21). Azine monoxides behave similarly (86), Eq. (22); this reaction may be applied to cyclic azine monoxides (87) and even to pyridazine oxides (88). In most cases, transient spectra of the diazo compounds have been recorded.

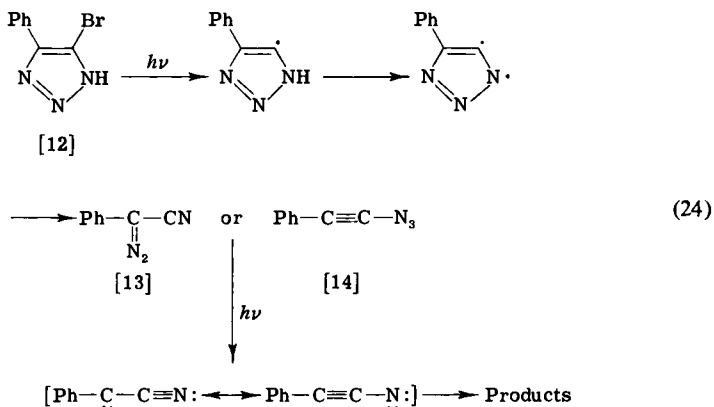


Diarylmethylene triphenylphosphazine ($\text{Ar}_2\text{C}=\text{N}-\text{N}=\text{PPh}_3$) decompositions appear to proceed in a stepwise fashion; first to the diazo compound and triphenylphosphine and then to the carbene *via* diazo decomposition (88a).

Di- and triaryl-1,2,3-triazoles [10] undergo photolysis with loss of nitrogen and the appearance of products resulting from 1,2-phenyl or hydrogen migration (89). The products suggest a carbenoid reaction but do not require a diazoimine [11] as an intermediate.

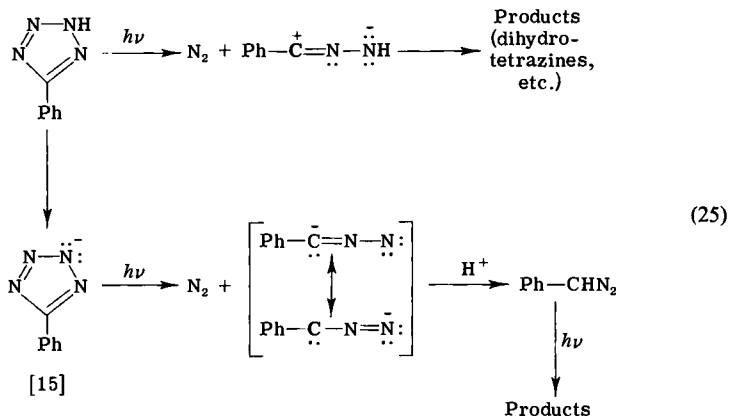


Since 4-phenyl-1,2,3-triazole undergoes photolysis slowly, it is assumed that the more rapid photoreaction of the 5-bromo derivative [12] is initiated by homolytic cleavage of the C—Br bond. Either simultaneous or subsequent abstraction of hydrogen leaves a residue which may be α -diazo- α -phenylacetonitrile [13] or phenylethynyl azide [14]. Both intermediates would ultimately lead to products derived from phenylcyanocarbene (90).

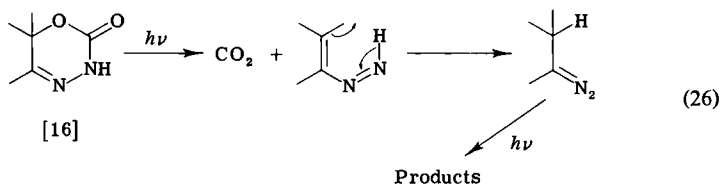


Irradiation of 5-phenyltetrazole gives one equivalent of nitrogen and a transient dipolar intermediate. Dimerization of the latter comprises the major reaction path. Photolysis of the anion [15], however, produces

two equivalents of nitrogen and products derived from the reaction of phenylcarbene with the solvent. This reaction is believed to occur via phenyldiazomethane (91).

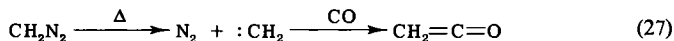


Dihydrooxadiazinones [16] undergo smooth photolytic decomposition affording products which largely parallel those obtained from the corresponding diazoalkanes (92). The results indicate that the successive loss of CO_2 and N_2 proceeds largely through a carbene intermediate.



V. PYROLYSIS OF DIAZO COMPOUNDS

The pyrolysis of diazomethane has long been thought to yield methylene. Staudinger (93) pyrolyzed diazomethane in the presence of carbon monoxide and obtained some ketene, which probably arose from the combination of methylene and carbon monoxide:



The Paneth technique was applied to diazomethane by several workers (8, 9, 94). The decomposition products of diazomethane were able to remove mirrors of Se, Tb, Sb, and As, but not mirrors of Zn, Cd, Tl, Pb

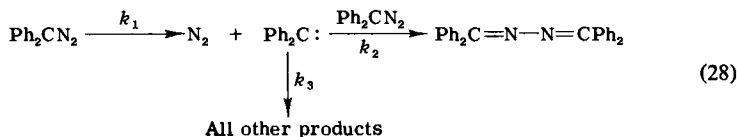
Bi, and Hg. (All of these metals react with methyl radicals.) The product obtained from Te was identified as polymeric telluroformaldehyde, $(\text{CH}_2\text{Te})_x$, whereas methyl radicals yielded volatile $(\text{CH}_3\text{Te})_2$. The apparent half life of methylene determined by this technique, however, is by far too long in view of our present knowledge of the rate of methylene reactions. Therefore it appears improbable that the removal of metal mirrors is due to free methylene.

The kinetics of the pyrolysis of diazomethane have been investigated by several research groups (95-97). Above 250° the decomposition appeared to be homogeneous and of first order. Shantarovitch (95), studying the decomposition of diazomethane in the presence of nitrogen in a flow system, obtained $k = 8 \times 10^{10} \exp(-31,750/RT) \text{ sec}^{-1}$. Rabinovitch and Setser (96) pyrolyzed diazomethane in the presence of hydrocarbons, $k = 1.2 \times 10^{12} \exp(-34,000/RT) \text{ sec}^{-1}$. The products were the same as those formed by photolysis at room temperature. Kinetic studies over the range 293° - 393° in the presence of excess hydrogen (97) afforded $k = 9 \times 10^{11} \exp(-32,000/RT) \text{ sec}^{-1}$.

Schenck *et al.* (98) have argued that, on thermochemical grounds, the rate data reported above cannot refer to the unimolecular dissociation $\text{CH}_2\text{N}_2 \rightarrow \text{CH}_2\cdot + \text{N}_2$. Recent estimates of $\Delta H_f^\circ (\text{CH}_2)$ are 92 kcal/mole (99) and 94 kcal/mole (100). Whereas a number of arguments have advocated various values of $\Delta H_f^\circ (\text{CH}_2\text{N}_2)$ ranging from 49 to 103 kcal/mole (101-103), no agreement on the magnitude of this quantity has been reached. Schenck *et al.* (98) have combined $\Delta H_f^\circ (^1\text{CH}_2) = 96$ kcal/mole and $\Delta H_f^\circ (\text{CH}_2\text{N}_2) = 49$ kcal/mole to make the dissociation of CH_2N_2 endothermic by 47 kcal/mole. This is more than the observed energy of activation. However, one should not expect to obtain a reliable estimate by combining a very high value of $\Delta H_f^\circ (\text{CH}_2)$ with the lowest value of $\Delta H_f^\circ (\text{CH}_2\text{N}_2)$. It should be remembered that $\Delta H_f^\circ (\text{CH}_2\text{N}_2) = 49$ kcal/mole is obtained from appearance potential data which, on the other hand, lead to an unreasonably low value of 66.4 kcal/mole for $\Delta H_f^\circ (\text{CH}_2)$ (104). Furthermore, the close agreement of the rate constants obtained in the presence of different reactants is hardly consistent with a bimolecular decomposition of diazomethane.

The thermal decomposition of diphenyldiazomethane in aprotic (hydrocarbon) solvents gives benzophenone azine and tetraphenylethane as the principal identifiable products (105), whereas in hydroxylic solvents the appropriate derivative of benzhydrol accompanies the azine (106). Kinetic studies of the decomposition of diphenyldiazomethane in xylene (107)

and in 1-methylnaphthalene (108) at about 100° have shown that the reaction is of first order in diazo compound; this has been interpreted as supporting the intermediate formation of diphenylcarbene.



Results for acetonitrile, benzene, and toluene solutions of diphenyldiazomethane (109) are given in Table IV. k_2/k_3 has been evaluated from

TABLE IV
Thermal Decomposition of Diphenyldiazomethane at 85° (109)

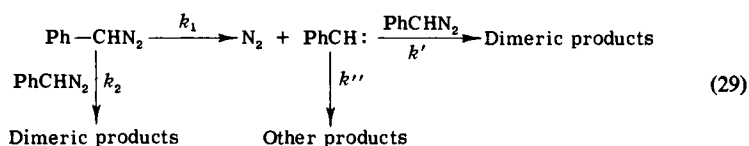
Solvent	$[\text{Ph}_2\text{CN}_2]_0 (M)$	$10^4 k_{\text{obs}} (\text{sec}^{-1})$	$10^4 k_1 (\text{sec}^{-1})$	Ketazine (%)
CH_3CN^a	0.0533	1.73	1.55	19.7
	0.0148	1.60	1.58	7.0
Benzene	0.0538	1.60	0.92	61.5
	0.0182	1.30	1.10	36.5
Toluene	0.0504	0.90	0.82	10.6
	0.0252	0.97	0.85	6.9

^a $\Delta H^\ddagger = 27.2 \pm 0.2 \text{ kcal/mole}^{-1}$; $\Delta S^\ddagger = 0.0 \pm 0.4 \text{ eu}$, from data at 65°, 75°, 85°, and 95°.

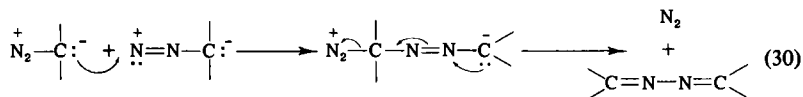
the yield of ketazine, and k_1 has been derived from k_{obs} by means of a steady-state treatment of Eq. (28). Values of k_1 do not differ significantly in the two aromatic solvents. The somewhat larger value of k_1 in acetonitrile indicates a small medium effect. Clearly, the nature of the solvent has a marked influence on the partitioning of the intermediate, though not on its formation.

In aqueous acetonitrile the disappearance of diphenyldiazomethane followed first-order kinetics at all water concentrations (109). The observed velocity constants varied little in the range 0–10 *M* water and, moreover, *decreased* in that range where the yields of benzhydrol rise from zero to > 90 % of the total product. The value of k_2/k_3 did not change significantly when D_2O replaced H_2O . The reaction of diphenylcarbene with water

The thermal decomposition of phenyldiazomethane in anhydrous acetonitrile is of intermediate order, between first and second, in a diazo compound (110). Benzalazine and *cis*- and *trans*-stilbene are formed as primary products. It has been assumed that the reaction proceeds by two paths, a unimolecular reaction in which phenylcarbene is formed, and a bimolecular reaction involving two molecules of phenyldiazomethane.



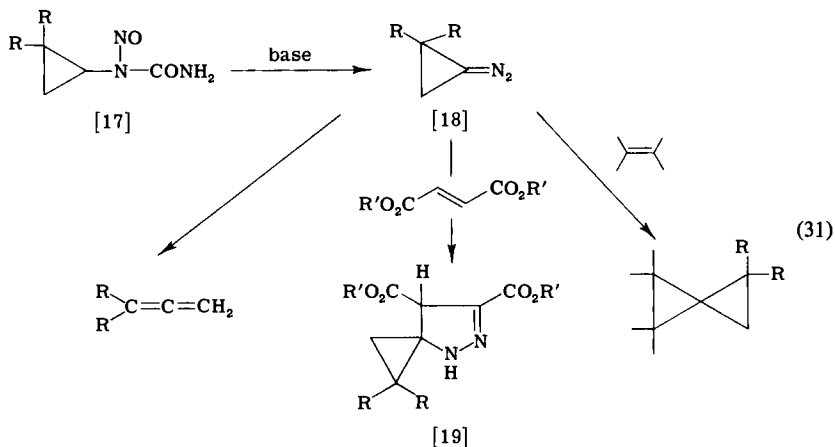
The mechanism in Eq. (30) has been suggested for the bimolecular formation of azines from diazo compounds (111).



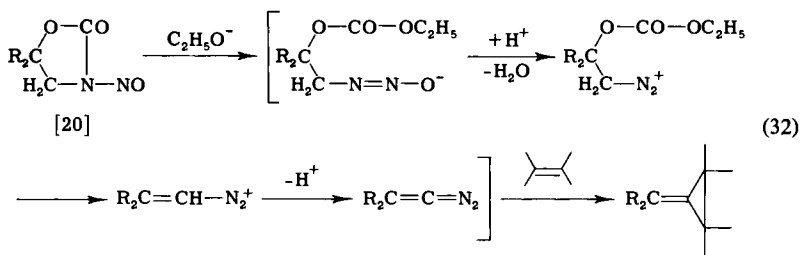
Kinetic data are not available for the less stable diazoalkanes. It should be pointed out, however, that the pyrolysis and photolysis of branched-chain diazoalkanes do not afford identical product distributions (112). Similar effects have been observed with alkyldiazirines (Section VII). The lower temperatures at which photolyses are usually carried out offer no reasonable explanation, because photolysis appears to promote the intramolecular reactions with greater activation energies. We cannot exclude the possibility that some of the intramolecular reactions of diazoalkanes are concerted with the elimination of nitrogen. Incomplete dissipation of the excess energy absorbed in the photolysis of diazoalkanes is an alternative (and more widely accepted) explanation of the observed discrepancies.

The thermal instability of various types of diazo compounds precluded their isolation. Spontaneous evolution of nitrogen was observed in attempts to generate diazocyclopropanes [18] by treatment of the corresponding nitrosoareas [17] with base (*III*, *II*). Pyrazoline [19] formation in the presence of diethyl fumarate suggests the intermediacy of [18]. In the absence of efficient traps for [18], the products are derived from

carbenoid rearrangement (Chapter 12, Section II) and addition (Chapter 8, Section III).



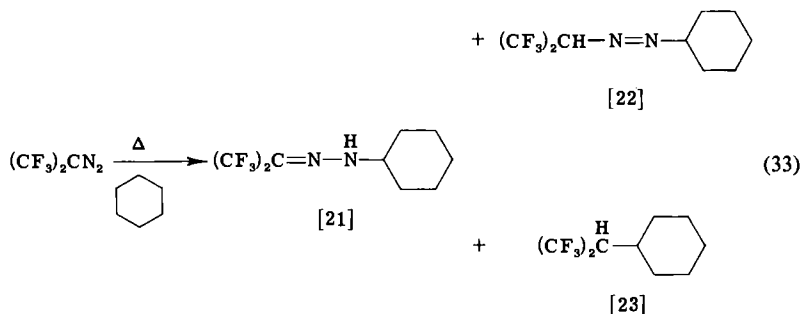
Treatment of 5,5-disubstituted *N*-nitrosooxazolidones [20] initiates a series of reactions which are best explained by postulating the formation of unsaturated carbenes, $R_2C=C\dot{}$. Unsaturation is introduced by the base-promoted elimination of ethyl bicarbonate, probably at the stage of an α -acyloxydiazonium ion (115).



Halogenation of diazomethane with less than molar amounts of *t*-butyl hypohalites at -100° gives halodiazomethanes in good yield. The halodiazomethanes undergo thermolysis at -10° or may be photolyzed at -50° (116). Similarly, reaction of 1-diazopropane and *t*-butyl hypobromite at -100° and subsequent warming of the reaction mixture to -30° led to the formation of products derived from 1-bromo-1-diazopropane (117). Halogenation of diazomethane with two equivalents of

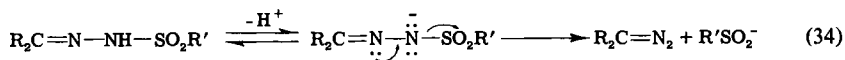
t-butyl hypohalites probably leads to dihalodiazomethanes which are too unstable to be characterized and decompose spontaneously even at -100° (116).

In interpreting any reaction of a diazoalkane, care has to be taken that products have not arisen by acid catalysis (cf. Section VI). The danger of protonation increases, of course, with increasing basicity of the diazo compound. Diazoalkanes may undergo acid catalyzed reactions even under strongly alkaline conditions. On the other hand, the decomposition of diethyl diazosuccinate in deuterated organic acids and alcohols proceeded largely through a carbenic process, as shown by the lack of deuterium incorporation (117a). Other noncarbenoid reactions are rarely encountered in the pyrolysis of diazoalkanes. Bis(trifluoromethyl)diazomethane was found to react anomalously with cyclohexane to give a hydrazone [21] and an azo compound [22] in addition to the expected carbene insertion product [23]. The formation of [21] and [22] is suppressed by the addition of hydroquinone, and evidence for a radical chain mechanism has been presented (118).



VI. BAMFORD-STEVEN'S REACTION

p-Toluenesulfonylhydrazones (tosylhydrazones) of aldehydes and ketones undergo base-catalyzed thermal decomposition with loss of *p*-toluenesulfinate to give intermediate diazo compounds (119).

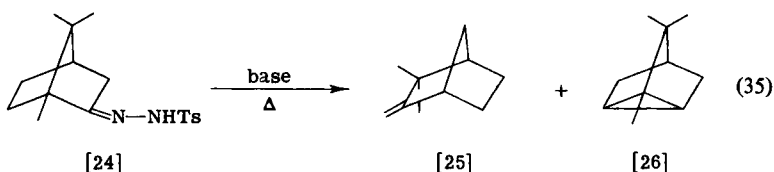


Kinetic studies have confirmed that the cleavage of the anion of the tosylhydrazone is rate-determining (120). The fate of the diazo compounds

is dependent on their structures and their interactions with their environment. Aryldiazomethanes (119, 121) and diazoketones (122) have been obtained by treatment of the corresponding tosylhydrazones with aqueous or alcoholic base. Diazoalkanes can be prepared conveniently and in high purity by vacuum pyrolysis of dry lithium or sodium salts of tosylhydrazones (123). More frequently, however, the Bamford-Stevens reaction is used as a method of *in situ* formation and decomposition of diazo compounds. The decomposition processes may be generally categorized as carbenic, in which nitrogen is expelled to give a divalent intermediate, or as cationic, in which there is coordination with an electron-deficient reagent (Brønsted or Lewis acid) to give diazonium or carbonium ion intermediates or both.

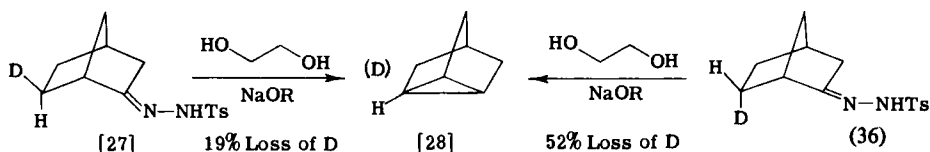
A. Effect of Solvent

The problem of distinguishing between carbenic and cationic mechanisms of decomposition of diazoalkanes has usually been studied by examination of the proportions of the various reaction products, supplemented by isotopic labeling experiments. A favored system for study has long been camphor tosylhydrazone [24], which gives mixtures of camphene [25] and tricyclene [26]. Tricyclene, which could be regarded as an intramolecular insertion product of the carbene derived from diazocamphane, predominates in solvents of low protonating ability, whereas the rearranged olefin, camphene, is favored in the more acidic alcohols like ethylene glycol (120, 124)



Shapiro *et al.* (125) allowed [24] to decompose in diglyme with increasing concentrations of sodium methoxide, and in the presence of D_2O . The tricyclene from their experiments contained deuterium in an amount which decreased with increasing base concentration. This result suggests a cationic path to tricyclene. Similar conclusions have been reached from studies of the Bamford-Stevens reaction of norcamphor tosylhydrazone [27] stereospecifically deuterated in either the 6-*exo* or the

6-*endo* position (126). Under aprotic conditions, the product is entirely nortricyclene [28], formed without loss of deuterium by intramolecular insertion of the carbene. In glycol (with 2–3 equivalents of base), [28] still constitutes the major product, but it is now formed with preferential loss of hydrogen (deuterium) from the 6-*endo* position. This result is inconsistent with the intermediacy of a nonclassical or rapidly equilibrating norbornyl cation; 1,3 elimination at the diazonium ion has been suggested.

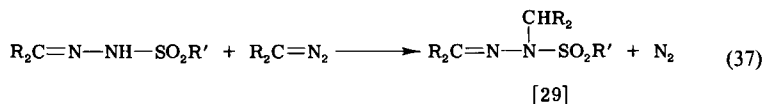


Accordingly, tricyclene formation does not provide a reliable estimate of the carbenic and cationic paths in tosylhydrazone decomposition. 2-Methylpropanal and 2,2-dimethylpropanal tosylhydrazones were chosen to obtain further information concerning the relative "protonicity," i.e., proton donor ability, of various hydroxylic solvents (127). The effects of the solvents can be followed by observing the relative amounts of cyclopropane formation and Wagner-Meerwein rearrangement. It has been found that "protonicity" of solvents is a function of their relative acidity (pK_a or K_e , an acidity scale inversely related to pK_a), and of their "proton equivalence" (PE), defined as milliequivalents of hydroxyl per gram of solvent. On the basis of cyclopropane formation, triethylcarbinol (PE 8.6, $K_e < 0.2$) appears to be as "aprotic" as diethyl Carbitol, a hydroxyl-free solvent. On the other hand, 1,3-propanediol (PE 26.3, K_e 12), diethylene glycol (PE 18.8, K_e 33), and ethylene glycol (PE 32.3, K_e 43) are strong proton donors. The importance of K_e becomes apparent by comparing solvents of equal PE. For example, at PE 10, neat hexanol ($K_e \sim 0.5$) is significantly more "aprotic" than diethylene glycol/diethyl Carbitol (50 : 50).

More information is supplied by investigation of diazo compounds, such as diazoneohexane, which undergo two or more competing intramolecular insertion reactions (112). Not only the relative amount, but also the selectivity of the intramolecular insertion was found to change with increasing "protonicity" of the solvent. There appears to be a gradual, rather than abrupt, transition from carbenic to cationic processes which may be interpreted as a carbenoid catalysis by weak proton donors.

The effect of solvent manifests itself also in the rate at which the tosylhydrazones decompose (128). At room temperature, the half life of the anion of *p*-nitrobenzaldehyde tosylhydrazone was 2 min in dimethylformamide versus about 30 min in ethanol. A blue shift of the primary absorption band of tosylhydrazone anions in hydroxylic solvents has also been noted (128).

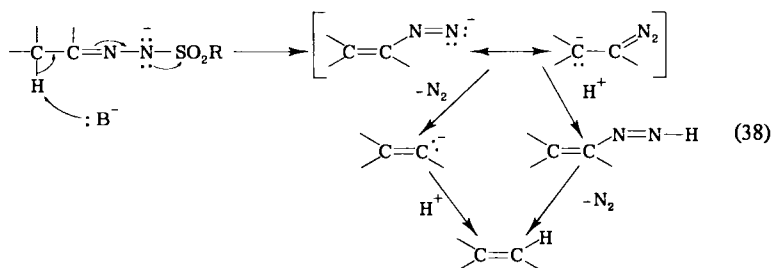
In aprotic solvents, the tosylhydrazone itself is an important source of protons. Incomplete neutralization of the tosylhydrazones leads to the formation of *N*-alkyltosylhydrazones [29], arising from the reaction of tosylhydrazone with diazoalkane (129–131).



The excess of base required for complete conversion of camphor tosylhydrazone [24] into tricyclene [26] was found to increase in the order of solvents: decalin, diglyme, and dimethylformamide (125). Dimethyl sulfoxide (DMSO) is not a suitable solvent for the decomposition of tosylhydrazones; some carbenes (or diazoalkanes) were oxidized by DMSO to the corresponding aldehydes or ketones (132).

B. Effect of Base

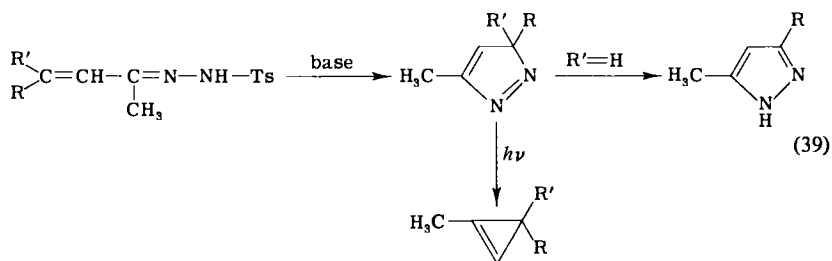
Sodium methoxide (2–5 fold excess) is the base most commonly employed in the Bamford-Stevens reaction. Sodium methoxide is preferred to the higher alkoxides because methanol is most easily removed from the reaction mixture. Sodium hydride, sodamide, and lithium alkyls may be employed in slight excess to neutralize tosylhydrazones and subsequently pyrolyze the corresponding sodium or lithium salts. With more than two equivalents of these bases, at elevated temperatures, the reaction takes an entirely different course (133–136). Olefins are formed without carbon skeleton rearrangements or insertion leading to cyclopropanes. Terminal olefins are the major products from tosylhydrazones of methylalkylketones, and *cis* olefins predominate in other cases. In contrast, olefin formation via carbenes shows a preference for internal olefins with *trans* geometry. The mechanism, Eq. (38), has been supported by experiments with deuterated tosylhydrazones.



Reduction of tosylhydrazones to saturated hydrocarbons is brought about by lithium aluminum hydride and sodium borohydride (137-141). Aluminum alkoxides are capable of generating diazoalkanes from tosylhydrazones, but subsequently act as Lewis acids to give carbonium ion-derived products (142).

C. Effect of Structure

Even with a proper choice of solvent and base, not all tosylhydrazones can be induced to give carbene intermediates. Tosylhydrazones of α,β -unsaturated aldehydes and ketones afford pyrazolenines which may be converted into cyclopropenes via diazoalkenes (79) (Section IV). If hydrogen is present in position 3, rearrangement to pyrazoles takes place (143).



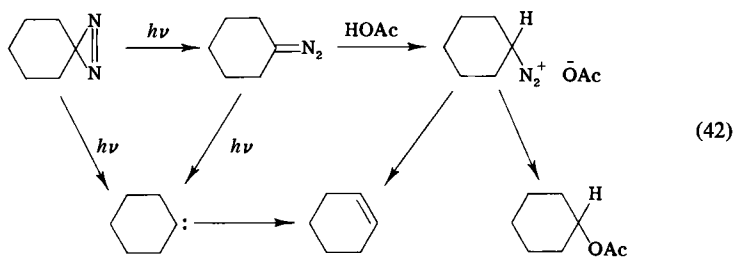
Tosylhydrazones of certain α,β -epoxyketones undergo a fragmentation reaction to yield an acetylene and a ketone as shown in Eq. (40) (144-146). By a similar mechanism, the aprotic decomposition of tosylhydrazones of benzoin acetate and benzoin benzoate afforded diphenylacetylene (164a).

in the gas phase with added nitrogen. They conclude that at least 20% of the primary decomposition of diazirine is an isomerization to diazomethane. Moore and Pimentel (53) photolyzed diazirine isolated in a solid nitrogen matrix. The photolysis did produce diazomethane but, by a careful labeling experiment with ^{15}N , they concluded that the diazomethane was produced by reaction of methylene with the nitrogen matrix and not by photoisomerization of diazirine. Moore and Pimentel also failed to observe any diazomethane in the gas-phase photolysis of diazirine.

The photoisomerization of diazirine to diazomethane presents unique problems. On the basis of the appearance potentials, the heats of formation of diazomethane and diazirine have been estimated as 49 and 79 kcal/mole, respectively (101). If diazomethane is, in fact, produced by photoisomerization, it cannot have been initially in its electronic ground state. With the excess energy it would contain (at least the difference between the heats of formation of diazirine and diazomethane), collisional stabilization in the gas phase is highly improbable. One possible solution to this difficulty is that some of the excited diazirine molecules undergo intersystem crossing to yield excited triplet diazomethane, which may well have a lifetime sufficiently long to allow its collisional stabilization (152).

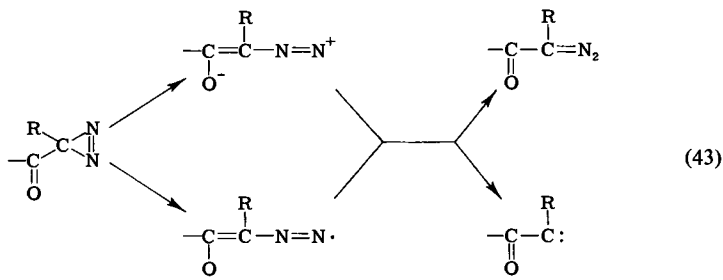
These reservations do not apply to substituted diazirines with more efficient internal energy redistribution. There is ample evidence that substituted diazirines can isomerize to diazo compounds. In the attempted preparation of 3,3-diphenyldiazirine by aerial oxidation of the corresponding diaziridine, only evidence for diphenyldiazomethane was obtained (153). Photolysis of pentamethylenediazirine in the liquid phase gave, in addition to the hydrocarbon products cyclohexene, bicyclo[3.1.0]hexane, and methylenecyclopentane, 15–20% of dicyclohexylazine (152, 154). IR examination of the reaction mixture immediately following partial photolysis showed the presence of diazocyclohexane. It is likely that the dicyclohexylazine is formed from the diazo compound.

Photolysis of pentamethylenediazirine in acetic acid led to the formation of 39% of cyclohexyl acetate (152, 155). Since the diazirine does not react with acetic acid in the dark, it is probable that cyclohexyl acetate arises from trapping of the intermediate diazocyclohexane. The fraction of olefin derived from the carbonium ion route was determined by photolyzing pentamethylenediazirine in O-deuterated acetic acid. The cyclohexene produced contained $33 \pm 2\%$ of the monodeuterated species (155). This means that, in the photolysis of the diazirine in acetic acid, about 75% of the primary process is the isomerization to its linear isomer.



Similar results have been obtained with a variety of diazirines. Pyrolysis of diazirines in acetic acid afforded somewhat smaller yields of acetates than did photolysis. Azine formation has even been observed in the gas phase pyrolysis of bis(trifluoromethyl)diazirine at 300° (156). It is not surprising, therefore, that the decomposition of diazoalkanes and alkyl-diazirines (157) give nearly identical product distributions (Chapter 7, Section IV). In both cases, the difference between photolysis and pyrolysis is quite striking. In view of the well-documented isomerization of diazirines to diazoalkanes, a comparison of the products from both precursors does not provide independent evidence of a carbene intermediate.

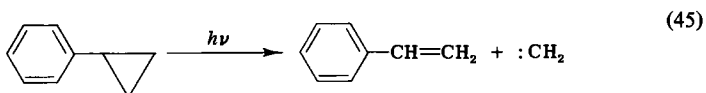
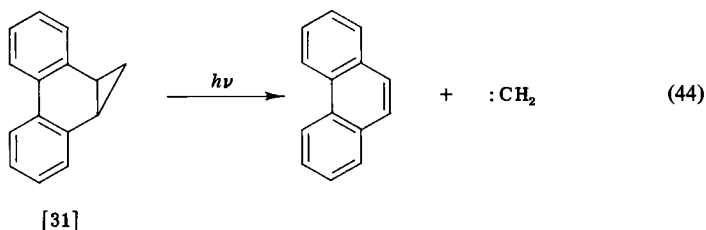
The nature of the pathway of ring rupture is not completely understood. The thermal gas-phase reactions of alkyl diazirines were homogeneous and of first order (158, 159). An unusually high preexponential *A* factor was observed in the pyrolysis of 3,3-dimethyldiazirine at relatively low temperatures (160), and the authors concluded that the transition state was noncyclic and probably radical in its nature. On the other hand, Schmitz (161) has argued that an ionic mechanism was the most likely, as the presence of an electron-withdrawing group strongly aids the ring rupture (α -ketopentamethylenediazirine loses nitrogen readily at 40°, whereas pentamethylenediazirine requires the elevated temperature of 160°). However, the homolytic process can also be aided by an electron-withdrawing group, and this pathway cannot be ruled out as yet.



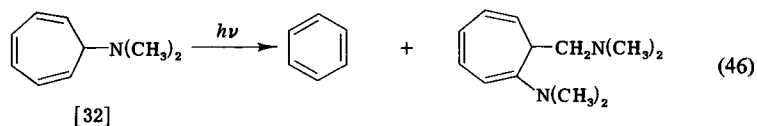
VIII. DECOMPOSITION OF CYCLOPROPANES

A. Photolysis of Arylcyclopropanes

Irradiation of 9,10-dihydro-9,10-methanophenanthrene [31] and of phenylcyclopropane generates methylene which displays the same reactivity as singlet CH_2 from other sources (random insertion into carbon-hydrogen bonds, stereospecific addition to olefins) (162).

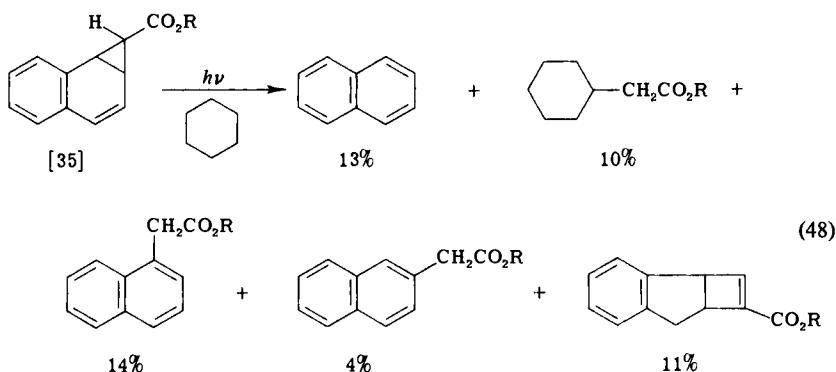
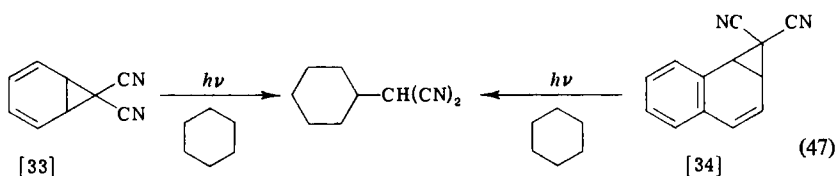


Reaction (45) has been considered as a possibility in the vapor-phase photolysis of phenylcyclopropane (163), but it seems to be much more important in solution. With reference to the norcaradiene structure of [31], the possibility of generating methylene from cycloheptatriene was also investigated. Examination of the products gave no evidence of the production of CH_2 (162). A formal transfer of dimethylaminocarbene, however, occurred in low yield on irradiation of 7-dimethylaminocycloheptatriene [32] (164).

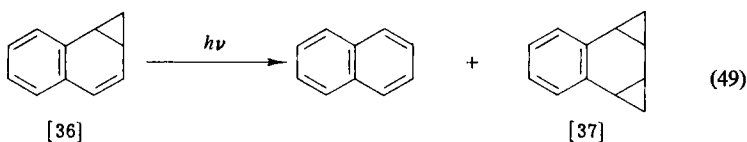


Photolysis of a cyclohexane solution of 7,7-dicyanonorcaradiene [33] gave cyclohexylmalonitrile in 60% yield. The same product (22%) was obtained from the photolysis of 7,7-dicyano-2,3-benzonorcaradiene [34] in cyclohexane (165). The yields of ethoxycarbonylcarbene transfer from 7-ethoxycarbonyl-2,3-benzonorcaradiene [35] to cyclohexane are even

lower (8–10%) (165, 166). Photoisomerization of the benzonorcaradienes constitutes a major reaction path.



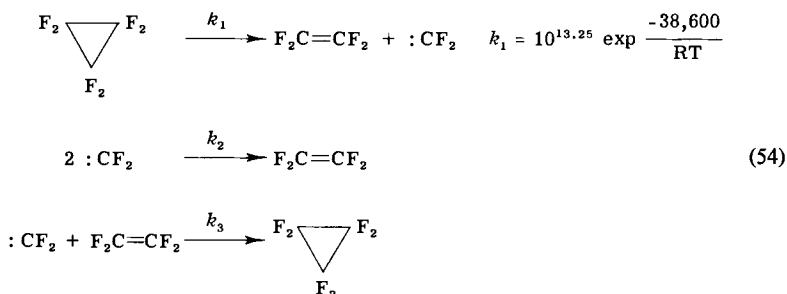
Prolonged irradiation of benzonorcaradiene [36] produced naphthalene and bismethanonaphthalene [37] (167). The conversion of [36] into [37] is best rationalized by assuming a photolytic cleavage of [36] into naphthalene and methylene. This hypothesis was supported by a trapping experiment in which photolysis of [36] in cyclohexene gave norcaradiene and naphthalene.



Diphenylcarbene appears to be generated in the photofragmentation of 1,1,2,2-tetraphenylcyclopropane, 1,1,2,3-tetraphenylcyclopropane, and 1,1,2-triphenylcyclopropane (168). Irradiation in methanol–benzene gave benzhydryl methyl ether; irradiation in 2-methyl-2-butene afforded 1,1,2,2-tetraphenylethane. These are the same products as have been obtained in the photolysis of diphenyldiazomethane. Irradiation of *trans*-1,2-diphenylcyclopropane in methanol–benzene produced methylbenzyl ether (6%), among other products, demonstrating that phenylcarbene was generated. Phenylcarbene was also trapped by 2-methyl-2-butene to give

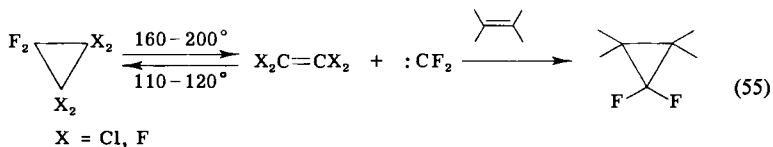
B. Pyrolysis of Halocyclopropanes

Perfluorocyclopropane decomposes thermally to tetrafluoroethylene and difluorocarbene (171). The fluorocarbon is much less stable than cyclopropane. Pressure-time curves can be fitted quantitatively to an integrated rate equation derived from the mechanism, Eq. (54). The

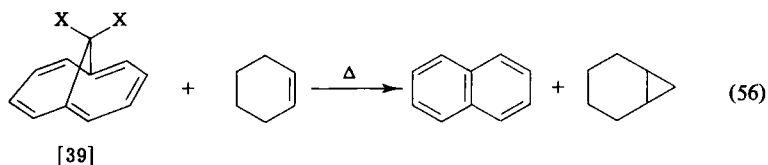


presence of $:\text{CF}_2$ in the reaction mixture has been confirmed by addition to perfluoropropene and ethylene. Similar extrusion of difluorocarbene has been observed in the pyrolysis of perfluoroallylcyclopropane (172) and difluoromethylpentafluorocyclopropane (173).

The thermal decomposition of chlorofluorocyclopropanes provides a useful source of difluorocarbene, as the required compounds are readily obtained by the gas-phase reaction of dichlorocarbene with fluoroolefins (174). The decomposition of 1,1-dichlorotetrafluorocyclopropane at 160°–170° is slow but quantitative. The liberated $:\text{CF}_2$ reacts with olefins to give the corresponding 1,1-difluorocyclopropanes, often in 85–95% yield. Thermal decomposition of 1,1,2-trichlorotrifluorocyclopropane or 1,1,2,2-tetrachlorodifluorocyclopropane requires temperatures near 200°. The decompositions involve predominantly (>70%) ejection of difluoro- rather than chlorofluoro- or dichlorocarbene and thus provide clear examples of the stabilization of a carbene by fluorine. The pyrolysis of tetra- and pentachlorocyclopropane (500°) takes an entirely different course to give tetra- and pentachloropropenes, with no evidence of $:\text{CCl}_2$ formation (175).

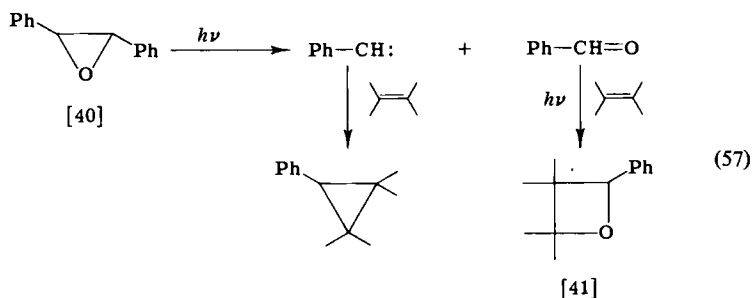


Surprisingly, an inverse sequence of reactivities has been found for the ejection of dihalocarbenes from 11,11-dihalo-1,6-methano[10]annulenes [39] (176). The difluoro compound required heating to 250°, whereas transfer of :CCl_2 from [39], $\text{X} = \text{Cl}$, to cyclohexene occurred almost quantitatively at 80° within 24 hr.



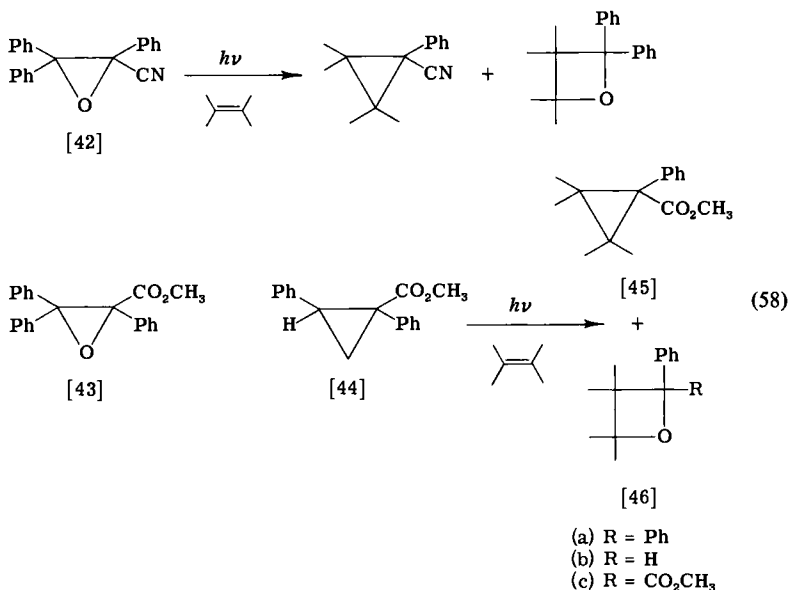
IX. PHOTOLYSIS OF OXIRANES

Aryl-substituted oxiranes undergo photofragmentation to arylcarbenes and ketones or aldehydes. Irradiation of *trans*-2,3-diphenyl-oxirane [40] in olefins as solvents affords phenylcyclopropanes in 60–75% yield (127, 178). A second product, the oxetane [41], invariably arises from the photoaddition of benzaldehyde to the olefin. The relative rates of insertion reactions of phenylcarbene from diverse sources, including [40], were found to be identical (179).



Substituted phenyloxiranes provide convenient precursors for substituted arylcarbenes, e.g., diphenylcarbene (177), phenylmethylcarbene (180), cyanophenylcarbene (181–183), and methoxycarbonylphenylcarbene (182). Selective cleavage was observed with unsymmetrical precursors; the thermodynamically more stable isomer appears to be favored. Compound

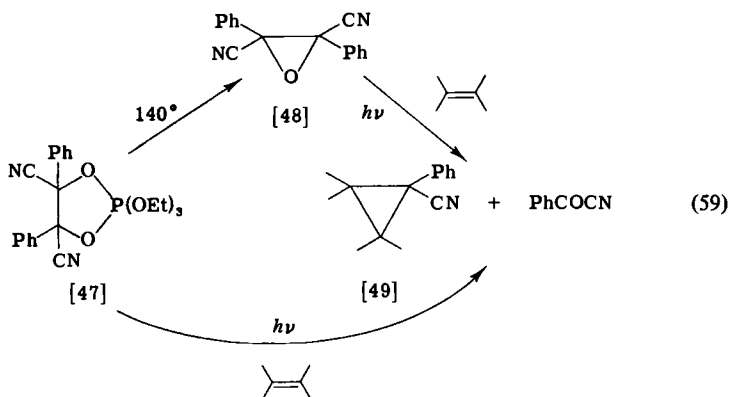
[42] affords cyclopropanes derived from cyanophenylcarbene and oxetanes derived from benzophenone. The alternative manner of fragmentation [42] $\rightarrow$ $\text{Ph}_2\text{C}:$ + PhCOCN , is less than 5% (181). In the photolysis of [43] and [44], the expected oxetanes of benzophenone and benzaldehyde [46a,b] are obtained in addition to the cyclopropane [45]. A small amount of [46c] indicates that fragmentation to diphenylcarbene also occurs (182).



The photochemistry of several aryloxiranes has been studied in rigid organic glasses at 77°K (184, 185). Irradiation at 2720 Å produces a colored intermediate, stable at 77°K, which can be eradicated either by warming or by irradiating into the visible absorption band (5000–6000 Å). Becker *et al.* (185) suggested a diradical resulting from C—O bond cleavage whereas Trozzolo *et al.* (184) presented evidence that the colored intermediates are most probably carbonyl ylides. The interconversion of aryloxiranes and the colored species proved to be stereospecific, in accordance with conservation of orbital symmetry. No ESR signals were observed in the region where monoradicals or triplets with smaller spin-spin interaction might exhibit absorption. The final photoproducts, arylcarbenes and

carbonyl compounds, were identified by comparison of their emission spectra with those of authentic samples. ESR absorption signals of the arylcarbenes in their triplet states were also recorded (184). When triphenyloxirane was photolyzed, no ESR signals corresponding to those of phenylcarbene were detected (184). The emission of phenylcarbene, however, has been observed (185), and products derived from both diphenylcarbene and phenylcarbene were obtained in solution.

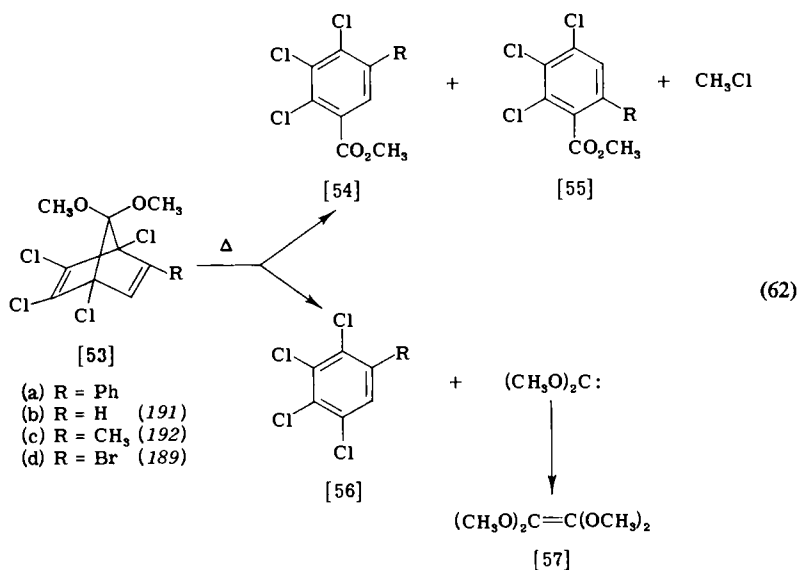
Some photolytic reactions closely related to the fragmentation of oxiranes have been reported. The 1,3,2-dioxaphosph(V)olane [47] decomposes thermally to give *trans*-2,3-dicyano-2,3-diphenyloxirane [48]. Irradiation of [47] in the presence of olefins provides the cyclopropanes [49] in yields comparable to those obtained from [48] (186).



Photofragmentation of tetraaryl and diaryl cyclic carbonates and sulfites [47, CO and SO instead of P(OEt)₃] produced diaryl and arylcarbenes, respectively (186a). The insertion selectivities of phenylcarbene from these sources agreed very well with those obtained with *trans*-stilbene oxide and phenyldiazomethane as precursors. The data indicate that a common species is generated in all the systems studied.

Photolysis of the dioxole [50] leads to products derived from 9-carbenafluorene [51] [nonstereospecific addition to *cis*-2-butene (23%), reaction with methanol to give 9-fluorenyl methyl ether (30%), etc.]. A variety of dioxoles fragment in a similar fashion with formation of arylcarbenes and 1,2-diketones, although in relatively low yield (187).

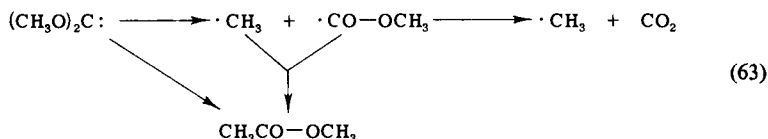
triene derivatives. When pyrolyzed as a melt or in concentrated solution, [53a] yields (in addition to tetrachlorodiphenyl [56]) the esters [54] and [55], methyl chloride, and tetramethoxyethylene [57] in 70% yield (based on [56]) (189–192). Of the two competing reactions, bridge loss and bridge opening, only the latter increases in rate with increasing polarity of the solvent (189). Formation of [54], [55], and methyl chloride most likely proceeds by a polar mechanism, whereas loss of the bridge is radical or concerted in nature.



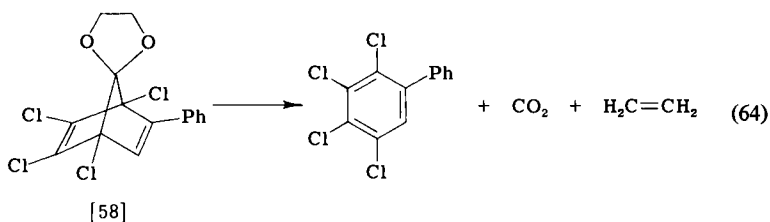
Since bridge loss has been shown to be unimolecular (190, 192), tetramethoxyethylene probably arises through the dimerization of dimethoxycarbene. In accord with this hypothesis, no tetramethoxyethylene was obtained from the liquid-phase pyrolysis of [53a] under conditions of high dilution, or from the gas-phase pyrolysis of [53c] (192). Attempts to intercept the carbene with olefins have met with failure. Pyrolysis of [53a] in the presence of oxygen afforded dimethyl carbonate (189, 192); sulfur reacted to give dimethyl thiocarbonate (189). Whether or not the carbonates are derived from dimethoxycarbene, however, is uncertain.

Compounds [53a] (193) and [53c] (192) were pyrolyzed in a furnace mounted at the inlet of a mass spectrometer. A peak of m/e 74 was assigned

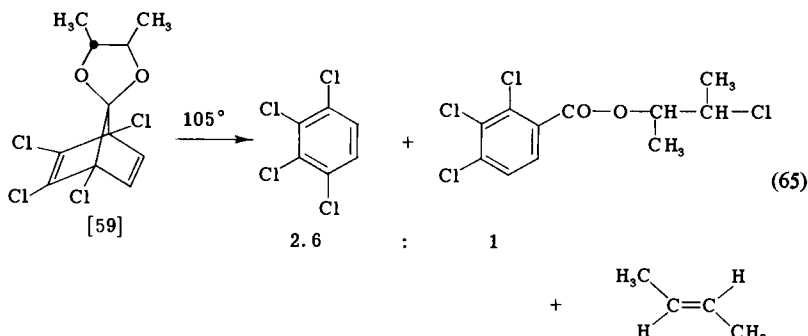
to methyl acetate, rather than dimethoxycarbene, on the basis of appearance potential data. The identification of methyl radicals and CO_2 , in addition to methyl acetate, suggests a rapid radical fragmentation process for the carbene (192).



Pyrolysis of the cyclic ketal [58] affords an almost quantitative yield of tetrachlorodiphenyl, and 95% of the ketal bridge is accounted for by the equimolar quantities of ethylene and CO_2 evolved (190, 192). A concerted pathway for the fragmentation of [58] is rendered unlikely, however, by the fact that [58] decomposes much more slowly than does [53a].

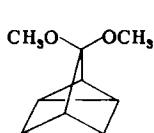


Small structural changes suffice to promote ester formation from cyclic norbornadienone ketals, e.g., [59] (191).



Quadricyclanone ketals have been investigated as potential sources of dialkoxycarbene. Benzene is produced in good yield when [60] is pyrolyzed,

but the products derived from the ketal bridge are highly dependent on the choice of reaction conditions (194). Dimethyl oxalate is generated in the neat liquid at 200°–250°; trimethyl orthoformate is a major product in dilute solution at 150°. Both products have been obtained from [53a] under suitable conditions (189), suggesting similar reaction paths in the decomposition of [53] and [60]. The isolation of tetramethoxyethylene from the pyrolysate of [60] has not been achieved. Compound [61] undergoes fragmentation in a fashion parallel to that of [58]: >95% yields of benzene, CO₂, and ethylene are obtained (194).



[60]



[61]

XI. REARRANGEMENT OF CARBONYL COMPOUNDS

Three major reaction paths have been observed in the solution photochemistry of cyclobutanones, Eq. (66): (a) cycloelimination, with formation of olefins and ketenes; (b) decarbonylation, with formation of cyclopropanes; and (c) ring expansion. All of these reactions may be explained in terms of one primary photochemical process, i.e., an α -cleavage from the n, π^* state of the cyclobutanone to yield the diradical [62] (195). See also Table V.

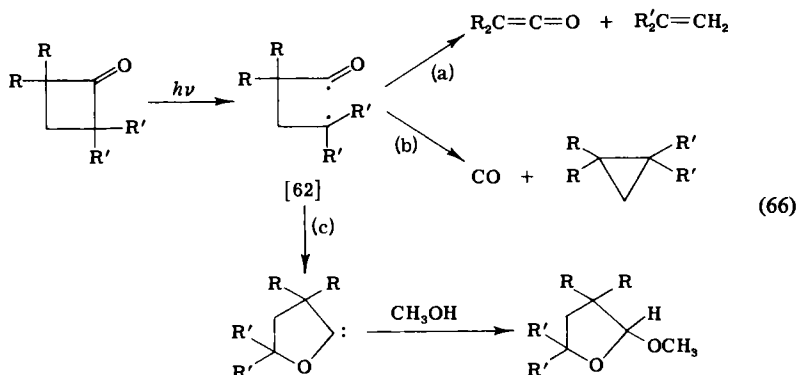
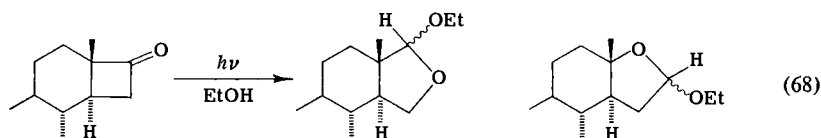
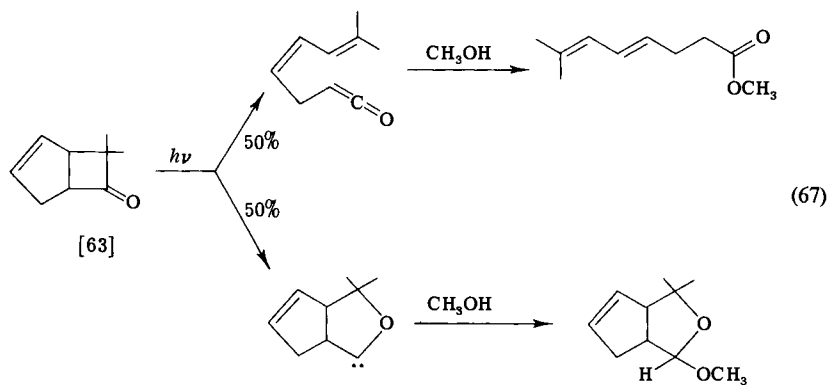


TABLE V
Photolysis of Cyclobutanones in Methanol (195)

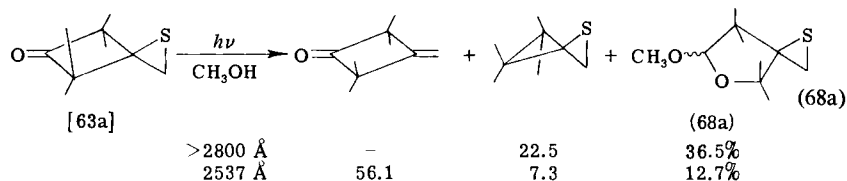
R	R'	Path (a) (%)	Path (b) (%)	Path (c) (%)
H	H	48	Trace	8
H	CH ₃	32	7	41
CH ₃	CH ₃	13	11	68

Alkyl substitution α to the carbonyl group enhances the yield of ring expansion products relative to decarbonylation and cycloelimination. The more electron-rich α bond (most highly alkyl-substituted) cleaves and migrates preferentially [$R = H$, $R' = CH_3$ in Eq. (66)]. The photochemistry of 7,7-dimethylbicyclo[3.2.0]hept-2-ene-6-one [63] provides another example of the ring expansion of cyclobutanones in competition with cycloelimination (196). The results of Quinkert (197) with steroidal cyclobutanones indicate that the reaction may be stereospecific, Eq. (68).

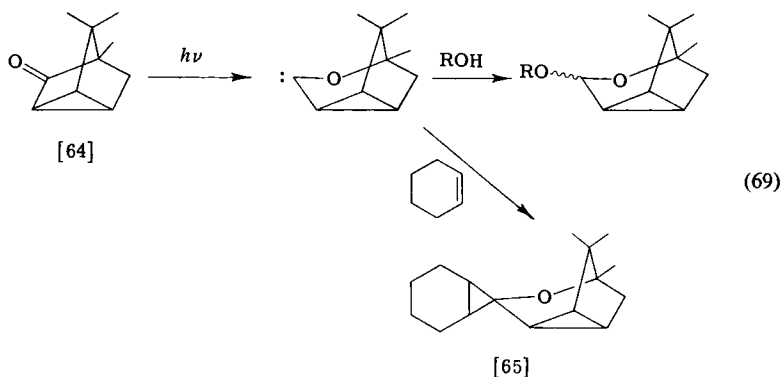
The photochemistry of 4,4,6,6-tetramethyl-1-thiaspiro[2,3]hexan-5-one [63a] displayed a remarkable dependence on the wavelength of the exciting



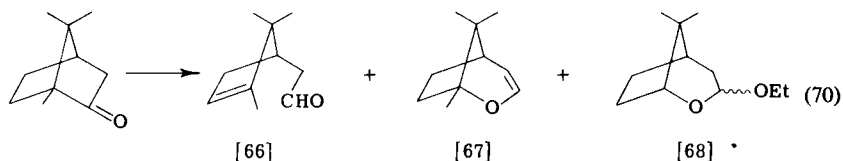
light (197a). The extrusion of sulfur probably occurs from the n, σ^* state associated with S , whereas the remaining products result from the n, π^* state of the carbonyl group.

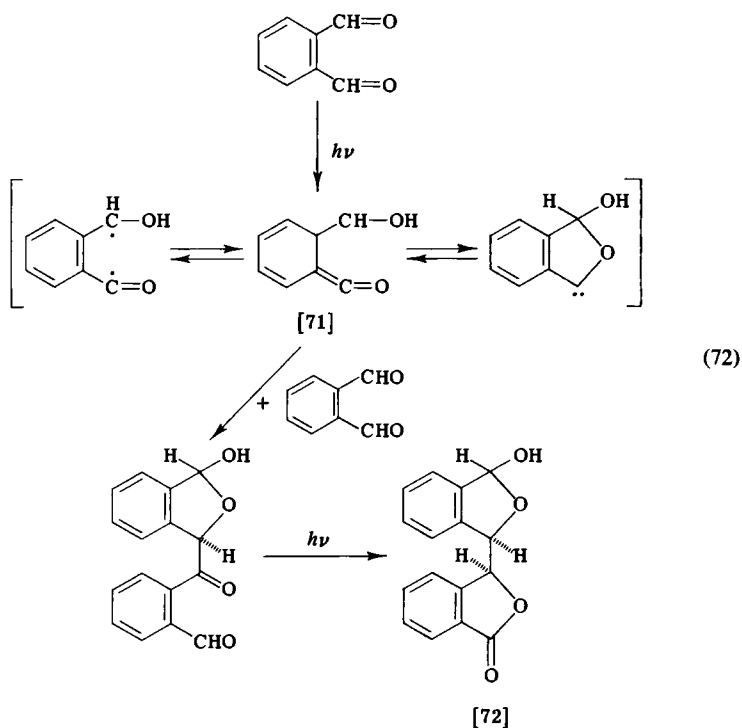


Although there is no indication that the ring expansion reaction occurs with simple cyclopentanones (195), an analogous reaction of cyclocamphanone [64] is known (198). Irradiation of [64] in dry cyclohexene afforded an adduct [65] in low yield.



Irradiation of camphor in ethanol or *n*-heptane or both gives rise to α -campholenic aldehyde [66] (70–80%), enol ether [67], and acetal [68] (10–15%) as primary products (199). Deuterium labeling demonstrates an alkoxy-carbene intermediate in the formation of [67] and [68]. Related observations have been made when camphenilone was irradiated (199a).





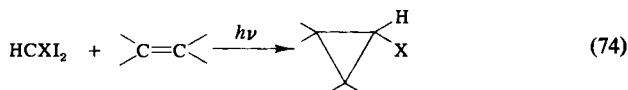
XII. DECOMPOSITION OF POLYHALOMETHANES

A. Photolysis

Methylene iodide has a rich spectrum with bands at 2120, 2400, and 2900 Å. Photolysis of methylene iodide in cyclohexene afforded norcarane with only a trace of other C₇ hydrocarbons. Cyclopropane formation from the isomeric 2-butenes and 3-hexenes proceeded stereospecifically (203). Moderate yields of cyclopropanes were also obtained from the photolysis of methylene bromide in cyclohexene and 1-hexene (204).

Three intermediates were considered as possible precursors of the cyclopropanes: (i) iodomethyl radical, (ii) methylene, and (iii) electronically excited methylene iodide (203). Iodomethyl radicals are considered unlikely

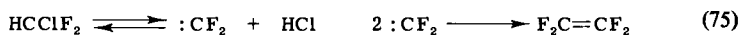
with no detectable isomerization. Chlorocarbene derivatives were isolated from the photolysis of diiodochloromethane.



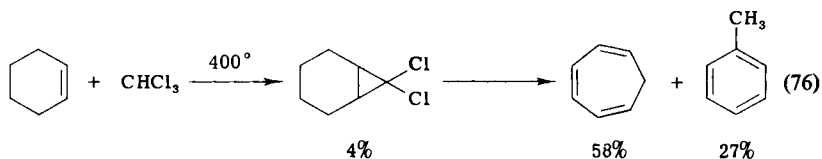
Spectra of difluorocarbene were observed after flash photolysis of CHClF_2 , CCl_2F_2 , CBr_2F_2 , perfluoropropene, and tetrafluoroethylene (208). The flash photolysis of CHClBr_2 and CHBr_2F afforded transient absorption spectra belonging to chlorocarbene and fluorocarbene, respectively (209).

B. Pyrolysis

The kinetics of the pyrolysis of CHClF_2 have been studied in a flow system between 670° and 750° (210). The reaction obeys first-order kinetics at low conversions, but is retarded by hydrogen chloride, in accordance with the mechanism, Eq. (75).



On a similar kinetic basis, the existence of dichlorocarbene as an intermediate in the pyrolysis of chloroform at 450° – 600° has been postulated (211, 212). The thermal decomposition of chloroform in the gas phase in the presence of olefins led to the isolation of dichlorocyclopropanes and to the formation of products which are known to arise from dichlorocyclopropanes under the prevailing conditions (213, 214). Difluoronorcarane (1–4%) and tetrafluoroethylene were obtained in the pyrolysis of NC-CClF_2 and cyclohexene at 370° – 420° (215).

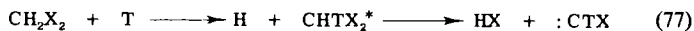


In the experiments mentioned so far, olefins were present at the site of carbene formation. Alternatively, :CCl_2 was generated by the vacuum

pyrolysis of CHCl_3 or CCl_4 at 1500° and was allowed to react with olefinic substrates on a liquid nitrogen-cooled surface (216). This technique afforded dichlorocyclopropanes in fair yields, and variable amounts of tetrachloroethylene which depended on the pyrolysis time (the probability of gas-phase dimerization of $\cdot\text{CCl}_2$ increases with increasing pyrolysis time). Attempts to condense the pyrolysate of CCl_4 on KBr plates at 83°K led to the detection of $\cdot\text{CCl}_3$, but not of $\cdot\text{CCl}_2$, by its IR spectrum (217).

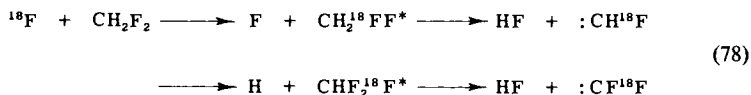
C. Chemical Activation

Chlorocarbene (218) and fluorocarbene (219) have been formed in the gas phase through dehydrohalogenation of highly excited dihalomethane molecules. The dihalomethane molecules were excited through the hot atom substitution of recoil tritium for hydrogen, Eq. (77). The carbenes were detected through the stereospecific formation of cyclopropyl halides in the presence of olefins. (The alternative mode of decomposition,



$\rightarrow \text{TX} + \cdot\text{CHX}$, would ultimately lead to inactive cyclopropyl halides which are not detected by radio gas chromatography.)

Energetic ^{18}F atoms from nuclear recoil react with fluorocarbons by both substitution pathways shown in Eq. (78). Both $\cdot\text{CH}^{18}\text{F}$ and $\cdot\text{CF}^{18}\text{F}$ are formed in appreciable quantities from the reactions of ^{18}F with CH_2F_2 or CHF_3 , whereas $\cdot\text{CF}^{18}\text{F}$ is formed from CF_4 (220).

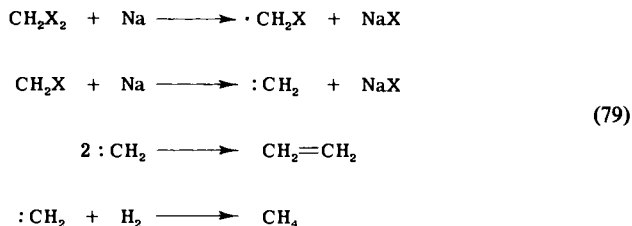


D. Reaction with Alkali Metals

The interaction of methylene halides with various metals and organo-metallic compounds in solution produces carbenoid species rather than free methylene (Chapter 3, Sections II, III). This subsection summarizes some studies carried out in the vapor phase, where the intervention of carbenoids is less likely.

The formation of alkyl radicals from alkyl halides and sodium in the

gas phase is a well-known reaction [Hartel and Polanyi; for a review, see (221)]. Sodium vapor, diluted by an inert carrier gas, is introduced into a stream of vaporized alkyl halide. Methylene halides were investigated under similar conditions by Bawn *et al.* (222–224). Starting with methylene chloride, methylene bromide, or methylene iodide in nitrogen as a carrier gas, they obtained ethylene, whereas in a hydrogen atmosphere methane was the major product. They proposed the reaction scheme in Eqs. (79).

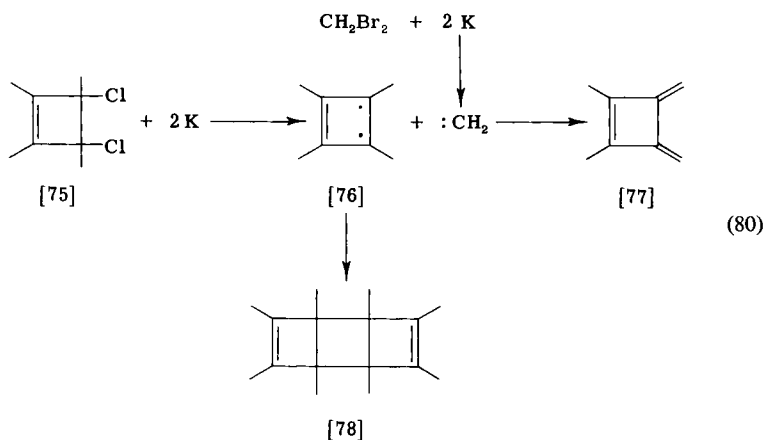


The observation that ethylene was the major product even in methane as a carrier gas casts some doubt on the intermediacy of methylene. According to our present knowledge of the reactions of methylene, ethane formed by insertion should be expected. An alternative mechanism of ethylene formation involving haloalkyl radicals should be considered:

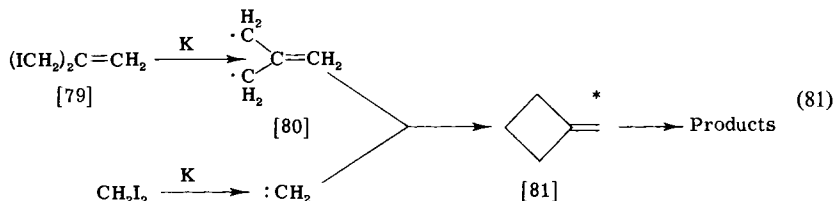


Ethylene has in fact been obtained from 1,2-dihaloethanes under the conditions of the Polanyi experiment.

This line of research has recently been revived by Skell and his co-workers, using a sodium-potassium alloy spray apparatus (225) in which the predominant species would be monoatomic potassium. An intriguing feature of their work is the generation of triplet molecules which may act as traps for triplet methylene. Thus the reaction of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene [75] with potassium vapor produces a dimer [78] of tetramethylcyclobutadiene [76] as the major product. Some minor components are also related to [76]. Introduction of an excess of methylene bromide profoundly influences the course of the reaction, the major product now being 3,4-dimethylene-1,2-dimethylcyclobutene [77]. The formation of [77] is thought to involve hydrogen transfer from triplet [76] to triplet methylene (226).



In another set of experiments (227), trimethylenemethane [80] was prepared by the reaction of potassium vapor with 2-iodomethyl-3-iodopropene [79]. Simultaneous reaction of [79] and a fivefold excess of methylene iodide with potassium vapor afforded, in addition to the usual products from trimethylenemethane, a number of C_5 olefins. The products can be rationalized by assuming the formation of excited methylenecyclobutane [81] which is partially quenched, the remainder isomerizing to C_5 dienes which are hydrogenated to the observed C_5 olefins.

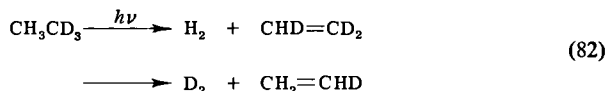


XIII. DECOMPOSITION OF ALKANES

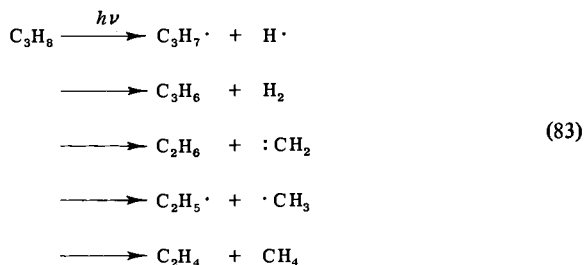
Methylene has been postulated quite often as an intermediate in the "cracking" of hydrocarbons under the action of heat, catalysts, electrical discharge, and radiation [for a review, see Knunyants *et al.* (228)], but positive evidence is rare. CH_2D_2 was obtained as the major product from mixtures of CH_4 and D_2 , and CH_4 and CD_4 , under electrical discharge (229). Photolysis of such mixtures with 1470 and 1295 Å radiation (xenon resonance lines) yielded a similar product distribution (230). These observations suggest the abstraction of molecular hydrogen with concomitant

formation of methylene. Methylene would be expected to insert into the C—H bonds of methane; products derived in this fashion have been obtained from the vacuum ultraviolet photolysis of methane (231)

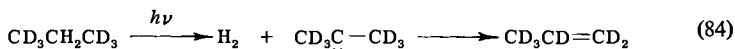
A complete analysis of the products of the photolysis of CH_3CD_3 and of $\text{C}_2\text{H}_6 + \text{C}_2\text{D}_6$ at $1470 \text{ \AA}$ led to the conclusion that nearly all molecular hydrogen produced in the primary process comes from the end carbon (232, 233). Methylcarbene is a plausible intermediate in the formation of deuterated ethylenes, Eq. (82).



The vacuum ultraviolet photolysis of propane has been studied in the gas phase (234–237) and the solid phase (77°K) (237). On the basis of the isotopic analysis of the products from $\text{CD}_3\text{CH}_2\text{CD}_3$, $\text{CH}_3\text{CD}_2\text{CH}_3$, and $\text{C}_3\text{H}_8-\text{C}_3\text{D}_8$ mixtures, primary fragmentation processes have been suggested, Eqs. (83).



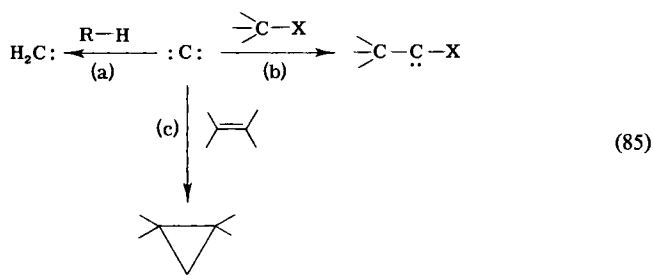
Hydrogen, ethane, and ethane are mainly formed by elimination processes from a single carbon atom; the result is the simultaneous formation of a carbene. In the solid phase, methylcarbene and dimethylcarbene rearrange quantitatively to ethylene and propylene, respectively. Secondary fragmentations have been noted to occur in the gas phase where at least 4 eV has to be distributed between the two fragments. In the photolysis of $\text{CD}_3\text{CH}_2\text{CD}_3$, H_2 accounts for 67% of all the hydrogen, indicating the prevalence of the process, Eq. (84).



Evidence of the intramolecular insertion of isopropylcarbene to give methylcyclopropane has been found in the direct photolysis of isobutane at $1470 \text{ \AA}$ (238).

XIV. REACTIONS OF ATOMIC CARBON

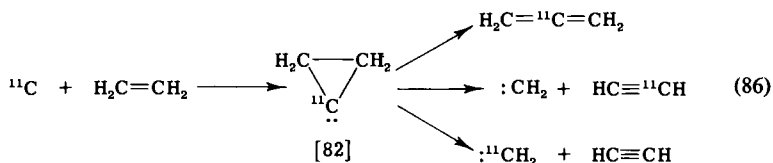
Several reactions of carbon atoms leading to carbenes may be envisaged: (a) abstraction of hydrogen from alkanes to produce methylene, (b) insertion into C—H or C—X bonds to generate alkylcarbenes, and (c) addition to olefins with formation of carbenacyclopropanes.



Many reactions of atomic carbon have been studied by the use of radioactive ^{11}C atoms (half-life 20.4 min) formed in nuclear processes (239, 240). Owing to the high energies of the reacting species and intermediates in these systems, skeletal fragmentation and rearrangements occur which cloud the basic mechanism. Such decomposition is particularly favored in the gas phase, where collisional deactivation is slow. The yield of fragmentation products becomes very small when the reactants are dispersed in a solid xenon matrix.

The interaction of recoiling ^{11}C atoms, produced by the $^{12}\text{C}(n, 2n)^{11}\text{C}$ reaction, with hydrocarbons (ethane, propane, pentane) appears to involve methylene. The product composition showed a definite phase dependence. The change from gas to liquid and solid phase reduced the yields of ethylene and acetylene, with a concomitant increase of apparent methylene insertion products (241). Observations on the statistical nature of the formation of various hexanes from *n*-pentane (242) were confirmed with propane. The ratio of *n*-butane to isobutane approached 3 : 1 in the liquid and solid phases (241). Indiscriminate reaction with carbon-hydrogen bonds is characteristic of methylene.

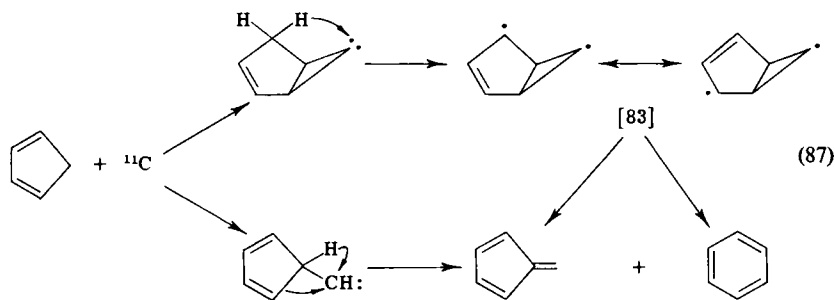
The reaction of thermal ^{11}C atoms with ethylene produces methylene by fragmentation of the initially formed adduct [82]. This type of reaction is greatly diminished in the solid phase, where [82] is rapidly deexcited and rearrangement to allene becomes more probable (243), Eq. (86).



Under the conditions of high dilution in a solid xenon matrix there is also evidence that some cyclic adducts survive sufficiently long to react with a second molecule of olefin to form spiro compounds (244).

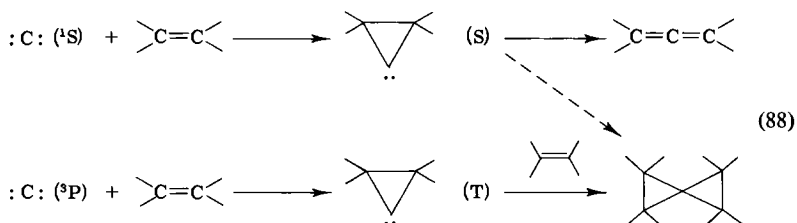
Addition of hot carbon atoms to H_2 gives rise to excited methylene which either can be stabilized by collisional deactivation or can dissociate to CH . This process is less efficient than addition of carbon atoms to ethylene, and the yield of products derived from CH_2 is in the order of 4–6% (245). Attempts to form CH_2 in spectroscopically observable amounts by the reaction of carbon atoms with H_2 or D_2 in an argon matrix were unsuccessful, although its existence was inferred from the observed production of methane (with H_2) and ketene (with CO) (246).

^{11}C atoms produced by nuclear recoil techniques react with cyclopentadiene to yield benzene and fulvene, possibly via diradical [83] which has also been suggested as an intermediate in the photoisomerization of benzene to fulvene (247, 248). Labeled products obtained from hot-atom reactions of ^{14}C ions of 5 keV kinetic energy in solid benzene at -196° included toluene, cycloheptatriene, phenylacetylene, diphenyl and diphenylmethane (248a). The results of partial degradation of these products indicate the formation of methylene, phenylcarbene, and cycloheptatrienylidene. Cycloheptatrienylidene and cycloheptatriene apparently undergo extensive isomerization (cf. Chapter 12, Section VI).

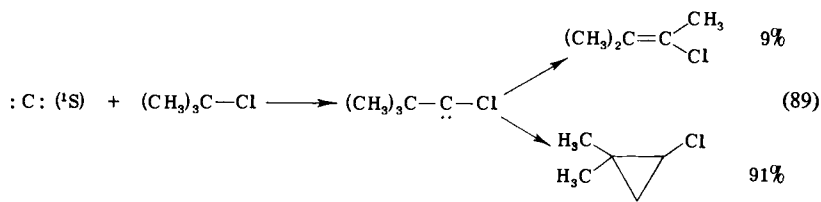


Carbon atoms have also been produced in a low-intensity carbon arc under high vacuum, a method which yields a mixture of ground state (^3P)

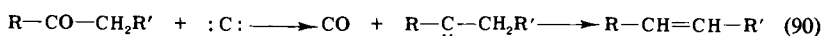
and metastable excited state species (^1D and ^1S) (249). C_2 and C_3 are also constituents of the carbon vapor (see below). The vacuum employed in this technique is such that the carbon atoms would have to travel one mean free path or less to the walls of the chamber which are cooled to -196° . With simultaneous deposition of carbon vapor and olefins, both allenes and spiropentanes are produced. If the carbon atoms are allowed to age in an inert matrix, and olefins are added after a time delay of 2 min or more, spiropentanes are the sole products. Obviously, the allenes arise from reactions of the metastable excited species, whereas ground-state carbon atoms react with two molecules of olefin to form spiropentanes. These results can be rationalized in terms of the different multiplicity of the intermediates (249) (Chapter 8, Section I, B).



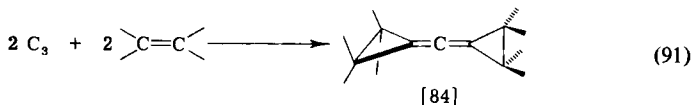
Toluene and cycloheptatriene are among the reaction products when benzene is treated with carbon vapor (250). Carbenic addition and insertion steps are likely, but the necessary hydrogen abstractions have not been explored. $C(^1S)$ inserts into C—H bonds of alkanes, with initial formation of alkylcarbenes (251). The product compositions differ significantly from those observed with alkylcarbenes from other sources. Hydrogen abstraction from the surrounding alkanes is an important process which is not encountered in the decomposition of diazoalkanes. The process has a *per* hydrogen selectivity which correlates with bond dissociation energy (251a). Inclusion of a radical trap (butadiene) inhibited the methyl producing reactions whereas a singlet carbene trap (methanol) had little effect. Triplet carbenes should result from the reaction of $C(^3P)$ with C—H bonds. Insertion of atomic carbon into C—Cl bonds, with initial formation of alkylchlorocarbenes, has also been reported (252). These intermediates undergo intramolecular cyclization more readily than do alkylchlorocarbenes from other sources. Although the differences in reactivity are not fully understood, minimum solvation and efficient relaxation in the low-temperature matrix may be important factors.



Carbon atoms produced in a low-intensity carbon arc react with aldehydes and ketones at -196° to produce carbenes and carbon monoxide, Eq. (90) (253). Deoxygenating capacity has been attributed only to the metastable states (^1D and/or ^1S) of C_1 (253a). The distribution of the intramolecular insertion products (253a) as well as the isotope effects of such reactions (253b) were nearly the same as with tosylhydrazone-derived carbenes. The deoxygenation technique has been applied to produce dichlorocarbene from phosgene and methoxycarbene from methyl formate (253c).



C_3 , a second major constituent of carbon vapor, reacts with olefins (254) and imines (255) to give bisethanoallenes [84] and their nitrogen analogs, respectively. The stereochemistry of the addition depends on the mode of deposition of the reactants, whether simultaneous or with time delay. The ground state of C_3 appears to be singlet (254). Excited state C_3 reacts with alcohols and other hydrogen-containing substrates to form C_3 hydrocarbons (allene, propyne, propene, propane) (256).



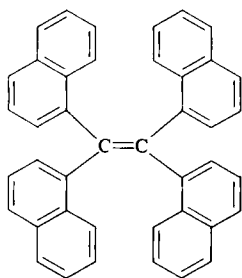
Recently, carbon vapor has been produced from graphite by a focused laser pulse (257). The major product obtained in the presence of hydrogen, methane, ethane, ethylene, or cyclopropane was invariably acetylene (257a). No spiropentanes or bisethanoallenes were produced. C_2 apparently played the dominant role in the laser-induced reaction. The photolysis of cyanogen azide appears to be an elegant method of generating carbon atoms at very low temperatures. Studies on the photolysis of $N_3\text{CN}$ in the presence of chlorine in argon and nitrogen matrices at 14°K provide

evidence for the formation of dichlorocarbene by the reaction of photo-lytically produced carbon atoms with Cl_2 (258). Dichlorocarbene has been identified by its IR spectrum, which disappears when the sample is warmed above 30°K .

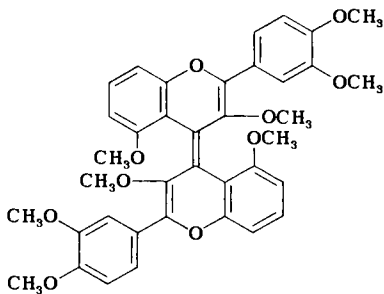
XV. DECOMPOSITION OF OLEFINS

A. Thermal Dissociation

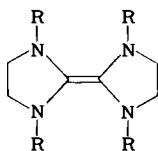
Olefins having substituents which are expected to stabilize a carbene or exhibit torsional strain, or both, have been investigated with respect to their dissociation. Products containing "one-half" of the olefin were obtained from [85] (259), [87] (260–262), and [88] (263–266) with various reagents at elevated temperatures. Molecular weights lower than those calculated for the olefin were observed for [86] (267) and [87] (268) when the method of Rast (freezing-point depression of camphor) was applied.



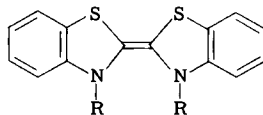
[85]



[86]



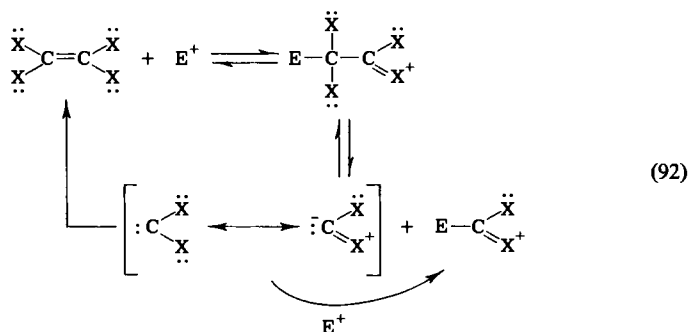
[87]



[88]

Little of the "evidence" in favor of carbene intermediates remained unchallenged. Many electrophilic reagents have been shown to react with olefins such as [87] and [88] according to the mechanism, Eq. (92) (265,

269). The electrophile initiates dissociation of the C=C bond and eventually traps the carbene generated in the first step.



The possibility of dissociation of **[87]** and **[88]** was tested in crossover experiments (i.e., heating of mixtures of symmetrical compounds with different but similar groups R, and thorough investigation of the products for unsymmetrical dimers). No evidence of crossover was obtained with **[87]**, R = aryl (269) and R = alkyl (270). "Crossed dimers" were observed with **[88]**, R = alkyl although not R = aryl (271). A proton-catalyzed crossover [Eq. (92), E = H], with the α -C—H bonds acting as a source of protons, cannot be definitely excluded.

Contrary to the negative results with tetraamino- and tetraalkoxyethylenes, the dissociation of polyfluoroolefins is well established. The flash photolysis of tetrafluoro-, chlorotrifluoro-, and 1,1-dichloro-2,2-difluoroethylene yields $\cdot\text{CF}_2$, the carbene decaying over a period of ≥ 20 msec (272). A weak spectrum of $\cdot\text{CFCl}$ has been observed in addition to the intense absorption bands of $\cdot\text{CF}_2$ in flash photolysis experiments with chlorotrifluoroethylene vapor (273). Gas chromatographic and mass spectrometric analyses of the volatile products of flash photolysis of $\text{CF}_2=\text{CCl}_2$ and $\text{CF}_2=\text{CFCl}$ have revealed $\text{CF}_2=\text{CF}_2$ and $\text{CCl}_2=\text{CCl}_2$, and $\text{CF}_2=\text{CF}_2$ and $\text{CFCl}=\text{CFCl}$, respectively (274).

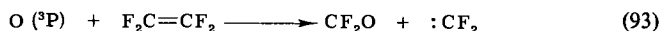
The thermal dissociation of tetrafluoroethylene was first investigated in shock-tube experiments (275). More recently, a mass spectrometric study of the thermal decomposition of $\text{CF}_2=\text{CF}_2$ in a graphite Knudsen cell showed that tetrafluoroethylene can be maintained in thermal equilibrium with difluorocarbene at $1130^\circ\text{--}1240^\circ\text{K}$ (276). From the measured heat of reaction, $\Delta H_{r,298}^\circ = 76$ kcal/mole, the heat of formation of difluorocarbene was calculated to be -39 kcal/mole. The matrix isolation technique has

been successfully adapted to the trapping of difluorocarbene formed in low-pressure pyrolysis of tetrafluoroethylene at 1300°C (276a). CF_2 was identified on the basis of known IR spectra (Chapter 6, Section I,B).

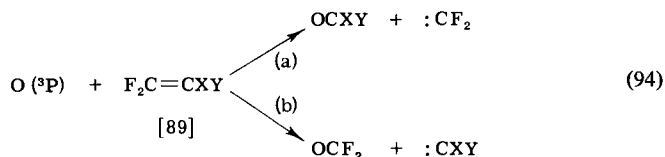
B. Bond Fission by Additional Reagents

The photochemical or thermal dissociation of olefins discussed above yields two carbene fragments. This subsection summarizes a group of reactions in which only one-half of an olefin is liberated as a carbene, whereas the other half is converted into more stable compounds by combination with suitable reagents.

This principle is nicely illustrated by the reaction of atomic oxygen with fluoroolefins. Oxygen atoms, $\text{O}(^3P)$, were prepared from the mercury-photosensitized photolysis of N_2O (277–281) or from the direct photolysis of NO_2 (279). In the presence of tetrafluoroethylene, the final products were CF_2O and hexafluorocyclopropane (277). If the reaction follows the simple course, Eq. (93), conservation of net electron spin requires one or the other of the primary products to be initially in a triplet state.

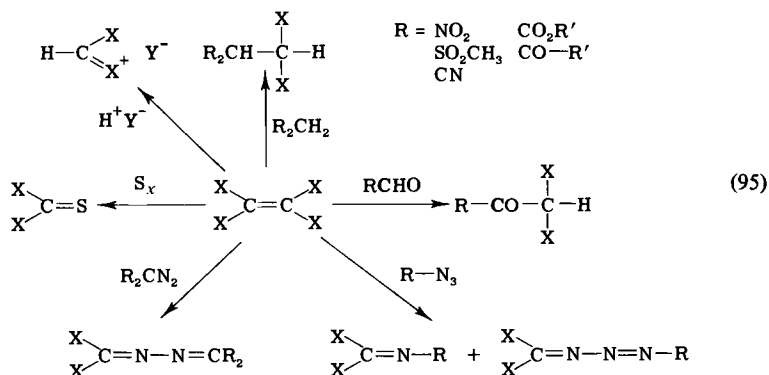


Heicklen *et al.* (277, 278) interpret their kinetic data in favor of the primary production of triplet $: \text{CF}_2$ which can react with O_2 or undergo spin inversion to form singlet $: \text{CF}_2$ (in the presence of molecular oxygen, the yield of CF_2O is enhanced). Mitchell and Simons (279), on the other hand, find no evidence for the intervention of triplet $: \text{CF}_2$. These authors have extended the reaction to a variety of olefins of the type [89]. When X, Y = halogen, Eq. (94b) is followed preferentially. CO (instead of the expected CH_2O) is a major product from $\text{CF}_2=\text{CH}_2$.



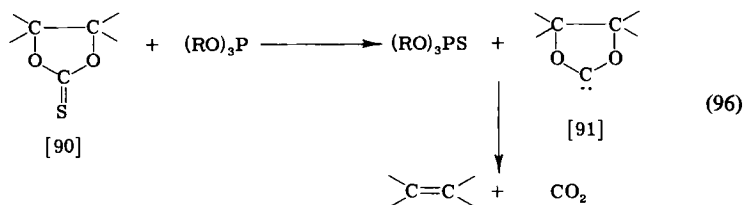
The reaction of oxygen atoms with perfluoropropene is analogous to that with tetrafluoroethylene, CF_2O , CF_3CFO , and C_5F_{10} [bis(trifluoromethyl)tetrafluorocyclopropane] being among the products (280, 281).

The attack of electrophiles on electron-rich olefins, outlined in Eq. (92), is another group of reactions belonging to the present category. Acids, including "C-H acidic" compounds (261, 268), aldehydes (261, 264), sulfur (262-264, 266), tetracyanoethylene (260, 264), diazo compounds (262, 266, 282), and azides (265, 282) were among the electrophiles employed. The mechanistic ambiguity of these reactions has not yet been resolved: the carbene intermediate formulated in Eq. (92) may either be trapped by the reagents mentioned above, or it may revert to the olefinic "dimer." Both pathways yield the same final product.

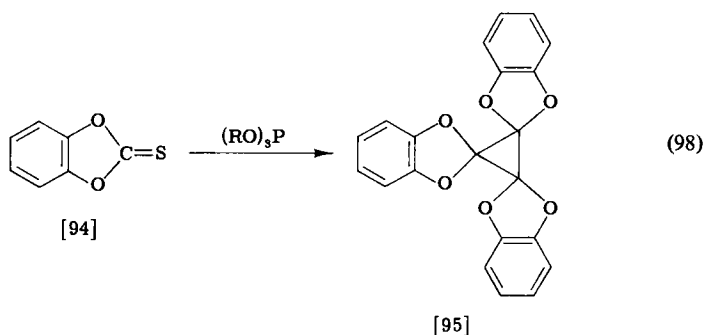
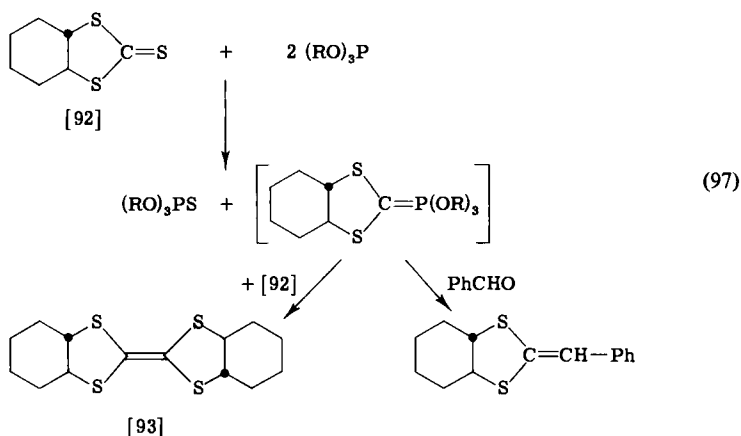


XVI. DESULFURIZATION AND DEOXYGENATION REACTIONS

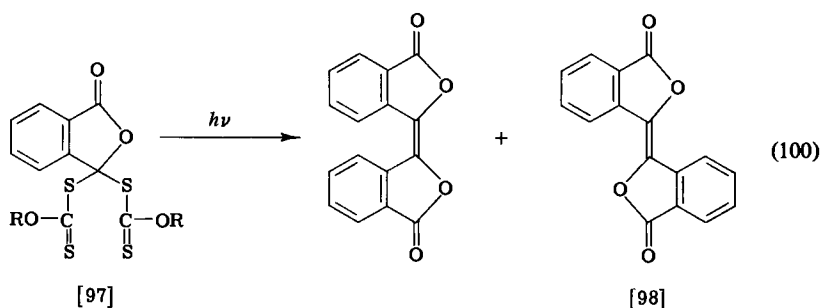
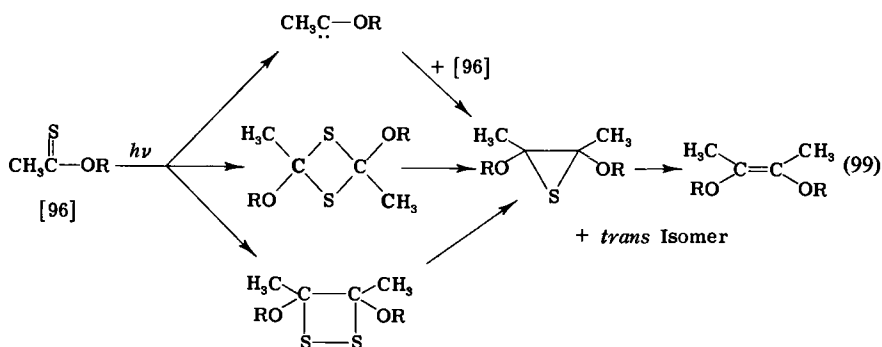
Corey and Winter (283) devised a stereospecific synthesis of olefins from 1,2-thionocarbonates [90] or 1,2-trithiocarbonates, assuming that a carbene of the type [91] might be unstable relative to olefin and carbon dioxide.



Although the synthetic procedure proved to be very useful, the intermediacy of [91] has not been established beyond doubt. Some "abnormal" cases of the reaction, Eq. (96), are of particular interest. *trans*-1,2-Cyclohexene trithiocarbonate [92] gives the coupling product [93], whereas the *cis* isomer yields cyclohexene. *o*-Phenylene thionocarbonate [94] was found to decompose to the cyclopropane derivative [95] (284). Compounds [94] and [95] may be produced by dimerization and trimerization, respectively, of a carbene intermediate. More probably, however, these products arise from intermediate phosphite ylides (285). In certain cases the ylides are easily diverted from olefin formation, e.g., by reaction with benzaldehyde.

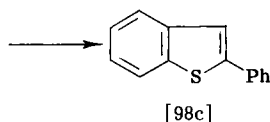
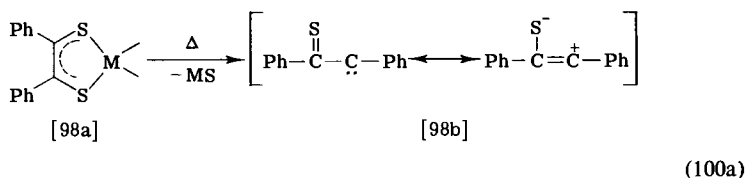


The photochemical desulfurization of thio esters [96] (286) and of the dioxanthate [97] (287) has been reported. In addition to a mechanism involving carbenes, several other pathways are conceivable.

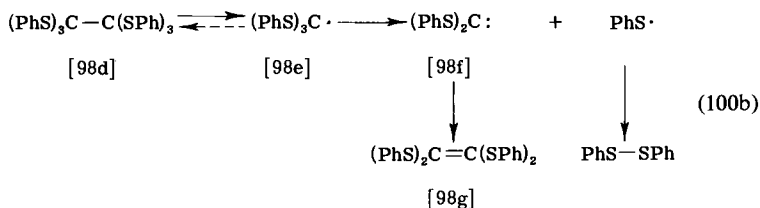


Biphtalyl [98] is also formed from phthalic anhydride and triethyl phosphite in a deoxygenation reaction which appears to be analogous to the desulfurization, Eq. (97) (288). Thiophthalic anhydride reacted some thousand times faster than phthalic anhydride, whereas both *N*-methyl and *N*-phenylphthalimide did not react (288a). The reactivity sequence $\text{S} > \text{O} \gg \text{NR}$ is that expected for nucleophilic attack of triethyl phosphite at the carbonyl carbon atom. Evidence for a phosphorane intermediate was provided by its reaction with benzaldehyde to give benzylidene phthalide.

1,2-Diphenylthioketocarbene [98b] has been suggested to occur in the pyrolysis of certain metal dithienes [98a], and could account for the formation of 2-phenylthianaphthene [98c] (288b).

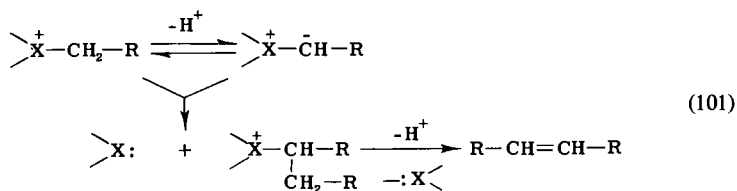


When hexa(phenylthio)ethane [98d] was heated to 110–130° in chlorobenzene or mesitylene, tetra(phenylthio)ethylene [98g] and diphenyl disulfide were produced (288*c, d*). The reaction is thought to involve intermediates [98e] and [98f]; the radical [98e] has been detected by ESR spectroscopy, and the carbene [98f] has been trapped by addition to S—H and C=S bonds.

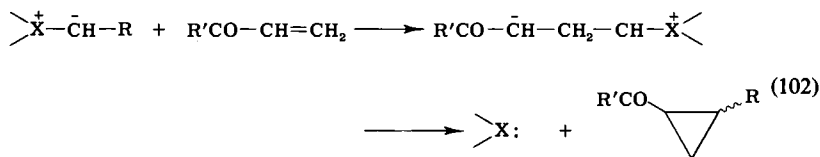


XVII. DECOMPOSITION OF YLIDES

The major problem faced in the investigation of methylene transfer from ylides is their instability. Many ylides are generated *in situ* by deprotonation of the corresponding onium salts. The presence of the onium salt opens a route, Eq. (101), to the formation of olefinic “dimers” which might otherwise be attributed to the intervention of carbenes.

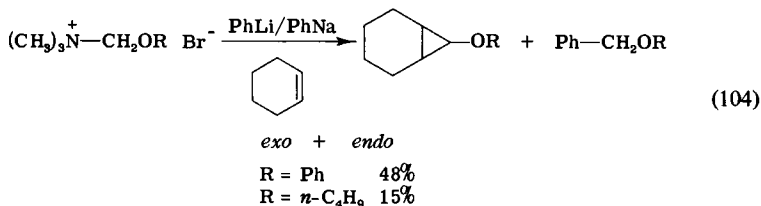
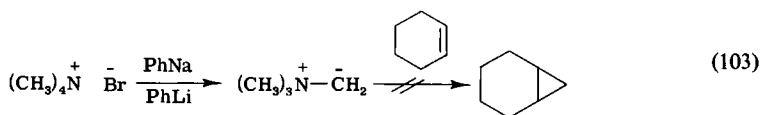


The ready reaction of many ylides with polar double bonds to produce cyclopropanes, Eq. (102), should also be considered in evaluating the products of ylide decomposition.



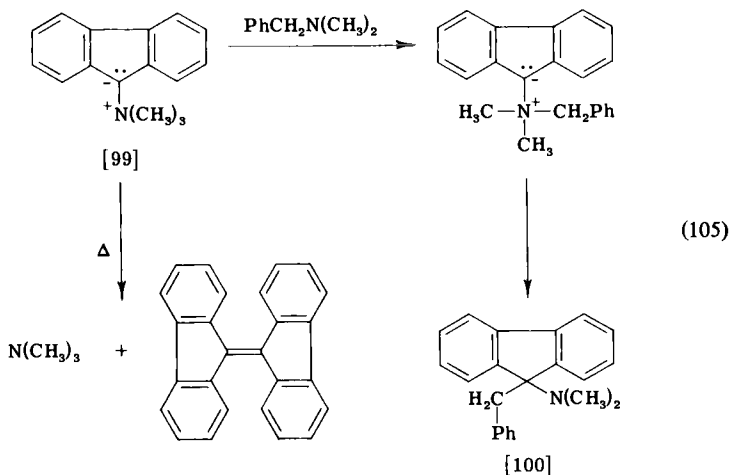
A. Nitrogen Ylides

Franzen and Wittig (289) claimed that a solution of trimethylammonium methyide, prepared from tetramethylammonium salts with phenylsodium and phenyllithium, converted cyclohexene into norcaradiene in 5–18% yield. More recently, Wittig and Krauss (290) have been unable to repeat this work. They were able, however, to isolate 7-(*n*-butoxy)norcaradiene and 7-phenoxy norcaradiene from treatment of *n*-butoxymethyltrimethylammonium bromide and phenoxyethyltrimethylammonium bromide, respectively, with organolithium reagents in the presence of cyclohexene.

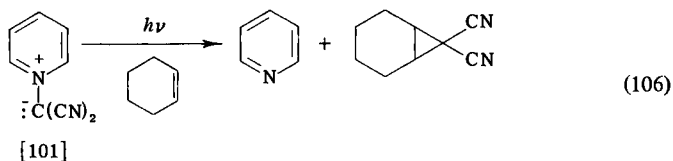


Decomposition of trimethylammonium 9-fluorenylide [99] in aqueous solution at 170° afforded trimethylamine and difluorenylidene (291). Compound [99] was converted into 9-dimethylamino-9-benzylfluorene [100] by heating with benzyldimethylamine (292). The latter reaction obviously proceeds by way of an amine exchange followed by Stevens rearrangement. The amine exchange may be explained by a carbene mechanism or by displacement. Compound [100] was also obtained from

the decomposition of 9-diazofluorene in the presence of benzyldimethylamine (293).

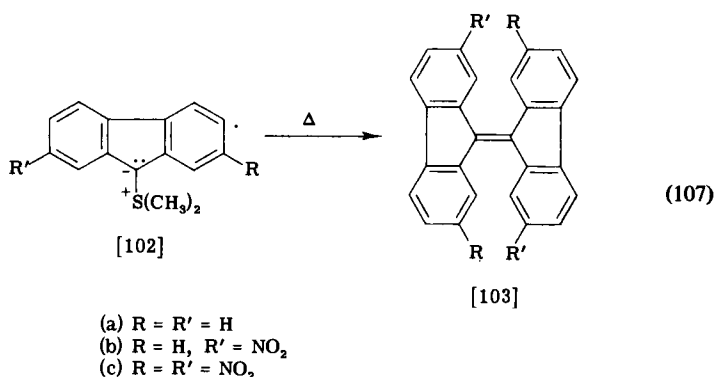


The most conclusive evidence of a carbene intermediate has been obtained in the photochemical cleavage of pyridinium dicyanomethylide [101]; the resulting dicyanocarbene adds to benzene with formation of 7,7-dicyanonorcaradiene (294).



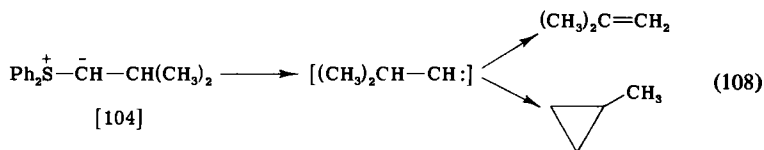
B. Sulfur Ylides

Several examples of olefin formation from sulfonium ylides have been recorded. Dimethylsulfonium 2-nitro-9-fluorenylide [102b] decomposed on heating in nitromethane to give 2,2'-dinitrodifluorenylidene [103b] (295). Likewise, dimethylsulfonium 2,7-dinitro-9-fluorenylide [102c] was thermally decomposed to [103c]. On the other hand, the unsubstituted difluorenylidene [103a] was only a minor by-product in the decomposition of [102a] (196).



Johnson *et al.* (297) found that solutions of diphenylsulfonium benzylide were stable at -70° but slowly formed a mixture of *cis*- and *trans*-stilbenes in 78 % yield when the temperature was raised to -40° . Dimethyl sulfonium dicyanomethylide decomposed at 190° – 230° . Dimethyl sulfide and tetracyanoethylene were among the products, but in addition at least six other compounds were isolated (298). The precise mechanism of these reactions is still obscure.

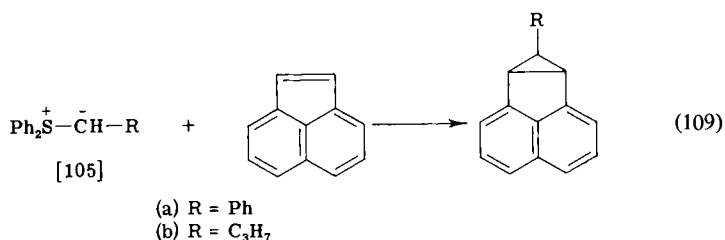
Treatment of isobutyldiphenylsulfonium salts with trityl sodium afforded a 35 % yield of a 3 : 1 mixture of isobutylene and methylcyclopropane (299). Thermolysis of 1-diazo-2-methylpropane gives the same products in a slightly different ratio (1.5 : 1). The formation of methylcyclopropane provides adequate reason to suspect the intervention of isopropylcarbene in the decomposition of diphenylsulfonium isobutylide [104].



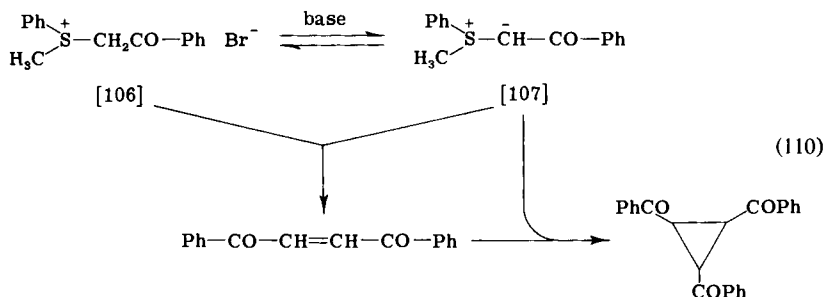
Photolysis of diphenylsulfonium allylide produced cyclopropene in addition to products resulting from phenyl migration (299a). The formation of cyclopropene suggests the intermediacy of vinylcarbene which undergoes intramolecular addition (Chapter 8, Section VI.A).

Trapping of carbenes by intermolecular addition may have occurred when the sulfonium ylides [105a,b] were decomposed in the presence of acenaphthylene (297). However, it also is possible that the ylides themselves

carried out a nucleophilic addition to the double bond, Eq. (102). In the case of a highly conjugated olefin such as acenaphthylene, the intermediate carbanion could be stabilized by resonance. The formation of the propylcarbene adduct [105b] must be regarded with particular suspicion; rearrangement of propylcarbene to butene is known to be fast compared to intermolecular addition.

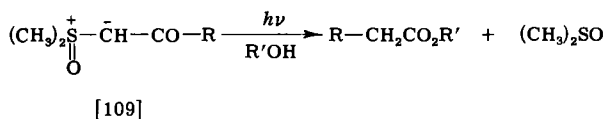
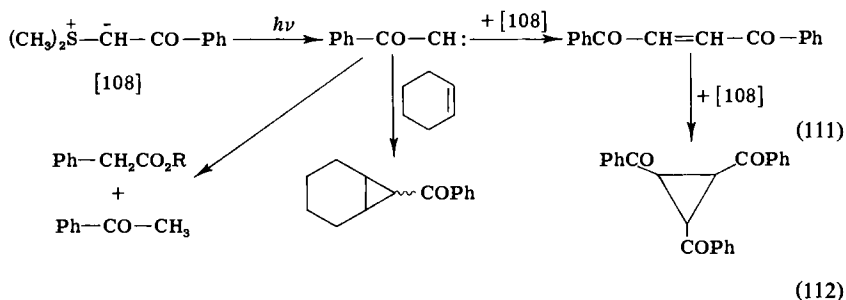


Methylphenylsulfonium phenacylide [107] was isolated as a stable solid on treatment of the bromide [106] with bases. Compound [107] could not be decomposed thermally but reacted with [106] to give tribenzoylcyclopropane (300). Tribenzoylcyclopropane was also obtained from [106] with less than one equivalent of base. This is an excellent demonstration of the alkylation-elimination route outlined in Eqs. (101) and (102).



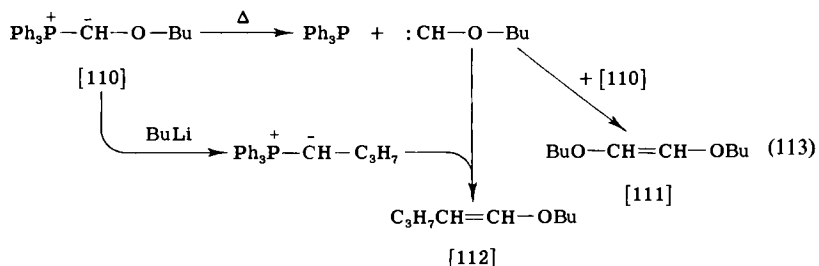
It is very unlikely, however, that the same mechanism operates in the photolytic decomposition of dimethylsulfonium phenacylide [108] in chloroform and benzene which led to nearly quantitative yields of *trans*-1,2,3-tribenzoylcyclopropane (301). A carbene intermediate is indicated by the formation of 7-benzoylnorcaradiene when cyclohexene is used as a solvent. In alcoholic solution, Wolff rearrangement and hydrogen abstraction occurred in a ratio nearly identical with that observed in the photosensitized decomposition of diazoacetophenone (Section IV). The evidence

clearly supports the intermediacy of benzoylcarbene in the photolysis of **[108]**. β -Ketosulfoxonium ylides **[109]** are also susceptible to photochemical fission of the dipolar C—S bond, followed by Wolff rearrangement (302).

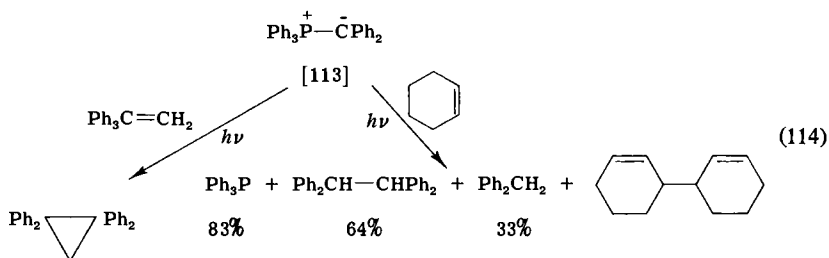


C. Phosphorus Ylides

Triphenylphosphonium *n*-butoxymethylide **[110]** undergoes the familiar Wittig reaction with carbonyl compounds at low temperatures. Above -10° , **[110]** decomposes with formation of triphenylphosphine and a variety of products among which 1,2-*di-n*-butoxyethylene **[111]** and 1-*n*-butoxy-1-pentene **[112]** are the most interesting ones (303). These products are pictured as arising from *n*-butoxycarbene in Eq. (113), but attempts to trap the carbene by addition to olefins have been unsuccessful. Analogs of **[111]** have been obtained from triphenylphosphonium *t*-butoxymethylide and -diphenoxymethylide.

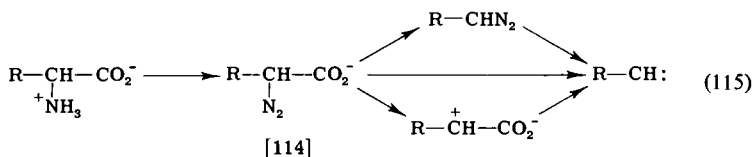


Diphenylcarbene appears to be generated in the photolysis of triphenylphosphonium diphenylmethide [113]. In cyclohexene, which does not add diphenylcarbene readily, tetraphenylethane has been obtained as the major product (304). In the presence of 1,1-diphenylethylene, however, 1,1,2,2-tetraphenylcyclopropane was formed in 73% yield (305). In addition to these compounds, 2537 Å irradiation produced benzene, a phosphorus—phenyl bond being broken (305a).



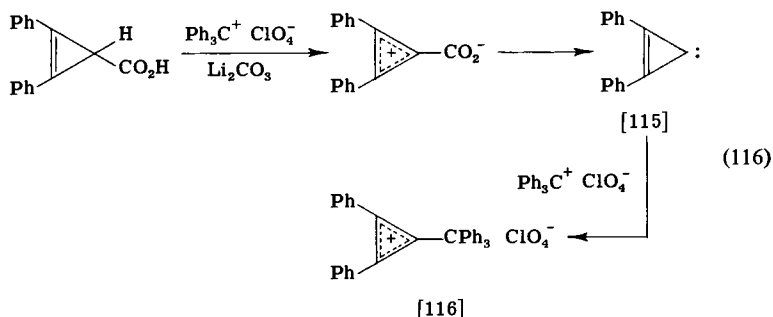
D. Betaines

In contrast to the ylides discussed so far, betaines are doubly but oppositely charged species in which the formal charges are not on adjacent atoms. The zwitterionic forms of amino acids are well-known betaines which by diazotization give rise to the likewise zwitterionic diazonium carboxylates [114]. Simultaneous loss of CO₂ and N₂ from [114] would produce an alkylcarbene. Some cyclopropane formation has indeed been observed when α-amino acids were treated with isoamyl nitrite at 63° (306). The relative yields of cyclopropanes, however, were small, and alkylcarbenes can at best play a minor part in the overall reaction.

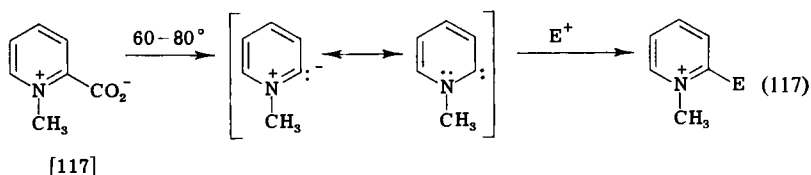


As a possible source of 2,3-diphenylcyclopropenyldiene [115], the hydride abstraction-decarboxylation sequence pictured in Eq. (116) has been explored (307). Hydride abstraction by trityl perchlorate occurred

in methylene chloride in the presence of lithium carbonate to give 1,2-diphenyl-3-triphenylmethylcyclopropenium perchlorate **[116]**. Formation of this material suggests, but does not demand, a mechanism involving **[115]** as an intermediate.



Heterocyclic betaines, such as **[117]** and its 2-quinoline and 1-isoquinoline analogs, lose CO_2 readily at $60\text{--}80^\circ$. The nucleophilic carbenes thus produced may be trapped by electrophiles. The rate of CO_2 evolution is independent of the nature of the electrophile (308).



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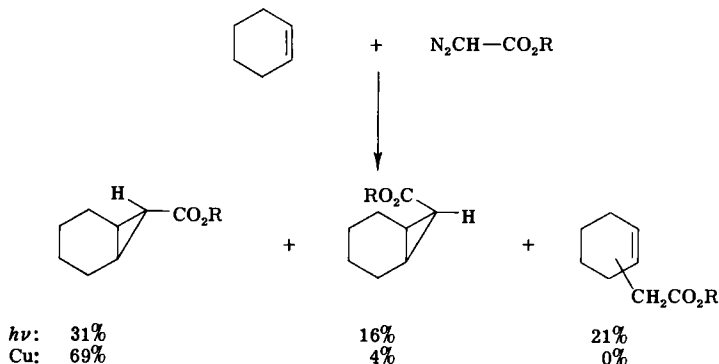
Organometallic Methylene Transfer Agents

I. CATALYTIC DECOMPOSITION OF DIAZOALKANES

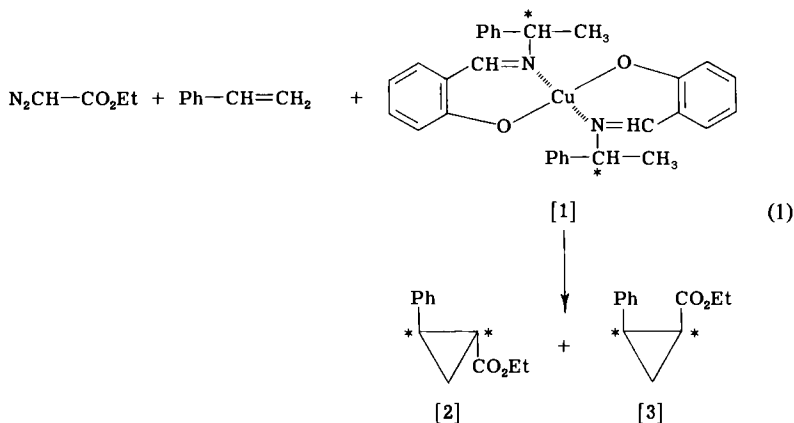
DIAZOALKANES DECOMPOSE under the influence of metal halides and other Lewis acids to produce α -haloalkyl derivatives of the metal (1, 2), polymethylene, and ethylene. *Isolable* organometallic products which are capable of methylene transfer are treated in the following sections. This section is concerned with catalytic reactions of diazoalkanes for which the formation of organometallic intermediates has not so far been observed directly but is suggested by indirect evidence.

A. Catalysis by Copper and Copper Salts

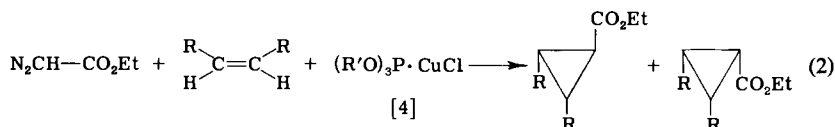
The copper-catalyzed decomposition of diazo esters and diazoketones is an old reaction (3-6) which has been the subject of several recent investigations. For example, the reactive intermediate from the CuSO_4 -catalyzed decomposition of ethyl diazoacetate converts olefins into cyclopropanes but does not appear to undergo insertion into carbon-hydrogen bonds (7). Its stereoselectivity in cyclopropane formation is quite different from that of the carbene obtained by photolysis of ethyl diazoacetate (8).



Evidence such as this does no more than indicate that the intermediate formed in copper-induced reactions is different from the "free" carbene thought to be produced in photolysis. However, the view that a carbene-copper complex is involved in the catalyzed reactions gains strong support from the observation that the decomposition of ethyl diazoacetate, catalyzed by the chiral complex **[1]** in the presence of styrene, gives a mixture of the optically active ethyl 2-phenylcyclopropanecarboxylates **[2]** and **[3]** (optical yield $\sim 6\%$) (9).

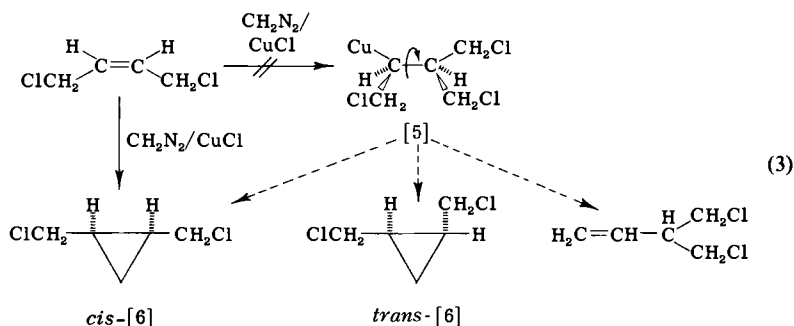


The homogeneous catalyzed addition of ethyl diazoacetate to olefins utilizing (trialkyl phosphite)-copper(I) chloride complexes **[4]** revealed systematic changes in the isomeric cyclopropane product distribution as a function of the steric bulk and electronic effects of the ligand (10). Again, asymmetric induction was observed with [(−)tribornyl phosphite]-copper(I) chloride as the catalyst.

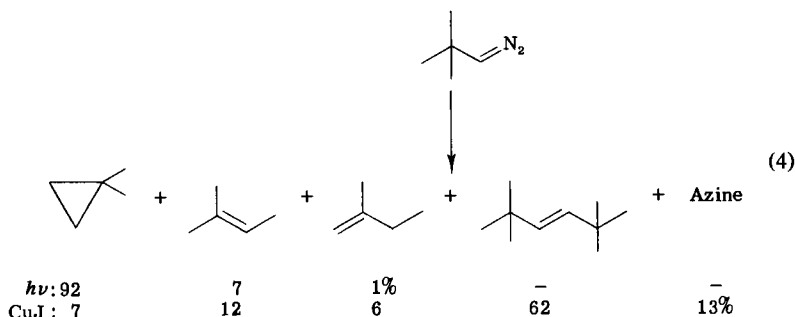


Diazomethane had not been subjected to copper-catalyzed decomposition before 1959 (11), but since then the reaction has found wide application (12). The copper-complexed methylene does not insert into carbon-hydrogen bonds but is capable of addition to olefins and aromatic hydrocarbons. Asymmetric induction is brought about by chiral catalysts such as **[1]** (9). Although the nature of the bonding is not yet clear, there is considerable

evidence that the intermediate in CuX-catalyzed reactions of diazomethane behaves as an electrophile (12) and reacts with olefins in a concerted rather than stepwise fashion. Intermediates such as [5] have been excluded in the reaction of $\text{CH}_2\text{N}_2/\text{CuCl}$ with *cis*-1,4-dichloro-2-butene, which is entirely stereospecific (13). Intervention of [5] would lead to both *cis*- and *trans*-[6].

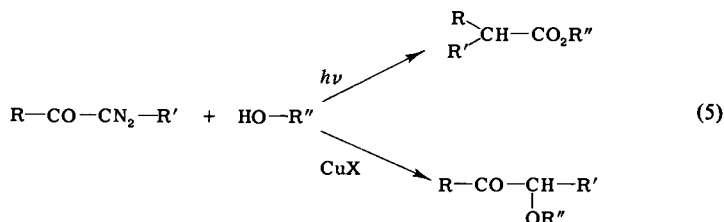


Alkylcarbenes give almost entirely intramolecular insertion products when generated photochemically or thermally. Copper-catalyzed decomposition of diazoalkanes diverts part of the intermediates to intermolecular reaction paths. The remaining portion (10–30%) still undergoes intramolecular insertion, but with increased selectivity and accompanied by alkyl shifts (14). These observations suggest that the reactive site of the carbenoid is more positive than that of the “free” carbene, i.e., the function of the carbene within the complex is that of a donor.

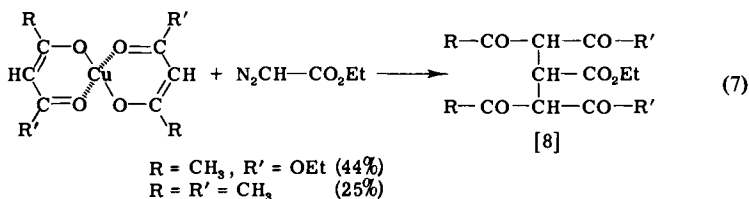
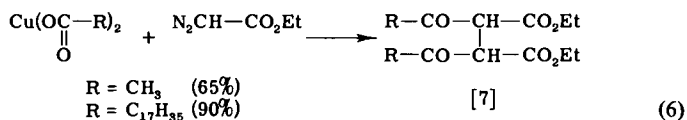


Similarly, the Wolff rearrangement of α -diazoketones in the presence of water, alcohols, carboxylic acids, etc., may be virtually eliminated by copper powder (15), cupric chloride (16), and copper chelates (17). The products of these catalyzed reactions are ketols and their alkyl and acyl

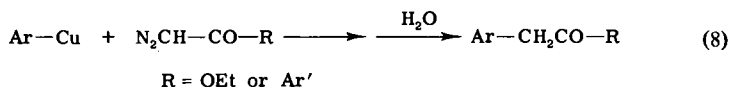
derivatives, respectively. In the absence of hydroxylic solvents, "dimerization" to give diacylethylenes (6), addition to olefins (18), and 1,3-dipolar additions (19) were observed.



Products arising from interaction of the carbenoid with the anion or ligand of the copper catalyst have occasionally been obtained when olefinic or other acceptors were absent. Reaction of ethyl diazoacetate with cupric stearate and cupric acetate in refluxing cyclohexane afforded diethyl 2,3-diacylsuccinates [7] (20). Compounds [8] were formed from copper(II) chelates of 1,3-dicarbonyl compounds and ethyl diazoacetate (21).



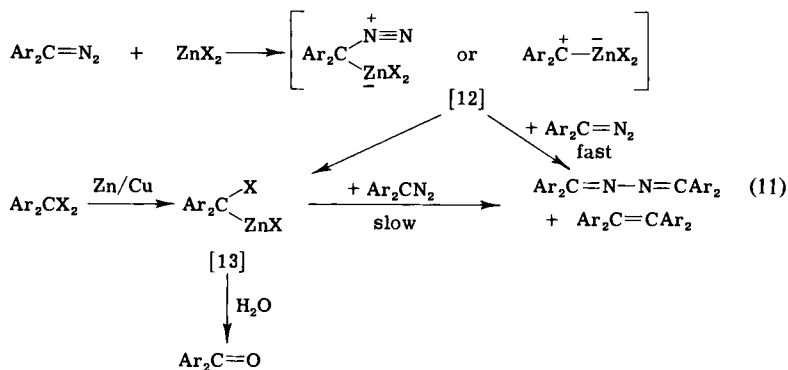
The reaction between arylcoppers and diazo compounds, followed by hydrolysis, afforded derivatives of phenylacetic acid and benzyl phenyl ketone (22, 23).



B. Catalysis by Lithium and Zinc Halides

Because of poor yields, the lithium bromide-catalyzed decomposition of aryldiazomethanes in the presence of olefins has little preparative value (24). However, comparison with the halogen-lithium exchange at benzal

remainder disappears much more slowly according to a second-order rate law. Obviously, at least two intermediates are involved in the overall reaction.



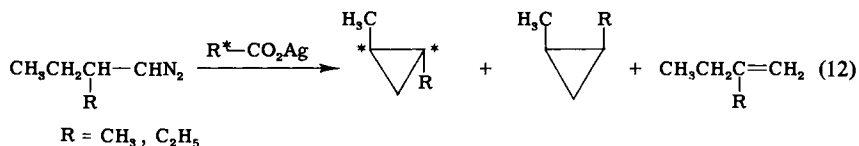
The product proportions and the kinetics fit the scheme shown in Eq. (11). For $\text{X} = \text{I}$, more of [12] is diverted to [13]; this diversion results in a slower decomposition and a lower yield of azine. Strong support for Eq. (11) comes from the fact that the organometallic reagent obtained from 9,9-diiodofluorene and zinc-copper couple reacted with 9-diazo fluorene at a rate virtually identical with that of the slow step of the zinc iodide-catalyzed decomposition of diazo fluorene.

Only traces of cyclopropanes were formed from diphenyldiazomethane and zinc salts in the presence of olefins (24, 26), whereas olefin adducts were obtained from diazo fluorene and 1-phenyldiazoethane in modest yields (24). The mechanism of the reaction of organozinc and organolithium intermediates with olefins is discussed in Sections II and III, respectively.

C. Miscellaneous Catalysts

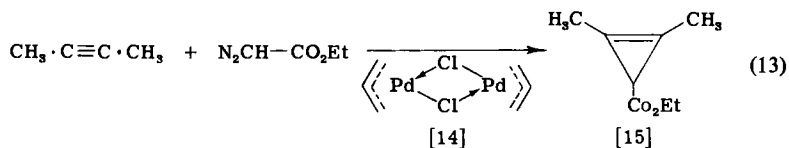
Silver catalysts are well suited to induce intramolecular carbenoid reactions. The accelerating effect of silver salts on the decomposition of diazoketones had already been noticed by Wolff (4). Ag^+ -ammonia, Ag^+ -thiosulfate, silver oxide (27), and silver benzoate-triethylamine (28) have been recommended for carrying out the Wolff rearrangement under mild conditions. The decomposition of diazoalkanes by silver salts gives high yields of cyclopropanes and olefins formed by intramolecular insertion and

rearrangement (14). Cyclopropane formation proceeds with considerable preference for secondary and tertiary carbon-hydrogen bonds, in contrast to the behavior of the thermally generated carbenes. Decomposition of 2-methyl-1-diazobutane and 2-ethyl-2-diazobutane by silver salts of optically active acids give optically active cyclopropanes (29).

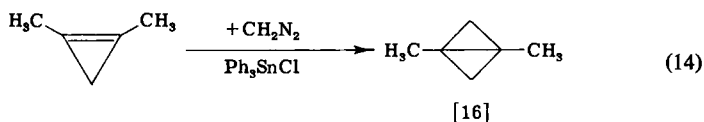


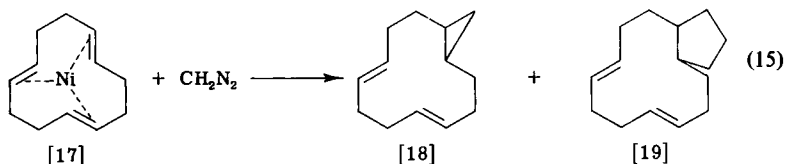
These observations confirm the participation of the catalyst in the product-determining step of the silver ion-catalyzed decomposition of diazoalkanes. Coordination to silver affects the chemical behavior of a carbene much less than does coordination to copper.

Ethyl diazoacetate reacts with dimethylacetylene in the presence of di- μ -chloro-di- π -allyldipalladium [14] to give 3-ethoxycarbonyl-1,2-dimethylcyclopropene [15] (30). Catalyst [14] has also been utilized in the catalytic decomposition of diazomethane, with methylene transfer to C=C bonds (31).



The conversion of 1,2-dimethylcyclopropene into 1,3-dimethylbicyclo [1.1.0] butane [16] was achieved with diazomethane and triphenyltin chloride, whereas copper catalysts failed to produce [16] (32). Treatment of *trans,trans,trans*-cyclododecatrienickel(0) [17] with diazomethane afforded the bicyclic products [18] and [19] (33). The formation of five-membered rings as in [19] has no precedent in metal-catalyzed decompositions of diazomethane.

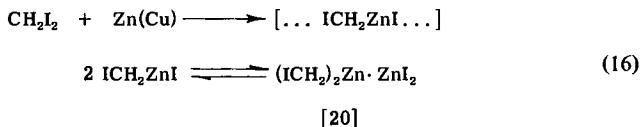




II. SIMMONS-SMITH REACTION

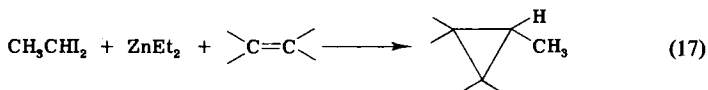
The Simmons-Smith reaction is an extremely valuable method for transferring methylene and a few substituted methylenes to olefins. In addition to the α -haloalkylzinc compounds employed in the original Simmons-Smith procedure (34), some closely related reagents derived from cadmium, magnesium, and aluminum are also covered in this section.

Methylene iodide and zinc-copper couple react in ether solution to give a stable organozinc intermediate, probably bis(iodomethyl)zinc · zinc iodide [20]. An unequivocal structure has not been established; [20] is probably not a simple monomeric species, and equilibria of the Schlenk type may exist.



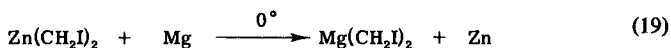
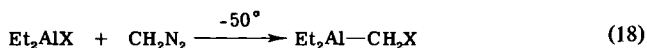
The preparation of a highly active zinc-copper couple has been reported which, in the presence of olefins, forms cyclopropane not only with methylene iodide, but also with methylene bromide (35). The separate preparation of the zinc-copper couple is not required; a mixture of zinc dust and cuprous halide may be even more effective (35a). A modification of the Simmons-Smith reaction which involves prior reaction of ethyl iodide with zinc-copper couple, followed by addition of methylene iodide and olefin, was proposed (35b). Improved yields of cyclopropanes were obtained with various olefinic substrates. The reaction of olefins with diethyl zinc and methylene iodide also affords cyclopropanes in excellent yields (36). This modification of the Simmons-Smith reaction is particularly suitable for the synthesis of methylcyclopropanes from ethylene iodide, diethylzinc, and olefins (37). In its reaction with a zinc-copper couple, ethylene iodide produces mainly ethylene and affords only minor amounts

of intermolecular addition products (38). Reaction of olefins with diethylcadmium and methylene iodide (ethylene iodide, benzal iodide) also gave olefins in good yield by stereospecific *cis*-addition (38a).



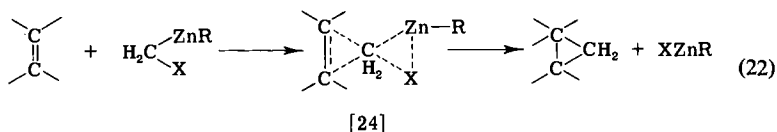
Another way to α -haloalkyl derivatives of zinc, cadmium, and indium has been explored by Wittig and his group (2). The reaction of diazomethane with zinc halides gives reagents of the general formula $\text{Zn}(\text{CH}_2\text{X})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) which are distinguished from the Simmons-Smith reagent by the absence of zinc halides. Zinc halides have a catalytic effect in some reactions of α -haloalkylzinc derivatives (39), and differences in reactivity between the Simmons-Smith and Wittig reagents may thus be explained.

Hoberg (40) has shown that diethylaluminum halides and diazomethane form diethylhalomethylaluminum compounds which are stable at -50° but react with olefins at -10° to give cyclopropanes. A similar, but less efficient, reagent was obtained from triethylaluminum and methylene iodide (41). Halomethyl derivatives of magnesium which have been prepared by metal exchange from the corresponding zinc compounds appear to be even less stable but are also capable of methylene transfer in moderate yields (42).



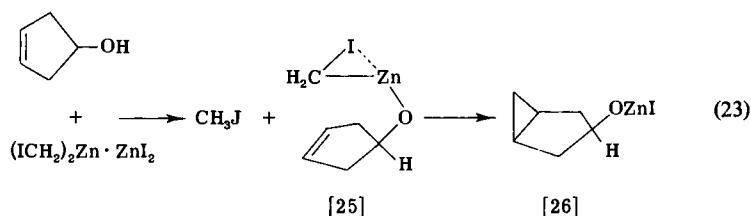
Intermediate [20] and its analogs react with iodine to regenerate methylene iodide and are hydrolyzed by water to methyl iodide (34). The iodine exchanges rapidly with external halide ions (43, 44). In the absence of other reactants, formation of ethylene and reduction to methyl iodide by the solvent occur (44, 45).

The reaction of [20] with olefins was shown to be a bimolecular process, being of the first order both in [20] and in olefin concentrations. Since the competing decomposition of [20] is unimolecular, high concentrations of [20] are required to obtain good yields of cyclopropanes (39, 45). Competition of mixtures of olefins for [20] revealed the electrophilic character and high steric demand of α -haloalkyl zinc derivatives. The reactivity of the olefin increases with increased substitution of the double bond with



The participation of the halogen X in the transition state [24] is open to question. Blanchard and Simmons (45) report that the nature of the halogen in XCH_2ZnR is not critical in determining whether methylene transfer to a double bond occurs. An investigation utilizing metal films and gaseous reactants (46) is of interest in this connection. When methylene chloride was adsorbed on magnesium or zinc films, subsequent hydrolysis afforded only methane, rather than methyl chloride. Exposure of olefin-methylene chloride mixtures to magnesium or zinc films led to the stereospecific synthesis of cyclopropanes. These observations indicate that organometallic reagents containing the unit $[\cdots \text{M}-\text{CH}_2-\text{M} \cdots]$ may also serve as methylene transfer agents.

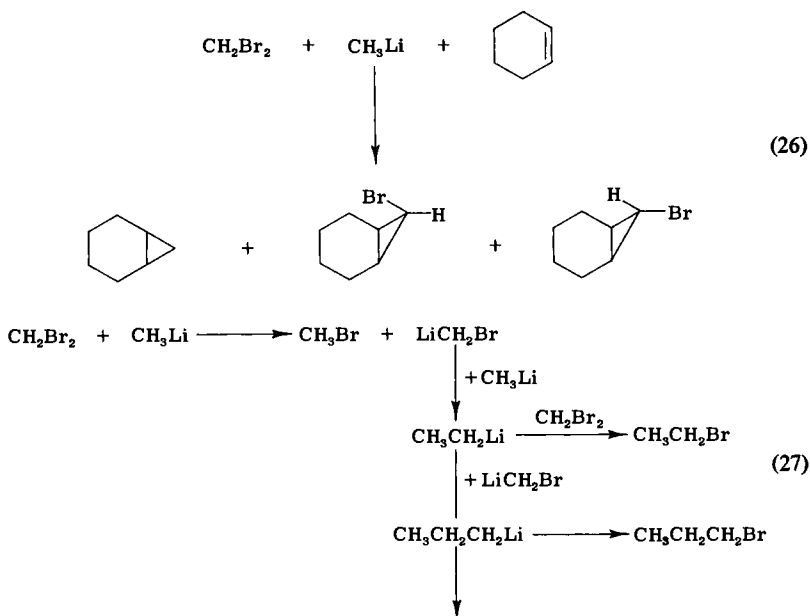
There is ample evidence that R (but not X) in Eq. (22) may be an alkoxy or acyloxy group. It has been found that oxygen-containing functions α or β to the double bond coordinate the reagent, increase the rate, and control the stereochemistry of the addition (34, 47-49). For example, in the reaction of cyclopenten-4-ol with Simmons-Smith reagent, Eq. (23), cleavage of the reagent by the acidic hydroxyl group gives an intermediate [25] and methyl iodide. Intramolecular methylene transfer then affords *cis*-bicyclo [3.1.0] hexan-3-ol [20], uncontaminated by the trans isomer.



Simmons-Smith reaction of various achiral olefins in the presence of 0.3 mole of free (–)-menthol afforded the corresponding cyclopropanes with optical activity (50). It seems likely that a prior reaction of (–)-menthol with the Simmons-Smith reagent occurs to form iodomethylzinc (–)-mentholate, and then the latter reacts with olefins to form a transition state incorporating the chiral moiety.

A. Alkyl Derivatives

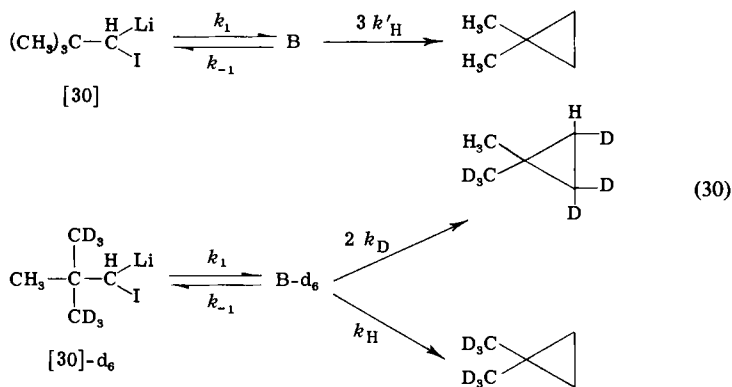
Several attempts to prepare the elusive iodomethyl lithium have failed (42). Chloromethyl lithium was obtained from bromochloromethane and *n*-butyllithium at -100° (53). Carbonation afforded chloroacetic acid in 4–7.5% yield, but addition of cyclohexene did not lead to the formation of norcaradiene. Bromomethyl lithium may be an intermediate in the halogen–lithium interchange of methylene bromide at ambient temperature (54–56). The reaction of cyclohexene with methylene bromide and ethereal methyl–lithium gave a 5% yield of norcaradiene derivatives which consisted of norcaradiene (75–93%) and *endo*- (4–14%) and *exo*-7-bromonorcaradiene (3–11%) (56). The bromonorcaradienes obviously arise from some dibromomethyl lithium formed via H–Li interchange. The product distribution does not, however, reflect the true proportions of reactions (25a) and (25b). The preferred reaction of bromomethyl lithium is substitution, leading ultimately to homologous bromides (55), as shown in Eq. (27).



The yields of cyclopropanes from (26) and related reactions may be increased to 30–40% by the use of butyllithium in a hydrocarbon solvent at low temperatures (-50 to 0°) (56*a,b*). A concerted addition has been demonstrated with 1,4-dichloro-2-butene and 1,6-dichloro-3-hexene as

Closer scrutiny has revealed that α -haloalkyllithium compounds are more selective in their intramolecular reactions than are the "free" carbenes generated in the decomposition of diazoalkanes. Discrimination in favor of tertiary and secondary C—H bonds is more pronounced in the organometallic reaction (59). The isotope effect of the carbenoid intramolecular insertion depends on the nature of the halogen (60) and is appreciably greater than that observed in the photolysis and thermolysis of diazoalkanes (61).

α -Iodoneopentyllithium [30] has been prepared in ether at -116° and characterized by protolysis to provide $>91\%$ of neopentyl iodide. Goldstein and Dolbier (60) have attempted to decide on the basis of isotope effects whether the formation of 1,1-dimethylcyclopropane (97% yield) from [30] proceeds in one step or by way of an intermediate B (carbene or carbene-LiI complex).

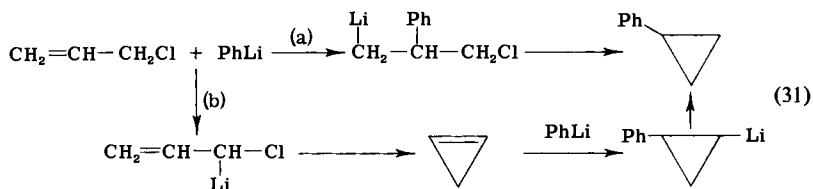


From a correlation of the intramolecular ($k_\text{H}/k_\text{D} = 2.76$) and intermolecular ($k_{d_0}/k_{d_6} = 1.50$) kinetic isotope effects according to the kinetic scheme, Eq. (30), they found k'_H/k_{-1} close to zero (assuming $k_\text{H} \simeq k'_\text{H}$). This means either that B is absent, or that $k_{-1} \gg k_\text{H}$ (fully established pre-equilibrium). The authors prefer the former interpretation (60).

B. Allyl and Benzyl Derivatives

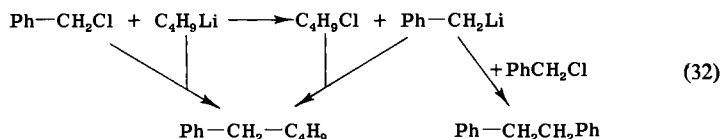
The reaction of allyl chloride with phenyllithium yields phenylcyclopropane in addition to the major product, allylbenzene (62). Two mechanisms have been offered for the formation of phenylcyclopropane. The first one suggested an attack of phenyllithium on the β -carbon atom of the halide, followed by an intramolecular cyclization to the cyclopropane,

Eq. (31a) (62). The second one suggested α -metalation of allyl chloride, followed by cyclization to cyclopropene which reacts with phenyllithium to give phenylcyclopropane, Eq. (31b) (63).

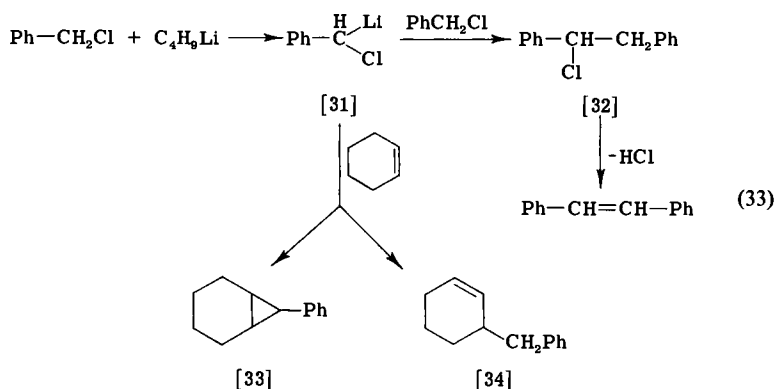


Mechanism (31b) has been confirmed with the aid of allyl-1,1- d_2 chloride and allyl-1- ^{14}C chloride, demonstrating (i) loss of one α -hydrogen, and (ii) intervention of an intermediate in which the α - and β -carbon atoms of allyl chloride are equivalent (63). Phenyllithium reacted with *cis*- and *trans*-1-chloro-2-butene to give *cis*- and *trans*-1-methyl-2-phenylcyclopropane in addition to olefinic products. The ratio of the isomeric cyclopropanes was similar to that obtained from the addition of phenyllithium to 3-methylcyclopropene (64).

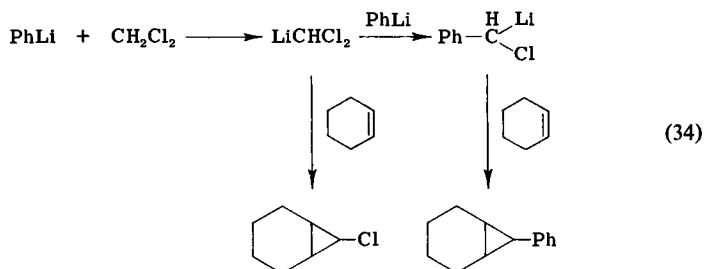
Earlier studies (65) had indicated that the reaction of benzyl chloride with *n*-butyllithium proceeds via halogen-metal interconversion, leading to the formation of benzyl lithium as a transient intermediate which is rapidly consumed in subsequent coupling reactions to form the observed products, 1,2-diphenylethane and *n*-amylbenzene.



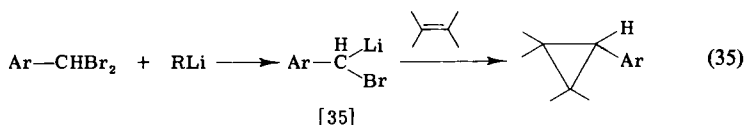
More recently, however, hydrogen-metal interchange was shown to be a second important reaction path (66, 67). At low temperature in tetrahydrofuran, *n*-butyllithium reacts with benzyl chloride almost exclusively by attack of the α -hydrogen atoms to form α -chlorobenzyl lithium [31]. 1-Chloro-1,2-diphenylethane [32] was isolated in over 80% yield, and base-catalyzed or thermal dehydrohalogenation of [32] at elevated temperature gave *trans*-stilbene (67). Slow addition of *n*-butyllithium in ether to a solution of benzyl chloride in excess cyclohexene at 10° afforded 7-phenyl-norcarane [33] (14%) and 3-benzylcyclohexene [34] (19%) in addition to the products of reaction (32) (66).



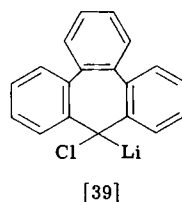
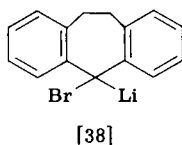
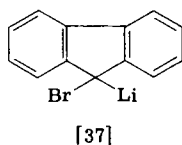
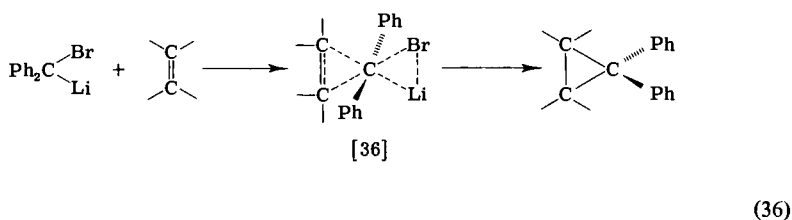
Compound [31] was also generated from methylene chloride and phenyllithium by the sequence of reactions shown in Eq. (34). Transfer of both $\text{PhCH}_2\cdot$ and $\text{ClCH}_2\cdot$ to olefins occurred in yields of 10–20% (68, 69). Very small yields of phenylcyclopropanes were obtained when butyllithium reacted with phenyl benzyl ether in the presence of olefins (70).



Halogen-metal interchange at benzal bromides in the presence of olefins proved to be a more efficient method for preparing arylcyclopropanes (71). Suggestive evidence that the α -bromobenzyl lithium [35] reacts directly with olefins first came from comparative precursor experiments (72). These studies showed, for example, that phenylcarbene generated from phenyldiazomethane exhibits a different selectivity toward olefins than does [35]. The chemistry of the species derived from ArCHI_2 and CH_3Li differs from that of the intermediate derived from ArCHBr_2 and CH_3Li (73). In an elegant series of experiments, Closs showed that [35] reacts bimolecularly with cyclohexene (74).



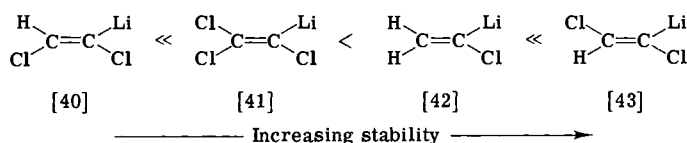
The same type of reaction may be applied to dibromodiarlylmethanes. The organolithium intermediate generated by treatment of dibromodiphenylmethane with methyllithium added stereospecifically to *cis*-2-butene, whereas diphenylcarbene from diphenyldiazomethane adds nonstereospecifically (74). Addition to ethyl vinyl ether has also been achieved (76). In contrast, the organolithium compounds derived from 9,9-dibromofluorene [37], 5,5-dibromo-10,11-dihydro-5*H*-dibenzo[*a, d*]cycloheptene [38], and 9,9-dichloro-9*H*-tribenzo[*a, c, e*]cycloheptene [39] did not afford cyclopropanes (76, 77). An *sp*-like transition state [36] has been proposed to account for the cyclopropane formation with Ph_2CBrLi and the failure of the reaction with [37]–[39] (76).



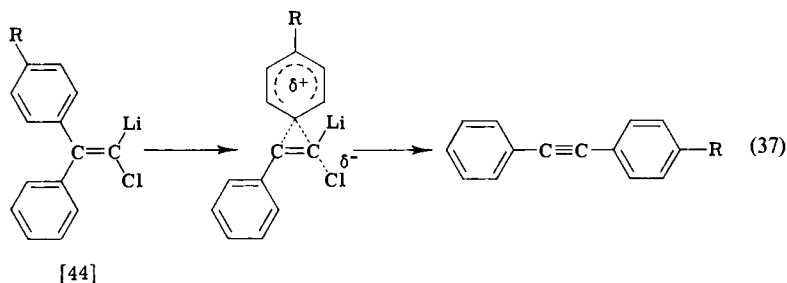
C. Vinyl Derivatives

Vinyl halides undergo halogen–metal interconversion and hydrogen–metal interconversion with ease; many of the resulting organolithium compounds are stable at low temperature, particularly in tetrahydrofuran. Among the least stable α -halovinyl lithium compounds are those with halogen and lithium in the *trans* position, e.g., [40] and [41]. Presumably they decompose via *trans*- β -elimination (78).

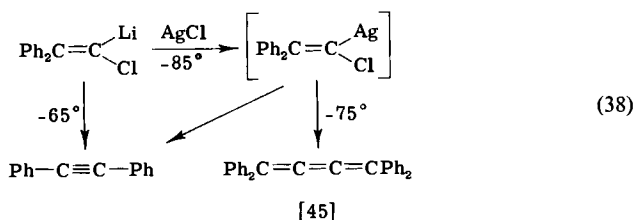
Dehydrohalogenation under the action of excess base (*E2cB* mechanism) is the preferred reaction of [42] and other α -halovinyl lithium compounds



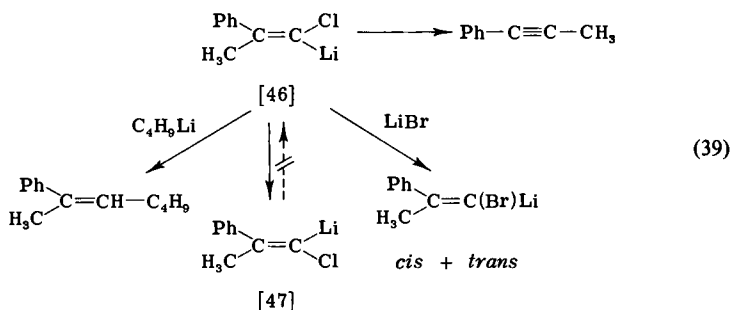
containing β -hydrogen (79). Reagents of the type $\text{Ar}_2\text{C}=\text{CClLi}$ undergo aryl migration to give diarylacetylenes (80–82). Their stability is a function of the substituent Ar, electron-releasing substituents on Ar facilitating decomposition (81). The aryl group trans to the halogen migrates exclusively.



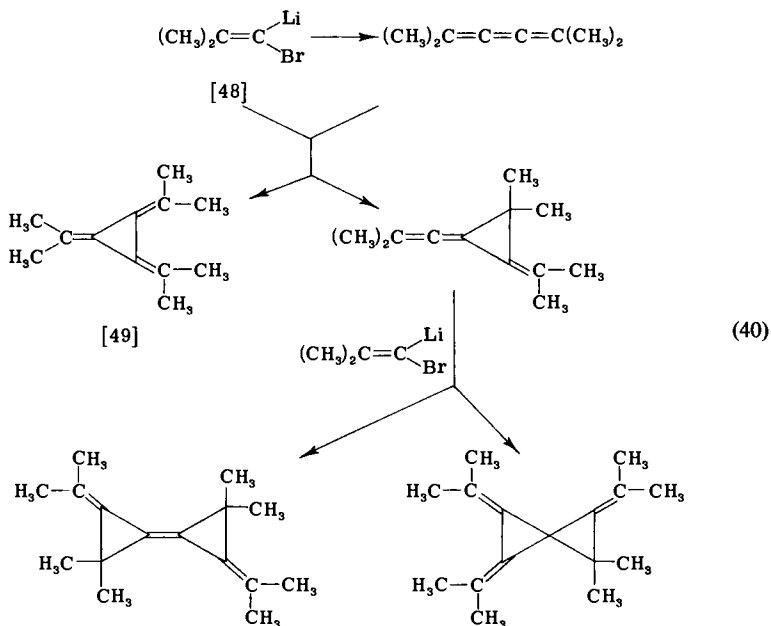
The dehydrohalogenation of β,β -diarylvinyl halides has previously been studied, with similar results, under a wide variety of experimental conditions (Fritsch-Buttenberg-Wiechell rearrangement) (83). There is now general agreement that carbenes are not involved. Compound [44] and its analogs are not capable of addition to olefins or of dimerization; they can be diverted, however, to give butatrienes [45] by addition of silver chloride at -75° to -85° (84).



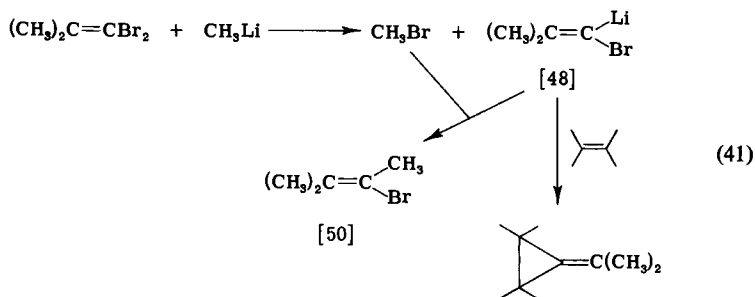
Much of this behavior remains unchanged when one β -aryl group is replaced by methyl, [46] rearranges to 1-phenylpropyne (despite the *cis* location of phenyl and chlorine!) and to the *trans* isomer [47]. Halogen exchange and reaction with excess butyllithium take place, but dimerization and cyclopropanation of olefins have not been observed (85).



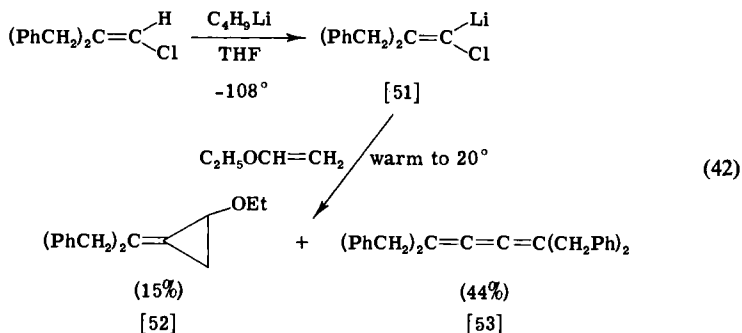
Halogen-metal interchange at 1,1-dibromo-2-methylpropene afforded the vinyl lithium reagent [48], which was stable in tetrahydrofuran at -110° but decomposed slowly at -90° . Tetramethylbutatriene was isolated in good yield from solutions of [48] which had been warmed to ambient temperature with exclusion of oxygen (86). Under suitable conditions, [48] may transfer $(\text{CH}_3)_2\text{C}=\text{C}:$ to tetramethylbutatriene, giving rise to a variety of methylenecyclopropanes among which the [3]radialene [49] is of particular interest (87, 88).



Although [48] is not stable in ether even at -110° (86), moderate yields of isopropylidenecyclopropanes were obtained when 1,1-dibromo-2-methylpropene was treated with methyllithium in ether in the presence of olefins (89) or allenes (90). A by-product, 2-bromo-3-methyl-2-butene [50], formed by the reaction of [48] with methyl bromide, became the sole product when very unreactive olefins such as vinyl chloride were used. The low stationary concentration of [48] in ether eliminates the formation of tetramethylbutatriene.



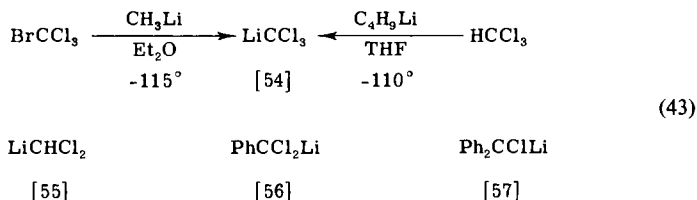
Equation (42) summarizes the only case in which cyclopropane formation from a preformed α -halovinyl lithium reagent has been achieved (91). Warming of [51] in the presence of excess ethyl vinyl ether afforded a modest yield of [52], the butatriene [53] still being the major product.



D. Polyhalomethyl Derivatives

Trichloromethylithium [54] has been prepared from bromotrichloromethane by halogen-metal interchange in ether at -115° (92), and from chloroform by hydrogen-metal interchange in tetrahydrofuran at -110°

(93, 94). The latter method also afforded dichloromethylithium [55] (93, 94), phenyldichloromethylithium [56] (94), and diphenylchloromethylithium [57] (94).



Whereas [54]–[57] are indefinitely stable in tetrahydrofuran at -100° , [54] and [56] decompose above -70° , [55] and [57] at -40° to -30° (94–96). If olefins are present during this decomposition, good yields of cyclopropanes are obtained with [54] and [56]. In contrast, the same procedure does not produce cyclopropanes with [55] and [57]. 1,2-Dichloroethylene and chloroacetylene appear to be formed in the decomposition of [55] (96). With [57], the major product was tetraphenylethylene (94). Chlorocyclopropanes are formed, however, when an ethereal solution of *n*-butyllithium is added slowly to a mixture of olefin and methylene chloride at ambient temperature (97). The different behavior of [55] in tetrahydrofuran may be attributed to an increased solvation of the lithium cation which promotes nucleophilic, rather than electrophilic, reactions of [55].

The remaining discussion of methylene transfer to olefins from [54] and [56] concentrates on the question: Does the α -halomethylithium compound react directly with the substrate, or does it lose LiX, affording a carbene which then reacts with the substrate? Contrary to a previous report (92), no reaction between [54] and olefins has been observed at -100° , where [54] is stable (94, 98, 99). Cyclopropane formation becomes significant at -80° to -70° , when [54] and [56] begin to decompose. Semiquantitative data have been obtained by hydrolysis or carbonation of the organometallic reagents after 25–75% conversion (Table I).

Table I reflects the experimental difficulties encountered in kinetic work at low temperatures. Some olefins appear to accelerate the decomposition of [54], whereas others produce cyclopropanes without appreciable kinetic effect. 1,1-Diphenylethylene, which for all practical purposes does not react with [54] at -78° , reacts to give an excellent yield of the cyclopropane as [54] is decomposed at -65° (94). Clearly, Table I does not justify the statement that [54] reacts with olefins in a bimolecular mechanism. Although the accelerating effect of cyclohexene on the decomposi-

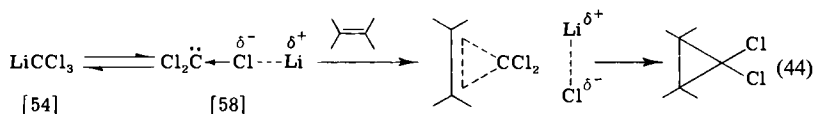
tion of [54] has been confirmed by recent, more accurate experiments (99a), the selectivity for different olefins displayed by [54] was found to be identical with that of dichlorocarbene from other precursors (99a,b) (cf. Chapter 3, Section IV and Chapter 8, Section III). An equilibrium

TABLE I
Effect of Olefins on the Decomposition of Trichloromethylithium [54]
and Phenylidichloromethylithium [56]^a

Olefin added	[54], -72° (99)		[54], -78° (94)		[56], -78° (94)	
	(1)	(2)	(1)	(2)	(1)	(2)
None	36	0	23	0	48	0
Cyclohexene	54	16	73	30	—	—
2,3-Dimethyl-2-butene	48	33	52	10	72	26
<i>trans</i> -2-Butene	35	15	—	—	—	—
<i>cis</i> -2-Butene	28	16	—	—	—	—
Styrene	—	—	41	Trace	—	—
α -Methylstyrene	41	29	—	—	—	—
Butadiene	—	—	42	<5	39	<5

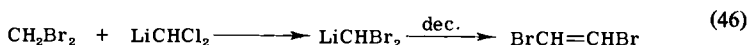
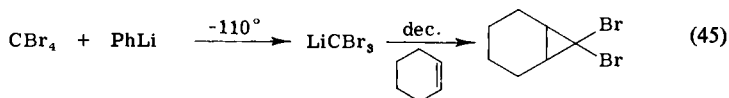
^a (1) % Decomposition; (2) % cyclopropane formation.

between trichloromethylithium and dichlorocarbene (99a) or a weak "carbene-salt complex" [58] (94) has been suggested to accommodate the results of rate and selectivity studies.



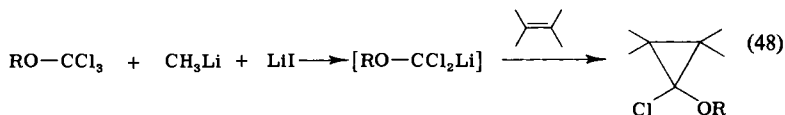
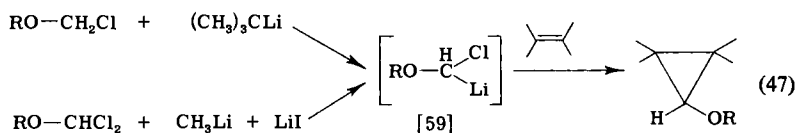
Tribromomethylithium has been prepared from bromoform and lithium metal at -105° in tetrahydrofuran–hexamethylphosphoric triamide (2 : 1) (100), and from tetrabromomethane and phenyllithium in tetrahydrofuran at -110° (101). Tribromomethylithium appears to be less stable than [54], significant decomposition occurring even at -100° . No reaction with cyclohexene has been observed at -100° : at somewhat higher temperature, a 19% yield of 7,7-dibromonorcarane was obtained (101). Dichloromethylithium [55] undergoes hydrogen–metal interchange with polybromomethanes such as CH_2Br_2 , CHBr_3 , and PhCHBr_2 (butyl- and methyl-lithium give halogen–metal interchange!) (102). Dibromomethylithium

thus prepared afforded some 1,2-dibromoethylene upon warming; other carbenoid reactions have not been reported.

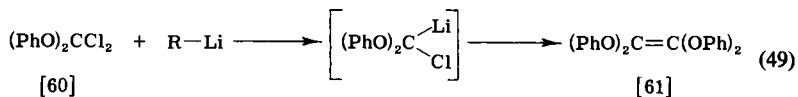


E. Derivatives of Ethers and Thio Ethers

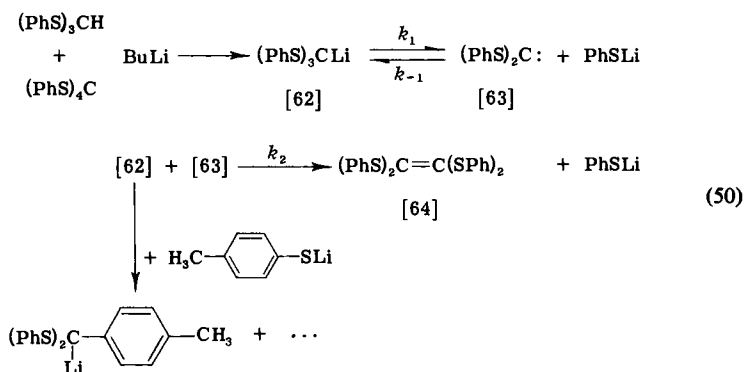
Aryloxycyclopropanes (103) and alkoxycyclopropanes (104) have been obtained by treatment of α -chloro ethers with organolithium compounds in the presence of olefins. These reactions presumably proceed by hydrogen-metal interchange via intermediate [59], but no attempts to trap [59] have been made. Because α -chloro ethers undergo $\text{S}_{\text{N}}2$ displacement very readily, *t*-butyllithium was often required in order to obtain fair yields of cyclopropanes. Treatment of dichloromethyl ethers with methyllithium in the presence of lithium iodide proved to be a convenient modification which probably involves displacement of one chlorine by iodide and, subsequently, by lithium (105, 106). Following this procedure, 1-alkoxy-1-chlorocyclopropanes have been prepared from α,α,α -trichloroethers (105)



Treatment of dichlorodiphenoxymethane [60] with methyllithium in ether-cyclohexene at -70° gave as the only isolated product tetraphenoxymethylene [61] in 88% yield (107). This reaction is reminiscent of the dimerization of dimethoxycarbene (Chapter 2, Section X), but could also proceed by the mechanism outlined for the formation of stilbene from benzyl halides, Eq. (33).



α -Chlorothio ethers are easily deprotonated by potassium *t*-butoxide, with subsequent addition of alkylthiocarbenoids to olefins (Chapter 4, Section III). Tri(phenylthio)methyl lithium [62] is accessible from triphenyl orthothioformate (108) or from tetraphenyl orthothiocarbonate (109) and butyllithium. From a variety of preparative results, the authors concluded that [62] is in equilibrium with bis(phenylthio)carbene [63] in tetrahydrofuran solution. Alkylating agents have a dual effect on the $[62] \rightleftharpoons [63]$ system: very reactive alkyl halides (methyl iodide, allyl bromide) trap [62], but others (butyl bromide, isopropyl iodide, cyclohexene oxide) remove PhSLi from the equilibrium, thereby promoting the formation of tetra(phenylthio)ethylene [64]. Addition of PhSLi, on the other hand, slows down the formation of [64], and the tolyl groups of added C_7H_7SLi are incorporated into [62] (108).



Kinetic measurements (110) are fully consistent with the rate equation derived from Eq. (50) by making the assumption that the second step is rate-determining ($k_{-1} \gg k_2$). A similar scheme, although with less supporting evidence, had been suggested previously for the reaction of trialkyl orthothioformates with potassium amide in liquid ammonia (111). Compound [63] adds to ketene acetals and thioacetals with formation of cyclopropanes (108); reaction with excess butyllithium yields 1,1,2-tris(phenylthio)-1-hexene [65] (109).

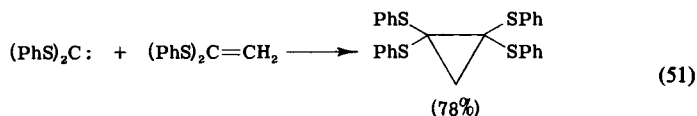
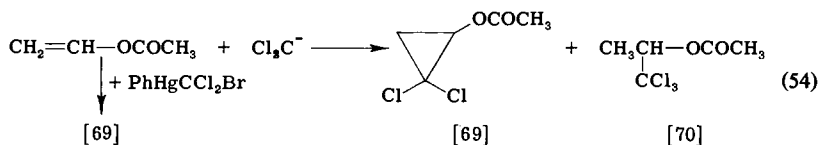


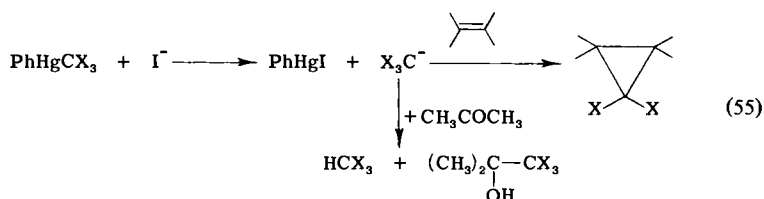
TABLE II
Methylene Transfer by Organomercury Reagents

[illegible]

The methylene transfer reactions of PhHgCX_3 do not involve radicals or trihalomethide ions (117). Acrylonitrile, the acrylic acid esters, vinyl acetate, styrene, and butadiene were not polymerized during their reactions with phenyl(bromodichloromethyl)mercury. Vinyl acetate also served as a diagnostic tool in excluding the intermediacy of trihalomethyl anions. Cl_3C^- , generated by the decarboxylation of sodium trichloroacetate in the presence of vinyl acetate, gives both 2,2-dichlorocyclopropyl acetate [69] and the addition product, 1-trichloromethylethyl acetate [70] in comparable yields (123). In contrast, the reaction of vinyl acetate with $\text{PhHgCCl}_2\text{Br}$ produced [69] as the sole product in 80% yield. The absence of a Michael-type addition product with acrylonitrile may also be noted (117).



The action of sodium iodide in acetone or dimethoxyethane on phenyl(trihalomethyl)mercury compounds results in displacement of trihalomethyl anions from mercury with formation PhHgI (124). This reaction proceeds faster than the thermal decomposition of PhHgCX_3 . In acetone, the X_3C^- species is intercepted by protonation or addition to the solvent; in dimethoxyethane, good yields of cyclopropanes are obtained with the more reactive olefins. BrCl_2C^- is partitioned to give minor amounts of *gem*-chlorobromocyclopropanes along with *gem*-dichlorocyclopropanes as the major products (with cyclohexene, the ratio of 7,7-dichloronorcarane to 7-chloro-7-bromonorcarane is 6 : 1). In contrast, the thermolysis of $\text{PhHgCCl}_2\text{Br}$ produces dichlorocyclopropanes *only* (125).



Although the thermolysis of phenyl(trihalomethyl)mercury compounds does not involve trihalomethyl anions, the relative rates of various olefins toward reagents producing PhHgCX_3 and X_3C^- are virtually identical (Table III) (124).

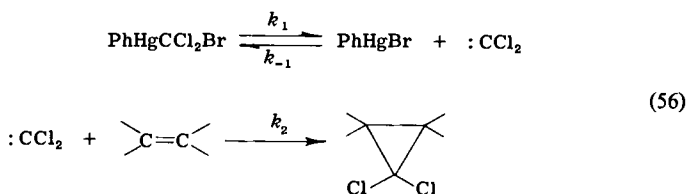
TABLE III
Relative Rates of CCl_2 Transfer to Olefins^a (124)

	$\text{PhHgCCl}_2\text{Br}$	PhHgCCl_3 + NaI	$\text{Cl}_3\text{CO}_2\text{Na}$
2,3-Dimethyl-2-pentene	22.5	23.2	24.8
3-Ethyl-2-pentene	3.54	3.13	3.52
2-Ethyl-1-pentene	2.31	2.30	
Cyclohexene	1.00	1.00	1.00
<i>cis</i> -3-Heptene	0.83	0.835	0.80
<i>trans</i> -3-Heptene	0.52	0.537	0.52
1-Heptene	0.24	0.218	0.22

^a In dimethoxyethane at 80°.

The following picture has emerged from a kinetic study of the $\text{PhHgCCl}_2\text{Br}$ -olefin reaction (126): The initial rates are essentially in-

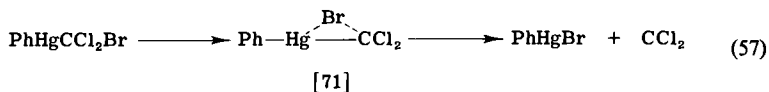
dependent of olefin concentration and are of first order in mercurial. They do, however, show a small dependence on the nature of the olefin, the observed reaction rates decreasing as k_{rel} of the olefin (Table III) decreases. The initial rates are retarded by added phenylmercuric bromide. These observations provide strong evidence that the rate-determining decomposition of $\text{PhHgCCl}_2\text{Br}$ is reversible and suggest the mechanism, Eq. (56).



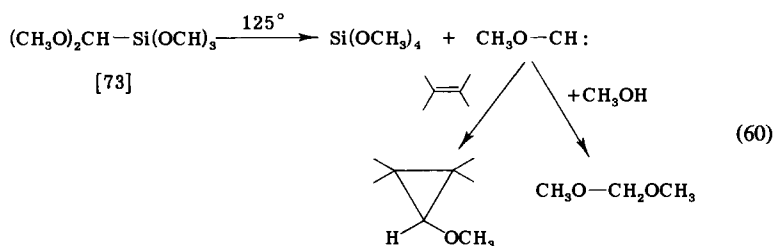
$\text{PhHgCCl}_2\text{Br}$ reacts with *p*-tolylmercuric chloride in benzene solution at 80° to give *p*-tolyl(trichloromethyl)mercury and PhHgBr (127), a fact which is easily explained in terms of the reversible dissociation of $\text{PhHgCCl}_2\text{Br}$.

The effect of added phenylmercuric bromide on the rate of the $\text{PhHgCCl}_2\text{Br}$ -olefin reaction is greatest for 1-heptene ($k_{-1}/k_2 = 6.0$), less for cyclooctene ($k_{-1}/k_2 = 1.1$), and not perceptible for 2,3-dimethyl-2-pentene ($k_{-1}/k_2 = 0.06$) (126). The variation in the k_{-1}/k_2 ratio, derived from the kinetic scheme, Eq. (56), would serve to explain the variations of both the initial rate and the inhibiting effect of PhHgBr . The activation parameters of the 2,3-dimethyl-2-pentene- $\text{PhHgCCl}_2\text{Br}$ reaction in benzene ($\Delta H^\ddagger = 24.3$ kcal/mole, $\Delta S^\ddagger = -2.8$ eu) are also in accord with a unimolecular mechanism. The available evidence suggests that the reactive intermediate is dichlorocarbene, and the small variation in rate observed upon changing the solvent from benzene to dimethoxyethane speaks against a strongly solvent-complexed CCl_2 intermediate.

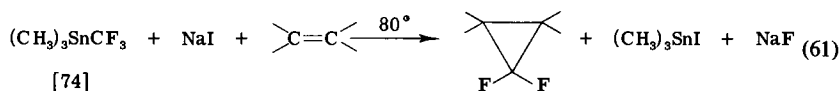
These conclusions were fully confirmed by a kinetic study of the $\text{PhHgCCl}_2\text{Br}$ - Et_3SiH reaction which was found to be of first order in the mercurial, and of zero order in Et_3SiH (128). The rates of CCl_2 extrusion from substituted aryl(bromodichloromethyl)mercury compounds differed only slightly as a function of the substituent (129). This insensitivity to electronic factors supports a concerted CCl_2 extrusion process proceeding via the cyclic transition state [71].



Rearrangement predominates if a β -chlorine atom is present. $\text{CHF}=\text{CFCl}$ was obtained from $\text{CHFCl}-\text{CF}_2\text{SiCl}_3$ (133), and $\text{CFCl}=\text{CFCl}$ was the major product derived from $\text{CFCl}_2\text{CF}_2\text{SiCl}_3$ (130). Thermolysis of (dimethoxymethyl)trimethoxysilane [73] at 125° in the presence of olefins gave high yields of methoxycyclopropanes (134). Methanol was converted into dimethoxymethane. The thermolysis of [73] is of first order in [73] and of zero order in the trapping agents, the rate of disappearance of [73] is nearly identical in the presence of drastically different trapping agents. The kinetic data support the formation of free methoxycarbene. Similarly, α,α -dimethoxybenzylsilanes eliminated phenylmethoxycarbene which was trapped by addition to dimethylfumarate and diphenylacetylene, and by insertion into Si-H and Ge-H bonds (134a).

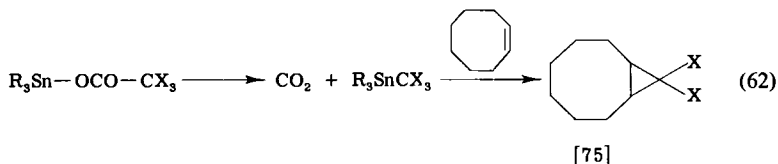


Pyrolysis of trimethyl(trifluoromethyl)tin [74] at 150° , either alone or with tetrafluoroethylene, afforded perfluorocyclopropane, presumably via difluorocarbene (135). This method for CF_2 transfer was made more useful by application of the sodium iodide procedure (Section IV) (136).



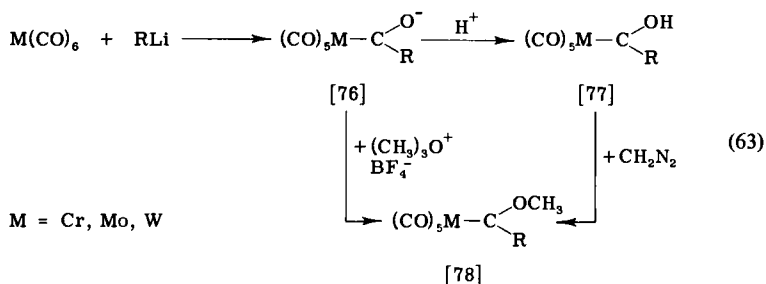
Trimethyl(trichloromethyl)tin was found to be an effective CCl_2 transfer agent at 140° , and the action of sodium iodide in 1,2-dimethoxyethane at 85° induced CCl_2 transfer from this tin compound in fair yield (137, 138). $(\text{CH}_3)_3\text{SnCCl}_2\text{Br}$ transferred CCl_2 to olefins very slowly at 80° , rapidly at 140° , but a small amount of CClBr transfer was also noted. Trimethyl(dichloromethyl)tin proved to be stable at 140° , and secondary reactions obscured the transfer of PhCCl from trimethyl(α,α -dichlorobenzyl)tin (138). CX_2 extrusion from organotin precursors appears to be mechanistically similar to the process suggested for the pyrolysis of PhHgCX_2Br (Section IV), no trihalomethyl anions being involved.

Thermolysis of trimethyltin and triphenyltin trichloroacetates in diglyme-cyclooctene solution gave 9,9-dichlorobicyclo[6.1.0]nonane [75] (88%); the corresponding dibromo compound (35%) was prepared from triphenyltin tribromoacetate (139). An NMR investigation has shown that the process involves decarboxylation and CX_2 transfer from the R_3SnCX_3 intermediate thus formed (140).



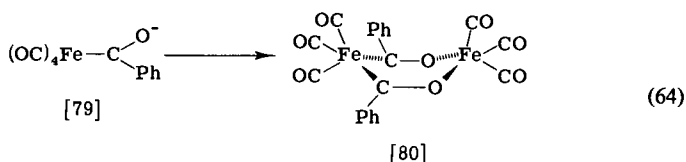
VI. CARBENE COMPLEXES OF THE TRANSITION METALS

E. O. Fischer and his group have prepared a large variety of stable alkoxyalkylcarbene and alkoxyarylcabene complexes by the following route: The addition of methyllithium or phenyllithium to Group VI metal carbonyls leads to the formation of metallates [76] which can be isolated as their tetramethylammonium salts. Subsequent methylation to yield the neutral carbene complexes [78] can be achieved by treatment with diazomethane after acidification or, better, by reaction with trimethyl-oxonium fluoborate (141, 142). The hydroxycarbene complexes [77] decompose rapidly to give acetaldehyde and metal carbonyl; only few of them have been isolated (e.g., the complex $C_5H_5Re(CO)_2C(OH)CH_3$ derived from cyclopentadienyl-tricarbonyl-rhenium) (143).

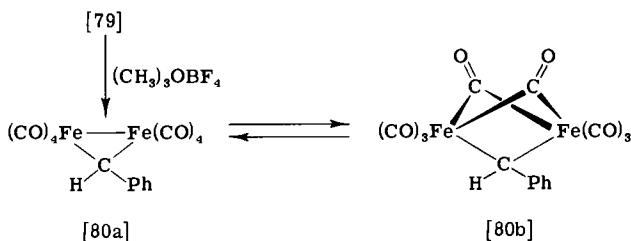


The synthetic procedure outlined in Eq. (63) has been applied to mono-substituted $LM(CO)_5$ complexes, where $L = Ph_3P, Ph_3As$, and Ph_3Sb (144). In the carbene complexes obtained, $L(CO)_4M-C(OCH_3)R$, L , and the carbene ligand are exclusively cis oriented. Dimanganesedecacarbonyl, $Mn_2(CO)_{10}$, afforded complexes of the type $(CO)_9Mn_2C(OCH_3)R$, with

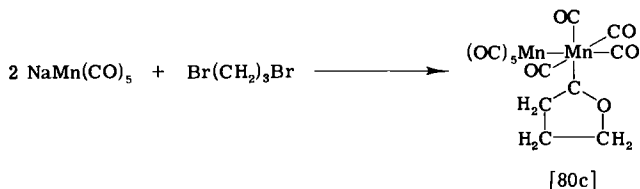
the carbene ligand equatorial if $R = CH_3$, and axial if $R = Ph$ (145). The tetracarbonyliron species [79] was also prepared, but reaction with alkylating agents led to binuclear complexes [80] the structure of which was elucidated by X-ray diffraction methods (146). Although in the anion [79] the carbene carbon is attached to the metal, in the dimer both of these carbon atoms are attached to the same metal. Complex [80] may be described as a phenylferroxy carbene complex, or as a benzoyl complex.



[79] and trimethyloxonium fluoborate afforded another type of binuclear complex which apparently exists in two isomeric structures, [80a] and [80b], depending on temperature and polarity of the solvent (146a). Iron-carbene complexes of structure [78] were finally prepared by photochemical transfer of the carbene ligand from $C_5H_5Mo(CO)(NO)(CH_3O-C-Ph)$ to $Fe(CO)_5$ (146b).

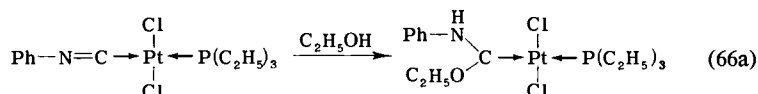


The structure of a compound prepared by the reaction of sodium pentacarbonylmanganese (-1) and 1,3-dibromopropane was shown to be the cyclic alkoxycarbene complex **[80c]** (146c).



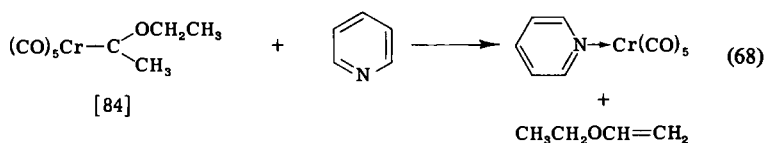
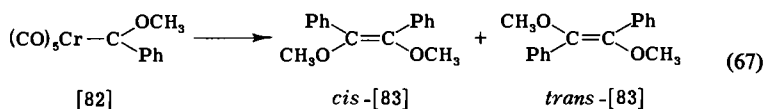
A different approach to alkoxycarbene complexes was opened by the reaction of *trans*-PtCl(CH₃)₂L₂ [L = PhP(CH₃)₂ or As(CH₃)₃] with

Alkoxy(dialkylamino)carbene complexes may be prepared according to Eq. (63), using lithium diethylamide (152a). An alternative route involves addition of alcohols to isocyanide complexes of platinum (152b). A typical example is shown in Eq. (66a).

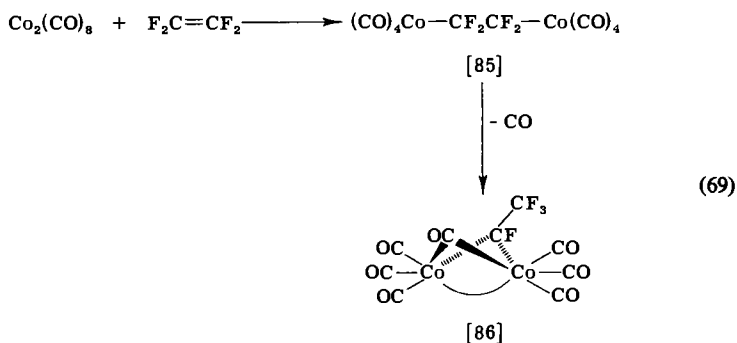


The structural properties of alkoxy-carbene and aminocarbene complexes, as determined by X-ray diffraction studies (153, 154), seem to be best described in terms of electron donation from the sp^2 hybridized carbene carbon atom to the metal, together with associated, but competitive, back donation from both the metal and oxygen (nitrogen) into the empty p_z orbital on the carbon. This results in partial double-bond character of both the metal-carbon and carbon-oxygen (nitrogen) bonds. The metal-carbene distance is always greater than the metal-carbonyl distance; it is not significantly greater in pentacarbonyl-methylaminocarbene-chromium (2.09 Å) than in phenylmethoxycarbene-pentacarbonyl-chromium (2.04 Å). The effect of ring substituents in arylmethoxycarbene complexes on C—O force constants has been used as a probe of σ donor and π acceptor properties of the carbene ligands (154a). *Cis*, *trans* isomerism of alkoxy and alkylaminocarbene complexes, arising from hindered rotation about the C—O and C—N bonds, has been investigated by NMR techniques (154b,c).

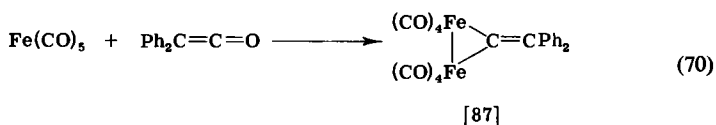
The potential of alkoxy- and aminocarbene complexes as methylene transfer agents has not yet been fully explored. The mass spectra of the alkoxy-carbene-pentacarbonylchromium complexes show peaks corresponding to the mass of the carbene ligand; in some cases, peaks appear corresponding to the mass of the carbene dimer (155). These results suggest that the carbene may be liberated by thermolysis of the complex. Dimethoxystilbene [83] has indeed been isolated after thermal decomposition of phenylmethoxycarbene-pentacarbonyl-chromium [82], but it has not been possible to intercept the carbene with nonpolar olefins (156). *trans*-Methyl crotonate was converted to the corresponding cyclopropane by treatment with [82], but the intermediacy of a free carbene in this methylene transfer reaction has not been substantiated (156a). Ethyl vinyl ether, the product of intramolecular stabilization of methylethoxycarbene, was obtained by treatment of methylethoxycarbene-pentacarbonyl-chromium [84] with pyridine (157).



Few stable carbene complexes have been prepared so far which do not contain stabilizing α -hetero atoms. Reaction of octacarbonyldicobalt with tetrafluoroethylene gives the compound [85] which slowly loses CO at 45° under reduced pressure. The resulting product shows two ^{19}F NMR signals in the ratio 1 : 3, consistent with the presence of a CF_3CF group, and is therefore considered to be [86] (158). Bis(trifluoromethyl)diazomethane reacts with octacarbonyldicobalt to produce a complex of $\text{CF}_3-\text{C}=\text{CF}_3$ which has been assigned a structure analogous to [86] (159).

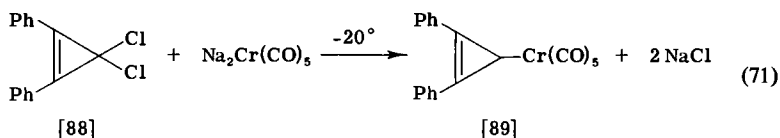


A stable, crystalline complex obtained in low yield from the irradiation of a mixture of diphenylketene and pentacarbonyliron in benzene has been shown by X-ray structural and mass spectroscopic methods to be octacarbonyldiphenylvinylidene-di-iron [87] (160). Of the two possible descriptions, carbene complex and substituted ethylene, the former is preferred since the $\text{Fe}-\text{C}-\text{Fe}$ angle is compressed from the normal sp^2 value of 120° to one of 83° , similar to the value found for bridging carbonyl groups.

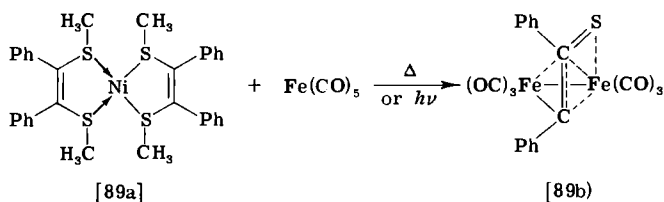


The reaction of $\text{Ru}_3(\text{CO})_{12}$ with phenyllithium gave low yields of $\text{Ru}_3(\text{CO})_9(\text{Ph}_2\text{C})$ which was identified by X-ray crystallography as a metal cluster derivative of diphenylcarbene (160a).

Treatment of 3,3-dichloro-1,2-diphenylcyclopropene [88] with $\text{Na}_2\text{Cr(CO)}_5$ afforded (2,3-diphenylcyclopropylidene)pentacarbonylchromium [89] (161). X-ray structural analysis (162) revealed a chromium-carbene distance of 2.05 Å (virtually the same as in alkoxycarbene-chromium complexes), indicating substantial double-bond character. The C—C bond lengths of the cyclopropene ring are significantly different (1.35 and 1.40 Å); the average C—C distance is close to that of the cyclopropenium ion (1.37 Å). Related palladium complexes have been prepared in a similar fashion (162a).

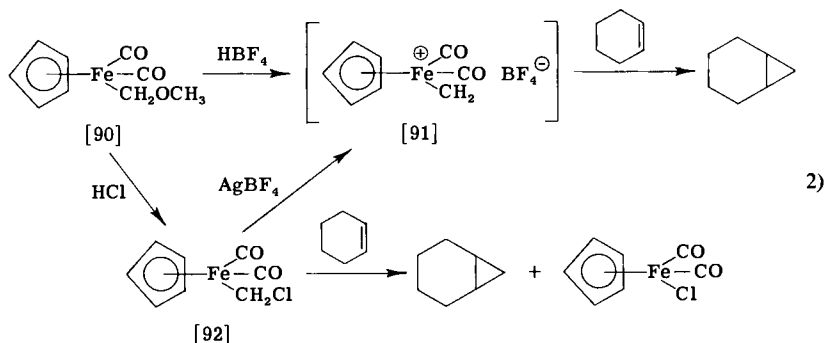


The degradation of dialkyl derivatives of nickel (II) bisethylenedithiolates [89a] with Fe(CO)_5 produced *trihapto*-1,2-diphenylthioketocarbene-hexacarbonyldiiron [89b] which appears to be the first example of a compound containing a coordinated thioketocarbene moiety (162b).

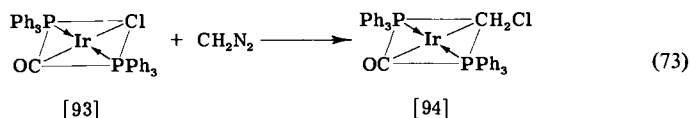


With respect to methylene transfer, some transient metal-carbene complexes are more interesting. Jolly and Pettit (163) obtained evidence for an unstable iron-methylene complex. (Methoxymethyl)cyclopentadienyliron dicarbonyl [90] reacted rapidly with HBF_4 ; when conducted at 0° in the presence of cyclohexene, the reaction produced a 46% yield of norcaradiene. Treatment of [90] with hydrogen chloride gave the dichloromethyl derivative [92]. When the reaction of [92] with AgBF_4 was performed at -60°, the silver chloride was removed, cyclohexene was added

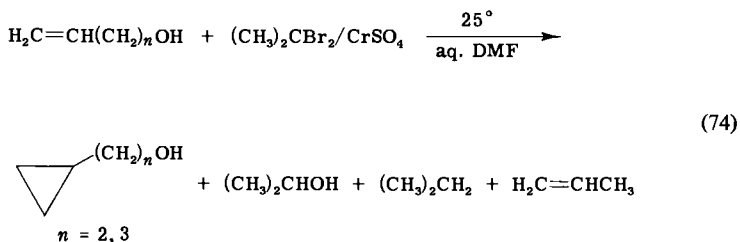
to the supernatant liquid and allowed to warm, small amounts of norcarane were produced. These observations can be rationalized through the intermediacy of the cation [91].



Derivative [92], on heating with cyclohexene at 50° for several hours, afforded a high yield of norcarane. This reaction, which is clearly distinguished from those mentioned above, appears to be analogous to the Simmons-Smith reaction. Similarly, the introduction of methylene into iridium chlorocarbonyl bis(triphenylphosphine) [93] gives the chloromethyl derivative [94] (164). The alternative structure as an iridium-carbene complex was rejected on the basis of spectroscopic data. The derivative [94] was found to transfer CH₂ to the double bond of styrene, but not to cyclohexene.



The reduction of certain *gem*-dihalides with chromous sulfate generates a unique dialkyl carbenoid entity which has the capacity to react with olefins and water in addition to being reduced and undergoing rearrangement (165, 166).



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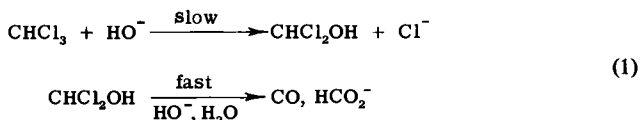
Base-Induced α -Elimination

I. BASIC HYDROLYSIS OF HALOFORMS

THE IDEA THAT dichlorocarbene is an intermediate in the basic hydrolysis of chloroform was first expressed by Geuther in 1862 (1). He suggested that chloroform is actually $\text{CCl}_2 \cdot \text{HCl}$ from which hydrogen chloride may be removed by alkali to give "carbon dichloride." The formation of carbon monoxide, in addition to formate ion, was taken as evidence for the intermediacy of dichlorocarbene by Geuther and a number of other authors [see Hine (2) for references]. It was not until 1950, however, that the mechanism of the basic hydrolysis of chloroform was elucidated by J. Hine and his co-workers. Today the reactions of haloforms with base are the most thoroughly investigated examples of α -elimination.

A. Two-Step (Carbanion) Mechanism

The rate of the basic hydrolysis of chloroform is of first order with respect to both chloroform and hydroxide ion concentrations [in 66.7% aqueous dioxane (2), and in pure water (3)]. Nucleophilic attack of hydroxide ion on chloroform ($\text{S}_{\text{N}}2$ displacement) [Eq. (1)] may be ruled out by several lines of argument.

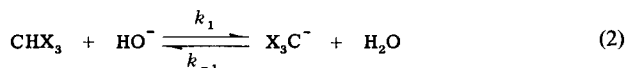


In general, the replacement of a hydrogen attached to the α -carbon of an alkyl halide by halogen decreases $\text{S}_{\text{N}}2$ reactivity. Chloroform, however, is much more reactive (about one thousandfold) in basic hydrolysis than is methylene chloride or carbon tetrachloride (2, 4). Every bromine-containing haloform studied (5) (CHBrClF , CHBrCl_2 , CHBr_2Cl , CHBr_3) is

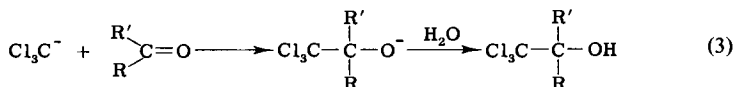
at least 600 times as reactive toward hydroxide ions in 66.7% aqueous dioxane as bromochloromethane or methylene bromide.

Toward weakly basic nucleophiles the predicted reactivity order is obeyed; haloforms have been found to be less reactive than the related methylene halides in all cases studied (4, 6). The reaction of chloroform, bromodichloromethane, dibromochloromethane, and bromoform with sodium thiophenoxide, or sodium *p*-thiocresolate (2, 5), is strongly accelerated, however, by the presence of hydroxide ions.

This observation is quite unexplainable in terms of Eq. (1). Apparently the strongly basic hydroxide ions are required to furnish an intermediate which is more susceptible to nucleophilic attack than the starting haloform. The base would be expected to abstract a proton from the haloform to produce a trihalocarbene, Eq. (2).



The formation of trichloromethylcarbinols from ketones, chloroform, and base is evidence for the occurrence of the trichlorocarbene (7-11), Eq. (3), and also the reaction of chloroform with sodium hypobromite to give bromotrichloromethane (12) [$\text{CHBr}_3 \rightarrow \text{CBr}_4$ (13)].

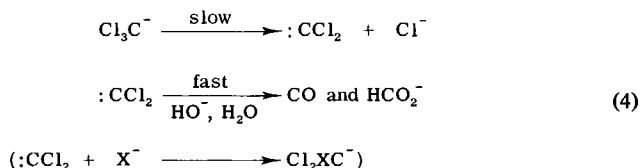


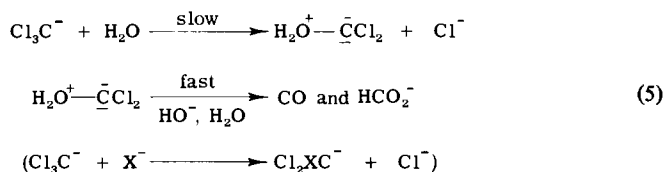
Quantitative information on reaction (2) was provided by investigation of the base-catalyzed hydrogen-deuterium exchange of haloforms. By use of a heterogeneous mixture of chloroform and alkaline heavy water, Sakamoto (14) has shown that the exchange reaction is rapid compared to the basic hydrolysis. Hine *et al.* (15-19) have measured the rates of the hydroxide-catalyzed transformations of deuterated haloforms to the corresponding protonated compounds in homogeneous aqueous solution. With nonfluorine-containing haloforms, the rate constant for the basic hydrolysis was only 0.1-0.001% of that for deuterium exchange, i.e., the exchange reaction was pseudounimolecular. With haloforms such as CHCl_2F , CHBrClF , and CHBr_2F , which contain one fluorine atom, the rates of hydrolysis and deuterium exchange were comparable, and the kinetic treatment was considerably more complicated. (For difluorinated compounds, see below.)

Comparison of the resultant data gave the reactivity series $\text{CDI}_3 \sim \text{CDBr}_3 > \text{CDBr}_2\text{Cl} > \text{CDBrCl}_2 \sim \text{CDCl}_2\text{I} > \text{CDFI}_2 > \text{CDBr}_2\text{F} > \text{CDCl}_3 > \text{CDBrClF} > \text{CDCl}_2\text{F}$ (17, 19), showing that the α -halogen substituents facilitate carbanion formation in the order $\text{I} \sim \text{Br} > \text{Cl} > \text{F}$. To account for the effect of the α -halogens (which is almost the reverse of that expected from the inductive effect) several factors might be considered (17). B-strain (repulsions between the three halogen atoms in the tetrahedral haloform) does not seem to be important in view of the equal reactivity of CDBr_3 and CDI_3 . d -Orbital resonance, i.e., contribution of structures with ten electrons in the outer shell of the halogen, may explain why fluorine is least effective in facilitating deuterium exchange. On the other hand, polarizability also increases in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$, the largest change occurring between fluorine and chlorine, and it is difficult to assess the relative importance of polarizability and d -orbital resonance.

The kinetic isotope effect in the abstraction of a proton from haloforms [Eq. (2)] is of interest with regard to the nature of the transition state. It has been measured directly with the rapidly hydrolyzing haloforms CHCl_2F ($k_{\text{H}}/k_{\text{D}} = 1.76$ at 0° and 1.52 at 20°) (16) and CHBrClF ($k_{\text{H}}/k_{\text{D}} = 1.74$ at 0° and 1.69 at 15°) (17). With chloroform the rate of exchange of CDCl_3 in alkaline H_2O has been compared to the rate of exchange of CHCl_3 in alkaline D_2O (15). From these data the isotope effect may be estimated if it is assumed that the reactivity of DO^- in D_2O relative to that of HO^- in H_2O is in the same range (1.36–1.42) as it is for the reaction with nitroethane and 2-nitropropane. The resultant estimate for chloroform is $k_{\text{H}}/k_{\text{D}} = 1.48$ at 20° (16). The small isotope effects suggest a transition state with little stretching of the carbon-hydrogen bond, i.e., the proton transfer either has not proceeded very far, or is nearly complete. The latter explanation appears more probable, taking into account the effect of the α -halogens as discussed in the preceding paragraph.

Having shown that trihalocarbanions are formed by most haloforms in a fast and reversible reaction, the rate-determining step of the overall hydrolysis remains to be located among the subsequent reactions of the trihalocarbanions. Two possible mechanisms, (4) and (5), which fit the observed kinetics should be considered.

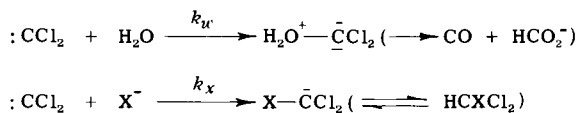




Mechanism (4) is an $\text{S}_{\text{N}}1$ reaction of the trihalocarbanion, proceeding via the dihalocarbene intermediate, whereas mechanism (5) involves an $\text{S}_{\text{N}}2$ displacement at the trihalocarbanion. In the dihalocarbene mechanism (4), the nucleophilic attack on carbon occurs *after* the rate-controlling step of the reaction, whereas in mechanism (5) the rate-controlling step is itself a nucleophilic attack. It is impossible to distinguish between (4) and (5) if water, present in large excess, is the only nucleophile available. The two mechanisms lead to different predictions concerning the effect of additional nucleophilic anions, however. The case of chloride ion, added to the basic hydrolysis of chloroform, is particularly instructive. No kinetic effect at all will result from the operation of mechanism (5), as products and reactants of the displacement $\text{Cl}_3\text{C}^- + \text{Cl}^- \rightarrow \text{Cl}_3\text{C}^- + \text{Cl}^-$ are identical. With mechanism (4), however, the combination of Cl^- with $:\text{CCl}_2$ to give Cl_2C^- is a reversal of the rate-determining step. Therefore the overall rate will be slowed by a "mass law" effect.

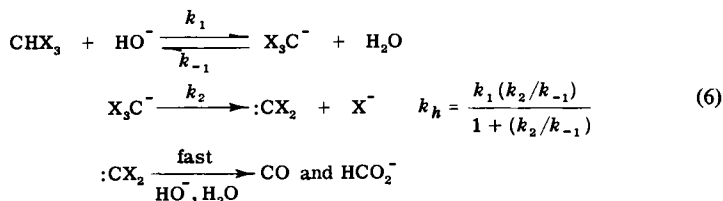
The rate of the basic hydrolysis of chloroform in the presence of 0.08- and 0.16 *N* sodium chloride was shown to be 92.9% and 86.6%, respectively, of that observed in the presence of an equal amount of sodium perchlorate, nitrate, or fluoride (3). A specific salt effect appears improbable, as chloride ions slow the basic hydrolysis of chloroform as effectively in the presence of 1.5 *N* sodium perchlorate as in its absence ("swamping salt" principle).

The rate of the basic hydrolysis of chloroform is diminished even more by the presence of bromide and iodide ions. Dichloriodomethane has been isolated from the latter reaction. The halide ions are thought to compete with water for the dihalocarbene intermediate, reverting some of it to haloform:



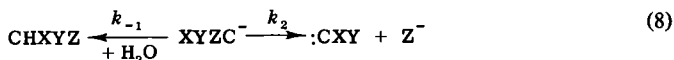
Competition factors $k_{\text{X}}/k_{\text{W}}$ have been evaluated from the rate equation, and $\log k_{\text{X}}/k_{\text{W}}$ was shown to be a linear function of the nucleophilic constants (n) of Swain and Scott (20).

Accepting the carbene mechanism (4) as generally valid, the overall rate constants for the basic hydrolysis of haloforms may be expressed in terms of the rate constants of the individual steps as follows.



The values of k_1 are known or may be closely approximated from data obtained on deuterated haloforms by use of deuterium kinetic isotope effects. A correlation of the values of k_2/k_{-1} has been attempted by means of Eq. (7), which refers to the generalized reaction (8) (21).

$$\log \frac{(k_2/k_{-1})\text{CHXYZ}}{(k_2/k_{-1})\text{CHCl}_3} = M_x + M_y + N_z + \log (n_z/3) + (c-d) \log \frac{(k_1)\text{CHXYZ}}{(k_1)\text{CHCl}_3} \quad (7)$$



Equation (7) contains parameters for : (i) the relative abilities of the various halogens to stabilize dihalocarbenes (M); (ii) the relative ease with which halogens separate as anions from the intermediate trihalocarbanions (N); and (iii) the relative carbanion character of the transition states for protonation and carbene formation ($c-d$). $\log (n_z/3)$ is a statistical correction for the number of Z atoms present in the haloform. The parameters derived from rate measurements on 12 haloforms (22) are given in Table I.

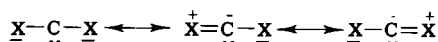
The k_2/k_{-1} values calculated with the aid of these parameters approximate the experimental values with a maximum deviation of 12%. Because

TABLE I
 M and N Parameters of Eq. (7)

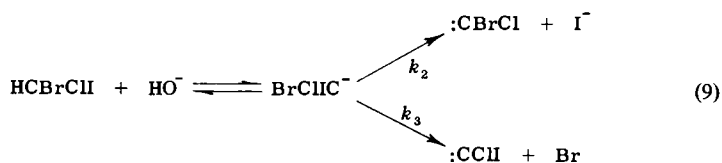
$M_F = 3.071$	$N_{Br} = 1.090$
$M_{Cl} = 0.000$ (standard)	$N_I = 0.327$
$M_{Br} = -1.164$	$N_{Cl} = 0.000$ (standard)
$M_I = -1.696$	$c-d = 0.114$

of the large number of parameters contained in Eq. (7), the excellent agreement cannot be taken as additional evidence supporting the carbene mechanism [Eqs. (4) and (6)]. But, inasmuch as the reaction mechanism is established by independent evidence given above, Eq. (7) affords a consistent quantitative estimate of the factors operating in carbene formation.

According to the values of the M parameters (Table I), halogens facilitate carbene formation in the order $F \gg Cl > Br > I$. Assuming a singlet state of the dihalocarbenes, this order may be attributed to the relative abilities of the halogens to supply electrons to the carbon atom by mesomeric effects:



The N parameters indicate the order $Br > I > Cl$ for the abilities of the halogens to depart as halide ions from the trihalocarbanions. This reactivity series is not the most common one in nucleophilic displacements, but it has been observed occasionally (6, 23). The superiority of bromide as a leaving group has been substantiated by studying the hydrolysis of bromochloriodomethane (22).



Kinetic measurements in the presence of added sodium iodide gave $k_3/(k_2 + k_3) = 0.72$, i.e., the production of chloriodocarbene and bromide ion is the major path of the reaction.

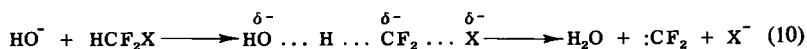
The knowledge of the activation volume (ΔV^*) has also been helpful in distinguishing between mechanisms (4) and (5) (24, 25). Since in the equilibrium, Eq. (2), neither the number of ionic charges nor the number of molecules changes, ΔV is likely to be very small. Any participation of water in the rate-determining step, Eq. (5), is expected to lead to a negative activation volume, whereas simple dissociation of Cl_3C^- , Eq. (4), would be characterized by a volume expansion. The observed value, $\Delta V^* = +16 \text{ cm}^3/\text{mole}$, suggests that the transition state leads to free dichlorocarbene.

B. One-Step (Concerted) Mechanism

As mentioned above, the replacement of a bromine or chlorine atom in haloforms by fluorine considerably *decreases* the rate constant of carbanion formation, k_1 , Eqs. (2) and (6). The overall rate of basic hydrolysis, however, *increases* because fluorine facilitates carbene formation from the trihalocarbanion. Because of the increase in k_2 , the ratio k_2/k_{-1} of haloforms such as CHBr_2F , CHBrClF , and CHCl_2F is in the order of 2–10.

One should expect carbanion formation to become rate-controlling upon introduction of a second fluorine atom, with a corresponding *decrease* of the overall rate of hydrolysis. The difluorinated compounds, chlorodifluoromethane (18, 26, 27), bromodifluoromethane (18), and difluoroiodomethane (27), however were found to hydrolyze much faster than they were expected (from extrapolation of data on other haloforms) to form carbanions. The basic hydrolysis of deuterobromodifluoromethane, CDBrF_2 , was shown to proceed with negligible isotopic exchange (18). ($\text{S}_\text{N}2$ displacement at the haloform has been ruled out by the same evidence as presented for the carbanion mechanism.)

The lack of isotopic exchange would be consistent with irreversible carbanion formation, i.e., formation of a carbanion which invariably loses a halide ion and never reverts to the starting material, k_2/k_{-1} infinite. This assumption does not account for the increase in rate. It has been inferred, therefore, that the carbanion is not a real intermediate with difluorinated haloforms. Instead, Hine has suggested (18) that the removal of the hydrogen and the cleavage of the carbon–halogen bond are concerted processes:



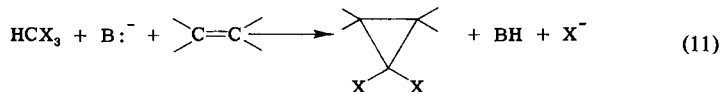
The loss of halide ion appears to add driving force to the proton removal Thus it is possible to go directly to what is probably the most stable of the dihalo-carbenes and by-pass what would be a relatively unstable trihalomethyl anion (18).

The kinetic isotope effect was measured by comparing the rates of the hydrolyses of CHBrF_2 and CDBrF_2 . The observed value (2.02 ± 0.14) is somewhat greater than those found in carbanion formation, a fact which is also consistent with a concerted mechanism. The participation of HO^- in the transition state leads to an activation volume, $\Delta V^\ddagger = 8.5 \text{ cm}^3/\text{mole}$, which is smaller than in the two-step (carbanion) mechanism (25).

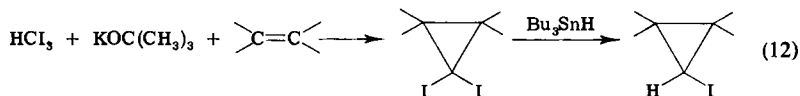
II. TRIHALOMETHIDES IN APROTIC MEDIA

A. Deprotonation of Haloforms

The basic hydrolysis of haloforms discussed in the preceding paragraphs is excellently suited for mechanistic studies. It has been seen, however, that the reactions of the dihalocarbene intermediates with added nucleophiles will, at best, compete with the attack on water, giving carbon monoxide and formate ion. In order to achieve addition of dihalocarbenes to nucleophiles (e.g., olefins) in good yields, aprotic media are required. Potassium *t*-butoxide has been the favored base, following the first successful application of this technique by Doering and Hoffmann (28), but sodium methoxide (29–31), potassium isopropoxide (32), and a dispersion of anhydrous sodium hydroxide (33) have also been applied. The success of the latter method suggests that the sensitivity of the dichlorocyclopropanation reaction toward water should not be exaggerated. A two-phase system involving olefin and chloroform in the presence of 50% sodium hydroxide and catalytic amounts of triethylbenzylammonium hydroxide also afforded good yields of dichlorocyclopropanes (33a). Even tetraethylammonium fluoride in acetonitrile effected the α -elimination of hydrogen halides from haloforms (34).

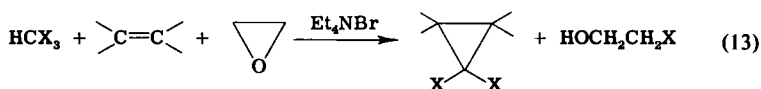


Reaction of olefins with iodoform in the presence of potassium *t*-butoxide gave rise to high-boiling products which, because of rapid decomposition, could not be purified. Evidence that these products contained 1,1-diiodocyclopropanes was obtained from their mass spectra. Reduction with tri-*n*-butyltin hydride afforded 1-iodocyclopropanes in high yields (35).



Dihalocarbene adducts were also prepared by heating equimolar amounts of haloform and olefin in the presence of ethylene oxide and an anionic catalyst such as tetraethylammonium bromide (36, 37). This method generates dihalocyclopropanes under essentially neutral conditions but requires elevated temperatures (130°–170°) and high-pressure equipment.

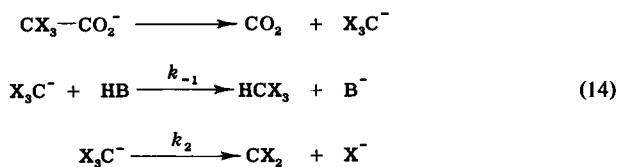
Tri- and tetraalkyl-1,1-dihalocyclopropanes undergo rearrangement and dehydrohalogenation under these reaction conditions, with formation of halo-1,3-dienes (38). On the other hand, moderate yields of difluorocyclopropanes have been obtained from difluorochloromethane and olefins by the ethylene oxide procedure (37), whereas other bases failed (cf., however, Section II,B).



Trihalomethides may be displaced from organometallic reagents such as PhHgCX_3 (Chapter 3, Section IV) and Me_3SnCF_3 (Chapter 3, Section V) by treatment with sodium iodide. The reactivity of various olefins toward the $\text{PhHgCCl}_2\text{Br-NaI}$ and $\text{CHCl}_3\text{-KOC(CH}_3)_3$ reagents has been compared and was found to be virtually identical (39). This observation may be quoted as evidence in favor of a dihalocarbene, rather than a trihalomethide, as the species attacking the olefin. The two reagents mentioned give rise to different trihalomethides, $\text{BrCl}_2\text{C:}^-$ and $\text{Cl}_3\text{C:}^-$, but to a common carbene, :CCl_2 . No further proof for the intervention of carbenes in reactions (11)–(13) has been given, and the assumption of divalent carbon intermediates rests largely on analogy with Hine's studies in aqueous solution.

B. Decarboxylation of Trihaloacetates

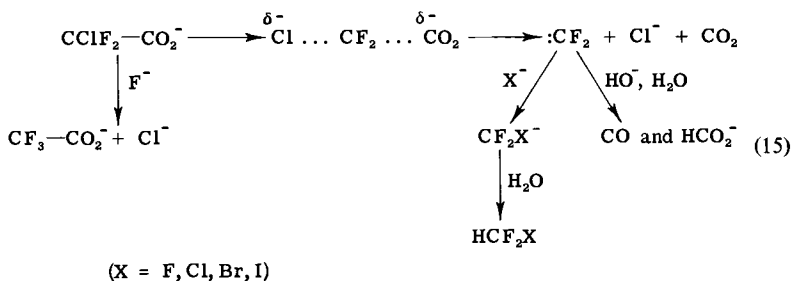
The reaction of trichloroacetic acid to give chloroform and carbon dioxide on heating with various bases was first observed by Silberstein (40) in 1884. Detailed kinetic studies of the decarboxylation of various trihaloacetic acids (41–45) revealed a first-order reaction of the carboxylate anion, forming carbon dioxide and a trihalomethyl anion. Subsequent protonation of the trihalocarbanion in protic solvents gives the haloform.



Stabilization of the carbene should increase k_2 with respect to k_{-1} . In fact, only 72% of dichlorofluoromethane has been obtained from the decarboxylation of dichlorofluoroacetate in aqueous solution; about 30%

of the dichlorodifluorocarbanions loses chloride ion to give chlorodifluorocarbene, which is subsequently hydrolyzed to carbon monoxide and formate ion (46).

The decarboxylation of chlorodifluoroacetate ion (47) produces very little chlorodifluoromethane, but the yield increases on addition of chloride ion. Fluoride, bromide, and iodide bring about the formation of fluoroform, bromodifluoromethane, and difluoroiodomethane, respectively. It appears, therefore, that chlorodifluoroacetate ion decomposes by a concerted mechanism to give carbon dioxide, chloride ion, and difluorocarbene without any intermediate formation of the chlorodifluoromethyl anion:

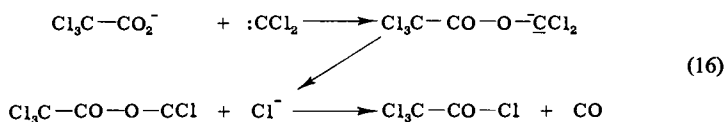


Some $\text{S}_{\text{N}}2$ attack of fluoride ion on the chlorodifluoroacetate ion to give trifluoroacetate also occurs, but trifluoroacetate decarboxylates too slowly to yield a significant amount of fluoroform under the reaction conditions employed here. The rate of decarboxylation of chlorodifluoroacetate is about 40 times as large as would be expected from an interpolation of the data on trichloro-, dichlorodifluoro-, and trifluoroacetates. The abnormal rate provides further evidence for the concerted character of the reaction (cf. Section I, B).

The decarboxylation of salts of trichloroacetic acid in an aprotic solvent is a convenient method to produce the trichloromethyl anion, and dichlorocarbene, under neutral conditions (48, 49). 1,2-Dimethoxyethane is a suitable solvent; the decompositions in tetrahydrofuran and ethyl acetate are notably slower. The rates of decarboxylation of the alkali trichloroacetates are in the order $\text{K} > \text{Na} > \text{Li}$, but the sodium salt is more easily prepared in a dry state. The intermediacy of the trichlorocarbanion is shown by the addition to the carbonyl group of ketones, and by chlorine abstraction from various perchloro compounds to give carbon tetrachloride (50). In the presence of olefins, including some base-sensitive compounds, dichlorocyclopropanes are formed in good yields. Difluorocarbene, produced by the thermal breakdown of sodium chlorodifluoroacetate in diglyme, has been trapped by cyclohexene (51).

The relative rates of cyclopropane formation from a wide range of olefins were found to be identical in the decarboxylation of sodium trichloroacetate and in the thermolysis of $\text{PhHgCCl}_2\text{Br}$, both at 80° in dimethoxyethane (39) (Chapter 3, Section IV). Since the organomercurial does not react via trihalocarbanions, these competitive studies provide convincing evidence of a dichlorocarbene intermediate.

The thermal decarboxylation of sodium trichloroacetate in 1,2-dimethoxyethane without added acceptor leads to a variety of products, but has been shown to proceed by way of trichloroacetic anhydride (50). Trichloroacetic anhydride was also the major product of the decarboxylation of silver trichloroacetate (52). Trichloroacetyl chloride, arising from attack of dichlorocarbene on the trichloroacetate ion, is thought to be an intermediate in anhydride formation:



The treatment of trichloroacetic acid with concentrated aqueous silver nitrate afforded chloropicrin, $\text{Cl}_3\text{C}-\text{NO}_2$, as the major product, which arises from a sequence similar to Eq. (16) (53). Only minor amounts of dichloronorcarane could be obtained in the presence of cyclohexene.

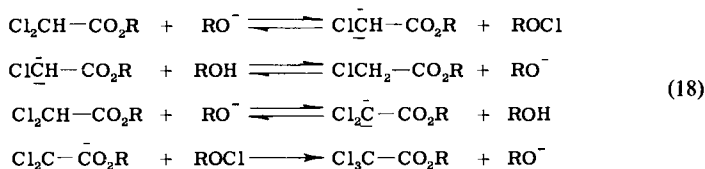
C. Basic Cleavage of Trihalocarbonyl Compounds

The reaction of alkyl trichloroacetates with alkoxide in the presence of olefins represents a convenient synthesis of dichlorocyclopropanes (54, 55). The alkyl trichloroacetates undergo carbonate cleavage to give dialkyl carbonates and, presumably, the trichloromethyl anion. No attempts to trap the anion have been made, but the yields of dichlorocyclopropanes are excellent regardless of the base used (potassium *t*-butoxide, sodium ethoxide, sodium methoxide).



Dichlorocarbene adducts are produced in much lower yield from *t*-butyl dichloroacetate under similar conditions (54, 56) (13% of 1,1-dichloro-2,2-dimethylcyclopropane was obtained in the presence of isobutene, compared to 86% from trichloroacetate). It has been proposed (56) that, in the presence of potassium *t*-butoxide, *t*-butyl dichloroacetate

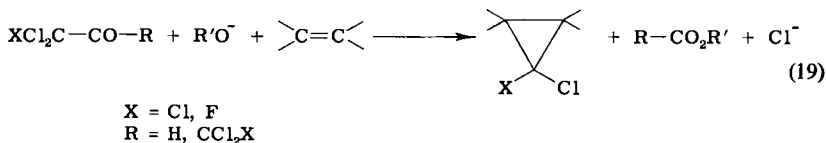
is converted into a mixture of *t*-butyl chloroacetate and *t*-butyl trichloroacetate, the latter giving dichlorocarbene and di-*t*-butyl carbonate according to Eq. (17).



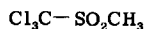
The mechanism suggested for this disproportionation involves abstraction of positive chlorine as well as of hydrogen from the dichloroacetate by base. Whereas this step has not been substantiated, the reaction of dichloroacetate with *t*-butyl hypochlorite in the presence of base has been shown to give dichlorocarbene and some *t*-butyl trichloroacetate (56). A similar mechanism probably operates in the reaction of diethyl dichloromalonate with potassium *t*-butoxide in cyclohexene, which affords a 21% yield of 7,7-dichloronorcaradiene (57).

The most efficient of these reactions, Eq. (17), has also been employed to produce chlorofluorocyclopropanes from methyl dichlorofluoroacetate, olefin, and base (58, 59), but has failed to give difluorocyclopropanes with methyl chlorodifluoroacetate as the trihalomethide precursor (58).

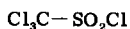
As in alkyl trihaloacetates, the carbonyl group of trihaloketones and trihaloaldehydes is highly reactive toward nucleophiles which initiate the elimination of trihalomethyl anions. Hexachloroacetone (60, 61) and chloral (62) readily yield dichlorocyclopropanes on treatment with alkoxides in an aprotic solvent in the presence of olefins. *sym*-Difluorotetrachloroacetone and potassium *t*-butoxide have been used as a convenient source of chlorofluorocyclopropanes (63, 64). Again, *sym*-tetrafluorodichloroacetone does not afford difluorocyclopropanes (58).



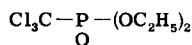
The reactions of methyl trichloromethylsulfinate [1] (65), trichloromethylsulfonyl chloride [2] (65), and diethyl trichloromethylphosphonate [3] (66) with base present a mechanistically similar situation. The yields of dichlorocyclopropanes are inferior to those obtained in reactions (17) and (19).



[1]



[2]



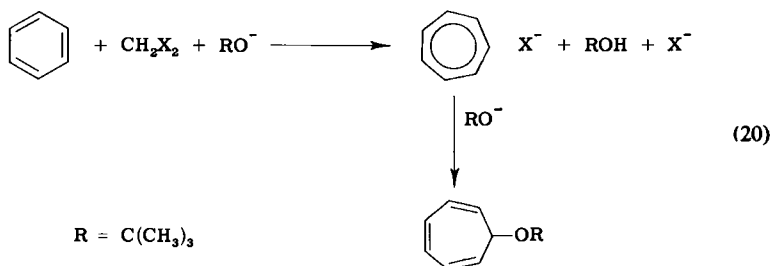
[3]

D. Dehalogenation of Tetrahalomethanes

Halogen-lithium interchange is the most frequently employed method for the dehalogenation of tetrahalomethanes with formation of dihalo-carbenes or -carbenoids (Chapter 3, Section III, D). However, moderate yields of dichlorocyclopropanes have also been obtained in the electrolytic reduction of CCl_4 in acetonitrile in the presence of 2,3-dimethyl-2-butene (67) and in the reactions of CCl_4 and BrCCl_3 with potassium *t*-butoxide in cyclohexene-tetrahydrofuran (68). The latter reaction involves formation of *t*-butyl hypohalite and is related to Eq. (18).

III. α -ELIMINATION AT METHYLENE HALIDES

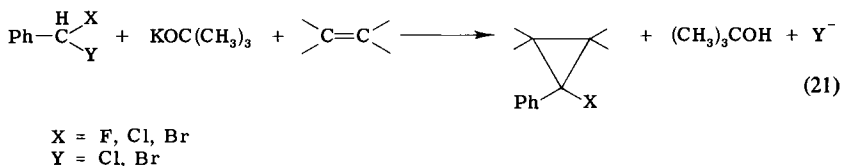
Closs and co-workers have shown that, when methylene chloride is treated with alkyl lithium compounds, a major fraction of the ensuing reaction involves hydrogen-lithium interchange with subsequent transfer of CHCl to suitable acceptors (Chapter 3, Section III, D). Using the more weakly basic reagent potassium *t*-butoxide, Volpin *et al.* (69) found that methylene halides are capable of transforming benzene into tropylium *t*-butoxide in yields ranging from 0.1 % to 1.4 %.



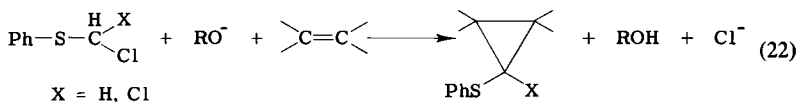
From these observations it is clear that *alcohol-free* potassium *t*-butoxide is capable of dehydrohalogenating methylene halides to an extent of at least 0.1–1.4 %. Hine *et al.* (70) have investigated the mechanism of the reaction of methylene halides with alkali metal alkoxides in alcohol solution, concluding that an α -elimination mechanism is improbable. Methylal isolated from the reaction of methylene bromide with sodium methoxide

in methanol-*d* contained only a small amount of deuterium, and 0.5 *M* sodium iodide did not decrease the rate of reaction of methylene iodide with sodium methoxide. These findings as well as the relative rates of methylene halides toward alkoxides (methoxide > isopropoxide > *t*-butoxide) are in sharp contrast to the behavior of haloforms (Section I, A).

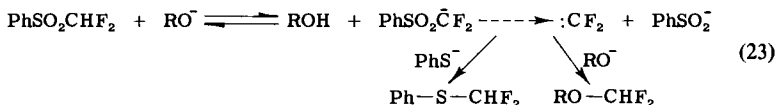
The propensity of methylene halides toward α -elimination is greatly increased by substituents which are capable of delocalizing a negative charge. The reaction of benzal chloride with potassium *t*-butoxide in excess olefin gave 1-phenyl-1-chlorocyclopropanes in yields ranging from 50% to 90% (71-73). The same procedure has been applied successfully to benzal bromide (74), α -bromo- α -fluorotoluene (75, 76), and α -chloro- α -fluorotoluene (77).



Dichloromethyl phenyl sulfide (78, 79) and even chloromethyl phenyl sulfide (80, 81) are easily dehydrochlorinated by potassium *t*-butoxide (79, 80) or ethylene oxide (81), transferring $\text{PhS}-\text{C}-\text{X}$ to olefins.



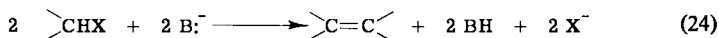
Difluoromethyl phenyl sulfone, on the other hand, undergoes elimination of phenylsulfinate, rather than fluoride, in the base-catalyzed reaction with sodium thiophenoxide to give difluoromethyl phenyl sulfide (82). Deuterium exchange is quite rapid compared to displacement.



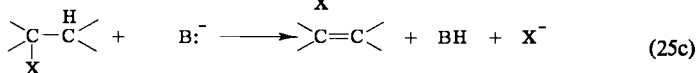
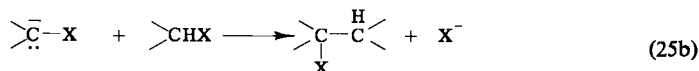
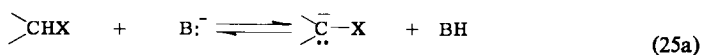
The reaction of dichloroacetophenone with potassium *t*-butoxide and olefins in aprotic media at -10° affords chlorocyclopropanes (83). The process is essentially the same as that described by Eq. (19).

IV. DEHYDROHALOGENATION OF BENZYLIC HALIDES

In basic media, a number of benzylic halides undergo dehydrohalogenation with formation of dimeric olefins, Eq. (24). The reaction depends critically on the structure of the halide, and on the solvent-base system employed. 4-Nitrobenzyl chloride is converted into 4,4'-dinitrostilbene by aqueous alkali (84), but this reaction is greatly retarded by one methyl group in the 3 position and completely inhibited by two methyl groups in the 3 and 5 positions (85); instead, alcohols are formed by S_N2 displacement of the halogen.

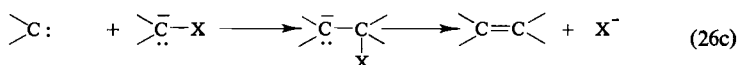
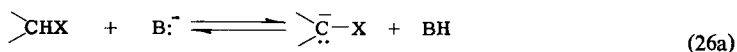


Whereas solutions of potassium *t*-butoxide in *t*-butyl alcohol react only slowly with benzhydryl chloride to produce benzhydryl *t*-butyl ether, potassium *t*-butoxide effects quantitative transformation of benzhydryl chloride into tetraphenylethylene with dimethyl sulfoxide as solvent (86). The latter reaction is of third order overall, of first order in the base, and of second order in benzhydryl chloride (87). It can be formulated as a bimolecular displacement of halide ion by an α -halocarbanion, followed by rapid β -elimination.



9-Halogenofluorenes also undergo this type of elimination, forming 9,9'-bifluorenylidene (88). A thorough kinetic study of this system has established that the conversion of 9-bromofluorene into bifluorenylidene is much slower than the proton transfer to and from the 9-carbon (89). The initial rate of formation of bifluorenylidene was proportional to the square of the concentration of 9-bromofluorene. These observations are consistent with Eqs. (25a) and (25b). The rate of bifluorenylidene formation from 9-bromo-9,9'-bifluorenyl (the "dimeric halide"), Eq. (25c), was found to be 30–50 times that of bifluorenylidene formation from 9-bromofluorene (90). Thus, after the first 2–3 % of reaction, the rate of appearance of bifluorenylidene from 9-bromofluorene is indeed the rate of formation of 9-bromo-9,9'-bifluorenyl.

A different type of kinetic behavior—of first order in benzylic halide—has also been observed, and has sometimes been interpreted in terms of a carbene mechanism, Eqs. (26). On the assumption that carbenes are highly energetic species, step (26b) should be rate-limiting, and the rate of the overall reaction should show a first-order dependence on the concentration of the starting material.



With potassium *t*-butoxide as base, certain 9-halofluorenes carrying electron-withdrawing substituents (2-Cl, 2-Br, 2-CN, 4-CN, 2-NO₂, 4-NO₂) follow first-order kinetics (91). Dipolar aprotic additives (e.g., dimethyl sulfoxide) also promote the change in kinetic form from second to first-order of several 9-halofluorenes. Detailed consideration of substituent effects, particularly the insensitivity of the rate of elimination to changing the 9-halogen, led to the exclusion of the carbene mechanism (92). The first-order kinetic law in this case appears to arise from a rate-limiting dissociation of an α -halocarbanion-alkali metal ion pair, as evidenced by the effect of added electrolytes (92).

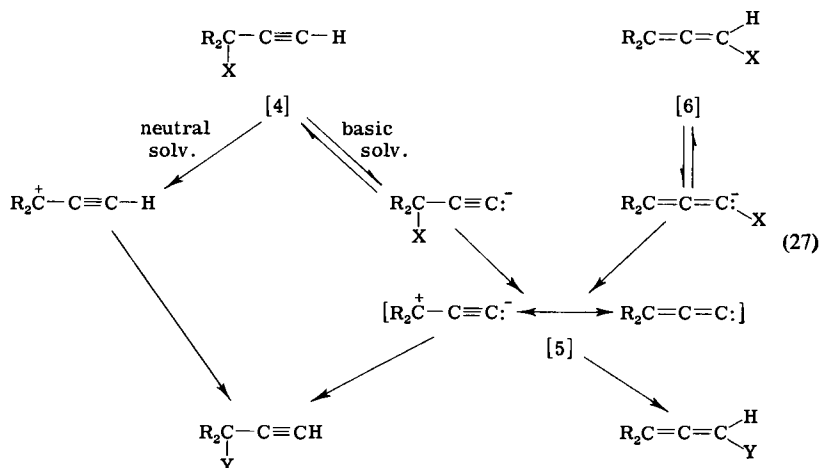
The only other published case of first-order kinetics is the conversion of 4-nitrobenzyl derivatives into 4,4'-dinitrostilbenes in aqueous organic solvents containing hydroxide ion (84, 85, 93, 94). Exchange of the α -hydrogen is again rapid compared with the elimination, and the intermediate carbanion can be trapped using carbonyl compounds (95, 96). If the reaction is carried out in the presence of a reactive aldehyde, deprotonation becomes rate-determining and is followed by a faster attack by the α -halocarbanion on the aldehyde to give *cis*- and *trans*-epoxides. The effect of ion pairing mentioned above appears unlikely in aqueous organic solvents. However, radical anions are readily formed from nitrobenzyl compounds under basic conditions, and may be responsible for stilbene formation (91).

V. SOLVOLYSIS OF PROPARGYL AND ALLENYL HALIDES

The rate of solvolysis of 3-halo-3-alkyl-1-butyne [4] is very slow compared to the rate of solvolysis of *t*-alkyl halides, but is strongly increased by added base. Under these conditions the kinetics are of first-order in

both halide and base concentrations, and the reaction proceeds predominantly with displacement of the halogen (only 3% elimination was observed under basic conditions, compared to 35% in the neutral solvolysis) (98-100). Replacement of the acetylenic hydrogen by an alkyl group speeds the rate of neutral solvolysis by a factor of 10^3 , but base catalysis is no longer observed (101).

The base-catalyzed exchange of the acetylenic protons in C_2H_5OD/D_2O is appreciably (at least 16 times) faster than the base-promoted solvolysis (102). This result eliminates rate-determining formation of the conjugate base and suggests S_N1 ionization of the acetylenide ion to give a zwitterion carbene [5], Eq. (27). Additional support for this mechanism comes from the observation of the "mass law effect" of added common ion salts (102). In the presence of 0.22 *M* sodium bromide, the initial rate of the second-order reaction of 3-bromo-3-methyl-1-butyne is depressed about 40%. The same concentration of either sodium perchlorate or sodium depresses the rate only about 18%.

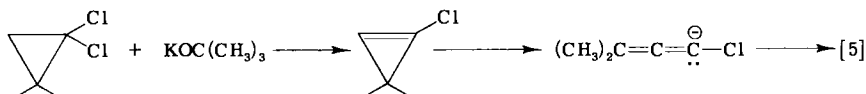


Hexadeutero-3-bromo-3-methyl-1-butyne [4], ($R = CD_3$) undergoes the neutral solvolysis 1.84 times slower than the protonated analog. The second-order hydroxide-promoted solvolysis is slowed by this deuterium substitution by only a factor of 1.31 (103). The smaller deuterium isotope effect is reasonably explained in terms of differing demand for stabilization of positive charge in the two transition states.

Similar conclusions have been drawn from the effects of hydrostatic pressure on the solvolysis of 3-chloro-3-methyl-1-butyne (25). The activation volume of the neutral solvolysis is $-15 \text{ cm}^3/\text{mole}$, in close agreement

with the values observed for *t*-alkyl halides. The net effect of pressure on the base-promoted reaction is small ($\Delta V^* = +2 \text{ cm}^3/\text{mole}$). The most reasonable interpretation is that the departure of chloride ion is accompanied by the creation of another pair of charges, i.e., the zwitterion carbene [5].

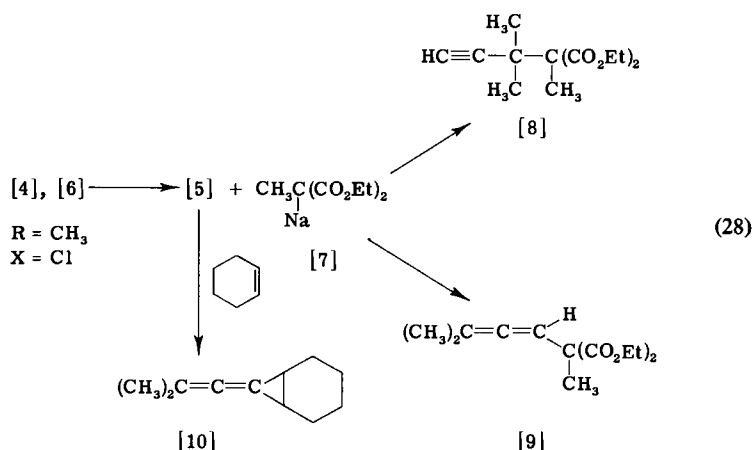
The kinetic evidence for the course of the base-promoted reaction of the allenyl halides [6] is entirely analogous to that presented above for the propargyl halides (104), and establishes that the rate-determining step also involves the loss of halide ion from the conjugate base (allenyl hydrogen exchange is 10–20 times faster than the rate of reaction). The activation volume of the base-promoted solvolysis of 1-chloro-3-methyl-1,2-butadiene equals $+5 \text{ cm}^3/\text{mole}$ (104a). A combination of this value with that measured for 3-chloro-3-methyl-1-butyne and with the densities of these two substrates shows that the two transition states have virtually identical volumes. The products in both the presence and absence of added nucleophiles show that the two reactions share a common intermediate, [5]. The same species was found to arise by treatment of 1,1-dichloro-2,2-dimethylcyclopropane with potassium *tert*-butoxide in hexamethylphosphoramide (104b).



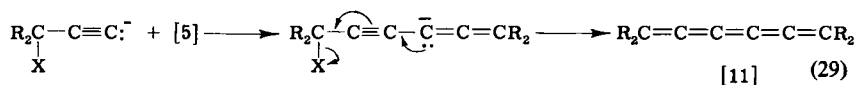
The ambident zwitterion carbene [5] can react with nucleophiles to give products originating from both α and γ attack. Hydroxide and ethoxide ions prefer the propargyl to the allenyl position exclusively, while azide prefers the propargyl position by a factor of 8, thiophenoxide by a factor of 1.6, and bromide attacks the two positions almost equally (104). A tentative hypothesis has been offered to explain why different nucleophiles give such widely differing acetylene/allene product ratios (104). Relative rates of ether formation from alcohols are: methyl 100, ethyl 45, isopropyl 4, *t*-butyl 0 (105). Unlike alcohols, amines of all types are excellent nucleophiles and lead to amine products in good yield. The reaction with trimethylamine produces quaternary ammonium halides, which have propargylic structure when $\text{R} = \text{CH}_3$ or $\text{R}, \text{R} = (\text{CH}_2)_5$. When R is larger than CH_3 , the products are allenic (106).

Diethylsodiummethyl malonate [7] affords propargylic [8] and allenic [9] products in the ratio 2.6 : 1 (107). The close agreement of product ratios from [4] and [6] again supports a common intermediate. By adding

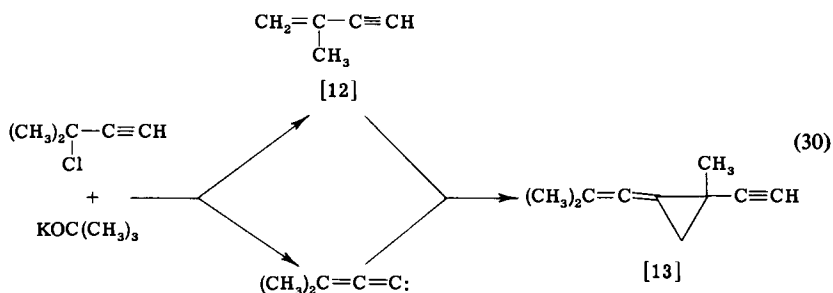
cyclohexene, the zwitterion carbene [5] can be competitively trapped as [10].



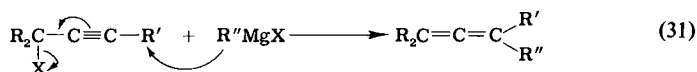
Alkenylidenecyclopropanes are the major products obtained from [4] (108) and [6] (109) in the presence of olefins in aprotic media, using potassium *t*-butoxide as base. The relative rates of addition to olefins of the intermediates generated from [4] and [6] ($\text{R} = \text{CH}_3$) were found to be identical (109). In the absence of olefins, hexapentaenes [11] are formed by reaction of [5] with the conjugate base of the starting halide, [4] or [6] (110–112).



Reaction (29) is successful with $\text{R} = \text{Ph}$ (110, 112) and with $\text{R} = \text{C}(\text{CH}_3)_3$. With $\text{R} = \text{CH}_3$, however, β -elimination of HX followed by addition of [5] to the enyne [12] takes place to give [13] (107).

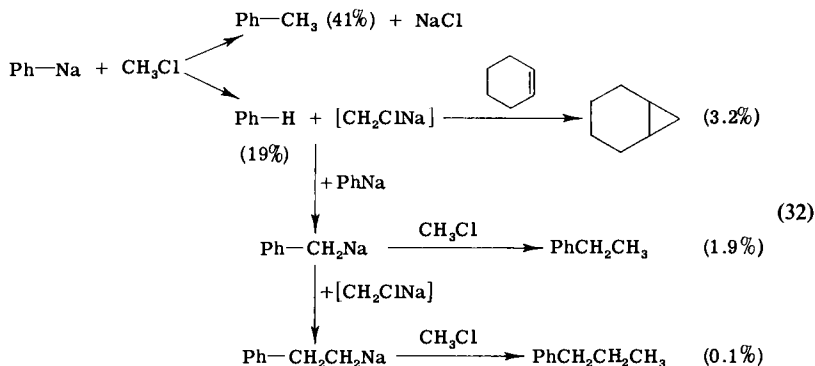


In contrast to the many reactions which are reasonably ascribed to the zwitterion carbene [5], the preparation of allenes from propargyl halides and Grignard reagents (113) appears to proceed by S_N2' displacement (114). The success of the allene synthesis with propargyl halides not carrying acetylenic hydrogen (115) excludes, among other facts, the intervention of [5].

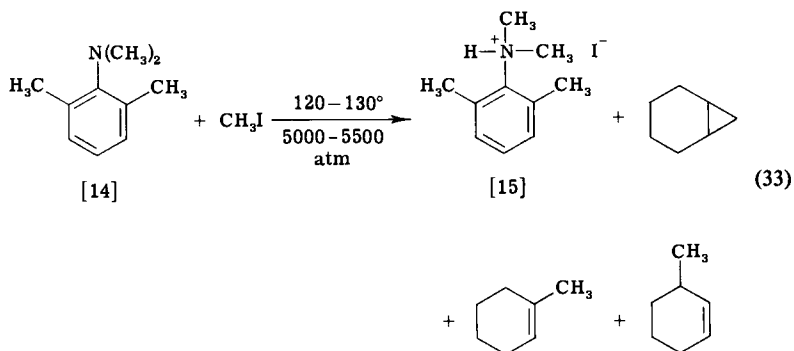


VI. α -ELIMINATION AT ALKYL HALIDES

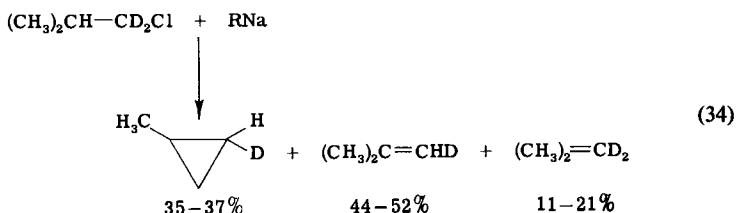
Toluene is the major product the reaction of methyl chloride with phenylsodium, originating from the familiar Wurtz reaction. The minor products, ethylbenzene (1.9%) and *n*-propylbenzene (0.1%), are probably the result of an α -elimination (cf. Chapter 3, Section III, A). In the presence of cyclohexene, norcaradiene was obtained in 3.2% yield (116). The absence of methylcyclohexenes (products of insertion into carbon-hydrogen bonds) indicates that the intermediate in this reaction is a carbenoid rather than free methylene. Relative olefin reactivities (cyclohexene 1.0; isobutene 1.3; 2,3-dimethyl-2-butene 0.85) indicate a considerable steric demand of the attacking species (116a). The observation that a higher yield of norcaradiene is obtained when total conversion to products is low also suggests an important role of the phenylsodium surface in the heterogeneous system.



The highly sterically hindered amine 2,6-*N,N*-tetramethylaniline [14] reacted with methyl iodide under high pressure to yield 2,6-*N,N*-tetramethylanilinium iodide [15] instead of the expected 2,6-*N,N*-pentamethylanilinium iodide (117). Compound [15] could result from the α -elimination of hydrogen iodide from methyl iodide. When the reaction was carried out in the presence of cyclohexene, norcaradiene (3–5%), 3-methylcyclohexene (15–20%), and 1-methylcyclohexene (6–8%) were isolated. The formation of an apparently unselective methylene by α -elimination is without precedent in carbene chemistry and deserves further investigation.



1,1-Dimethylcyclopropane is the major product of the treatment of neopentyl chloride with sodium (118) or sodium alkyls (119). Cyclopropane derivatives are found to be minor products in the reaction of less branched primary alkyl chlorides with sodium (120, 121) or phenylsodium (121). The mechanism of the production of the cyclopropanes has been formulated as a γ -elimination by Whitmore (118, 119). However, the methylcyclopropane obtained from 1-chloro-2-methylpropane-1,1- d_2 contained less than 1% of dideuterated material (120). Neopentyl chloride-1,1- d_2 also afforded monodeuterated 1,1-dimethylcyclopropane (121–122). Only the α -elimination-insertion path is compatible with the experimental results.

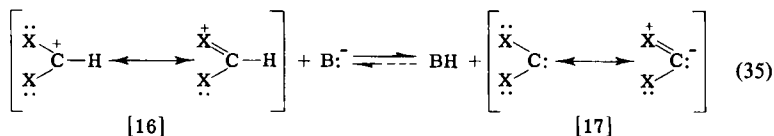


The distribution of deuterium in the isobutene produced along with the methylcyclopropane in reaction (34) defines the ratio of α - to β -elimination. In this experiment, α -elimination predominated, but 2-chloroalkanes reacted preferentially via β -elimination (120).

The nature of the intermediate in these α -elimination reactions is still a matter of concern. The product distribution in the reaction of many primary chlorides with sodium closely parallels that observed in the decomposition of diazoalkanes (120, 121, 123). Intramolecular competition for different types of C—H bonds, however, revealed a slightly higher selectivity of the species generated by α -elimination in favor of secondary and tertiary C—H bonds (123). This observation suggests some participation of metal halide in the cyclopropane formation.

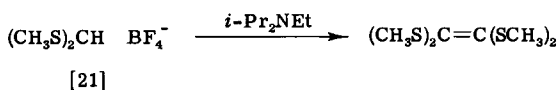
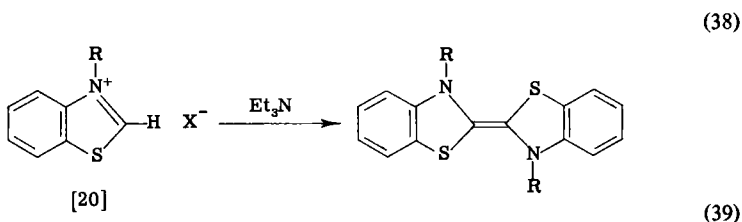
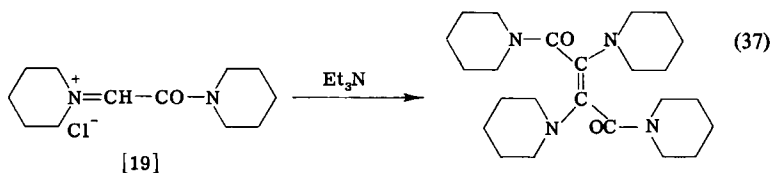
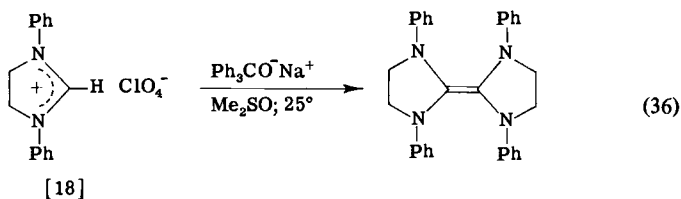
VII. DEPROTONATION OF CARBONIUM IONS

The α -elimination reactions discussed so far involve generation of a negative charge in their first step, followed by elimination of a nucleophile. One might construct an alternative mode of α -elimination in which the two steps are just reversed in order, the nucleophile being removed before the electrophile (proton) is eliminated. This type of α -elimination would be expected in the reaction of a base with "stable" carbonium ions (i.e., carbonium ions with heavily contributing ammonium, oxonium, etc., resonance structures).

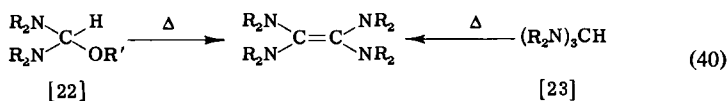


The investigation of intermediates of the general structure [17] was foreshadowed by the pioneering work of Breslow (124, 125) on the mechanism of thiamine action. Breslow demonstrated that imidazolium and, particularly, thiazolium salts suffer deuterium exchange at C₂ under extraordinarily gentle conditions. The various factors affecting the rate of deuterium exchange were elucidated by Olofson and his co-workers (126–129). Not surprisingly, the presence of a positive charge in the system undergoing deprotonation has an enormous influence on the rate of base catalyzed exchange (typically ten powers of ten compared to uncharged systems). Although there is evidence that the contribution of carbenic resonance forms to [17] is of minor importance, the deprotonation of [16] frequently affords dimers of [17], e.g., from the formamidinium salt [18] (130), from the α -chloroamide [19] (131), from *N*-alkylbenzthiazolium

salts [30] (132–135) and some of their aliphatic analogs (135a), and from dithiomethoxymethyl fluoborate [21] (136).

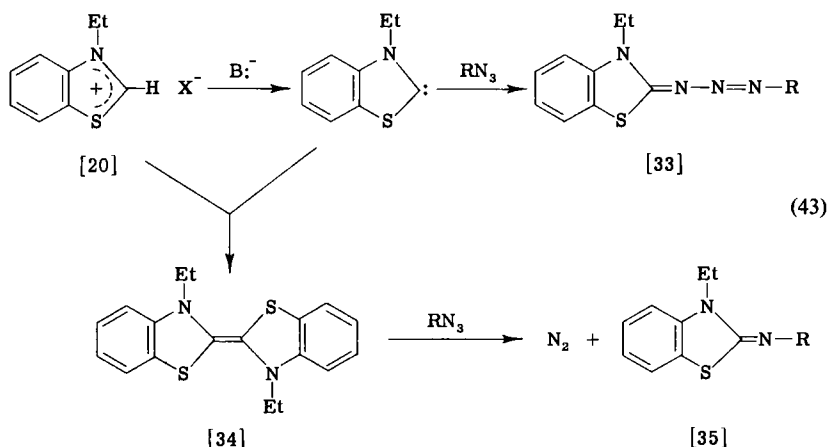


For the synthesis of tetraaminoethylenes the pyrolysis of either [22] (prepared from amine and alkyl orthoformate) (137–140) or [23] (141) is preferred to the deprotonation of formamidine salts. Both reactions, Eq. (40), probably involve intermediates of the type of [16] and [17].

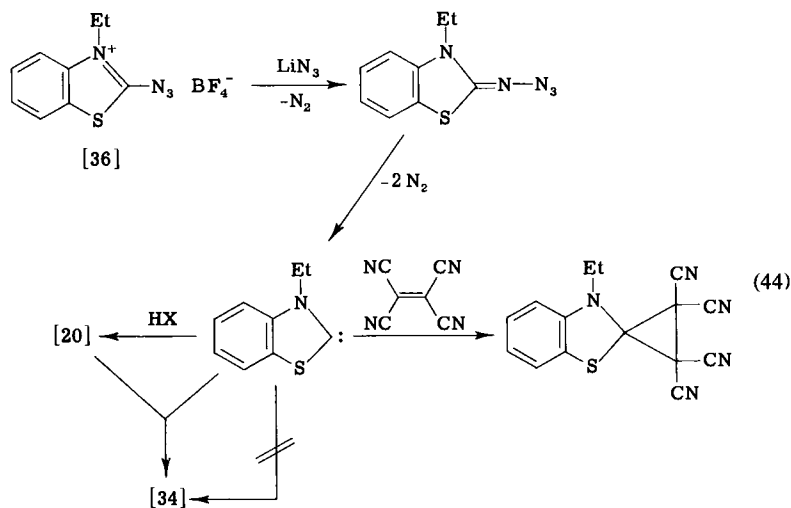


Some of the strongly nucleophilic olefins undergo secondary reactions under the conditions of deprotonation of their onium salt precursors. Base treatment of dimethoxymethyl fluoborate [24] affords the esters [25] and [26] almost certainly via tetramethoxyethylene (136).

of benzthiazolium salts could be trapped as diazoimines [33], whereas the dimers [34] afforded imines [35].



On the other hand, carbenes alone do not produce dimers. Balli (142) developed a method for generating the carbene involved in Eq. (43) which did not depend on deprotonation of a cation. Treatment of the azidinium salt [36] with azide ion yielded 3 moles of nitrogen and a carbene which could be trapped with a variety of electrophiles, but did not afford the dimer [34]. The dimer was readily obtained, however, in the presence of acids which protonate the carbene to give [20].



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CHAPTER 5

The Structural Theory of Carbenes*

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I. AN APPROACH TO THE ELECTRONIC STRUCTURE OF CARBENES

A. Nature of the Problem—CH₂

WE INTRODUCE THE PROBLEMS associated with the theoretical description of the electronic structure of carbenes with a discussion of the parent compound, methylene. Orient the methylene radical as shown in Fig. 1,

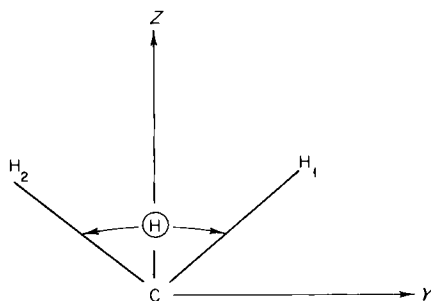


FIG. 1. CH₂ coordinate system.

with the x axis perpendicular to the molecular plane. For concreteness assume that we construct the molecular orbitals for CH₂ using the carbon $1s$, $2s$, and $2p$ orbitals and $1s$ on each hydrogen. We assume that the molecule has C_{2v} symmetry and therefore label each of the molecular orbitals by the irreducible representation which it spans. Because each molecular

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orbital (MO) is of definite symmetry, it will be composed entirely of atomic orbitals of like symmetry and consequently we expect MO's of the form

$$Na_1 = C_{N1} \phi_C(1s) + C_{N2} \phi_C(2s) + C_{N3} \phi_C(P_z) + C_{N4} [\phi_{H1}(1s) + \phi_{H2}(1s)] \quad N = 1, \dots, 4 \quad (1)$$

$$Nb_2 = C_{N5} \phi_C(P_y) + C_{N6} [\phi_{H1}(1s) - \phi_{H2}(1s)] \quad N = 1, 2 \quad (2)$$

$$1b_1 = \phi_C(P_x) \quad (3)$$

The unknown coefficients appearing in the MO's are determined by solving the Hartree-Fock-Roothaan (HFR) equations (1) for the indicated basis. In practice, a significantly larger atomic basis is employed and the solutions of the HFR equations in the larger basis yields the energy levels schematically represented in Fig. 2. The lowest singlet state of CH_2 is

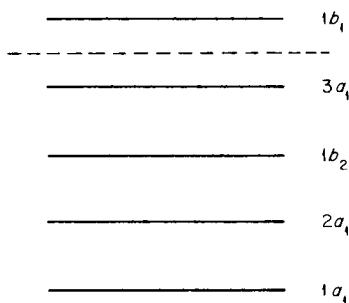


FIG. 2. Schematic representation of CH_2 MO energies.

described by the configuration $(1a_1)^2 (2a_1)^2 (1b_1)^2 (3a_1)^2$, where we have doubly occupied the first four levels. The spatial distribution of electrons in these molecular orbitals (and therefore their bonding characteristics) is vividly displayed in the contour plots shown in Figs. 3, 4, and 5.

We do not present a contour map for the $1a_1$ orbital since it is essentially a carbon $1s$ orbital and therefore nonbonding. The $2a_1$ orbital is an intimate mixture of carbon $2s$, $2P_z$ and hydrogen $1s$ orbitals and is C—H and H—H bonding. Note that, since this orbital must correlate with a σ_g orbital as the molecule approaches a linear geometry, the $2P_z$ contribution must decrease as we open the H—C—H angle. This decrease in sp hybridization coupled with a decreased overlap between the two hydrogens causes the $2a_1$ to become destabilized with increasing angle. The $1b_2$ orbital

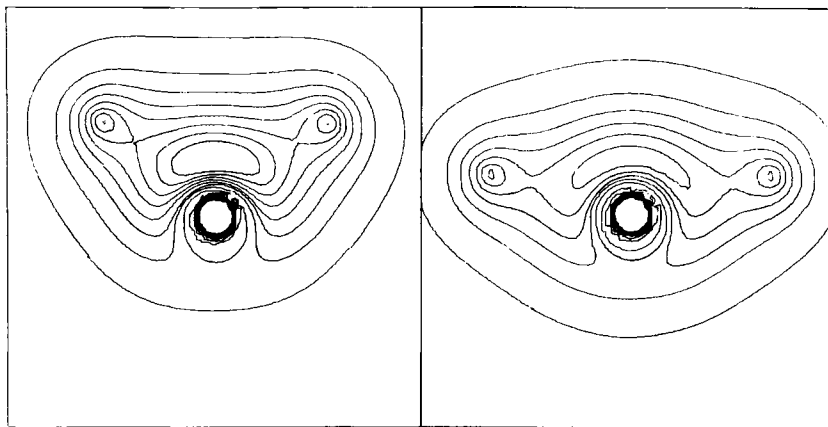


FIG. 3. Contours of the $2a_1$ MO of CH_2 ($105^\circ \rightarrow 150^\circ$).

is C—H bonding and, because of the characteristic nodal (ZX) plane, H—H antibonding. As the H—C—H angle opens up, the $1b_2$ MO will be stabilized because of the reduced confinement of the electrons which were formerly clashing against the nodal XZ plane. This effect may be interpreted as bond-bond repulsion and is manifested in the contour plots by the relaxation of the electron distribution and its expansion in a direction normal to the C—H line. The $3a_1$ MO is essentially a carbon lone pair lying along the C_2 axis, and at small angles it has a large spatial extension to the rear of

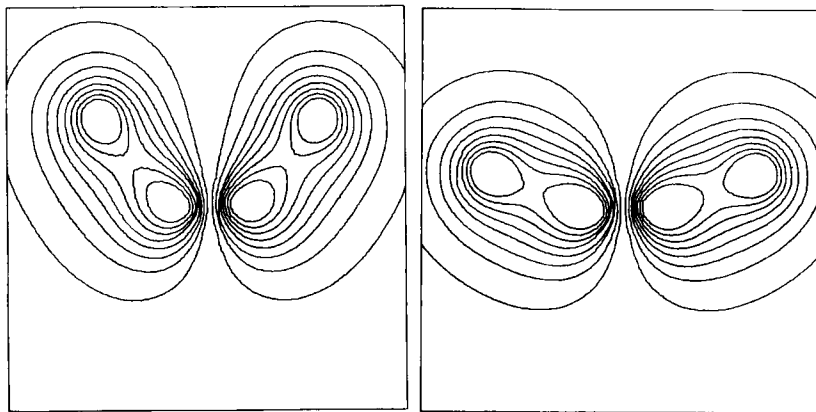


FIG. 4. Contours of the $1b_2$ MO of CH_2 ($105^\circ \rightarrow 150^\circ$).

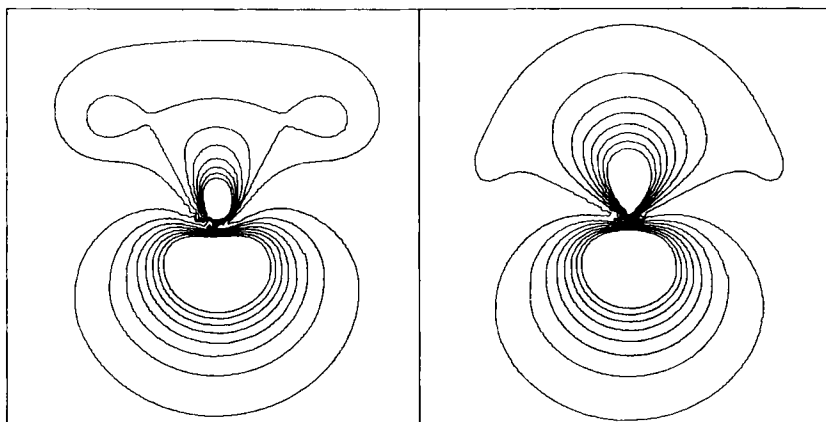


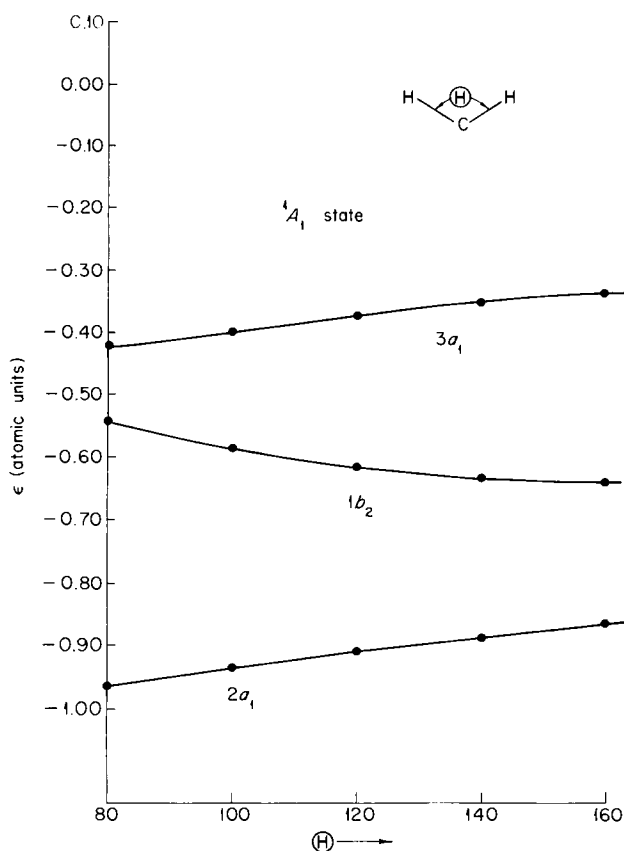
FIG. 5. Contours of the $3a_1$ MO of CH_2 ($105^\circ \rightarrow 150^\circ$).

the carbon atom. This MO is the result of a significant sp hybridization and at small angles is slightly H—H bonding. Since this MO must correlate with a π orbital in the linear molecule, it must lose s character as the H—C—H angle opens and consequently is destabilized. The first virtual (empty) MO (not shown) is the $1b_1$ orbital which has a node in the molecular plane and is localized entirely on carbon. The inclusion of P_π orbitals on hydrogen does not significantly alter this conclusion. These trends are also evident in the plot of the MO energies versus angle [Walsh diagrams (2)] shown in Fig. 6. In summary, we note that the $2a_1$ and $1b_2$ molecular orbitals play a major role in the bonding of carbon to hydrogen and the $3a_1$ and $1b_1$ are accurately described as nonbonding.

The total energy of CH_2 computed with the MO's described above is plotted versus angle in Fig. 7 [curve labeled $^1A_1$ (MO)]. The calculations (3) were carried out at the experimental bond length (4) (1.11 Å) and the predicted equilibrium angle of 105° agrees well with the experimental value of 103° . In Hartree-Fock theory (HFT) (1) the total energy associated with a sequence of MO's is given by

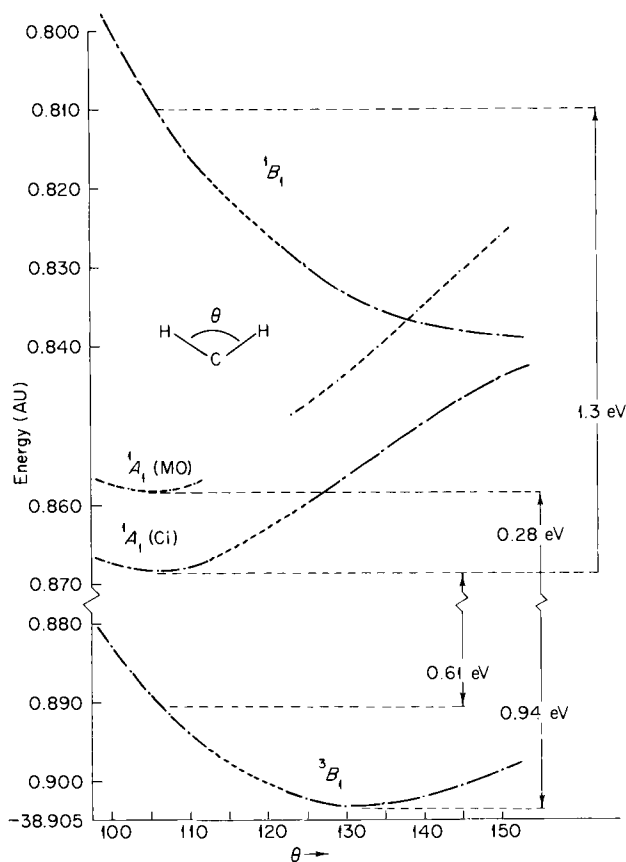
$$E = \sum_{i=1}^N \varepsilon_i - \sum_{i < j}^N (J_{ij} - K_{ij}) + \sum_{\mu < \nu} z_\mu z_\nu / R_{\mu\nu}$$

i.e., a sum over the molecular orbital energies minus a sum over Coulomb and exchange integrals which corrects for the electron-electron repulsion within and among the MO's, and then a sum representing the nuclear

FIG. 6. Walsh diagram of CH_2 .

repulsion energy. Consider now exciting an electron from an occupied to an empty MO. The molecular energy changes for two reasons:

1. The sum of the molecular orbital energies increases.
2. The electron interaction terms change but, unlike the sum of the MO energies, these terms may increase or decrease. Consequently, if the electron interaction terms decrease more than the orbital energy sum increases, the energy of the molecule decreases. We conclude that promoting an electron to a higher MO could result in a state which has a lower total energy than that state which minimizes the sum of the molecular orbital energies. Methylene chemistry receives its unique flavor because the proximity of

FIG. 7. Energies of various electronic states of CH_2 .

the $3a_1$ and $1b_1$ orbital energies is such as to allow the decrease in electron repulsion on excitation to dominate the situation and to permit the triplet state ($^3B_1$) of the configuration $(1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^1(1b_1)^1$ to have a lower energy than the lowest $^1A_1$ state (5). In order to extend our discussion to include all carbenes we introduce a slight modification in our notation.

B. Generalization to Arbitrary Carbenes

Given a carbene RCR' with a particular nuclear configuration, we can in principle construct the solution to the Hartree-Fock-Roothaan equations

(*I*) and arrive at an electron configuration describing the lowest doubly occupied singlet state. The molecular orbitals so generated will be assumed to consist of:

1. A core which includes the orbitals associated with the inner shells of the constituent atoms and the chemical bonds in the molecule (in CH_2 the core is $1a_1$, $2a_1$, and $1b_2$).
2. A doubly occupied MO which is either of σ symmetry in the sense that it is "in the plane" containing the C—R and C—R' bonds, or one of

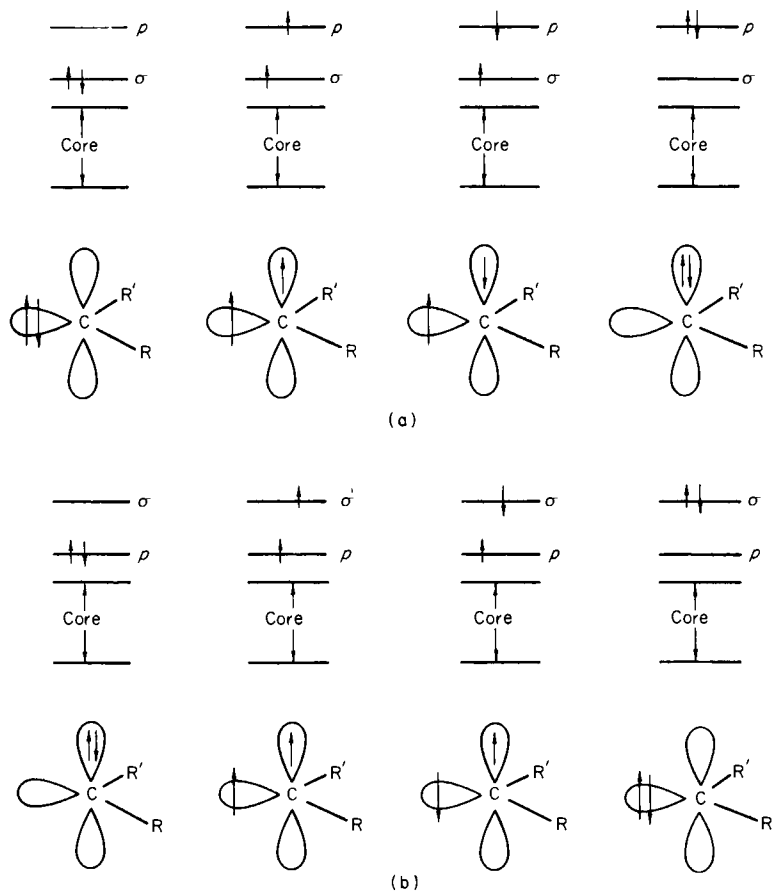


FIG. 8. Schematic representation of the ground and excited configurations of (a) σ^2 and (b) p^2 carbenes.

p symmetry which is perpendicular to this plane. This σ , p notation was introduced by Hoffmann *et al.* (6). A carbene whose lowest singlet state is described by $(\text{core})^2\sigma^2$ will be called a σ^2 carbene (CH_2 is in this category), and one with $(\text{core})^2p^2$ will be called a p^2 carbene. These two possibilities are depicted schematically in Fig. 8. Note that we do not mean to imply that σ or p orbital is completely localized on the carbene carbon. Since σ and p are molecular orbitals, they will have contributions from those atomic orbitals on any center, which are permitted by symmetry, to mix with the carbene carbon orbitals.

It is often the case that the σ MO is localized on the carbene carbon, but the p MO runs the gamut from a localized orbital on the carbene carbon to a highly delocalized orbital with significant contributions from many atoms in the molecule.

C. Implications of Hartree-Fock Theory

Consider that we have carried out the appropriate MO calculations for a given carbene and have the molecular orbitals appropriate for the lowest doubly occupied singlet. Assume for concreteness that we are dealing with a σ^2 carbene. The configuration $(\text{core})^2\sigma^2$ gives rise to the state (5)

$${}^1\psi(\sigma^2) = (\text{core } \sigma \mid \text{core } \sigma) \quad (5)$$

where the wavefunction is represented by a single determinant with the orbitals having α spin to the left of the vertical bar and those with β spin to the right. The doubly excited $(\text{core})^2p^2$ configuration gives rise to the state

$${}^1\psi(p^2) = (\text{core } p \mid \text{core } p) \quad (6)$$

These two states have the same symmetry and will mix in a CI calculation to yield the states

$${}^1\psi_- = {}^1\psi(\sigma^2) \sin \chi - {}^1\psi(p^2) \cos \chi \quad (7)$$

$${}^1\psi_+ = {}^1\psi(\sigma^2) \cos \chi + {}^1\psi(p^2) \sin \chi \quad (8)$$

with the energies

$$E_{\pm} = [E(\sigma^2) + E(p^2)]/2 \pm K_{\sigma p}R \quad (9)$$

where

$$R = \sqrt{\{[E(\sigma^2) - E(p^2)]/2K_{\sigma p}\}^2 + 1} \quad (10)$$

$$E(\sigma^2) = \langle {}^1\psi(\sigma^2) | \hat{H} | {}^1\psi(\sigma^2) \rangle \quad (11)$$

$$E(p^2) = \langle {}^1\psi(p^2) | \hat{H} | {}^1\psi(p^2) \rangle \quad (12)$$

$$K_{\sigma p} = \langle {}^1\psi(\sigma^2) | \hat{H} | {}^1\psi(p^2) \rangle = \int \sigma(1)p(1)(1/r_{12})\sigma(2)p(2) dV(1, 2) \quad (13)$$

$E(\sigma^2)$ and $E(p^2)$ are the energies of the σ^2 and p^2 configurations before they are permitted to interact, $K_{\sigma p}$ is the exchange integral connecting the σ and p molecular orbitals, and $\hat{H}$ is the exact Schrödinger Hamiltonian. The integral $K_{\sigma p}$ is always greater than zero and so $E_- < E_+$. The angle χ is determined by the equation

$$\tan 2\chi = 2K_{\sigma p}/[E(\sigma^2) - E(p^2)] \quad (14)$$

and, for a σ^2 carbene, $\tan 2\chi < 0$.

This restricts χ to the range $45^\circ \leq \chi \leq 90^\circ$. We see therefore that, the larger the energy separation $E(\sigma^2) - E(p^2)$, the closer χ is to 90° and the more ${}^1\psi_\pm$ resembles ${}^1\psi(p^2)$ and ${}^1\psi(\sigma^2)$, respectively, as required intuitively. The argument for a p^2 carbene is analogous, and in this instance $E(\sigma^2) - E(p^2) > 0$ and $\tan 2\chi > 0$. This restricts χ to the range $0^\circ \leq \chi \leq 45^\circ$ and, the larger the energy separation, the closer χ is to 0° and the more ${}^1\psi_\pm$ resembles ${}^1\psi(\sigma^2)$ and ${}^1\psi(p^2)$, respectively. Thus both σ^2 and p^2 carbenes may be treated simultaneously by working with ${}^1\psi_\pm$ and recognizing the relationship between these states and ${}^1\psi(\sigma^2)$ and ${}^1\psi(p^2)$.

The wavefunction for the singlet state arising from the $(\text{core})^2\sigma^1p^1$ configuration (of either a p^2 or a σ^2 carbene) is

$${}^1\psi(\sigma p) = [(\text{core } \sigma | \text{core } p) + (\text{core } p | \text{core } \sigma)]/\sqrt{2} \quad (15)$$

with an energy

$${}^1E(\sigma p) = [E(\sigma^2) + E(p^2)]/2 + [J_{\sigma p} - (J_{\sigma\sigma} + J_{pp})]/2 + K_{\sigma p} \quad (16)$$

where

$$J_{\sigma p} = \int \sigma(1)\sigma(1)(1/r_{12})p(2)p(2) dV(1, 2) \quad (17)$$

and

$$J_{\sigma\sigma} = \int \sigma(1)\sigma(1)(1/r_{12})\sigma(2)\sigma(2) dV(1, 2) \quad (18)$$

while the triplet ($S_z = 0$ component) is described by

$${}^3\psi(\sigma p) = [(\text{core } \sigma | \text{core } p) - (\text{core } p | \text{core } \sigma)]/\sqrt{2} \quad (19)$$

with an energy

$${}^3E(\sigma p) = {}^1E(\sigma p) - 2K_{\sigma p} \quad (20)$$

If we use the inequality derived by Roothaan (1):

$$0 \leq K_{\sigma p} \leq J_{\sigma p} \leq (J_{\sigma\sigma} + J_{pp})/2 \quad (21)$$

we may develop the following inequalities.

$${}^3E(\sigma p) \leq {}^1E(\sigma p) \quad (22)$$

$${}^1E_- \leq {}^1E_+ \quad (23)$$

$${}^3E(\sigma p) \leq {}^1E_+ \quad (24)$$

$${}^1E(\sigma p) \leq {}^1E_+ \quad (25)$$

Since these inequalities must be simultaneously satisfied by a given carbene, they restrict the relative positions of the various states to one of the three shown in Fig. 9. In this figure

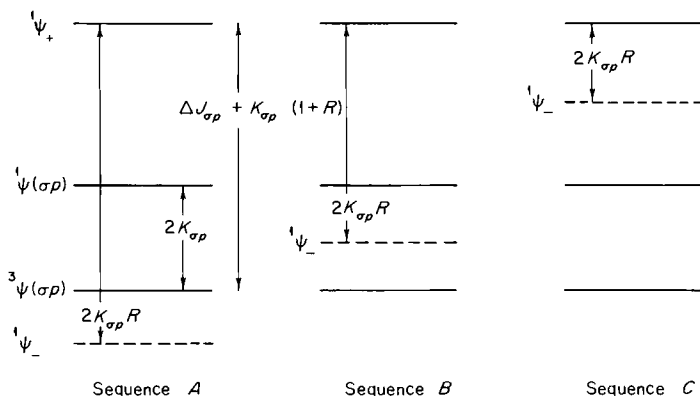


FIG. 9. Permitted state sequences for carbenes.

$$\Delta J_{\sigma p} = (J_{\sigma\sigma} + J_{pp})/2 - J_{\sigma p} > 0 \quad (26)$$

The relative positions of all states with the exception of ${}^1\psi_-$ are determined by the structure of the theory. Although the ${}^1\psi_-$ state must be located by detailed calculation, one can construct arguments for the probable occurrence of a given state sequence. In particular, in methylene, $\Delta J_{\sigma p}$ is approximately equal to $2K_{\sigma p}$ (an equality in the linear configura-

tion), and if we *assume* this to be “approximately” true in general we note that

$${}^1E(\sigma p) - {}^1E_+ = K_{\sigma p}(1 + R) \quad (27)$$

and since

$$K_{\sigma p}(1 + R) < 2K_{\sigma p}R \quad (28)$$

sequence *C* is not possible. Also, in this approximation

$${}^3E(\sigma p) - {}^1E_+ = K_{\sigma p}(R + 3) \quad (29)$$

$${}^1E_- - {}^1E_+ = 2K_{\sigma p}R \quad (30)$$

So we will have a singlet ground state (sequence *A*) when

$$2K_{\sigma p}R > K_{\sigma p}(R + 3) \quad (31)$$

or

$$R > 3 \quad (32)$$

and, using the definition of *R* in Eq. (10), this reduces to

$$|[E(\sigma^2) - E(p^2)]/K_{\sigma p}| > 5.6 \quad (33)$$

It is interesting to note that Eq. (33) requires that, whenever $E(\sigma^2) = E(p^2)$, a triplet state is lower than either of the two possible singlets $\psi_{\pm}$. If a carbene is (effectively) cylindrically symmetric in the linear configuration, then by symmetry, $E(\sigma^2) = E(p^2)$, the lowest state is a triplet, and, by continuity, the ground state remains a triplet when we bend the molecule slightly, i.e., state sequence *B* obtains. Exactly when and if a singlet state intersects this triplet and we pass from state sequence *B* to *A* is of considerable concern, and we shall return to this later.

If, however, we have a carbene in which the σ and *p* MO's are not equivalent in the linear configuration we have the possibility of a linear singlet, although from Eq. (33) we see that the two configurations must be separated by a large energy and a linear singlet is not expected to be a very common occurrence.

D. Range of Validity of the Preceding Theory

The most serious deficiency of the preceding theory is that it is a molecular orbital theory and thus does not take into consideration the correlation energy (7) of the various states. Since we are concerned about the

relative ordering of states, we must consider differences in correlation energy. If we assume that in going from σ^2 to a σp configuration we lose correlation energy simply from the dissolution of the σ^2 pair and if we assume also that the σ^2 pair is essentially a lone pair, we estimate, using the results of Scarzafava (8), that the correlation energy loss is approximately 1 eV. This means that the σ^2 equilibrium molecular energy calculated in an *ab initio* MO-SCF calculation should be displaced downward by about 1 eV while the states arising from the σp configuration remain unchanged.

The second deficiency arises because we have used virtual orbitals (those orbitals which are unoccupied in the σ^2 state) to construct representations of the excited states. This effect is difficult to quantify. The error comes about because the virtual orbital, say p in a σ^2 carbene, is constructed in the field of a neutral species and is more diffuse than it would be if it were occupied during the SCF procedure. This results in the energies of the σp and p^2 configurations being higher than they should be. Estimates using FCH and FCF indicate that the effect can be as large as 0.8 eV for a σp configuration. The two effects are schematically represented in Fig. 10.

Reformulating the energetics with these corrections in mind, the requirements for a singlet ground state becomes

$$K_{\sigma p} R > 3K_{\sigma p} - \Delta E_{\text{corr}} + \Delta E_{\text{virt}} \quad (34)$$

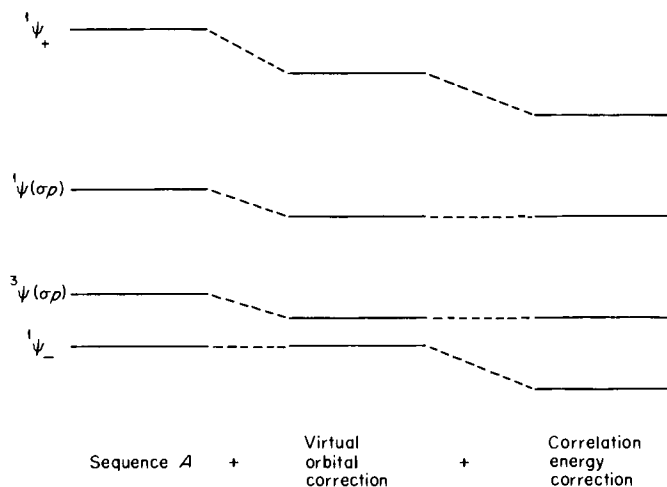


FIG. 10. Schematic representation of the correlation energy and virtual orbital effects on the order of the molecular energy states.

where $\Delta E_{\text{corr}}(>0)$ is the correlation energy in the σ^2 configuration and $\Delta E_{\text{virt}}(>0)$ is the energy decrease that would result in a state arising from the σp configuration if we used the proper occupied excited p orbital. The net result of these effects is to decrease the spacing $E(\sigma^2) - E(p^2)$ necessary for a singlet ground state (assuming $\Delta E_{\text{corr}} > \Delta E_{\text{virt}}$). An estimate of the magnitude of the correction may be obtained as follows.

From Eq. (34) we have

$$R > 3 - (\Delta E_{\text{corr}} - \Delta E_{\text{virt}})/K_{\sigma p} = 3 - \delta/K_{\sigma p} \quad (35)$$

Using Eq. (10), we arrive at

$$|[E(\sigma^2) - E(p^2)]/K_{\sigma p}| > 2\sqrt{8 - (6\delta/K_{\sigma p}) + (\delta/K_{\sigma p})^2} \quad (36)$$

Now, since ΔE_{virt} is effectively zero in semiempirical theories (adequate parameterization will ensure this) and may be compensated for in *ab initio* theories, we will assume that δ is essentially the correlation energy correction, ~ 1.0 eV. Then, taking $K_{\sigma p} \sim 1$ eV, we arrive at the approximate but useful criteria for a triplet ground state.

$$|[E(\sigma^2) - E(p^2)]/K_{\sigma p}| > 3.5 \quad (37)$$

II. THE ELECTRONIC STRUCTURE OF CH₂*

Having a reasonably clear idea about the mechanisms operative in determining the multiplicity of a carbene and the problems associated with a particular theoretical approach, we will discuss the CH₂ radical. A study of the history of the effort to understand CH₂ seems in order not only because it is one of the most important molecules in chemistry but because of the insight we gain from correlating the diverse theoretical approaches taken by many workers since about 1930.

Speculation about the electronic structure of methylene dates from the work of Mulliken (9) in 1932. He reasoned that, if carbon were sp^3 hybridized, the H-C-H angle would be a little larger than the tetrahedral value, while, if the atom were not hybridized, the angle would be about 90°. Therefore the H-C-H angle was judged to have an intermediate value (the possibility of sp^2 or sp hybridization was not mentioned). A $^1A_1$ ground state and a first excited $^3B_1$ state were assumed. Lennard-Jones (10) in 1934 constructed a correlation diagram for the series O, NH, CH₂, and from the known atomic levels in O he deduced that the one-electron orbitals in CH₂ should decrease in stability along the sequence $1a_1, 2a_1,$

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$1b_2$, $3a_1$, $1b_1$. He also concluded that the ground state should be $^1A_1$ and the first excited state $^3B_1$. This prediction was made at a time when no detailed knowledge could be obtained about the difference in stability between the $3a_1$ and $1b_1$ orbitals or its dependence on the H-C-H angle. Voge (11) cautioned against using only the carbon sp^3 configuration in considering the CH_2 angle. He pointed out that, if one considered VB structures which included sp hybridization, the equilibrium angle would be much larger than the tetrahedral angle. Lennard-Jones and Pople (12) made a qualitative prediction that the methylene triplet was linear and that the singlet would be bent. They noted also that detailed calculation would be necessary to ascertain the ground-state multiplicity. Linnet and Poë (13) present a very interesting argument for a nonlinear triplet. They write the determinantal wavefunction ψ corresponding to the ^3p state of oxygen and form the electron distribution function ψ^2 . The electronic coordinates which maximize this function are sought subject to the constraint that the symmetry of the resulting electron distribution is C_{2v} . They concluded that the configuration of maximum probability was that which had (i) two electrons at the oxygen nucleus, (ii) four electrons distributed in two pairs which are separated by an angle of 133.5° , and (iii) two single electrons being separated by an angle of 103° . The plane of the pairs is at right angles to the plane of the single electron, and the angle between a single electron and a pair is 104.5° . Linnett and Poë argue that the free carbon atom has as its configuration of maximum probability four electrons at the vertices of a tetrahedron (109.5°), while in the united atom limit the angle between electron pairs is 133.5° . Since the methylene triplet is an intermediate configuration, it should have an H-C-H angle between 109.5° and 133.5° .

The first calculation to consider all electrons was a semiempirical attempt by Niira and Oohata (14). They employed the VB method, including the covalent states that may be constructed from the atomic configurations $k^2s^2p^2h^2$ and $k^2sp^2h^2$. This results in six determinants with carbon as s^2p^2 and seven with carbon as sp^3 . They symmetrize this basic set and construct secular equations for the various singlets and triplets of CH_2 . Overlap integrals are neglected, and the matrix elements of the Hamiltonian over the determinantal wave functions are approximated by: (a) expressing part of each matrix element in terms of atomic valence-state energies which are obtained from spectroscopy; (b) parameterizing the interaction between the k shell of carbon and the $1s$ orbital of hydrogen, the parameter being evaluated from the electronic spectrum of CH ; (c) obtaining the interaction energy between the two hydrogen atoms from the

Morse curve for hydrogen; and (d) evaluating the remaining two electron and nuclear attraction integrals using single-term STO's for the carbon 2s and *sp* orbitals. Their results were ${}^3B_1$ (140°) < ${}^1B_1$ (~120°) < ${}^1A_1$ (~110°) with a dissociation energy of 9.25 eV, ${}^3B_1 - {}^1B_1$ separation of 1.5 eV, and ${}^1B_1 - {}^1A_1$ approximately 0.6 eV.

Walsh (2) in his discussion of the geometry of AH₂ molecules suggests that, in the ground state, methylene is probably bent and that the multiplicity depends on the H-C-H angle. He expects that, if the molecule is found to have a large angle, the ground state is probably a triplet, whereas a small angle indicates a singlet ground state. He predicts that the allowed transition ${}^1A_1 \rightarrow {}^1B_1$ will be similar to the α bands of NH₂, and he anticipates a large change in angle in going to the ${}^1B_1$ state. These predictions seem well borne out by experiment (4).

Gallup (15) attempted to ascertain the multiplicity of the ground state by employing a Hückel-like theory. He took an atomic orbital basis consisting of carbon valence orbitals and a 1s on each hydrogen atom. The elements of the Hamiltonian were taken to have the form

$$H_{ij} = [(H_{ii} + H_{jj} - 10.0)S_{ij}]/2 \quad (38)$$

where the diagonal elements H_{ii} were not given but were said to be "empirically determined atomic orbital energies for carbon and hydrogen." Slater orbitals were used to calculate the overlap integrals. The sum of the one-electron energies over the first three spatial MO's is taken as the singlet energy. To estimate the triplet energy, one promotes an electron from the highest filled to the lowest empty MO, takes the sum of the one-electron energies, and then adds -1.3 eV to this sum. The 1.3 eV is the difference between the ${}^3P$ and ${}^1D$ states of free carbon (16) and is taken as a measure of the energy increase in pairing two electrons of opposite spin. Gallup arrives at the conclusion that the triplet state is lower than the singlet for the angles he considered (100°-180°). The energy difference is, of course, never greater than 1.3 eV.

The first *ab initio* calculation in which all integrals were evaluated was carried out by Foster and Boys (17). They consider six STO's on the carbon atom and a 1s orbital on each hydrogen which they form into orthogonal MO's. These MO's are used to define exclusive orbitals, i.e., that orthonormal set of functions which have their centroids of charge as far apart from one another as is possible. Then, for each occupied exclusive orbital they define a set of oscillator orbitals composed of a linear combination of the unoccupied exclusive orbitals. These oscillator orbitals have the

property that the square of the dipole moment matrix elements between them and the corresponding occupied exclusive orbital is a maximum. The variation calculation is carried out over the determinants formed from the exclusive orbitals and single and double replacements of these exclusive orbitals by their corresponding oscillator orbitals. Foster and Boys report that this leads to 128 functions for the ${}^3B_1$ symmetry. They predict the level order ${}^3B_1$ (129°) $< {}^1A_1$ (90°) $< {}^1B_1$ (132°) for all angles between 90° and 180° .

The raw data predict the following separations: ${}^3B_1 - {}^1A_1$, 1.06 eV; ${}^1A_1 - {}^1B_1$, 1.55 eV, and ${}^3B_1 - {}^1B_1$, 2.61 eV. These authors then estimated how well their basis accounted for the correlation energy difference by computing the energy separation between the ${}^1D$ and ${}^3P$ states of atomic carbon. They found an error of 0.82 eV and concluded that their molecular calculations of the ${}^3B_1 - {}^1A_1$ separation is in error by something less than this number. This results in a ${}^3B_1 - {}^1A_1$ separation greater than 0.24 eV (5.5 kcal) but less than 1.06 eV (24 kcal) with the triplet still the ground state.

Padgett and Krauss (18) carried out the first molecular orbital SCF treatment. They used an STO basis with Slater exponents and used the Mulliken approximation (19) for the three-center electron interaction integrals. They predict ${}^3B_1$ (120°) $< {}^1A_1$ (90°) $< {}^1B_1$ (130°) for all angles from 90° to 180° . Because of the small separation between their ${}^3B_1$ and ${}^1A_1$ states, they are reluctant to make a choice as to which is the ground state since the effect of Mulliken approximation could not be assessed.

King and Malli (20) have carried out an MO-CI on linear methylene. They consider the carbon 1s electrons as shielding the nucleus and treat the methylene as a six-electron problem. They use single exponentials for the carbon orbitals and the two hydrogen 1s functions. The atomic orbitals are combined into basis functions for the $D_{\infty h}$ group. Since there are six one-electron functions, one may form $({}^6_3)^2 = 400$ determinants having $S_z = 0$. Of these 400 they neglect those 20 which would place each of the six electrons in a different spatial orbital. The variation calculation is then carried out for states of definite symmetry and spin. The order of the first three states is ${}^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma^+$, in accordance with Hund's rules.

Jordan and Longuet-Higgins (21) used a novel semiempirical approach in considering the electronic structure of AH_2 molecules. They write the total energy as

$$E(\lambda, \theta) = E_A(\lambda) + 2E_H(\theta, \lambda) + 2E_H \quad (39)$$

where λ is a measure of the $2s$ - $2p$ hybridization and θ is the H-C-H angle. $E_A(\lambda)$ is the energy of atom A in the valence state appropriate to the molecular state under consideration, $E_{AH}(\theta, \lambda)$ is the A-H bond energy, and E_H is the energy of an isolated hydrogen atom. The hybrid orbitals defined by λ do not necessarily lie along the line joining the A and H nuclei. For CH₂, $E_c(\lambda)$ is expressed in terms of the energies of the various spectroscopic levels of carbon; $E_{CH}(\theta, \lambda)$ is written as the sum of three exchange integrals $(2s(1)h(2) | 1/r_{12} | h(1)2s(2))$, $(2p(1)h(2) | 1/r_{12} | h(1)2p(2))$, and $(2s(1)h(2) | 1/r_{12} | h(1)2p(1))$, which are not calculated but are given values consistent with the observed energy of formation of CH₄, CH₃, and CH (their energy of formation expression assumes perfect pairing). Minimization with respect to λ at each θ results in ${}^3B_1(180^\circ) < {}^1A_1(105.5^\circ) < {}^1B_1(180^\circ)$. They calculate an energy of formation of $-64,320 \text{ cm}^{-1}$ and

$$\begin{aligned} {}^3B_1(180^\circ) &\longleftrightarrow {}^1A_1(105.5^\circ) = 0.450 \text{ eV} \\ {}^3B_1(180^\circ) &\longleftrightarrow {}^1A_1(180^\circ) = 0.981 \text{ eV} \\ {}^1A_1(105.5^\circ) &\longleftrightarrow {}^1B_1(180^\circ) = 0.981 \text{ eV} - 0.450 \text{ eV} = 0.531 \text{ eV} \\ {}^1A_1(105.5^\circ) &\longleftrightarrow {}^1B_1(105.5^\circ) \cong 1.8 \text{ eV} \end{aligned}$$

Using an approximate equation proposed by Mulliken (22) for the heat of formation of a molecular system, Pedley (23) calculated that the triplet state of CH₂ is more stable than the singlet state. He hybridized the $2s$ and $2p$ orbitals of carbon into four linearly independent functions. The hybridization depends on the H-C-H angle being sp in the linear molecule and passing through sp^2 and sp^3 as the angle is varied. The assumption of perfect pairing is maintained for all angles, and one always has two nonbonding electrons in different spatial orbitals. The difference between the singlet and triplet states, in this theory, is due to a single exchange integral between these nonbonding orbitals. However, this integral was not calculated but was estimated from the atomic spectrum of free carbon.

A most interesting attempt has been a semiempirical approach by Ellison (24). He uses an atomic basis consisting of carbon $1s$, $2s$, $2p_z$, $2p_y$, $2p_x$, and two hydrogen $1s$ functions. The carbon $2s$, $2p_z$, $2p_y$ orbitals are hybridized such that one orbital lies along the C₂ axis, while the other two point directly toward the hydrogen atoms. The $2p_x$ orbital has a node in the molecular plane (b_1 sym). He writes determinantal wave functions for the singlet and triplet B_1 states as well as the first two states of ${}^1A_1$ symmetry. The energy expression for a given structure is reduced to the form

$$E_i = E_{C\bullet} + E_{H_2\bullet} + J + \bar{X} - \bar{Y} \quad (40)$$

where E_{C^*} and E_{H2^*} are the valence-state energies of the carbon and hydrogen atoms, respectively. $\bar{J}$ is proportional to the Coulomb energy, $\bar{X}$ is proportional to the exchange energy which arises from single and multiple permutations of covalently bonded electrons, and $\bar{Y}$ is proportional to the exchange energy involving single permutations of nonbonded electrons. The energy expression contains three undetermined parameters which are fixed by calibrating the theory with the heat of atomization of the $^2\pi$, $^2\Delta$ states of CH and the ground state of CH_4 . The predicted order of the first four states is $^3B_1(180^\circ) < ^1A_1(100^\circ) < ^1B_1(180^\circ) < ^1A_1(180^\circ)$. The estimated vertical transition energies are

$$\begin{aligned} ^1A_1(100^\circ) &\longleftrightarrow ^1B_1(100^\circ) = 4.35 \text{ eV} \\ ^3B_1(180^\circ) &\longleftrightarrow ^1A_1(180^\circ) = 0.92 \text{ eV} [\equiv ^3B_1(180^\circ) \longleftrightarrow ^1B_1(180^\circ)] \\ ^3B_1(180^\circ) &\longleftrightarrow ^1A_1(100^\circ) = 0.62 \text{ eV} \end{aligned}$$

Coulson and Stamper (25) have studied the Rydberg levels in CH_2 which are associated with the carbon $3d$ orbital. They restricted the molecule to the linear configuration and confirmed Herzberg's (4) assignment of the vacuum ultraviolet bands ($^3\Sigma_g^- \rightarrow ^3\Sigma_u^-$ and $^3\Sigma_g^- \rightarrow ^3\Pi_u$) as transitions to essentially Rydberg levels involving the carbon $3d$ electron.

Dixon (26) has carried out a rather extensive study of the $^3B_1$, $^1A_1$, and $^1B_1$ states of methylene as a function of the H-C-H angle. He employed the basis functions and integrals used by Padgett and Krauss (18). Both the VB and ICC (27) methods were employed. For the (limited) VB method, his results are

$$^3B_1(165^\circ) < ^1A_1(\sim 100^\circ) < ^1B_1(\sim 150^\circ)$$

with a $^1A_1 - ^3B_1$ separation of 1 eV, while, for the ICC, he obtains

$$^3B_1(180^\circ) < ^1A_1(105^\circ) < ^1B_1(180^\circ)$$

with a singlet-triplet separation of 0.11 eV.

However, on correcting for using the wrong C-H bond length for the triplet state and estimating the effect of a bad parameter choice, the singlet-triplet separation is estimated as 0.0 to 0.6 eV.

Recently, Hoffman *et al.* (6) applied the extended Hückel method to a series of methylenes among which was the parent compound, methylene. The criterion for assigning the ground-state multiplicity was the same as Gallup's. The triplet was taken as the ground state if the sum of the one-electron energies of the lowest singly excited configuration was not greater

than the comparable sum for the lowest doubly occupied configuration by more than 1.5 eV (recall that Gallup used 1.3 eV). A triplet state with a very shallow minimum at about 155° and a highly bent singlet with an angle around 115° are predicted. Detailed discussion of the $^3B_1 - ^1A_1$ separation in the theory is meaningless.

Harrison and Allen (5) constructed valence bond wavefunctions for the first three states of CH₂ for several angles. They deduce the order

$$^3B_1(138^\circ) < ^1A_1(108^\circ) < ^1B_1(148^\circ)$$

with a very large energy separation (1.77–2.10 eV) between the $^3B_1$ and $^1A_1$ states. This calculation is a complete configuration interaction within the valence shell, and the high singlet–triplet separation seems to have its origin in the inadequacy of the atomic orbital basis to account for the correlation energy in the $^1A_1$ state. This basis (28) was of Hartree-Fock quality for the isolated atoms but did not adequately allow for polarization in the molecular environment.

Meyer (29) has carried out extended Hartree-Fock calculations for CH₂ as a function of angle and bond length. His results are

$$^3B_1(1.076 \text{ \AA}, 135^\circ) < ^1A_1(1.105 \text{ \AA}, 103^\circ) < ^1B_1(1.068 \text{ \AA}, 147^\circ)$$

with a singlet–triplet separation of 1.16 eV. With an estimation of a correlation correction, he reduces his estimate of the separation to 0.74 eV (17 kcal).

In a recent calculation, Harrison (3) constructed the MO-SCF solution for the lowest $^1A_1$ state. The energies of the $^3B_1$, $^1B_1$ states were determined by using the b_1 orbital generated in an MO-SCF calculation for the first excited $^1A_1$ state [configuration $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$]. This eliminates the virtual orbital effect discussed in Section I,D as a possible major deficiency. The results are

$$^3B_1(132^\circ) < ^1A_1(105^\circ) < ^1B_1(>150^\circ)$$

The potential curves are displayed in Fig. 7. The raw numbers would indicate a singlet–triplet separation of 1.22 eV, but when coupled with our estimate of the correlation energy effect, they yield a probable separation greater than 0.22 eV (5 kcal) but considerably less than 1.22 eV (27 kcal). These results are very similar to those of Foster and Boys (17) and Meyer (29). In addition, Harrison (3) has constructed a configuration interaction representation of the various states which predicts the order of the states given above with essentially the same geometry but with a singlet–triplet separation of 19 kcal.

Bender and Schaeffer (29a) have constructed (via extensive configuration interaction) the most accurate representation of the triplet ground state to date and predict a bond angle of 135° and a bond length of $1.096 \text{ \AA}$.

Allen and Franceschetti (29b) have constructed molecular orbital wavefunctions for both the $^3B_1$ and $^1A_1$ as a function of angle and basis set. Their most extensive calculation (with d orbitals on carbon) predicts

$$^3B_1 (126^\circ) < ^1A_1 (101^\circ)$$

with a singlet triplet separation of 25 kcal. These authors estimate that this separation would be lowered to 11 kcal/mole if one corrected for electron correlation, and it is abundantly clear that the singlet-triplet separation in CH_2 is dominated by the differential in the electron correlation energy.

III. USE OF EXTENDED HÜCKEL THEORY IN THE ELUCIDATION OF CARBENE STRUCTURE

A. Applicability

In the EHT(30) one defines the energy associated with a particular MO as an eigenvalue ε of the secular equation

$$|H_{ij} - S_{ij}\varepsilon| = 0 \quad (41)$$

There are as many eigenvalues as there are atomic orbitals in the problem, and the total energy of the molecule is taken as the sum of the molecular orbital energies for the occupied MO's. The Hamiltonian matrix elements H_{ij} are parameterized in terms of the corresponding overlap integral S_{ij} and a number akin to an ionization potential for the i th and j th atomic orbitals. A most remarkable conclusion that we are being drawn toward is that this very simple technique is capable of simulating many aspects of *ab initio* molecular electronic structure theory, although not so many as to warrant its indiscriminate use for any problem (31). It still remains a tool to be used very cautiously and with a good deal of chemical common sense.

One of the most widely heralded failings of this technique is that it does not distinguish between different states of the same configuration. So, in the current context, EHT would say

$$^3E(\sigma p) - ^1E(\sigma p) \equiv 0 \quad (42)$$

This would seem to preclude applying EHT to elucidate carbene structure except for the existence of Eq. (37). This inequality says that, given an estimate of $K_{\sigma p}$, we may estimate the possibility of a singlet or triplet ground state by considering the energy difference between two closed-shell singlet configurations. These are precisely the type of states for which experience indicates that the EHT is somewhat reliable. This fact was used by Hoffmann *et al.* (6) in their investigation into the electronic structure of carbenes.

B. Hoffmann's Procedure

1. Preliminaries

In the EHT the energy difference, $E(\sigma^2) - E(p^2)$ becomes $2(\varepsilon_\sigma - \varepsilon_p)$, where ε_σ and ε_p are the Hückel molecular orbital energies. Note that since, in EHT,

$$\varepsilon_\sigma - \varepsilon_p \equiv E(\sigma^2) - E(\sigma p) \quad (43)$$

the inequality (37) becomes

$$|E(\sigma^2) - E(\sigma p)|/K_{\sigma p} > 1.8 \quad (44)$$

Hoffmann actually employed the empirical criterion

$$|E(\sigma^2) - E(\sigma p)| > \sim 1.5\text{--}2.0 \text{ eV} \quad (45)$$

but, since $K_{\sigma p}$ is often of order 1 eV, the empirical and theoretical criteria are usually equivalent.

2. Definition of p_o and p_i Orbitals

We shall refer to the σ and p orbitals in the linear configuration of a carbene as p_o (for out of plane) and p_i (for in plane). Figure 11 illustrates the distinction with methylene and phenylmethylene. In methylene the choice is irrelevant because p_o and p_i are degenerate, while in phenylmethylene the orbital in the plane of the benzene ring (p_i) is significantly different from the orbital perpendicular to this plane (p_o). Which of the two, p_o or p_i , becomes σ or p as the molecule is bent is immaterial when p_o and p_i are degenerate but depends on the mode of bending when these two orbitals are distinguishable. For example, if we bend phenylmethylene in plane, $p_o \rightarrow p$ and $p_i \rightarrow \sigma$, while bending out of plane induces the correspondence $p_o \rightarrow \sigma$, $p_i \rightarrow p$.

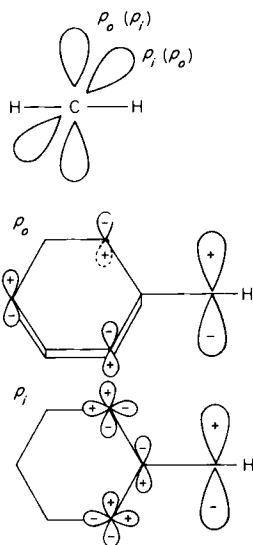


FIG. 11. Distinction between p_o and p_i (methylene and phenylmethylene).

3. Generalizations from EHT of importance in Carbene Structure Considerations

The detailed results of EHT for a particular carbene may be anticipated from the following generalizations.

a. The p orbital in the linear carbene which goes into the σ orbital on bending always becomes more stable, i.e., ϵ_σ decreases. This stabilization is a consequence of the increased s character in this "lone pair-like" orbital and was noted in the discussion of the $3a_1$ MO of methylene in Section I.

b. On the other hand, the p orbital in the linear carbene which goes into the p orbital on bending is often little affected, i.e., $\epsilon_p \sim \text{constant}$. For example, the $1b_1$ orbital of CH₂ remains essentially inviolate for all values of the H—C—H angle.

c. There exists a b_2 -like orbital in a bent carbene, similar to that in CH₂, which increases in energy rather dramatically as the carbene is bent. Recall that in our discussion of the $1b_2$ orbital in CH₂ we interpreted the increase of this orbital energy with bending as the result of bond-bond repulsion. This interpretation accounts for the universality of the existence of this orbital.

d. The remaining MO's in a carbene need not enter the discussion.

The total EHT energy of a carbene is the sum of the occupied MO energies weighted according to their occupancy. The $E(\sigma^2)$ configuration usually decreases with bending because the increased stability of the σ MO outweighs the decreased stability due to bond-bond repulsion. However, if we now remove an electron from the σ MO and place it in the p MO, we may no longer be able to contain the energy rise due to the bond-bond repulsion. The result of this tradeoff is that the energy, $E(\sigma p)$, changes slightly with bending until the carbene is sufficiently bent for the bonds to interact significantly, at which time the energy increases rapidly. The p^2 configuration has no electron in the σ orbital, and there is nothing to prevent the repulsions from dominating even at small deviations from linearity. The energy $E(p^2)$ invariably increases rapidly with bending.

4. Results and Predictions of EHT

In discussing the results of EHT it is convenient to classify carbenes according to the relative values of p_o and p_i .

a. p_o and p_i Equivalent. Carbenes in this class are cylindrically symmetric, or effectively so. A typical example is linear CH_2 , and the energetics as predicted by EHT for this molecule are presented in Fig. 12. Note that, since the σ^2 and σp curves are never more than 1 eV apart for angles $> 110^\circ$, we expect the triplet component of the σp configuration to be the ground state and anticipate an angle of 155° (recall that the *ab initio* predictions range from 130° to 140°). Molecules in this class which have been studied by Hoffmann *et al.* (6) include $\text{H}-\text{C}-\text{CH}_3$, $\text{CH}_3-\text{C}-\text{CH}_3$, $\text{H}-\text{C}=\text{C}=\text{C}-\text{H}$, $\text{N}\equiv\text{C}-\text{C}-\text{H}$, $\text{N}\equiv\text{C}-\text{C}-\text{C}\equiv\text{N}$, and the halocarbenes. All have potential energy curves exhibiting the same general behavior as CH_2 , differing only in the σ^2 , σp energy gap. The predictions of EHT for these molecules (with the exception of the halocarbenes which are discussed in Section IV) are summarized in Table I.

Olsen and Burnelle (32) have employed the EHT as well as the INDO method in a study of CCO and $(\text{NC})_2\text{C}$ and find that both methods predict linear triplet ground states for both molecules.

b. p_o and p_i Not Equivalent. Consider a case in which p_i is slightly higher than p_o . As we bend the carbene in plane, p_i becomes σ and is stabilized while p_o becomes p and is affected only slightly. Since we have assumed that the separation between p_o and p_i is small, we expect the two levels to intersect at some angle.

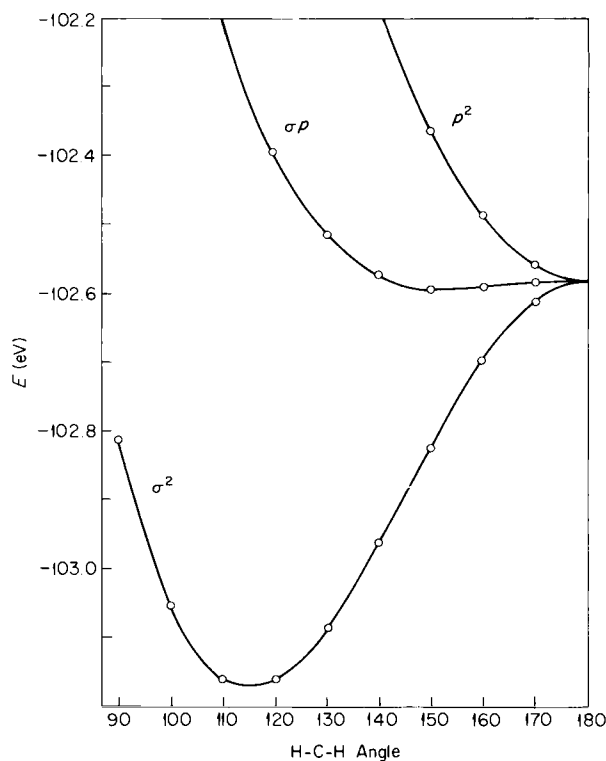
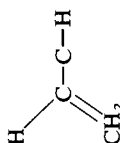
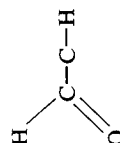
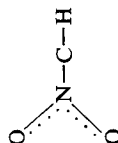
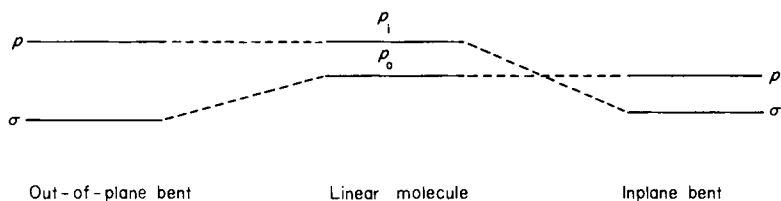


FIG. 12. CH_2 energies in extended Hückel theory. Reprinted from *J. Amer. Chem. Soc.* **90**, 1485 (1968). Copyright 1968 by the American Chemical Society. Reprinted by permission of the copyright owner.

The σ orbital in the bent molecule will trace its lineage to the p_i orbital of the linear molecule. If we consider out-of-plane bending, p_o becomes σ and is stabilized further while p_i becomes p and is unaffected. In this instance the σ orbital in the bent carbene will trace its lineage to the p_o orbital of the linear molecule. These two modes are represented schematically in Fig. 13. We anticipate that the in-plane triplet will be lower than the out-of-plane triplet, since the p orbital in the σp configuration arising from the in-plane bending traces its lineage to the more stable p_o orbital. The geometry of the lowest singlet may be anticipated by noting that a p_o orbital is stabilized in an out-of-plane bending mode to a lesser extent than a p_i orbital is stabilized in an in-plane bending mode. This is so because

TABLE I
Predictions of Extended Hückel Theory (δ)

Molecule	ϵp_o (eV)	ϵp_i (eV)	Lowest singlet	Lowest triplet	Predicted ground state
CH ₂	-11.40	-11.40	Bent, 115°	Bent, 155°	Triplet
CH ₃ -C-H	-11.00	-11.00	Bent, 116°	Bent, 146.5°	Triplet
CH ₃ -C-CH ₃	-10.63	-10.63	Bent, 121.5°	Bent, 143.0°	Triplet
ϕ -C-H	-11.08	-10.90	Bent, in plane 115°	Bent, in plane 143°	Triplet
ϕ -C- ϕ	N.G.	N.G.	Bent, out of plane 134°	Bent, in plane 165°, then twist about each ϕ -C bond 45°	Triplet
	-11.16	-11.00 +	Bent, in plane 115°—methylene H either cis or trans relative to vinyl group	Bent, in plane 140°—methylene H is cis to vinyl group	Triplet
	-12.13	-11.21	Linear	Bent, in plane, trans 140°	Possibly a singlet
	-12.09	-11.15	Bent, out of plane 125°	Bent, in plane 130°	Triplet
NC-C-H	-11.73	-11.73	Bent, 126°	Linear	Triplet
(NC) ₂ C	-11.93	-11.93	Bent, 140°	Linear	Triplet
HCC-C-H	-11.16	-11.00	Bent, 126°	Linear	Triplet

FIG. 13. Influence of bending when p_o is slightly higher than p_i .

the p_o stabilization comes about because of an increase in s character with a concomitant decrease in overlap with the π system of the attached substituent. On the other hand, the p_i stabilization comes about solely because of increased s character with no concomitant loss of stability. Thus we expect an in-plane bent σ^2 carbene as the lowest singlet. The detailed EHT results

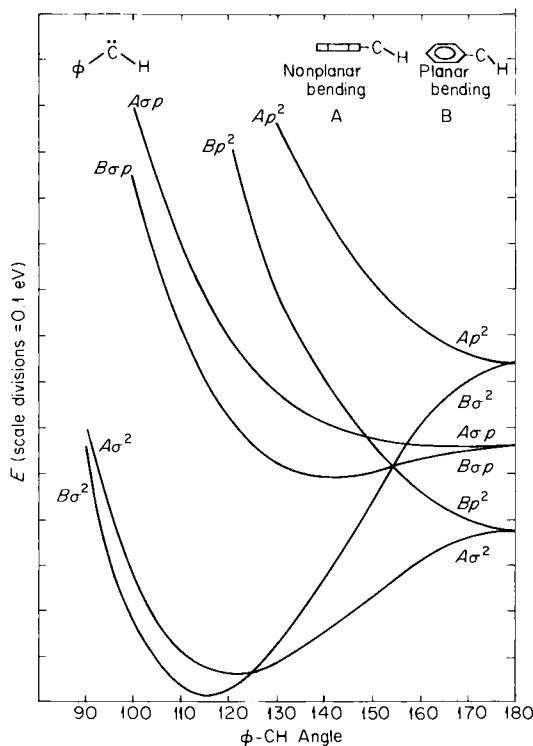


FIG. 14. Phenylmethylene energies in extended Hückel theory. Reprinted from *J. Amer. Chem. Soc.* **90**, 1485 (1968). Copyright 1968 by the American Chemical Society. Reprinted by permission of the copyright owner.

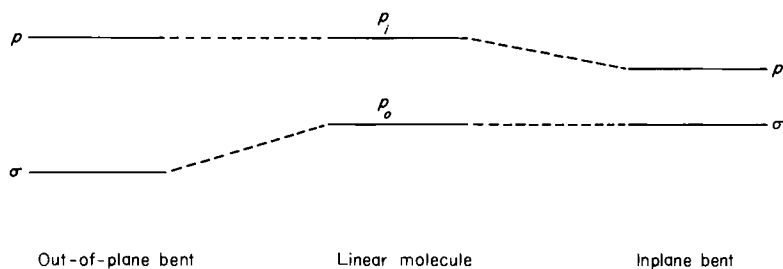


FIG. 15. Influence of bending when p_o is much higher than p_i .

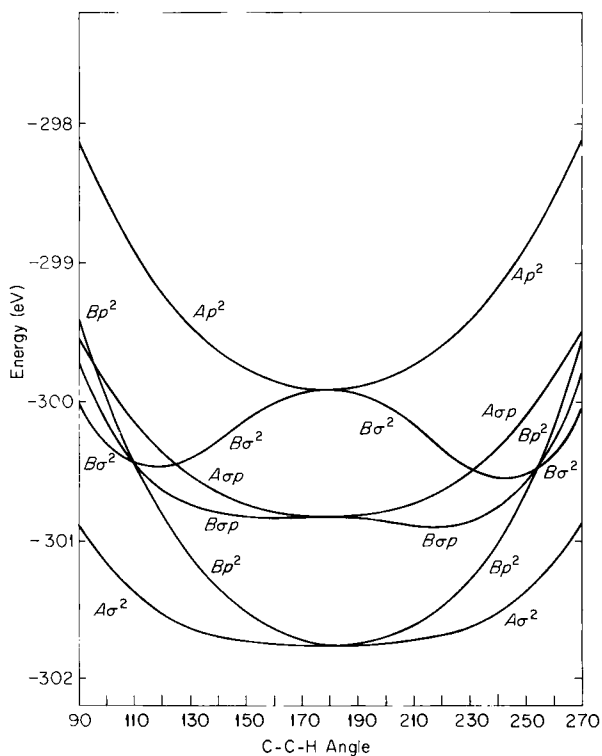


FIG. 16. Formylmethylene energies in extended Hückel theory. A = out-of-plane. B = in-plane. Reprinted from *J. Amer. Chem. Soc.* **90**, 1485 (1968). Copyright 1968 by the American Chemical Society. Reprinted by permission of the copyright owner.

for phenylmethylene illustrate this behavior and are presented in Fig. 14. From the detailed calculations we would predict a triplet ground state. Vinylmethylene is expected to behave in a similar manner, whereas diphenylmethylene is complicated by steric effects (6),

An interesting situation arises if the p_o orbital is much lower than the p_i orbital. In this case, the possibility arises that the p_i orbital may never be stabilized sufficiently by in-plane bending to intersect the p_o level. This situation is schematically represented in Fig. 15. We anticipate an out-of-plane singlet and an in-plane triplet both arising because of the extraordinary stability of the p_o orbital. Hoffmann *et al.* (6) offered formylmethylene and nitromethylene as examples of this case. The detailed EHT results for formylmethylene are presented in Fig. 16. These numerical results suggest the possibility of a singlet ground state.

IV. HALOCARBENES

The theoretical work on halocarbenes is recent and limited almost exclusively to CF_2 and HCF . In 1965, Simons (33) used a semiempirical technique due to Green and Linnett (34) (essentially a slightly different parameterization of EHT) and studied the electronic structure of FCF . Only the $2p$ orbitals of fluorine and the $2s$ and $2p$ orbitals of carbon were used to construct the molecular orbitals. Overlap integrals and resonance integrals between nonadjacent atoms were taken to be zero. With these rather drastic approximations the input to the calculation consists of:

- a. the difference between the Coulomb integrals for the carbon $2s$ and $2p$ orbitals (estimated from spectroscopic data on free carbon) and between the carbon $2p$ and fluorine $2p$ orbitals (taken as proportional to the Pauling electronegativity difference with the constant of proportionality fixed by Green's and Linnett's estimate of the difference between the nitrogen and oxygen coulomb integrals);
- b. resonance integrals connecting the carbon and fluorine $2p$ orbitals; these integrals are estimated by parameterizing the $B \leftarrow X(^2\pi)$ transition of CF and correcting for the different bond lengths by assuming that the resonance integral is proportional to the respective overlap integral;
- c. the $\text{C}-\text{F}$ bond length which is taken as 1.32 Å and the $\text{F}-\text{C}-\text{F}$ angle, taken as 110° .

The end product of this calculation is a series of molecular orbital energies which are to be interpreted as in the EHT. The highest occupied MO is $5a_1$, (i.e., σ) and the lowest empty is $2b_1$ (i.e., p), with an energy

separation of 4.2 eV. This large spacing augurs of a $^1A_1$ ground state with a first excited state of $^3B_1$ symmetry. Simons presents qualitative arguments for CCl_2 and CBr_2 having singlet-triplet separations similar to CF_2 . Unfortunately there was no geometry search in this calculation.

Hoffmann *et al.* (6) have studied the halo- and dihalocarbenes using EHT, and their results are presented in Table II. These data indicate that

TABLE II
Extended Hückel Theory Predictions for Halocarbenes (6)

Molecule	$E(\sigma p) - E(\sigma^2)$ (eV)	Bond angle	
		Lowest singlet	Lowest triplet
CF_2	3.6	98°	108°
CCl_2	1.8	112°	124°
CBr_2	1.4	114°	126°
CHF	1.6	103°	116°
CHCl	1.1	110°	129°
CHBr	1.0	111°	131°

CF_2 and most likely CCl_2 , CBr_2 , and CHF would be ground-state singlets. This is in accord with the spectroscopic data available for HCF (35) and CF_2 (36). Also, whereas EHT suggests that HCCl and HBr may have triplet ground states, spectroscopic evidence (37) indicates that HCCl is a ground-state singlet. This apparent exception to Eq. (44) may be rationalized in terms of the inadequacy of the halogen parameters in this application of EHT or by a value of $K_{\sigma p}$ significantly smaller than 1 eV or, as is most likely, a combination of these.

Sachs *et al.* (38) studied CF_2 using an *ab initio* LCAO-MO-SCF technique. They employed Gaussian basis sets of various sizes and studied the lowest $^1A_1$ state. With the experimental bond length of 1.30 Å (36) they computed an equilibrium angle of 105.8° (experimental value 104.9°). The MO sequence corresponding to the lowest $^1A_1$ state is found to be $(1b_2)^2(1a_1)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(5a_1)^2(1b_1)^2(4b_2)(1a_2)^2(6a_1)^2$, the $2b_1$ being the first virtual orbital. These authors felt that the differences in the geometry of the lowest $^1A_1$ and the $^1B_1$ state (F-C-F angle = 122.3°, $R_{\text{CF}} = 1.32$ Å) (36) precluded any meaningful estimate of the $^1B_1$ and $^3B_1$ energies using the $^1A_1$ virtual orbitals.

TABLE III^a
Ab Initio Results^b for CH₂, FCH, CF₂

Molecule	¹ A ₁		³ B ₁		¹ B ₁	
	θ	Energy (au)	θ	Energy (au)	θ	Energy (au)
CH ₂	105° (102.4°)	-38.85831	132.4° (~ linear)	-38.90306	>150° (140 ± 15)	<-38.83874
FCH	103° (101.8°)	-137.72451	123.5° (?)	-137.70045	127° (127.2°)	-137.63256
CF ₂	105° (104.9°)	-236.60744	120° (?)	-236.52784	122.5° (122.3°)	-736.42522

^a Experimental numbers are in parentheses.

^b Harrison (3). Bond lengths employed: CH₂, ¹A₁ (1.11 Å) ^{1,3}B₁ (1.05 Å); FCH, R_{CF} - 1.30 Å, R_{CH} = 1.12 Å for all states; FCF, R_{CF} - 1.30 Å for all states.

Harrison (3) has constructed an MO-SCF function for the lowest singlet state of FCF and HCF as a function of angle. The lowest-lying triplet and its companion singlet were constructed using the virtual orbitals from the lowest singlet. The results are shown in Table III. This calculation substantiates the experimental evidence supporting ground-state singlets for both CF₂ and HCF. Harrison also reports more extensive configuration interaction results which predict a singlet-triplet separation of 39 kcal for CF₂ and approximately 0 kcal for HCF.

V. CHARGE DISTRIBUTION

We will attempt to develop insight into the significance of the charge on the carbene carbon by considering first the charge distribution in the sequence CH₂, CHF, and CF₂. These molecules are described in detail by Harrison (3), and we limit ourselves to the highlights of his discussion. The MO's for these three molecules were constructed for the lowest singlet state at 105°, using the experimental bond length, and were then subjected to a Mulliken population analysis. The more relevant part of this analysis is presented in Table IV. This table shows the total charge on a given atom, the distribution of the two electrons in the σ lone pair, and the distribution of the electrons in the π system. We note that the positive charge on the carbene carbon increases almost linearly with F substitution, and contri-

TABLE IV

Some Aspects of the Charge Distribution in CH_2 , FCH , and CF_2 (3)

	$\text{CH}_2(105^\circ)$		$\text{FCH}(105^\circ)$			$\text{CF}_2(105^\circ)$	
	C	H	C	H	F	C	F
Q	-0.10	+0.05	+0.16	+0.12	-0.28	+0.53	-0.26
σ	1.84	0.08	1.64	0.18	0.18	1.64	0.18
π	0.00	0.00	0.14	0.00	1.86	0.24	1.88

buting to this loss of electrons from C is the increased delocalization of the σ orbital in the halocarbenes compared to that in CH_2 . Also, as the σ electron leaves the carbon, there is an influx of π electrons from the fluorines.

With these results in mind, we recall that the electrophilic character of singlet carbenes has been associated in the experimental literature (39, 40) with the existence of an almost empty p orbital on the carbene carbon. This contention has recently received support from extended Hückel calculations of Hoffmann *et al.* (41) on the dimerization of CH_2 . These authors find that one CH_2 utilizes its empty p orbital to initiate the attack on the electron-rich lone pair of the second CH_2 , and the system subsequently follows a minimum energy path, involving no activation energy to form ethylene in its ground electronic state (the lack of activation energy is due of course to the constraint of a fixed geometry along the reaction coordinate). If this, or a comparable, mechanism is operative in the addition of carbenes to olefins, then the electrophilic character within a series of carbenes would be governed not so much by the total charge on the carbene carbon as by the charge in the carbon p orbital. This is so because a considerable contribution to the formal charge on the carbene carbon comes from the polarity of the C—R bonds, and to the extent that these bonds are not broken in a reaction this charge should not dictate the course of the reaction.

In the sequence CH_2 , CHF , and CF_2 the carbene carbon becomes increasingly positive, and yet we would predict, on the basis of the occupancy of the carbon p orbital, that the electrophilicity should decrease with increasing fluorination. Furthermore, since the electronegativity of the halogens decreases as we go down the series from F to I, we would expect less charge transfer in the σ system and consequently less transfer

from halogen to carbon via the π system. We would then expect the occupancy of the carbon p orbital to decrease in the sequence CF_2 , CCl_2 , CBr_2 , Cl_2 , CH_2 , and so would anticipate an increase in the electrophilic character as we proceed from CF_2 to CH_2 . This order was first predicted by Simons (33), and there is some evidence that it is the experimental order (40).

The change in the occupancy of the carbene p orbital in going from CH_2 to CF_2 is slight, and therefore the difference in their electrophilic character is slight. Gleiter and Hoffmann (42) have examined molecules in which the change in chemical character is more dramatic. Consider, for example, cyclopropylcarbene [1]. According to EHT the charge on the carbene carbon, is -0.21 and, since this is expected to be localized in the



[1]

σ system and is of the same magnitude as the corresponding number in CH_2 , we expect this molecule to behave as an electrophile. If we now remove two hydrogen atoms to form cyclopropene carbene [2], rather



[2]

drastic changes ensue. The carbon p orbital now participates significantly in the lowest doubly occupied π orbital and, since the σ (lone-pair) orbital is also occupied (a σ^2 carbene), we have no "almost empty" orbitals on the carbene carbon suitable for initiating an electrophilic attack and so anticipate nucleophilic behavior. EHT associates a charge of -0.68 with the carbene carbon.

As another example, consider the carbene in structure [3]. Ignoring for



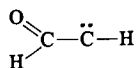
[3]

the moment the two electrons from the carbene carbon and noting that

each nitrogen contributes two electrons to the π system, we have six π electrons in a five-membered ring. By analogy with the cyclopentene MO's we anticipate that the two empty π MO's are antibonding and so expect the electrons from the carbene carbon to go into the stabilized σ orbital, which is probably largely localized on carbon.

The carbene carbon receives charge from the participation of its p orbital in the occupied π MO's and also because of the occupancy of the σ lone pair. We expect the σ MO's (bonding and lone-pair) to lose electron density to the nitrogen (electronegativity effect) and thus increase the charge transfer from nitrogen to carbon via the π system. A rather nucleophilic carbene is expected, and EHT associates a charge of -0.43 with this carbene carbon. Adding two hydrogen atoms to carbene (3) (forming 3,5-diazocyclopentene) results in a charge of $+0.50$ on the central carbon atom, illustrating the profound effect of the π system on the nucleophilic reactivity of the carbene.

As an example of an electrophilic carbene, these authors suggest (linear) formylcarbene [4]. As discussed in Section III, B,4, this is a p^2 carbene and



[4]

consequently its σ orbital is formally empty and would be used in attacking an electron-rich species. A population analysis of the extended Hückel wavefunction associates a charge of $+0.33$ with the carbene carbon.

Gleiter and Hoffmann (42) summarize their analysis with the useful rule: σ^2 carbenes attached to a π electron system are nucleophilic, and p^2 carbenes are electrophilic.

VI. CONCLUSIONS

Although carbenes are of considerable importance in chemical theory, with the exception of CH_2 they have attracted little attention from the theoretical chemist until rather recently. The few *ab initio* studies carried out to date indicate that the prediction of the geometry in the ground and low-lying excited states is reliable and, although the relative order of these states seems to be predictable, there is still considerable difficulty in calculating the precise value for the singlet-triplet separation. This difficulty may be traced to the nonuniform treatment of electron correlation in the

two states, a recurring problem in most theoretical discussions of electronic structure.

Our increasing ability to treat small organic molecules (carbenes in particular) on an *ab initio* level will have a profound effect on organic chemistry. The detailed information obtainable from these calculations, such as the charge distribution from reliable contour maps or population analysis, will require that we formulate our qualitative ideas with the understanding that they must bear up under scrutiny at a most fundamental level.

The significance of the role played by semiempirical theories cannot be overstated. The ability of these techniques to capture a large part of the essence of an intricate problem coupled with the technical ease of performing such studies augurs well for their continued usefulness.

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The Spectra of Carbenes

OBSERVATION AND ANALYSIS of the spectra of carbenes is extremely important as a source of structural information, and may also serve as an unequivocal demonstration of carbene intermediates in methylene transfer reactions. As a consequence of the high reactivity of carbenes, their spectra have rarely, if ever, been obtained under the conditions of chemical transformation. Nevertheless, the fact that spectroscopically identifiable carbenes may be obtained from certain carbene precursors under "special conditions" lends some credit to the assumption that the same method will also produce carbenes in the presence of reactants. The "special conditions" referred to are: (i) flash photolysis of dilute gaseous systems, and (ii) matrix isolation, i.e., the generation of carbenes in rigid matrices (crystals or glasses) at low temperatures, conditions under which the carbenes are quite stable. Gas phase studies have been used for the simplest structures such as methylene and the halocarbenes whereas the matrix isolation technique has been applied to more complicated carbenes.

I. ELECTRONIC AND VIBRATION-ROTATION SPECTROSCOPY

A. Methylene

After a prolonged search, Herzberg and Shoosmith (*1*) were able to obtain the absorption spectrum of methylene on flash photolysis of diazomethane at low pressure using a high-resolution spectrograph. Isotopic substitution of both hydrogen and carbon established beyond doubt that methylene was the carrier of the spectra. Absorption at 1415 Å was favored at high pressures of nitrogen, whereas a band at 5500–9500 Å showing rotational fine structure was more prominent at high ratios of diazomethane to nitrogen. The results indicate a metastable species

absorbing fairly strongly in the red region of the visible spectrum and weakly in the near ultraviolet (3000–3500 Å), and the true ground state of methylene giving rise to a spectrum in the vacuum ultraviolet region. It appears that the metastable state is produced first and then decays to the ground state on collision with inert gas molecules such as nitrogen.

Complete analysis of the spectra indicated the molecular dimensions (2, 3). The metastable state is highly bent, with a bond angle of 102° and a C—H bond length of 1.12 Å. The metastable species almost certainly should be identified as the $^1A_1$ (lowest singlet) state of methylene and the 5500–9500 Å absorption associated with the $^1A_1 \rightarrow ^1B_1$ transition. The ground state appears to be linear or nearly linear with a C—H bond length of 1.07 Å. Although the triplet splitting in the spectrum of the ground-state molecule was not observed, the state is believed to be $^3\Sigma_g^-$, and the transition is thought to be $^3\Sigma_g^- \rightarrow ^3\Sigma_u^-$. Unfortunately, the spectral data provide no answer to the interesting question of the energy difference between singlet and triplet states.

Attempts to preserve methylene for spectroscopic observation by matrix isolation (4–7) have led to ambiguous results. Diazomethane has been irradiated in argon, nitrogen (4–6), and perfluoroether matrices (6) at 20°K. Alternatively, irradiation was carried out during codeposition of diazomethane and krypton at 4.2°K (7). The spectra of the matrices obtained by the two techniques were extraordinarily different. Although some of the new bands disappeared on warming, none could be assigned to methylene with any conviction.

B. Halocarbenes

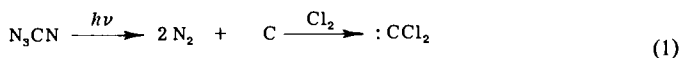
The emission spectrum of an excited state of difluorocarbene, obtained by electric discharge through CF_4 , was the first authenticated spectroscopic observation of a carbene (8, 9). Absorption by the ground state of the species was reported almost simultaneously (10). Analysis of the early spectral data (11) led to the conclusion that the upper limits of the F—C—F angle in the lower and upper states were 110° and 120° , respectively, and that the ground state must be a singlet. More recent studies used flash photolysis of difluorodibromomethane (12) and trifluoromethylphosphines (13) as well as discharge techniques (14, 15). The considerable stability of difluorocarbene, compared to that of methylene, is obvious from its decay period of 4–10 msec, depending on the precursor and its pressure (14). An analysis of one of the absorption bands of difluorocarbene (2540 Å) based

on rotational fine structure led to the following molecular dimensions: $r_{\text{C-F}}$ 1.30 Å, F-C-F angle 104.9° (15). The microwave spectrum of difluorocarbene produced in fluorocarbon discharges was in agreement with the deductions from UV data (16). The absence of fine structure and observable Zeeman shifts in the microwave spectrum confirms the singlet ground state of difluorocarbene.

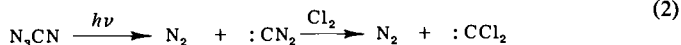
Isolation of difluorocarbene in an argon matrix was achieved by condensing the products of a discharge through C_4F_8 -Ar mixtures on a surface cooled by liquid helium (17). The UV absorption of the trapped species corresponded to that of gaseous CF_2 . At low temperature (4 – 20°K), infrared studies of the photolysis products of difluorodiazirine in inert matrices yielded the three vibrational fundamentals of CF_2 at 668, 1102, and 1222 cm^{-1} (18). Detection of the stretching fundamentals of $^{13}\text{CF}_2$, present in natural abundance, has permitted an estimate of the F-C-F angle ($\sim 108^\circ$).

Absorption spectra of fluorocarbene (19) and chlorocarbene (20) have been obtained by flash photolysis of fluorodibromomethane and chlorodibromomethane, respectively. HCF showed a long progression of absorption bands in the region 4300–6000 Å, HCCl in the region 5500–8200 Å. Observation of chlorine and deuterium isotope shifts, together with the rotational analysis, showed that the carrier of the bands was chlorocarbene with a ground-state H-C-Cl angle of $\sim 103^\circ$, $r_{\text{C-H}}$ 1.12 Å, and $r_{\text{C-Cl}}$ 1.69 Å (20).

Matrix isolation has so far been the favored technique for dichlorocarbene. Milligan and Jacox (21) photolyzed cyanogen azide in an argon matrix in the presence of chlorine molecules and reported absorption at 748 and 721 cm^{-1} which they assigned to dichlorocarbene made by the reaction of photolytically produced carbon atoms with chlorine:



or



Andrews (22) obtained similar absorptions (745.7 and 719.5 cm^{-1}) when molecular beams of lithium atoms and carbon tetrachloride at high dilution in argon were simultaneously condensed on a salt window at 15°K . The agreement of the IR data, using different methods of production, conclusively supports the validity of their assignment to CCl_2 . Normal-coordinate calculations gave a Cl-C-Cl bond angle of $100 \pm 9^\circ$. Since the

C—Cl frequencies are similar to those in dichloromethane, it has been suggested that there is no appreciable amount of electron donation to the electron-deficient carbon atom (23) (cf. Chapter 5, Section V). On warming the argon matrix to 40°K, the absorption of dichlorocarbene disappeared completely, while absorptions due to tetrachloroethylene appeared. It is not surprising, therefore, that CCl_2 was not detected when the products of chlorocarbon pyrolyses were condensed at 83°K (24).

C. Arylcarbenes

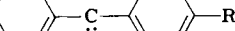
The divalent carbon intermediates prepared by the low-temperature photolysis of aryldiazomethanes in a suitable inert matrix have been identified as ground-state triplet molecules by their ESR spectra (Section II). More recently the optical spectroscopy of these species has been developed by correlating ESR studies, fluorescence, fluorescence excitation, and absorption measurements.

The emission of diphenylcarbene consists of a broad band (λ_{max} 480 nm) with a shoulder at longer wavelength (~ 510 nm). The same spectrum was obtained for all excitation wavelengths in the range 230–470 nm (25). The intensity of the 480-nm emission correlated linearly with the intensity of the low-field ESR absorption of diphenylcarbene. The emission spectrum is different from that of other possible products of the photolysis of diphenyldiazomethane (e.g., benzophenone, tetraphenylethane, tetraphenylethylene, diphenylmethyl radical, and benzophenone azine), and it disappeared on warming the photolyzed matrix.

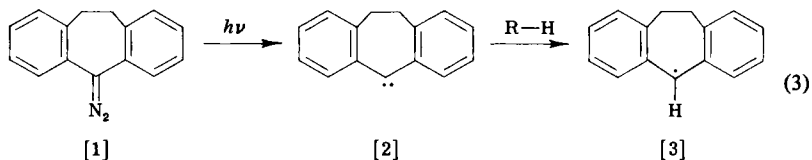
The absorption spectrum of a photolyzed sample of diphenyldiazomethane showed the same bands (300 and 465 nm) as the fluorescence excitation spectrum of diphenylcarbene (25). When a known concentration of diphenyldiazomethane was destroyed quantitatively, the following minimum extinction coefficients were estimated: ϵ 25,000 (300 nm) and 300 (465 nm). There is a qualitative resemblance between the spectra of diphenylcarbene and those of the diphenylmethyl radical (absorption maxima at 336 and 515 nm). This suggests that the π systems of both species are similar (13π electron odd-alternant hydrocarbon radicals), and that the second unpaired electron of diphenylcarbene is not involved in the transitions.

Polarization studies have been made by observing the long-wavelength absorption band of diphenylcarbene oriented in single crystals of 1,1-diphenylethylene (26). It was found that only light which was polarized

Data obtained from substituted diphenylcarbenes are collected in Table I. The maxima of both the absorption and emission bands were

		Absorption maxima (nm)	Emission maximum (nm)
H	H	300, 465	480
Cl	H	311, 475	487
Br	H	316, 475	488
CH ₃	H	301, 472	487
OCH ₃	H	335, 345 ^a	495
NO ₂	H	265, 370, 555	No emission
Ph	H	355 ^a	555
OCH ₃	OCH ₃	335–345 ^a	507

Moritani *et al.* (27, 28) have obtained the electronic spectrum of 10,11-dihydrodibenzo[*a,d*]cycloheptenylidene [**2**] (λ_{max} 510 nm) by photolysis of the corresponding diazo compound [**1**] in a variety of rigid matrices at 77°K (27), and also in liquid paraffin at room temperature (28). Under these conditions the spectrum of [**2**] was observed at delay times of 3–50 μsec after the photolysis flash. The decay of [**2**] was accompanied by the appearance of a long-lived transient spectrum which was assigned to the radical [**3**].



D. Ethynylcarbenes

The flash photolysis of diazopropyne in the gas phase provided a very strong absorption spectrum of C_3 . Below 370 nm, the C_3 spectrum was overlapped by absorption bands which were assigned to ethynylcarbene (propargylene) (29). The vibrational structure of this system proved to be extremely complex, and analysis has not yet been possible.

II. ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY

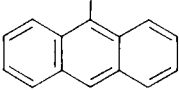
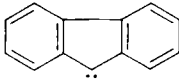
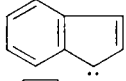
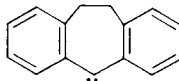
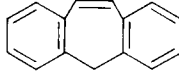
Much information about the structure of polyatomic carbenes comes from ESR studies. This technique is limited to triplet carbenes obtained in a stable form by photolysis of the corresponding diazoalkane in a solid matrix at low temperature. The matrix serves to prevent the molecules from rapid rotation. ESR spectra may be obtained from carbenes which are either aligned in a crystalline matrix (30, 31) or randomly oriented in a rigid glass (32, 33).

For an organic molecule possessing two interacting unpaired spins, the spectrum is described using the spin Hamiltonian

$$\mathcal{H} = g\beta HS + DS_z^2 + E(S_x^2 - S_y^2) \quad (4)$$

where S is the spin operator and S_x , S_y , and S_z its components along the molecular axes. H is the magnetic field, β the Bohr magneton, and g the Landé splitting factor. The spectrum may be analyzed in terms of the zero-field splitting parameters D and E which describe the separation of the three energy levels when no external field is present. Each energy level corresponds to a principal magnetic axis. The parameter D measures the magnetic dipole interaction along the z axis and is roughly proportional to $1/r^3$, where r is the average separation of the unpaired spins. The other parameter, E , is a measure of the difference between similar magnetic dipole interactions along the x and y axes. It follows that a molecule with three different axes should exhibit a finite E , whereas this quantity would vanish for linear molecules with degenerate p orbitals. The value of E indicates qualitatively the magnitude of the deviation of the spin-spin interaction from cylindrical symmetry. A fairly good correlation of the E/D ratio and the bond angle on the divalent carbon has been observed (34, 35). Values of D and E obtained from ESR spectra of carbenes are collected in Table II (30, 32, 34, 36-44).

TABLE II
Zero-Field Splitting Parameters and Derived Bond Angles
for Triplet Carbenes

Carbene	D/hc (cm ⁻¹)	E/hc (cm ⁻¹)	Angle	Refs.
Ph-CH:	0.515	0.0251	~155°	(32, 34)
α -C ₁₀ H ₇ CH:				
<i>anti</i>	0.456	0.0202	—	(36)
<i>syn</i>	0.435	0.0208	—	(36)
β -C ₁₀ H ₇ CH:				
<i>anti</i>	0.471	0.0243	—	(36)
<i>syn</i> : CH	0.493	0.0209	—	
	0.301	0.0132	—	(36)
Ph-C-CH ₃	0.496	0.0265	—	(37)
Ph-C-CH ₂ Ph	0.493	0.0289	—	(38)
Ph-C-CO-Ph	0.3815	0.0489	—	(39)
Ph-C-Ph	0.405	0.0194	~150°	(30, 32)
	0.408	0.0283	~135°	(40)
	0.378	0.0160	—	(40)
	0.409	0.0120	—	(40)
	0.393	0.0170	~150°	(41)
	0.379	0.0162	—	(41)
CF ₃ CH:	0.712	0.021	~160°	(37)
CF ₃ CF ₂ CF ₂ CH:	0.723	0.027	~160°	(37)
CF ₃ (CF ₂) ₆ CH:	0.72	0.024	~160°	(37)
(CF ₃) ₂ C:	0.744	0.0437	~140°	(37)
CF ₃ -C-Ph	0.518	0.0313	—	(37)
HC≡C-CH:	0.628	0.000	180°	(42)
CH ₃ C≡C-CH:	0.626	0.000	180°	(42)
Ph-C≡C-CH:	0.541	0.0035	—	(42)
CH ₃ C≡C-C≡C-CH:	0.609	0.000	180°	(42)
(CH ₃) ₃ C-C≡C-C≡C-CH:	0.606	0.000	180°	(42)
Ph-C≡C-C≡C-CH:	0.533	0.000	180°	(42)
NC-CH:	0.863	0.000	180°	(42, 43)
(NC) ₂ C:	1.002	0.002	180°	(44)

A. Methylene

The ESR spectrum of methylene trapped in a xenon matrix at 4,2°K has been one of the most recent achievements in this field (35*a,b*). Diazo-methane or diazirine were cocondensed with xenon and photolyzed at liquid helium temperature. The ESR signal survived warming to 20°K but disappeared upon warming to 77°K (35*a*). The two groups engaged in this work offered different interpretations of their spectra. Bernheim, Skell *et al.* reported $D = 0,69 \text{ cm}^{-1}$ and $E = 0,003 \text{ cm}^{-1}$, indicating a "slightly bent" structure (35*a*). Wasserman *et al.* (35*b*) observed two species with $D = 0,6636 \text{ cm}^{-1}$, $E < 0,002 \text{ cm}^{-1}$ and $D = 0,6844 \text{ cm}^{-1}$, $E = 0,00347 \text{ cm}^{-1}$, respectively. These they ascribed to different sites in the crystal. The site with the lower D and E is believed to allow greater motional freedom; a bent molecule which rotates freely about the long axis will have $E = 0$. Taking into account the extensive motional possibilities of the small, light methylene, Wasserman *et al.* arrived at a HCH angle of 136°, in good agreement with most theoretical calculations (cf. Chapter 5). These geometrical conclusions were supported by the ESR spectra of CHD ($D = 0,7443 \text{ cm}^{-1}$, $E = 0,00640 \text{ cm}^{-1}$) and CD₂ ($D = 0,7563 \text{ cm}^{-1}$, $E = 0,00443 \text{ cm}^{-1}$) (35*c*). The largest E arises with CHD, a trend which does not fit a smooth change of angle with increasing isotopic mass, but is explained by the larger barrier seen by CHD on rotation about the z axis.

B. Arylcarbenes

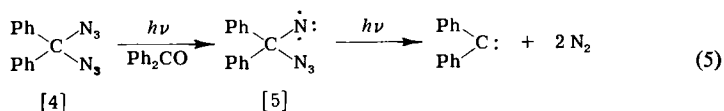
From the results in Table II it can be seen that a common feature of arylcarbenes is the nonlinear bond angle on the divalent carbon. Angles of 150–155° have been estimated for phenylcarbene and diphenylcarbene. It was found that for diphenylcarbene the magnitudes of D and E show a small dependence on the nature of the host matrix (Table III). The smallest values of D and the narrowest lines were found with matrix molecules of benzophenone geometry (35). The zero-field splitting parameters of diphenylcarbene in single crystals of benzophenone and 1,1-diphenylethylene likewise differed appreciably (45). A high degree of orientation in the matrix was also revealed when diphenyldiazomethane was photolyzed with polarized light (46). Because the matrix acts as a significant restraint, it becomes questionable whether the observed bond angles correspond to the preferred geometry of the carbene. Some reassurance that the influence of the host may not be overwhelming comes from the observation that the

TABLE III

Influence of the Host Matrix on Zero-Field Splitting Parameters
for Diphenylcarbene (35, 45)

Matrix	D/hc (cm ⁻¹)	E/hc (cm ⁻¹)	Linewidth (G)
"Fluorolube"	0.415	0.0197	93
<i>n</i> -Hexane	0.408	0.0188	88
Diphenyl ether	0.402	0.0182	18
Benzophenone	0.405	0.0192	19
Diphenyldiazomethane	0.405	0.0188	17
Diphenylmethane	0.407	0.0187	67
Fluorene	0.409	0.0187	95
Diphenylacetylene	0.409	0.0189	89
1,1-Diphenylethylene	0.396	0.0149	—

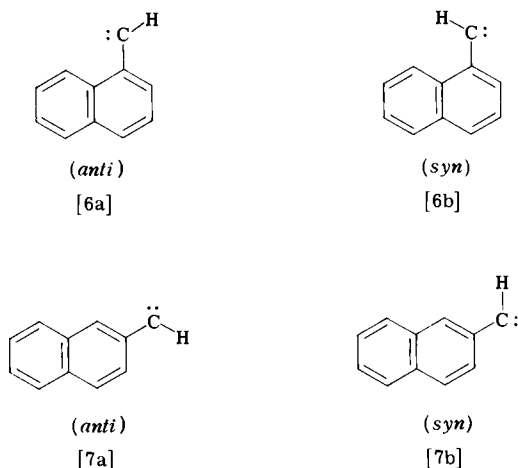
use of diphenylacetylene, which is linear, as the matrix does not lead to the formation of linear diphenylcarbene (Table III). Furthermore, the photolysis of diphenyldiazidomethane [4], proceeding by way of the azidonitrene [5], produced ESR spectra identical with those obtained from diphenyldiazomethane (47). The geometry about the central carbon atom of [4] is tetrahedral rather than trigonal in diphenyldiazomethane. There appears to be enough freedom in the cage for the carbene to take its preferred angle even though extensive reorientation of the molecule is not possible.



The E/D values and hyperfine structure data for fluorenylidene, indenylidene, and cyclopentadienyldiene (40) suggest interorbital angles ($>135^\circ$) which are much larger than the internuclear angles that can be accommodated in an undistorted five-membered ring. This has led to the assumption that the bonds to the divalent carbon atom are bent (40, 41).

In addition to the central bond angle, another structural parameter of interest in the arylcarbenes is the dihedral angle between the plane defined by the bonds on the divalent carbon and the aryl plane. The carbenes obtained by photolysis of α - and β -naphthyldiazomethanes each show two triplet signals in their ESR spectra which were assigned to geometric

isomers of the carbenes [6a,b; 7a,b] (36). The ESR spectra of such isomers are distinguishable provided that the spin densities on nearby carbon atoms in the π system are different. Of course, this result is compatible with any dihedral angle except 90° .



More information on the dihedral angle of diarylcarbenes has become available from electron nuclear double resonance (ENDOR) studies (48, 49). This technique permits the investigation of the hyperfine interactions of the unpaired spins with the constituent atomic nuclei (which are otherwise not accessible because of the broad lines which are observed). ENDOR measurements of planar fluorenylidene (48) confirm that one electron moves in a π orbital which extends over the whole carbon skeleton, while the second unpaired electron occupies an orbital which is localized at the divalent carbon and lies in the σ plane. Planar diphenylcarbene would show a similar electron distribution. However, ENDOR studies of diphenylcarbene in a 1,1-diphenylethylene crystalline matrix revealed a dihedral angle of 34° (49). The rotation of the phenyl planes out of the molecular plane diminishes the delocalization of the π electron and increases that of the σ electron. It should be remembered that this specific geometry does not necessarily represent the equilibrium conformation of the isolated molecule, because the host crystal may exert some distorting influence.

C. Perfluoroalkylcarbenes

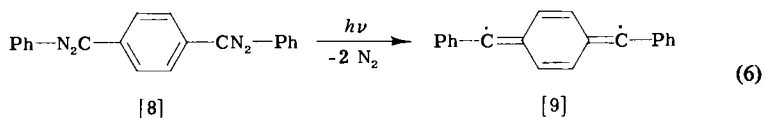
The ESR spectroscopy of alkylcarbenes has been limited so far to the structures $R_f-CH\cdot$ and $CF_3-\ddot{C}-CF_3$ (37). All of them were found to be bent at the divalent carbon. If one extrapolates the angles measured for bis-trifluoromethylcarbene (140°) and trifluoromethylcarbene (160°) to the unsubstituted system, a linear geometry for methylene is indicated. It is likely that the bond angle for triplet alkylcarbenes does not deviate much from linearity because $Ph-CH\cdot$ and $Ph-\ddot{C}-CH_3$ have similar E values whereas those of $Ph-CH\cdot$ and $Ph-\ddot{C}-CF_3$ differ appreciably (Table II). The reason why an attached CF_3 group reduces the angle at a divalent carbon remains obscure.

D. Ethynyl- and Cyanocarbenes

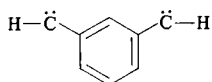
A series of carbenes with the general structure $R-(C\equiv C)_n-CH\cdot$ [$n = 1, 2$; $R = H, CH_3, C(CH_3)_3$] has been investigated by ESR, and in all cases E was found to be zero within experimental error (42). Linear structures are the only ones compatible with the experimental data. Similar considerations apply to cyanocarbene (43) and dicyanocarbene (44). Ethynylcarbene (propargylene) has been discussed in terms of a superposition of two π electron systems having the same spin density distribution as the allyl radical. The lower D value obtained for phenylpropargylene (Table II) reflects the delocalization of one of the two triplet electrons into a π orbital of the phenyl group. A nonzero though small E value was obtained for phenylpropargylene.

E. Dicarbenes

The photolysis of 1,4-bis(α -diazobenzyl)benzene [8] in solid solution in dibenzoylthane at $77^\circ K$ yielded ESR absorptions consistent with $D/hc = 0.0521 \text{ cm}^{-1}$ and $E/hc < 0.002 \text{ cm}^{-1}$ (50). The observed zero-field splittings correspond to an average separation of the unpaired electrons by $\sim 4 \text{ \AA}$. The most reasonable structure which explains this low spin-spin interaction is [9] in which the two electron-deficient atoms are $\sim 5.6 \text{ \AA}$ apart.

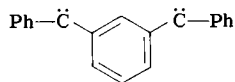


The ESR spectra obtained by photolysis of 1,3-bis(diazomethyl)benzene (51) and 1,3-bis(α -diazobenzyl)benzene (51, 52) were much more complex than those observed with triplet states. The data have been analyzed in terms of a quintet ground state ($S = 2$) of [10] and [11].



$$\begin{aligned} D/hc &: 0.0844 \text{ (51)} \\ E/hc &: 0.0233 \text{ (51)} \end{aligned}$$

[10]



$$\begin{aligned} &0.0701 \text{ (51)}, 0.0713 \text{ (52)} \\ &0.020 \text{ (51)}, 0.0190 \text{ (52)} \end{aligned}$$

[11]

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CHAPTER 7

Reactions with Carbon–Hydrogen Bonds

I. INSERTION AND ABSTRACTION MECHANISMS

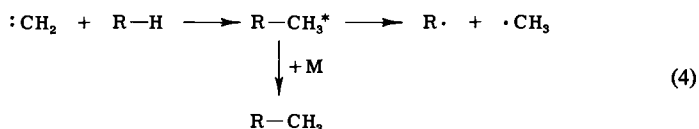
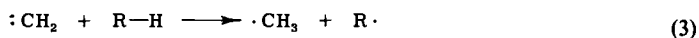
THE PRODUCTS ARISING from many reactions of carbenes with alkanes depend strongly on the carbene precursor, wavelength of actinic light, phase (gas or liquid), pressure, and other variables. As an example, the methylene–propane reaction system will be considered in some detail.

Ethane, ethylene, isobutane, *n*-butane, 2,3-dimethylbutane, and 2-methylpentane were major products from the ketene–propane photochemical reaction; *n*-hexane was produced only in small amount (1, 2). Ethylene is formed by the interaction of methylene with ketene (Chapter 2, Section I). The remaining products are qualitatively accounted for by the production and recombination of methyl, *n*-propyl, and isopropyl radicals. Quantitatively, this mechanism is inconsistent with the high relative yield of butanes obtained at 2800 Å (Table I). The formation of butanes in

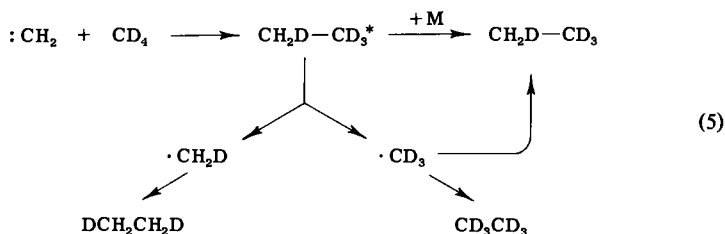
TABLE I
Products of Ketene–Propane Photochemical Reaction (2)^a

Product	2800 Å	3800 Å	
	54 mm	54 mm	100 mm
Ethane	1.000	1.000	1.000
Ethylene	1.239	0.317	0.246
<i>n</i> -Butane	7.18	0.602	0.537
Isobutane	3.79	1.608	1.468
2,3-Dimethylbutane	0.298	0.575	0.435
2-Methylpentane	0.130	0.245	0.179
<i>n</i> -Hexane	Trace	Trace	Trace

^a 27 ± 1°, ketene/propane = 0.10.



Strong evidence in favor of Eq. (4) has been obtained in an investigation of the photolysis of diazomethane in the presence of methane- d_4 (7). The isotopic distribution of the ethane produced was consistent with Eq. (5). As expected, the relative amount of ethane-1,1,1,2- d_4 increased with increasing pressure. In the presence of oxygen the ethane formed was almost exclusively ethane- d_4 . Flash photolysis of diazomethane in the presence of methane resulted in the appearance of a strong CH_3 spectrum (8).

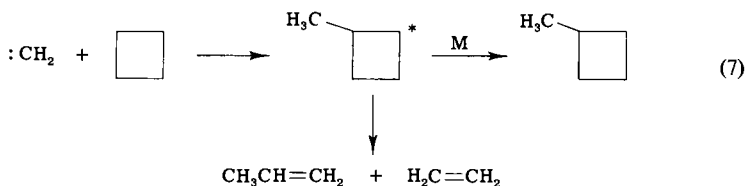
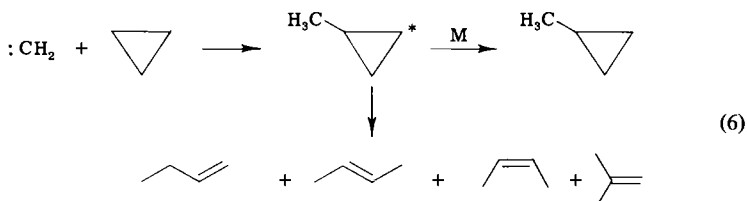


The initial excitation energy of the ethane is at least equal to the exothermicity of the insertion reaction ($\Delta H = -95.3$ kcal/mole, using the recent estimate of $\Delta H_f^\circ(\text{CH}_2) = 93$ kcal/mole; cf. Chapter 2, Section V). To this value we must add any excess energy of methylene available from its generic reaction and carried into the activated molecules. Estimates of the latter quantity are in the order of 9–12 kcal/mole (3). The rate of dissociation of ethane may be calculated to be approximately ten times as great as the rate of collisional deactivation, even with an unexcited methylene precursor (9). Decomposition of the activated ethane into ethylene and hydrogen does not occur to an appreciable extent (10).

When activated alkanes are formed through the insertion of methylene into C—H bonds, the enthalpy of reaction must be unsymmetrically distributed at the instant of reaction. There is evidence, however, of a rapid flow of vibrational energy through a molecule (11, 12). With an increasing number of effective oscillators, dissociation of activated alkanes becomes

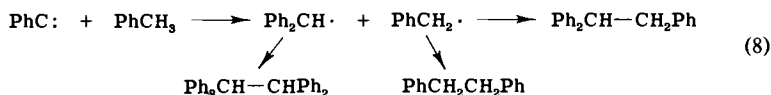
less likely. As mentioned above, ethyl radicals occur in the diazomethane-propane photolysis system, Eq. (2), but they do not occur in the ketene-propane photochemical reaction (2). The absence of pentanes in the latter case suggests that the dissociation of "hot" butane molecules into ethyl radicals may be neglected.

Reaction paths of comparatively low activation energy, such as structural isomerization and fragmentation, are available to some activated molecules, and these proceed to the exclusion of any dissociation into alkyl radicals. The reaction of methylene with cyclopropane gives excited methylcyclopropane which is deactivated or undergoes structural isomerization to 1-butene, *cis*- and *trans*-2-butene, and isobutene (11, 13, 14). When cyclobutane was used as the substrate, the yield of methylcyclobutane approached 100% asymptotically at high pressures, and the fragmentation products at low pressures were propylene and ethylene (15).



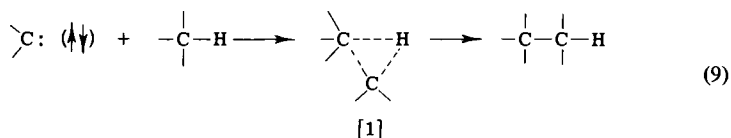
Reaction (4) is not an acceptable mechanism for the formation of alkyl radicals in the liquid phase because collisional deactivation of vibrationally excited alkanes should be rapid. Although methylene in solution does not give products attributable to radical coupling, other carbenes do. For example, in the thermal (16) or photolytic (17) decomposition of diphenyldiazomethane or photolysis of diphenylketene (18) in toluene solution, the product of insertion of diphenylcarbene into the benzylic carbon-hydrogen bonds, 1,1,2-triphenylethane, was accompanied by substantial amounts of 1,1,2,2-tetraphenylethane and bibenzyl. This is a strong indication that discrete diphenylmethyl and benzyl radicals are formed. Diphenylmethyl radicals have been identified by ESR spec-

troscopic examination of diphenyldiazomethane during thermolysis (19).

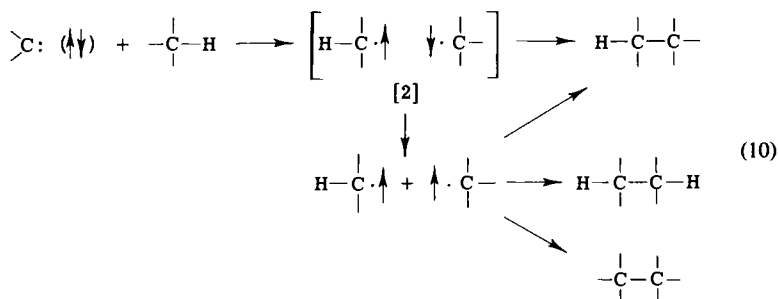


To summarize, the formation of alkyl radicals in carbene-alkane systems by dissociation of vibrationally excited alkanes, Eq. (4), should be considered as an exception rather than the rule. In contrast, the abstraction of hydrogen by carbenes, Eq. (3), appears to be quite general. Having identified radical and nonradical primary processes in carbene-alkane systems, the question then arises whether the two modes of reaction and their variation with reaction conditions can be correlated with some property of the carbenes.

A widely held view is that carbenes of different multiplicity react in qualitatively different ways: singlet carbenes insert into carbon-hydrogen bonds, whereas triplet carbenes abstract hydrogen according to Eq. (3). Consideration of the rule of spin conservation leads to the formulation of the insertion of a singlet carbene as a one-step process involving a three-center cyclic transition state [1].

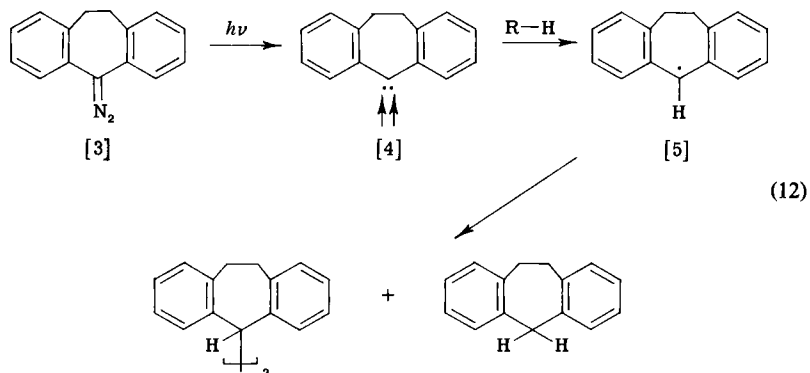


DeMore and Benson (9) have argued in favor of a mechanism similar to Eq. (3) for the insertion of singlet carbenes, the initially formed radical pair [2] being held together and undergoing efficient recombination because of contributions from ionic states. Spin inversion and dissociation of the radical pair would be comparatively rare, and [2] would not be trapped by radical scavengers.



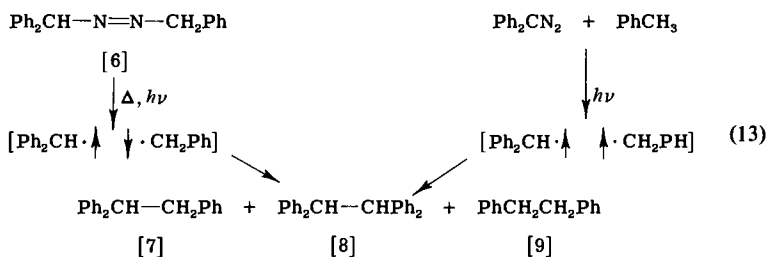
by methylene from its generic reaction. The less energetic methylene produced at longer wavelengths may indeed be expected to behave more selectively. Similar trends would be predicted, however, in ketene and diazomethane photolysis, and this is in contrast to the experiment. Moreover, the increased production of alkyl radicals at longer wavelengths is not easily understood. Decreasing excess energy of the radical pair [2] should promote, rather than inhibit, recombination to give the products of C—H insertion.

The idea that alkyl radicals are generated by the interaction of triplet carbenes with alkanes is supported by recent spectroscopic studies. Flash photolysis of 5-diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene [3] in liquid paraffin at room temperature (21) produced the electronic absorption spectrum of the triplet carbene [4] which was already known from rigid solvent studies (22). The lifetime of [4] was estimated to be in the range 1–50 μ sec. The spectrum of the radical [5] was also observed, disappearing within 25 msec. The consecutive appearance of the two spectra suggests (but does not prove) that [5] originates from [4].



Closs and his group have used chemically induced nuclear spin polarization as a tool for determining the spin multiplicities of radical-pair precursors (23). The NMR emission or enhanced absorption displayed by organic compounds immediately after their formation from radical intermediates is a consequence of nonequilibrium population of nuclear spin states (24). Closs compared the photolysis of diphenyldiazomethane in toluene solution and the thermal or photolytic decomposition of the azo compound [6]. Both reactions afforded the same products, [7]–[9], but the ratio of unsymmetrical to symmetrical products, [7]/[8] + [9] was higher

in the reaction of [6] (1.5 : 1) than in the diphenylcarbene reaction (1 : 1). The NMR spectra obtained from both reactions showed opposite polarizations, in confirmation of theoretical predictions for radical pairs of different multiplicity (25). Since there is little doubt that acyclic azo compounds decompose through the singlet state (26), this experiment assigns triplet multiplicity to the radical pairs intervening in the diphenylcarbene reaction.

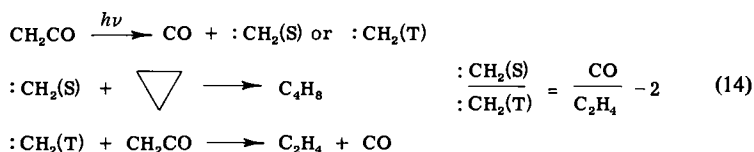


If it is accepted that only triplet carbenes undergo abstraction reactions, then the fraction of triplet species in a specific carbene-alkane system may be estimated from the product distribution. In the ketene-propane photochemical reaction [Eq. (1); Table I] the concentration of *n*-propyl radicals is small, and the formation of *n*-butane by radical recombination may be neglected in a first-order approximation. The fraction of triplet methylene then corresponds to $2\text{C}_2\text{H}_6$ + isobutane from triplet CH_2 . The latter quantity was derived from a steady-state treatment by use of the known relative rate constants of radical recombinations. On this basis the fraction of triplet methylene was calculated to be 20% at 2800 Å and 77% at 3800 Å (2).

The diazomethane-isopentane system has been analyzed by comparing the absolute yields of products in the presence and absence of oxygen. The underlying assumption is that all the products eliminated by added oxygen arise through reactions involving triplet methylene. The proportion of the methylenes that are triplet was calculated to be 15–20% (6).

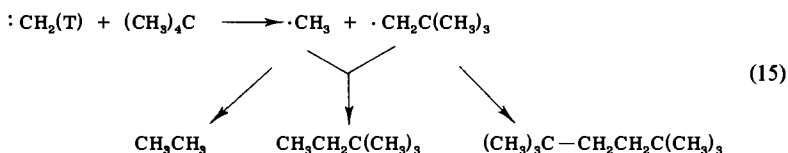
The ketene-cyclopropane photolytic reaction is suitable for a very simply approach (27). The absence of methane and ethane as by-products in this system must indicate that the rate of hydrogen abstraction by triplet methylene from cyclopropane is considerably slower than from *n*-alkanes. This is to be expected if the reactivity of triplet methylene is similar to methyl whose relative rates of attack on cyclopropane and *n*-butane are 1 : 228 (28). At high cyclopropane/ketene ratios all singlet methylenes will insert into the C—H bonds of cyclopropane, whereas all triplet methy-

lenes will react with ketene to produce ethylene and carbon monoxide, Eq. (14). The carbon monoxide/ethylene ratio became constant when the cyclopropane/ketene ratio exceeded 20, and the resultant triplet methylene fractions were 14% at 2700 Å and 16% at 3130 Å (27). These values agree reasonably well with those derived from methylene-olefin systems (Chapter 8, Section I).



The fraction of triplet methylene in gas-phase photolysis systems increases greatly on addition of inert gases. For example, hexanes arising by radical coupling constituted only 3% of the butanes produced in the high-pressure region of the diazomethane-propane photolytic reaction (3). Addition of 800 mm of N₂ resulted in a 15% relative yield of hexanes (4). Collisionally induced conversion of singlet methylene to its triplet state explains the enhanced production of alkyl radicals. It is matter of controversy, however, whether the experimental conditions (800 mm N₂, total pressure ~2 atm) are sufficient for *complete* spin inversion (see also Chapter 8, Section I). More C_{n+1} alkanes were formed than could be accounted for by a kinetic analysis based on conventional radical-radical reactions, and the additional insertion products were not eliminated by addition of O₂ to the system. Ring and Rabinovitch (4) have concluded that triplet methylene can insert into C—H bonds (or react by some process which does not involve conventional long-lived radical intermediates). Even the presence of a small amount of singlet methylene would invalidate this conclusion which, therefore, has not been generally accepted.

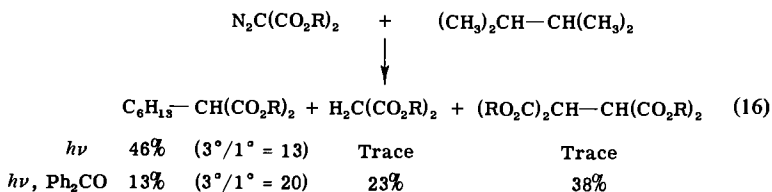
Similar observations have been made in the mercury-photosensitized decomposition of ketene, previously believed to be a source only of triplet methylene. The sensitized photolysis of ketene in the presence of neopentane afforded the products of radical recombination, ethane, 2,2-dimethylbutane, and 2,2,5,5-tetramethylhexane (29). The yield of 2,2-dimethylbutane, however, was about twice that expected from collision theory and the measured yields of ethane and tetramethylhexane. Thus either the insertion reaction of triplet methylene is a major reaction pathway, or there must be an appreciable quantity of singlet methylene in this system. The authors prefer the second alternative on the basis of independent evidence (Chapter 2, Section I).



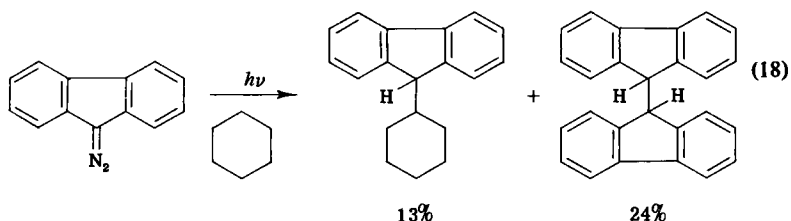
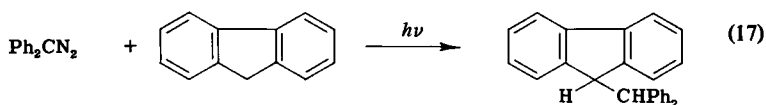
In recent flash photolysis experiments, triplet methylene was monitored by kinetic spectroscopy at 1415 Å (29a). Singlet CH₂ was not observed directly, but the growth of the triplet absorption as a function of the pressure of various additives permitted the estimation of rate constants. The insertion of singlet CH₂ into C—H bonds of methane and the collisionally induced spin inversion [$: \text{CH}_2(\text{S}) + \text{CH}_4 : \text{CH}_2(\text{T}) + \text{CH}_4$] proceeded at comparable rates, *ca.* 100 times faster than the reaction of triplet methylene with methane. The low reactivity of triplet CH₂ toward methane has been confirmed in steady-state photolysis studies (29b). In the ketene-CD₄ photolysis, triplet CH₂ reacted predominantly with methyl radicals originating from the C—H insertion of singlet CH₂, Eq. (5).

Triplet methylene does not intervene in the liquid-phase photolysis of diazomethane-alkane (C_n) systems. The absence of C_{2n} products is inconclusive evidence because the initially formed radical pair might be held together in a solvent cage to give predominantly C_{n+1} products. However, the indiscriminate nature of the liquid-phase insertion reactions (Section III) excludes any selective intermediate from serious consideration. In the benzophenone-sensitized photolysis of diazomethane no detectable attack on solvent alkanes occurred (30). Considerable amounts of polymethylene and of hydrocarbons of low molecular weight were formed, indicating that attack of triplet CH₂ on diazomethane was the principal reaction.

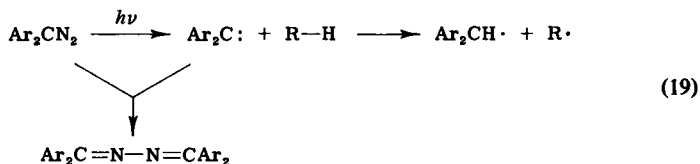
Apparent triplet carbene insertion was observed in the benzophenone-sensitized photolysis of dimethyl diazomalonate (31). Compared to the direct photolysis, a drop in yield of insertion products was obvious, and two new products, dimethyl malonate and 1,1,2,2-tetracarboxymethoxyethane, were formed. The triplet bis(methoxycarbonyl)carbene "inserted" slightly more selectively than did the singlet.



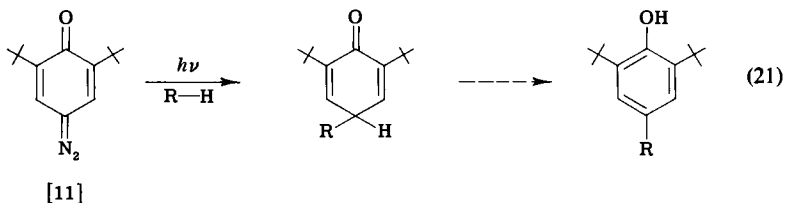
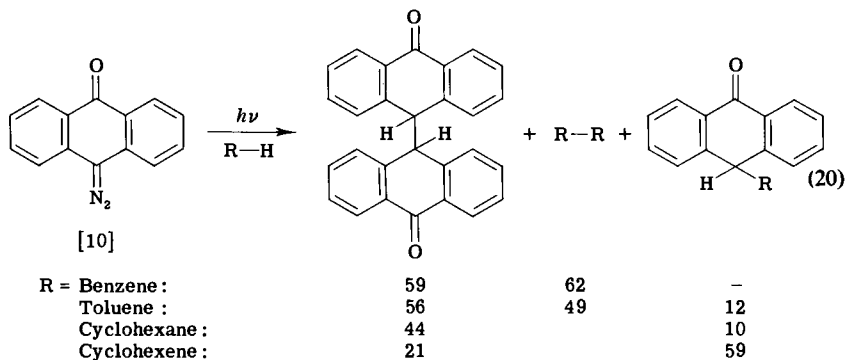
Aryldiazoalkanes produce triplet carbenes on direct photolysis in solution. Singlet-triplet interconversion of either the electronically excited aryldiazoalkanes or the arylcarbenes must be rapid compared to that of diazomethane and methylene, respectively. Triplet arylcarbenes abstract hydrogen from the solvent with formation of radicals and, ultimately, products of radical recombination [Eqs. (8), (12), (13)]. The radicals have been detected by ESR spectroscopy (19, 21, 32) and by the autoxidation induced in oxygen-saturated hydrocarbon solvents (33). In some cases not all the possible products of radical recombination have been isolated, but direct insertion appears nevertheless unlikely. 9-Benzhydrylfluorene has been obtained as the major product by photolysis of diphenyldiazomethane in the presence of fluorene (34). The photolysis of diazofluorene in cyclohexane solution afforded 9-cyclohexylfluorene and bifluorenyl (34).



In the absence of suitable hydrogen donors, azine formation by attack of the arylcarbenes on excess aryldiazoalkanes predominates. Photolysis of diphenyldiazomethane in benzene gave only benzophenone azine, whereas much hydrogen abstraction occurred in toluene, cyclohexene, and petroleum ether (34, 35). The azine was the only product obtained from 4-methoxy- and 4,4'-dimethoxydiphenyldiazomethane regardless of the solvent used in the photolysis (36).



Unlike diphenylcarbene, the carbene derived from diazoanthrone [10] was found capable of hydrogen abstraction from benzene, but coupling between anthranyl and phenyl radicals did not occur (37). The reactivity of [10] may be contrasted with that of simple 1,4-diazoxides, e.g., [11], which undergo clean insertion into aromatic and aliphatic C—H bonds (38). Ferrocenylcarbenes behave very much like arylcarbenes (39, 40).

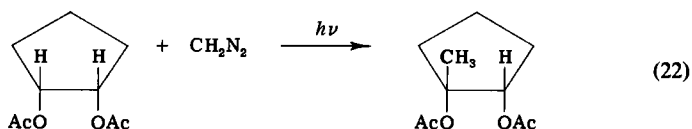


II. STEREOCHEMISTRY

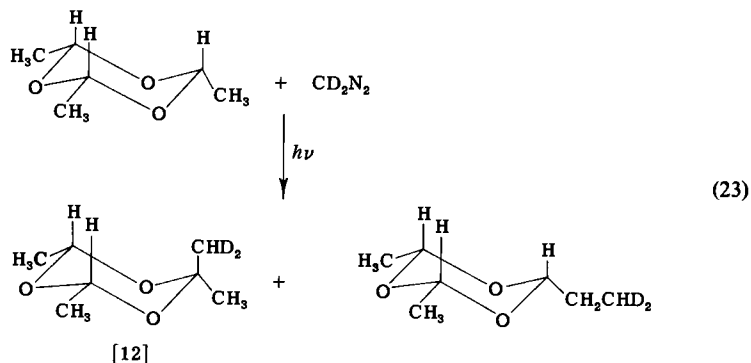
In spite of the considerable number of investigations bearing on the mechanism of the insertion reactions of carbenes, there are only few accounts that establish the stereochemistry of carbene insertion into carbon-hydrogen bonds. This has been due partly to the experimental difficulties encountered in observing this reaction at an asymmetric carbon atom. The simplest aliphatic hydrocarbon capable of supporting optical activity both in itself and in the products obtained from insertion of methylene is 2-methyl-3-ethylhexane. With methylene, this compound would be expected to give at least eight products, all isomeric. Their separation, not only from each other but also from a large excess of starting material, would be a formidable task. The problem has been simplified by

studying insertion reactions into C—H bonds α to OR groups. Most probably, the hetero atom does not affect the insertion mechanism although it enhances the rate of insertion into α -C—H bonds (Section III).

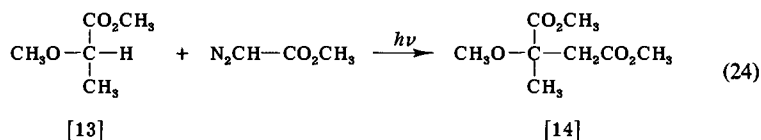
The first experiment aimed at evaluating the configurational relationship between substrate and insertion product is mentioned in an abstract (41) which claims that both the *cis*- and *trans*-1,2-cyclopentanediol diacetates were methylated at the acetoxy-bearing carbon atoms with no change in configuration. The recently published full paper, however, reports *inversion* of configuration (41a). Strangely enough, this kind of stereochemistry is presented as evidence for a three-center transition state [1], Eq. (9).



The photolysis of diazomethane- d_2 in the presence of paraldehyde (all methyl groups equatorial) afforded 2,2,4,6-tetramethyl-1,3,5-trioxane [12] in which all ($\pm 5\%$) of the deuterium was located in *one* of the geminal methyl groups (42). On the basis of convincing NMR evidence, the deuterium-containing group was assigned the axial position. Insertion with retention of configuration is the obvious conclusion from this assignment.



When methyl (–)(*S*)-2-methoxypropionate [13] was allowed to react with methoxycarbonylcarbene generated photolytically from methyl diazoacetate, a small amount of dimethyl (+)(*R*)-2-methoxy-2-methyl succinate [14] could be isolated from the product mixture (43). The optical rotation of [14] indicated that $99 \pm 4\%$ of the insertion reaction proceeded with retention of configuration.



Both methylene (in solution) and methoxycarbonylcarbene would be expected to react from their singlet states in a one-step insertion mechanism. The stereochemistry of the abstraction-recombination sequence initiated by triplet carbenes has not yet been studied, although its knowledge would be essential for an unequivocal mechanistic interpretation. Insertion with retention by singlet carbenes, and "insertion" with racemization by triplet carbenes has been observed, however, with the more reactive Si—H bond (44) (Chapter 11, Section I).

III. SELECTIVITY

A. C—H Bonds of Alkanes

Early work on the gas-phase interaction of methylene with alkanes (13, 45) showed selective reactivity in the order tertiary C—H > secondary C—H > primary C—H. Methylene from diazomethane (45) was found to be less selective than methylene from ketene (13). The differences in the relative reactivity of methylene from the two sources have been attributed to excess translational energy of methylene from diazomethane (11, 46). More recently, however, it has been recognized that the photolysis of ketene produces more triplet methylene than the photolysis of diazomethane (Section I). Part of the reported selectivity (13, 45) must be due to triplet methylene effects.

On the basis of recent work with added radical scavengers (3, 6, 47, 50), it appears that there is no real difference in the reactivity of singlet methylene from diazomethane and that from ketene toward C—H bonds (Table II). Very probably methylene is translationally thermalized before it inserts into C—H bonds. This assumption is consistent with the lack of wavelength dependence for singlet methylene insertion (6, 31). The collision yield for C—H insertion is much less than that for addition to double bonds (Table IV) or that for insertion into Si—H bonds (Chapter 11, Section I). Obviously, insertion does not occur on every collision of methylene with hydrocarbons, and only a few collisions would be needed for translational thermalization.

Whereas a small but significant selectivity of methylene in gas-phase reactions is well established, the evidence for liquid-phase reactions is less

definitive. Studies using diazomethane (48–50), phenylcyclopropane (51), or 9,10-dihydro-9,10-methanophenanthrene (51) as the methylene precursor have indicated random attack on primary, secondary, and tertiary C—H bonds (deviations from statistical values are within the experimental error). However, some results for the liquid phase indicate slight selectivity, particularly in favor of tertiary C—H bonds (6, 48).

TABLE II
Relative Rates of Singlet Methylene Reactions with Alkanes
(Gas Phase)

Photolytic reaction		Relative rate per C—H bond			Ref.
		1°	2°	3°	
Propane,	CH ₂ N ₂ , O ₂	1.00	1.20	—	(3)
	CH ₂ CO, NO	1.00	1.30	—	(47)
<i>n</i> -Butane,	CH ₂ N ₂ , O ₂	1.00	1.35	—	(50)
	CH ₂ CO, NO	1.00	1.31	—	(47)
Isobutane,	CH ₂ CO, NO	1.00	—	1.2	(47)
Isopentane,	CH ₂ N ₂ , O ₂	1.00	1.22	1.39	(6)
	CH ₂ CO, O ₂	1.00	1.22	1.42	(6)

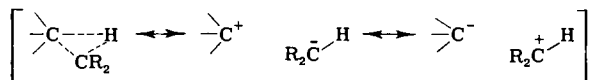
Various carbenes are capable of insertion into C—H bonds but behave more discriminatingly than methylene. Pertinent data are collected in Table III (6, 31, 48, 52–60). Only a few standard alkanes have been used, and it is difficult to say how much the rate ratios “per bond” depend on the structure of the alkane (steric hindrance etc.). The structure of the carbene is clearly more important. Resonance stabilization by donor groups is expected to lower the reactivity of the divalent carbon. Table III shows the dramatic effect of one halogen substituent. Thermolysis of phenyl(bromodichloromethyl)mercury in cyclohexane afforded dichloromethylcyclohexane (32% yield) (61), but this unique insertion was not achieved with other dichlorocarbene precursors. Insertion of CCl₂ into other secondary and tertiary (not primary) C—H bonds has been reported (61a). The selectivity is very high, i.e., secondary C—H bonds did not react detectably if a tertiary C—H bond was present. The formation of by-products (e.g., alkyl bromides) resulting from radical side reactions was not considered indicative of the mechanism of the insertion of CCl₂ into C—H bonds.

TABLE III
Relative Rates of Carbene Insertion into C—H Bonds
(Liquid Phase)

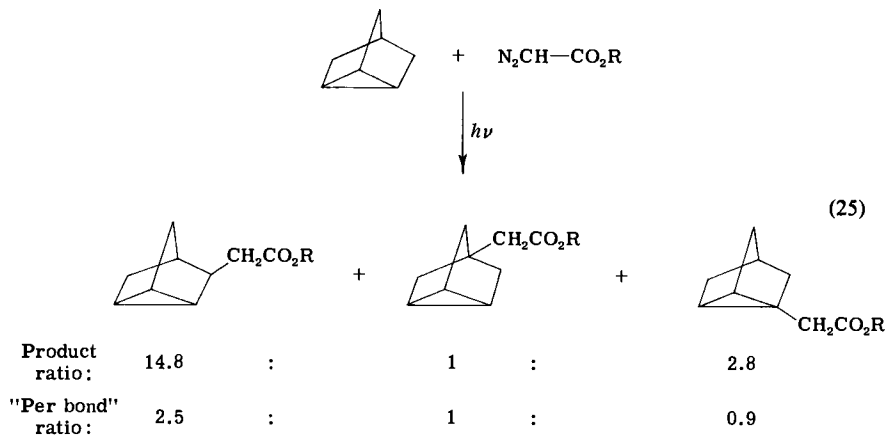
Carbene	Method ^a	Alkane	Rate 2°/1°	Ratio 3°/1°	Ref.
:CH ₂	a	Isopentane	1.2	1.5	6
	a	2,3-Dimethylbutane		1.2	48
:CH—CF ₃	a	<i>n</i> -Butane	1.0		52
	a	Isobutane		1.3	52
: 	a	2,3-Dimethylbutane		7.3	53
:CH—Ph	a	<i>n</i> -Pentane	6.3		54
	a	<i>n</i> -Pentane	8.3		55
:CH—CO ₂ CH ₃	a	<i>n</i> -Pentane	2.3		56
	a	Isobutane		3.1	56
	a	2,3-Dimethylbutane		2.9	56
:C(CO ₂ CH ₃) ₂	a	<i>n</i> -Butane	4.7		31
	a	<i>n</i> -Pentane	3.4		31
	a	2,3-Dimethylbutane		13.1	31
:C(CO ₂ C ₂ H ₅) ₂	a	<i>n</i> -Pentane	8.4		56
	a	Isobutane		21.0	56
	a	2,3-Dimethylbutane		12.5	56
:C(CN) ₂	b	<i>n</i> -Butane	4.0		57
	b	Isobutane		12.0	57
	b	2,3-Dimethylbutane		8.0	58
F—  —CHF ₂	c	Propane	18		59
	c	<i>n</i> -Butane	14.5		59
	c	<i>n</i> -Hexane	18		59
	c	Isobutane		> 500	59
:CHCl	a	<i>n</i> -Pentane	20		60
:CHBr	a	<i>n</i> -Pentane	25		60

^a a. Photolysis of diazo compound; b. thermolysis of N₂C(CN)₂, 80°;
c. thermolysis of CHF₂CF₂SiF₃, 150°

The increase in selectivity by acceptor groups, such as CO_2R and CN , has been explained in terms of polar resonance structures contributing to the transition state of the insertion reaction (56). The "weight" of the resonance structure with negative charge on the carbene carbon will increase if the charge can be dispersed over CO_2R or CN groups. Thus the relative stabilities of the transition states and the relative rates of $\text{C}-\text{H}$ insertion will reflect the usual order of carbonium ion stabilities, $3^\circ > 2^\circ > 1^\circ$.



Evidence supporting the postulated charge separation in the transition state comes from the reactivity of bridgehead hydrogens. Methylene reacts with bicyclo[2.2.1]heptane to give all of the possible $\text{C}-\text{H}$ insertion products in essentially statistical amounts (62). The product mixture obtained with methoxycarbonylcarbene, however, reflected a relative reactivity ratio of 0.7 : 1 for a bridgehead $\text{C}-\text{H}$ compared to a secondary one (62). The bridgehead $\text{C}-\text{H}$ bonds of nortricyclene were found to be even less reactive toward ethoxycarbonylcarbene (63).



B. $\text{C}-\text{H}$ Bonds of Alkenes

Addition to the carbon-carbon double bond is the major reaction of carbenes with olefins, competing insertion into the $\text{C}-\text{H}$ bonds being observed only with the more reactive carbenes. The isomeric distribution of the products of methylene insertion has been studied in some detail (Table IV) (11, 30, 46, 48, 64-68). Comparatively few data are available

TABLE IV
Relative Rates of Singlet Methylene Reactions with Olefins

Photolytic reaction		Relative rates of insertion (addition = 1.00)			Ref.
		Vinyllic C—H	Allylic C—H	Nonallylic C—H	
Propene, CH_2CO , O_2		0.070	0.097	—	(64)
CH_2N_2		0.09	0.11	—	(11)
3,3,3-Trifluoropropene, CH_2CO , O_2	H—1	0.033	—	—	(64)
	H—2	0.030	—	—	(64)
1-Butene, CH_2CO , O_2		0.070	0.125	0.12	(64)
4,4,4-Trifluoro-1-butene, CH_2CO , O_2	H—1	0.050	0.015	—	(64)
	H—2	0.023	—	—	(64)
<i>trans</i> -2-Butene, CH_2CO , O_2		0.088	0.13	—	(65)
CH_2N_2		0.11	0.15	—	(66)
Isobutene, CH_2N_2		0.09	0.11	—	(46)
Cyclohexene, CH_2N_2		0.125	0.155	0.155	(48)
		0.12	0.16	0.16	(30)
Allene, CH_2N_2		0.11	—	—	(67)
1,3-Butadiene, CH_2N_2		0.085	—	—	(68)

for methylene-olefin systems with added radical scavengers. Since the triplet fraction in the photolysis of diazomethane is known to be small (<20%), some diazomethane reactions without added scavengers have also been added to Table IV. Any contribution of triplet methylene to the apparent insertion reaction is expected to increase the selectivity in favor of allylic C—H bonds.

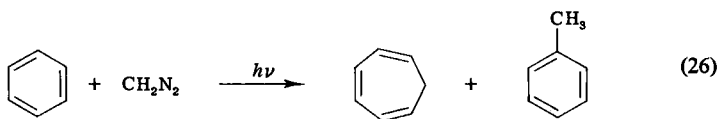
The data collected in Table IV show a fair constancy of the rates of insertion per bond. The slight upward trend with increasing alkyl substitution scarcely exceeds the limits of experimental error. The presence of a trifluoromethyl group, however, decreases the rates of methylene insertion relative to addition significantly (64). The deactivation becomes as great as a factor of 7–8 for the rate of allylic C—H insertion to addition for 4,4,4-trifluoro-1-butene, compared to the corresponding rate ratio for 1-butene. With the remaining olefins, it appears that vinylic C—H is slightly less reactive than allylic C—H or aliphatic C—H.

No reliable data for the relative rates of insertion and addition exist for the simplest olefin, ethylene. Diazomethane-ethylene reactions were studied under the aspects of "hot molecule" chemistry and were not extended to sufficiently high pressures (69). The products from the photolysis of ketene in the presence of ethylene (3100 and 3600 Å) extrapolate to a 85% yield of cyclopropane at 1600–2400 mm (70), i.e., the relative rate of insertion into a carbon-hydrogen bond compared with addition to the double bond is 0.044. An even smaller ratio of 0.028 has been observed with ketene-ethylene mixtures at 7 atm total pressure (71). In the latter case, irradiation was performed with pyrex-filtered light from a medium-pressure mercury arc. Only the longer wavelengths are effective under these conditions, and a large fraction of triplet methylene should be expected. Correction for 70% of triplet methylene (cf. Section I) gives a rate ratio of approximately 0.09 which agrees with those reported in Table IV.

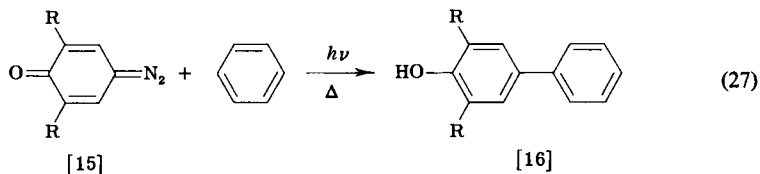
The relative rates of insertion and addition of bis(trifluoromethyl)carbene, generated by thermolysis of bis(trifluoromethyl)diazirine at 150°, are very similar to those observed with methylene (72). Again, vinylic C—H is slightly less reactive than allylic C—H. Frequently, analysis of the minor insertion products for structural isomers has not been carried out, and only rough estimates of C—H/C=C rate ratios are available for cyclopentadienylidene (0.06) (53), methoxycarbonylcarbene (0.045) (73), bis(methoxycarbonyl)carbene (0.03) (31), and dicyanocarbene (0.06) (57).

C. C—H Bonds of Arenes

The photolysis of diazomethane in benzene solution yields 32% of cycloheptatriene and 9% of toluene (74). Cycloheptatriene is the stable valence isomer of the presumed addition product norcaradiene. Toluene formed from benzene and $^{14}\text{CH}_2\text{N}_2$ contains all of the ^{14}C in the methyl group (75). The relative amounts of cycloheptatriene and toluene formed by attack of methylene on benzene were found to depend on the solvent (76). The ratio of cycloheptatriene/toluene increased from 3.3 (vapor phase) to 3.7 (2 *M* solution of benzene in cyclohexane), 4.8 (pure benzene), and 7.0 (2 *M* solution of benzene in *t*-butylnaphthalene). The obvious effect of aromatic solvents has been discussed in terms of π complexes of methylene.

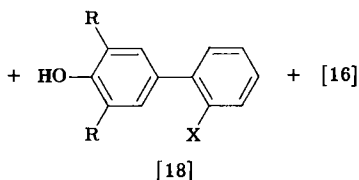
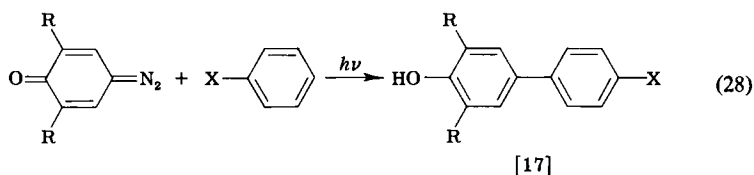


Insertion into the C—H bonds of benzene has also been observed with bis(trifluoromethyl)carbene (72) and phenylcarbene (77), whereas many other carbenes recorded in Table III add cleanly without concurrent insertion. Photolysis and thermolysis of 1,4-quinonediazides [15] in aromatic solvents afforded 4-hydroxybiphenyls [16] (78–84), sometimes accompanied by polymers (78–82). Partial elimination of halogen occurred with halobenzenes as the reactants, Eq. (28) (79, 81, 83).

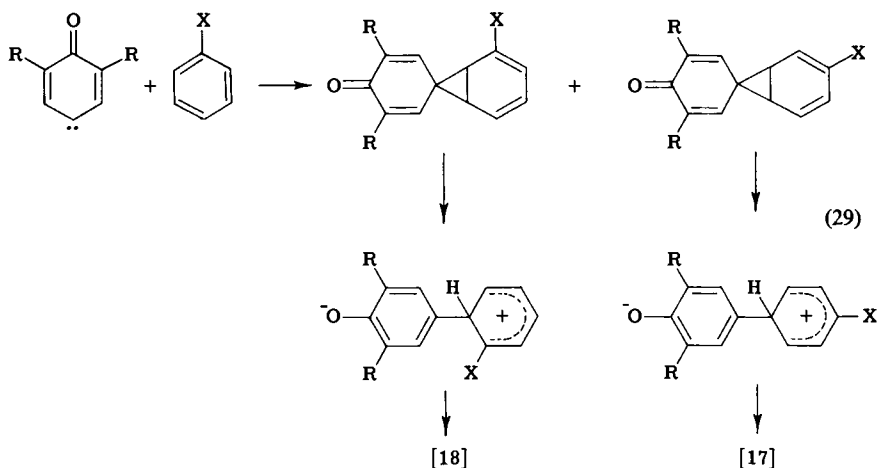


R = H (80), CH₃ (81), C(CH₃)₃ (84)

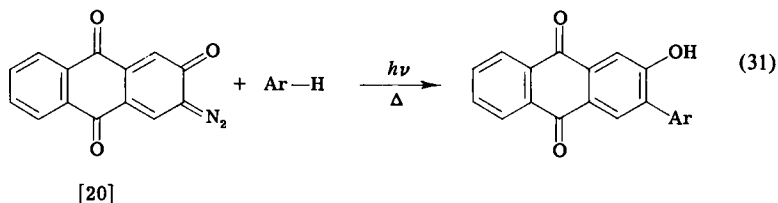
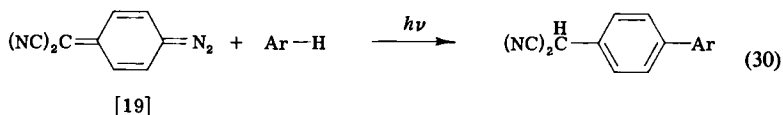
Cl (83), Br (79)



The carbenes derived from [15] have triplet ground states (84, 85). The ESR spectra show that one unpaired electron is largely localized in a σ orbital at C₁, and another is delocalized in a π orbital. A radical mechanism of reactions (27) and (28) has been considered (79, 81); it would be consistent with the ground-state structure of the carbenes. The complete absence of *m*-isomer (<0.5%) in the products from anisole, chlorobenzene, and bromobenzene (Table V), however, seems to rule out a radical mechanism. Addition of the carbene, followed by polar ring opening and proton transfer, plausibly explains the observed orientation (83).



The apparent insertion into C—H bonds of arenes has also been observed with compounds [19] (86) and [20] (87), although 1,2-quinone diazides normally undergo Wolff rearrangement (Chapter 12, Section V).



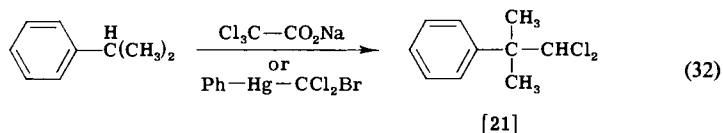
Benzylic carbon-hydrogen bonds are the most reactive sites of alkylbenzenes. With increasing alkyl substitution of the benzene nucleus [xylene (88), mesitylene (89), durene (90), prehnitene (91)], insertion of ethoxycarbonylcarbene gradually increases at the expense of cycloheptatriene formation. Even dichlorocarbene was found to insert into the benzylic C—H bonds of ethylbenzene, cumene, tetralin, and diphenylmethane. Fair yields resulted when dichlorocarbene was generated from sodium trichloroacetate (92) or phenyl(bromodichloromethyl)mercury

TABLE V

Reaction of 3,5-Dichlorobenzene-1,4-diazooxide [15], R=Cl) with
Substituted Benzenes (83)

Substituent	Rel. rate	Product distribution			
		Unsubst.	Ortho	Meta	Para
H	1.000	—	—	—	—
F	0.388	0	62.1	0	37.8
Cl	0.429	6	62	0	32
Br	0.345	26	42.3	0	31.6
CH ₃ O	1.276	0	72.8	0	27.2
CH ₃ O ₂ C	0.522	0	35.1	42.2	17.7
NC	0.335	0	45.0	16.5	38.5

(61), whereas chloroform-potassium *t*-butoxide (reacting at a much lower temperature) afforded only 0.5–5% of [21] and its analogs (92). Dichlorocarbene reacted with optically active 2-phenylbutane to give inactive 2-dichloromethyl-2-phenylbutane (41a). The deuterium isotope effect of benzylic insertion was 1.8 ± 0.2 (41a). An example of the insertion of dibromocarbene into a benzylic C—H bond (8.5% yield) was provided by the decomposition of PhHgCBr₃ in ethylbenzene at 85° (61a).



The photolytic reaction of azulenes with diphenyldiazomethane, various diazo ketones, and ethyl diazoacetate gave 1-substituted azulenes (93). The intervention of carbenes in this apparent insertion reaction is not definitively established; acid catalysis afforded the same products.

D. C—H Bonds of Ethers, Thio Ethers, and Amines

The insertion of methylene into C—H bonds was discovered when Meerwein, Rathjen, and Werner (94) irradiated diazomethane in diethyl ether, in tetrahydrofuran, and in isopropanol. In each case they found all the products that could arise from insertion of CH₂ into C—H bonds. More than a decade passed, however, before the insertion mechanism was recognized (48). Meerwein concluded that free methylene was not involved

[illegible]
$$\text{C}_2\text{H}_5\text{O}-\text{CH}_2\text{CH}_3 + \text{H}_2^{14}\text{CN}_2 \xrightarrow{h\nu} \text{C}_2\text{H}_5\text{O}-\text{CH}_2\text{CH}_2^{14}\text{CH}_3 \quad (34)$$

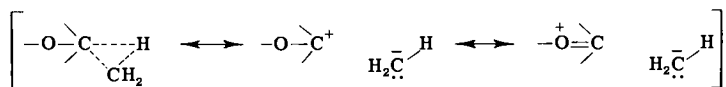
The oxygen atom of aliphatic ethers has a small promoting effect on methylene insertion into neighboring C—H bonds (97–102). In analogy to the behavior of alkanes, discrimination appears to be more pronounced in the gas phase than in the liquid phase (Table VI). Insertion is accompanied by minor side reactions which may be explained by an attack of methylene on oxygen (Chapter 11, Section IV). Triplet methylene abstracts hydrogen almost exclusively from the α position, giving rise to products of apparent α insertion (101, 102). Because of the differences in reactivity, it has been possible to estimate the percentage of singlet and triplet methylene under

TABLE VI
Insertion of Singlet Methylene into C—H Bonds of Ethers
(Photolysis of Diazomethane)

Ether	Conditions	Relative rates				Ref.
		α	β	γ	CH ₃ O—	
CH ₃ OCH ₂ CH ₃	Gas, O ₂	1.49	1.00		1.13	101, 102
	Liquid	1.30	1.00		1.00	
(CH ₃ CH ₂) ₂ O	Liquid	1.23	1.00			97
CH ₃ OCH ₂ CH ₂ CH ₃	Gas, O ₂	1.12	1.00	0.95	1.00	99, 101
	Liquid	1.00	1.00	0.98	0.98	
CH ₃ OCH(CH ₃) ₂	Gas, O ₂	1.73	1.00		1.39	101
	Liquid	1.21	1.00		1.13	
CH ₃ OC(CH ₃) ₃	Gas, O ₂		1.00		1.54	101
	Liquid		1.00		1.25	
	Gas, O ₂	1.35	1.00			97, 100
	Liquid	1.26	1.00			

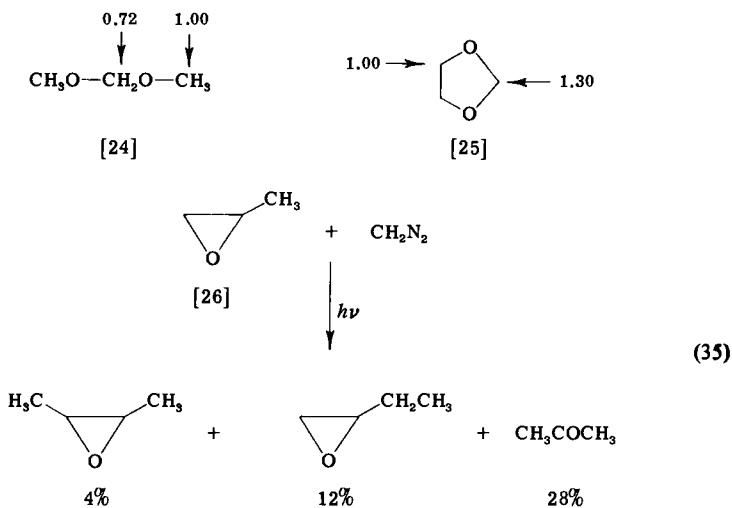
various conditions. In fair agreement with the data presented in Section I, the direct photolysis of diazomethane was found to produce about 10% of triplet methylene. The proportion of the selectively reacting species could be greatly increased by the addition of perfluoropropane. In the presence of a tenfold excess of perfluoropropane the amount of triplet methylenes increased to 33% and, when the C₃F₈/ether ratio was 40 : 1, about 56% of the reacting methylene was triplet. This is good evidence for collision-induced spin inversion. Methylene produced by the mercury-photosensitized decomposition of ketene was essentially all in the triplet state.

The photolytic reaction of diazomethane with triethylamine proceeded with insertion into the α - and β -C—H bonds in the ratio 1.17 : 1 (103). The small preference for insertion into the α -C—H bonds of ethers and amines was rationalized in terms of polar resonance structures of the transition state (97) (cf. Section A).



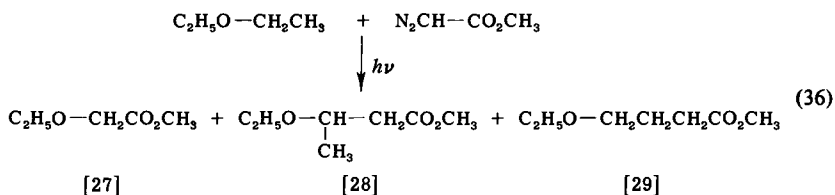
In contrast to expectations based on this concept, the O—CH₂—O hydrogens of methylal [24] were found to be less reactive than the CH₃O hydrogens (104). The reverse relation holds with 1,3-dioxolane [25]. These

results suggest that the conformation of ethers and acetals may be an important factor in determining the relative rates of methylene insertion. 2-Methyloxirane [26] also showed surprisingly small reactivity of the α -C—H bonds, essentially no 2,2-dimethyloxirane being formed (105). Energy transfer from excited diazomethane to [26] followed by rearrangement was suggested as a mechanism for the production of acetone.

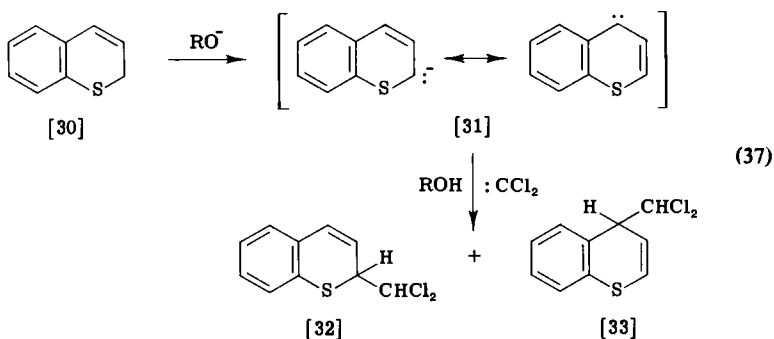


Insertion of alkoxycarbonylcarbenes into the C—H bonds of ethers competes less efficiently with cleavage at the O—alkyl bond than does the insertion of methylene. Methyl ethoxyacetate [27], methyl β -ethoxybutyrate [28], and γ -ethoxybutyrate [29] were produced in the ratio of $\sim 4:4:1$ when methyl diazoacetate was photolyzed in the presence of diethyl ether (106). The photolytic reaction of ethyl diazoacetate with dibutyl ether likewise afforded all products that would result from C—H insertion and C—O cleavage (107).

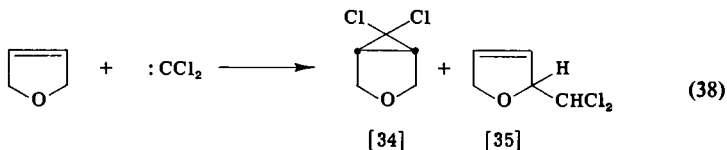
Apparent C—H insertion was observed when 2-*H*-1-benzothiopyran [30] reacted with dichlorocarbene (108). Two products, 2-dichloromethyl-2-*H*-1-benzothiopyran [32] and 4-dichloromethyl-4-*H*-1-benzothiopyran



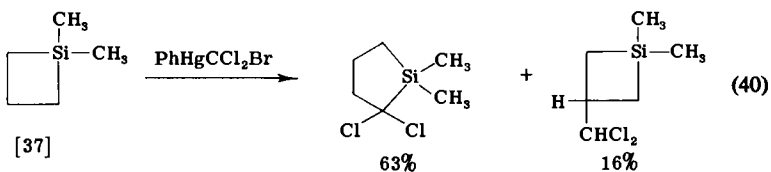
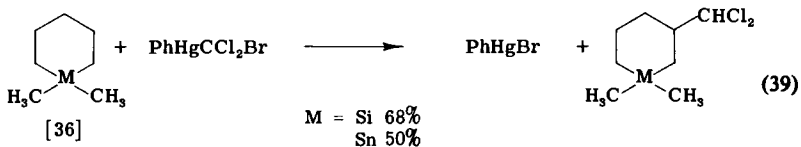
[33], were obtained in a 2.4 : 1 ratio with ethyl trichloroacetate–sodium methoxide as the dichlorocarbene source. The product ratio was 1 : 1 if the dichlorocarbene was generated from sodium trichloroacetate. The distribution of products in the allylic system suggests that an ambident ion [31] is involved, and the reaction may proceed as in Eq. (37). In contrast to [30], 4-*H*-1-benzothiopyran afforded a dichlorocyclopropane derivative under the same conditions.



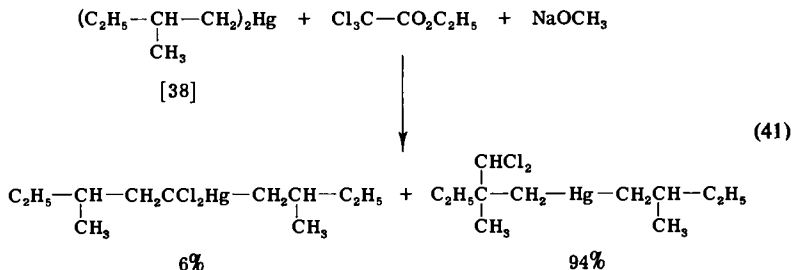
Dichlorocarbene and dibromocarbene both yielded an insertion product as well as the expected adduct with 2,5-dihydrofuran (109). The ratio of 6,6-dichloro-3-oxabicyclo[3.1.0]hexane [34] to 2-dichloromethyl-2,5-dihydrofuran [35] was 1.88 when dichlorocarbene was generated from ethyl trichloroacetate and sodium methoxide, 1.12 with sodium trichloroacetate, and 1.18 with phenyl(bromodichloromethyl)mercury (110). The high reactivity of cyclic ethers toward the mercurial reagent was confirmed by the formation of 2-dichloromethyltetrahydrofuran in 67% yield from tetrahydrofuran and $\text{PhHgCCl}_2\text{Br}$ in refluxing benzene (110). Yields of dichlorocarbene insertion products ranging from 10 to 60% were obtained from aliphatic ethers (110a). No reaction occurred at OCH_3 groups. Allyl ethers were found to be particularly reactive, C–H insertion competing efficiently with addition to the $\text{C}=\text{C}$ bond (110a,b). Noteworthy is the observation that difluorocarbene does not insert into those C–H bonds which are reactive toward dichlorocarbene (111).



Seyferth and Washburne (112) reported surprisingly specific insertions of dichlorocarbene into the β -C—H bonds of tetraalkylsilanes and -stannanes, e.g., [36]. Competitive insertion into the Si—C and β -C—H bonds occurred with silacyclobutanes, e.g., [37] (113). A consideration of product yields in 36 such reactions and the results of relative reactivity studies suggest that it is metal-carbon hyperconjugation and, to a lesser extent, the +I inductive effect of the alkylmetal substituents which are the important factors involved (113a). Noteworthy is the total absence of CCl_2 insertion into C—H bonds α to the silicon and tin atoms.



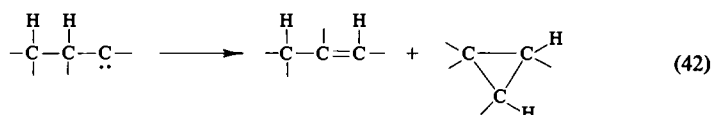
The attack of dichlorocarbene on dialkylmercury compounds results in the formation of both the C—Hg and the β -C—H insertion product (114, 115). The ratio of β -C—H to C—Hg insertion increased from 0 to 9 as the β -C—H bond went from primary to tertiary. Dichlorocarbene insertion into the β -C—H bond of bis(*S*)-2-methylbutylmercury [38] proceeded with overall retention of configuration to the estimated degree of 23% (115). The authors agree that the metal atom is most probably involved in these specific β -C—H insertion reactions, but the mechanism of participation remains speculative.



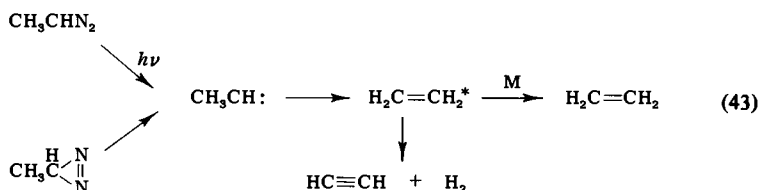
IV. INTRAMOLECULAR INSERTION

A. Competitive Formation of Olefins and Cyclopropanes

Alkyl- and dialkylcarbenes react predominantly by insertion of the divalent carbon into β - and γ -C—H bonds to give olefins and cyclopropanes, respectively. The intramolecular reactions of alkylcarbenoids, derived from organometallic precursors, often proceed in a similar fashion, differing only in product distribution from the decomposition of diazoalkanes.



The photolysis of diazoethane (116, 117) and methyldiazirine (118) in the gas phase produced ethylene and acetylene as the major products. The ratio of ethylene to acetylene increased linearly with pressure (116–118). Photolysis of CD_3CHN_2 showed that acetylene is formed from excited ethylene, and not from $\text{CD}_3\text{CH:}$ directly (117). Small amounts of 2-butene ($\sim 1\%$) were obtained in the photolysis of diazoethane (116, 117), and addition of CH_3CH to propene could be achieved in low yield (116). It remains doubtful, however, whether these products indicate true intermolecular reactions of methylcarbene since they were not observed in the photolysis of methyldiazirine (118). Similarly, dimethylcarbene could not be added to olefins, propene being the only product which emerged from the high-pressure photolysis of dimethyldiazirine (119).



Effects of excess energy have been observed in other gas-phase reactions of alkylcarbenes. Excited cyclohexene (produced by photolysis of pentamethylenediazirine at pressures below 10 mm) decomposed into butadiene and ethylene (120). 1,1-Dimethylcyclopropane, a major product in the photolysis of *t*-butyldiazirine (Table IX), isomerized at low pressures

TABLE VII
 Products from Ethylcarbene, $\text{CH}_3\text{CH}_2\text{CH}$

Reaction			
$\text{CH}_3\text{CH}_2\text{CHN}_2$, Photolysis	(122)	88	12
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}-\text{NH}-\text{Ts} + \text{NaOCH}_3$	(123)	90	10
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{Na}$	(124)	96	4
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{OCH}_3 + \text{Mg}$	(125)	99.4	0.6
$\text{CH}_3\text{CH}_2\text{CHI}_2 + \text{Zn}(\text{Cu})$	(126)	99.7	0.3

to give a mixture of 2-methylbutenes (121). These products are not obtained in the liquid phase where most of the alkylcarbenes have been studied.

The data collected in Table VII (122–126), Table VIII (122–130), Table IX (123, 127, 128, 131–134), Table X (123, 127, 129, 133, 138), and Table XI (123, 127, 129, 133) refer to intramolecular reactions of alkylcarbenes and -carbenoids in solution. The relative yields of cyclopropanes increase with increased branching of the alkyl groups. This behavior distinguishes carbenes from carbonium ions, for which the yields of cyclopropanes decrease with increased branching (136–138). Different

 TABLE VIII
 Products from Isopropylcarbene $(\text{CH}_3)_2\text{CH}-\text{CH}$

Reaction					
$(\text{CH}_3)_2\text{CH}-\text{CHN}_2$, Photolysis	(122)	54	36.5	5.5	4
Pyrolysis	(123)	67	33		
$(\text{CH}_3)_2\text{CH}-\text{C}(\text{N})=\text{N}$, Photolysis	(127)	53.6	29.4	9.3	7.7
Pyrolysis	(127)	53.6	45.5	0.5	0.3
$(\text{CH}_3)_2\text{CH}-\text{CH}=\text{N}-\text{NH}-\text{Ts} + \text{NaOCH}_3$	(123)	63	37		
	(122)	59	41		
$(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{Cl} + \text{Na}$	(124)	65	35		
+ PhNa	(128)	66	34		
$(\text{CH}_3)_2\text{CH}-\text{Li} + \text{CH}_2\text{Cl}_2$	(124, 129)	75	25		
$(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{SPh}_2^+ + \text{Ph}_3\text{Na}$	(130)	75	25		
$(\text{CH}_3)_2\text{CH}-\text{CH}(\text{Cl})\text{OCH}_3 + \text{Mg}$	(125)	74.5	24.5		
$(\text{CH}_3)_2\text{CH}-\text{CHI}_2 + \text{Zn}(\text{Cu})$	(126)	99	0.3	0.6	0.3

TABLE IX
Products from *tert*-Butylcarbene, $(\text{CH}_3)_3\text{C}-\text{CH}$

Reaction				
$(\text{CH}_3)_3\text{C}-\text{CHN}_2$, Photolysis	(131)	51.6	46.6	1.8
$(\text{CH}_3)_3\text{C}-\text{C} \begin{smallmatrix} \text{H} \diagup \text{N} \\ \parallel \\ \text{N} \end{smallmatrix}$	Photolysis	(127,132)	51	49
	Pyrolysis	(127,132)	92	8
$(\text{CH}_3)_3\text{C}-\text{CH}=\text{N}-\text{NH}-\text{Ts} + \text{NaOCH}_3$	(123)	92	7	1
$(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Cl} + \text{PhNa}$	(128)	96.5	3.5	
$(\text{CH}_3)_3\text{C}-\text{CHI}_2 + \text{CH}_3\text{Li}$	(133)	96	4	
$(\text{CH}_3)_3\text{C}-\text{Li} + \text{CH}_2\text{Cl}_2$	(134)	69	13	18

TABLE X
Products from Ethylmethylcarbene, $\text{CH}_3\text{CH}_2\text{C}-\text{CH}_3$

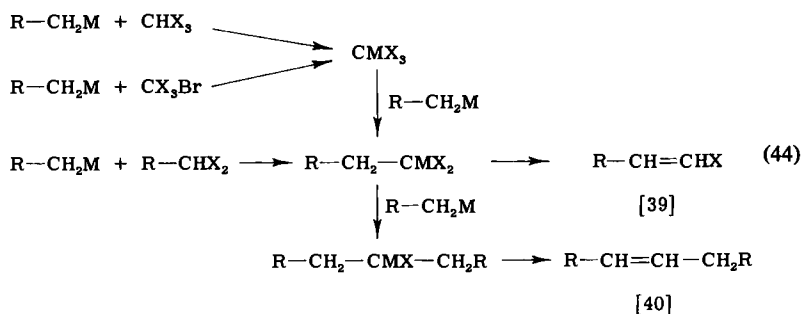
Reaction					
$\text{CH}_3\text{CH}_2-\text{C} \begin{smallmatrix} \text{N} \diagup \\ \parallel \\ \text{N} \end{smallmatrix}$	Photolysis	(127,135)	23	38	35
	Pyrolysis	(127,135)	3.5	66.5	29.5
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{N}-\text{NH}-\text{Ts} + \text{NaOCH}_3$	(123)	5	67	28	0.5
$\text{CH}_3\text{CH}_2\text{CBr}_2\text{CH}_3 + \text{CH}_3\text{Li}$	(133)	1	74	25	
$\text{CH}_3\text{CH}_2\text{Li} + \text{Cl}_2\text{CH}-\text{CH}_3$	(129)	7	44	47	

TABLE XI
Products from *tert*-Butylmethylcarbene, $(\text{CH}_3)_3\text{C}-\text{C}-\text{CH}_3$

Reaction				
$(\text{CH}_3)_3\text{C}-\text{C} \begin{smallmatrix} \text{N} \diagup \\ \parallel \\ \text{N} \end{smallmatrix}$	Photolysis	(127)	55.1	34.5
	Pyrolysis	(127)	51.4	48.2
$(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)=\text{N}-\text{NH}-\text{Ts} + \text{NaOCH}_3$	(123)	52	47	Trace
$(\text{CH}_3)_3\text{C}-\text{CBr}_2\text{CH}_3 + \text{CH}_3\text{Li}$	(133)	35	65	
$(\text{CH}_3)_3\text{C}-\text{Li} + \text{Cl}_2\text{CH}-\text{CH}_3$	(129)	57	43	

product distributions were obtained not only from carbenes and carbenoids, but also from the photolytic and thermal decomposition of diazoalkanes and alkyldiazirines. Photolysis of either diazoneopentane or *t*-butyldiazirine afforded ~50% of 2-methyl-2-butene, a product of methyl migration which was only a minor component in the thermal reactions (Table IX). Similar effects, although less pronounced, were observed with diazoisobutane and isopropyldiazirine (Table VIII). Ethylmethylcarbene (Table X) and diethylcarbene (127, 139) yielded more of the *cis*-2-olefins in the photochemical than in the thermal reaction. These results may be explained in terms of incomplete thermalization of the photolytically generated carbenes. It is difficult, however, to exclude the participation of electronically excited carbene precursors in these intramolecular reactions.

Carbenoids intervening in organometallic reactions sometimes approach the reactivity of "thermal" carbenes but frequently give lower yields of cyclopropanes. Olefins [40] essentially free from cyclopropanes may be synthesized from metal alkyls and 1,1-dichloroalkanes (129), haloforms (140), ortho esters (141), or tetrahalomethanes (142). The ratio of 1-haloalkenes to olefins, [39]/[40], depends on the reactivity of the α -hydrogen. Virtually no [39] was formed when $R = H$; [39] predominated when *sec*-alkyl derivatives, $RR'CHM$, were employed.



The complex nature of these carbenoid reactions is illustrated by the fact that different combinations of precursors selected to produce the same organometallic intermediate (e.g., $CH_3CH_2CHCl_2 + CH_3Li$, $CH_3CHCl_2 + CH_3CH_2Li$) gave different product mixtures (129).

The greater selectivity of carbenoids also emerges from the deuterium isotope effects of intramolecular C-H insertion reactions (Table XII). In the case of organometallic precursors, the unambiguous halogen dependence demands the presence of this atom in the transition state (143).

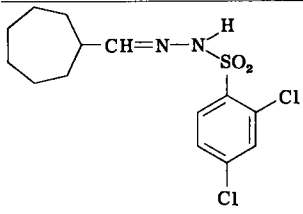
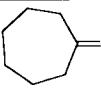
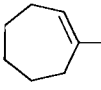
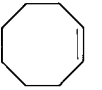
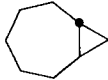
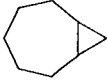
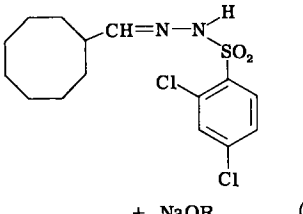
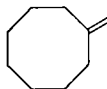
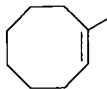
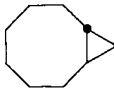
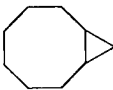
TABLE XII
Deuterium Isotope Effects of Intramolecular Insertion Reactions

planar arrangement of the divalent carbon, the ring carbon to which it is attached, and the C—H bond may be favorable for insertion (147, 148). The decrease in insertion by cyclohexylcarbene may be ascribed to the strain introduced in attaining a nearly eclipsed conformation. Consequently, 3-cyclohexenylcarbene gave more bicyclic products than did

TABLE XIII
Products from Cycloalkylcarbenes and —Carbenoids

Reaction, reference	Products (%)			
 $\text{CH}=\text{N}-\text{NH}-\text{Ts}$ $+ \text{NaOR}$ (146)	 37	 30	 23	 10
 $\text{CH}_2\text{Cl} + \text{Na}$ (147)	17	8	10	6
		 59		
 $\text{CH}=\text{N}-\text{NH}-\text{Ts}$ $+ \text{NaOR}$ (148)	 27.5	 72.5		
 $\text{CH}_2\text{Cl} + \text{Na}$ (147)	10	34	54	2
 $\text{CH}=\text{N}-\text{NH}-\text{Ts}$ $+ \text{NaOR}$ (148)	 92	 8		
 $\text{CH}_2\text{Cl} + \text{Na}$ (147)	36	3	61	
 $\text{CH}=\text{N}-\text{NH}-\text{Ts}$ $+ \text{NaOR}$ (149, 150)	 65	 5	 24	 6

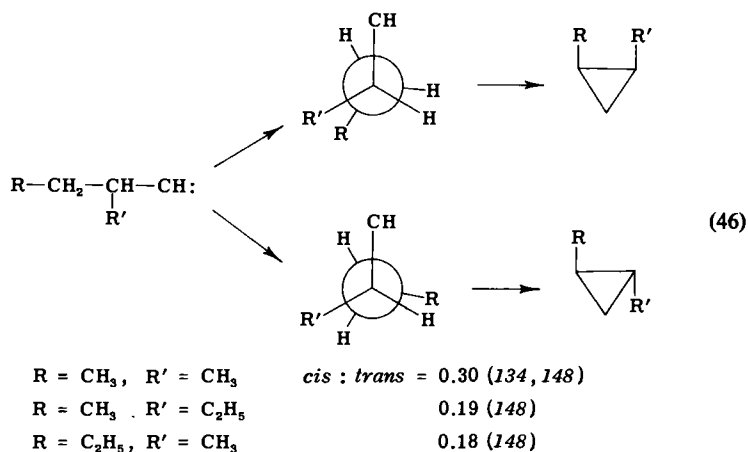
TABLE XIII (continued)

Reaction, reference	Products (%)		
 + NaOR (151)	 48	 2	 1
	 12	 37	
 + NaOR (151)	 44.5	 1.5	 33
		 18	

cyclohexylcarbene, and insertion into the allylic C—H bonds predominated (149, 150). This is not a substituent effect (cf. Section C), but is rather due to the smaller dihedral angle between carbons 1 and 2 ($\sim 45^\circ$) compared to that between carbons 1 and 6 ($\sim 60^\circ$).

Because of ring strain, cyclopentylcarbene and cyclohexylcarbene gave only *cis*-bicyclo[*n*.1.0]alkanes. Cycloheptylcarbene afforded *trans*-bicyclo[5.1.0]octane as the minor cyclopropane product, whereas *trans*-bicyclo[6.1.0]nonane predominated in the insertion reaction of cyclooctylcarbene (151).

The intramolecular reactions of acyclic carbenes start from low-energy staggered conformations of the carbene or carbene precursor and lead ultimately to the eclipsed conformation of the cyclopropane products. Nonbonding interactions of partially eclipsed groups are expected to determine the relative energies of the various transition states and, consequently, the product distributions. Suitable *sec*-alkylcarbenes afforded more *trans*- than *cis*-1,2-dialkylcyclopropanes, Eq. (46).



Competitive formation of structural isomers may also be affected by the eclipsing of groups which are not directly involved in the insertion process. The higher energy of the transition states [42] and [43] compared to that of [41] leads to an apparent selectivity in favor of primary C—H bonds (Table XIV). The formation of *trans*-1,2-dialkylcyclopropanes

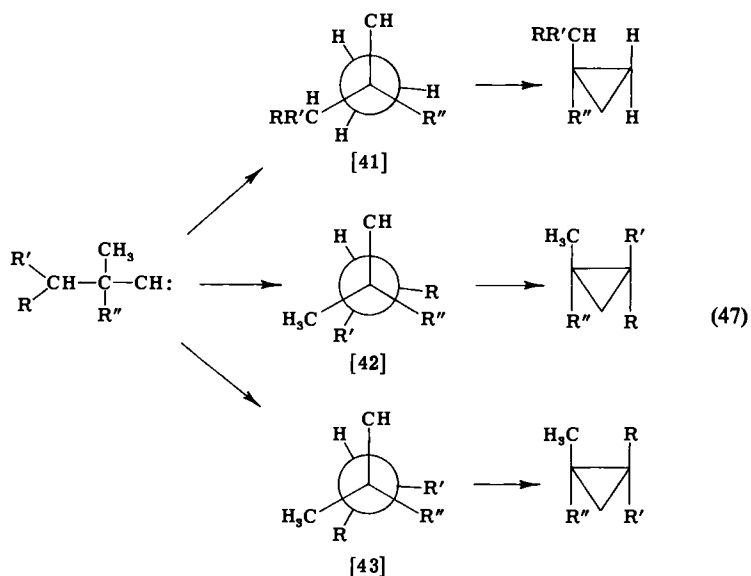


TABLE XIV
Relative Rates of Intramolecular γ -C—H Insertion, Eq. (47) (148)

R	R'	R''	2°/1°	3°/1°
CH ₃	H	H	1.60 (<i>trans</i>) 0.49 (<i>cis</i>)	—
CH ₃ CH ₂	H	H	2.54 (<i>trans</i>) 0.47 (<i>cis</i>)	—
CH ₃	H	CH ₃	0.78	—
CH ₃ CH ₂	H	CH ₃	0.85	—
(CH ₃) ₂ CH	H	CH ₃	0.95	—
CH ₃	CH ₃	H	—	0.83
CH ₃	CH ₃	CH ₃	—	0.38

which proceeds without significant steric hindrance (alkyl-hydrogen interactions only) shows the "normal" preference for secondary C—H bonds. The effect of steric compression may be overcome by increasing the selectivity of the intermediate, i.e., by employing carbenoids instead of carbenes. Table XV (131, 148, 152) shows that in many cases α -elimination

TABLE XV
Relative Rates of Intramolecular Insertion—Comparison of Carbenes and Carbenoids

Reaction ^a	2°/1°	3°/1°
R—CHN ₂ , photolysis (131)	0.81	0.63
R—CHN ₂ , thermolysis (diglyme) (148)	0.78	0.38
R—CHN ₂ , thermolysis (PhCH ₂ CH ₂ OH) (131)	2.4	—
R—CHN ₂ , thermolysis (PhCH ₂ OH) (131)	1.95	—
R—CHN ₂ , CuI (131)	4.8	1.5
R—CHN ₂ , AgI (131)	2.5	2.1
R—CH ₂ Cl + NaNH ₂ (152)	1.59	1.06
R—CHI ₂ + Na (152)	1.44	0.74
R—CHI ₂ + Li (152)	1.70	0.60
R—CHI ₂ + Mg (152)	2.18	1.74
R—CHI ₂ + Zn(Cu) (152)	6.4	4.0

^a 2°/1°, R = CH₃CH₂C(CH₃)₂; 3°/1°, R = (CH₃)₂CH—C(CH₃)₂.

and catalytic decomposition of diazoalkanes exhibit increased 2°/1° and 3°/1° rate ratios.

Several rules concerning the reactivity of cyclic carbenes emerge from Table XVI (63, 120, 139, 153–185c). β -C—H insertion with formation of

TABLE XVI
 Products from Cyclic Carbenes (Carbenoids)

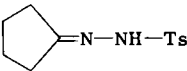
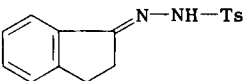
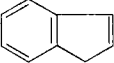
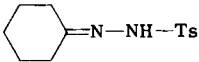
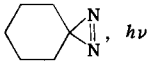
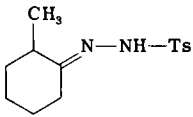
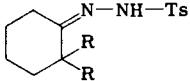
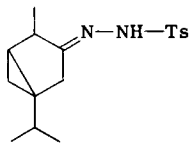
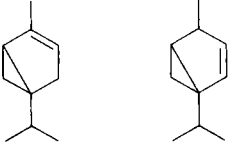
Carbene (carbenoid) Precursor		Products				
	(153)					
	(139)					
	(154)	 10%				
	(153)					
	(139)					
	(120)	 97.0	 2.5	 0.5		
	(155)	 63	 27	 0.2	 4	 60%
	(156)	 (75-90%)				
	(157)	 50				

TABLE XVI (continued)

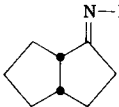
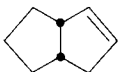
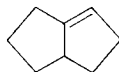
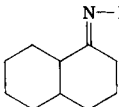
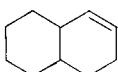
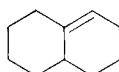
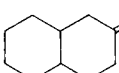
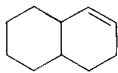
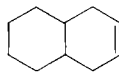
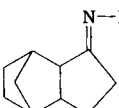
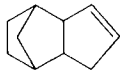
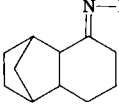
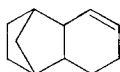
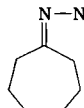
Carbene (carbenoid) Precursor		Products	
	(158)		
		97	3
	(159)		
	<i>cis</i>	75	25
	<i>trans</i>	26	74
	(159)		
	<i>cis</i>	51	49
	<i>trans</i>	35	65
	(160)		
	(161)		
Steroid diazirines	(162)	Δ^2 -Olefins	
Steroid tosylhydrazones	(163)	Δ^{11} -Olefins	
Terpenoid tosylhydrazones	(164)	Olefins	
	(153) ,		
	(165)	82	18
Cyclododecanone tosylhydrazone	(166)	Cyclododecene (<i>cis/trans</i> = 1 : 3)	

TABLE XVI (continued)

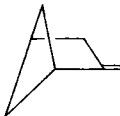
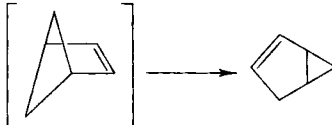
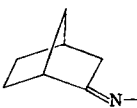
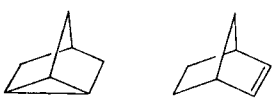
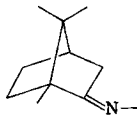
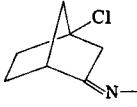
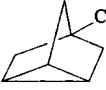
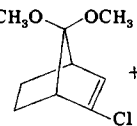
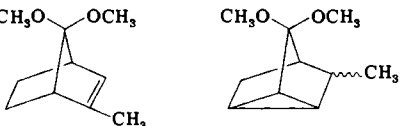
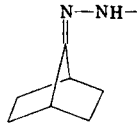
Carbene (carbenoid) Precursor	Products
 <chem>C12CCC3C1CCC2C3=N-NH-Ts</chem> (167)	 Rearranges at $> 150^\circ$
 <chem>C12CCC3C1CCC2C3=N-NH-Ts</chem> (168)	 99.5 0.5
Methylnorbornanone tosylhydrazones 1-(169, 170); 4- (169); 3- <i>endo</i> (169, 171); 3- <i>exo</i> (171); 5- <i>endo</i> (169); 6- <i>endo</i> (169); 7- <i>anti</i> (171)	Methylnortricyclenes (70-90%)
 <chem>CC12CCC3C1CCC2C3=N-NH-Ts</chem> (172, 173)	
 <chem>CC12CCC3C1CCC2C3=N-NH-Ts</chem> (63)	 (ca. 100%)
 <chem>COC12CCC3C1CCC2C3=N-NH-Ts</chem> (174) + <chem>CH3Li</chem>	 8.5 91.5
 <chem>C12CCC3C1CCC2C3=N-NH-Ts</chem> (175)	 14 12 74 (80%)

TABLE XVI (continued)

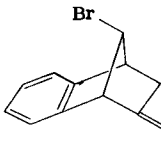
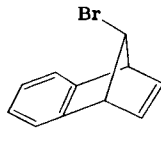
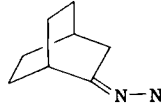
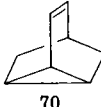
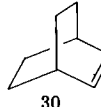
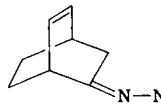
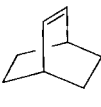
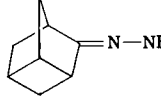
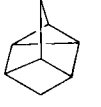
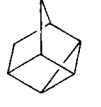
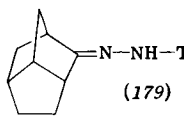
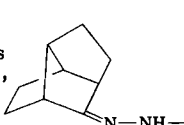
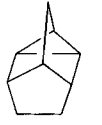
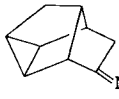
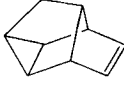
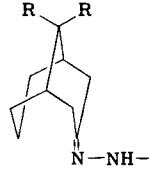
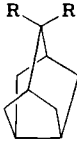
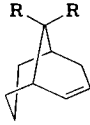
Carbene (carbenoid) Precursor		Products	
 (176)			
 (177)		 70	 30
 (177)		 (71%)	
 (178)		 65	 35 (44%)
 (179)			
 (180)			
 R = R = H R, R = —OCH ₂ CH ₂ O—	 (181)	 65 60	 35 (90%) 40 (35%)

TABLE XVI (continued)

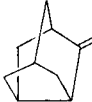
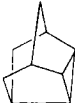
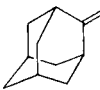
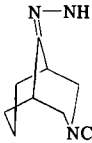
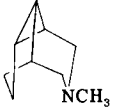
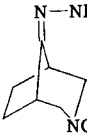
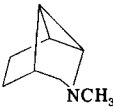
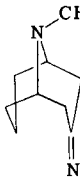
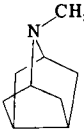
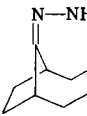
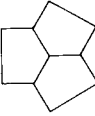
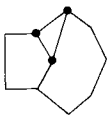
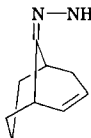
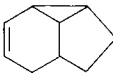
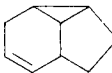
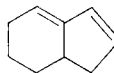
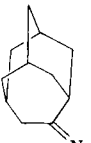
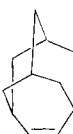
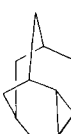
Carbene (carbenoid) Precursor	Products
 (182)	 $\equiv$ 
 (183)	 (65%)
 (184)	
 (184)	
 (185)	 (80%)
 (185a)	 (87%)  (4%)

TABLE XVI (continued)

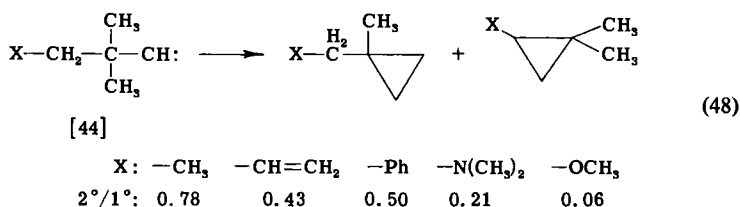
Carbene (carbenoid) Precursor	Products		
 (185b)	 (18%)	 (18%)	 (31%)
 (185c)	 (54%)	 (44%)	

olefins occurs almost exclusively when the divalent carbon is incorporated in five- and six-membered rings. In contrast, carbenacycloheptane produced substantial amounts of norcarane. Carbenes derived from medium-sized rings (C_8 – C_{10}) undergo transannular insertion which is considered more explicitly in Section D. In the bicyclo[2.2.1]heptane series, carbenes give nortricyclenes in strong preference to norbornenes. An increased production of olefins was observed in the bicyclo[2.2.2]octane and bicyclo[3.3.1]nonane series, but Bredt's rule enforces cyclopropane formation from adamantane and noradamantane structures. Tetraalkyl substituted *gem*-dibromocyclopropanes react with methyllithium to afford bicyclobutanes rather than allenes (Chapter 12, Section II) (185*d-f*). The intermediate cyclopropylidenes, free or complexed, must suffer sufficient steric hindrance to opening that γ -C–H insertion takes precedence. Some cases of transannular (1,5) insertion of bicyclo[3.3.1]nonane-derived carbenes have also been included in Table XVI. Conformational analysis has been helpful in understanding the selectivity of some of these reactions. The potential of intramolecular C–H insertion in the synthesis of fascinating tricyclic and quadricyclic compounds will be obvious.

C. Substituent Effects

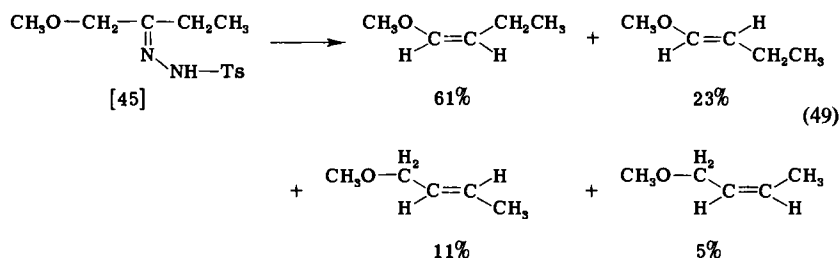
1. Substituents α to the Site of Insertion

The influence of substituents on the rate of γ -C-H insertion may be estimated from the proportions of isomeric cyclopropanes produced by substituted *t*-butylcarbenes [44]. The C-H bonds of the methyl groups are assumed to react at approximately the same rates regardless of the substituent X. The $2^\circ/1^\circ$ rate ratios thus provide an estimate of the reactivity of the CH_2X groups (186).



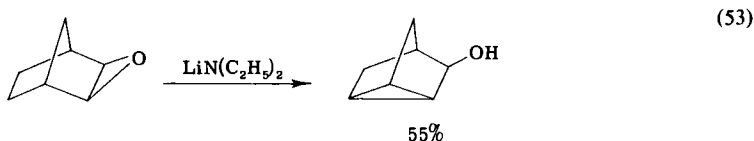
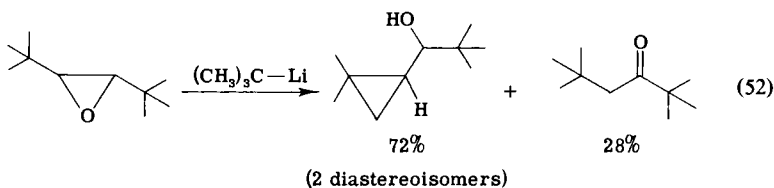
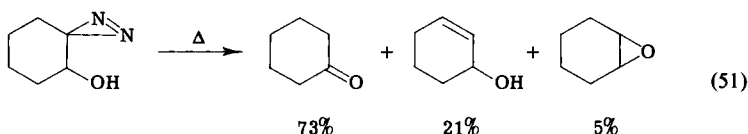
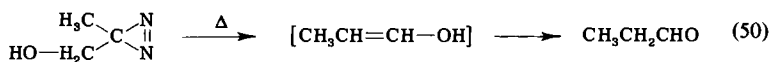
The data in Eq. (48) indicate a largely inductive effect of X. Stabilization of (partial) charge by resonance does not appear to be an important factor. The small contribution of resonance suggests concerted hydrogen transfer and C—C bonding in γ -C—H insertion reactions.

β -Alkoxy groups promote the transfer of hydrogen to the divalent carbon, in contrast to the deactivating effect of γ -OCH₃. The Bamford-Stevens reaction of 1-methoxy-2-butanonesulphhydrazone [45] afforded 1-methoxy-1-butenes and 1-methoxy-2-butenes in a 5.3 : 1 ratio (187).



β -Hydroxyalkylcarbenes behave similarly. These intermediates may be generated either from hydroxyalkyldiazirines (188, 189) or in a carbenoid

version, by metalation and α -elimination of epoxides (190, 191). The hydrogen α to the hydroxyl group was found to react preferentially with formation of carbonyl compounds, Eqs. (50) and (51), but in some cases allyl alcohols, Eq. (51), and cyclopropylcarbinols, Eq. (52), were also obtained. The notoriously γ -inserting bicyclo[2.2.1]heptane system produced nortricyclanol exclusively (190), Eq. (53).

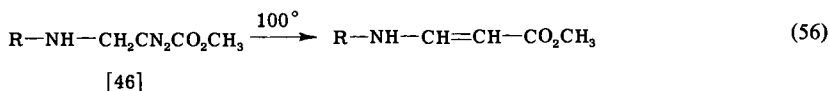
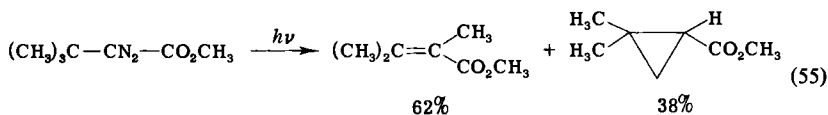
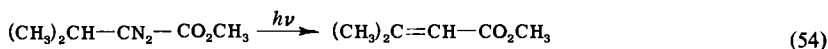


The bis-tosylhydrazone of hexane-2,5-dione afforded exclusively *cis*- and *trans*-2,4-hexadiene (21 : 79) (191a). This result may be due to a substituent effect of the first-formed double bond, but also to a base-catalyzed isomerization of nonconjugated dienes.

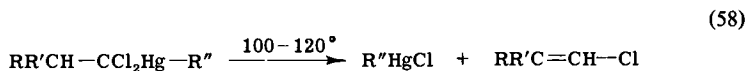
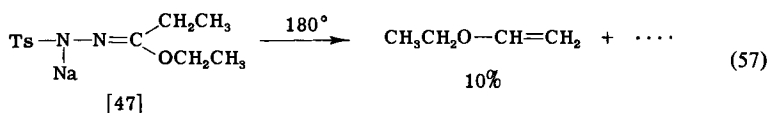
2. Substituents α to the Divalent Carbon

β -C—H insertion and alkyl migration predominate among the reactions of alkyl(alkoxycarbonyl)carbenes (192). Equations (54) and (55) provide two examples which should be compared with the products from isopropylcarbene (Table VIII) and *t*-butylcarbene (Table IX), respectively.

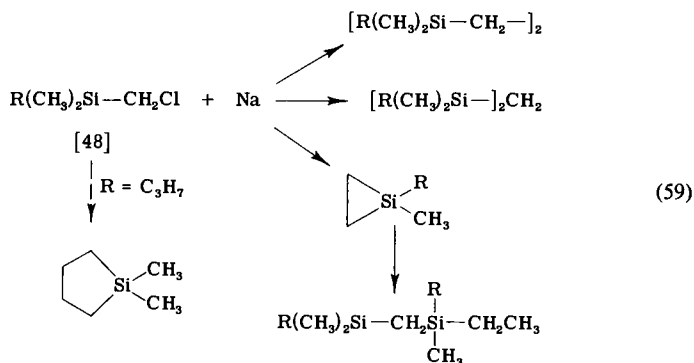
In contrast to β,β -dimethyl- α -diazobutyrate, the silicon analog $(\text{CH}_3)_3\text{SiCN}_2\text{CO}_2\text{R}$ did not undergo intramolecular reactions but inserted into C—H bonds of hydrocarbon solvents (192a)—another example of the inertness of C—H α to silicon toward attack by carbenes (cf. Section III. E). Methyl β -amino- α -diazopropionates [46] produced β -aminoacrylates in fair yields on pyrolysis (193).



Vinyl ethers were only minor products from the Bamford-Stevens reaction of the tosylhydrazones [47]. Fragmentation of the presumed alkyl(alkoxy)carbenes and noncarbenic side reactions of [47] predominated (194). Chloroalkenes were formed by β -C—H insertion of mercurial-derived alkylchlorocarbenes (195), Eq. (58) [see Section A, Eq. (44), for another organometallic route]. γ -C—H insertion was a major path only when the alkylchlorocarbenes were generated from alkyl chlorides and atomic carbon [Chapter 2, Section XIV, Eq. (89)].



The attempted generation of trialkylsilylcarbenes or -carbenoids by reaction of compounds [48] with sodium led to a variety of products which may be attributed to nucleophilic displacement at carbon and silicon, and to α -elimination. Some of the silanes obtained are suggestive of 1,3 and 1,5 insertion, but the presumed silacyclopropanes undergo nucleophilic ring cleavage (196, 197).

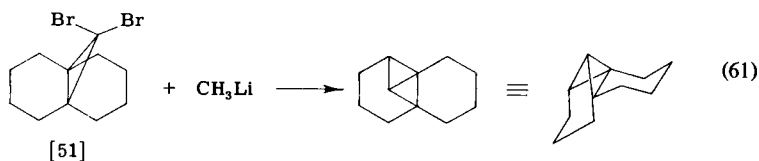
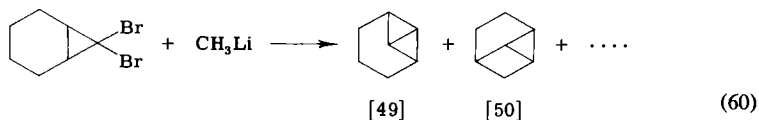


D. Long-Range Insertion

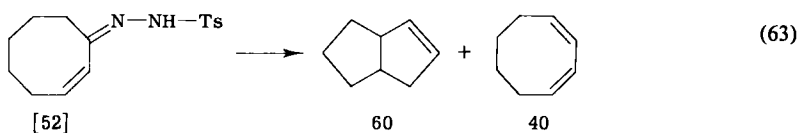
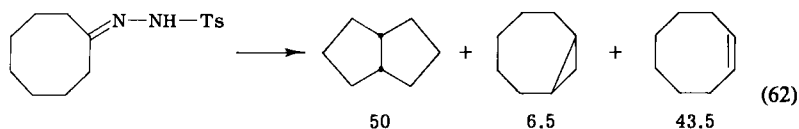
The formation of four-, five-, and six-membered rings by intramolecular insertion is quite exceptional in carbene chemistry. Among the carbenes capable of "long-range" insertion are those derived from medium-sized rings ($\text{C}_8\text{--C}_{10}$), and several aryl- and carbonylcarbenes not containing β - and $\gamma\text{-C-H}$ bonds.

1. Transannular Insertion

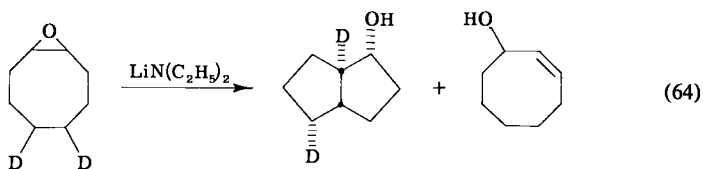
Carbenacycloheptane produces some norcarane but no bicyclo[3.2.0]heptane (Table XVI) (153, 165). A small amount of 1,4 insertion was observed, however, with the carbenoid generated from 7,7-dibromonorcarane and methyllithium (198, 199). Compounds [49] and [50], arising by intramolecular insertion in 30–40% yield and in a ratio of 23 : 1, were accompanied by products of intermolecular reaction with the solvent and with excess methyllithium, and by the dimeric olefin. The carbenoid derived from 11,11-dibromotricyclo[4.4.1.0^{1,6}]undecane [51] underwent 1,3 insertion exclusively and did not produce an analog of [50] (200).



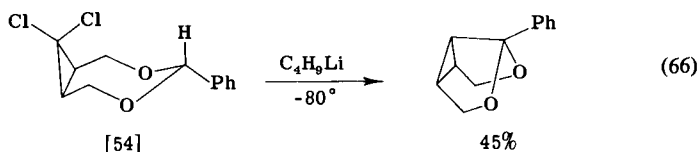
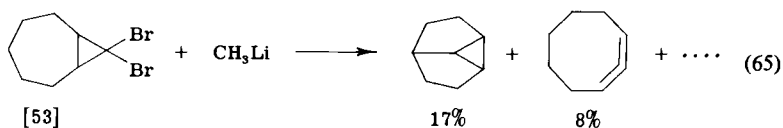
cis-Bicyclo[3.3.0]octane was obtained in ~50% yield from the aprotic Bamford-Stevens reaction of cyclooctanonetosylhydrazone (153, 201). 1,2 and 1,3 (but not 1,4) insertion were found to compete with the transannular reaction. A phenyl group in the 2 and 3 positions of cyclooctanone reduced the yields of bicyclo[3.3.0]octane derivatives to 18% and 17%, respectively (202). This result may be due to a slight flattening of the cyclooctane ring. The tosylhydrazones of 2-cycloocten-1-one [52] and 3-cycloocten-1-one, on the other hand, produced *cis*-bicyclo[3.3.0]octene in yields of 60% and 55%, respectively (203).



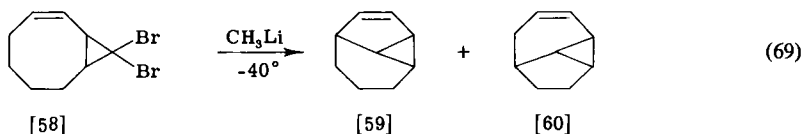
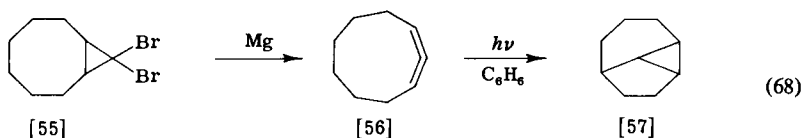
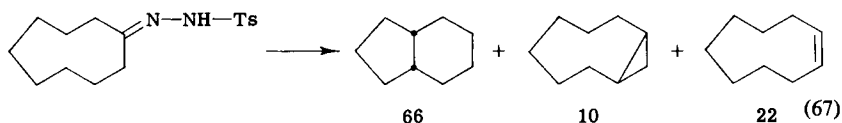
Cyclooctene oxide gave bicyclo[3.3.0]octan-2-ol and 2-cycloocten-1-ol on treatment with lithium diethylamide (204). The fate of the deuterium label in cyclooctene oxide-5,6- d_2 clearly showed that an α -elimination-insertion mechanism is involved.



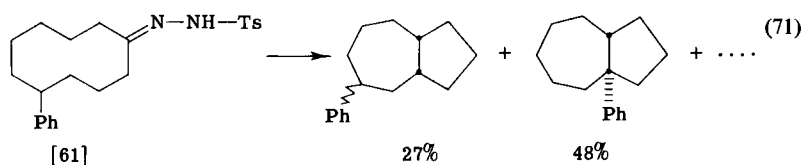
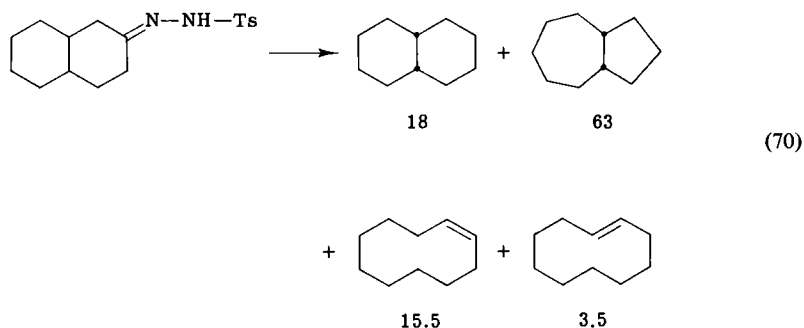
The reaction of 8,8-dibromobicyclo[5.1.0]octane [53] with methyl-lithium led to some transannular insertion. However, [53] appears to be the smallest bicyclic system where the cyclopropylidene-allene rearrangement (Chapter 12, Section II) can take place, producing 1,2-cyclooctadiene as a labile compound which rapidly dimerized (205). In contrast to [53], the carbenoid derived from the cyclic acetal [54] did not reveal any evidence of allene formation but inserted cleanly into the benzylic C—H bond (206).



Carbenacyclononane may be generated from cyclononanonetosylhydrazone in the aprotic Bamford-Stevens reaction (153), and by photolysis of bicyclo[5.2.1]decan-10-one via octamethyleneketene [Chapter 2, Section II, Eq. (10)]. *cis*-Bicyclo[4.3.0]nonane was a major product from both reactions. 9,9-Dibromobicyclo[6.1.0]nonane [55] was converted into 1,2-cyclononadiene [56] without competing intramolecular C—H insertion (207), but the benzene-sensitized photolysis of [56] afforded tricyclo[3.3.0.0^{2,9}]nonane [57] as the major product (208). The most reasonable pathway for the conversion of [56] into [57] is the closing of the allene to the cyclopropylidene and subsequent C—H insertion. In contrast to [55], the unsaturated analog [58] did not give a cyclononatriene but rather two products of intramolecular insertion, [59] and [60], in a 2 : 1 ratio (209).



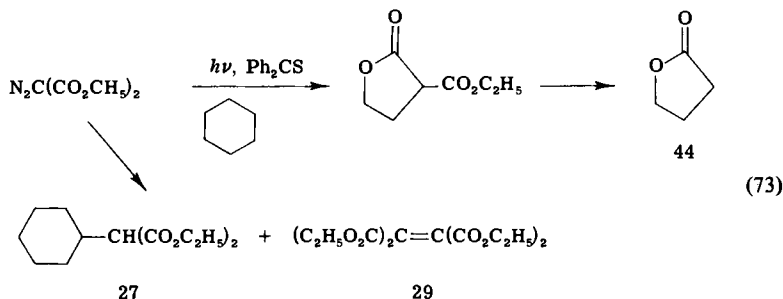
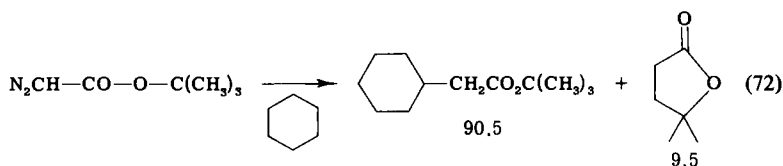
Cyclodecanonetosylhydrazone afforded both *cis*-decalin and *cis*-bicyclo[5.3.0]decane as transannular insertion products (153, 201). The corresponding 2-ols were obtained from cyclodecene oxide and lithium diethylamide (204). A preference for 1,5 insertion toward the benzylic position was noted in the decomposition of 5-phenylcyclodecanonetosylhydrazone [61] (210).



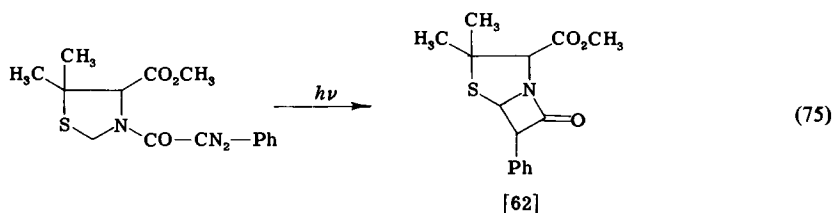
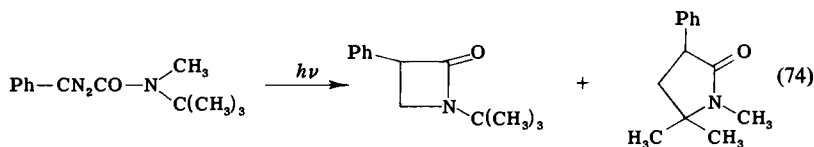
In all transannular insertion reactions, only *cis* junctures were observed in the bicyclic products, regardless of the thermodynamic stability of the *cis* and *trans* bicycloalkanes. This stereospecificity is a result of concerted transfer of an axial hydrogen in the insertion reaction and is in accord with the observation that C—H insertion proceeds with retention of configuration.

2. Long-Range Insertion of Carbonylcarbenes

Pholysis of ethyl diazoacetate, even in the vapor phase, did not produce butyrolactone. *t*-Butyl diazoacetate and *t*-amyl diazoacetate, however, afforded small amounts of lactones when photolyzed in cyclohexane solution (211). The $2^\circ/1^\circ$ rate ratio of the *t*-amyl compound was 1.63. The otherwise intermolecular reactions of diethyl diazomalonate were diverted in part to intramolecular insertion when the photolysis was carried out in the presence of thiobenzophenone (212).

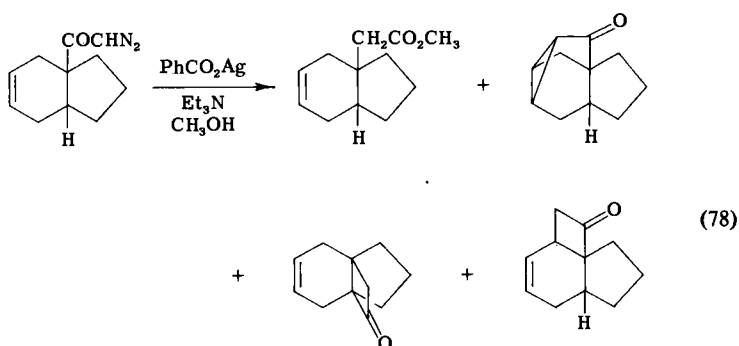
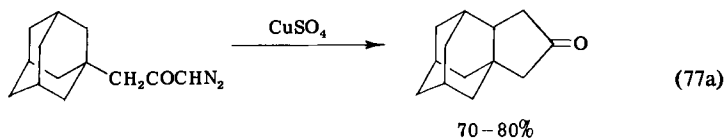
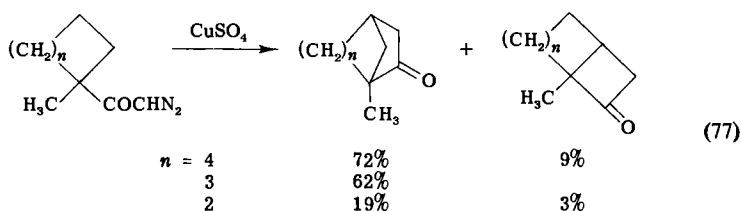
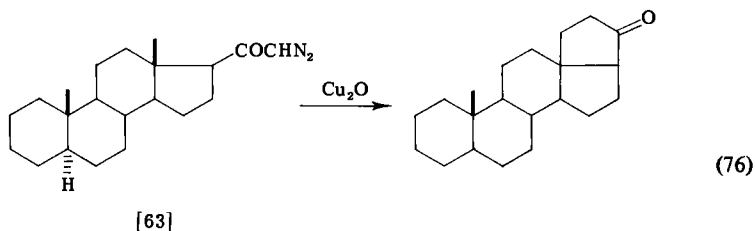


Several diazoamides were found to undergo intramolecular insertion into α -C—H bonds of the *N*-alkyl groups with formation of β -lactams (192, 213). This method was applied in a synthesis of methyl 6-phenylpenicillanate [62] (213).



The formation of cycloalkanones from diazoketones was first observed when 21-diazo-5 α -pregnan-20-one [63] was heated in toluene in the presence of copper(I) oxide (214). This method has also been used for intramolecular functionalization of the isopropyl group in dehydroabietic acid (215). A study of the CuSO_4 -catalyzed intramolecular C—H bond insertions of diazo ketones is summarized in Eqs. (77) and (77a) (216, 216a). When silver catalysts were employed, Wolff rearrangement (Chapter 12,

Section V) was found to compete with C—H insertion (216, 217). Equation (78) provides an example of three competing reactions, rearrangement, addition, and insertion (217).



Photolysis of 2-diazo-2-phenylacetophenone O-benzoyloxime [64] resulted in the formation of triphenylisoxazolines [65] (*cis* and *trans*) and triphenylisoxazole [66]. Compound [65] arises by 1,5 insertion into the benzylic C—H bonds and is dehydrogenated by [64] to give [66] (218).

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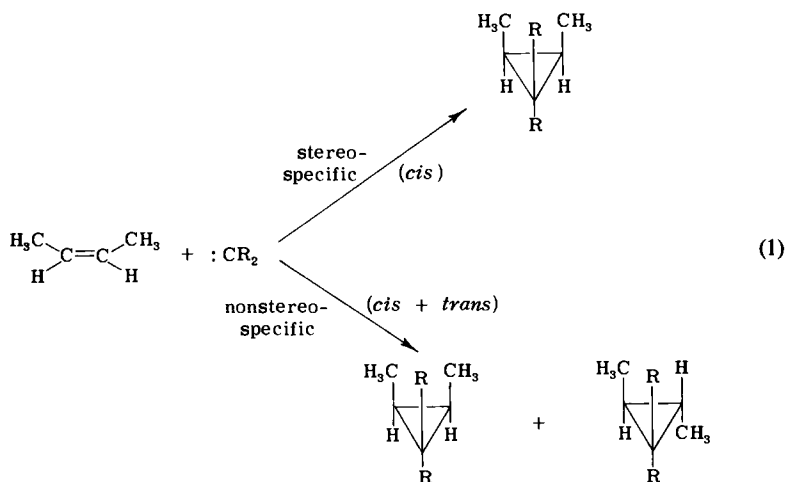
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Addition to Alkenes

I. STEREOSPECIFICITY

OLEFINS LACKING A symmetry axis along the carbon-carbon double bond, e.g., 2-butene, can form two adducts with a symmetrical carbene, Eq. (1). In a stereospecific reaction the geometrical relationship of the substituents is retained, i.e., *cis*-1,2-dialkylcyclopropanes are produced from *cis*-olefins, and *trans*-1,2-dialkylcyclopropanes from *trans*-olefins. This stereochemical course is also referred to as a *cis* addition. The reaction is called nonstereospecific if cyclopropanes are formed in which the arrangement of substituents relative to the plane of the ring does not correspond to the configuration of the olefin. An entirely nonstereospecific carbene addition is expected to yield identical product mixtures from *cis,trans* pairs of alkenes. If different product distributions are observed, the reaction exhibits some degree of stereospecificity. (In this text, the term "stereoselective" will refer to the ability of unsymmetrical carbenes to discriminate between the two possible modes of *cis* addition; Section II.)

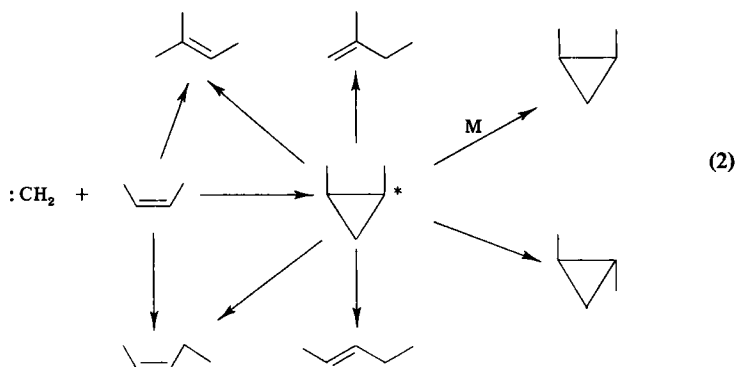


Two major causes of nonstereospecific formation of cyclopropanes can be envisioned: (i) initial stereospecific addition, followed by geometrical isomerization of the products, and (ii) nonstereospecific addition, proceeding through an intermediate whose geometry is less rigid than that of ground-state olefins and cyclopropanes. The first mechanism will be important in the gas phase where relaxation of vibrationally excited products is slow because of a low collision frequency with other molecules. The contributions of both mechanisms to the gas-phase reactions of methylene have been distinguished only after an extended effort of many research groups (Section A). Nonstereospecific addition in the liquid phase may be reasonably attributed to the second mechanism.

A. Reactions in the Gas Phase

Careful investigations of some of the simplest systems involving reactions of methylene have shown them to be of considerable complexity. *In statu nascendi*, the product of the reaction of methylene with an organic molecule is vibrationally excited by an amount of energy at least equal to the exothermicity of the reaction. With most olefins the addition of CH_2 will be exothermic by ~ 90 kcal/mole, while the activation energy of cyclopropane isomerization is known to be only 64 kcal/mole. Further transformation of the initial products by structural or geometrical isomerization is almost always a possibility in gas-phase reactions.

The first systematic study of the stereochemistry of the addition of methylene to olefins was carried out by Frey (1), who photolyzed diazomethane in the presence of either *cis*- or *trans*-2-butene. Two observations were of importance: (i) the yields of cyclopropanes increased with rising total pressure, and (ii) the cyclopropane formation was more stereospecific at higher pressures and longer wavelengths of the incident light. The results were rationalized in terms of Eq. (2) which assumes initial stereospecific addition to the double bond in competition with insertion into the allylic and vinylic C—H bonds. Deactivating collisions of the vibrationally excited 1,2-dimethylcyclopropane molecules will inhibit rearrangement to the isomeric cyclopropane and to the thermodynamically more stable pentenes. Consequently, more of the initial adducts are preserved at higher pressures. It was found that the geometrical isomerization of the cyclopropanes proceeds considerably faster than structural rearrangement to the pentenes. This observation was supported by independent thermochemical studies on the 1,2-dimethylcyclopropanes (2).



The rates of geometrical and structural isomerization of activated *cis*-1,2-dimethylcyclopropane have been determined by an internal comparison method (3) (Table I). The success of RRKM (Rice-Ramsperger-Kassel-Marcus) theory in predicting rates in chemical activation

TABLE I
Rates of Geometrical and Structural Isomerization
in Diazomethane-*cis*-2-butene Systems (3)

Isomerization	3660 Å	4358 Å
Geometrical	$k = 9.0 \cdot 10^8 \text{ sec}^{-1}$	$5.5 \cdot 10^8 \text{ sec}^{-1}$
Structural	$k = 0.96 \cdot 10^8 \text{ sec}^{-1}$	$0.68 \cdot 10^8 \text{ sec}^{-1}$

systems (4) encourages its use, combined with experimental rates, to determine the energy of a chemical activation system. According to RRKM calculations, the energies carried into the activated 1,2-dimethylcyclopropane molecules by methylene were 113.0 and 116.8 kcal/mole at 4358 Å and 3660 Å, respectively. Methylene carries into the addition reaction a relatively small fraction of the excess energy available from its formation (a difference in photon energies of 12.5 kcal/mole corresponds to a difference of only 3.8 kcal/mole in methylene energies).

Studies of the reactions of methylene produced by the thermal decomposition of diazomethane indicate that at about 350° the resulting 1,2-dimethylcyclopropane has approximately the same energy content as

the same molecule formed by the photolysis of diazomethane with *cis*-2-butene using 4358 Å radiation (5).

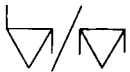
According to Eq. (2), all products derived from activated 1,2-dimethylcyclopropane should be eliminated at pressures which are high enough to ensure complete collisional deactivation. Although the yields of 2-methyl-1-butene and *trans*-2-pentene approach zero with increasing pressure, the yield of *trans*-1,2-dimethylcyclopropane does not (1). Similarly, the photolysis of diazomethane or ketene in the presence of *cis*-3-hexene gave rise to some *trans*-1,2-diethylcyclopropane, even at pressures where all the initially formed *cis* compound would be stabilized (6). These observations suggest that a second mechanism of nonstereospecific cyclopropane formation is involved.

Skell (7) introduced the idea of relating the stereospecificity (or lack of it) observed in the reactions of methylene with olefins to the singlet (or triplet) nature of the methylenic species. The underlying mechanistic assumptions are discussed in Section D. The following paragraphs summarize the experimental evidence which supports the correlation of stereospecificity with the spin state.

One approach to this problem was foreshadowed by the spectroscopic findings of Herzberg and Shoosmith (8, 9). Their results indicated that the flash photolysis of diazomethane yields methylene molecules in excited singlet states which are subsequently energetically degraded to the triplet ground state through collision with inert gas molecules. The stereochemistry of methylene addition to olefins is strongly affected when the reaction is carried out at a high pressure of inert gas, such as nitrogen or argon, the olefin accounting only for a small fraction of the total pressure (10, 11). Under those conditions, cyclopropane formation may show little stereospecificity (Table II). It should be remembered, however, that any geometrical isomerization of vibrationally excited cyclopropanes would invalidate the conclusions drawn from the experiments with added inert gas.

While this condition has well been recognized, the actual pressure limit has been controversial. Anet *et al.* (10) studied the products obtained from the photolysis of small partial pressures of diazomethane and *cis*-2-butene in the presence of a large excess of nitrogen. They found that much of the stereospecificity of the reaction was lost and concluded that singlet methylene had been converted into the triplet state through collision with inert gas molecules. Frey (11) has criticized the work of Anet *et al.* on the grounds that the inert gas pressures employed by these workers (~560 mm)

TABLE II
Stereochemistry of Methylene Addition to 2-Butene

Precursor	Wavelength (Å)	Additive	Additive/ butene		Ref.
<i>trans</i> -2-Butene					
CH ₂ CO	3660	—	—	4.0	(17)
	3660	CH ₃ I	4	2.94	(17)
	3660	O ₂	0.02	> 30	(17)
CH ₂ CO	3130	—	—	3.7	(18)
	3130	CH ₃ I	10	8.3	(17)
	3130	O ₂	0.02	> 100	(17)
CH ₂ CO, Hg	2537	—	—	3.85	(19)
CH ₂ N ₂	Unfilt.	N ₂	1500	9.3	(15)
<i>cis</i> -2-Butene					
CH ₂ CO	3660	—	—	1.9	(18)
	3660	CH ₃ I	4	2.78	(17)
CH ₂ CO	3130	—	—	0.27	(17)
	3130	CH ₃ I	10	0.92	(17)
	3130	O ₂	0.02	0.02	(17)
CH ₂ CO, Hg	2537	—	—	1.3	(19)
				1.6	(20)
CH ₂ N ₂	4358	Ar	1600	0.97	(11)
	4358	Ar	314	0.69	(11)
	4358	Ar	356	0.07	(11)
		O ₂	0.5		
	4358	N ₂	1500	0.40	(15)

were not sufficient to quench the geometrical isomerization of the highly energized *cis*-1,2-dimethylcyclopropane molecules. Frey (11) repeated these experiments with inert gas pressures up to 2000 mm Hg and observed the same lack of stereospecificity, which he attributed to triplet methylene. DeMore and Benson (12) have questioned the existence of triplet CH₂ even in Frey's experiments. They argue that dilution of the reaction mixture with nitrogen and argon in place of *cis*-2-butene leads to a decreased deactivation efficiency and that the loss of stereospecificity observed by Frey could still be due to geometrical isomerization of the initially formed *cis*-1,2-dimethylcyclopropane.

Much of this contradictory argumentation has been resolved by the work of Bader and Generosa (13). The experiments consist of photolyzing

mixtures of fixed, small amounts of diazomethane (0.9 mm Hg) and *cis*-2-butene (0.35 mm Hg) in the presence of an increasing partial pressure (0–850 mm Hg) of an inert gas (He, Ar, Xe, N₂, or CF₄). The variation of the relative yield of *trans*-1,2-dimethylcyclopropane as a function of the inert gas pressure indicates that two basic mechanisms are responsible for its formation. An initial decrease in the yield of the *trans* isomer with increasing pressure shows that a source is the isomerization of energized molecules. A subsequent rise in the yield of the *trans* isomer with further increase in the pressure is attributed to a mechanism involving triplet methylene. The participation of this mechanism is proved for any pressure above the value at the minimum. It should be noted that the minimum occurred at 100 mm Hg with CF₄ and at 250 mm Hg with N₂ and Xe, while no well-defined U-shape was observed with He. Helium is the least effective both in deactivating and in causing the spin inversion.

Estimates of the relative deactivation efficiencies of inert gases have been made in various ways. Either the reaction of singlet CH₂ with ketene itself (13a) or the reaction with added propane (13b) was used as the reference monitoring singlet CH₂. In a flash photolysis study (13c), triplet CH₂ was observed by kinetic spectroscopy at 1415 Å. The deactivation efficiency ratios He:Ar:N₂ obtained were only in moderate agreement: 1,0 : 0,8 : 2,9 (13a); 1,0 : 2,7 : 4,1 (13b); 1,0 : 2,2 : 3,0 (13c). Deactivation by nitrogen poses a special problem in that N₂ is not inert toward singlet methylene (cf. Chapter 2, Section IV).

When a constant ratio of *cis*-2-butene/diazomethane/nitrogen was maintained at 20 : 1 : 30,000, and reaction pressures were varied from 0.3 to 3.5 atm, the ratio of *trans* : *cis*-1,2-dimethylcyclopropane increased to a plateau or shallow maximum with rise of pressure (14, 15). The relative yields of some alkene products decreased as the reaction pressure was raised. These results indicate that the partitioning of the triplet reaction intermediate(s) may be pressure-dependent.

Confirmatory evidence for spin inversion of methylene by inert gas molecules comes from the effect of added radical scavengers. Addition of a few percent of oxygen to methylene-alkene-inert gas systems was found to restore the stereospecificity of the cyclopropanation reaction (11, 13). A recent report has demonstrated that O₂ eliminates triplet methylene directly by oxidation to carbon oxides (16). In contrast, methyl iodide prevents the formation of triplet products involving monoradicals (abstraction of H) in their genesis, but does not suppress the nonstereospecific addition to alkenes (17) (Table II) (11, 15, 17–20).

A second method of generating methylene in its triplet state utilizes the decomposition of ketene, photosensitized by the excited triplet state (6^3P_1) of mercury atoms. Duncan and Cvetanović (19) found that methylene produced in this manner added nonstereospecifically to the 2-butenes (Table II). The results are consistent with a mechanism in which triplet ketene, formed by transfer of excitation from mercury triplets, decomposes with direct formation of triplet methylene. The mercury-sensitized photolysis of ketene has long been considered a source of triplet methylene uncontaminated by the singlet species. Recent studies, however, have detected a minor stereospecific reaction which could not be quenched by the addition of oxygen (20). The presence of $\sim 13\%$ of singlet methylene in mercury-ketene-butene photolysis systems may be due to direct photolysis of ketene.

Several attempts have been made to calculate the fraction of triplet methylene intervening in specific methylene-butene systems from the degree of stereospecificity displayed in the formation of 1,2-dimethylcyclopropane. This method requires some estimate of the *trans* : *cis* ratio of 1,2-dimethylcyclopropane formed from triplet methylene. It is by no means certain that the addition of triplet CH_2 to 2-butene is entirely nonstereospecific (cf. Section D), and any numerical value of the *trans* : *cis* ratio would be even less reliable. Table II shows that only in $\text{CH}_2\text{CO}-\text{CH}_3\text{I}$ -alkene systems at 3660 Å (17) has approximately the same cyclopropane composition been obtained from *cis*- and *trans*-alkene precursors. The presence of methyl iodide could be a complicating factor in these experiments. Appreciable discrepancies between the *cis*- and *trans*-2-butene series have been observed with the inert gas-modified and mercury-photosensitized reactions. It is not surprising, therefore, that "triplet methylene fractions" determined under similar experimental conditions have sometimes differed significantly, e.g., for the direct photolysis of ketene at 3130 Å, the values 15 (21, 22), 20–30 (6), 29 (23), and 37% (24) have been reported. Triplet methylene fractions ranging from 40% to 77% have been estimated at 3660 Å (21, 25).

Comparison of the absolute product yields in the absence and presence of oxygen appears to be a more satisfactory method (which is based on the premise that all "triplet products" are suppressed by oxygen). The average values for the direct photolysis of ketene obtained in this way were $87 \pm 2\%$ at 3660 Å and $29 \pm 3\%$ at 3130 Å (18).

As discussed in previous paragraphs, nonstereospecific addition of methylene to olefins has been attributed either to the intervention of triplet

methylene or to rearrangements of cyclopropanes carrying excess vibrational energy. The hot-molecule mechanism for nonstereospecific addition in the gas phase should be much less important for derivatives of methylene. Almost any substituent can be expected to stabilize the divalent carbon intermediate, thereby decreasing the exothermicity of the addition process. Unfortunately, very few gas-phase addition reactions have been reported for substituted methylenes.

The behavior of fluorocarbene has been studied utilizing the tritium-labeled carbene :CTF (26). The species CTF was formed by the unimolecular decomposition of excited CHTFX , which was itself formed by energetic tritium atom reactions with polyhalomethanes, particularly CH_2F_2 . The addition of CTF to the double bond of either *cis*- or *trans*-2-butene was 99% stereospecific and was not affected by small amounts of oxygen. These observations are consistent with CTF reacting in a singlet electronic ground state. The absence of isomerization of excited fluorocyclopropane to the fluoropropenes indicates that less than 75 kcal/mole is released by CTF addition to ethylene.

Difluoromethylfluorocarbene ($\text{CHF}_2-\dot{\text{C}}-\text{F}$), generated by pyrolysis of $\text{CHF}_2\text{CF}_2\text{SiF}_3$ at 150° , was 100% stereospecific in its addition to *cis*- and *trans*-2-butene (27). In contrast, the vapor phase photolysis of 2,2,2-trifluorodiazaoethane in the presence of *cis*-2-butene led to 60% nonstereospecific addition of $\text{CF}_3\text{CH:}$ (28). Bis(trifluoromethyl)carbene, produced by pyrolysis of the corresponding diazine, yielded 17% of *trans* adduct in its reaction with *cis*-2-butene (29). Nonstereospecific addition of triplet carbenes may well explain these observations. Fluorine attached directly to the divalent carbon has a strong stabilizing effect on the singlet state. Trifluoromethyl groups show an opposite trend (30). In fact, the spectroscopically observed ground state of fluorocarbene is singlet, whereas that of trifluoromethylcarbene and bis(trifluoromethyl)carbene is triplet (Chapter 6).

B. Reactions in the Liquid Phase

Hot-molecule rearrangements are extremely unlikely in the liquid phase in view of the very high collision frequencies. Collisional deactivation of excited molecules will be much faster than even the more readily occurring rearrangements. Consequently, nonstereospecific behavior of carbenes in the liquid phase must be attributed to the mechanism of the addition reaction. The results of many investigations in this field may be

summarized by stating that nonstereospecific addition has been observed only for those carbenes which have a readily accessible triplet state. Although the observation of stereospecific addition most certainly means that the reaction has occurred with the singlet state, it does not guarantee that this is the ground state, since intersystem crossing may be slower than reaction with the alkene. In fact, methylene, when generated by direct photolysis of diazomethane in the liquid phase, adds to olefins with complete retention of configuration (7, 31).

Because of the high reactivity of singlet methylene, it is difficult to promote intersystem crossing by inert solvents. A liquid system involving triplet methylene was produced by photolysis of diazomethane in a 200-fold excess of perfluoropropane (32). Table III shows a significant decrease in

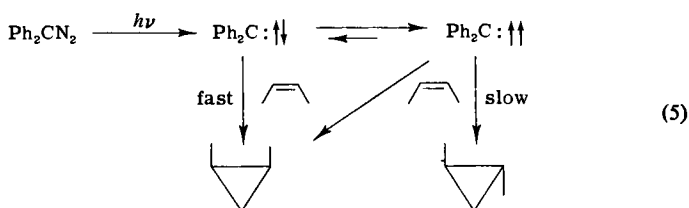
TABLE III
Liquid-Phase Photolysis of Diazomethane in the Presence
of *cis*-2-Butene (32)

Products	<i>cis</i> -2-Butene, neat	<i>cis</i> -2-Butene + C ₃ F ₈ (1 : 200)
<i>cis</i> -1,2-Dimethylcyclopropane	47.5	60.4
<i>trans</i> -1,2-Dimethylcyclopropane	0.4	13.3
<i>cis</i> -2-Pentene	39.1	9.3
<i>trans</i> -2-Pentene	0.0	7.1
2-Methyl-2-butene	12.5	1.9
2-Methyl-1-butene	0.3	1.9
3-Methyl-1-butene	0.2	6.1

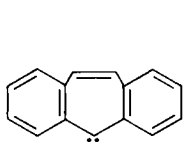
both stereospecificity and C—H insertion as compared to the photolysis in neat *cis*-2-butene.

The dilution technique has been applied successfully to other carbenes which have triplet ground states. Fluorenylidene, generated by photolysis of 9-diazo fluorene in *cis*-2-butene as the solvent, afforded *cis* [1] and *trans* [2] adducts in a ratio of 1.95 (33). This ratio decreased to 0.25 on dilution of *cis*-2-butene with 90–100 mole % of hexafluorobenzene. Irradiation in *trans*-2-butene gave the same products in a ratio of 0.06 which increased to 0.14 when C₆F₆ was added. Extrapolation of the available data to infinite dilution suggests a common product ratio of approximately 0.16. Added oxygen or 1,3-butadiene caused the reaction to become more stereospecific, triplet fluorenylidene being scavenged and leaving behind

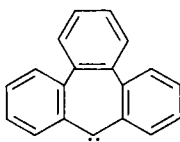
butene the *trans* addition products do not account for more than 3% and 1%, respectively (40). The loss of stereospecificity observed with diphenylcarbene is also relatively small (41, 42). At -10° with *cis*-2-butene as the trapping olefin, *cis*- and *trans*-1,2-dimethyl-3,3-diphenylcyclopropane were formed in a ratio of 3.2 (at -60° this ratio was 9.0). At a given temperature, the product ratio was unaffected by dilution with cyclohexane and by addition of oxygen (although oxygen lowered the total yield of diphenylcarbene products). As an explanation of these results, it has been postulated that intersystem crossing is much faster than any other reaction in this system. A rapid equilibrium would provide a constant ratio of triplet and singlet diphenylcarbene, with the triplet (ground state) predominating but reacting slowly, and the singlet as a minor component of high reactivity (43).



The related systems dibenzo[*a,d*]cycloheptenyliene [5] and tribenzo[*a,c,e*]cycloheptenyliene [6] added stereospecifically to the 2-butenes, although ESR studies have shown them to have triplet ground states (44, 45). The addition of cycloheptatrienyliene [7] to fumaronitrile and maleinitrile was completely stereospecific if extreme precautions were taken to exclude all excess base in the generation of [7] from tropone-silylhydrazone (46). Previous reports of a nonstereospecific reaction of [7] with diethyl maleate and diethyl fumarate (47) were due to some isomerization of diethyl maleate to diethyl fumarate, combined with a much higher reactivity of the latter toward [7] (46). The stereospecificity of [7] was unaffected by high dilution and heavy atom solvents.



[5]



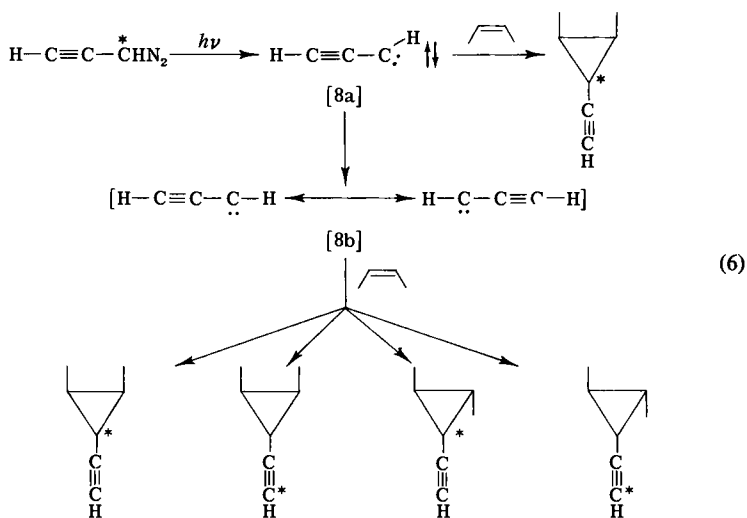
[6]



[7]

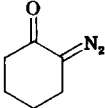
Other carbenes which have been reported to add in a stereospecific manner to the 2-butenes include benzylcarbene (48), 4,4-dimethylcyclohexadienylidene (48a), methoxycarbonylcarbene (49), ethoxycarbonylhalocarbenes (50), methoxycarbene (51), and arylsulfonylcarbenes (52). Some of these may have singlet ground states. All carbenoids generated from organometallic precursors (Chapter 3) or by α -elimination (Chapter 4) are stereospecific in their reactions with olefins. The stereochemistry of the cyclopropanation reaction has often been used to distinguish carbenes from carbenoids, e.g., in the arylcarbene series.

Carbenes with alkynyl substituents reveal a particularly interesting correlation of structure and stereospecificity (53–55). The addition of ethynylcarbene (propargylene) [8] to *cis*- and *trans*-2-butene was not stereospecific, but different product ratios were obtained from the isomeric olefins. Triplet scavenging experiments with butadiene increased the stereospecificity. Studies using diazopropyne-3- ^{14}C revealed that carbons 1 and 3 become equivalent in the nonstereospecific reaction. In contrast, no scrambling of the label was found in the product resulting from stereospecific *cis* addition. These observations are consistent with a linear resonance hybrid [8b] of triplet ethynylcarbene. The bent structure [8a] of the singlet species prevents delocalization of the π and n electrons.



Several carbenes have been generated in their triplet states by photosensitized decomposition of the corresponding diazo compounds. Benzo-

TABLE IV
 Photosensitized Decomposition of Diazo Compounds
 in the Presence of Olefins

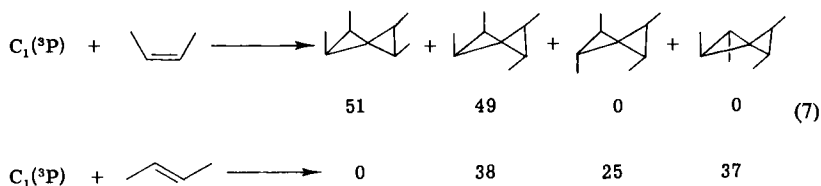
Diazo compound	Photolysis	Olefin	1,2-Dialkylcyclopropane		Refs.
			<i>trans</i>	<i>cis</i>	
CH ₂ N ₂	Direct	<i>cis</i>	0	100	(7, 31)
	Sens.	<i>cis</i>	34	66	(56)
PhCN ₂ CH ₃	Direct	<i>cis</i>	4	96	(57)
	Sens.	<i>cis</i>	15	85	
PhCOCHN ₂	Direct	<i>cis</i>	50	50	(58)
	Sens.	<i>cis</i>	55	45	
	Direct	<i>trans</i>	73	27	
	Sens.	<i>trans</i>	74	26	
CH ₃ COCHN ₂ 	Sens.	<i>cis</i>	56	44	(59)
	Sens.	<i>trans</i>	89	11	
	Sens.	<i>cis</i>	86	14	(59)
	Sens.	<i>trans</i>	86	14	
N ₂ C(CO ₂ CH ₃) ₂	Direct	<i>cis</i> ^a	8	92	(60)
	Sens.	<i>cis</i>	90	10	
	Direct	<i>trans</i>	90	10	
	Sens.	<i>trans</i>	86	14	

^a 4-Methyl-2-pentene; all other studies with 2-butene.

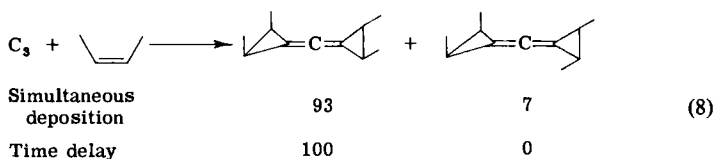
phenone has been the favored photosensitizer in liquid-phase reactions. Most of the systems studied (Table IV) (7, 31, 56–60) showed a decrease in stereospecificity compared to that obtained in direct photolysis. Identical mixtures of *cis*- and *trans*-dialkylcyclopropanes have been obtained in some cases from either of the isomeric *cis*- and *trans*- alkenes (59, 60). A complication in the interpretation of the photosensitized decomposition of diazo compounds is the possibility that the triplet states of the diazo compounds are relatively long-lived and may undergo addition reactions by themselves. At least, no conclusive evidence exists that loss of nitrogen occurs before the addition process is initiated.

Additional support for the correlation of stereospecificity with spin states comes from the elegant studies of Skell and his group, who allowed constituents of carbon vapor (C₁ and C₃) to react with alkenes on a liquid nitrogen-cooled surface (Chapter 2, Section XIV). The time-delay technique employed in some of these experiments is equivalent to the dilution

technique in liquid-phase studies; it gives the carbon fragment an opportunity to find its ground state before it adds to the substrate. "Aged" (ground state) C_1 (^3P) afforded spiropentanes by reaction with two molecules of alkene (61). The stereochemistry of the products is entirely consistent with a stereospecific first step and a nonstereospecific second step of the double addition, Eq. (7). Excited state C_1 (^1S) was scavenged by simultaneous deposition of the olefin. The first step of the addition of C_1 (^1S) is identical with that of C_1 (^3P), but the singlet cyclopropylenes thus produced rearrange to allenes (Chapter 12, Section II).



The reaction of C_3 with two molecules of an alkene afforded bisethanoallenes (62). "Aged" (ground state) C_3 was 100% stereospecific in both steps of its addition to the isomeric 2-butenes. Partial loss of stereospecificity was observed when C_3 and 2-butene were deposited simultaneously. C_3 is the only example recorded so far of a carbenic species which may be generated in an excited triplet state and then relaxes to its singlet ground state. The multiplicity assigned to the ground state on the basis of its stereochemistry is consistent with the analyses of the spectra and theoretical calculations.



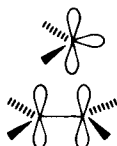
C. Mechanism of Singlet Carbene Addition

The one-step addition of a carbene to a double bond is a sufficient (but not a necessary) condition of stereospecificity. Cyclopropane formation in one step can be viewed as a cycloaddition reaction, being subject to the rules of conservation of orbital symmetry which have been extremely valuable in predicting stereochemical results in other cycloadditions (63). It must be recalled that singlet methylene has C_{2v} symmetry in its low-

energy conformation with a bond angle of 102° . Two extreme geometries of approach of a singlet methylene to an olefin are shown in formulas [8] and [9]. Formula [8] gives the most symmetrical transition state and has been called σ approach because the σ orbital of the methylene impinges on the ethylene π system. Formula [8] is closest in geometry to the addition product, cyclopropane, but the construction of correlation diagrams reveals that this approach is symmetry-forbidden (64). The π approach [9], with the p orbital of the methylene impinging on the π system of the alkene, has only one plane of symmetry, making this reaction symmetry-allowed. However, [9] is only one example of various less symmetrical reaction paths, and the relative merits of these are not easily estimated (64). Formula [9] has been chosen in view of the electrophilic character of carbenes. Only the p orbital of a singlet carbene is able to accept additional electrons. It may be postulated that the most efficient overlap would occur in a transition state resembling [9].



[8]

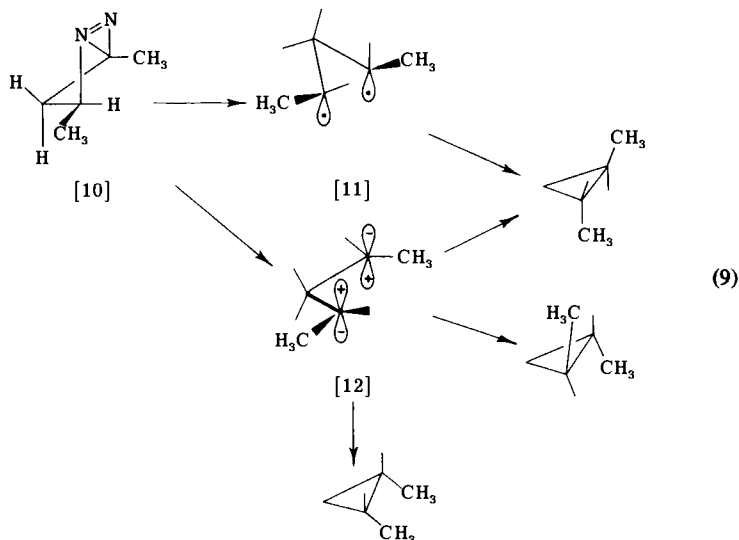


[9]

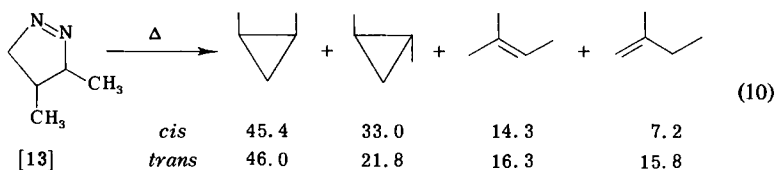
The symmetrical cycloaddition of a linear carbene is allowed in terms of orbital symmetry correlations (65). Calculations and spectroscopic work place the lowest linear singlet of methylene ($^1\Delta_g$) 10–20 kcal/mole above the lowest bent singlet ($^1A_1$). This excess energy may be available in some photochemical reactions when methylene is generated from diazomethane by short-wavelength irradiation.

The possible intervention of a trimethylene intermediate in the addition of singlet carbenes to olefinic double bonds should also be examined. The stereospecificity of cyclopropane formation would be retained in a two-step process if conformational or stereoelectronic effects lead to stereospecific closure of a trimethylene intermediate. Studies of the pyrolysis of alkyl-1-pyrazolines have demonstrated the existence of a nitrogen-free intermediate which is capable of conversion into alkenes and cyclopropanes (66–68). The thermolysis of (3R : 5R)(+)-*trans*-3,5-dimethyl-1-pyrazoline [10] produces 1% each of *cis*- and *trans*-2-pentene, 73% of *cis*-1,2-dimethylcyclopropane, and 23% of *trans*-1,2-dimethylcyclopropane of 23% optical purity, having the (*S* : *S*) configuration (69). The minor reaction path leading to double inversion is rationalized in terms of a

pyramidal diradical [11] (70). The major path, leading to racemic product, appears to proceed by a planar trimethylene intermediate [12]. According to Hoffmann's EHT calculations (64), [12] represents an energy minimum.



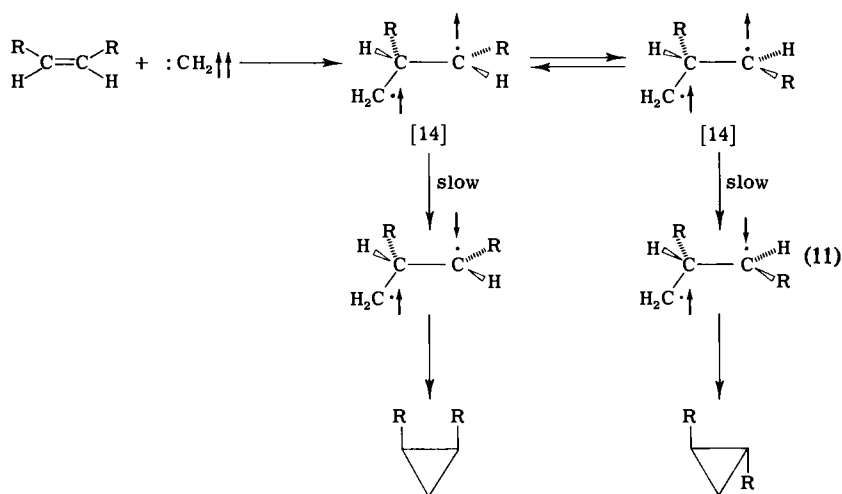
The trimethylene [12] has the same stoichiometry and spin state as the possible adduct of a singlet carbene to an alkene. It is important, therefore, to see whether two substituents on carbon atoms 1 and 2 retain their relative configuration during ring closure. The thermolysis of *cis*- and *trans*-3,4-dimethylpyrazoline [13] was found to produce 1,2-dimethylcyclopropane in a nonstereospecific reaction (71). Obviously, the intermediate(s) involved in the pyrolysis of [13] are not on the reaction coordinate in the addition of singlet methylene to *cis*- and *trans*-2-butene.



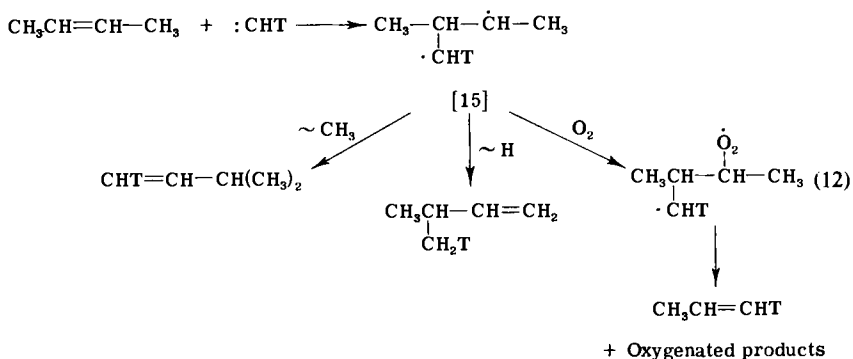
D. Mechanism of Triplet Carbene Addition

Two two-step mechanism for the addition of a triplet carbene outlined in Eq. (11) was conceived by Skell and Woodward (7). They postulate that

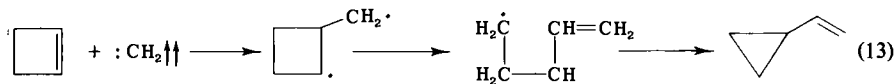
spin inversion is much slower than any other molecular process. Consequently, a triplet carbene will react with an olefin to give as the initial product a trimethylene diradical in its triplet state. Again it is assumed that rotation about C—C bonds in this intermediate is fast compared to ring closure.



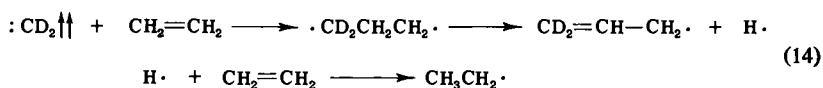
The reaction of triplet methylene with the 2-butenes produces olefins (2-methyl-1-butene and 3-methyl-1-butene; cf. Table III) which cannot arise by insertion or abstraction-recombination mechanisms. 3-Methyl-1-butene was not detected in any experiments run in the presence of oxygen, and only trace amounts were produced in the presence of carbon monoxide (71a). Formation of these products has been attributed to rearrangement of the diradical [15]. Information about these rearrangements has been obtained through tritium labeling of the methylene and subsequent determination of the location of the T label (72). The 3-methyl-1-butene contained tritium activity in both alkyl and olefinic positions. The presence of an olefinic T component indicates that 1,2-methyl migration is an important process. When oxygen was present, 3-methyl-1-butene was not observed and propylene appeared as a product. Propylene formed from $:CHT$ showed no T activity in the methyl group, in agreement with the sequence in Eq. (12).



Vinylcyclopropane was obtained in almost quantitative yield when triplet methylene, generated by mercury-photosensitized decomposition of ketene, was added to cyclobutene (73). The initial products of the reaction of singlet CH_2 were bicyclo[2.1.0]pentane, 3-methylcyclobutene, and 1-methylcyclobutene. Equation (13) accounts for the production of vinylcyclopropane by way of an 1,3 diradical.



Bell (74) has argued that the intermediate in the addition of triplet carbenes to olefins might not be a trimethylene diradical but, instead, a triplet state of cyclopropane. This hypothesis has been supported by the appearance of 3-methyl-1-butene as a product in the photosensitized reaction of 1,2-dimethylcyclopropane. The triplet cyclopropane intermediate implies that any of the three C—C bonds of the incipient cyclopropane ring can break when the intermediate rearranges to acyclic isomers. In the case of methylene addition to ethylene, the three carbons would be entirely indistinguishable. When triplet CD_2 (formed by mercury-photosensitized decomposition of CD_2CO) was allowed to react with ethylene, products resulting from the combination of ethyl and allyl radicals (*n*-butane, 1-pentene, 1,5-hexadiene) were obtained in addition to cyclopropane and propylene (75). The deuterium content of the compounds indicated that essentially all ethyl radicals were d_0 and all allyl radicals were d_2 . The only simple mechanism leading to these radicals is Eq. (14), which involves a trimethylene intermediate carrying no deuterium on carbon atom 2. Similarly, the results of the reaction of :CHT with ethylene (76) are not easily reconciled with a triplet cyclopropane intermediate.



The most questionable part of Skell's mechanism, Eq. (11), appears to be the postulate of slow spin relaxation in the trimethylene diradical compared to rotamer equilibration. This postulate demands that identical mixtures of *cis*- and *trans*-1,2-dialkylcyclopropanes are obtained from each of the geometrical isomers of a suitable alkene. The experimental data collected in Tables II–IV indicate that entirely nonstereospecific addition is an exception rather than the rule. Although the participation of singlet carbenes may account for some of the partially stereospecific reactions, comparable rates of rotation and ring closure in the trimethylene intermediate have often been invoked. The energy separation between the singlet and triplet states of the trimethylene diradical cannot be large because of a small electron interaction, and the rate of intersystem crossing increases with a decreasing energy difference between the two spin states. Consequently, there is some probability that spin relaxation competes with rotation about C–C bonds. Two groups, studying the rates of geometrical isomerization and racemization of optically active 1,2-dialkylcyclopropanes, have rationalized their data by invoking diradical intermediates having competitive rates of cyclization and rotation about single bonds (76*a,b*). It may be inferred at this point that the 1,5 diradicals [16], generated by photolysis of 3*H*-indazoles in the presence of alkenes, produce mixtures of stereoisomeric indanes (77). Both 1,3 and 1,5 diradicals involved in the sequence of reactions, Eq. (15), have been identified by their ESR spectra at 77°K.

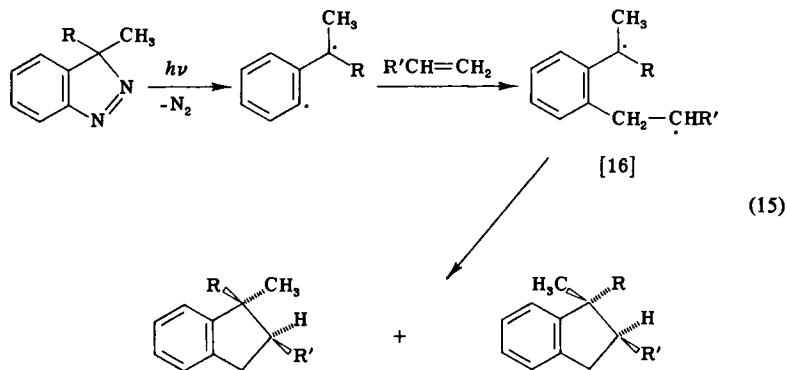
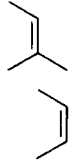
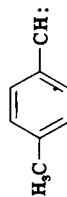
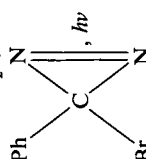


TABLE V
Syn/Anti Product Ratios in Cyclopropanes Obtained by the Addition
of Carbenes and Carbenoids to Olefins

Carbene (carbenoid)	Source	<i>syn/anti</i>		Refs.
				
$\text{CH}_3\text{CH:}$	$\text{CH}_3\text{CHI}_2 + \text{ZnEt}_2$ $\text{PhCO}_2\text{CH}(\text{CH}_3)\text{I}$ $+ \text{Zn}(\text{Cu})$	1.5	—	(78)
	$\text{CH}_3\text{CHI}_2 + \text{CH}_3\text{Li}$	1.0	—	(79)
	$\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Li}$	1.4	—	(80)
$\text{CF}_3\text{CH:}$	$\text{CF}_3\text{CHN}_2, h\nu$	1.5	—	(81)
Ph-CH:	$\text{PhCHN}_2, h\nu$	—	0.74	(28)
	$\text{PhCH-CHPh}, h\nu$	—	1.1	(82)
		—	0.6	(83)
	$\text{PhCHN}_2 + \text{ZnX}_2$	3.0	4.7	(84)
	$\text{PhCHBr}_2 + \text{CH}_3\text{Li}$	—	2.4	(82)
	$\text{PhCHI}_2 + \text{ZnEt}_2$	17	—	(78)
	$\text{ArCHN}_2, h\nu$	—	1.7	(82)
	$\text{ArCHBr}_2 + \text{CH}_3\text{Li}$	—	2.3	(82)
	$\text{ArCHN}_2 + \text{LiBr}$	—	7.5	(84)
	$\text{ArCHN}_2 + \text{LiClO}_4$	—	12.0	(84)
	$\text{ArCHN}_2 + \text{ZnCl}_2$	—	6.6	(84)
	$\text{ArCHN}_2 + \text{ZnBr}_2$	—	8.5	(84)
	$\text{ArCHN}_2 + \text{ZnI}_2$	—	21.0	(84)
	$\text{ArCHN}_2 + \text{MgBr}_2$	—	10.0	(84)
	$\text{ArCHN}_2 + \text{CoBr}_2$	—	18.0	(85)

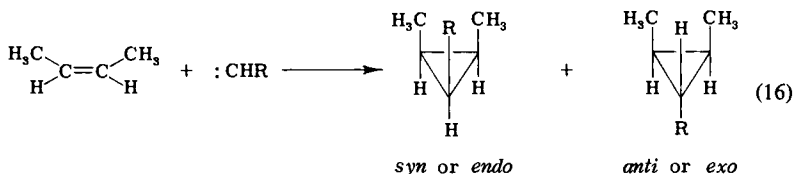


$\text{EtO}_2\text{C}-\text{CH}:$	$\text{N}_2\text{CH}-\text{CO}_2\text{Et}, h\nu$	0.53	—	(85)	
	$\text{N}_2\text{CH}-\text{CO}_2\text{Et}, \Delta$	0.14	—	(85)	
	$\text{N}_2\text{CH}-\text{CO}_2\text{Et}, \text{Cu}$	0.10	—	(85)	
$\text{Ph}-\text{COCH}:$	$\text{PhCOCHN}_2, h\nu$	—	0.3	(58)	
$\text{CH}_3\text{COCH}:$	$\text{CH}_3\text{COCHN}_2, h\nu, \text{Ph}_2\text{CO}$	—	0.3	(59)	
$\text{FCH}:$	$\text{CH}_2\text{F}_2 + \text{recoil T}$	—	1.0	(26)	
	$\text{CHBr}_2\text{F} + \text{BuLi}$	2.3	—	(86)	
$\text{ClCH}:$	$\text{ClCHN}_2 (\text{dec. } -30^\circ)$	—	1.0	(87)	
	$\text{CH}_2\text{Cl}_2 + \text{BuLi}$	—	5.5	(88)	
	$\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Li}$	2.1	—	(81, 89)	
$\text{BrCH}:$	$\text{PhHgCHClBr}, 130^\circ$	1.14	—	(90)	
	$\text{BrCHN}_2 (\text{dec. } -30^\circ)$	—	1.0	(87)	
	$\text{PhHgCHBr}_2, 132^\circ$	1.16	—	(90)	
$\text{ICH}:$	$\text{CHI}_3, h\nu$	1.0	2.0	(91)	
$(\text{CH}_3)_3\text{SiCH}:$	$(\text{CH}_3)_3\text{SiCHN}_2, \text{CuCl}$	0.11	—	(92)	
$\text{CH}_3\text{OCH}:$	$(\text{CH}_3\text{O})_3\text{SiCH}(\text{OCH}_3)_2,$	0.14	0.66	(51)	
	$\text{CH}_3\text{OCH}_2\text{Cl} + \text{BuLi}$	0.25	—	(93)	
	$\text{CH}_3\text{OCHCl}_2 + \text{CH}_3\text{Li} + \text{LiI}$	0.59	7.1	(94)	
$\text{Ph}-\text{OCH}:$	$\text{PhOCH}_2\text{Cl} + \text{BuLi}$	0.5	3.7	(95, 96)	
$\text{Ph}-\text{SCH}:$	$\text{PhSCH}_2\text{Cl} + \text{KOC}(\text{CH}_3)_3$	1.3	7.0	(97)	
$\text{PhSO}_2\text{CH}:$	$\text{PhSO}_2\text{CHN}_2, h\nu$	0.47	—	(98)	
	<i>syn-Hal/anti-Hal</i>				
$\text{Ph}-\ddot{\text{C}}-\text{F}$	$\text{PhCHClF} + \text{KOC}(\text{CH}_3)_3$	2.1	2.0	(99)	
	$\text{PhCHBrF} + \text{KOC}(\text{CH}_3)_3$	—	1.23	(100)	
$\text{Ph}-\ddot{\text{C}}-\text{Cl}$	$\text{PhCHCl}_2 + \text{KOC}(\text{CH}_3)_3$	2.0	3.0	(101)	
	$\text{PhCHCl}_2 + \text{BuLi}$	—	3.0	(102)	
$\text{Ph}-\ddot{\text{C}}-\text{Br}$		—	1.55	(103)	
$\text{F}-\ddot{\text{C}}-\text{Cl}$	$\text{FCl}_2\text{C}-\text{CO}-\text{CCl}_2\text{F}$ + $\text{KOC}(\text{CH}_3)_3$	<i>syn-Cl/anti-Cl</i>			(104)
		—	3.08	2.35	

Theoretical support for a two-step addition of triplet carbenes comes from Hoffmann's EHT calculations on trimethylene (64). In the light of his theory, triplet methylene adds nonstereospecifically not because it is a triplet but because the complex of it and a ground-state ethylene correlates with a triplet state of an excited configuration of trimethylene, one in which there are no barriers to rotation around terminal bonds.

II. STEREOSELECTIVITY

Two different adducts may be obtained from the stereospecific reaction of a monosubstituted carbene or carbenoid with olefins lacking both a center of symmetry and a twofold symmetry axis along the C=C bond (e.g., *cis*-2-butene). The ability of the carbene to discriminate between the two possible ways of *cis* addition is referred to as its stereoselectivity. The isomeric adducts are designated as *syn/anti* or *endo/exo* pairs, the *syn* or *endo* configuration being assigned to the cyclopropane in which the carbene substituent has a *cis* relationship to the larger number of alkyl groups. This nomenclature may be extended to adducts from disubstituted, unsymmetrical carbenes by adding the group to which the *syn/anti* definition applies (e.g., *syn*-Br).



The data collected in Table V (26, 28, 51, 58, 59, 78–104) reveal that a large number of carbene and carbenoid addition reactions show a preference for the formation of the presumably thermodynamically less stable *syn* isomers. (For R = Ar, equilibration experiments proved the greater thermodynamic stability of the *anti* isomers, but no such evidence exists for R = Hal). In most reactions known to proceed through free carbenes, the stereoselectivity is not very large, whereas the corresponding carbenoids display enhanced stereoselectivity. Because of its relevance with respect to the carbene–carbenoid problem, the stereoselectivity of some systems has been studied in detail.

The *syn* adducts are preferred in the addition of both arylcarbenes and arylcarbenoids to *cis*-2-butene (82). The effect of substituents is small in the free carbene reactions [photolysis of aryldiazomethanes; *syn/anti* = 1.1 (*p*-Cl), 1.7 (*p*-CH₃), 2.8 (*p*-OCH₃)]. In the related carbenoids, generated

from benzal bromides and lithium alkyls, both substituents with negative and positive σ increase the selectivity [syn/anti = 2.4 (H), 2.9 (*p*-Cl), 3.7 (*m*-Cl), 4.5 (*p*-CH₃), 8.1 (*p*-OCH₃)]. The carbenoids generated from ArCHN₂ + LiBr showed higher selectivity than those produced from ArCHBr₂ + RLi (Table V), although the same intermediate, ArCHLiBr, would be expected in both reactions (cf. Chapter 3, Section I, B). When a series of olefins R-CH=CH₂ was investigated, syn/anti ratios were found to fall off as R became larger (105) (Table VI). Preferential anti

TABLE VI
Syn/Anti Product Ratios in Cyclopropanes Obtained by the Addition
of *p*-Tolylcarbenoids to 1-Alkenes (105)

R in R-CH=CH ₂	ArCHI ₂ + BuLi in pentane	Syn/anti	
		ArCHBr ₂ + BuLi in pentane	ArCHBr ₂ + MeLi in Et ₂ O
CH ₃ CH ₂	2.68	2.60	2.14
(CH ₃) ₂ CH	1.92	1.89	1.43
(CH ₃) ₃ C	0.42	0.76	0.45

addition to 3,3-dimethyl-1-butene is the only well-documented observation of its kind for arylcarbenes or carbenoids.

The effect of LiX (leaving group and solute) and solvent shown in Table VI has been confirmed by other authors (106) who reported decreasing syn/anti ratios in the order hydrocarbon solvents > diethyl ether > tetrahydrofuran > dimethoxyethane. The syn/anti selectivity of cyclohexene-benzal halide-butyllithium systems increased from ~6 to ~30 on dilution with hydrocarbon solvents.

Steric hindrance by *t*-butyl groups was also observed in the CuSO₄-catalyzed addition of ethyl diazoacetate to alkenes (107). Trimethylalkenylsilanes afforded higher yields of the syn adducts than did the corresponding carbon compounds (108) (Table VII). The homogeneous catalyzed addition of ethyl diazoacetate to olefins utilizing (trialkyl phosphite)-copper(I) chloride complexes was studied thoroughly (85). In every case where an element of higher substitution was introduced on the ligand, the syn/anti isomer ratio was found to increase (!). The effect of electron donation via the ligand of (triaryl phosphite)copper(I) complexes caused a decrease in the syn/anti ratio which correlated linearly with the normal σ substituent constants (85). Data on the stereoselectivity of the copper-catalyzed addition of ethyl diazoacetate to various cycloalkenes have been collected in Table VIII (85, 109-116).

TABLE VII

Syn/anti Product Ratios in Cyclopropanes Obtained by the CuSO_4 -Catalyzed Addition of Ethyl Diazoacetate to Alkenes (107, 108)

Alkene	Syn/ anti	Alkene	Syn/ anti
$(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2$	0.16	$(\text{CH}_3)_3\text{Si}-\text{CH}=\text{CH}_2$	0.44
$(\text{CH}_3)_3\text{CCH}_2\text{CH}=\text{CH}_2$	0.50	$(\text{CH}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$	0.64
$(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	0.52	$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	0.53
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}_2$	0.70		

The free halocarbenes show little or no stereoselectivity at all in their reactions with alkenes. The carbenoids generated from methylene halides and lithium alkyls produce syn adducts preferentially; fluoro- and chloro-carbenoids afforded similar syn/anti product ratios (86). With fluoro-chlorocarbene and *cis*-2-butene, however, the two 1-chloro-1-fluoro-*cis*-2,3-dimethylcyclopropanes were formed in a ratio of 3 : 1 in favor of the *syn*-Cl isomer (104). On the other hand, a marked *syn*-F selectivity has been observed in the addition of fluoro-chlorocarbene to 10-methyl- Δ^8 -2-octalone ethylene acetal, a steroid model compound (104a). The syn

TABLE VIII

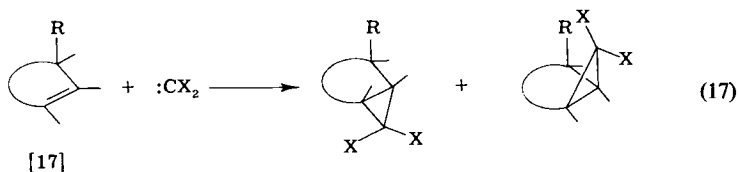
Syn/Anti Product Ratios in Cyclopropanes Obtained by the Copper-Catalyzed Addition of Ethyl Diazoacetate to Cycloalkenes

Cycloalkene	Syn/anti	Refs.
Ethyl 1,2-dipropylcyclopropene-3-carboxylate	0.24	(109)
Cyclobutene	0.18	(110)
Cyclopentene	0.25	(110)
	0.17	(111)
Cyclopentadiene	0.20	(112)
Cyclohexene	0.10	(85)
1,3-Cyclohexadiene	0.20	(113)
1,4-Cyclohexadiene	0.14	(113)
	0.02	(114)
Cycloheptene	0.20	(115)
1,3,5-Cycloheptatriene	0.20	(115, 116)

directive powers of the phenyl group and of the halogen atoms compete with each other in the reactions of phenylhalocarbenes. Both phenylchlorocarbene (101) and phenylbromocarbene (103) add with predominant formation of the isomer in which the halogen has the syn orientation. The stereoselectivity of alkoxy- and phenoxycarbenoids was found to depend on the nature of the alkoxy group, the solvent-base system employed, and on the steric requirements of the acceptor olefin (94-96).

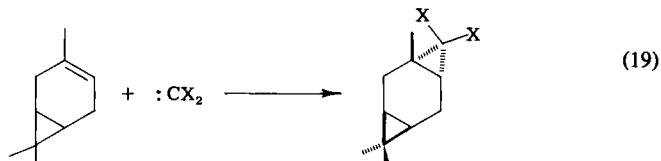
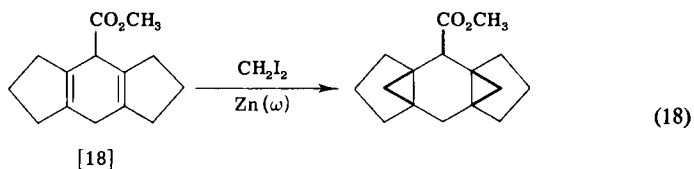
Any rationalization of the observed stereoselectivities requires the assumption of attractive forces between many carbene substituents and the alkyl groups of the alkene. The nature of the attractive forces is unknown, although some plausible hypotheses have been advanced (43, 82). Non-bonded repulsive interactions appear to operate in delicate balance with the attractive forces (Tables V and VI). Detailed models of the transition state will be of limited value in view of the well-documented solvent and salt effects (84, 96, 105, 106). Probably some of the carbenoids exhibiting large stereoselectivities are oligomers whose reactivities are strongly affected by the state of aggregation.

Another type of stereoselectivity is encountered with substituted cycloalkenes [17] where carbenes and carbenoids may add *cis* or *trans* to the substituent R, Eq. (17). The *cis* directive powers of hydroxyl and carboxyl functions in the Simmons-Smith reaction have been explained by complexation of the organozinc reagent (Chapter 3, Section II). Cyclopenten-3-ol (117), cyclopenten-4-ol (118), cyclohexen-3-ol (117), and cyclohepten-4-ol (119) afforded *cis* products exclusively, whereas the *cis/trans* ratio observed with cyclohepten-3-ol was 91 : 9 (119). Cycloocten-3-ol and cyclononen-4-ol produced more than 99% of the *trans* adduct (119a). The abrupt switch from *cis* to *trans* direction as the ring size is increased is consistent with attack of the complexed organozinc reagent on the nearest face of the neighboring double bond (cf. Chapter 3, Section II). The related methyl ethers follow the same reaction course, but the acetates are attacked from the unhindered side and they form *trans* products in low yield.

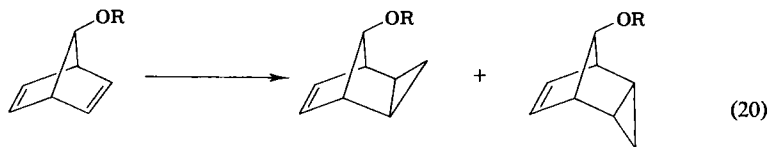


Methyl 1,4-dihydrobenzoate (120) and its tricyclic derivative [18] (121) yield bis adducts of all-*cis* configuration on treatment with an excess of the

Simmons-Smith reagent. The preferred *cis* relationship between the two cyclopropane rings must be ascribed to the directing effect of the CO_2R group. The parent compounds 1,4-dihydrobenzene (122) and dihydroindacene (121) gave predominantly *trans* orientation of the two cyclopropane rings in the Simmons-Smith reaction. Similarly, 3-carene reacted with halocarbenes to produce derivatives of *trans*-tricyclo[5.1.0.0^{3,5}]octane exclusively (123), Eq. (19).



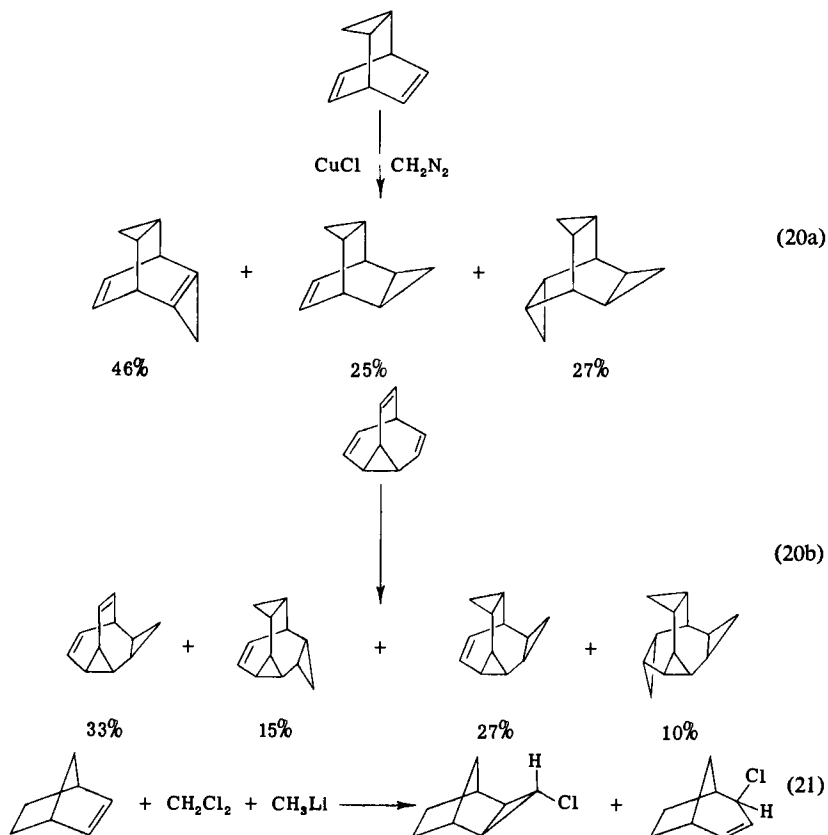
Norbornene affords *exo* adducts with both the Simmons-Smith reagent (124) and ethyl diazoacetate (125). In contrast, norbornadiene and a variety of 7-substituted norbornadienes yield mixtures of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octanes with *exo*/*endo* ratios ranging from 5.7 to 1.5 (124–130). Alkoxy and acyloxy groups in the 7 position of norbornadiene direct the addition to the *exo*-syn route (127–130), Eq. (20). The bis adduct of ethoxycarbonylcarbene to norbornadiene was shown to have the *exo*-*exo* configuration (131).



R = COCH_3	$\text{CH}_2\text{N}_2/\text{CuCl}$	80	20	(127)
R = COC_6H_5	$\text{CH}_2\text{N}_2/\text{CuCl}$	80	20	(130)
R = $\text{C}(\text{CH}_3)_3$	ICH_2ZnI	64	36	(129)

The directive effect of cyclopropane rings on further methylenation by $\text{CH}_2\text{N}_2/\text{CuCl}$ is comparatively small, as shown in Eqs. (20a) and (20b) (131a).

The addition of chlorocarbenoid ($\text{CH}_2\text{Cl}_2 + \text{RLi}$) to bridged bicyclic olefins proceeds *exo* with predominant *anti* orientation (132–134) (Table IX). Only rearranged *exo*-syn adducts of various bicyclo[2.2.1]heptenes



and of bicyclo[2.2.2]octene were detected (cf. Section IV). In contrast, the *syn*-F adducts obtained from norbornene with :CFCl and :CFBr proved to be stable (135).

TABLE IX
Syn/anti Ratios of Carbenoid *exo* Addition to Bicyclic Olefins
(132–135)

Bicyclic olefin	$[\text{:CHCl}]$ (syn/anti)	$[\text{:CFCl}]$	$[\text{:CFBr}]$
		syn-F/anti-F	
Norbornene	0.17	1.1	0.77
1-Methylnorbornene	0.67	—	—
2-Methylnorbornene	0.10	—	—
Bicyclo[2.2.2]octene	0.20	—	—

TABLE X

Carbene (carbenoid)	Source	$R-CH=CH_2$	$\begin{array}{c} R \\ \diagup \\ C=C \\ \diagdown \quad \diagup \\ H \quad R \end{array}$
$:CH_2 (S)$	CH_2CO , 2600 Å	0.89	0.79
$:CH_2 (T)$	CH_2CO , Hg, 2537 Å	0.56	0.31
$[:CH_2]$	CH_2N_2 , Cu(II) ^a	0.60 ^b	—
$[:CH_2]$	$CH_2J_2 + Zn(Cu)$	0.14 ^c	0.17 ^d
$:C:(^3P)$	C vapor	0.6 ^g	2.0
C_3	C vapor	0.6 ^g	0.35
$Ph_2 \triangle :$	$Ph_2 \triangle =N_2$, Δ	0.22 ^h	0.42
 (T)	$C(^3P) + trans\text{-butene}$	2.0 ^g	5.0
	 $=N_2$, $h\nu$	0.94 ^c	—
$(CH_3)_2C=C=C:$	$(CH_3)_2C-C\equiv CH + KOC(CH_3)_3$ Cl	0.05	—
PhCH:	PhCHN ₂ $h\nu$, syn	0.56	1.10
	anti	0.56	—
[PhCH:]	PhCHBr ₂ + RLi, syn	0.65	0.59
	anti	0.30	—
$[:CH-CO_2C_2H_5]$	$N_2CH-CO_2C_2H_5 + CuSO_4$	0.90 ^c	—
$:C(CO_2CH_3)_2 (S)$	$N_2C(CO_2CH_3)_2$, $h\nu$	0.47	0.23 ^t
$:C(CO_2CH_3)_2 (T)$	$N_2CH(CO_2CH_3)_2$, $h\nu$, Ph ₂ CO	0.46	0.13 ^t
$:C=C=O$	C_3O_2 , $h\nu$	0.15	0.21
$:CHF$	$CH_2F_2 + \text{recoil T}$	0.73	1.40
$:CHCl$	N_2CHCl (dec. -30°)	0.74	1.09
$[:CHCl]$	$CH_2Cl_2 + RLi$, syn	0.35 ^h	0.45
	anti	0.10	—
$:CHBr$	N_2CHBr (dec. -30°)	0.75	1.10
$:CF_2$	$FeC \begin{array}{c} \diagup N \\ \\ \diagdown N \end{array}$, $h\nu$	—	—
$:CFCl$	$Cl_2FC-CO-CFCl_2$ + $KOC(CH_3)_3$	0.009	0.097

Relative Rates of Carbene and Carbenoid Addition to Alkenes*

$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{R} \end{array}$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	Refs.
0.78	—	1.00	1.17	1.13	(136)
0.33	—	1.00	0.64	0.96	(136)
—	1.00	—	3.32	3.46	(137)
0.33 ^e	0.40	0.00 ^f	0.86	0.51	(138)
1.6	—	1.0	—	—	(139)
0.50	—	1.0	—	—	(62)
1.15	1.24	1.00	—	0.41	(140)
3.5	—	1.0	—	—	(139)
—	1.00	—	0.75	0.74	(141)
—	0.25	1.00 ^f	0.94	3.56	(142)
1.01	—	1.00	1.9	—	(82)
0.93	—	—	1.8	—	
1.29	—	1.00	1.2	—	(82)
0.53	—	—	0.82	—	
—	1.00	—	1.62	1.6	(143)
0.55 ^j	—	—	1.00	0.88	(60)
0.15 ^j	—	—	1.00	0.33	(60)
0.22	—	1.00	1.57	3.44	(144)
1.08	—	1.00	1.48	2.10	(26)
0.99	—	1.00	1.18	1.20	(87)
1.55	0.91	1.00	2.2	2.8	(88)
0.28	0.28	—	1.38	—	
1.02	—	1.00	—	1.18	(87)
0.08	—	1.00	—	—	(145)
0.14		1.00	6.5	31	(104)

TABLE X (Continued)

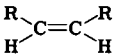
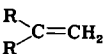
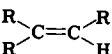
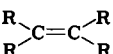
Carbene (carbenoid)	Source	$R-CH=CH_2$	$\begin{array}{c} R \\ \diagup \\ C=C \\ \diagdown \quad \diagup \\ H \quad R \end{array}$
$:CCl_2$	$CHCl_3 + KOC(CH_3)_3$	0.011	0.15
$:CBr_2$	$CHBr_3 + KOC(CH_3)_3$	0.045	—
$[Ph-\ddot{C}-F]$	$PhCHBrF + KOC(CH_3)_3$	—	0.10
$Ph-\ddot{C}-Cl$	$\begin{array}{c} Ph \\ \diagup \\ C \\ \diagdown \quad \diagup \\ Cl \quad N \\ \quad \parallel \\ \quad N \end{array}, h\nu$	—	0.20
$[Ph-\ddot{C}-Cl]$	$PhCHCl_2 + KOC(CH_3)_2$	—	0.11
$Ph-\ddot{C}-Br$	$\begin{array}{c} Ph \\ \diagup \\ C \\ \diagdown \quad \diagup \\ Br \quad N \\ \quad \parallel \\ \quad N \end{array}, h\nu$	—	0.25
$[Ph-\ddot{C}-Br]$	$PhCHBr_2 + KOC(CH_3)_3$	—	0.15
$Br-\ddot{C}-CO_2C_2H_5$	$BrCN_2CO_2C_2H_5, h\nu$	—	0.8
$J-\ddot{C}-CO_2C_2H_5$	$JCN_2CO_2C_2H_5, h\nu$	—	0.9
$[PhOCH:]$	$PhOCH_2Cl + BuLi$	—	—

* The standard olefins are 1-butene, *trans*-2-butene, *cis*-2-butene, cyclohexene, isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. When other olefins have been used, reference is made to the following footnotes.

III. REACTIVITY

The relative reactivities of a series of olefins in addition reactions of carbenes and carbenoids have been obtained in competition experiments. The data collected in Table X (26, 50, 60, 62, 82, 87, 88, 96, 100, 103, 104, 136–148) have been arranged according to the type of substitution of the olefin. In many instances, the range of relative rates is quite small, suggesting a rather unselective attacking species. It is of interest that in the case of triplet carbenes the attack on 1,3-butadiene occurs appreciably more rapidly than on the monoolefins (60, 136, 139). This effect has been attributed to stabilization of the diradical intermediate in triplet carbene addition by allylic resonance (147).

TABLE X (Continued)

					Refs.
0.23	0.13	1.00	2.8	6.5	(104, 146)
—	0.27	1.00	2.0	1.85	(147)
0.12	—	1.00	1.2	2.7	(100)
0.37	—	1.00	3.2	5.1	(148)
0.31	—	1.00	1.6	2.6	(148)
0.53	—	1.00	2.5	4.4	(103)
0.29	—	1.00	1.3	1.6	(103)
1.1	—	1.0	2.2	3.4	(50)
0.9	—	1.0	1.1	1.1	(50)
—	0.2	1.0	1.05	0.43	(96)

^a Cu complex [1], (Chapter 3, Section I). ^b 1-Octene, ^c 1-Hexene, ^d *trans*-3-Hexene, ^e *cis*-3-Hexene. ^f 2-Methyl-1-butene, ^g Propene, ^h 1-Pentene, ⁱ *trans*-3-Methyl-2-pentene, ^j *cis*-3-Methyl-2-pentene.

The more selective carbenes and carbenoids behave like electrophiles toward olefinic C=C bonds, i.e., the reactivity of the olefin increases with increased substitution of the double bond with alkyl groups. If the divalent intermediate displays sizable steric requirements in the transition state, a reversal of reactivity with highly substituted olefins may be observed. The Simmons-Smith reagent—probably not a simple monomeric species—exhibits such behavior (138). The carbenoid derived from CH₂BrCl and butyllithium (probably an organometallic aggregate) transferred methylene about 4 times faster to 1-octene than to tetramethylethylene (138a).

Steric effects are obvious even with “free” carbenes. The mode of reaction of diphenylcarbene with olefins is most sensitive to olefin structure

(138*b*). With propene and isobutene addition to give cyclopropanes predominated, whereas tri- and tetramethylethylene reacted exclusively by way of allylic hydrogen abstraction. Similar effects were noticed with the singlet carbene derived from $(\text{CH}_3)_3\text{SiCN}_2\text{CO}_2\text{C}_2\text{H}_5$ which showed allylic C—H insertion with highly alkylated olefins but produced adducts with isobutene and 2-butene (138*c*). The steric effects in the addition of dichlorocarbene to 1-alkenes are specific because only alkylation at the α -carbon and not at the β -carbon of the olefinic alkyl group leads to substantial rate reductions (149) (Table XI).

TABLE XI

Relative Rates of Addition of Dichlorocarbene to
1-Alkenes $[\text{CHCl}_3 + \text{KOC}(\text{CH}_3)_3, -10^\circ]$ (149)

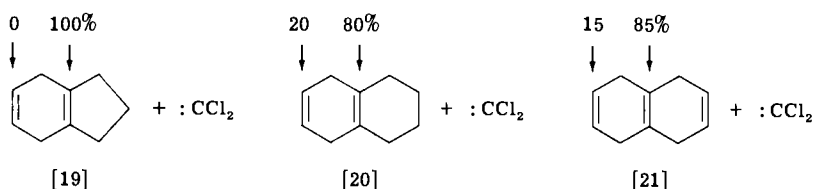
R in $\text{R}-\text{CH}=\text{CH}_2$	Relative rate
CH_3CH_2	1.00
$(\text{CH}_3)_2\text{CH}$	0.43
$(\text{CH}_3)_3\text{C}$	0.029
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$	1.24
$(\text{CH}_3)_2\text{CH}-\text{CH}_2$	0.99
$(\text{CH}_3)_3\text{C}-\text{CH}_2$	0.97

The relative rates of cyclopropane formation from cycloalkenes using iodomethylzinc iodide (Table XII) depend on the ring size in a fashion similar to those of epoxidation and reduction with diimide (150, 151). The dominant feature in establishing the observed order of reactivities appears to be the relief of torsional strain, diminished bond angle strain also playing an appreciable role in cyclopentene. The reactivity of the 1,4-cyclohexadienes [19]–[21] toward dichlorocarbene (152) may be explained by a combination of the substituent effects discussed above.

TABLE XII

Reactivity of Cycloalkenes in the Simmons-Smith Reaction
(150, 151)

Cycloalkene	Rel. rate	Cycloalkene	Rel. rate
Cyclopentene	1.60	1-Methylcyclopentene	5.14
Cyclohexene	1.00	1-Methylcyclohexene	2.14
Cycloheptene	1.18	1-Methylcycloheptene	2.46
Norbornene	1.70	1-Methylcyclooctene	5.35
		1-Methylcyclodecene	2.93
		1-Methylcyclododecene	2.29



trans-C₈-C₁₂ cycloalkenes react more readily (k_{trans}/k_{cis} 1,5-4,2) with dichlorocarbene than the corresponding *cis* isomers (152a).

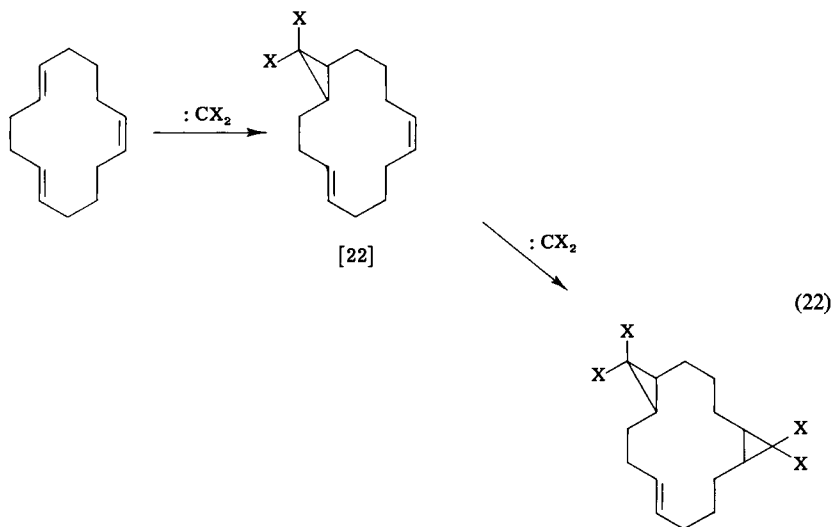
The *trans* double bonds of *cis,trans,trans*-1,5,9-cyclodecatriene (153-156) (Table XIII) and of *cis,trans*-1,5-cyclodecadiene (157,158) are preferentially attacked by various carbenes and carbenoids. A similar selectivity has been observed in other *cis* additions (diimide reduction, OsO₄ hydroxylation, epoxidation) of these cycloalkenes. The *trans*-bicyclo[10.1.0]trideca-4-*cis*-8-*trans*-dienes [22], however, add carbenes and carbenoids preferentially at the *cis* double bond (153-156).

Relative rates have been used as a tool for distinguishing between carbenes and carbenoids. A pattern of reactivities which is independent of the precursor would be indicative of a free carbene intermediate. This method is not well suited for rather indiscriminate species with a small range of relative rates. It may be applied, however, to the fairly selective dihalocarbenes. The reactivities of various olefins toward PhHgCX₃ and

TABLE XIII

Product Ratios in the Addition of Carbenes and Carbenoids
to *cis,trans,trans*-1,5,9-Cyclododecatriene

Carbene (carbenoid)	Source	Adduct to C=C Bond		Refs.
		Trans	Cis	
(:CH_2)	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	97	3	(153)
(:CH_2)	$\text{CH}_2\text{N}_2 + \text{Cu}(\text{II})$	90	10	(137)
:CCl_2	$\text{CHCl}_3 + \text{KOC}(\text{CH}_3)_3$	91	9	(154)
:CCl_2	$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}$	85	15	(154, 155)
:CCl_2	$\text{Cl}_3\text{C}-\text{CO}_2\text{Et} + \text{NaOR}$	80	20	(156)
:CBr_2	$\text{CHBr}_3 + \text{KOC}(\text{CH}_3)_3$	97	3	(154)

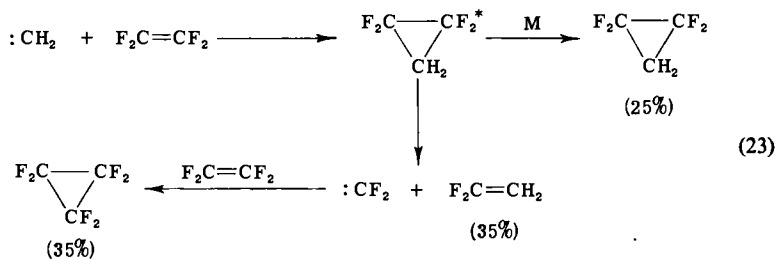


reagents producing X_3C^- were found to be virtually identical (Chapter 3, Section IV, Table III), The relative rates of reaction of olefins with CCl_2 ,

generated by pyrolysis of chloroform or carbon tetrachloride, were also investigated in the temperature range -80° to -150° , and were found to fall on the extrapolated Arrhenius plots determined for $MCX_3 + \text{olefin}$ reactions (159). Thus all methods of generating CCl_2 give an intermediate showing the same selectivity; quite probably this intermediate is free dichlorocarbene.

Activation parameters have been determined for a variety of dichlorocarbene addition reactions (159). The $\Delta\Delta F^*$ values vary with structure in a manner understandable in terms of the electrophilic character of CCl_2 . Separation of the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ terms showed that the $\Delta H^\ddagger$ differ by little more than the experimental uncertainty. $\Delta S^\ddagger$ is the dominant factor, suggesting that the less reactive olefins have tighter transition states than do the more reactive alkenes.

The effect of substituents other than alkyl on the relative rates of carbene addition to olefins has received little attention so far. Phenyl has a slightly accelerating influence; styrene and α -methylstyrene add CH_2 faster than does cyclohexene in both the Simmons-Smith (160) and Cu(II)-catalyzed diazomethane reactions (137). The relative reactivities of a series of 3- and 4-substituted α -methylstyrenes toward CCl_2 correlated well with the Hammett-Brown σ^+ constants, yielding a ρ value of -0.38 (160a). The rates of addition of methylene from the photolysis of ketene to ethylenes have been shown to decrease regularly with fluorine substitution (161). Tetrafluoroethylene reacts approximately 10 times slower than ethylene, producing 1,1,2,2-tetrafluorocyclopropane (25%) and hexafluorocyclopropane (35%) (162). The probable mechanism for the reaction of methylene with tetrafluoroethylene is outlined in Eq. (23). A decelerating effect of fluorine substitution was also noted in the photolysis of C_3O_2 in the presence of vinyl fluoride and 1,1-difluoroethylene (163).



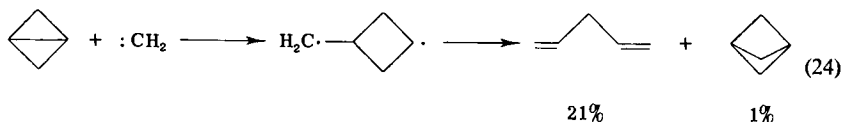
The rates of reaction of trimethylalkenylsilanes, $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{CH}=\text{CH}_2$, with ethyl diazoacetate (CuSO_4 -catalyzed) (164), dichlorocarbene (165), and diphenylcarbene (166) are shown in Table XIV. The maximum

TABLE XIV
Relative Rates of Carbene and Carbenoid Additions
to Unsaturated Silanes

$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ (<i>n</i>)	$\text{N}_2\text{CHCO}_2\text{Et}$ + CuSO_4 (164)	CHCl_3 + $\text{KOC}(\text{CH}_3)_3$ (165)	Ph_2CN_2 , 55° (166)
0	0.52	0.047	46.3
1	2.94	4.97	0.93
2	1.44	1.20	0.91
1-Heptene	1.00	1.00	1.00

at $n = 1$ observed with the electrophilic carbenes (carbenoids) probably reflects the opposite effects from p_{π} - d_{π} bonding from the double bond to silicon and of the inductive effect of the silyl group (the dipole moment also has a maximum at $n = 1$). The reactivity of diphenylcarbene is best explained by triplet and nucleophilic properties.

The reactivity of strained C—C bonds with increased p character toward carbenes has been studied. Cyclopropanes, including spiropentane, proved to be inert (C—H insertion only), but the central bond of bicyclobutane was found to react (167). Photolysis of diazomethane in the presence of bicyclobutane at -50° afforded 1,4-pentadiene and bicyclo[1.1.1]pentane as the major identified products. Derivatives of 1,4-pentadiene were also obtained from the reaction of dichlorocarbene with methyl bicyclobutane-1-carboxylate. A possible interpretation of the reaction course involves a diradical intermediate.

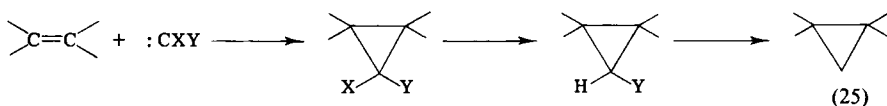


IV. SYNTHESIS OF CYCLOPROPANES

The addition of carbenes and carbenoids to olefins is a versatile method for the synthesis of cyclopropanes. It is impossible to record, within the scope of this volume, every cyclopropane which has been prepared by

carbene addition. Table XV provides a guide to the literature, and references have been arranged according to structural features of the carbenes (carbenoids) and olefins employed.

Indirect methods are sometimes preferred to the direct approach (167a). The easily accessible dihalocyclopropanes may be dehalogenated by various reducing agents to give either monohalocyclopropanes or halogen-free cyclopropanes. Complete reduction has been achieved by Raney nickel (168), sodium in methanol (31, 169–171), sodium in liquid ammonia (156, 172, 173), and lithium in *t*-butanol–tetrahydrofuran (174–176). The preferred reagent for partial reduction is tributyltin hydride (177–183), but electrochemical reduction (184, 185), methylmagnesium bromide (186), methyllithium (187), dimethyl sulfoxide anion (188), and zinc in acetic acid (189) have also been employed. Excess tributyltin hydride reduces 1,1-dibromocyclopropanes to the cyclopropane stage (190, 191). Partial reduction of 1-chloro-1-fluorocyclopropanes removes chlorine selectively and constitutes the only efficient synthesis of fluorocyclopropanes (178, 180, 181, 192, 193). Triphenyltin hydride has been reported to reduce 7-chloro-7-phenylnorcarane selectively to *endo*-7-phenylnorcarane (194).



An ether-soluble complex from two equivalents of alkyllithium to one of cuprous halide is an excellent reagent for the replacement of bromine in 1,1-dibromocyclopropanes by alkyl (195). Replacement of halogen by alkoxy and alkylthio groups has been achieved in some cases but is frequently accompanied by elimination. Neither of the products thus obtained is accessible by direct carbene addition (196).

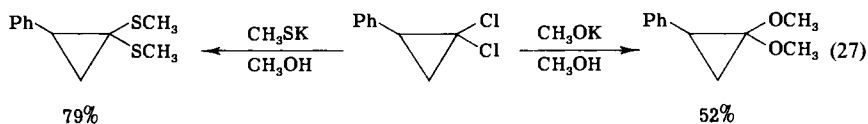
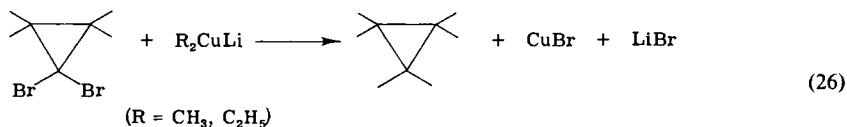
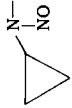
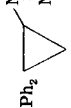
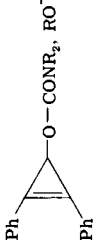


TABLE XV
Synthesis of Cyclopropanes by Methylene Transfer to Olefins

Species transferred	Source	Olefins	Refs.
:CH_2	$\text{CH}_2\text{N}_2, h\nu$	Alkenes (addition and insertion)	Table IV, Chapter 7
	$\text{CH}_2\text{N}_2, h\nu$	Fluoroethylenes	(161, 162)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Alkenes	(138, 203, 204)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Dienes	(205, 206)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Allenes	(207-211)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Cycloalkenes	(119, 150, 151, 212, 213)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Bicycloalkenes	(124, 214-216)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	1,4-Cyclohexadienes	(120-122, 124, 217)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Cyclododecatriene	(153)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Norbornadienes	(124, 129, 218)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Methylenecycloalkenes	(150, 219-225b)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Arylalkenes	(226, 227)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	1-Arylcycloalkenes	(228)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Benzocycloalkenes	(229-231)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Allyl alcohols	(232)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Cyclic	(117, 119, 233-241)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	2-Methylenecycloalkenols	(224, 225)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Allylcarbinols	(117-119, 216, 242-247)
	$\text{CH}_2\text{I}_2 + \text{Zn}(\text{Cu})$	Cycloalkenylcarbinols	(117, 248, 249)

:CH ₂ (Cont'd.)	CH ₂ I ₂ + Zn(Cu)	Allyl ethers + acetals	(117, 249–251)
	CH ₂ I ₂ + Zn(Cu)	Enol ethers + esters	(249, 252–254)
	CH ₂ I ₂ + Zn(Cu)	Ketene acetals	(252, 255)
	CH ₂ I ₂ + Zn(Cu)	Ketones, unsaturated	(256–258a)
	CH ₂ I ₂ + Zn(Cu)	Acids and esters	
		α,β-Unsaturated	(226, 259–262)
		Unsaturated fatty	(263)
		1,4-Dihydrobenzoic	(120, 121)
		Allenic	(207, 210)
		Steroids	(220, 235–237, 244)
	CH ₂ I ₂ + Zn(Cu)	Enamines	(264, 265)
	CH ₂ I ₂ + Zn(Cu)	Alkenylsilanes and -germanes	(266, 267)
	CH ₂ I ₂ + Zn(Cu)	Divinylmercury	(268)
	CH ₂ I ₂ + R ₂ Zn	Alkenes, cycloalkenes, enol ethers	(269)
	CH ₂ N ₂ + ZnX ₂	Alkenes, cycloalkenes, butadiene	(270, 271)
	CH ₂ N ₂ + R ₂ AlX	Alkenes, cycloalkenes	(272)
	CH ₂ N ₂ + CuX	Alkenes, cycloalkenes	(137, 273–278a)
	CH ₂ N ₂ + CuX	Polyenes and cyclopolynes	(137, 275, 279–281)
	CH ₂ N ₂ + CuX	Norbornenes, norbornadienes	(282, 127–130)
	CH ₂ N ₂ + CuX	Allenes	(283, 283a)
	CH ₂ N ₂ + CuX	Allyl halides	(284)
CH ₃ CH:	CH ₂ N ₂ + CuX	Allyl ethers and sulfides	(285)
	CH ₂ N ₂ + CuX	Allylamines	(286)
	CH ₂ N ₂ + CuX	Ketene acetals	(287)
	CH ₂ N ₂ + CuX	Vinylene carbonates	(288)
	Hg(CH ₂ Br) ₂	Alkenes, cycloalkenes	(289, 290)
	ICH ₂ Hgl + Ph ₂ I'g	Alkenes, cycloalkenes	(289, 290)
	CH ₃ CHN ₂ , hν	2-Butene	(291)

TABLE XV (Continued)

Species transferred	Source	Olefins	Refs.
$\text{CH}_3\text{CH:}$ (Cont'd.)	$\text{CH}_3\text{CHI}_2 + \text{R}_2\text{Zn}$ $\text{PhCO}_2\text{CH}(\text{CH}_3)\text{ZnI}$ $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Li}$ $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Li}$ $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{Li}$ $\text{CF}_3\text{CHN}_2, h\nu$ $(\text{CH}_3)_2\text{CBr}_2 + \text{CrSO}_4$ $(\text{CH}_3)_2\text{CCl}_2 + \text{COT}^{2-}$ $(\text{CF}_3)_2\text{CN}_2, 150^\circ$ $(\text{CF}_3)_2\text{CN}_2 + \text{C}_6\text{F}_5\text{Cu}$	Cycloalkenes, enol ethers Cyclohexene Alkenes, cycloalkenes Aryalkenes Cyclooctatetraene Alkenes, cycloalkenes 3-Buten-1-ol Cyclooctatetraene Alkenes, cycloalkenes Cyclohexene	(78) (79) (80, 81) (292) (293) (28, 294) (295, 296) (297) (29) (298)
$\text{CF}_3\text{CH:}$ $(\text{CH}_3)_2\text{C:}$ $(\text{CF}_3)_2\text{C:}$			
	$\text{N}-\text{CO}_2\text{R} + \text{RO}^-$ 	1,4-Cyclohexadiene	(299)
$\text{Ph}_2\text{C:}$ 	$\text{N}-\text{CONH}_2 + \text{RO}^-$ 	Alkenes, cycloalkenes	(140)
	 + CH_3Li	2-Butene	(140, 300)
		Dimethyl fumarate	(301-304)

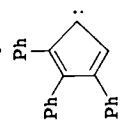
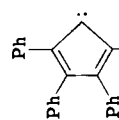
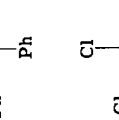
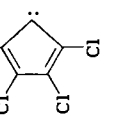
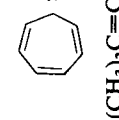
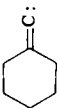
		Alkenes, cycloalkenes Dienes, COT	(39, 141, 305) (306)
		Alkenes, cycloalkenes	(307)
		Alkenes, cycloalkenes	(308, 308a, b)
		Alkenes, cycloalkenes	(309)
		$\text{RO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{R},$ $\text{NC}-\text{CH}=\text{CH}-\text{CN}$	(46, 47, 310)
		Cyclohexene	(311)
		Alkenes, cycloalkenes, enol ethers	(312)
		Allenes	(313)
		Butatrienes	(314)
		Enol esters	(315)

TABLE XV (Continued)

Species transferred	Source	Olefins	Refs.
	$(\text{CH}_3)_2\text{C}=\text{CBr}_2 + \text{Mg}$ $(\text{CH}_3)_2\text{C}-\text{O}-\text{C}(=\text{O})-\text{N}(\text{H}_2)-\text{NO}$ $+ \text{RO}^-$	Alkenes, cycloalkenes arylalkenes	(316)
$(\text{PhCH}_2)_2\text{C}=\text{C}:$	$(\text{PhCH}_2)_2\text{C}=\text{CHCl} + \text{RLi}$	Ethyl vinyl ether	(317)
	 + RO^-	Cyclohexene	(311)
	 + RO^-	Cyclohexene, enol ethers	(318)
$\text{Cl}_2\text{C}=\text{C}:$	$\text{PhHgCCl}=\text{CCl}_2, h\nu$	Cyclohexene	(319)
$\text{R}_2\text{C}=\text{C}=\text{C}:$	$(\text{CH}_3)_2\text{C}-\text{C}\equiv\text{CH} + \text{RO}^-$ 	Alkenes, cycloalkenes	(320, 320a)
	$(\text{CH}_3)_2\text{C}=\text{C}=\text{CHCl}, \text{RO}^-$ $\text{R}_2\text{C}-\text{C}\equiv\text{CH} + \text{RO}^-$ 	Alkenes, cycloalkenes Alkenes, cycloalkenes	(321) (322)
$\text{HC}\equiv\text{C}-\text{CH}:$	$\text{OAc} \quad [\text{R}=\text{C}(\text{CH}_3)_3]$ $\text{HC}\equiv\text{C}-\text{CHN}_2, h\nu$	Alkenes	(53)
$\text{Ph}-\text{CH}:$	$\text{PhCHN}_2, h\nu$ $\text{PhCHN}_2, h\nu$ Stilbene oxide, $h\nu$	Alkenes, cycloalkenes Butadiene Alkenes	(40, 82) (323) (83)

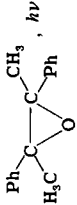
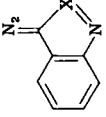
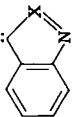
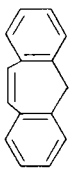
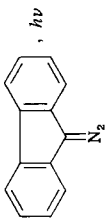
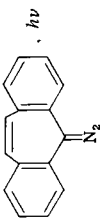
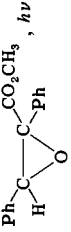
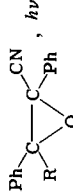
$\text{Ph}-\ddot{\text{C}}-\text{CH}_3$			
$\text{PhCHN}_2, \text{LiX or ZnX}_2$	Alkenes	(84)	
$\text{PhCH}_2\text{Cl} + \text{RLi}$	Cyclohexene	(324)	
$\text{PhLi} + \text{CH}_2\text{Cl}_2$	Cycloalkenes	(325, 326)	
$\text{PhCH}_2\text{OPh} + \text{RLi}$	Isobutene	(327)	
$\text{PhCH}_2\text{SPh}_2 + \text{BF}_4^-, \text{RLi}$	Acenaphthylene	(328, 329)	
$\text{PhCHBr}_2 + \text{RLi}$	Alkenes, cycloalkenes	(82, 105, 106)	
$\text{PhCHO} + \text{BF}_3 + \text{Zn}$	Alkenes, cycloalkenes	(330)	
$\text{PhCN}_2\text{CH}_3, h\nu$	Alkenes	(101)	
	Alkenes	(331)	
	Cyclooctene	(332)	
$\text{Ph}_2\text{C}:$			
			
$\text{X} = \text{N, CR}$			
$\text{Ph}_2\text{CN}_2, h\nu \text{ or } \Delta$	Alkenes	(41, 42)	
$\text{Ph}_2\text{CN}_2, h\nu \text{ or } \Delta$	Arylalkenes	(333, 334)	
$\text{Ph}_2\text{CN}_2, h\nu \text{ or } \Delta$	Dienes	(335, 336)	
$\text{Ph}_2\text{CN}_2, h\nu \text{ or } \Delta$	Allyl alcohol	(337)	
$\text{Ph}_2\text{CN}_2, h\nu \text{ or } \Delta$	Allyl acetate	(338)	
$\text{Ph}_2\text{CN}_2, h\nu \text{ or } \Delta$	Dihydrofuran	(339, 339a)	
$\text{Ph}_2\text{CN}_2, \text{Cu(II)}$	Enamines	(340)	
$\text{Ph}_2\text{CN}_2, \text{Cu(II)}$	Alkenylsilanes	(166, 341)	
$\text{Ph}_3\text{P}=\text{CPh}_2, h\nu$	$\text{Ph}_2\text{C}=\text{CH}_2$	(342)	
$\text{Ph}_2\text{CBr}_2, \text{RLi}$	Alkenes	(42)	
$\text{Ph}_2\text{CBr}_2, \text{RLi}$	Enol ethers	(343)	

TABLE XV (Continued)

Species transferred	Source	Olefins	Refs.
$\text{PH}_2\text{C:}$ (Cont'd.) 	 	Alkenes Alkenynes Maleic and fumaric esters Alkenylsilanes Alkenes	(33, 344, 345) (346) (347) (348) (44)
$\text{:CH-CO}_2\text{CH}_3$ $\text{:CH-CO}_2\text{C}_2\text{H}_5$	$\text{N}_2\text{CH-CO}_2\text{CH}_3, h\nu$ $\text{N}_2\text{CH-CO}_2\text{CH}_3, \text{CuSO}_4$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, h\nu$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \Delta$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \Delta$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \Delta$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \Delta$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \Delta$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \text{Cu}$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \text{Cu}$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \text{Cu}$ $\text{N}_2\text{CH-CO}_2\text{C}_2\text{H}_5, \text{Cu}$	Alkenes Cycloalkenes Cycloalkenes Arylalkenes Acenaphthylene Cyclooctatetraene Vinylpyridines Enol ethers Alkenes Dienes and trienes Allenenes Cycloalkenes Cyclopentadiene Cyclohexadienes	(49) (152) (85, 114, 349) (253, 350-352) (353) (354) (355, 356) (349) (357, 358, 358a) (359-361a) (207) Table VIII (85, 109-111, 349, 362-368a) (112, 369) (113, 114)

$N_2CH-CO_2C_2H_5$, Cu	Cycloheptatriene	(115, 116)
$N_2CH-CO_2C_2H_5$, Cu	Cyclooctatetraene	(370, 371)
$N_2CH-CO_2C_2H_5$, Cu	Norbornene	(125)
$N_2CH-CO_2C_2H_5$, Cu	Norbornadienes	(125, 126, 131)
$N_2CH-CO_2C_2H_5$, Cu	Methylenecycloalkanes	(222)
$N_2CH-CO_2C_2H_5$, Cu	Enynes	(372, 373)
$N_2CH-CO_2C_2H_5$, Cu	Allyl alcohol	(374)
$N_2CH-CO_2C_2H_5$, Cu	Enol ethers + esters	(375, 375a)
$N_2CH-CO_2C_2H_5$, Cu	Acids and esters, unsaturated	(376-378)
$N_2CH-CO_2C_2H_5$, Cu	Steroids	(379)
$N_2CH-CO_2C_2H_5$, Cu	Alkenes	(85, 107, 380)
$N_2CH-CO_2C_2H_5$, Cu(II)	Polyisoprene	(381)
$N_2CH-CO_2C_2H_5$, Cu(II)	Cycloalkenes	(85, 382-385)
$N_2CH-CO_2C_2H_5$, Cu(II)	Arylalkenes	(137, 352, 380, 386)
$N_2CH-CO_2C_2H_5$, Cu(II)	Allyl esters	(384, 387)
$N_2CH-CO_2C_2H_5$, Cu(II)	Allyl halides	(388)
$N_2CH-CO_2C_2H_5$, Cu(II)	Enol ethers + esters	(349, 384, 389, 390)
$N_2CH-CO_2C_2H_5$, Cu(II)	Alkenylsilanes	(108, 391, 392)
$N_2CH-CO_2C_2H_5$, Cu(II)	Allyl and vinyl phosphonates	(393)
$N_2CH-CO_2C_2H_5$, Cu(II)	Cycloalkenes, enol ethers	(394)
		
$N_2CH-CO_2C_2H_5$, NiCp ₂	Cyclohexene	(368)
$I_2CH-CO_2C_2H_5$, Zn(Cu)	Stilbene	(380)

TABLE XV (Continued)

Species transferred	Source	Olefins	Refs.
$:C(CO_2C_2H_5)_2$	$N_2C(CO_2C_2H_5)_2, h\nu$ $N_2C(CO_2C_2H_5)_2, h\nu$ $N_2C(CO_2C_2H_5)_2, Cu$	Alkenes 1,4-Cyclohexadiene Cyclohexene	(38, 60) (114, 395) (396)
$Ph-\ddot{C}-CO_2CH_3$	 , $h\nu$	Alkenes	(397)
$:CH-CN$ $:C(CN)_2$	N_2CH-CN, CuX $N_2C(CN)_2, \Delta$	Dienes Alkenes, cycloalkenes arylalkenes, COT	(398, 399) (36)
$Ph-\ddot{C}-CN$	 , $h\nu$	Alkenes	(397, 400, 401)
$:CH-CHO$ $:CH-COCH_3$	$N_2CH-CHO, Cu(II)$ $N_2CHCOCH_3, h\nu, Ph_2CO$ $N_2CHCOCH_3, Cu$	Alkenes Alkenes Cycloalkenes, styrene, vinyl acetate	(402) (59) (403)
	$N_2CHCOCH_3, CuSO_4$ $N_2CHCOCH_3, CuSO_4$	Dienes, enynes Methyl oleate <i>etc.</i>	(404) (405)
	 , $h\nu, Ph_2CO$	Alkenes	(59)
$:CH-COPh$	$N_2CH-COPh, h\nu$	Alkenes, cycloalkenes	(58)

:CH-COPh (Cont'd.)	$\text{N}_2\text{CH-COPh, Cu}$ $\text{N}_2\text{CH-COPh, CuSO}_4$	Alkenes Dienes	(406, 406a) (404)
	$\text{N}_2=\text{C}_6\text{H}_4=\text{O, } h\nu$	Alkenes	(37)
	$\text{N}_2=\text{C}_6\text{H}_3(\text{X})_2=\text{O, } h\nu, \Delta$	Alkenes, cycloalkenes	(407, 408)
	$\text{N}_2=\text{C}_{10}\text{H}_6=\text{O, } h\nu$	Arylalkenes	(409)
	$\text{N}_2=\text{C}_8\text{H}_5\text{N}_2=\text{O, } h\nu$	Cyclohexene, styrene	(410)
	$\text{CF}_3\text{COCN}_2\text{CO}_2\text{R, } h\nu$ $\text{CHBr}_2\text{F, RLi}$ $\text{N}_2\text{CHCl, } h\nu$ $\text{CH}_2\text{Cl}_2, \text{RLi}$ $\text{CH}_2\text{Cl}_2, \text{RLi}$	Cyclohexene Alkenes, cycloalkenes Alkenes Alkenes Cycloalkenes	(411) (86) (87) (88, 412) (80, 81, 89, 123, 152, 413)
$\text{CF}_3\text{CO-C(=O)-CO}_2\text{R}$:CHF :CHCl	$\text{CH}_2\text{Cl}_2, \text{RLi}$ $\text{CH}_2\text{Cl}_2, \text{RLi}$ $\text{CH}_2\text{Cl}_2, \text{RLi}$ $\text{CH}_2\text{Cl}_2, \text{RLi}$ $\text{CH}_2\text{Cl}_2, \text{RLi}$ $\text{CH}_2\text{Cl}_2, \text{Li}$ CHCl_3, Li $\text{CHCl}_3 + \text{COT}^{2-}$	Cyclooctatetraene Bicycloalkenes Methylenecycloalkenes Arylalkenes Enol ethers Cyclohexene Cyclohexene Cyclooctatetraene	(414) (132-134) (415) (292, 416) (417) (418) (419) (420)

TABLE XV Continued

Species transferred	Source	Olefins	Refs.
:CH-COPh (Cont'd.)	PhCOCHCl_2 , RO^-	Cyclohexene	(421)
:CHBr	PhHgCHClBr , 130° N_2CHBr , $h\nu$	Cyclohexene Alkenes	(90) (87)
:CHI	PhHgCHBr_2 , 130° CHI_3 , $h\nu$	Cyclohexene Alkenes, cycloalkenes	(90) (91)
:CF_2	$\text{F}_2\text{C} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array}$, $h\nu$ or Δ	Alkenes, cycloalkenes Haloalkenes	(145) (422)
	$\text{F}_2 \triangle \begin{array}{c} \text{X}_2 \\ \text{X}_2 \end{array}$, Δ ($\text{X} = \text{Cl}, \text{F}$)	Alkenes, cycloalkenes	(423)
	$\text{CF}_2\text{Cl}-\text{CO}_2\text{Na}$, Δ $\text{CF}_2\text{Cl}-\text{CO}_2\text{Na}$, Δ	Cycloalkenes Steroids	(424, 425) (426-430)
	CHF_2Cl , 	Alkenes, cycloalkenes	(431)
	$(\text{CH}_3)_3\text{SnCF}_3$, Δ $(\text{CH}_3)_3\text{SnCF}_3$, NaI $(\text{CH}_3)_3\text{SnCF}_3$, NaI	$\text{F}_2\text{C}=\text{CF}_2$ Alkenes, cycloalkenes Vinyl acetate, vinyl silanes, dihydrofuran	(432) (433, 434) (434)
	PhHgCF_3 , NaI CHCl_2F , NaOH CHCl_2F , RO^-	Alkenes, cycloalkenes Alkenes Alkenes	(435) (436) (192)
:CFCI	CHCl_2F ,  CHBr_2F , RLi	Alkenes, cycloalkenes arylalkenes Cycloalkenes	(431) (135)

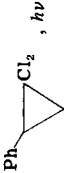
:CCl_2					
$(\text{CCl}_2\text{F})_2\text{CO}, \text{RO}^-$				Alkenes, cycloalkenes	(104, 437, 438)
$\text{CCl}_2\text{F}-\text{CO}_2\text{R}, \text{RO}^-$				Cycloalkenes	(180, 439)
$\text{CCl}_2\text{F}-\text{CO}_2\text{R}, \text{RO}^-$				Dihydropyran	(440)
$\text{PhHgCCl}_2\text{F}, \text{NaI}$				Alkenes, cycloalkenes, methyl acrylate, acrylonitrile, dihydrofuran	(435, 441)
				Alkenes, cycloalkenes	(442)
$\text{Cl}_3\text{C}-\text{SiCl}_3, 250^\circ$				Cyclohexene	(443)
$\text{Cl}_3\text{C}-\text{SiCl}_3, 250^\circ$				Alkenylsilanes	(444)
$\text{CHCl}_3, \text{NaOH}$				Alkenes, cycloalkenes	(436, 445)
$\text{CHCl}_3, \text{NaOH}$				Allyl halides and ethers	(446)
$\text{CHCl}_3, \text{RO}^-$				Alkenes	(146, 147, 149)
$\text{CHCl}_3, \text{RO}^-$				Dienes	(447-451)
$(\text{R} = \text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3)$				Allenes	(207, 452)
$\text{CHCl}_3, \text{RO}^-$				Enynes	(453)
$\text{CHCl}_3, \text{RO}^-$				Cycloalkenes	(152, 154, 174, 454-458)
$\text{CHCl}_3, \text{RO}^-$				Bicycloalkenes	(459-461)
$\text{CHCl}_3, \text{RO}^-$				Arylalkenes	(160, 182, 462, 463)
$\text{CHCl}_3, \text{RO}^-$				Enol ethers	(417, 464-469)
$\text{CHCl}_3, \text{RO}^-$				Ketene acetals	(470, 471)
$\text{CHCl}_3, \text{RO}^-$				Enamines	(472-474a)
$\text{CHCl}_3, \text{RO}^-$				Alkenylsilanes	(165, 475)
$\text{CHCl}_3, \text{RO}^-$				Alkenes, cycloalkenes	(431, 476)
$\text{CHCl}_3,$ 				Dienes	(477)
				Enol ethers	(476, 478)

TABLE XV (Continued)

Species transferred	Source	Olefins	Refs.
:CCl ₂ (Cont'd.)	CHCl ₃ or CCl ₄ , Li	Cyclohexene	(418)
	CCl ₄ , COT ²⁻	Cyclooctatetraene	(420)
	CCl ₄ , CCl ₃ Br, or CCl ₃ I, RLi	Cyclohexene	(479)
		Enol ethers	(466)
	Cl ₃ C-CHO, RO ⁻	Cyclohexene, styrene, ethyl vinyl ether	(480)
	Cl ₃ CCOCCl ₃ , RO ⁻	Cyclohexene	(481)
	Cl ₃ C-CO ₂ R, RO ⁻	Alkenes	(482)
	Cl ₃ C-CO ₂ R, RO ⁻	Dienes	(463, 483)
	Cl ₃ C-CO ₂ R, RO ⁻	Enynes	(484-486)
	Cl ₃ C-CO ₂ R, RO ⁻	Cycloalkenes	(156, 158, 180, 482, 487)
	Cl ₃ C-CO ₂ R, RO ⁻	Bicycloalkenes	(171, 488)
	Cl ₃ C-CO ₂ R, RO ⁻	Dihydrofuran	(489, 490)
	Cl ₃ C-CO ₂ R, RO ⁻	Dihydropyran	(491)
	Cl ₃ C-CO ₂ R, RO ⁻	Benzo(thio)pyran	(492, 493)
	Cl ₃ C-CO ₂ R, RO ⁻	Enol ethers	(173, 466, 494-497a)
	Cl ₃ C-CO ₂ Na, Δ	Alkenes	(498)
	Cl ₃ C-CO ₂ Na, Δ	Fluoroethylenes	(499)
	Cl ₃ C-CO ₂ Na, Δ	Trichloroethylene	(500)
	Cl ₃ C-CO ₂ Na, Δ	Tetrachloroethylene	(501, 502)
	Cl ₃ C-CO ₂ Na, Δ	Allenes	(503-505)
	Cl ₃ C-CO ₂ Na, Δ	Enynes	(506)

$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}, \Delta$	Cycloalkenes	(154, 155, 175, 498, 507, 508)
$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}, \Delta$	Ferrocenylethylenes	(509)
$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}, \Delta$	4- <i>H</i> -(Thio)pyran	(510)
$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}, \Delta$	Sugars, unsaturated	(511)
$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}, \Delta$	Enol acetates	(512, 513)
$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}, \Delta$	Steroids	(426, 513)
$\text{PhHgCCl}_3, 80^\circ$	Alkenes, cycloalkenes	(514, 515)
$\text{PhHgCCl}_3, 80^\circ$	Enol acetates	(516)
$\text{PhHgCCl}_3, \text{NaI}, 30^\circ$	Cyclohexene	(433)
$\text{PhHgCCl}_3, \text{NaI}, 30^\circ$	Fluoroalkenes	(499)
$\text{PhHgCCl}_2\text{Br}, 80^\circ$	Alkenes, cycloalkenes, arylalkenes, unsatd. acids, esters, and ketones, enol ethers and esters	(514, 517)
$\text{PhHgCCl}_2\text{Br}, 80^\circ$	Dihydropyran	(518)
$\text{PhHgCCl}_2\text{Br}, 80^\circ$	Steroids	(430, 519)
$\text{PhHgCCl}_2\text{Br}, 80^\circ$	Alkenylsilanes	(514, 520)
$\text{PhHgCCl}_2\text{Br}, 80^\circ$	Alkenylcarboranes	(521)
$\text{PhHgCCl}_2\text{Br}, \text{NaI}, 20^\circ$	Cyclohexene, acrylonitrile	(433)
$\text{PhHgCClBr}_2, \Delta$	Alkenes, cycloalkenes, styrene, acrylonitrile, vinyl acetate, dihydrofuran, alkenylsilanes	
	Fluoroalkenes	(523)
$\text{CHBr}_3, \text{RO}^-$	Alkenes	(31, 524, 525)
$\text{CHBr}_3, \text{RO}^-$	Dienes	(361, 447, 449, 451)
$\text{CHBr}_3, \text{RO}^-$	Allenes	(190, 207, 452, 526, 527)

:CClBr

:CBr₂

TABLE XV (Continued)

Species transferred	Source	Olefins	Refs.
:CBr_2 (Cont'd.) $\text{F}_2\text{CH}-\ddot{\text{C}}-\text{F}$ $\text{CH}_3-\ddot{\text{C}}-\text{Cl}$ $\text{CF}_3-\ddot{\text{C}}-\text{Cl}$ $\text{Ph}-\ddot{\text{C}}-\text{F}$	$\text{CHBr}_3, \text{RO}^-$	Enynes	(189, 261, 453, 528, 529)
	$\text{CHBr}_3, \text{RO}^-$	Cycloalkenes	(119, 122, 152, 158, 530)
	$\text{CHBr}_3, \text{RO}^-$	Bicycloalkenes	(123, 191, 460)
	$\text{CHBr}_3, \text{RO}^-$	Methylenecycloalkanes	(531)
	$\text{CHBr}_3, \text{RO}^-$	Arylalkenes	(160, 169, 462)
	$\text{CHBr}_3, \text{RO}^-$	Benzotropone	(532)
	$\text{CHBr}_3, \text{RO}^-$	Benzopyran	(533)
	$\text{CHBr}_3, \text{RO}^-$	Enol ethers	(534)
	$\text{CHBr}_3, \text{RO}^-$	Steroids	(168, 170, 535)
	CHBr_3 or CBr_4, Li	Cyclohexene	(537)
	CBr_4, RLi	Cyclohexene	(538)
	$\text{PhHgCBr}_3, 80^\circ$	Alkenes, cycloalkenes	(479)
	$\text{PhHgCBr}_3, 80^\circ$	Alkenes, cycloalkenes	(514, 539)
	$\text{PhHgCBr}_3, 80^\circ$	Alkenes, cycloalkenes	(514, 540)
	$\text{Hg}(\text{CBr}_3)_2, 80^\circ$	Alkenes, cycloalkenes	(514, 520)
$\text{F}_2\text{CH}-\ddot{\text{C}}-\text{F}$ $\text{CH}_3-\ddot{\text{C}}-\text{Cl}$ $\text{CF}_3-\ddot{\text{C}}-\text{Cl}$ $\text{Ph}-\ddot{\text{C}}-\text{F}$	$\text{CHF}_2\text{CF}_2\text{SiF}_3, 150^\circ$	Cyclohexene	(541)
	$\text{CH}_3\text{CCl}_3, \text{COT}^{2-}$	Alkenes, fluoroalkenes	(27, 542)
	$\text{PhHgCClBrCF}_3, 140^\circ$	Cyclooctatetraene	(293)
	$\text{PhCHFX}, \text{RO}^-$	Cyclooctene	(543)
		Alkenes, cycloalkenes	(99-100, 148) 544)

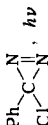
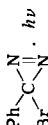
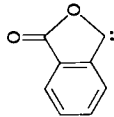
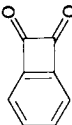
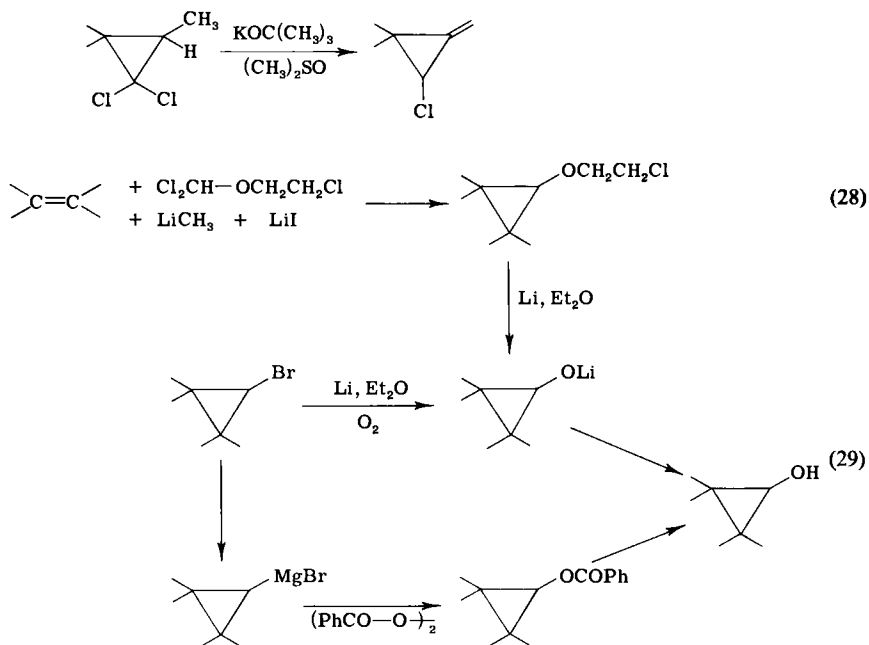
$\text{Ph}-\ddot{\text{C}}-\text{Cl}$	$\text{PhCHCl}_2, \text{RO}^-$	Alkenes, cycloalkenes	(99-102, 148, 194, 545-546a)
	 , $h\nu$	Alkenes, cycloalkenes	(100, 148, 547)
$\text{Ph}-\text{C}-\text{Br}$	$\text{PhCHBr}_2, \text{RO}^-$	Alkenes, cycloalkenes	(100, 103, 148, 548)
	 , $h\nu$	Alkenes, cycloalkenes	(100, 103, 148)
$\text{Cl}-\ddot{\text{C}}-\text{CO}_2\text{R}$	$\text{ClCN}_2\text{CO}_2\text{R}, h\nu$	Isobutene	(549)
$\text{Br}-\ddot{\text{C}}-\text{CO}_2\text{R}$	$\text{PhHgCCl}_2\text{CO}_2\text{R}, 140^\circ$	Cyclooctene	(543)
$\text{I}-\ddot{\text{C}}-\text{CO}_2\text{R}$	$\text{BrCN}_2\text{CO}_2\text{R}, h\nu$	Alkenes	(50)
$\text{CH}_3\text{OCH:}$	$\text{ICN}_2\text{CO}_2\text{R}, h\nu$	Alkenes	(50, 550)
	$(\text{CH}_3\text{O})_3\text{SiCH}(\text{OCH}_3)_2, 125^\circ$	Alkenes, cycloalkenes	(51)
	$\text{CH}_3\text{OCH}_2\text{Cl}, \text{RLi}$	Alkenes, cycloalkenes	(93)
	$\text{CH}_3\text{OCHCl}_2, \text{RLi}, \text{LiI}$	Alkenes, cycloalkenes	(94, 551, 551a)
	$\text{CH}_3\text{OCHCl}_2, \text{COT}^{2-}$	Cyclooctatetraene	(420)
$\text{RO}-\text{CH:}$	$\text{ROCH}_2\text{Cl}, \text{RLi}$	Alkenes, cycloalkenes	(93)
	$\text{ROCHCl}_2, \text{RLi}, \text{LiI}$	Alkenes, cycloalkenes	(94, 200)
$\text{PhO}-\text{CH:}$	$\text{ROCHCl}_2, \text{RLi}, \text{LiI}$	Dienes, enol ethers	(551, 552)
$\text{Ph}-\ddot{\text{C}}-\text{OCH}_3$	$\text{PhOCH}_2\text{Cl}, \text{RLi}$	Alkenes, cycloalkenes	(95, 96)
$\text{Cl}-\ddot{\text{C}}-\text{OCH}_3$	$\text{PhC}(\text{OCH}_3)=\text{N}-\text{NH}-\text{Ts}$	1-Decene	(553)
	$\text{Cl}_3\text{C}-\text{OR}, \text{RLi}, \text{LiI}$	Alkenes, cycloalkenes	(94, 200)
	 , $h\nu$	Alkenes, cycloalkenes, dienes	(554)

TABLE XV (Continued)

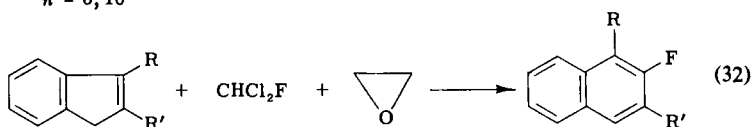
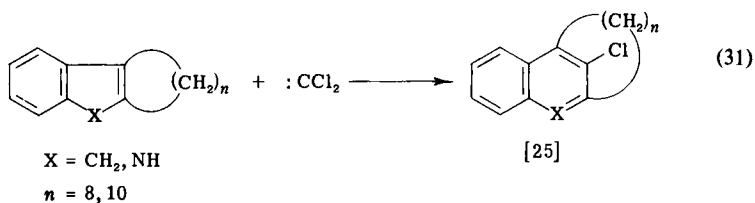
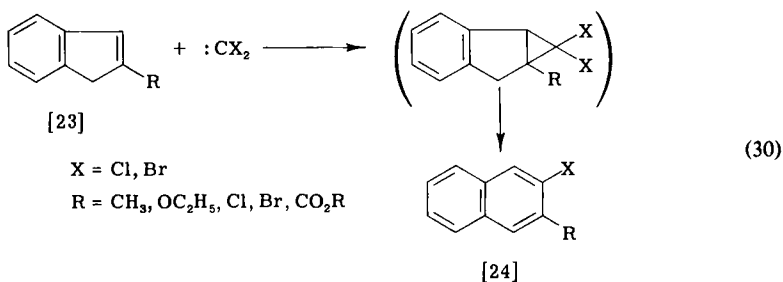
Species transferred	Source	Olefins	Refs.
$\text{PhS}-\text{CH}:$	$\text{PhSCH}_2\text{Cl}, \text{RO}^-$	Alkenes, cycloalkenes, ketene acetals	(97, 555, 556)
$\text{Cl}-\ddot{\text{C}}-\text{SPh}$	$\text{PhSCHCl}_2, \text{RO}^-$	Alkenes, cycloalkenes, ketene acetals	(577)
	$\text{PhSCCl}_3, \text{RLi LiI}$	Alkenes	(94)
$(\text{RS})_2\text{C}:$	$(\text{RS})_2\text{C}=\text{N}-\text{NH}-\text{Ts}, \text{RO}^-$	Enol ethers, ketene acetals, enamines	(558)
$(\text{PhS})_2\text{C}:$	$(\text{PhS})_3\text{CH}, \text{RLi}$	Ketene acetals	(559)
$\text{ArSO}_2\text{CH}:$	$\text{ArSO}_2\text{CHN}_2, h\nu$	Alkenes, cycloalkenes	(52, 98)
$\text{Ph}-\text{Se}-\text{CH}:$	$\text{PhSeCH}_2\text{Cl}, \text{RO}^-$	Alkenes, cycloalkenes	(560)
$(\text{CH}_3)_3\text{SiCH}:$	$(\text{CH}_3)_3\text{SiCHN}_2, \text{CuCl}$	Alkenes, cycloalkenes	(92)
$\text{R}_3\text{Si}-\ddot{\text{C}}-\text{CO}_2\text{R}$	$\text{R}_3\text{SiCN}_2\text{CO}_2\text{R}, h\nu$	Isobutene	(561)
$\text{R}_3\text{Si}-\ddot{\text{C}}-\text{Cl}$	$(\text{R}_3\text{SiCCl}_2)_2\text{Hg}, \text{Ph}_2\text{Hg}$	Cyclohexene	(562)
$\text{R}_3\text{Sn}-\ddot{\text{C}}-\text{CO}_2\text{R}$	$\text{R}_3\text{SnCN}_2\text{CO}_2\text{R}, h\nu$	Isobutene	(561)
$\text{Ph}-\ddot{\text{C}}-\text{P}(\text{OR})_2$	$\text{PhCN}_2\text{P}(\text{OR})_2, \text{Cu}$	Alkenes, cycloalkenes	(563, 563a)
$(\text{RO}_2\text{C}-\ddot{\text{C}})\text{Hg}$	$(\text{RO}_2\text{C}-\text{CN})_2\text{Hg}, h\nu$	Cyclohexene	(564)

Methylenecyclopropanes can be made by addition of carbenes to allenes (Table XV). They are also formed by treatment of some halocyclopropanes with base, probably by way of cyclopropene intermediates (197-199). Equation (29) summarizes some useful routes to cyclopropanols (200-202).

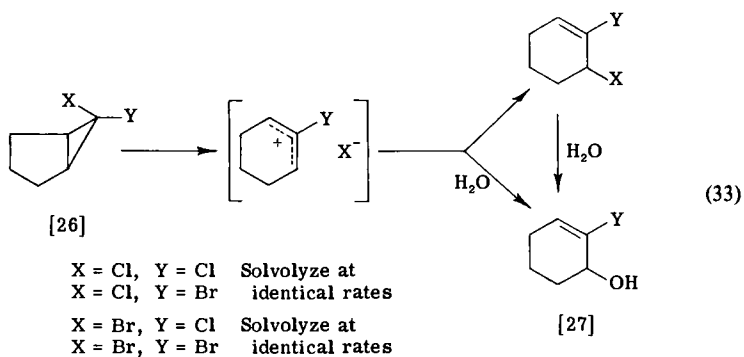


V. ADDITION ACCOMPANIED BY REARRANGEMENT

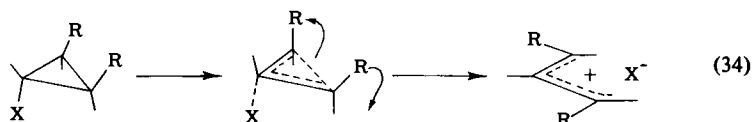
The rearrangements of highly energized cyclopropanes which arise by addition of carbenes to olefins in the gas phase have been discussed in Section I of this chapter. The present section is concerned with some reactions of labile carbene adducts in solution. The rearrangement of halocyclopropanes to give allyl halides or products derived therefrom has been observed quite frequently. Parham and his co-workers (565-567) provided the first examples when they found that the reaction of indenenes [23] with dihalocarbenes afforded 2-halonaphthalenes [24], Eq. (30). The preparative utility of this procedure is illustrated by the synthesis of naphthalene-2-¹⁴C from indene and chloroform-¹⁴C (568), and by the synthesis of a new class of metacyclophanes [25] (569, 570, 570*a,b*). Treatment of indenenes with dichlorofluoromethane and ethylene oxide provided 2-fluoronaphthalenes in high yields (571), Eq. (32).



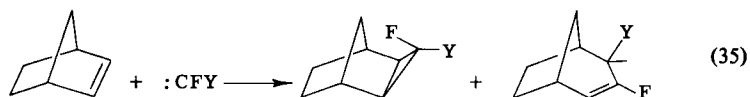
The dihalocarbene adducts of cyclopentene proved to be more stable, and their behavior sheds much light on the mechanism of the rearrangement (572–574). 6,6-Dihalobicyclo[3.1.0]hexanes [26] solvolyze in aqueous alcohol to give 2-halocyclohexen-3-ols [27]. One of the two isomeric chlorobromocarbene adducts solvolyzed at the same rate as the dichlorocarbene adduct; the other isomer solvolyzed at the same rate as the dibromocarbene adduct.



Similarly, *endo*-6-chlorobicyclo[3.1.0]hexane was converted into 3-chlorocyclohexene at 126° within 3 hr, whereas the *exo* isomer remained unchanged after 4 hr at 250° (413). These observations indicate that the stereochemical disposition of the leaving halogen is a crucial factor of the rearrangement. According to the Woodward-Hoffmann rules (63) the *concerted* rearrangement of a cyclopropyl derivative to an allyl cation should proceed by a stereospecific disrotatory process such that the groups *trans* to the leaving group rotate outward, and those *cis* to it rotate inward, as the C—X bond begins to break. If R, R in Eq. (34) form a small ring ($n \leq 7$), outward rotation becomes difficult on grounds of ring strain because it would lead to the incorporation of a *trans* allylic cation in a ring of size $n + 1$. As a consequence, the corresponding *exo*-halides and tosylates have been found to be particularly resistant to solvolysis (575–578).



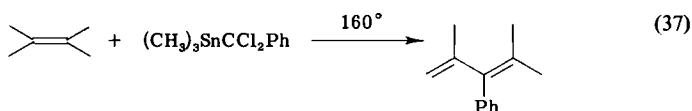
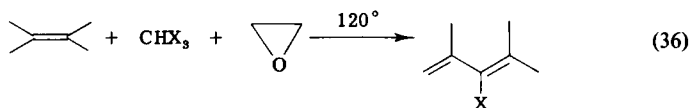
Dibromocarbene adducts rearrange more readily than the corresponding dichlorocarbene adducts, as might be expected from a mechanism involving heterolytic fission of the C—X bond. Thus, while 6,6-dibromobicyclo[3.1.0]hexane (26, X = Y = Br) was completely converted into 2,3-dibromocyclohexene in 1 hr at 120° (413, 572), the corresponding dichloro compound required 1.5 hr at 170° (413, 579). The dichlorocarbene adducts of 1,1-dialkyl-1-germacyclopent-3-enes and -1-silacyclopent-3-enes rearranged more readily than the cyclopentene derivatives (579a). Similar observations have been made with the adducts derived from dihydrofuran (490), camphene (580), and norbornene (581). Norbornene adducts of :CFCl and :CFBr which contain *endo*-fluorine are stable, whereas the *exo*-F isomers, carrying Cl or Br in the stereoelectronically preferred *endo* disposition, rearrange spontaneously to ring-expanded products (135, 582).



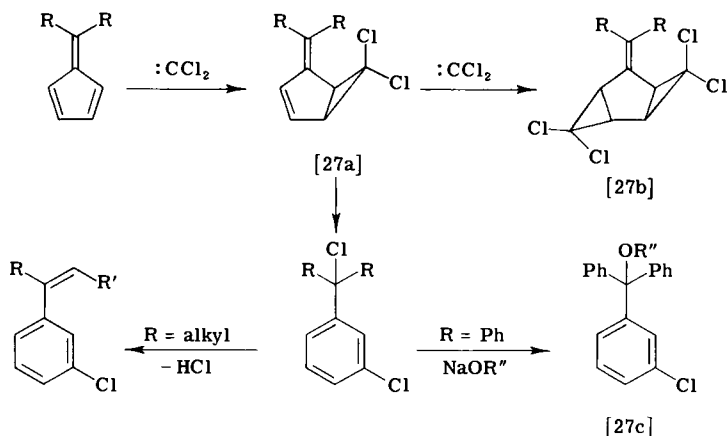
The norbornene case illustrates the effect of ring strain. In contrast to the rather stable 6,6-dichlorobicyclo[3.1.0]hexane (26, X = Y = Cl), the

dichlorocarbene adduct of norbornene has been isolated only with difficulty (581, 583). Several research groups have obtained only rearranged products from the reaction of dihalocarbenes with norbornenes (584–586), substituted norbornenes (585–588), and benzonorbornadiene (589). These reactions provide valuable synthetic routes to bicyclo[3.2.1]octenes. The stability of 7,7-dibromonorcarane (590) (rearrangement requires heating at 220° in quinoline solution) may be contrasted with the spontaneous ring expansion which was induced by the addition of dibromocarbene to bicyclo[2.2.2]octene (586).

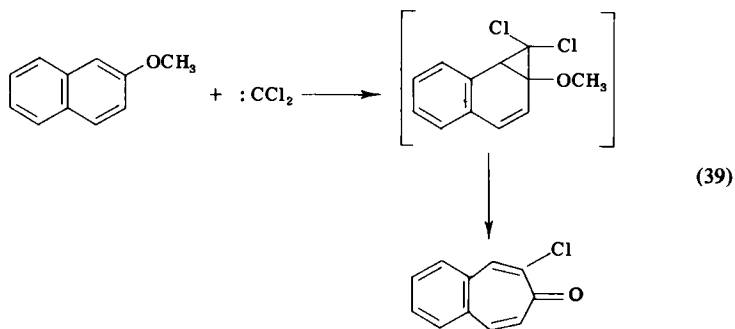
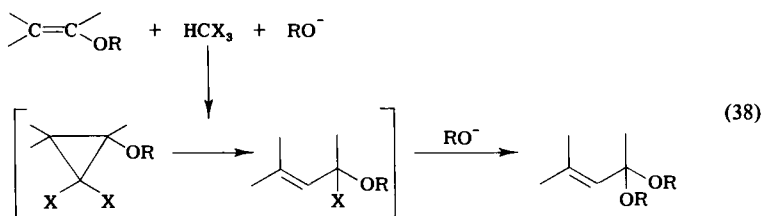
The dichlorocarbene adduct of 7-oxanorbornene is more stable (up to 165°!) than that of norbornene (591). The effect of oxygen may be attributed to inductive destabilization of the rearranged allylic cation. Inductive stabilization of the allyl cation, on the other hand, may promote rearrangement. Thus the dichlorocarbene adduct of 2-methyl-4,5-dihydrofuran could not be isolated (592), in contrast to that of 4,5-dihydrofuran itself (490). Rearrangement may even occur in the addition of halocarbenes to branched acyclic olefins when the carbene precursors require drastic reaction conditions (593, 594), Eqs. (36) and (37).



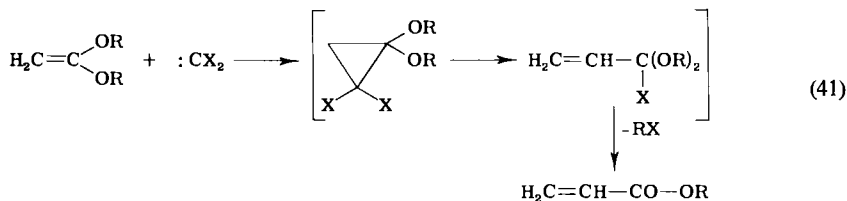
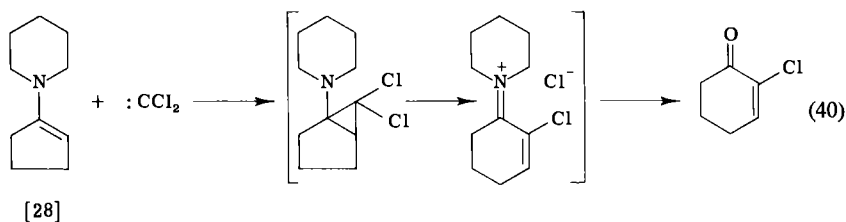
The addition of dichlorocarbene to 6,6-dialkylfulvenes proceeded with rearrangement to give *m*-chlorostyrenes (594a). The reaction of 6,6-diphenylfulvene with ethyl trichloroacetate and sodium methoxide at room temperature gave 70% of *m*-chlorophenyldiphenylcarbinol and its methyl ether [27a]. At –10° with a 5 : 1 carbene: fulvene ratio, 57% of the bis-adduct [27b] were obtained (594b). At –10° the mono-adduct [27a] apparently survives long enough for a second CCl₂ addition to occur, whereas at room temperature rapid rearrangement takes place.



Enol ethers afforded either unsaturated acetals (595, 596), Eq. (38), or carbonyl compounds. The latter reaction proceeds spontaneously with ethers of 1-naphthol, 2-naphthol, 9-phenanthrol (597), and 3-hydroxybenzothiophene (598), as illustrated in Eq. (39). Stable dibromocarbene adducts of enol ethers can be subjected to the same rearrangement by treatment with aqueous alcoholic silver nitrate (533–537). This sequence of reactions has been applied to the expansion of ring A in steroids.

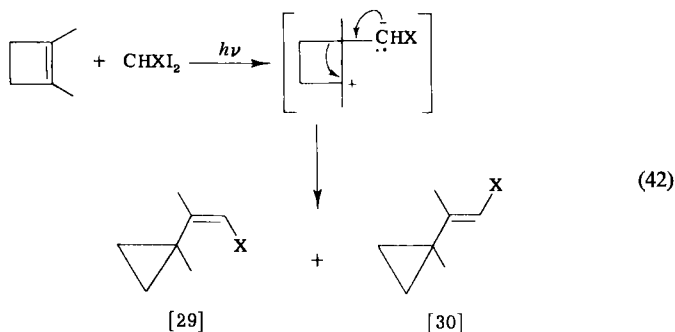


The reaction of some enamines, e.g., [28], with dichlorocarbene proceeded in obvious analogy to Eq. (39) (472, 473), whereas the adduct from isobutyryldimethylamine was stable at ambient temperature (474). Ketene acetals afforded α -haloacrylates on treatment with dihalocarbenes (287, 599).

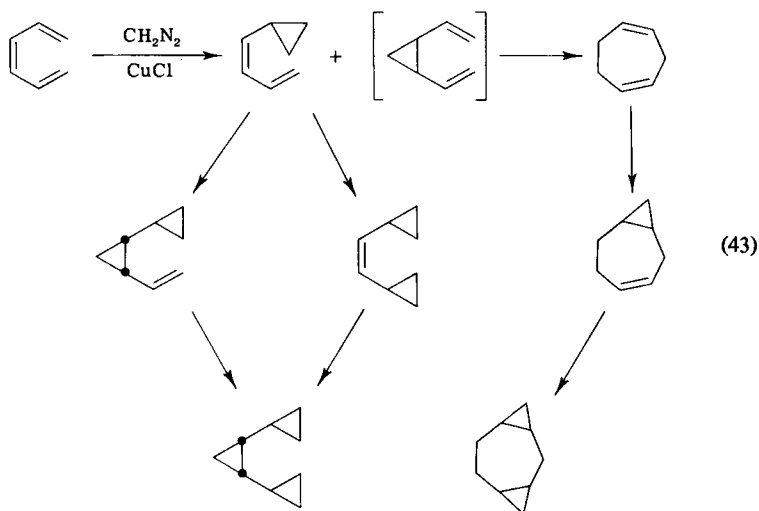


When iodoform (diiodochloromethane) was photolyzed in a solution of 1,2-dimethylcyclobutene in methylene chloride, two isomeric vinylcyclopropanes, [29] and [30], were isolated instead of the expected cyclopentenes (91). Other alkenes and cycloalkenes afforded halocyclopropanes under the same conditions. The authors suggest that halocarbenes generated from the photolysis of diiodohalomethanes may add to a strained olefin in a stepwise mechanism via a dipolar intermediate, Eq. (42).

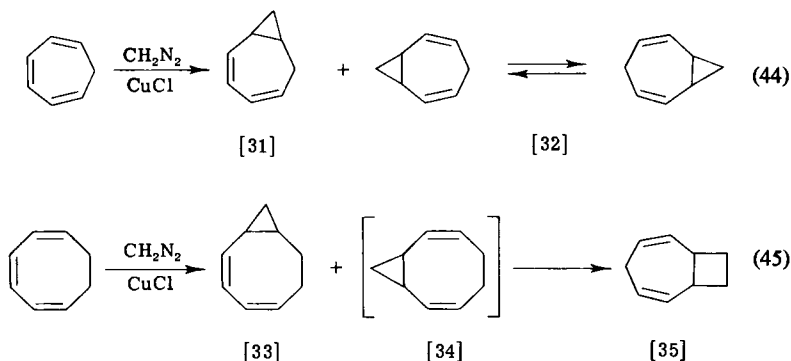
Some additions of carbenes and carbenoids to olefinic bonds generate structures capable of undergoing fast sigmatropic rearrangements.



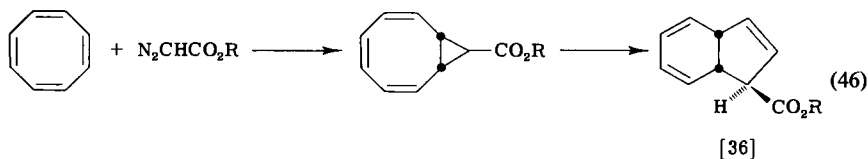
Thus *cis*-1,3,5-hexatriene afforded all possible cyclopropanation products on treatment with diazomethane–cuprous chloride, except *cis*-1,2-divinylcyclopropane. Instead, 1,4-cycloheptadiene (formed by Cope rearrangement of *cis*-1,2-divinylcyclopropane) and products of its further cyclopropanation were isolated (279).



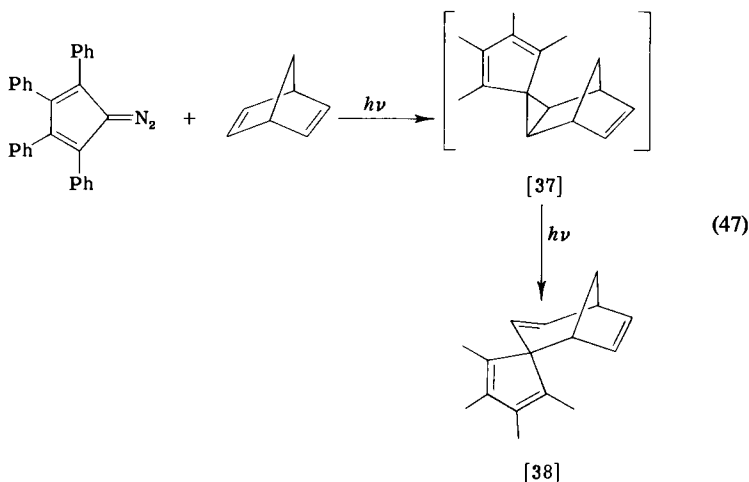
Application of the same method to cycloheptatriene afforded bicyclo[5.1.0]octa-2,4-diene [31] and bicyclo[5.1.0]octa-2,5-diene [32]; the latter undergoes a rapidly reversible, degenerate Cope rearrangement (279). The cyclopropanation of 1,3,5-cyclooctatriene gave bicyclo[6.1.0]nona-2,4-diene [33] and bicyclo[5.2.0]nona-2,5-diene [35], the latter resulting from the Cope rearrangement of bicyclo[6.1.0]nona-2,6-diene [34] (275).



Bicyclo[6.1.0]nona-2,4,6-trienes could be obtained by addition of carbenoids to cyclooctatetraene and were found to rearrange at elevated temperatures to *cis*-dihydroindenes (280, 354). When ethyl diazoacetate was decomposed thermally in the presence of cyclooctatetraene, the rearranged ester [36] was the major product (354).



The formation of the spiro compound [38] by photolysis of tetraphenyl-diazocyclopentadiene in the presence of norbornadiene has been viewed as a photorearrangement of the initial adduct [37] (600).



VI. INTRAMOLECULAR ADDITION

A. Vinylcarbenes

Divalent carbon intermediates with olefinic bonds in the α , β position are distinguished from those with more remote unsaturation by the lack of hydrogen shifts. The conversion of a vinylcarbene into an allene has never been observed; formation of cyclopropenes appears to be the only way of intramolecular reaction. The base-induced pyrolysis or photolysis

of tosylhydrazones of α, β -unsaturated carbonyl compounds is a convenient route to the hypothetical vinylcarbenes (601–604). Details of the reaction mechanism, such as the possible intervention of pyrazolenines and their photochemical reversion to diazoalkenes, have been discussed in Chapter 2, Section IV. Good yields of cyclopropenes were obtained only from unsaturated carbonyl compounds lacking a hydrogen in the β position (602). Otherwise pyrazole formation became the major reaction path. Moderate yields of arylcyclopropenes were obtained by the photolytic procedure but not by thermolysis (604) (Table XVI).

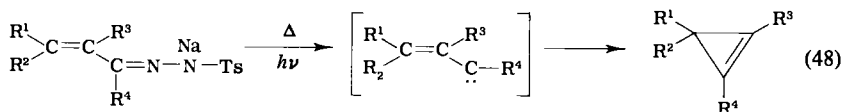
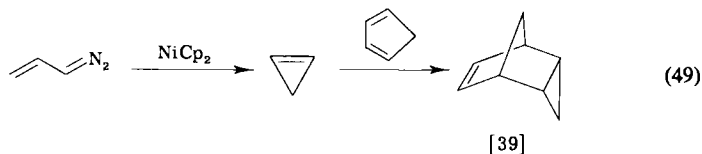


TABLE XVI

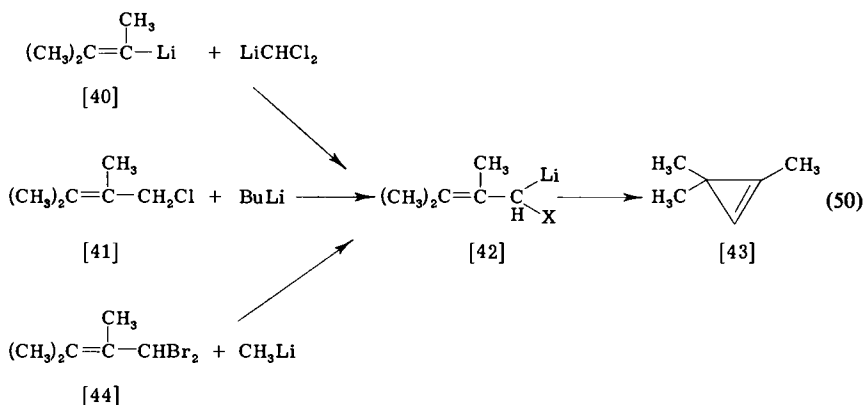
Cyclopropene Formation from Tosylhydrazones of α, β -Unsaturated Carbonyl Compounds, Eq. (48)

Substituents				Yield, %; and Ref.	
R ¹	R ²	R ³	R ⁴	Thermolysis	Photolysis
CH ₃	CH ₃	CH ₃	CH ₃	22 (603)	28 (604)
CH ₃	CH ₃	H	CH ₃	39 (604)	42 (604)
CH ₃	CH ₃	CH ₃	H	72 (602)	—
CH ₃	CH ₃	H	H	50 (602)	—
CH ₃	H	CH ₃	H	4 (602)	—
Ph	H	H	Ph	—	19 (604)
Ph	H	Ph	Ph	—	21 (604)

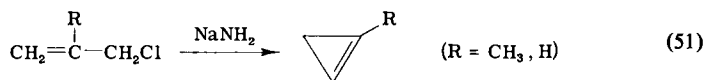
The nickelocene-catalyzed decomposition of 3-diazopropene in cyclopentadiene as solvent afforded *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene [39], the product of the Diels-Alder reaction of cyclopropene with cyclopentadiene (368).



Several methods have been described to generate vinylcarbenes from organometallic precursors. Thus 1,2-dimethylpropenyllithium [40] reacted with methylene chloride in tetrahydrofuran to give the lithium derivative of 1,3,3-trimethylcyclopropene [43] in fair yield (605). It is assumed that the initially formed chlorocarbenoid adds to the vinyl lithium compound to form the intermediate [42]. The same cyclopropene was obtained in poor yield from 1-chloro-2,3-dimethyl-2-butene [41] on treatment with *n*-butyllithium (606). Still another route to this compound is based on the halogen-metal interchange reaction with 1,1-dibromo-2,3-dimethyl-2-butene [44] (606).

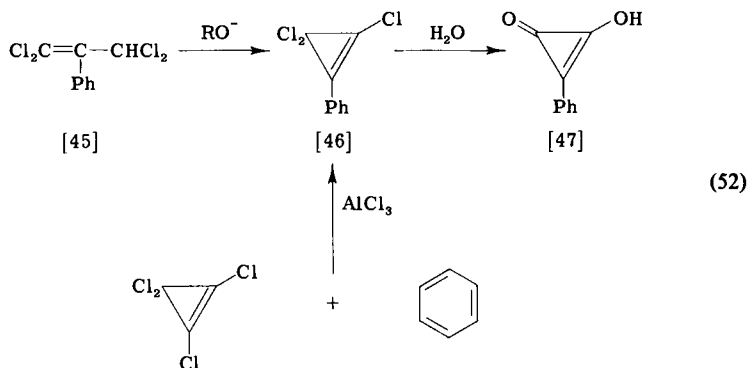


Probably closely related to the reactions in Eq. (50) is the formation of 1-methylcyclopropene (yield 50%) from sodium amide and 3-chloro-2-methylpropene (607). When potassium amide was employed as the base, a virtually complete isomerization of methylcyclopropene to methylenecyclopropane occurred (608). The unsubstituted cyclopropene was only obtained in about 10% yield from allyl chloride and sodium amide (609).

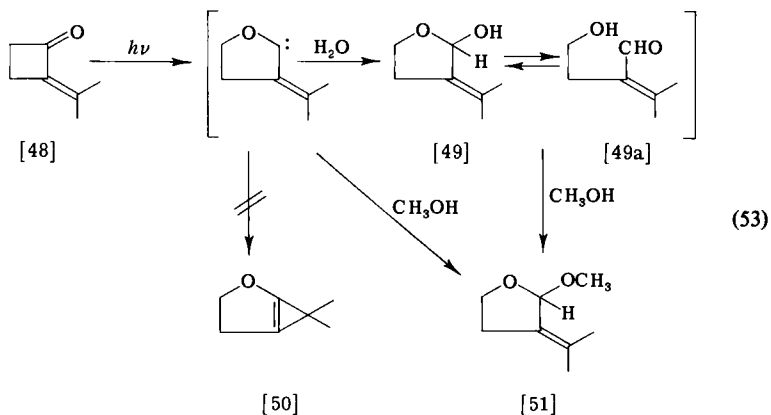


The synthesis of 1-hydroxy-2-phenylcyclopropenone [47] has been accomplished in 10% yield by the reaction of 1,1,3,3-tetrachloro-2-phenylpropene [45] with potassium *t*-butoxide followed by aqueous workup (610). 1-Phenyl-2,3,3-trichlorocyclopropene [46] seems to be a reasonable intermediate in this reaction. When prepared in an unambiguous way from

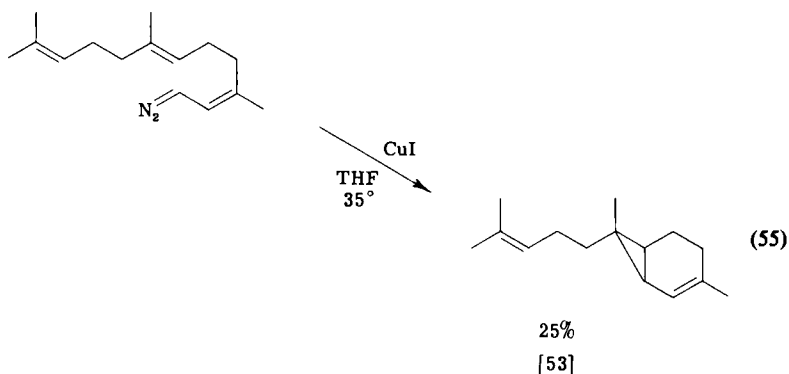
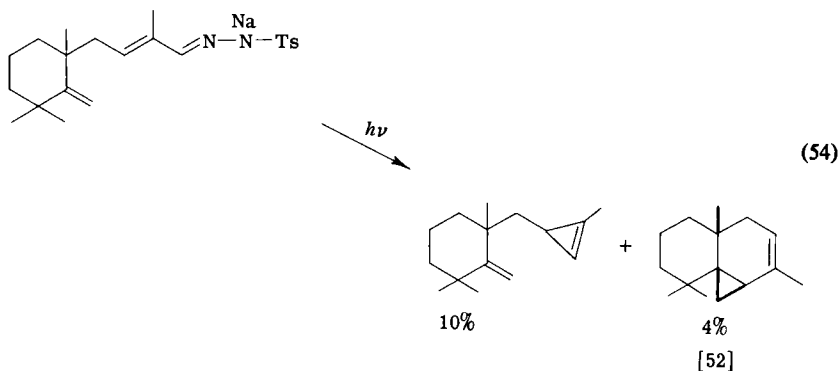
tetrachlorocyclopropene, benzene, and aluminum trichloride, [46] could be converted into [47] under the same conditions to which [45] was subjected (610).



Irradiation of 2-isopropylidenecyclobutanone [48] in benzene afforded an unstable intermediate which, when treated with methanol in the dark, produced the cyclic acetal [51] (611). In a preliminary report, the unstable intermediate was tentatively assigned the cyclopropene structure [50]. Later, the intermediate was identified as an equilibrium mixture of hemiacetal [49] and its hydroxyaldehyde [49a], formed by reaction of the oxacarbene with water present in the benzene (611a). The presumed intramolecular addition of the oxacarbene does not occur.



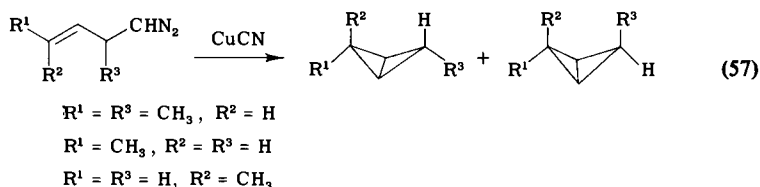
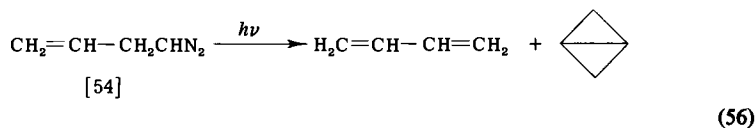
The addition of vinylcarbenes to a double bond located in the 6,7 position of the same molecule, with formation of norcarene structures, has been utilized in the synthesis of two terpenoid hydrocarbons, thujopsene [52] (612) and sesquicarene [53] (613) (for another synthesis of sesquicarene see Section VI, E).



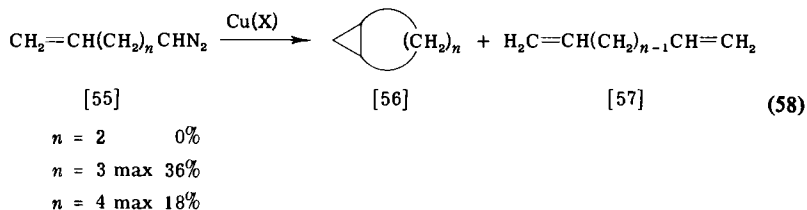
B. Alkenylcarbenes

When allyldiazomethane [54] was photolyzed in heptane solution at -78° , the products were 1,3-butadiene and bicyclo[1.1.0]butane in the

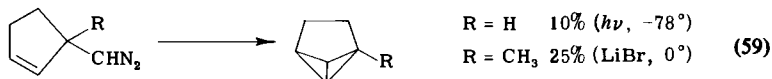
ratio 5 : 1 (614). Closs and Pfeffer (615) synthesized 2-methyl- and 2,4-dimethylbicyclobutanes via the cuprous cyanide-catalyzed decomposition of the appropriate diazo precursors and studied the stereochemistry of the bicyclobutane-butadiene rearrangement.

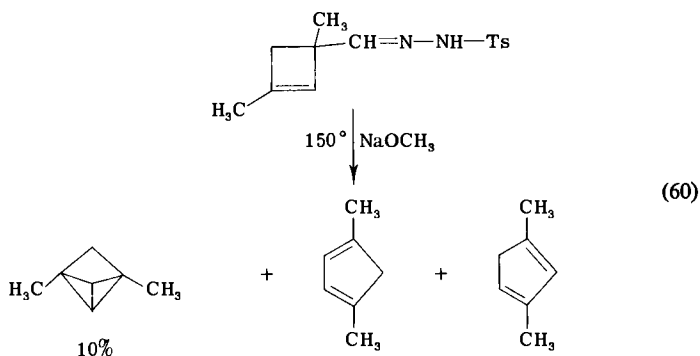


When the diazo and olefinic functions were separated by more than one carbon atom, photolysis did not lead to intramolecular addition. Some of the ω -diazoalkenes [55] were converted into bicyclo[$n.1.0$]alkanes [56] by catalytic decomposition, but the major products were 1, ω -dienes [57] arising by hydrogen shift (616).

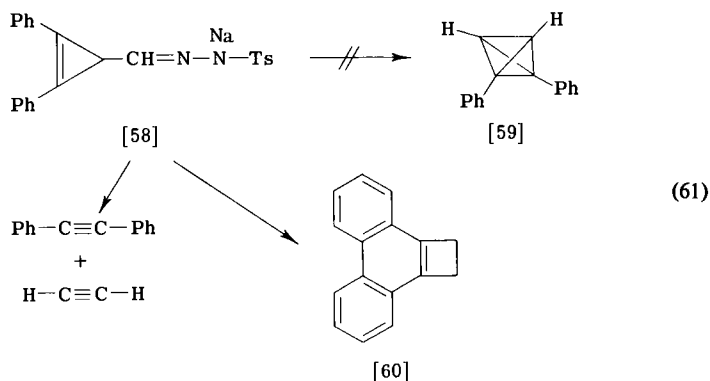


Intramolecular addition of cycloalkenylcarbenes opened an access to several interesting tricyclic structures. Thus, bridged bicyclobutanes have been obtained from cyclopentenyl diazomethanes (617, 618), and even from a cyclobutenyl diazomethane (618). Major reactions in both cases, however, were ring expansion and migration of hydrogen.



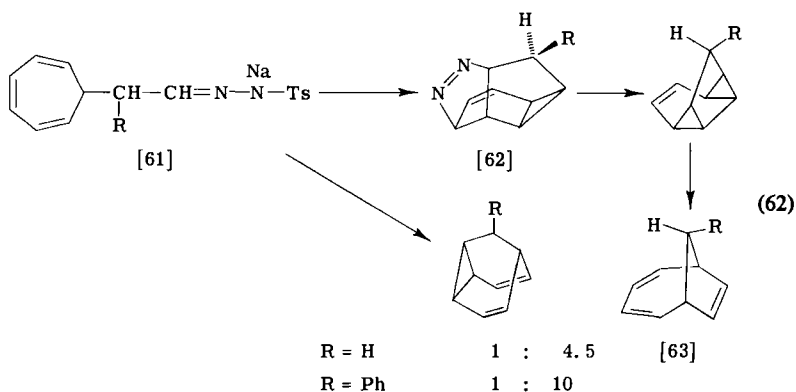


Attempts to synthesize a derivative of tetrahedrane by intramolecular addition of 1,2-diphenylcyclopropenylcarbene failed. Major products obtained from the thermal or photolytic decomposition of [58] were diphenylacetylene and acetylene, in analogy to the fragmentation of cyclopropylcarbenes (Chapter 12, Section III) (619, 620). A minor product (0.1 % yield) to which the tetrahedrane structure [59] had originally been assigned (619) turned out to be the cyclobutene derivative [60] (620, 621).

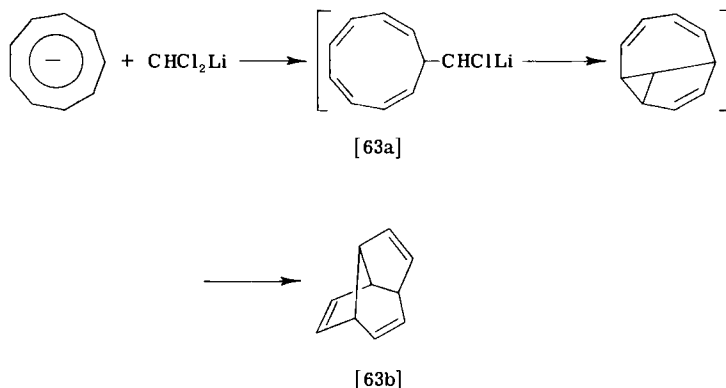


In analogy to the results obtained in the acyclic series, intramolecular addition was at best a minor reaction (2–3 %) in the case of cyclopentenylcarbenes, cyclohexenylcarbenes, and cycloheptenylcarbenes having the double bond in the 5,6 position (622). When the tosylhydrazones of cycloheptatriene-7-acetaldehydes [61] were decomposed, formation of bicyclo[4.2.1]nona-2,4,7-trienes [63] was the predominant reaction (623). The mechanism leading to [63] may involve carbene addition to the 1,2

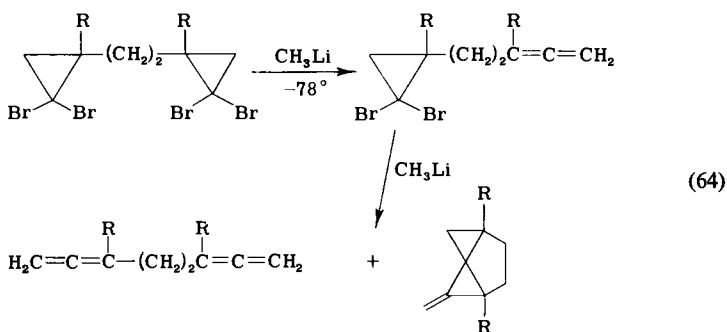
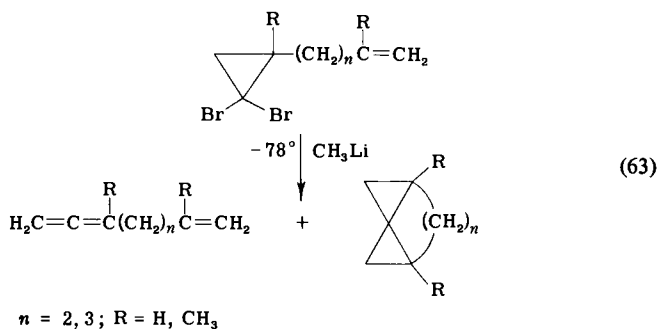
double bond, but pyrazolines [62] (isolated in small yield from the reaction mixture) are also potential intermediates.



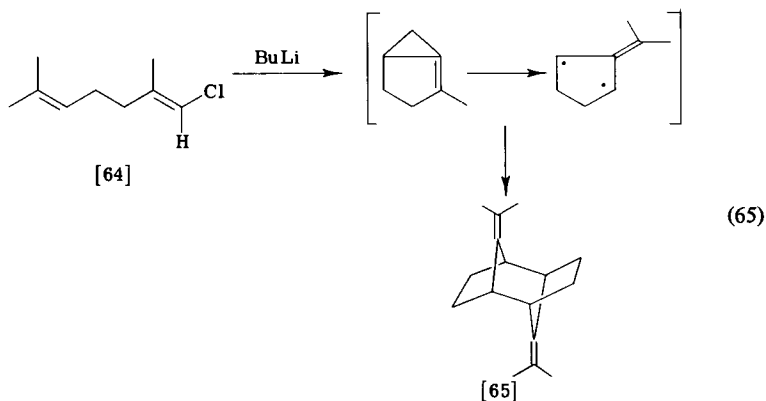
A synthesis for $\text{C}_{10}\text{H}_{10}$ hydrocarbons was devised by expanding the readily available C_9H_9^- ring (623a). When lithium cyclononatetraenide was reacted with CH_2Cl_2 and butyllithium at -40° , a hydrocarbon fraction was obtained in 35% yield which contained [63b] as the major product (85%). The simplest explanation for the formation of [63b] is intramolecular addition of the carbenoid [63a] followed by Cope rearrangement.



Skattebøl (624) reported on carbenoid intramolecular additions which start from the mono or bis adducts of dibromocarbene to $1,\omega$ -dienes. Halogen-metal interchange induces the competitive formation of bridged spiropentanes and of allenes, Eqs. (63) and (64).

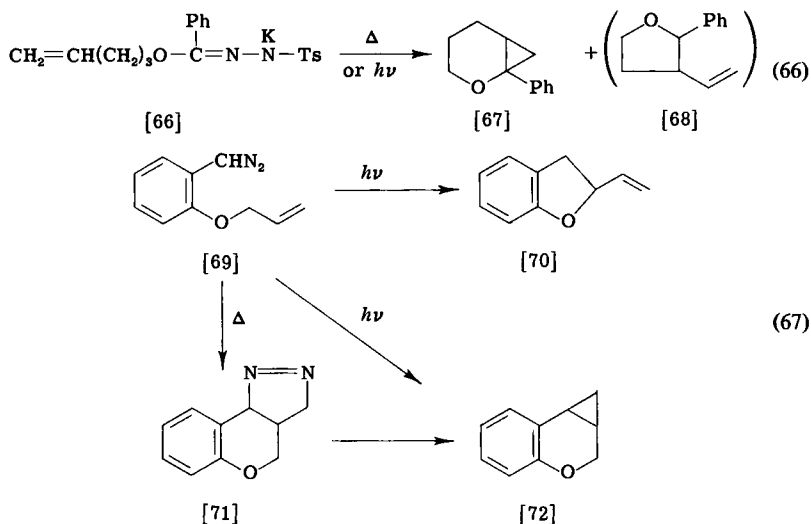


Intramolecular addition of an alkylidenecarbene (or carbenoid) may be the path by which [65] is formed on treatment of 1-chloro-2,5-dimethylhepta-1,5-diene [64] with *n*-butyllithium in tetrahydrofuran (625).



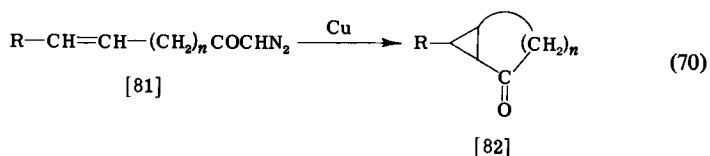
C. Arylcarbenes

Arylcarbenes with unsaturated chains attached either to the divalent carbon or to the ortho position of the aryl group have been investigated. The thermolysis or photolysis of potassium 4-pentenol benzoate tosylhydrazone [66] afforded [67] in 11–21 % yield (553). The product of insertion into the allylic C—H bonds [68] was not present in a yield greater than 1 %. Much more allylic insertion was observed in the photolysis of (2-allyloxyphenyl)diazomethane [69] which produced [70] and [72]. This reaction was complicated further by the conversion of [69] into the pyrazoline [71] which also afforded [72] on photolysis. By extrapolation of the product ratio to zero time it was concluded that [70] and [72] arise from (2-allyloxyphenyl)carbene in the ratio 2.5 : 1 (626).



D. Unsaturated Alkoxycarbonylcarbenes

Allyl diazoacetate [73] is the precursor prototype of this section. Despite the absence of β - and γ -C—H bonds, allyloxycarbonylcarbene undergoes intramolecular addition reluctantly. Photolysis of [73] in cyclohexane afforded only allyl cyclohexylacetate [75], the product of intermolecular C—H insertion. Catalytic decomposition of [73] produced the bicyclic lactone [74] with large amounts of diallyl fumarate and diallyl maleate (627). The optimal yield of [74] was 40 %, and the cyclization of *trans*-crotyl diazoacetate proceeded with similar results (628).

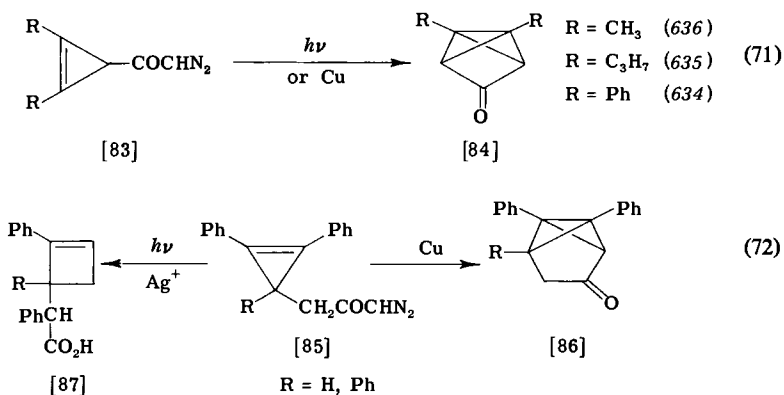


$n = 2$, R = H: 59%; R = Ph: 59%

$n = 3$, R = H: 37%; R = Ph: 30%

$n = 4$, R = H: 3%; R = Ph: Very low

The use of copper catalysts (CuSO_4 and CuCl have also been employed) is imperative to suppress the Wolff rearrangement of diazoketones (Chapter 12, Section V), which is brought about by light, heat, and silver catalysts. There are only few examples of intramolecular addition under conditions which normally lead to Wolff rearrangement. Equation (78) in Chapter 7 illustrates the complex mixture of products arising by rearrangement, addition, and insertion in the silver-catalyzed decomposition of a cyclohexenyl diazoketone (633). 3-Diazomethylketocyclopropenes [83] are the only unsaturated diazoketones known so far where both light (634, 635) and copper catalysis (636) effected intramolecular addition to produce the tricyclo[1.1.1.0^{4,5}]pentane skeleton [84]. In the homologous series [85], only copper catalysis afforded tricyclo[2.1.1.0^{5,6}]hexane derivatives [86], whereas photolysis and silver catalysis led to Wolff rearrangement (637–639). The unexpected structure of the “Wolff products” [87] is due to a second rearrangement at the ketene stage.



Under the appropriate conditions, the intramolecular reactions of unsaturated diazoketones appear to proceed more efficiently than those of diazoalkenes and unsaturated diazo esters. Applications of this reaction in the synthesis of natural products or otherwise intriguing polycyclic compounds have been collected in Table XVII (632, 640–665).

TABLE XVII
Carbenoid Intramolecular Addition Reactions of Unsaturated Diazo Ketones

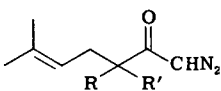
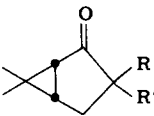
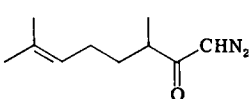
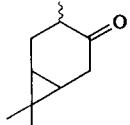
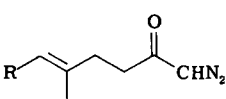
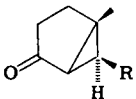
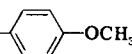
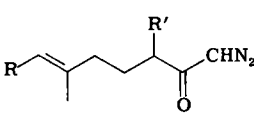
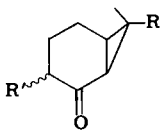
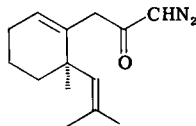
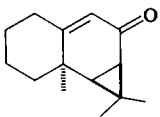
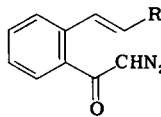
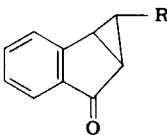
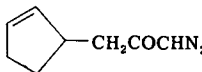
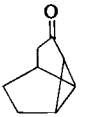
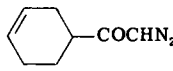
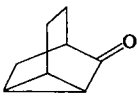
Diazo ketone	Product(s)	Yield	Ref.
		$R, R' = H$ 40% $R = CH_3, R' = H$ 70% $R, R' = CH_3$ 70% $R = CH_3, R' = CO_2R$ 48%	640, 641 641 642 643
		50%	644
		$R = (CH_2)_2CH=CHCH_3$ 80% $R = (CH_2)_2$ - 	645 646
		$R = (CH_2)_2CH=C(CH_3)_2$ 60% $R' = H$ 55% $\rightarrow \rightarrow d, l$ -Sesquicarene $R = (CH_2)_2CH=C(CH_3)CH_2OMs$ $R' = H$ $\rightarrow \rightarrow d, l$ -Sirenine	647 648, 649 650
		4-Demethylaristolone 15%	651
		$R = H$ 42% $R = Ph$ 74%	632 652
		53%	653
		31, 53%	654, 655

TABLE XVII (continued)

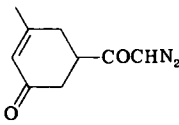
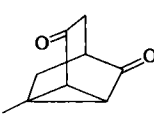
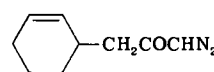
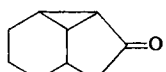
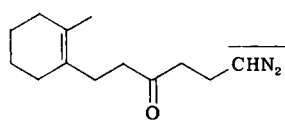
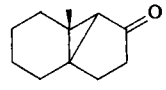
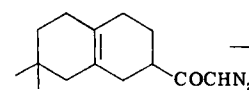
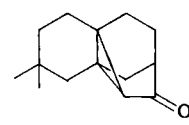
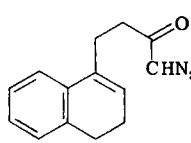
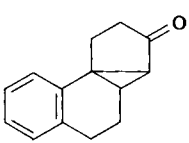
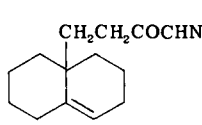
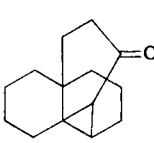
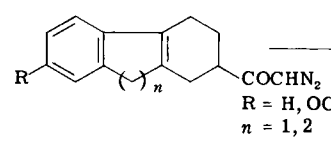
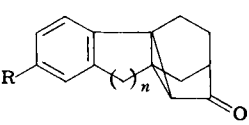
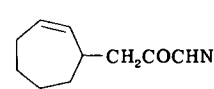
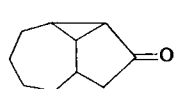
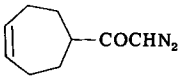
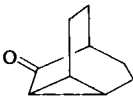
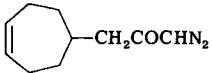
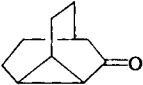
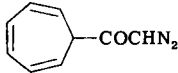
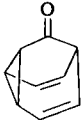
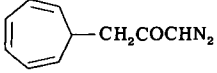
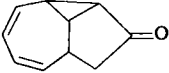
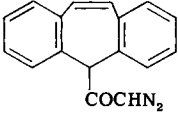
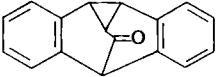
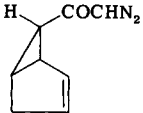
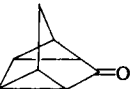
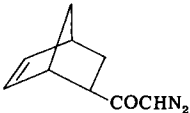
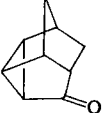
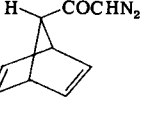
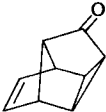
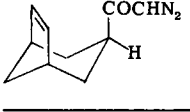
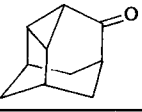
Diazo ketone	Product(s)	Yield	Ref.
 $\xrightarrow{\text{CuSO}_4}$		38%	656
 $\xrightarrow{\text{CuSO}_4}$		39%	654
 $\xrightarrow{\text{Cu}}$		29%	632
 $\xrightarrow{\text{CuSO}_4}$			657
 $\xrightarrow{\text{Cu}}$		22%	632
 $\longrightarrow$	 $\rightarrow$ [4.4.4] Propellane		658
 $\longrightarrow$ $\text{R} = \text{H}, \text{OCH}_3$ $n = 1, 2$	 $\rightarrow$ Gibberelins		659
 $\xrightarrow{\text{CuSO}_4}$		36%	654

TABLE XVII (continued)

Diazo ketone		Product(s)	Yield	Ref.
	$\xrightarrow[\text{or Cu}]{\text{CuSO}_4}$		47–55%	654, 655
	$\xrightarrow{\text{CuSO}_4}$		47%	654
	$\xrightarrow{\text{Cu}}$		"Barbaralone" 15–30%	660
	$\xrightarrow{\text{Cu}}$		45%	660
	$\xrightarrow[\text{or Cu}]{\text{CuCl}}$		30%	661
	$\xrightarrow{\text{Cu}}$		30%	662
	$\xrightarrow{\text{Cu}}$			663
	$\xrightarrow{\text{Cu}}$		50%	664
	$\xrightarrow{\text{CuSO}_4}$		27%	665

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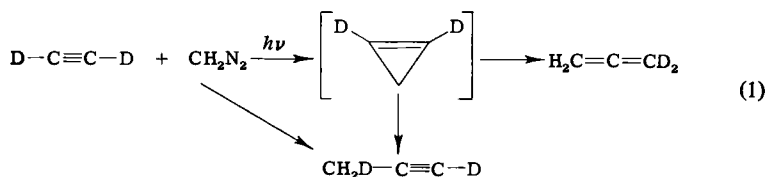
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Addition to Alkynes

I. FORMATION OF CYCLOPROPENES

CARBENES AND CARBENOIDs add to alkynes less readily than they add to alkenes. Two factors, the decreased nucleophilic reactivity of the carbon-carbon triple bond, and the instability of many cyclopropenes, contribute to the rather low efficiency of cyclopropene formation.

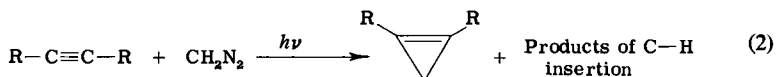
The photolysis of diazomethane in the presence of acetylene gave allene and propyne instead of the expected cyclopropene (1). The formation of allene-1,1- d_2 from acetylene-1,2- d_2 suggests that the allene arises by way of a cyclopropene intermediate.



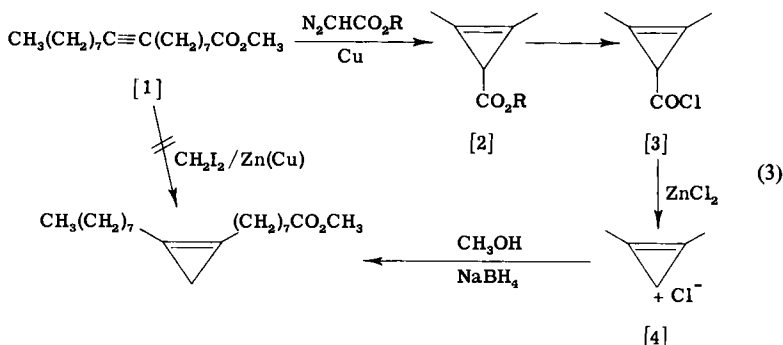
Trapping of the cyclopropene was impossible even under favorable conditions of collisional deactivation. No spectral evidence for the presence of either cyclopropene or methylacetylene was obtained after photolysis of solid argon-acetylene-diazomethane deposits at 4°K, allene being the only product (2). Reaction of methylene produced by ketene photolysis with acetylene in the gas phase afforded propyne and allene in a constant ratio of 1.5 ± 0.3 which was not affected by variation of pressure or by addition of oxygen or nitric oxide (3).

Alkyl substitution increases the stability of the cyclopropenes: 1,2-dimethylcyclopropene was obtained in 17% yield from the photolysis of diazomethane in 2-butyne-dimethyl ether mixtures at -70° (4). The photodecomposition of diazomethane in 4-octyne at -78° afforded

1,2-di-*n*-propylcyclopropene, 6-methyl-4-octyne, 7-methyl-4-octyne, and 4-nonyne in the ratio 23 : 19 : 19 : 38. This suggests that the relative reactivity of methylene with the acetylenic bond of 4-octyne is about eight times that with a C—H bond in the same molecule (5).

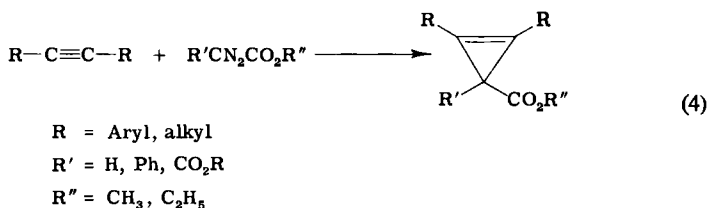


The photolytic synthesis of a methyl sterulate-containing mixture from methyl stearolate and diazomethane has been reported (6). The amount of methyl sterulate separable by chromatography on silicic acid was 9.5% (6a). The addition of CH_2 to methyl stearolate by the Simmons-Smith procedure has also been claimed (7), but in the hands of other authors this method failed to produce detectable amounts of cyclopropene material (8, 9). Diazomethane in the presence of cuprous chloride or bromide likewise failed to convert methyl stearolate into methyl sterulate (9). An unequivocal synthesis of methyl sterulate was achieved by an indirect route. Diazoacetic ester in the presence of Cu-bronze reacted with methyl stearolate to give the diester of the cyclopropene diacid [2]. Treatment of the corresponding diacid chloride [3] selectively decarbonylated the chloro-carbonyl group in the cyclopropene ring. The cyclopropenium intermediate [4] was converted into methyl sterulate by treatment with methanol and sodium borohydride (9).



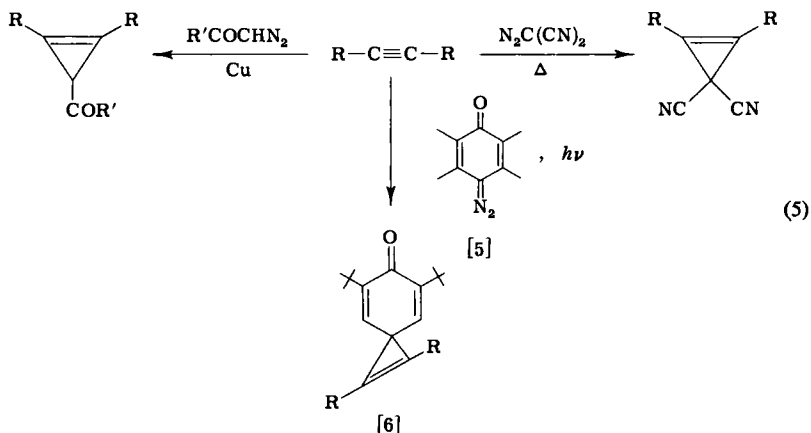
The first published example of cyclopropene formation from an acetylene and ethyl diazoacetate, by Dyakonov and Komendantov (10), involved 1-phenylpropyne. This reaction was extended to 1-phenylpropynes substituted in various nuclear positions (11–13), and to 1,3,3-triphenylpropyne (14). Breslow and his co-workers (15) reported independently on

the addition of ethoxycarbonylcarbene to diphenylacetylene. The synthesis of 1,2-dimethylcyclopropene-3-carboxylates was achieved by photolysis of methyl diazoacetate (4), and by decomposition of ethyl diazoacetate catalyzed by arylcopper (16) or di- μ -chlorodi- π -allylpalladium (17) in the presence of 2-butyne. Methyl phenyldiazoacetate (18) and diethyl diazomalonate (15) likewise afforded cyclopropenes in their thermal reactions with diphenylacetylene.

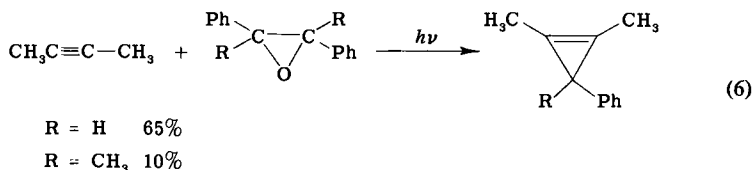


A method for preparing cyclopropenecarboxylic acids with hydrogen at the double bond involves reaction of methyl diazoacetate with trimethylsilyl-substituted acetylenes (18a). The trimethylsilyl groups were removed during alkaline hydrolysis of the ester, but yields of the addition step were poor (5–10%).

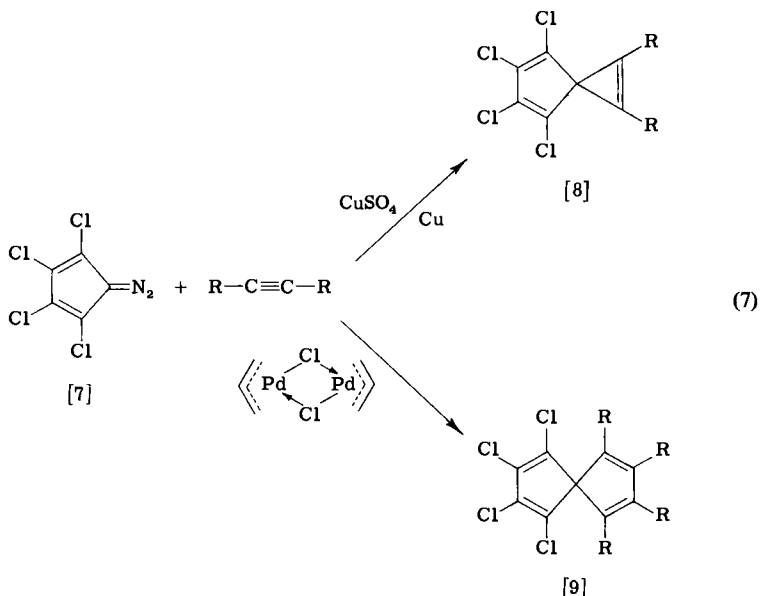
While the copper-catalyzed reaction of ethyl diazoacetate with various dialkylacetylenes produced cyclopropenes in 30–50% yield (19), the results obtained with diazoketones were much poorer (19, 20). As a rule, less than 10% of the corresponding acylcyclopropenes were isolated. The carbene derived from 3,5-di-*t*-butylbenzene-1,4-diazooxide [5] added to 2-butyne to give the spiro compound [6] in 63% yield (21), and the thermal reaction of dicyanodiazomethane proceeded with similar efficiency (22).



The photolysis of phenyldiazoacetone nitrile in the presence of diphenylacetylene was involved in the first synthesis of a cyclopropenium salt (23), but attempts to decompose simple aryldiazomethanes in the presence of alkynes fail because of pyrazole formation. The photolysis of stilbene oxides with excess 2-butyne, however, afforded the corresponding aryl-carbene adducts (24, 25).

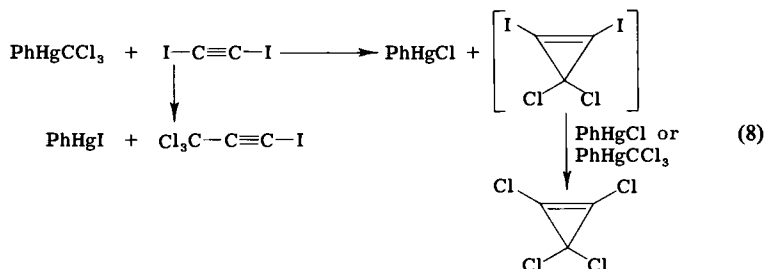


Decomposition of 1,2,3,4-tetrachlorodiazocyclopentadiene [7] at 80° in diphenylacetylene or 3-hexyne, using Cu or CuSO₄ catalysts, gave the expected spiro[2.4]heptatrienes [8]. However, the reaction of [7] with dialkylacetylenes, induced by di-μ-chlorodi-π-allyldipalladium, gave low yields of spiro[4.4]nonatetraenes [9]. These are thought to arise from the insertion reaction of a palladium-carbene complex with a tetraalkylcyclobutadiene-palladium complex (26).

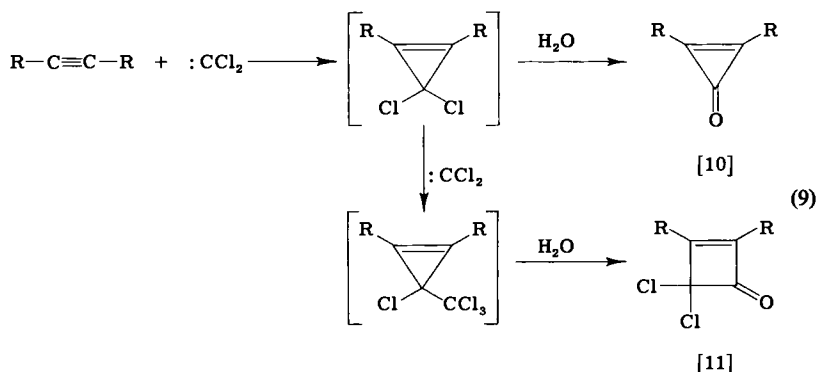


Only few cases of dihalocarbene addition to alkynes are known which

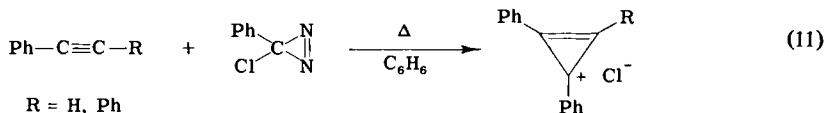
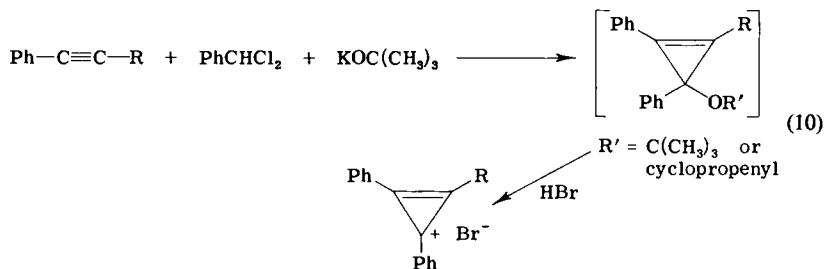
lead to isolable dihalocyclopropenes. They include the reaction of sodium difluorochloroacetate with steroidal alkynes (27, 27a), the reaction of $(\text{CF}_3)_3\text{PF}_2$ with hexafluoro-2-butyne (28), and the reaction of $(\text{CH}_3)_3\text{SnCF}_3$ with $(\text{C}_2\text{H}_5)_3\text{Ge}-\text{C}\equiv\text{C}-\text{CF}_3$ (29), $(\text{CH}_3)_2\text{As}-\text{C}\equiv\text{C}-\text{CF}_3$ (29a), and perfluoroalkynes (30). The thermolysis of phenyl(trichloromethyl)mercury in the presence of diiodoacetylene afforded tetrachlorocyclopropene and 1-iodo-3,3,3-trichloropropyne, both in 13% yield (31).



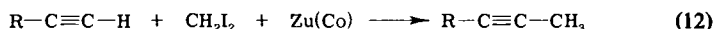
The unstable acetylene adducts of dichlorocarbene and dibromocarbene were hydrolyzed to give cyclopropenones [10] the isolation of which is facilitated by their solubility in aqueous acids (owing to the formation of cyclopropenium ions). Haloform and potassium *t*-butoxide (32, 33), lithium trichloromethide at -95° (34), and phenyl(bromodichloromethyl)mercury (35) have been used as the carbene precursors. The organomercury reagent appears to give the best yields of diarylcyclopropenones (63–79%). An excess of dihalocarbene (precursor) does not improve the yields of cyclopropenones but leads to dihalocyclobutenones [11] which probably arise by reaction of the dihalocyclopropene intermediates with dichlorocarbene or trichloromethide (36).

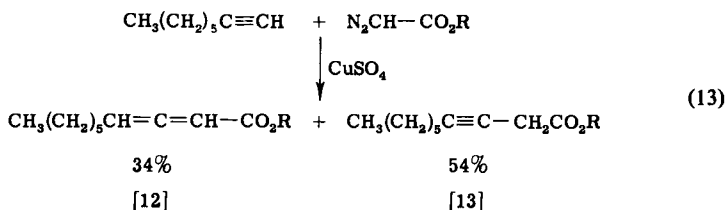


The addition of arylchlorocarbenes to arylacetylenes afforded cyclopropenium salts. When benzal chloride and potassium *t*-butoxide were employed as the carbene precursor, the initial products were cyclopropenyl ethers which are readily converted into cyclopropenium salts by treatment with strong acids, Eq. (10) (37, 38). Thermolysis of phenylchlorodiazirine in the presence of arylacetylenes gave cyclopropenium chlorides directly, and in high yields (39).



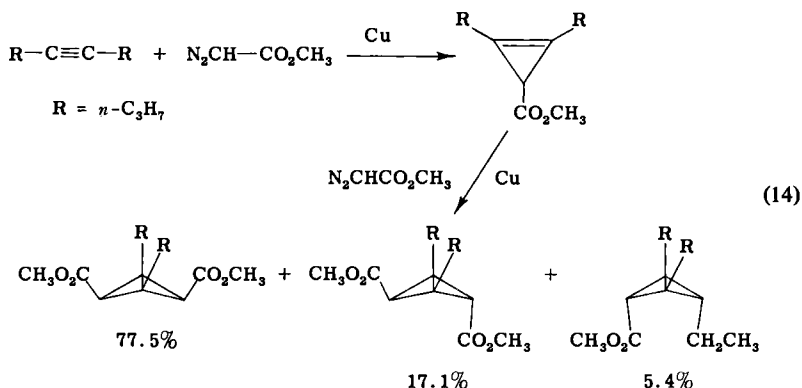
There is good reason why disubstituted acetylenes have been used in most of the cyclopropene syntheses recorded above. Alkynes with terminal triple bonds may be diverted to undesired products by reactions of the acetylenic hydrogen. Thus 1-alkynes and 1,3-diynes were converted into the corresponding methylacetylenes by treatment with the Simmons-Smith reagent (40-42). Similarly, the copper sulfate-catalyzed decomposition of ethyl diazoacetate in the presence of 1-octyne resulted in the formation of ethyl deca-2,3-dienoate [12] and ethyl deca-3-ynoate [13] (43). The irradiation of mixtures of 1-alkynes and ethyl diazoacetate, however, was reported to produce cyclopropene-3-carboxylates (44), and acetylenic hydrogen did not interfere with some addition reactions of halocarbenes (27, 29, 34, 38, 39).



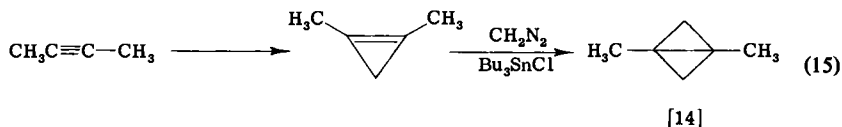


II. FORMATION OF BICYCLOBUTANES

The reactions of carbenes and carbenoids with alkynes may involve double addition, giving bicyclo[1.1.0]butanes. Several cases of bicyclobutane formation have been recorded for the copper (sulfate)-catalyzed decomposition of ethyl diazoacetate in the presence of alkynes (45-47), whereas the palladium-catalyzed reaction did not proceed beyond the cyclopropene stage (17). Careful analysis of the product mixture revealed the presence of all possible stereoisomers, although in largely different proportions (47).

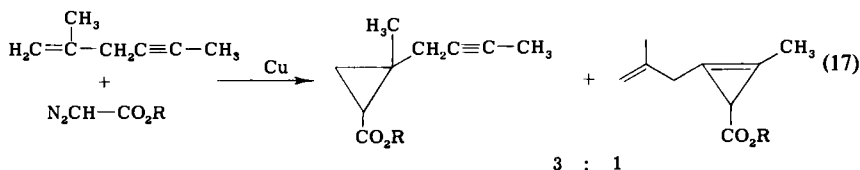
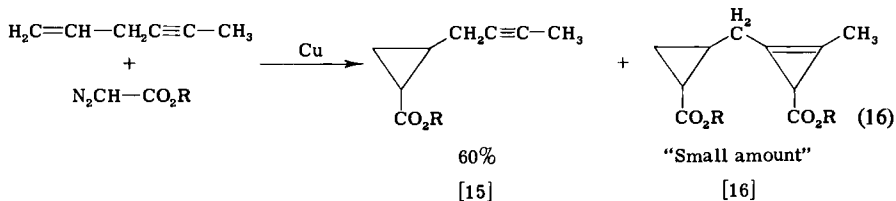


In contrast to the results obtained with alkyl diazoacetates, neither the photolytic nor the copper-catalyzed reaction of diazomethane with 1,2-dimethylcyclopropene led to any 1,3-dimethylbicyclobutane [14]. Modification of the catalytic reaction by the addition of tri-*n*-butyltin chloride allowed the generation of [14] in 13% yield (48). Successful double additions of difluorocarbene have also been reported (27, 29).

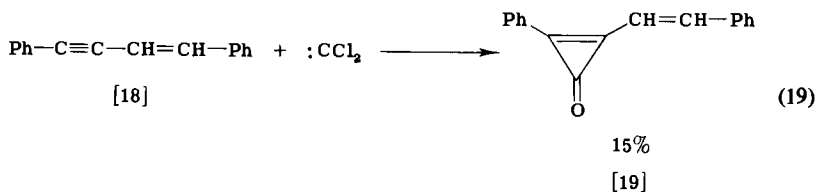
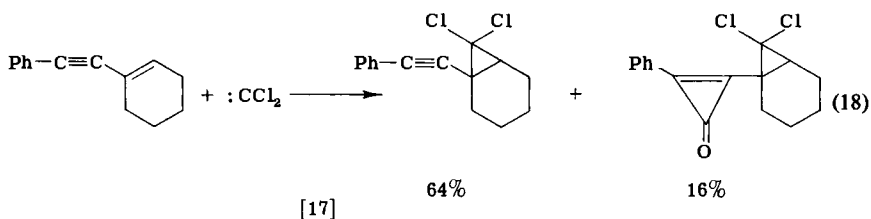


III. REACTIONS WITH ENYNES

The double bond of an enyne would be expected to be the preferred site of reaction with carbenes and carbenoids. In fact, 1-hexen-4-yne afforded a mono adduct of cyclopropane structure [15] and a bis adduct [16] when treated with ethyl diazoacetate in the presence of copper catalyst (49). 2-Methyl-1-hexen-4-yne, however, produced two mono adducts, one of which contained the unreacted double bond, Eq. (17) (50).

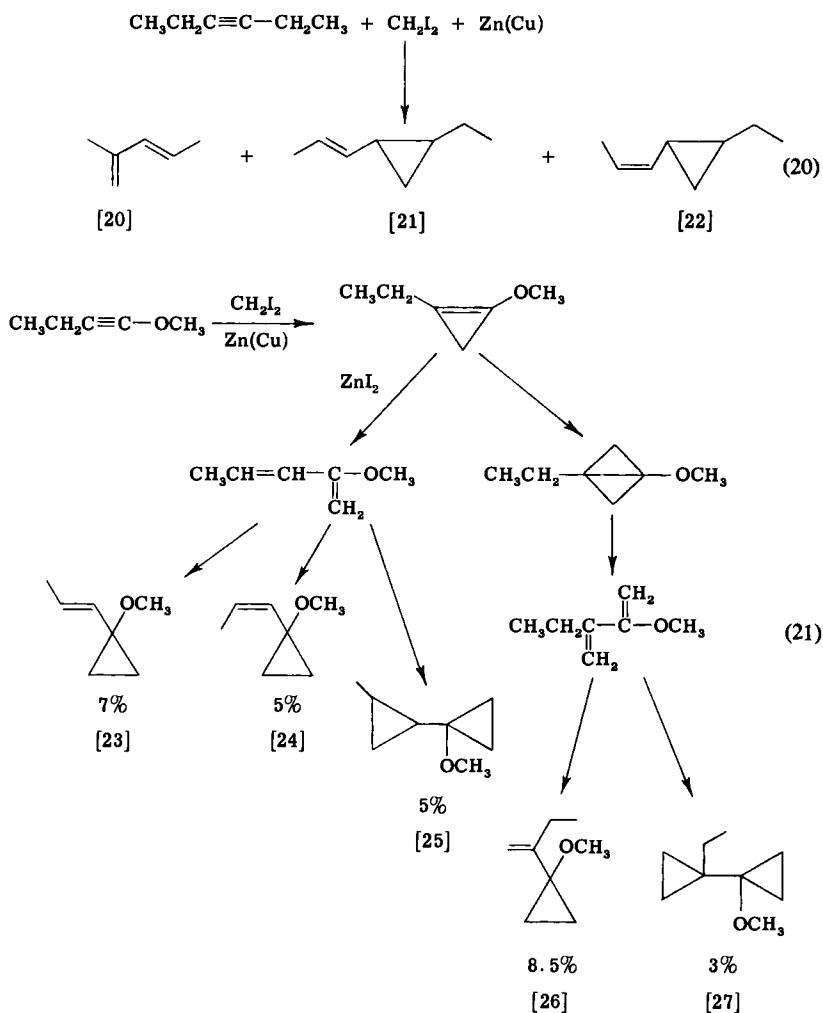


Dichlorocarbene was initially reported to react with enynes at the olefinic bond exclusively (51, 52). While this is true with 2-methyl-1-hexen-4-yne, straight-chain enynes were found to give 10–20% of cyclopropanones (53). Compound [17] is another example in which cyclopropane formation predominates, but *trans*-1,4-diphenylbutenyne [18] gave only the cyclopropene [19] (53).

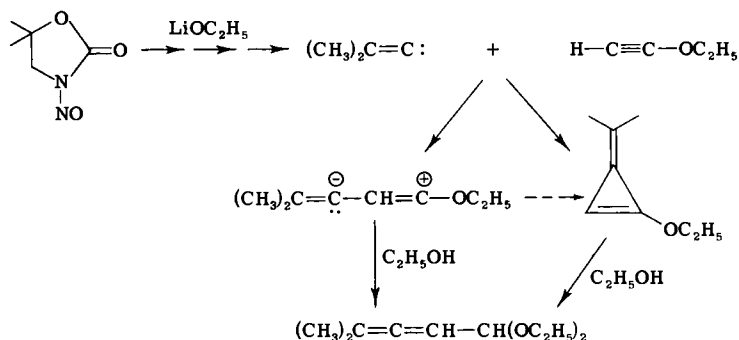


IV. ADDITION ACCOMPANIED BY REARRANGEMENT

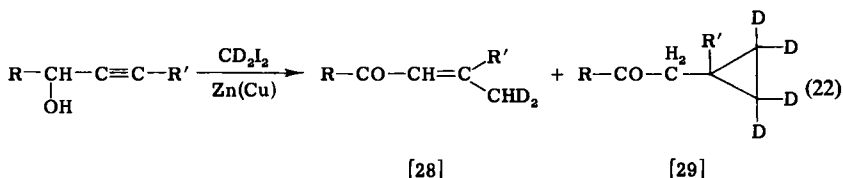
Three products, [20]–[22], were obtained from 3-hexyne, methylene iodide, and zinc–copper couple (8). The authors assume initial isomerization of the acetylene to the allene, but rearrangement of an initially produced cyclopropene, catalyzed by zinc iodide, is also a possible route. The latter mechanism, Eq. (21), has been suggested to explain the five products, [23]–[27], which were formed from 1-methoxy-1-butyne under Simmons-Smith conditions (54).



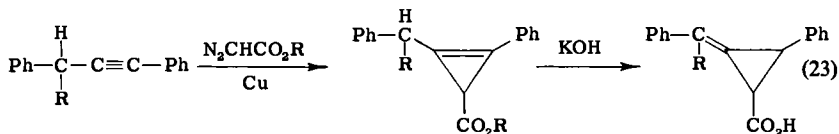
Treatment of a solution of ethoxyacetylene and 5,5-dimethyl-*N*-nitrosooxazolidone in dimethoxyethane with lithium ethoxide afforded 4-methyl-2,3-pentadienal diethylacetal [27a] in 35% yield (54a). The following mechanism has been proposed:



Secondary alkynols, when subjected to the Simmons-Smith reagent, afforded α,β -unsaturated ketones containing one additional carbon atom [28] and cyclopropylmethyl ketones containing two additional carbon atoms [29] (55). The use of CD_2I_2 led to deuterated products as shown in Eq. (22), but this result does not shed much light on the reaction mechanism.

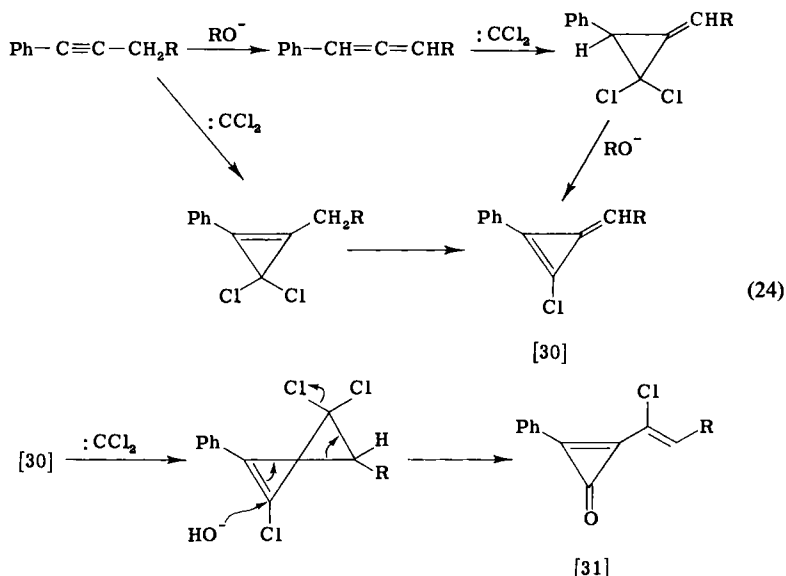


Rearrangement of cyclopropenes to methylenecyclopropanes was observed when the alkoxycarbonylcarbene adducts of 1,3-diphenylpropyne and 1,3,3-triphenylpropyne were treated with base during the workup procedure (14, 56).

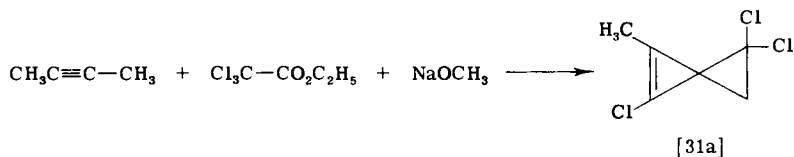


Treatment of several alkynes with haloform and base afforded (1-chlorovinyl)cyclopropenones [31] in addition to cyclopropenones and cyclobutenones, Eq. (9). The incorporation of an additional carbon atom may be explained either by initial isomerization of the acetylene to an allene, or by rearrangement of an intermediate cyclopropene to the corresponding methylenecyclopropane (36, 53, 57). 1,3-Diphenylallene gave the

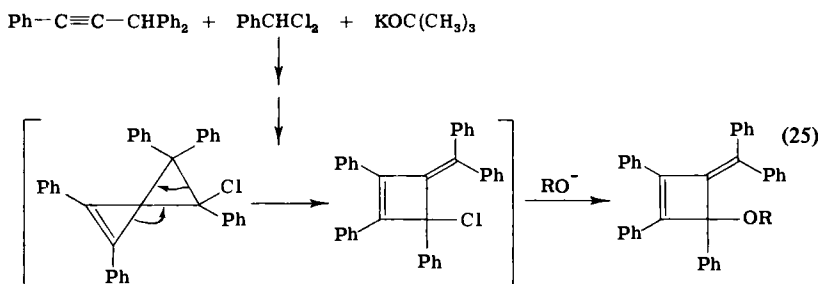
same results as did 1,3-diphenylpropyne. Compound [31] was not formed when dichlorocarbene was generated under neutral conditions by pyrolysis of sodium trichloroacetate.



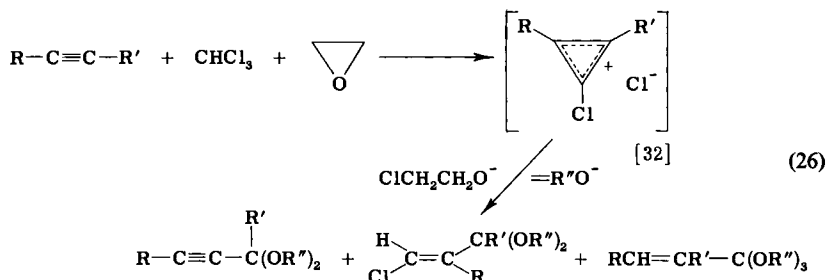
The spirocyclic compound [31a] has been isolated in 16% yield from the reaction of 2-butyne with ethyl trichloroacetate and sodium methoxide (57a). The mechanism of formation is analogous to Eq. (24).



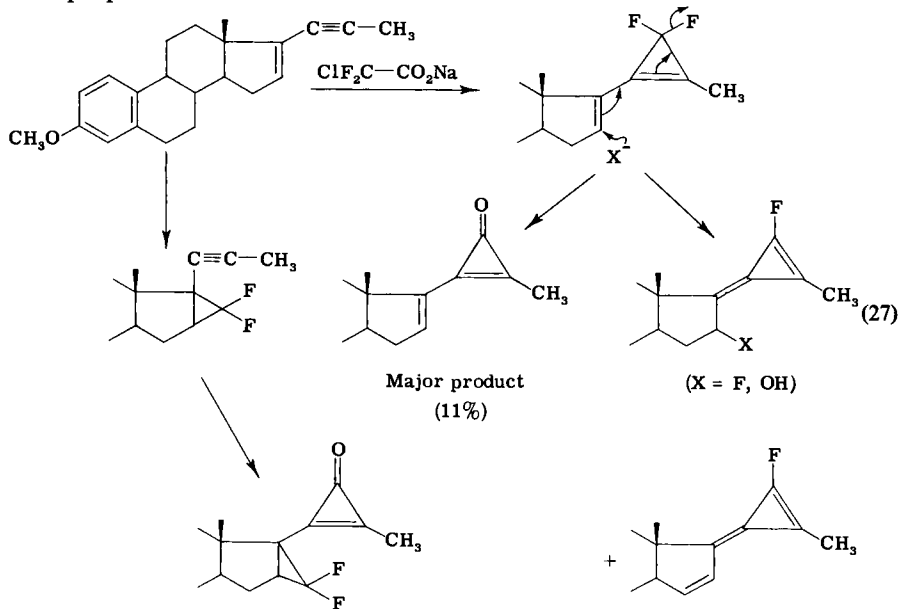
The reaction took a slightly different course in the last step when phenylchlorocarbene, generated from benzal chloride and potassium *t*-butoxide, was the attacking species (58).



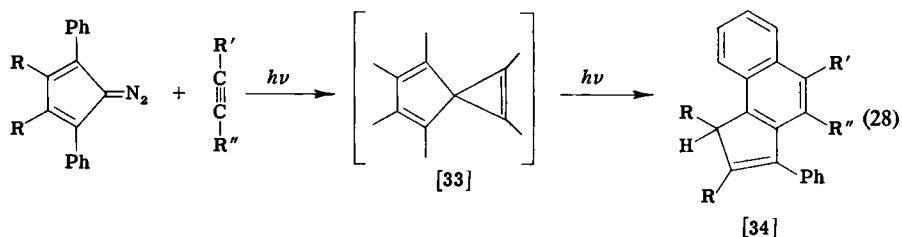
Acetals and ortho esters were obtained when alkynes reacted with dichlorocarbene generated from chloroform and ethylene oxide according to Nerdel's procedure (59). The chlorocyclopropenium chloride [32] has been assumed as an intermediate which is subject to nucleophilic attack by β -chloroethoxide.



The addition of difluorocarbene to a steroidal enyne proceeded in part with elimination of F^- from the CF_2 group to give a methylenecyclopropene structure (60). The major product, however, was the expected cyclopropenone.

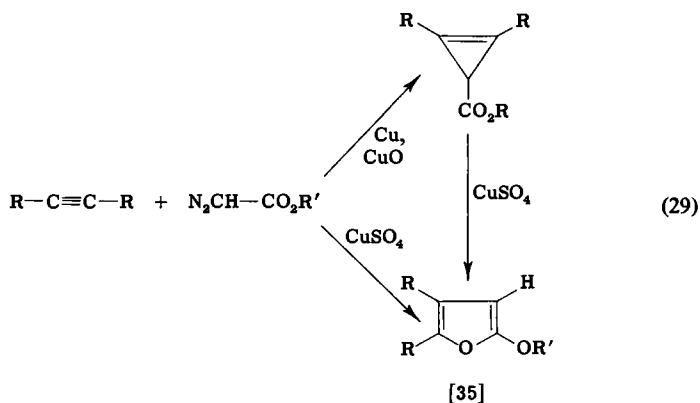


Photolysis of diazocyclopentadienes in the presence of alkynes afforded benzindenes [34] which are thought to arise by photorearrangement of the initial spiro compounds [33] (61).

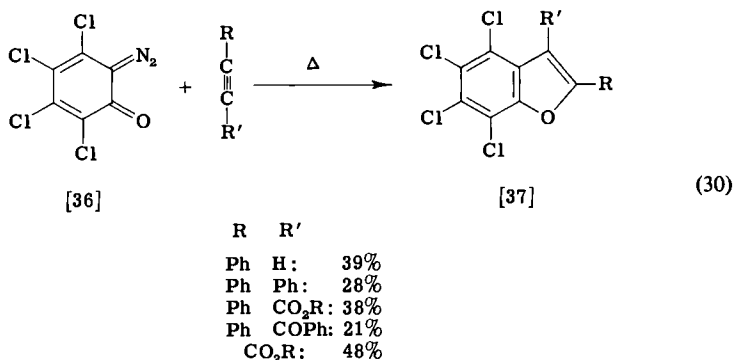


V. "1,3-DIPOLAR ADDITIONS" OF CARBONYLCARBENES

Dyakonov and his co-workers found that the reaction of ethyl diazoacetate with alkynes, when catalyzed by CuSO₄, produced isomers of the expected 1,2-diaryl(alkyl)cyclopropene-3-carboxylates which they initially considered to be 2,3-diaryl(alkyl)cyclopropene-1-carboxylates (62, 63). The correct furan structure [35] was elucidated by Breslow (64). This assignment was confirmed by Dyakonov (11, 65), who also showed that the amount of catalyst determined the course of the reaction. With CuSO₄ in amounts exceeding 0.005 mole per mole of alkyne, and with freshly prepared colloidal copper (66), furans were obtained, whereas copper powder, cupric oxide, and copper salts at concentrations of less than 0.001 mole per mole of alkyne induced the formation of cyclopropenes. These somewhat puzzling observations were recently unraveled by the Russian workers when they found that product mixtures initially rich in cyclopropene carboxylate were converted into pure furan by heating them in the presence of cupric sulfate or stearate (67). The previous results were apparently due to incomplete precipitation of the catalyst prior to distillation, and the alleged 1,3-dipolar addition of the carbene evidently does not take place at all.

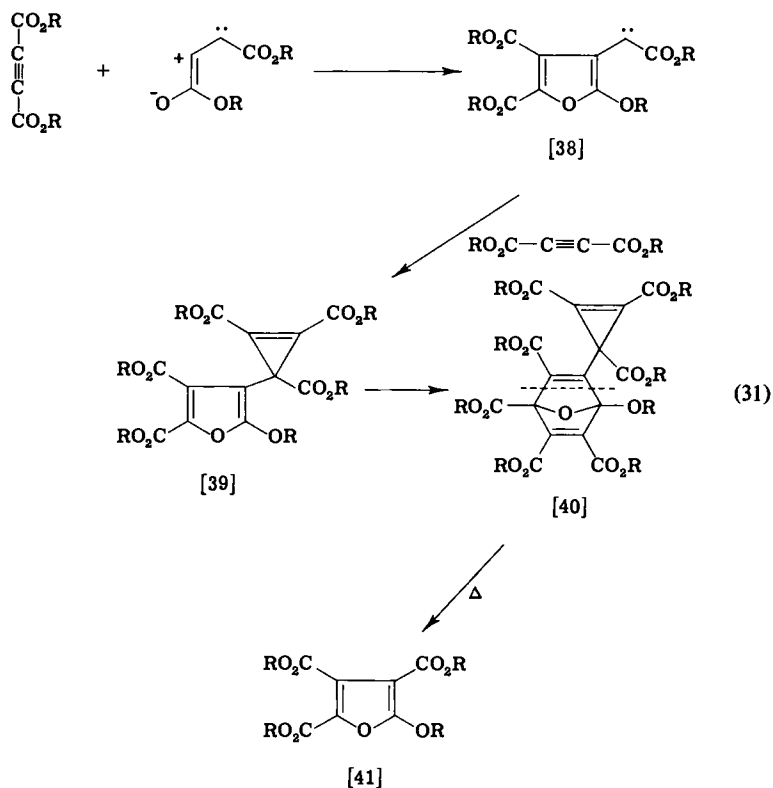


The reactions of diazoacetone (67) and of diazoacetophenone (68) with alkynes most probably proceed in an analogous manner, yielding 1,2,5-triaryl(alkyl)furans. The intermediacy of acyclopropenes appears less likely in the thermal, uncatalyzed reactions of tetrachlorobenzene-1,2-diazooxide [36] with alkynes which afforded fair yields of benzofurans [37] (69).



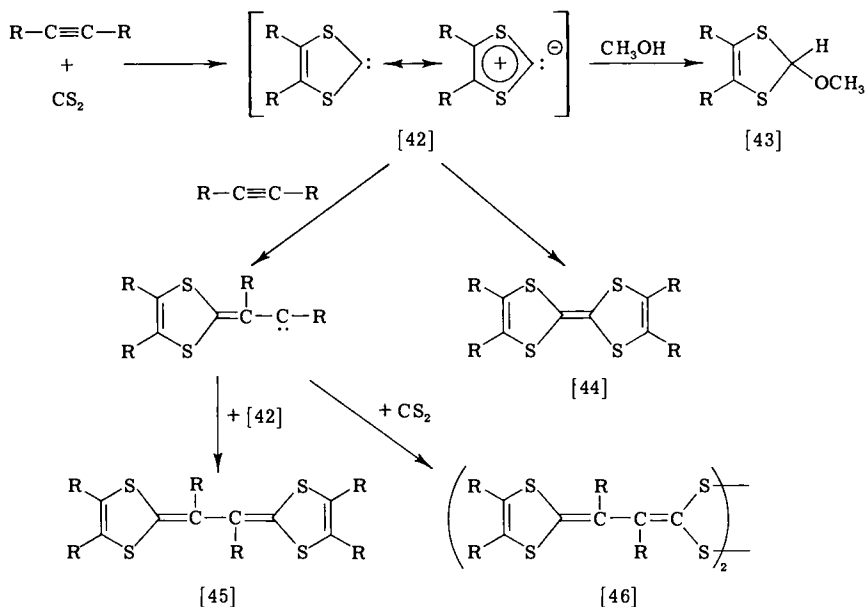
VI. THERMAL REACTIONS OF DIALKYL ACETYLENE-DICARBOXYLATES

Dimethyl and diethyl acetylenedicarboxylate spontaneously react to form tetramers which have been characterized as cyclopropenyl derivatives of 7-oxanorbornadiene [40] (70, 71). The mechanism suggested for the formation of [40] involves initial 1,3-dipolar addition of dimethyl acetylene dicarboxylate to itself to produce a carbenoid intermediate [38] which in turn reacts with a third mole of acetylenedicarboxylic ester to give the cyclopropenylfuran [39]. The latter undergoes a conventional Diels-Alder reaction to give [40]. Under more vigorous conditions the thermal reaction

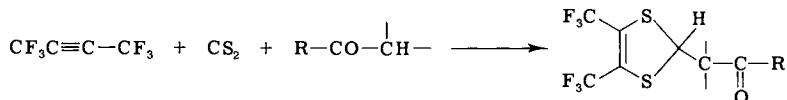


of dimethyl acetylenedicarboxylate afforded **[41]**, formally a dimer with loss of one carbon atom (72). Compound **[41]** most probably arises by a retro Diels-Alder reaction of **[40]**. Oligomerization of dimethyl acetylene dicarboxylate in the presence of diphenylacetylene led to incorporation of the alkyne (72).

Heating of dimethyl acetylenedicarboxylate or hexafluoro-2-butyne with carbon disulfide gave products **[44]**, **[45]**, and **[46]**, any of which could be made the predominant product by variation of the reaction conditions (73, 74). In the presence of methanol, the intermediate dithioliumcarbene **[42]** was diverted to produce predominantly **[43]**. Another general reaction



of 1,3-dithiolium carbenes has been found in the α -alkylation of aldehydes and ketones (75).



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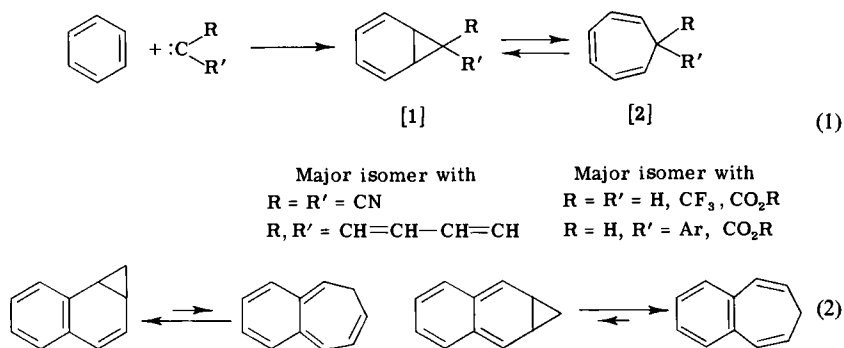
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Addition to Arenes

I. AROMATIC CARBOCYCLIC COMPOUNDS

THE ADDITION OF CARBENES to benzene affords bicyclo[4.1.0]heptadienes (norcaradienes) [1] or cycloheptatrienes [2] or both; they are "valence isomers" which rapidly equilibrate even at low temperatures. The position of the equilibrium is strongly affected by the substituents on carbon atom 7 (originally the carbene carbon) but also by incorporation of part of the triene system into additional benzene rings. The effect of substituents on carbon atom 7 has been attributed to deformation of the valence angle, whereas the effect of annelation is due to differences in the resonance energy of the valence isomers.



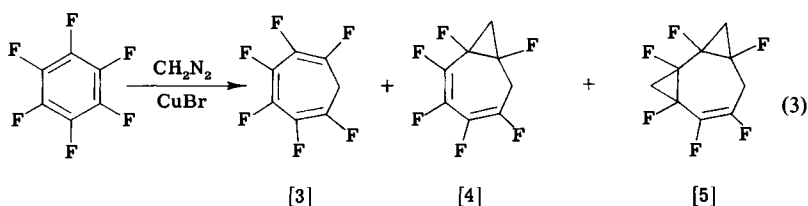
A. Methylene

The photolysis of diazomethane in benzene solution yielded cycloheptatriene (product of arene addition) and toluene (product of C—H insertion) in the ratio 4.8 : 1 (1-4). In the vapor phase the ratio was 3.3, and the highest value, 7.0, was observed with a 2 M solution of benzene in

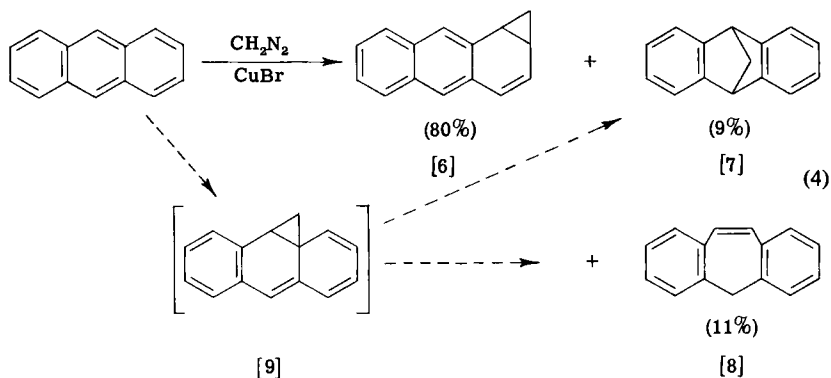
t-butylnaphthalene. The solvent effect has been discussed in terms of π -complexes of methylene (4).

7,7-Dideuterocycloheptatriene cannot be obtained in structurally homogeneous form from the photolytic reaction of benzene and CD_2N_2 , the product having significant but variable amounts of deuterium in the vinyl positions (5). The scrambling of the deuterium label was shown to be due to the photorearrangement of 7,7-dideuterocycloheptatriene. Structurally homogeneous 7,7-dideuterocycloheptatriene was prepared by the decomposition of CD_2N_2 in benzene catalyzed by copper sulfate (5).

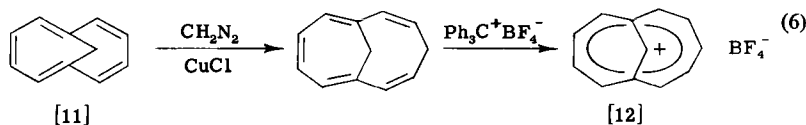
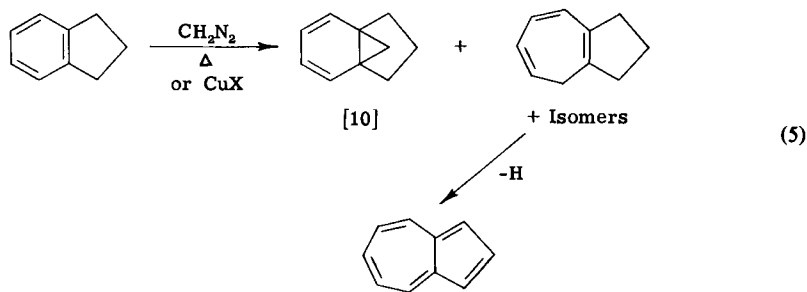
The catalyzed reaction of diazomethane with benzene afforded cycloheptatriene uncontaminated with toluene (6). Consequently, it became the method of choice for the ring expansion of substituted and annelated benzenes. The relative yields of cycloheptatriene isomers obtained from a series of alkyl-, halo-, and alkoxybenzenes were governed by steric and electronic effects, in agreement with the concept of electrophilic attack on the benzene nucleus (7, 8). In most of these reactions a large excess of the arene was employed. For the preparation of perdeuterocycloheptatriene from hexadeuterobenzene and CD_2N_2 , a procedure was developed which maintained a high benzene/cycloheptatriene ratio at the time of the reaction and yet achieved satisfactory overall conversion by the use of a distillation column packed with the supported cuprous chloride catalyst (9). Passing diazomethane into a refluxing mixture of hexafluorobenzene and cuprous bromide gave compounds [3]–[5] and three unidentified products (10).



Naphthalene accepts the diazomethane–CuBr reagent exclusively at the 1,2 bond (11); phenanthrene and pyrene (12, 13) react predominantly at their “olefinic” sites to give products of norcaradiene structure. Two interesting minor products, [7] and [8], were obtained from anthracene in addition to an 80% yield of the 1,2 adduct [6]. Both [7] and [8] may arise by isomerization of an unstable adduct to the 9,9a bond [9] (14).

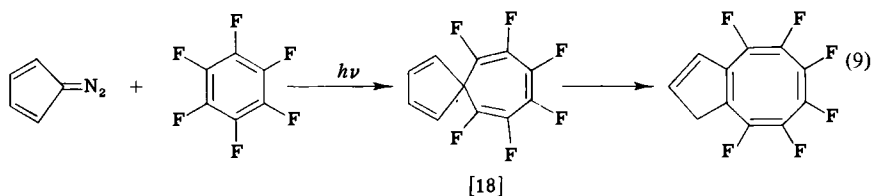
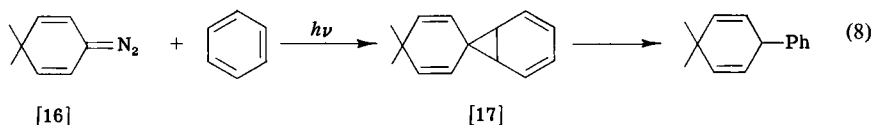
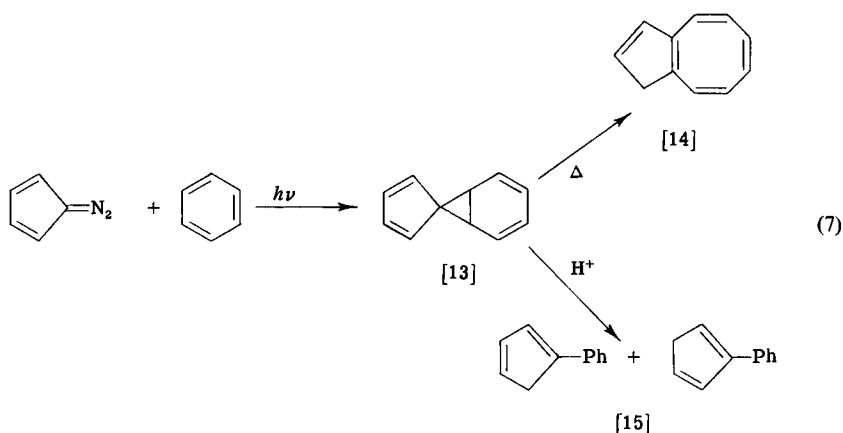


The crude product mixtures obtained from diazomethane and various indanes have been dehydrogenated to give azulenes without previous separation of the methylene adducts (15). Only 0.5–1% of the tricyclic hydrocarbon **[10]** (remarkable for its norcaradiene structure) was detected among the products of the indane–diazomethane–cuprous chloride reaction (16). Ring expansion with formation of an *A*-homosteroid has been achieved by treatment of β -estradiol dimethyl ether with diazomethane and cuprous chloride (17). Similarly, the ten π -electron system, 1,6-methanocyclodecapentaene **[11]**, was expanded to its cationic $n + 1$ analog **[12]** (18, 18a).



B. Vinylcarbenes

Photolysis of diazocyclopentadiene in benzene solution afforded a crystalline but rather sensitive adduct to which the spironorcaradiene structure [13] was assigned on the basis of NMR spectra (19). Thermal isomerization of [13] led to [14], whereas a mixture of phenylcyclopentadienes [15] resulted from acid-catalyzed rearrangement (19). Similarly, a norcaradiene-type adduct [17] was isolated from the photolysis of 1-diazo-4,4-dimethylcyclohexa-2,5-diene [16] and benzene (20, 20a). On the other hand, a cycloheptatriene structure was suggested by H and ^{19}F NMR evidence for the adduct of cyclopentadienylidene to hexafluorobenzene [18] (21).

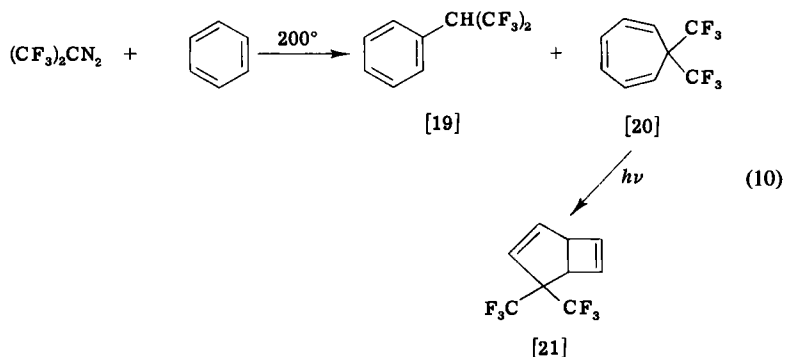


Only rearranged products corresponding in structure to either [14] or [15] were obtained from the photolytic reaction of substituted diazocyclo-

pentadienes (tetraphenyl-, tetrachloro-, 1,2,3-triphenyl-, and 1,4-diphenyl-) with benzene derivatives (22).

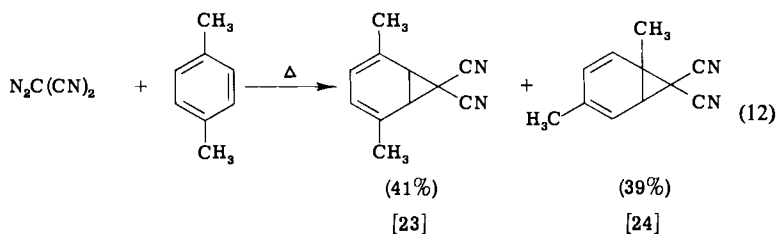
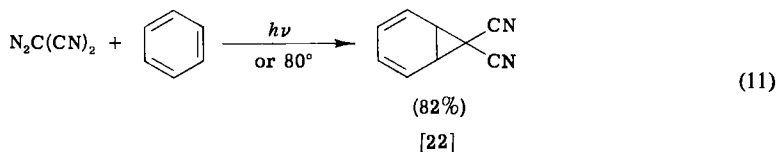
C. Trifluoromethylcarbenes and Cyanocarbenes

Thermolysis of bis(trifluoromethyl)diazomethane in benzene solution at 200° (autoclave) afforded 7,7-bis(trifluoromethyl)cycloheptatriene [20] (62%) and the product of C—H insertion, [19] (8%) (23). On photolysis, [20] was converted into its valence isomer [21]. Not surprisingly, [21] was a major product of the photolysis of bis(trifluoromethyl)diazomethane and benzene (23). Bis(trifluoromethyl)carbene was also added to hexafluorobenzene to give a 20% yield of perfluoro-7,7-dimethyl-1,3,5-cycloheptatriene (24). Similar yields of the corresponding cycloheptatriene were obtained from the thermal reaction of bis(pentafluoroethyl)diazomethane with benzene (23). It is noteworthy that the perfluoroalkylcarbenes add to benzene before they rearrange to perfluoroalkenes.

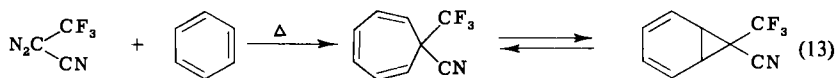


Thermolysis or photolysis of dicyanodiazomethane in benzene gave, as the sole product, in 82% yield, 7,7-dicyanonorcaradiene [22] (25). The norcaradiene structure was confirmed by a complete analysis of the NMR spectrum (26). *p*-Xylene, with the same reagent, afforded two isomeric adducts, [23] and [24]. The complete X-ray structure determination of [23] has been published (27). Thus the norcaradiene structure of the dicyanocarbene adducts is well established. There is less conclusive evidence with regard to the insertion of dicyanocarbene into aromatic C—H bonds. Whereas Ciganek (25) reported addition only, Berson and his co-workers (28) obtained the three isomeric tolylmalonitriles in addition to the three methyl-7,7-dicyanonorcaradienes when they thermolyzed a solution

of dicyanodiazomethane in toluene. They noted, however, that aromatization of the norcaradienes occurred on prolonged heating and on exposure to chromatographic adsorption materials.

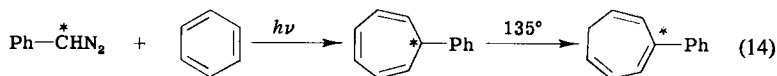


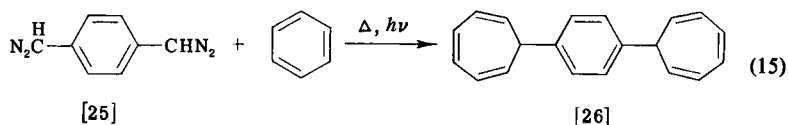
Trifluoromethyl groups on the carbon 7 atom favoring the cycloheptatriene structure, and cyano groups in the same position favoring the norcaradiene structure, one might expect properties "in between" of the cyanotrifluoromethylcarbene adduct. In fact, thermolysis of cyanotrifluoromethyldiazomethane in benzene gave 77% of a compound whose ^{19}F and H NMR spectra show two species which are in rapid equilibrium at room temperature (29).



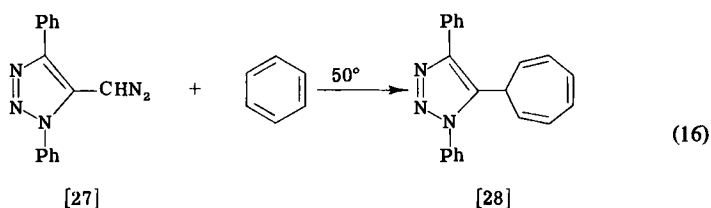
D. Arylcarbenes

7-Phenylcycloheptatriene was obtained by photolysis of phenyldiazomethane in benzene solution (30). This reaction has recently been used to prepare 7-phenylcycloheptatriene-7- ^{14}C (which on heating to 135° yielded 3-phenylcycloheptatriene as the major product) (31). Similarly, 1,4-bis(diazomethyl)benzene [25] was converted into 1,4-bis(cycloheptatrienyl)benzene [26], and to the bistropylium salt derived from [26] (32).





Decomposition of benzaldehyde tosylhydrazone in the presence of sodium methoxide in molten naphthalene at 140° gave an adduct of phenylcarbene to the 1,2 bond of naphthalene in 9% yield (33). Anthracene also afforded a 1,2 adduct together with small amounts of a 9,10 adduct [cf. Eq. (4)], whereas phenanthrene produced 9-benzylphenanthrene as the major product (33). One of the few hetero analogs of phenyldiazomethane studied, 5-diazomethyl-1,4-diphenyltriazole [27], reacted smoothly with benzene to give the cycloheptatriene derivative [28] in 66% yield (34). The carbene derived from [27] attacked cyclohexene ~10 times faster than benzene.

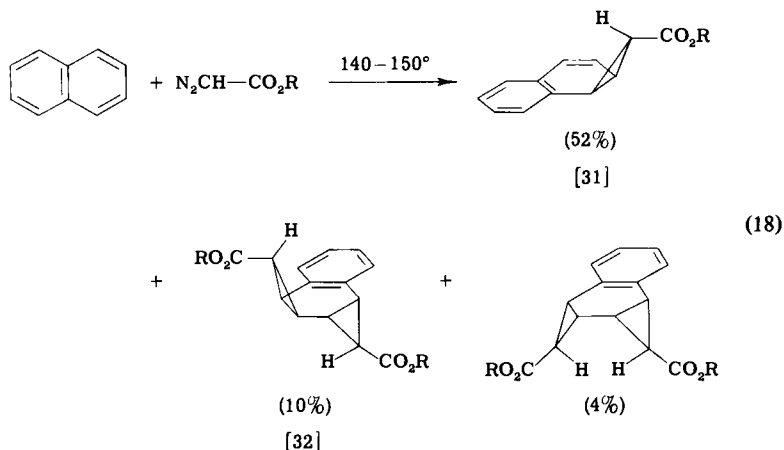


E. Carbonylcarbenes

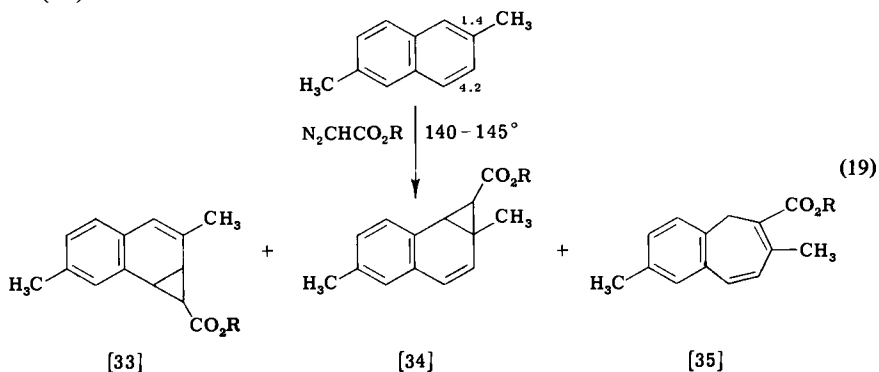
The thermolysis of ethyl diazoacetate in the presence of benzene is one of the oldest carbene reactions known. After a first report by Buchner and Curtius in 1885 (35), the norcaradiene structure was assigned to the product in 1896 (36). Investigation of this compound was impeded by its facile isomerization (under the conditions of formation and hydrolysis) to various cycloheptatrienecarboxylic acids ("Buchner acids"). After a long search, correct structures were finally assigned by Doering and his co-workers in 1956 (37). The NMR data definitely excluded the norcaradiene structure for any of the Buchner acids. The primary product undoubtedly is ethyl cycloheptatriene-7-carboxylate [29]. However, [29] cannot be isolated in a pure state from the thermal reaction. It appears that, on prolonged heating, rather uniform preparations of cycloheptatriene-3-carboxylic acids [30] may be obtained (38).

ethyl 1,2,3,4,5,6-hexafluorocycloheptatriene-7-carboxylate in fair yield (24).

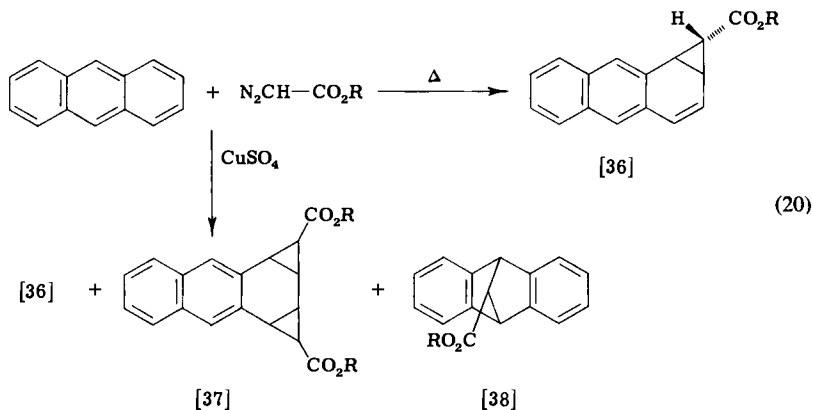
In contrast to the results obtained in the benzene series, the adduct of ethoxycarbonylcarbene to naphthalene (54) has been shown to contain a cyclopropane ring (55). NMR and degradative evidence support the exo configuration [31]. In addition to [31], two isomeric bis adducts were formed, as would be expected if exo addition applies also to the second step of the reaction. The major isomer has been assigned the trans structure [32] on the basis of its resolution into enantiomers (55).



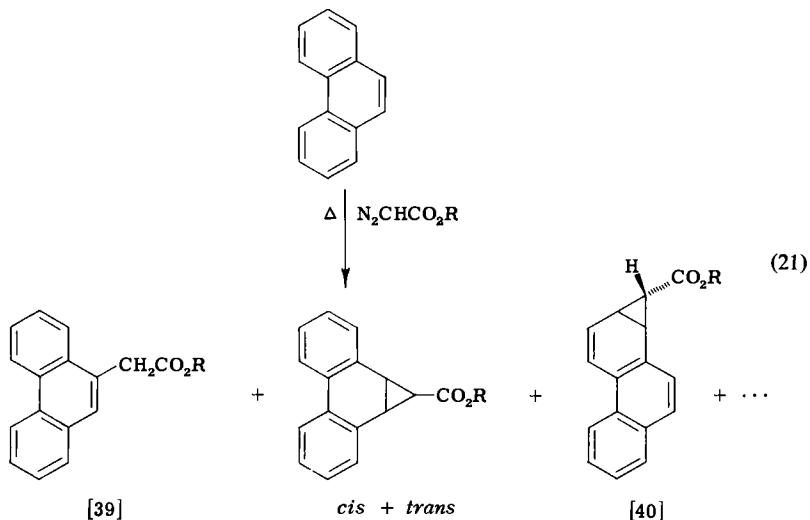
Ethoxycarbonylcarbene was found to attack 2,3-dimethylnaphthalene preferentially in the unsubstituted ring (58% versus 37%) (56). The results obtained with 2,6-dimethylnaphthalene, including partial rate factors referring to naphthalene = 1.00, are given in Eq. (19). The benzocycloheptatriene [35] is probably an artifact arising from [34], not from [33] (57).



Only one product was obtained from the thermal reaction of ethyl diazoacetate with anthracene (58) which was identified as the *exo*-1,2 adduct [36] (59). The CuSO_4 -catalyzed reaction, however, was reported to produce the 9,10 adduct [38] and the bis adduct [37] in addition to [36] (60) [cf. Eq. (4) for a possible route to 9,10 adducts of anthracene].

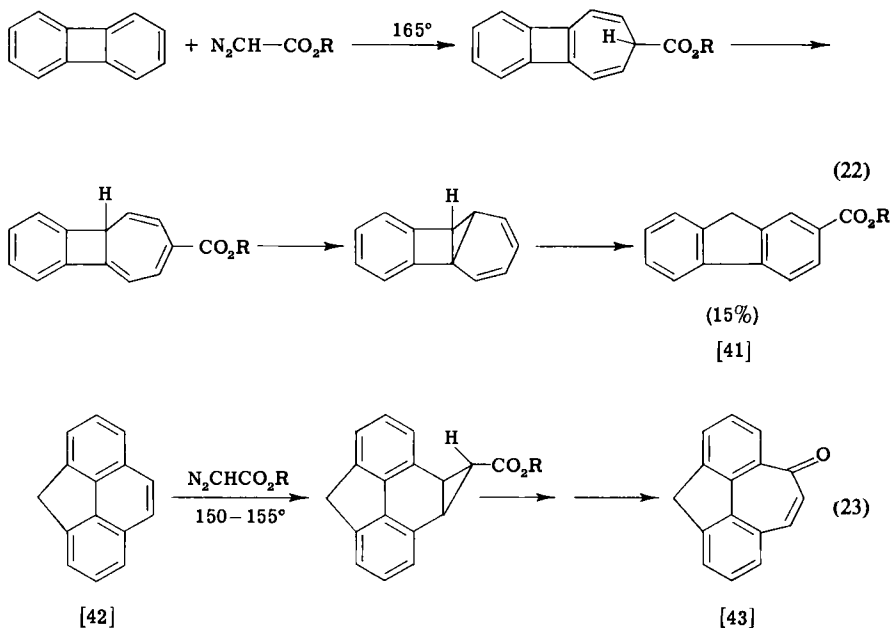


The reaction of ethyl diazoacetate with phenanthrene (61–64) appears to be more complex; five monocarboxylic acids have been isolated after hydrolysis of the product mixture (59). Phenanthrene-9-acetic acid [39] and [40] were the most abundant isomers.

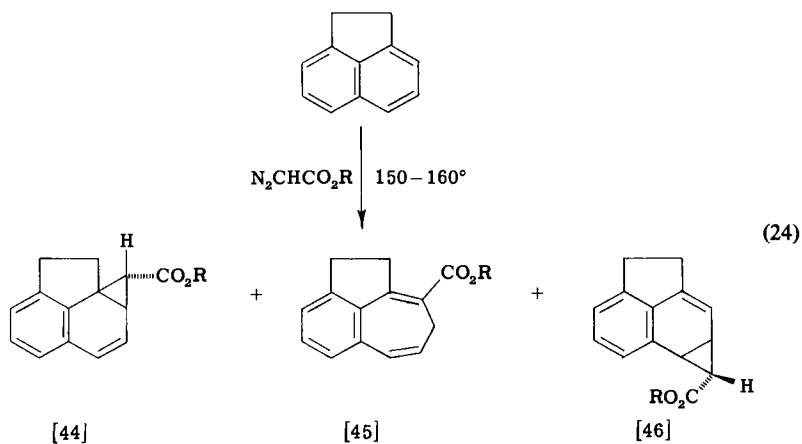


Thermolysis of ethyl diazoacetate in the presence of biphenylene led to ethyl fluorene-2-carboxylate [41]. Equation (22) rationalizes the formation

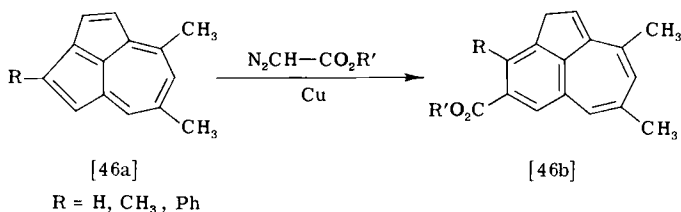
of [41] (65). A synthesis of cyclohepta[*def*]fluoren-8(4*H*)one [43] involves ring expansion of 4*H*-cyclopenta[*def*]phenanthrene [42] by means of ethyl diazoacetate (66).



When molten acenaphthylene was treated with ethyl diazoacetate at $150\text{--}160^\circ$, there formed in good yield the three mono adducts [44]–[46], plus some of a bis adduct (67). Adduct [45] is probably an artifact arising from the thermal rearrangement of [44] during distillation.

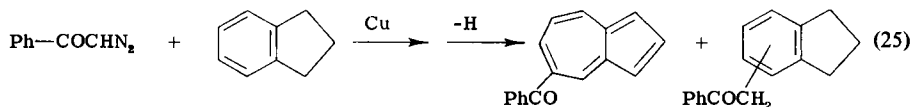


The 2*H*-benz[*c,d*]azulene system [46b] has been obtained from the copper-catalyzed reaction of cyclopent[*c,d*]azulenes [46a] with ethyl diazoacetate (67*a*).



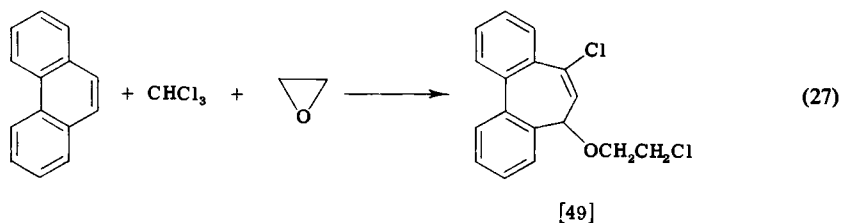
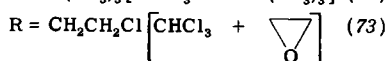
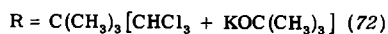
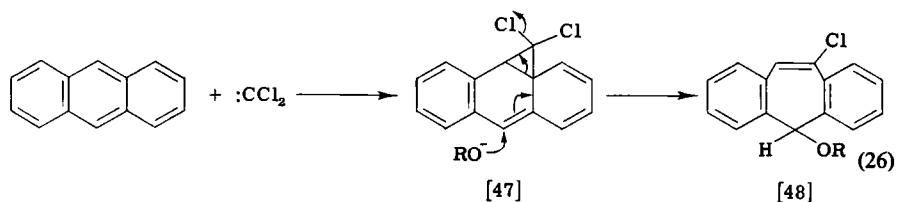
Ring expansion of the benzene nucleus of indans by alkoxy-carbonyl-carbenes has frequently been applied in the synthesis of azulenes (15). In most cases, crude product mixtures have been hydrolyzed, decarboxylated, and dehydrogenated. Although more efficient routes to azulenes are now available, some syntheses of substituted azulenes by the carbene procedure have been published recently (68, 68*a*).

Acetylcarbenoid from the copper-catalyzed decomposition of diazoacetone attacks anisole in low yield, but does not react with benzene (69). On the other hand, ring expansion as well as substitution by benzoyl-carbene and acetylcarbene has been observed in the indan series, Eq. (25) (70). Trifluoroacetyloxy-carbonylcarbene, CF₃CO-C(=O)-C(=O)-CO₂C₂H₅, is unique in its reactions with arenes: C-H insertion was found to take place without any competing addition (71).

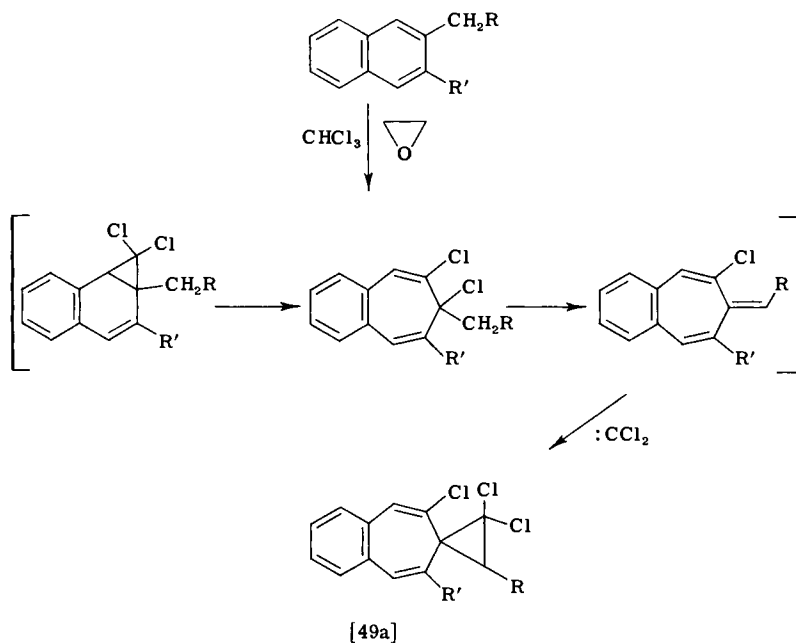


F. Halocarbenes

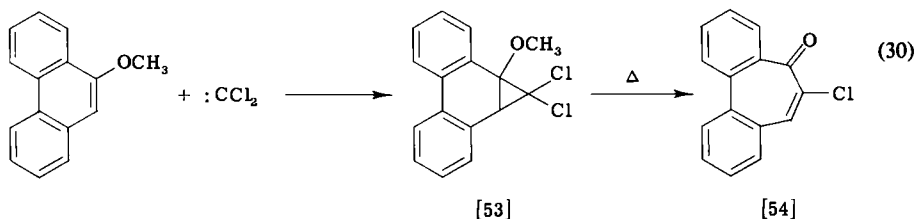
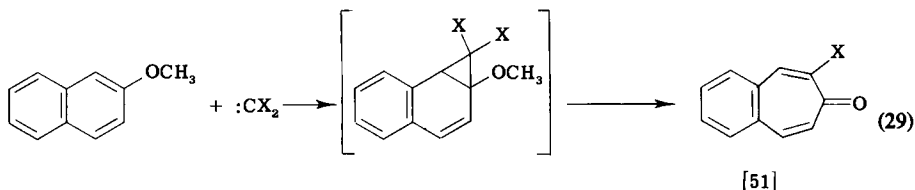
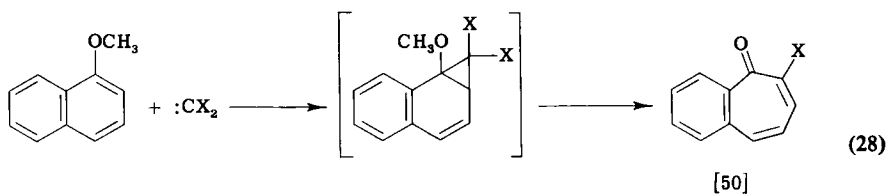
Most benzene derivatives are inert toward dihalocarbenes; only those most susceptible to electrophilic attack were found to react. Anthracene, when treated with chloroform and alkoxides, afforded products [48] which are derived from the hypothetical adduct [47] by nucleophilic displacement (72, 74). Similarly, phenanthrene produced [49] via cyclopropyl-allyl rearrangement (73).



Low yields of spirononatrienes [49a] were isolated from the reaction of alkylnaphthalenes with chloroform, ethylene oxide, and catalyst at $150\text{--}175^\circ$ (73a). They arise from the initial adducts by rearrangement, elimination of hydrogen chloride, and a second addition of CCl_2 .

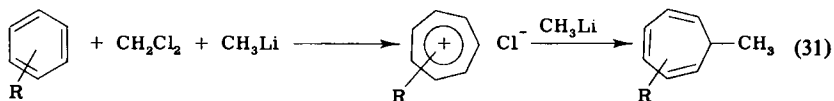


1- and 2-Methoxynaphthalene were converted into the halobenzo-tropones [50] and [51], respectively, by treatment with ethyl trichloroacetate and sodium methoxide (74) ($X = \text{Cl}$) or with phenyl(tribromomethyl)mercury (75, 75a) ($X = \text{Br}$). Reaction of anisole with bromoform and potassium *t*-butoxide gave 4-bromotropone in low yield, whereas phenyl(tribromomethyl)mercury gave *p*-anisic acid and 4,4'-dimethoxybenzophenone along with a host of other products (75). Halotropones were also obtained from 1,6-dimethoxynaphthalene and 6,12-diethoxychrysene (76). 9-Methoxyphenanthrene was the only compound of this series which afforded an adduct [52] of dichlorocyclopropane structure (74). Adduct [52] rearranged to the chlorodibenzotropone [53] on pyrolysis.

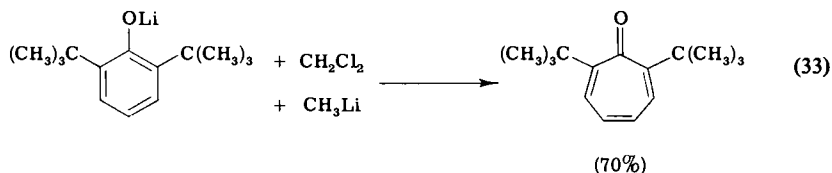
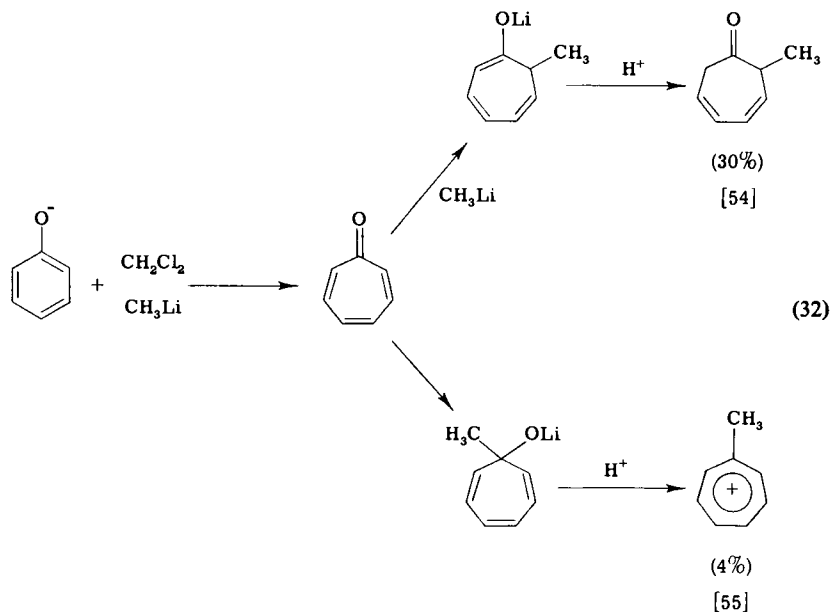


Chlorocarbene attacks arenes more readily. Tropylium halides were obtained in small yields by treatment of benzene with methylene halides and potassium *t*-butoxide, followed by acid extraction (77). If chlorocarbonoid was produced from methylene chloride and methyl lithium in the presence of benzene, 7-methylcycloheptatriene (20%) was the major product, probably formed via tropylium chloride which escaped the further

reaction with methyllithium only in trace quantities (<1%) (78). Application of the same procedure to alkylbenzenes afforded mixtures of 1,7-, 2,7-, and 3,7-dialkylcycloheptatrienes (20–40% yield) (79). Use of sodium *N,N*-bis(trimethylsilyl)amide as the base led to 7-*N,N*-bis(trimethylsilyl)-amino]cycloheptatrienes (80).

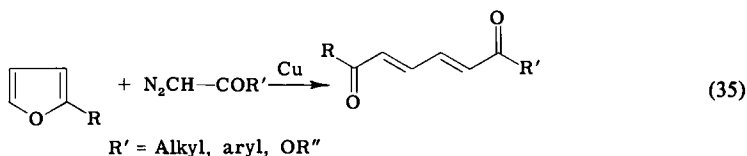
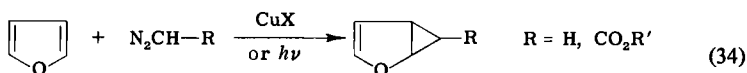


Reaction of lithium phenoxide with methylene chloride and methyllithium produced 2-methylcyclohepta-3,5-dien-1-one [54] and methyltropylium ion [55], both of which result from the intermediate tropone by further reaction with methyllithium (81). Initial formation of a tropone was clearly shown with 2,6-di-*t*-butylphenoxide where bulky ortho substituents prevent the addition of methyllithium, Eq. (33) (81).

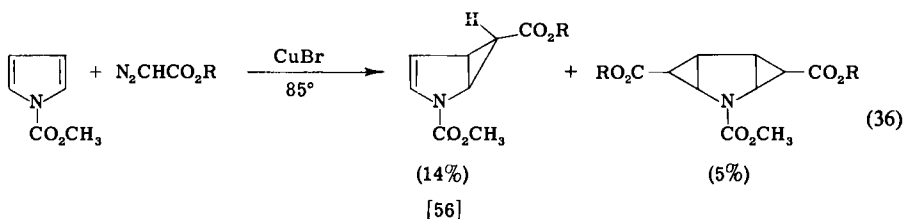


II. AROMATIC HETEROCYCLIC COMPOUNDS

With few exceptions, furans and thiophenes behave like dienes toward carbenes and carbenoids, giving bicyclic adducts. Thus methylene has been transferred to furan (82), 2-methylfuran (83), and thiophene (82) by means of diazomethane-cuprous halide. Ethoxycarbonylcarbene, generated by photolysis of ethyl diazoacetate, was added in an analogous way to furan (84), benzofuran (85), and thiophene (84, 86). Benzothiophene, however, accepted ethoxycarbonylcarbene at the benzene rather than the thiophene nucleus (87). 2-Alkylfurans afforded acyclic carbonyl compounds in their copper-catalyzed reactions with ethyl diazoacetate (83) and with diazo ketones (88). The furan adducts underwent the same type of rearrangement at 140–160° (84).

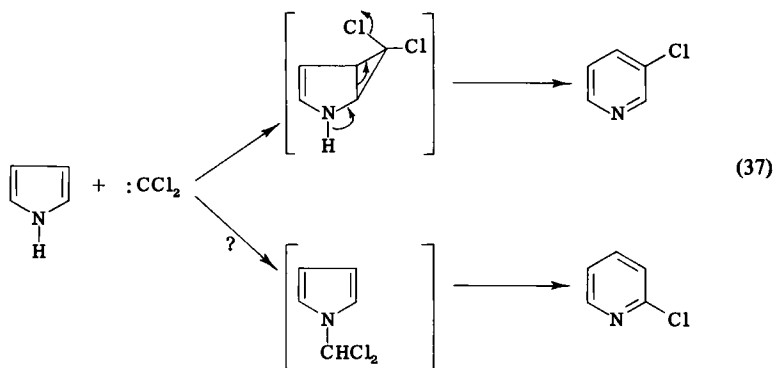


The decomposition of ethyl diazoacetate and of diazo ketones in the presence of pyrroles and indoles led to apparent C—H insertion. Pyrrole, *N*-methylpyrrole, and 2,4-dimethylpyrrole were attacked in the α (2 or 5) positions (89–91), whereas β -attack occurred with 2,3,5-trimethylpyrrole (89) and indole (69, 92). The 2,3-homopyrrole system [56] has recently been prepared by the CuBr-catalyzed decomposition of ethyl diazoacetate in the presence of *N*-methoxycarbonylpyrrole (93). Reaction of copper(II)-octaethylporphyrin with ethyl diazoacetate gave two isomeric chlorins



containing fused cyclopropane rings as well as *meso*-ethoxycarbonylmethyloctaethylporphyrin (94).

The interaction of pyrrole with haloform and base proceeds with ring expansion to give 3-halopyridines (10–12% yield) (95, 96). Better yields were obtained in the gas-phase reaction of pyrrole with dichlorocarbene generated by pyrolysis of chloroform at 550° (97). An improved procedure (98) afforded 58% of 3-chloropyridine and 28% of the 2-isomer. Addition of dichlorocarbene to the 2,3 bond of pyrrole followed by ring expansion accounts for the formation of 3-chloropyridine. The formation of 2-chloropyridine may result from attack at the pyrrole nitrogen or at the α -carbon atom.



2,5-Dimethyl-, 2,3,4,5-tetramethyl-, and 3,4-dimethyl-2,5-diphenyl-1*H*-pyrrole [57] reacted with dichlorocarbene in basic solution to give 2-dichloromethyl-2*H*-pyrroles [60] and 3-chloropyridines [58] in low yield, Eq. (38) (99, 100). However, in neutral aprotic solution, high yields of 3-chloropyridines were formed (100). The absence of 2*H*-pyrroles in the neutral reaction suggests that the pyridines [58] arise from initial cycloaddition of dichlorocarbene to neutral molecules, whereas the 2*H*-pyrroles [60] arise from electrophilic attack by dichlorocarbene on the ambident pyrrol anion. Although [60] has been converted into [58] in low yield by treatment with an excess of butyllithium (101), it does not appear very likely that this transformation occurs under neutral conditions, or that the anion [59] is an intermediate in the formation of both [58] and [60]. Table I lists the yields of [58] and [60] from Eq. (38).

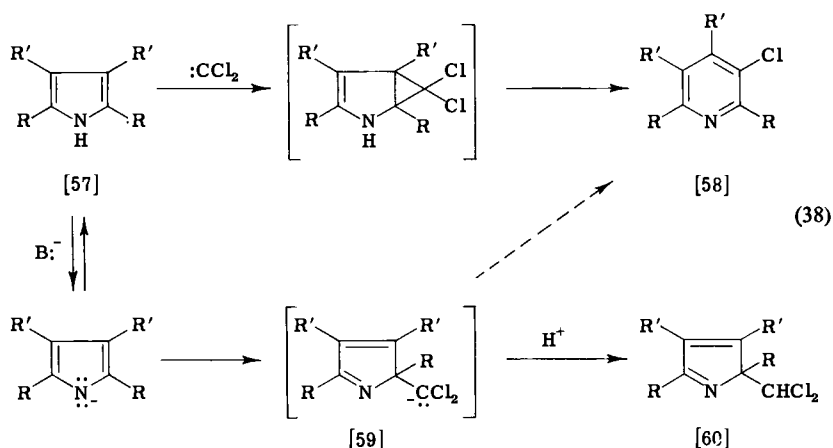


TABLE I
Yields of Products from Reaction (38)

R	R'	Carbene precursor	[58] (%)	[60] (%)
CH ₃	H	CHCl ₃ + C ₂ H ₅ ONa	9	6
	H	Cl ₃ C—CO ₂ Na	70	0
CH ₃	CH ₃	CHCl ₃ + C ₂ H ₅ ONa	5	12
	CH ₃	Cl ₃ C—CO ₂ Na	55	0
Ph	CH ₃	CHCl ₃ + C ₂ H ₅ ONa	1	8
	CH ₃	Cl ₃ C—CO ₂ Na	90	0

Observations related to those of the preceding paragraph were made more than 60 years ago in a study of 2,3-dimethylindole (102), and confirmed later by improved analytical (103, 104) and tracer techniques (105). Again the proportion of 3-haloquinolines [61] and 3-dihalomethylindolines [62] depended strongly on the reaction conditions and is not easily reconciled with a common intermediate (104). On the other hand, acetylation of the crude product mixture afforded a labile product which was shown to yield both [61] and [62] on alkaline hydrolysis (105). 1,2,3-Trimethylindole [63], lacking the N—H bond, loses a proton from the 2-CH₃ group to give products [64] and [65] which are otherwise analogous to [61] and [62] (104). Table II gives the product distribution from reaction (39).

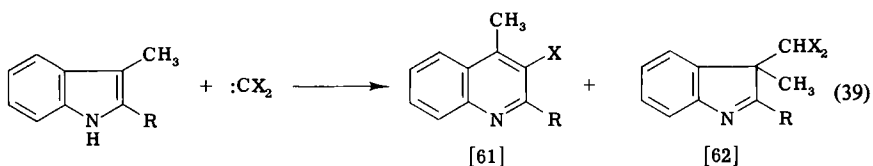
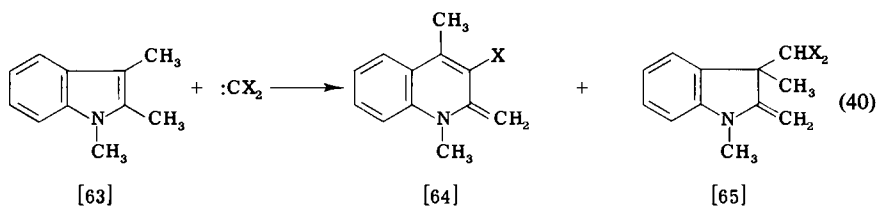
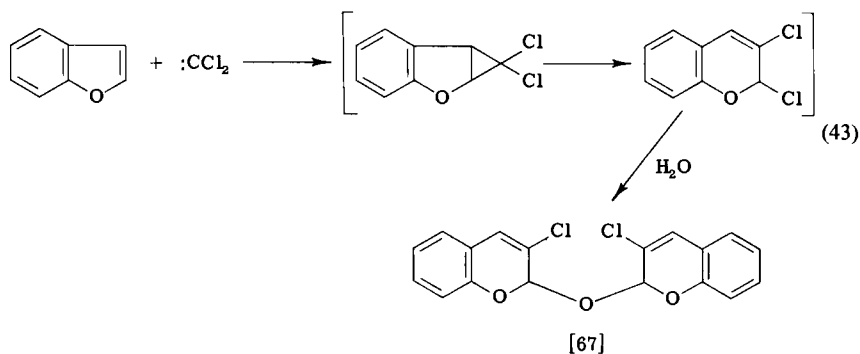
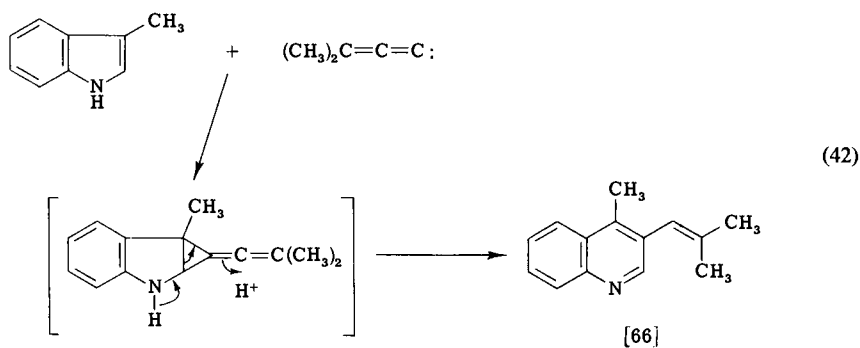
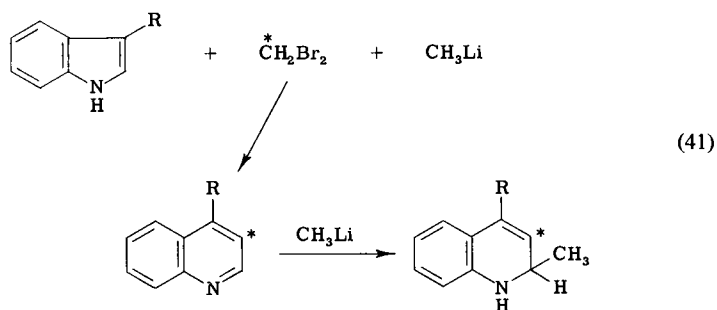


TABLE II
Product Distribution from Reaction (39)

X	R	Carbene precursor	Product ratio
Cl	H	$\text{Cl}_3\text{C}-\text{CO}_2\text{R} + \text{RONa}$	[61] only
Cl	CH_3	$\text{Cl}_3\text{C}-\text{CO}_2\text{R} + \text{RONa}$	[61]/[62] = 2.1
	CH_3	$\text{CHCl}_3 + \text{C}_2\text{H}_5\text{ONa}$	[61]/[62] = 0.8
	CH_3	$\text{Cl}_3\text{C}-\text{CO}_2\text{Na}$	[61]/[62] = 2.6
Br	CH_3	$\text{CHBr}_3 + \text{C}_2\text{H}_5\text{ONa}$	[61]/[62] = 1.2
	CH_3	$\text{Br}_3\text{C}-\text{CO}_2\text{Na}$	[61]/[62] = 6.4
F	CH_3	$\text{ClF}_2\text{C}-\text{CO}_2\text{Na}$	[62] only

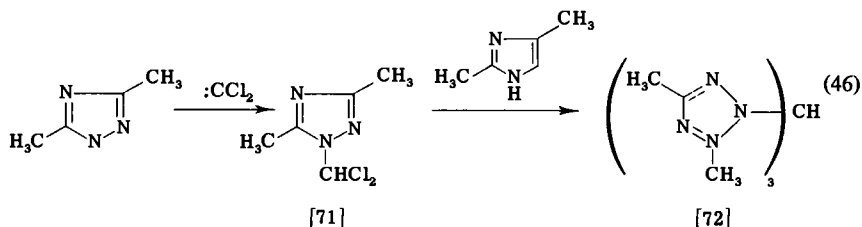
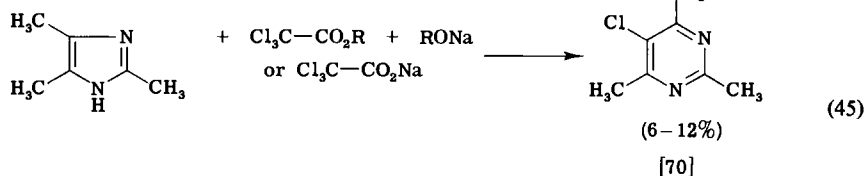
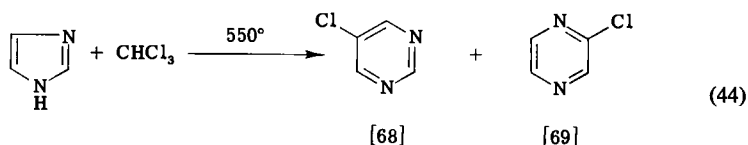


The carbenoid produced from methylene bromide and methyllithium reacted with indole and skatole to yield quinoline and lepidine, respectively (106). These two quinolines reacted further with methyllithium to give 1,2-dihydro-2-methylquinolines. The new carbon atom, originating from $\text{H}_2^{14}\text{CBr}_2$, enters the 3 position of the quinoline ring. Ring expansion of skatole to [66] was observed on treatment with 3-chloro-3-methyl-1-butyne and base (107). The latter components are known to produce $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}\cdot$, and the reaction presumably proceeds according to Eq. (42). No simple way of eliminating hydrogen chloride is available to the dichlorocarbene adduct of benzofuran which therefore gives rise to the "dimeric" ether [67] on hydrolysis (108).



The addition of dichlorocarbene to imidazoles, pyrazoles, and tetrazoles follows one or several of the routes discussed above, although the preferred one is not easily predicted. Reaction of imidazole with dichlorocarbene at 550° (pyrolysis of chloroform) gave a 10 : 1 mixture of 5-chloropyrimidine

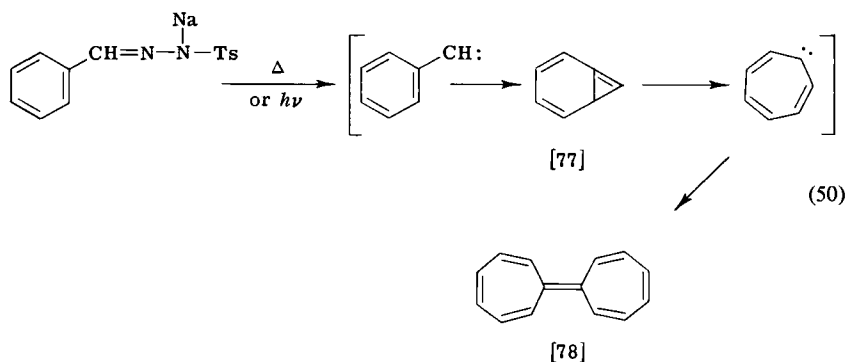
[68] and chloropyrazine [69] (109). It appears that the C=C bond is more susceptible to attack by dichlorocarbene than is the C=N bond of imidazole. 5-Chloro-2,4,6-trimethylpyrimidine [70] was the only product obtained from 2,4,5-trimethylimidazole and dichlorocarbene at ambient temperature (110). 3,5-Dimethyl-1,2,4-triazole gave exclusively tris(3,5-dimethyl-1,2,4-triazol-1-yl)methane [72], arising by way of the *N*-dichloromethyl compound [71] (110). 3,4,5-Trimethylpyrazole afforded small amounts of four products formed by competitive attack of dichlorocarbene on C=C, β -C, and N-H (110).



III. INTRAMOLECULAR REACTIONS

The copper-catalyzed decomposition of several β -aryldiazoketones [73] afforded the bicyclo[5.3.0]decane skeleton by intramolecular addition of the carbonylcarbenoid to the arene part of the molecule (*III*). Similar results were achieved with methyl benzyl diazomalonates (*IIIa*). 1-Aza-benz[*b*]azulene [75] was obtained in 62% yield after irradiation of the isocyanide [74] at 2537 Å (*II2*). It appears that irradiation may develop electrophilic carbenoid properties in an isocyanide function, leading to an aromatic ring expansion by addition of the isocyanide carbon atom.

heptafulvalene because it should favor "head-to-tail" dimerization, leading to benzenoid products.



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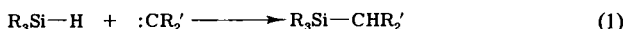
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Reactions Involving Hetero Atoms

I. SILANES AND GERMANES

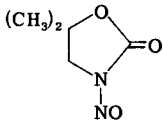
ALTHOUGH THERE IS a degree of resemblance in the behavior of Group IV elements toward carbenes, remarkable differences in reactivity have been observed. A very selective reaction of methylene was first reported with phenylsilane, diphenylsilane, and diphenylgermane (1). Photolysis of diazomethane in the presence of these compounds led to exclusive insertion of methylene into the Si—H and Ge—H bonds, respectively, with no detectable attack on the phenyl groups. Data about methylene transfer have been collected in Table I (1–17). The results of these studies, done in liquid solution, might be interpreted in terms of both direct insertion and abstraction–recombination mechanisms. More recent work in the gas phase with diazomethane–monosilane mixtures has shown, however, that the major path is direct insertion (2). Judging from the yields of products such as Si₂H₆ and C₂H₆, ~20% abstraction may have occurred. When the reactions of methylene with methylsilane and methyltrideuterosilane were studied (photolysis of diazomethane at 3660 Å), singlet methylene was found to insert into the Si—H bonds 8.9 times faster than into the C—H bonds of methylsilane (3). The deuterium isotope effect of Si—H insertion was determined to be 1.15. Liquid-phase photolysis of trifluorodiazomethane in trimethylsilane gave more rapid insertion into Si—H than into C—H bonds by a factor of 7.4 (4).



The high reactivity of Si—H bonds extends to carbenes and carbenoids which do not insert into C—H bonds. In its reaction with phenyl(tri-halomethyl)mercury compounds, triethylsilane was 0.8 times as reactive as cyclohexene, and triethylgermane was found to be 4 times more reactive

than triethylsilane (5). The insertion of dichlorocarbene and dibromocarbene (generated from PhHgCX_3) into the Si—H bond of optically active α -naphthylphenylmethylsilane proceeded with $\sim 93\%$ retention of configuration (6).

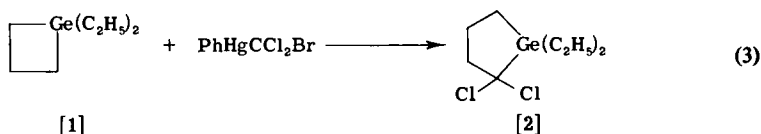
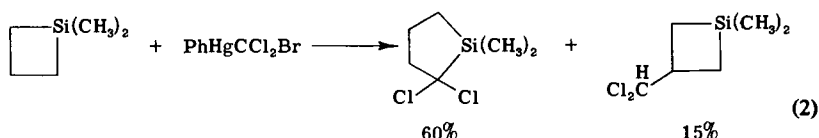
TABLE I
Methylene Transfer to Si—H and Ge—H Bonds

Species transferred	Precursor	Acceptor	Ref.
:CH ₂	CH ₂ N ₂ , <i>hν</i>	SiH ₄	2
		CH ₃ SiH ₃ , CH ₃ SiD ₃	3
		PhSiH ₃ , Ph ₂ SiH ₂	1
	XCH ₂ ZnX	Et ₃ SiH	7
	Hg(CH ₂ Br) ₂	R ₃ SiH, Et ₃ GeH	8
:CH—CF ₃	N ₂ CH—CF ₃	Me ₃ SiH	4
:C=C(CH ₃) ₂		Et ₃ SiH	9
:CH—CO ₂ R	N ₂ CH—CO ₂ R	Et ₃ SiH, Et ₃ GeH	10
:CHCl	PhHgCHClBr	R ₃ SiH	11
:CHBr	PhHgCHBr ₂	R ₃ SiH, Et ₃ GeH	11,12
:CCl ₂	PhHgCCl ₂ Br	R ₃ SiH, Ph ₃ SiH, R ₃ GeH	5,13
:CBr ₂	PhHgCBr ₃	R ₃ SiH, R ₃ GeH	5,13
F—C—CHF ₂	CHF ₂ CF ₂ SiF ₃	Me ₃ SiH, Me ₂ ClSiH, MeCl ₂ SiH, Cl ₃ SiH	14
Cl—C—CF ₃	PhHgCClBrCF ₃	Et ₃ SiH	15
Cl—C—SiMe ₃	(Me ₃ SiCCl ₂) ₂ Hg	Et ₃ SiH	16
:CH—OCH ₃	(CH ₃ O) ₃ SiCH(OCH ₃) ₂	(CH ₃ O) ₃ SiH	17

Both iodomethylzinc iodide and bromomethylzinc bromide reacted with trialkylsilanes to give trialkylmethylsilanes in good yield (7). When equimolar amounts of tri-*n*-butylsilane and cyclohexene were allowed to compete for the Simmons-Smith reagent, 51.5% of tri-*n*-butylmethylsilane and only 2.3% of norcarane were obtained. Similar rate ratios were encountered in methylene transfer from the halomethylmercury reagents Hg(CH₂Br)₂, ICH₂HgI-Ph₂Hg, and Hg(CH₂Br)₂-Ph₂Hg to a number of organosilicon hydrides (8). It is very likely that the latter process involves

a direct reaction between the organometallic reagent and the Si—H bond. A Hammett study of the reaction of $\text{Hg}(\text{CH}_2\text{Br})_2$ with substituted phenyldimethylsilanes showed a good correlation between $\log k_{\text{rel}}$ and σ° , giving a ρ value of -1.31 (8).

Carbon–silicon and carbon–germanium bonds are normally inert toward divalent carbon intermediates. The strained sila- and germacyclobutanes, however, were found to react by Si—C and Ge—C insertion, respectively, with dihalocarbenes. In the case of silacyclobutanes, competing reactions with β -C—H bonds were observed, Eq. (2) (18). 1,1-Diethyl-1-germacyclobutane [1] afforded the Ge—C insertion product [2] in yields up to 70%; minor products were not obtained in quantity sufficient to permit their identification (19).



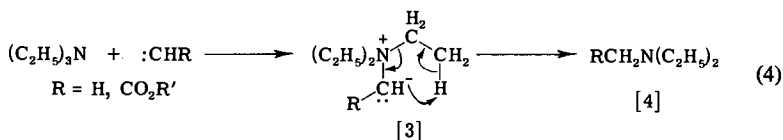
With certain chlorosilanes, insertion of F—C—CHF_2 into both Si—H and Si—Cl bonds was found to take place (14). Both the overall yield and the ratio of Si—H/Si—Cl insertion decreased sharply in the series $(\text{CH}_3)_2\text{ClSiH} > \text{CH}_3\text{Cl}_2\text{SiH} > \text{Cl}_3\text{SiH}$ (yield 98, 58, and 53 %, respectively; insertion ratio Si—H/Si—Cl, ∞ , 2.0, and 0.7, respectively). The copper-catalyzed reaction of diazomethane with trichlorosilane gave only $\text{ClCH}_2\text{SiHCl}_2$ (20).

II. NITROGEN COMPOUNDS

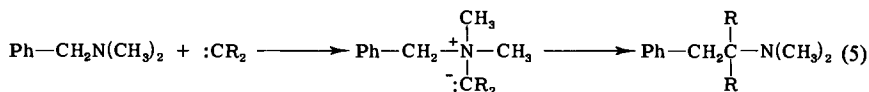
A. Amines

Insertion into the carbon–hydrogen bonds is the predominant reaction of methylene (21) and ethoxycarbonylcarbene (22) with triethylamine. Products [4] resulting from an α,β' -elimination within the hypothetical

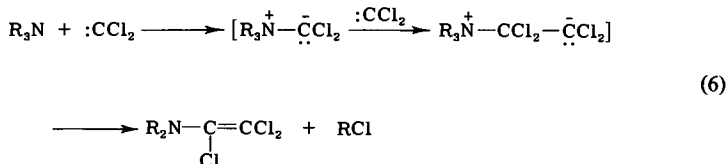
ylide [3] are formed only to a minor extent (4% of diethylmethylamine from the photolysis of diazomethane in triethylamine).



Benzyltrimethylamine reacts with ethyl diazoacetate (22) and with diazofluorene (23) by apparent insertion of the carbene into the N-benzyl bond. Most likely, these products arise from a Stevens rearrangement of the ylide intermediate. To a minor extent, rearrangement, followed by hydrolysis, was also observed in the reaction of dichlorocarbene with benzyltrimethylamine (24) and with (γ,γ -dimethylallyl)diethylamine (25). As a rule, allylamines do not undergo allylic rearrangements (21, 25), very much in contrast to the behavior of the corresponding ethers, sulfides, and halides (Section IV-VI).

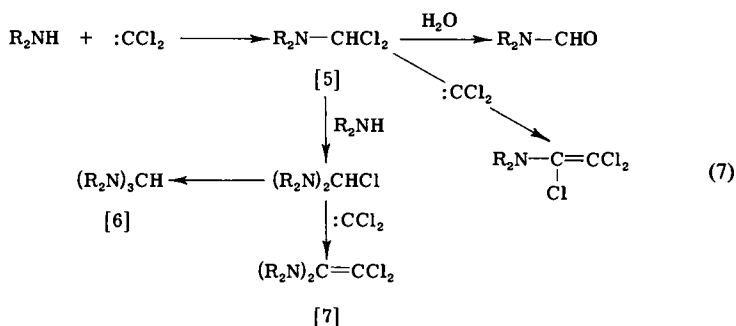


In aprotic media (PhHgCX_3 precursor), tertiary amines react with dichlorocarbene to produce trichlorovinylamines and alkyl (allyl) chlorides. A plausible mechanism is formulated in Eq. (6). This type of reaction was observed with triethylamine (comparable in reactivity to cyclohexene) (26), various allyldialkylamines (addition of CCl_2 to the double bond also taking place) (25), and even with dimethylaniline (27). Treatment of tertiary amines with chloroform and potassium *t*-butoxide led to a variety of minor products (24) some of which arise by protonation and hydrolysis of the intermediates postulated in Eq. (6).

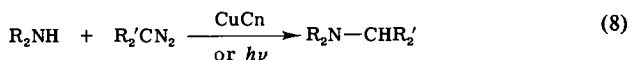


Secondary amines also afforded trichlorovinylamines when treated with PhHgCX_3 , but these were accompanied by 1,1-bis(dialkylamino)-2,2-dichloroethylenes [7] (28). Dichloromethylamines [5] were assumed as initial intermediates which can react further with dichlorocarbene or with excess amine as outlined in Eq. (7). Dialkylformamides were the

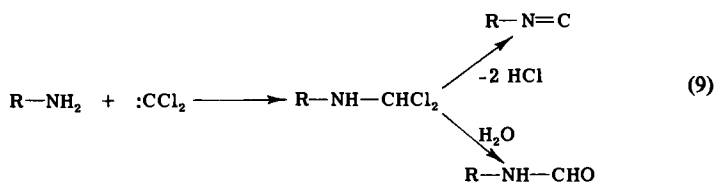
major products (30–60% yield) obtained from secondary amines, chloroform, and base (24, 29, 30). If hydrogen sulfide was introduced into the reaction mixture, thioformamides instead of formamides were produced (31). Decarboxylation of sodium trichloroacetate in the presence of methylaniline led to the formation of an ortho amide [6] (32). The various products are reasonably derived from [5].



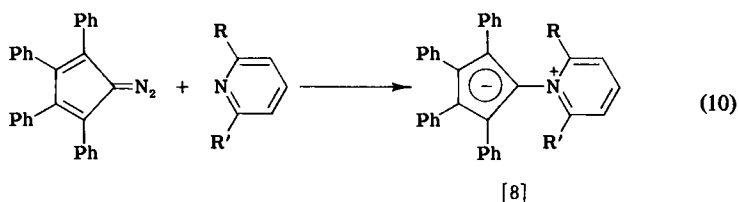
The first step of Eq. (7) may be viewed as "insertion" of dichlorocarbene into the N—H bond. Analogous "N—H insertion" has been achieved by the cuprous cyanide-catalyzed decomposition of diazomethane and ethyl diazoacetate (33), and by the photolysis of diphenyldiazomethane (34) in the presence of secondary and primary amines. No evidence is available to distinguish attack on the N—H bond from attack on nitrogen followed by a proton shift. The benzhydrylamines produced from diphenyldiazomethane were accompanied by tetraphenylethane, suggesting hydrogen abstraction as a third possibility.



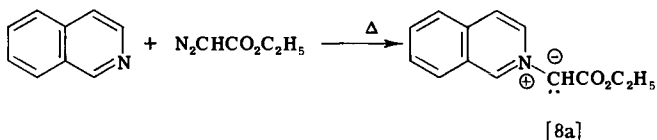
The reaction of primary amines with chloroform and base was discovered by Hoffmann in 1867 (35), and has been widely used for the synthesis of isocyanides (36, 37) and for the detection of primary amines. The intermediacy of dichlorocarbene was suggested by Nef (38) in 1897. The formation of formamides during the Hoffmann isocyanide synthesis was shown to proceed simultaneously with and not subsequent to isocyanide formation (36). Both types of product can be accounted for by a dichloromethylamine intermediate. Decarboxylation of sodium trichloroacetate, another source of dichlorocarbene, also afforded fair yields of isocyanides when carried out in the presence of arylamines (39).



Stable nitrogen ylides **[8]** were produced in almost theoretical yield by heating tetraphenyldiazocyclopentadiene under reflux with pyridine, the picolines, and 2,6-lutidine (**40**). No ylide could be isolated, however, from the parent diazocyclopentadiene.



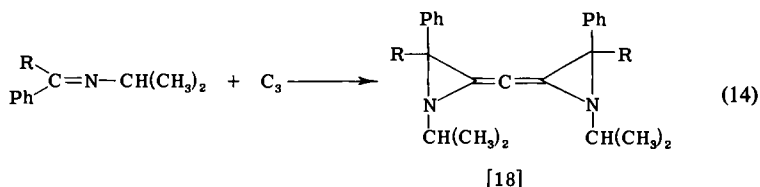
Isoquinolinium carboethoxymethylide **[8a]** has been obtained by the thermal decomposition of ethyl diazoacetate in the presence of isoquinoline (**40a**).



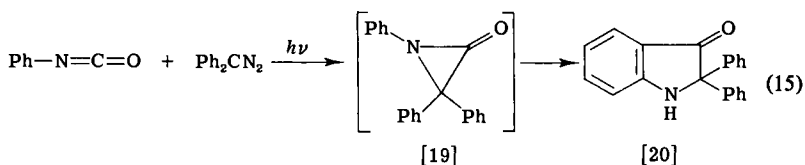
B. Carbon-Nitrogen Double Bonds

Copper-catalyzed reaction of ethyl diazoacetate with benzalaniline gave only ethyl 3-anilinoacrylate **[10]**, presumably by opening of the initial aziridine **[9]** (**41**). Dichlorocarbene adducts of various substituted benzalanilines and benzophenoneanils **[11]** have been isolated (**42-45**). Hydrolysis led to α -chloro- α -phenylacetanilides **[12]** or to α -hydroxy- α -phenylacetanilides **[15]**, depending on the reaction conditions (**42, 44, 46**). 1,3-Di-*t*-butylaziridinone **[17]** was obtained in 1-5% yield by mild hydrolysis of the dichlorocarbene adduct to *N*-neopentylidene-*t*-butylamine **[16]** (**47**). Treatment with sodium iodide in acetone converted **[11]** into ketenimines **[14]** (**45**). Rearrangement of **[11]** to the oxindoles **[13]** was observed

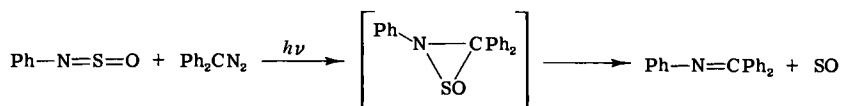
The reaction of *N*-benzylideneisopropylamine with carbon vapor, occurring on a surface cooled to -196° , afforded three stereoisomers of bis(*N*-benzylideneisopropylamino)allene (**18**, $R = H$) in the statistical ratio 1 : 1 : 2 (49). A single isomer was obtained from *N*-diphenylmethylenoisopropylamine ($R = Ph$).



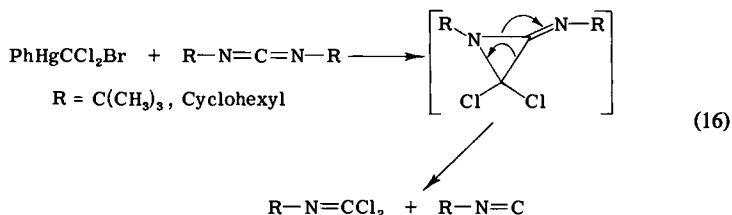
Diphenyldiazomethane and phenylisocyanate react under the influence of UV light to afford 2,2-diphenylindoxyl [**20**], presumably via diphenylcarbene addition to the $\text{C}=\text{N}$ bond and rearrangement of the α -lactam intermediate [**19**] (50).



Irradiation of *N*-sulfinylaniline and diphenyldiazomethane gave *N*-diphenylmethyleneaniline as the major product (50a). There is evidence that SO was given off.

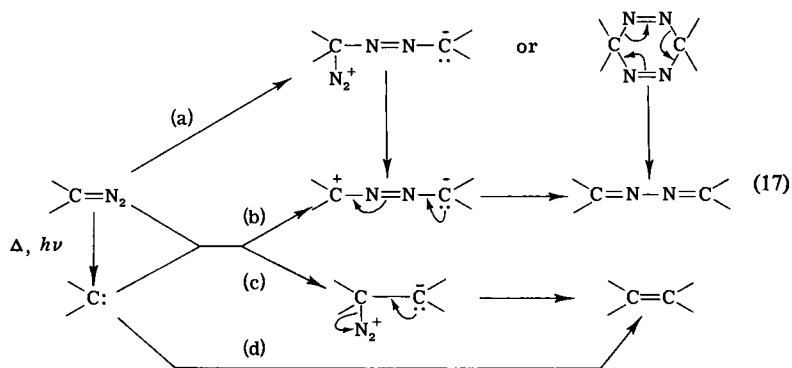


The cleavage of carbodiimides by phenyl(bromodichloromethyl)mercury, Eq. (16), probably involves a bimolecular reaction between mercurial and carbodiimide because it proceeds more readily than does the cyclopropanation of olefins (51).



C. Diazo Compounds

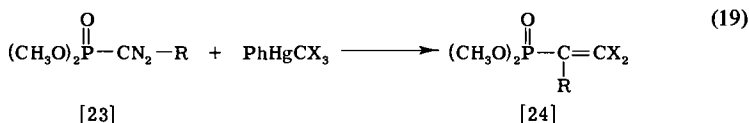
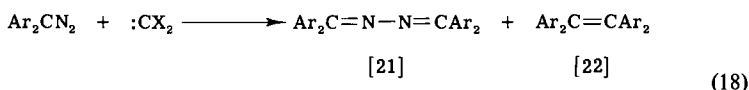
Carbenes attack diazo compounds to yield olefins or azines or both, Eq. (17). Most of these reactions occurred inadvertently when diazo compounds were photolyzed or pyrolyzed. Under these conditions, olefins could arise by dimerization of carbenes, Eq. (17d), or by reaction of a carbene with a second molecule of diazo compound, Eq. (17c). The former mechanism has been considered unlikely in view of the high reactivity and correspondingly small lifetime of most carbenes. Nevertheless, carbene dimerization may prevail in special cases. Sterically hindered diaryldiazomethanes with bulky ortho substituents afforded virtually quantitative yields of tetraarylethylenes on photolysis (52), much in contrast to their unhindered counterparts, which gave predominantly azines. It is conceivable that as a result of steric hindrance the triplet diarylcarbene concentration builds up to the point where dimerization occurs (52).



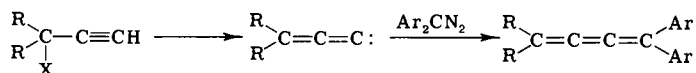
The duality of mechanisms leading to azine formation is even more obvious. Photolysis of 1-phenyldiazoethane in hexane at 0–5° produced 95% of acetophenone azine and less than 5% of styrene (53), whereas styrene was the major product obtained from phenylmethyldiazirine (54). By analogy with other alkylcarbenes, phenylmethylcarbene would be expected to undergo rapid hydrogen shift rather than to react with a second molecule of diazoalkane. Apparently the carbene is not an intermediate in the formation of acetophenone azine. The alternative is a bimolecular reaction between excited- and ground-state diazoalkane molecules. Photolysis of diphenyldiazomethane in substance at its melting point with 5460 Å radiation proceeded with a quantum yield of two (55) whereas the quantum yield in dilute solution was much lower (56). This result again suggests quenching of excited diazoalkane molecules by excess

diazo compound. The kinetics of the thermal decomposition of phenyldiazomethane show a second-order component (57), whereas the pyrolysis of diphenyldiazomethane follows a first-order rate law (58).

Further support for a two-step mechanism of azine and olefin formation comes from the reaction of dihalocarbenes with diazo compounds. As dihalocarbenes can be generated from organometallic precursors, they are uniquely suited for such studies. Treatment of diaryldiazoalkanes with haloforms and base afforded azines [21] and alkenes [22] in variable amounts (59). Only alkenes [24] were obtained from organophosphorus-substituted diazoalkanes [23] with the dihalocarbenes generated from $\text{PhHgCCl}_2\text{Br}$, PhHgCClBr_2 , and PhHgCBr_3 (60).



The base-induced elimination of HX from derivatives of ethynylcarbinols (Chapter 4, Section V) in the presence of diaryldiazomethanes produced the corresponding cumulenes in 5–26% yield (60a).



The effect of structure on the ratio of the two competing reactions, (17b) and (17c), remains obscure, as will be seen from Table II (34, 61–76). Intramolecular “dimerization” of bisdiazocarbonyl compounds [25] gave rise to alkynes [27] (77, 78). Under suitable conditions (aprotic solvent, 4360 Å radiation), cyclopropenones [26] have been isolated which give alkynes [27] on photodecarbonylation (78).

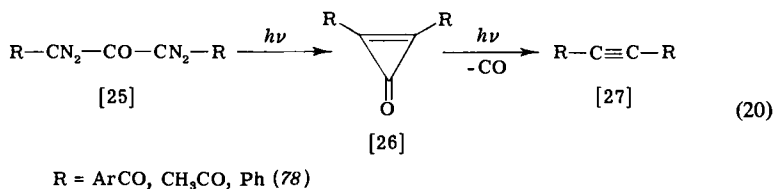
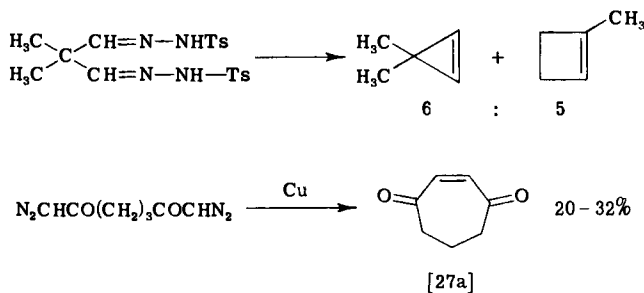


TABLE II
Formation of Alkenes and Azines from Diazo Compounds

Precursor	$R_2C=N-N=CR_2$	$R_2C=CR_2$	Ref.
CH_2N_2 , $h\nu$, Gas phase	—	64%	61
 $=N-NH-Ts$	—	+	62
Ar_2CN_2 , $h\nu$ or Δ	+	—	34, 63
Ph_2CN_2 , Cu(II)	4%	86%	64
Diazofluorene, Δ	—	+	63, 65
Diazoanthrone, Δ , Cu	+	+	66
5-Diazo-3-carene-2-one, $h\nu$, Δ	93%	—	67
2-Diazoacenaphthenone, Δ	+	+	68
N_2CH-CO_2R , Cu or Cu(II)	—	+	69-72
$N_2C(CO_2R)_2$, CuBr	—	40%	73
$N_2C(CN)_2$, 220°	—	+	74
$NC-C(=N)-N(Li)Ts$, $h\nu$ $\quad \quad \quad $ $\quad \quad \quad NH_2$	—	+	75
$(RS)_2C=N-N(Na)Ts$, Δ	—	50-55%	76

Cyclopropenes were among the products obtained from bistosylhydrazones of nonenolizable 1,3-diketones (78a). Intramolecular cyclization of bis- α -diazoketones afforded cycloalkenediones [27a] (78b).

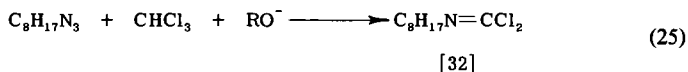


D. Nitriles and Isonitriles

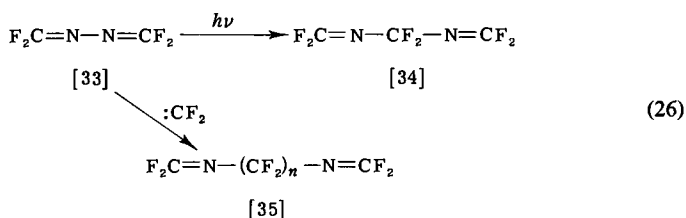
A variety of carbonylcarbenes derived from diazo ketones, arenediazooxides, and ethyl diazoacetate were found to react with nitriles by way of "1,3-dipolar addition" (79-81). The addition involves both the divalent

E. Nitrogen-Nitrogen Bonds

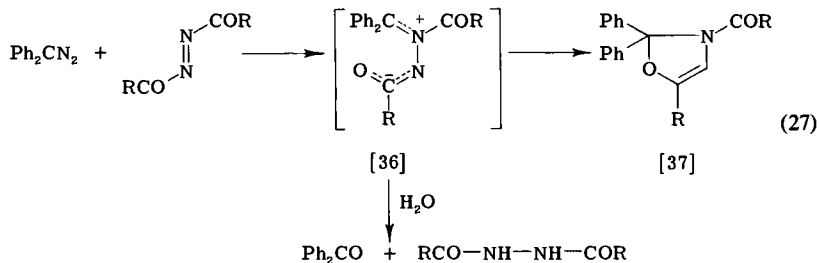
The reactions of alkylazides and of diazoalkanes with dichlorocarbene are very similar. When *n*-octyl azide in pentane at 0° was stirred with an excess of potassium *t*-butoxide and chloroform, it was smoothly transformed into *n*-octyl isocyanide dichloride [32] (85).

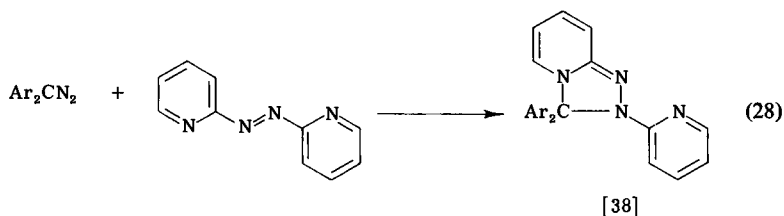


The photolysis of tetrafluoro-2,3-diaza-1,3-butadiene [33] in the absence of co-reactants resulted in almost quantitative conversion into hexafluoro-2,4-diaza-1,4-pentadiene [34] (86). This reaction was rationalized on the basis of decomposition of [33] into both $\text{F}_2\text{C}=\text{N}\cdot$ and $\cdot\text{CF}_2$. Difluorocarbene generated from difluorodiazirine inserted into the N—N bond of [33] to give the first four members of the perfluoro- α,ω -bisazomethines [35] in isolable quantities (86).



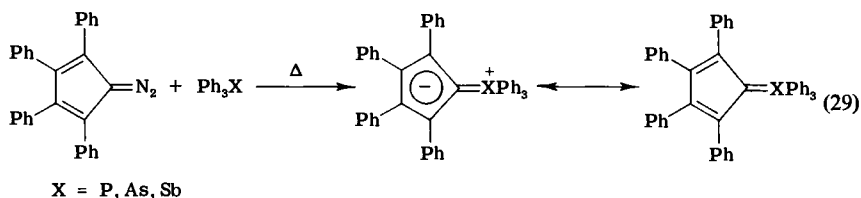
Azodicarbonyl compounds (87), 2,2'-azopyridine, and 2,2'-azoquinoline (88) accept diarylcarbenes with formation of five-membered heterocycles [37], [38]. Instead of cyclization, the hypothetical intermediate [36] may undergo hydrolysis (87). Whereas 2,2'-azopyridine had no effect on the rate of decomposition of diaryldiazoalkanes (88), an increase in rate was observed with several azodicarbonyl compounds (89). The intervention of carbenes in reaction (27) is therefore questionable.



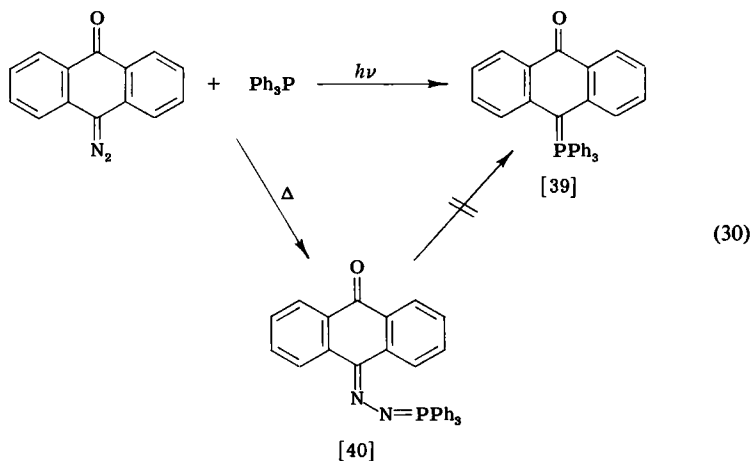


III. ORGANOPHOSPHORUS COMPOUNDS

Phosphines and phosphorus ylides have been utilized so far as carbene acceptors. Cyclopentadienylides of Group V elements (P, As, Sb) have proved to be readily obtainable by decomposition of diazotetraphenylcyclopentadiene in the molten triphenyl derivatives of these elements (90), Eq. (29).

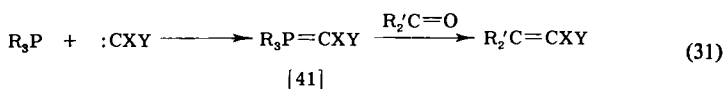


Photolysis of diazoanthrone at 25° in benzene containing triphenylphosphine led to 10-triphenylphosphoranylanthrone [39]. Formation of [39] involves trapping of the carbene rather than a direct reaction of diazoanthrone with triphenylphosphine. The two components were found to

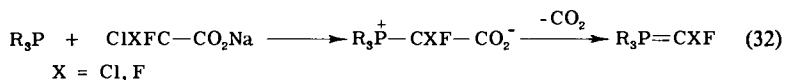


react very slowly at 25° to give anthraquinone monotriphenylphosphazine [40] rather than [39]; [40] was not converted into [39] by photolysis (66).

Phosphinemethylene reagents [41], obtained by the addition of halo-carbenes to phosphines, have been used *in situ* to convert carbonyl compounds into haloolefins. Triphenylphosphine chloromethylide ([41], X = H, Y = Cl) was prepared from methylene chloride-butyllithium (91, 92) or PhHgCHClBr (93) as the carbene precursor. CCl₂ and CBr₂ were transferred to triphenylphosphine by means of haloform and base (94, 95) or PhHgCX₃ (93). Three methods of generation were employed in the synthesis of triphenylphosphine chlorofluoromethylides ([41], X = Cl, Y = F), namely, the decarboxylation of sodium dichlorofluoroacetate (96), the dehydrohalogenation of dichlorofluoromethane (96), and the basic cleavage of methyl dichlorofluoroacetate (97). Decarboxylation of sodium chlorodifluoroacetate was the method of choice for preparing difluoromethylides of triphenylphosphine (98, 99) and tributylphosphine (100).

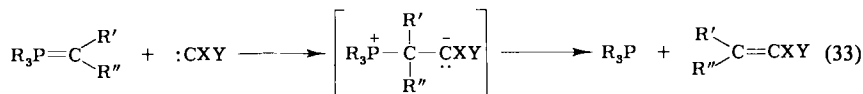


Not all of these methylene transfer reactions are likely to involve "free" carbenes. The decomposition of PhHgCX₃ in the presence of triphenylphosphine proceeded "much faster" than it did in the presence of olefins (93). No competitive trapping of CX₂ by olefins was observed when sodium dichlorofluoroacetate and sodium chlorodifluoroacetate were decarboxylated in the presence of olefin-phosphine mixtures (96, 99). Such trapping was successful, however, when :CClF was generated by dehydrohalogenation of dichlorofluoromethane (96). An alternative mechanism, involving the phosphobetaine salt [42], has therefore been suggested for CX₂ transfer by the trihaloacetate route (96, 99).



The Wittig reactions which followed ylide formation afforded yields in the range 50–80% which were generally better with aldehydes than with ketones. Triphenylphosphine difluoromethylide reacted with aldehydes (98) and perfluorinated ketones (99) only. Difluoromethylenecyclohexane was obtained, however, by the use of both tributylphosphine and *N*-methylpyrrolidone as the solvent (100).

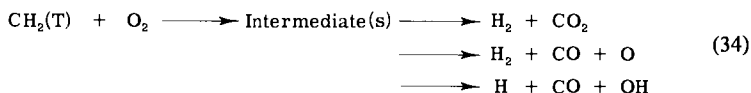
Phosphorus ylides were found to react with dihalocarbenes and aryl-halocarbenes to give olefins according to Eq. (33) (101). Electron-releasing groups on the α -carbon atom of the ylide increased the relative rates, whereas electron-withdrawing groups decreased them. The results support a mechanism which involves rate-determining attack of the carbene on the phosphorus ylide followed by rapid elimination of phosphine.



IV. OXYGEN COMPOUNDS

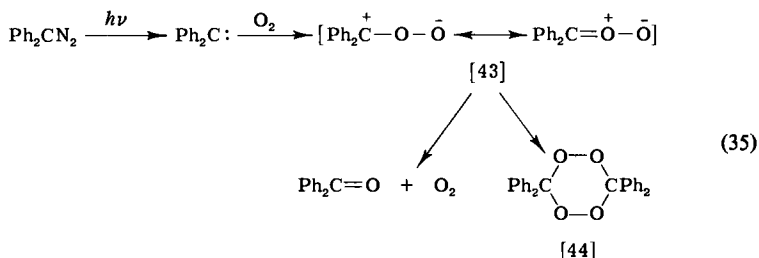
A. Molecular Oxygen

The addition of oxygen to gas-phase reactions of methylene has been widely used to remove products derived from the triplet species (Chapter 7, Section I). Photolysis of ketene- ^{14}C in the presence of O_2 and various hydrocarbons led to the formation of $^{14}CO_2$ and ^{14}CO (102). The sum of these products was very near the values given for percent of triplet methylene in these systems on the basis of reactivity (abstraction vs. insertion, non-stereospecific addition). The reactions producing CO and CO_2 , tentatively written as in Eq. (34), have not been fully elucidated. Molecular hydrogen derived from ketene was found in the photolysis of $CHT=C=O$, but the data do not establish whether molecular hydrogen is the complementary product of CO and CO_2 . Either excited formaldehyde or an excited form of CH_2O_2 is a possible intermediate in Eq. (34).

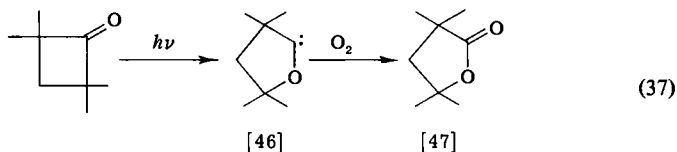
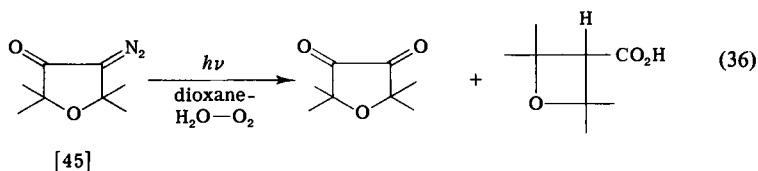


Photolysis of diphenyldiazomethane in the presence of oxygen afforded benzophenone (103), which may become the major product under suitable conditions (34). The isolation of the cyclic peroxide [44] from the photo-oxidation of diphenyldiazomethane suggests a carbonyl oxide [43] as the intermediate (104). Experiments with $^{36}O_2$ indicate that no decomposition of [44] (or a related polymeric peroxide) to give oxygen and benzophenone occurred under the conditions of the photooxidation (104). The processes leading to benzophenone and [44] appear to proceed in a parallel fashion rather than consecutively. Formation of benzophenone has been detected

after irradiation of diphenyldiazomethane in a solid air matrix at 20°K (105). The presence of oxygen caused a luminescent reaction during the warm-up of rigid fluorocarbon glasses containing triplet diphenylcarbene (106).



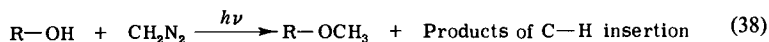
Autoxidation of the carbonylcarbene derived from diazo ketone [45] was found to compete with Wolff rearrangement (107). Oxacarbenes [46] originating from the photorearrangement of cyclobutanones afforded butyrolactones [47] in the presence of molecular oxygen (108). There may be more examples of oxidizable carbenes which remained undetected because careful chemists maintained an atmosphere of inert gas.



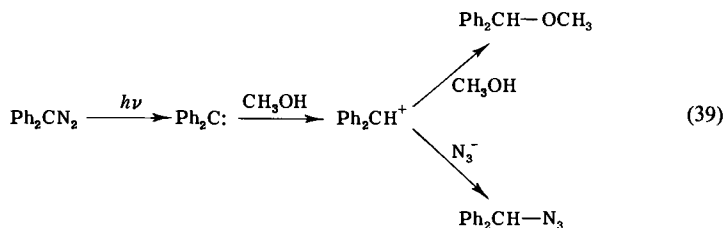
B. Hydroxyl Compounds

In their pioneer work on the reaction of methylene with propan-2-ol, Meerwein and his students isolated 2-propyl methyl ether, butan-2-ol, and *t*-butanol (109). In a study of the photolysis of ketene in the presence of methanol in the gas phase, approximately equal rates of insertion of CH₂ into the C—H and O—H bonds were observed (110). It is doubtful, however, whether this work should be relied on because the dark reaction to form methyl acetate was considerable. When diazomethane-*t*-butanol mixtures were photolyzed, the major products were *t*-butyl methyl ether and 2-methylbutan-2-ol (111). From the amounts formed, it was calculated

that in *t*-butanol the O—H bond is 10.9 ± 0.5 times as reactive as a C—H bond. Competitive reactions with roughly equimolar mixtures of alcohols gave the following relative reactivities of O—H bonds toward attack by methylene: methanol 2.01, ethanol 1.95, propan-2-ol 1.37, *t*-butanol 1.00. This is the order of decreasing acidity of the alcohols as well as the order of increasing steric hindrance.

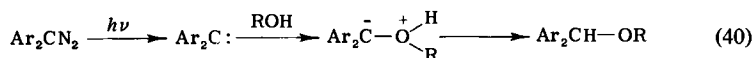


No experiments were performed to distinguish between direct insertion of methylene into the O—H bond and various alternative mechanisms. There has been much concern about this problem, however, in the aryl-carbene series. Photolysis of diphenyldiazomethane in methanol afforded benzhydryl methyl ether in 70% yield (34). The quantum yield of the photolyses in methanol and in aprotic solvents were identical within experimental error (112). The photooxidation of diphenyldiazomethane was suppressed by methanol but not by aprotic nucleophiles. Photolysis of diphenyldiazomethane in a methanolic solution of lithium azide produced benzhydryl methyl ether and benzhydryl azide in virtually the same ratio as that obtained by solvolysis of benzhydryl chloride. These results suggested a diphenylcarbonium ion intermediate, arising by protonation of diphenylcarbene, Eq. (39) (112).

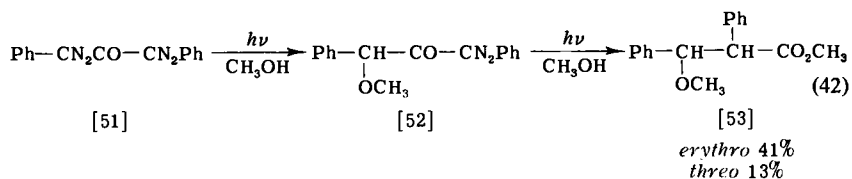
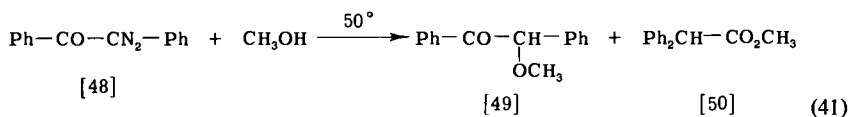


The thermolysis of diphenyldiazomethane in acetonitrile containing hydroxylic additives did not conform to Eq. (39) (113, 114). From studies of isotope effects of the product-forming steps (leading to Ph_2CHOR and benzophenone azine) it has been deduced that diphenylcarbene reacts with the oxygen atom of ROH, giving an ylide, subsequent rearrangement of which gives Ph_2CHOR , Eq. (40). The kinetics were rather complex because azine formation involved two mechanisms, following first- and second-order rate laws. On the other hand, it has been shown that the hydrogen-bonding ability of alcohols (which is related to their acidity) is

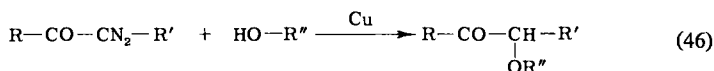
important in determining the extent to which they can capture 4,4'-dichlorodiphenylcarbene (relative reactivities: methanol 1.00, propan-2-ol 0.37, *t*-butanol 0.11, benzyl alcohol 1.9) (115). With isopropanol, hydrogen abstraction to give diphenylmethane and acetone competed with formation of benzhydryl isopropyl ether (115a). If hydrogen abstraction and autoxidation are attributed to triplet diphenylcarbene, the kinetics require the reversible interconversion of the singlet and triplet states (cf. Chapter 8, Section I.B). Substantial isotope effects of the product-forming steps were found in the thermal decomposition of 4,4'-dichlorodiphenyldiazomethane in acetonitrile containing tritiated alcohols (115) which is consistent with either proton transfer, Eq. (39), or direct insertion into the O—H bond. The evidence available at present indicates a delicate balance of mechanisms in the reactions of diarylcarbenes with hydroxyl compounds.



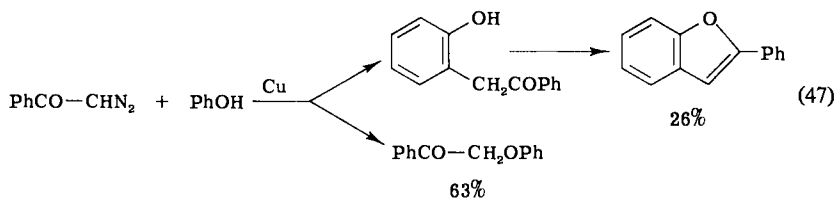
Arylcarbenes generated by photolysis of polyarylcyclopropanes (116) and -oxiranes (117, 118) have also been trapped by methanol, thus providing additional evidence that diazo compounds are not involved in the product-forming steps of Eqs. (39) and (40). Aryl substituents even divert carbonylcarbenes from the otherwise facile Wolff rearrangement in favor of methanol addition. Azibenzil [48], in methanol at 50°, afforded 30% of benzoin methyl ether [49] and 70% of methyl diphenylmethylacetate [50] (product of Wolff rearrangement) (119). Irradiation of 1,3-bisdiazo-1,3-diphenylpropan-2-one [51] in methanol-tetrahydrofuran yielded [53] as the major product (78). Compound [53] probably originates from Wolff rearrangement of the diazo compound [52] formed by methanol insertion into the initially produced carbene.



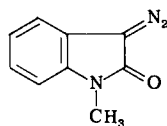
The Wolff rearrangement of diazo ketones in the presence of water, alcohols, carboxylic acids, etc., may be virtually eliminated by cupric oxide (125), copper powder (126), cupric chloride (127), and metal chelates, such as acetylacetonates of Cu(II), Ni(II), and Pb(II) (128). The products of these catalyzed reactions are ketols, and their alkyl and acyl derivatives, respectively.



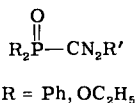
The copper-catalyzed reaction of diazoacetophenone with phenol involves nuclear attack (leading ultimately to formation of a benzofuran) as well as formation of a ketol ether, Eq. (47) (126).



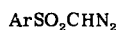
Diazocarbonyl compounds which do not readily undergo Wolff rearrangement, e.g., [29] (81) and [57] (129), diazophosphinoxides [58] (130), diazosulfones [59] (131) and [60] (132) all afford high yields of OH insertion products when photolyzed in methanol. Oxacarbenes originating from the photorearrangement of cyclobutanones, Eq. (37), were efficiently trapped by alcohols with formation of cyclic acetals (108).



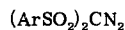
[57]

R = Ph, OC₂H₅

[58]

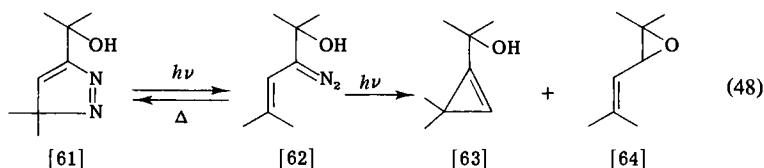


[59]

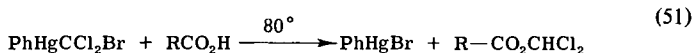
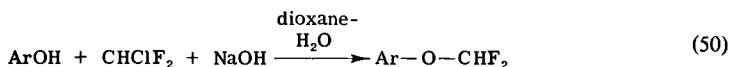
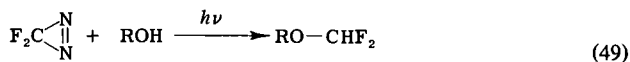


[60]

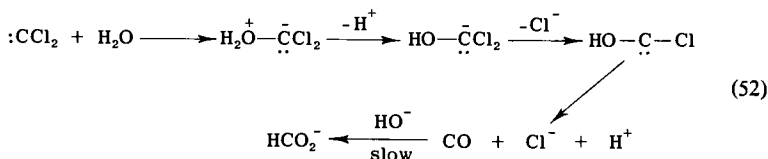
At least one example of intramolecular OH insertion has been recorded. Photolysis of the pyrazolenine [61], proceeding by way of the diazoalkene [62], resulted in intramolecular competitive C=C addition and OH insertion to give cyclopropene [63] and oxirane [64], respectively (133). As in other cases of diazoalkanes reacting with alcohols, proton transfer to the diazo compound, with formation of diazonium ions and carbonium ions, cannot be definitely excluded.



Products of the structure ROCHX_2 have rarely been obtained by attack of dihalocarbenes on hydroxyl compounds. Photolysis of difluorodiazirine in the presence of alcohols and carboxylic acids afforded difluoromethyl ethers and esters, respectively (134), Eq. (49). The preparation of aryl difluoromethyl ethers by the reaction of chlorodifluoromethane with phenols in aqueous dioxane and in the presence of an excess of sodium hydroxide, Eq. (50), has been described (135). Phenyl(bromodichloromethyl)mercury reacted with carboxylic acids in benzene at 80° to give high yields of dichloromethyl esters (136, 137), Eq. (51). Only highly acidic carboxylic acids such as trifluoroacetic acid caused cleavage of the $\text{Ph}-\text{Hg}$ bond to a major extent. However, the mercurial route failed to produce dichloromethyl ethers from alcohols; alkyl chlorides, alkyl formates, and chloroform were obtained which can be rationalized as resulting from an initially formed alkyl dichloromethyl ether (138).

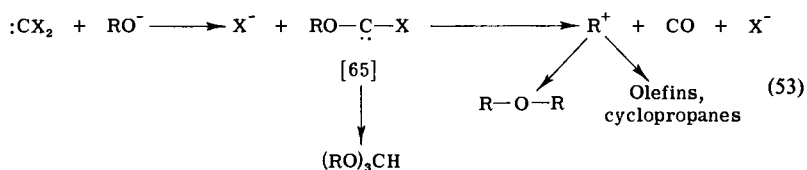


Secondary solvolytic transformations are very common when dihalocarbenes react in hydroxylic solvents. The hydrolysis of dichlorocarbene in aqueous solution to give carbon monoxide and formate ion probably proceeds as represented by Eq. (52) (139).

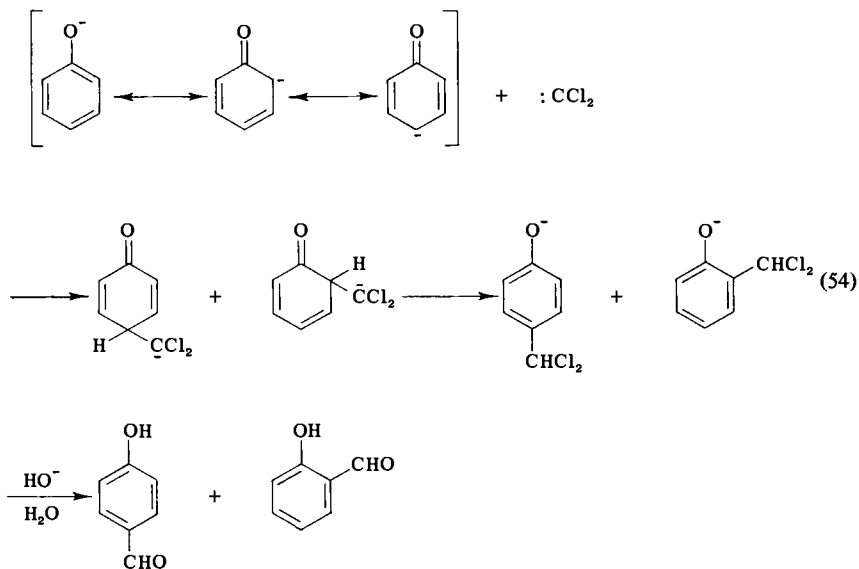


A similar sequence may be expected for the reaction of dihalocarbenes with alkoxides in alcoholic solution. The evolution of ethylene and carbon monoxide from a refluxing mixture of ethanol, potassium hydroxide, and bromoform was observed as early as 1885 (140). Hine *et al.* (141) studied

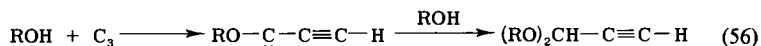
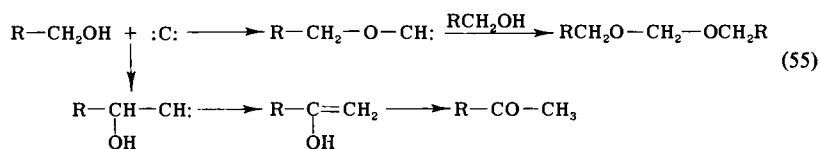
this reaction in various alcohols and obtained the olefins corresponding to the alcohols used. The formation of rearranged and cyclic products (essentially the same as those obtained by nitrous acid deamination of the corresponding amines) suggests a carbonium ion mechanism of the "deoxidation" reaction, Eq. (53) (142-144). If the structure of the carbonium ion does not permit elimination, reaction with excess alcohol occurs. Thus dibenzyl ether was a major product when benzyl alcohol was treated with chloroform and base (145). Tribenzyl orthoformate, another major product, probably arises by alcoholysis of the intermediate [65] in Eq. (53). Orthoformates were the only products from [65], X = F (146).



The familiar Reimer-Tiemann synthesis of phenolic aldehydes (*147*) probably involves attack of dichlorocarbene on the ambident phenoxide ions (*148*). Chloroform reacts with aqueous sodium phenoxide only very slowly, but in the presence of excess sodium hydroxide it reacts rapidly to give *o*- and *p*-hydroxybenzaldehyde (*149*). The arguments which have been advanced for the intermediacy of dichlorocarbene in the aqueous hydrolysis of haloforms (Chapter 4, Section I) apply analogously to the Reimer-Tiemann reaction.

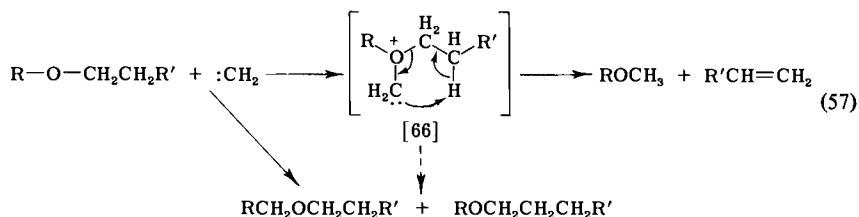


The constituents of carbon vapor behave like bifunctional carbenes toward hydroxylic reactants. All alcohols react with C_1 to undergo deoxygenation (giving carbon monoxide) and insertion into every O—H and C—H bond (150). O—H insertion leads to formals, the alcoholic OH group contributing the hydrogen atoms of the O—CH₂—O group. C—H insertion gave rise to both carbonyl compounds and unsaturated alcohols, Eq. (55). Ground-state C_3 reacted with alcohols by addition reactions producing propargyl aldehyde acetals, Eq. (56) (151).

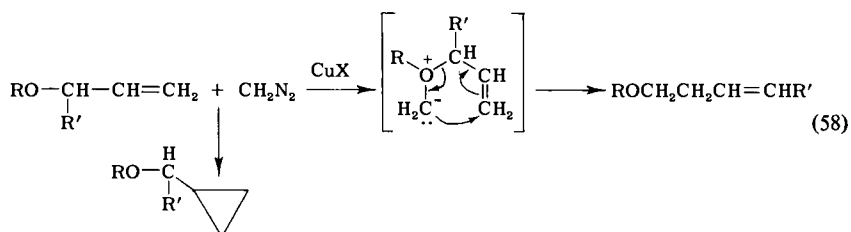


C. Ethers

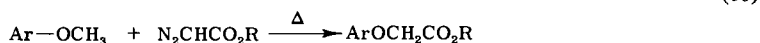
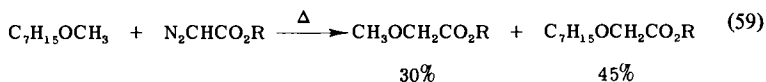
The major reaction of methylene with ethers is nearly random insertion into the various C—H bonds (Chapter 7, Section III). Two minor reactions are displacement, leading to methyl ethers, and apparent insertion into the C—O bonds. The displacement reaction with methyl alkyl ethers results in the formation of dimethyl ether and an olefin (152). It is not suppressed by the presence of oxygen, nor does it occur when the methylene is produced by mercury photosensitization. The reaction is therefore envisaged as resulting from the initial attack of singlet methylene on the oxygen atom to give an ylide intermediate [66], followed by α,β' -elimination. The same intermediate may be involved in C—O insertion. The formation of C—O insertion products was (in part) suppressed by oxygen. However, they were not found when mercury photosensitization was used as the source of methylene. The effect of oxygen cannot be due to trapping of triplet methylene; rather, oxygen must interfere with some later step of the reaction. That step may well be the rearrangement of [66]. Radical mechanisms are now well established for various types of Stevens rearrangements. Table III records the relative amounts of displacement and C—O insertion products which were obtained from various ethers and acetals (152–159).



The carbenoid generated by cuprous halide-catalyzed decomposition of diazomethane did not initiate the reactions outlined in Eq. (57). With allyl ethers, however, addition of CH_2 to the $\text{C}=\text{C}$ bond was accompanied by apparent insertion into the O-allyl bond (160). As was shown with 3-methoxy-1-butene, the reaction proceeds with allylic inversion, and is reasonably formulated as in Eq. (58).

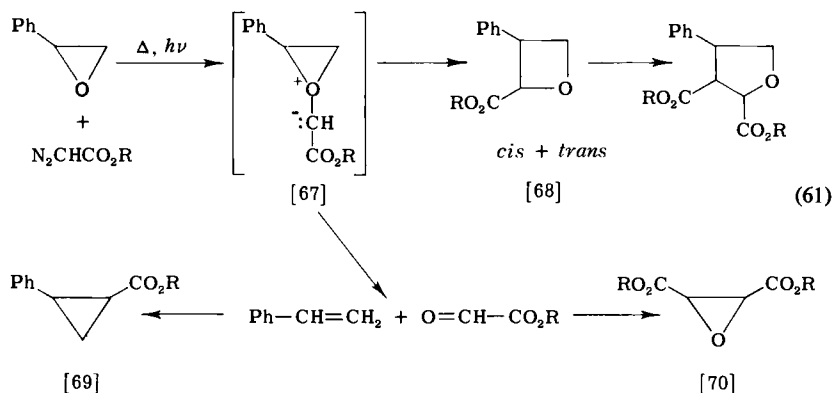


Photolysis of ethyl diazoacetate in diethyl ether led to ethyl ethoxyacetate as the principal product (155, 161). Thermolysis of ethyl diazoacetate in di-*n*-butyl ether afforded ethyl *n*-butoxyacetate and 1-butene in comparable yields (162). While these findings can be rationalized in terms of the ylide mechanism, Eq. (57), the reaction with *n*-heptyl methyl ether does not conform to this scheme. Elimination of the *n*-heptyl group, which can follow Eq. (57), is not even favored over displacement of the methyl group, the fate of which is unknown. Similarly, a large number of substituted anisoles gave rise to aryloxyacetates when treated with ethyl diazoacetate (162-166).

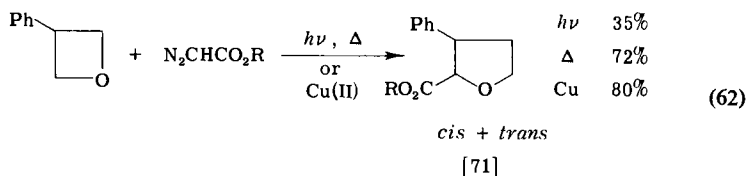


Thermal or photochemical decomposition of ethyl diazoacetate in 2-phenyloxirane gave a complex mixture of products, Eq. (61) (167).

The reaction probably involves formation of an oxygen ylide [67] which rearranges to the oxetane [68]. Fragmentation of [67] gives styrene and ethyl glyoxylate, which on further reaction afford ethyl 2-phenylcyclopropanecarboxylate [69] and diethyl epoxysuccinate [70], respectively.



2-Phenyloxetane reacted more selectively with ethoxycarbonylcarbene to produce a mixture of *cis*- and *trans*-2-ethoxycarbonyl-3-phenyltetrahydrofuran [71] (167). This apparent C—O insertion proceeded in high yield even when catalyzed by Cu(II) compounds; optically active copper complexes as catalysts afforded optically active [71] of unknown optical purity (168).



There are also some examples of apparent insertion of ethoxycarbonylcarbene into the C—O bonds of cyclic acetals (166, 169), Eqs. (63) and (64).

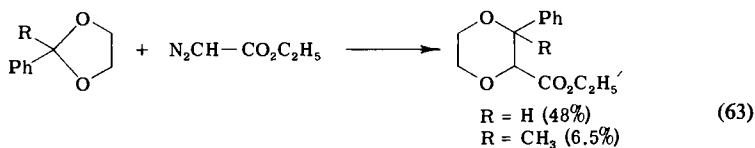
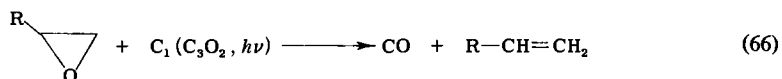
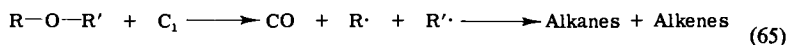


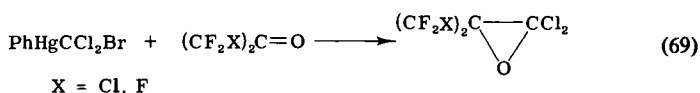
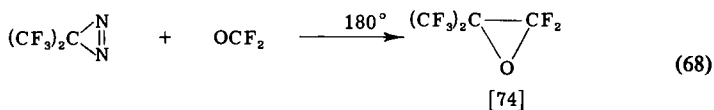
TABLE III
Displacement and Insertion Reactions of Methylene
with Ethers and Acetals

Compound	Phase	% Displacement	% C—O Insertion	Ref.
CH ₃ OCH ₂ CH ₃	Gas	4.0	0	152, 153
	Liquid	0	0	
CH ₃ OCH ₂ CH ₂ CH ₃	Gas	3.2	0	152, 154
	Liquid	0	0	
CH ₃ OCH(CH ₃) ₂	Gas	10.0	2	152
	Liquid	5.6	0	
CH ₃ CH ₂ OCH ₂ CH ₃	Liquid	Some	0	155
CH ₃ OC(CH ₃) ₃	Gas	3.3	3.5	152
	Liquid	0	0	
Tetrahydrofuran	Gas	2.1	12	152, 156
	Liquid	0	0	
CH ₃ CH(OCH ₃) ₂	Gas	3.9	4.6	158
	Liquid	1.6	11.3	
1, 3-Dioxolane	Gas	Trace	1.1	158
	Liquid	0	15.8	
2-Methyl-1, 3-dioxolane	Gas	6.7	13.6	158
	Liquid	13.7	3.9	
Paraldehyde	Liquid	10.0	0	159

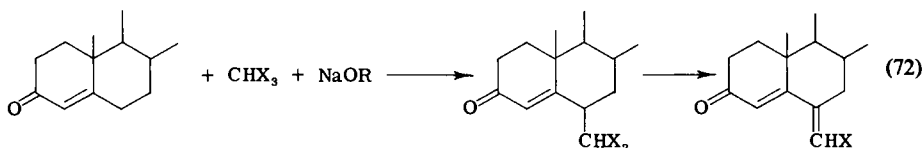
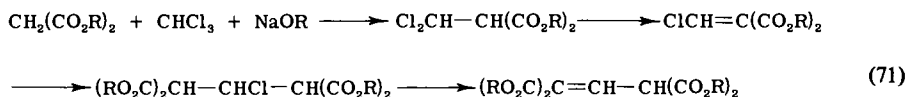
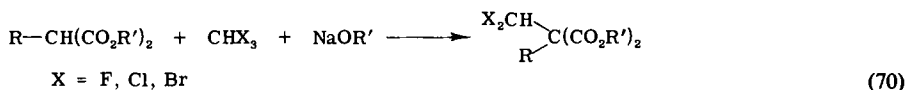
Atomic carbon was found to deoxygenate ethers with formation of carbon monoxide and of hydrocarbons which arise by combination and disproportionation of alkyl radicals (170). Oxiranes were converted into the parent olefins. Similar deoxygenation reactions were observed when carbon suboxide was photolyzed in the presence of oxiranes and oxetanes (171).



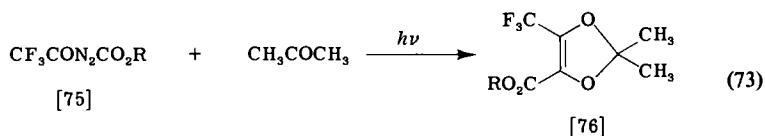
Epoxides of *cis*- and *trans*-2-butene were deoxygenated by atomic carbon to yield olefins in a nonstereospecific manner, suggesting that the

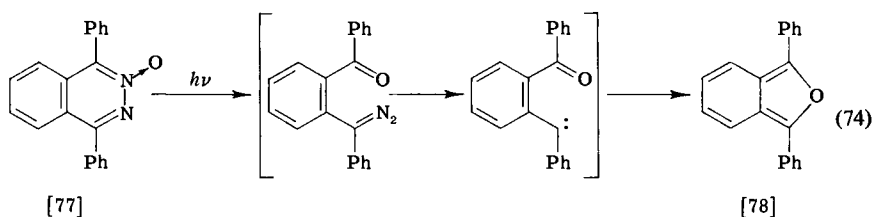


The reactions of carbonyl compounds with haloforms and base appear to proceed by attack of dihalocarbenes on the enolate ions, followed by dehydrohalogenation whenever possible. Examples include the dihalomethylenation of alkyl- and arylmalonic esters, Eq. (70) (178-180), the conversion of diethyl malonate into tetraethyl propene-1,1,3,3-tetracarboxylate, Eq. (71) (181), and the halomethylenation of testosterone and several of its derivatives, Eq. (72) (182).

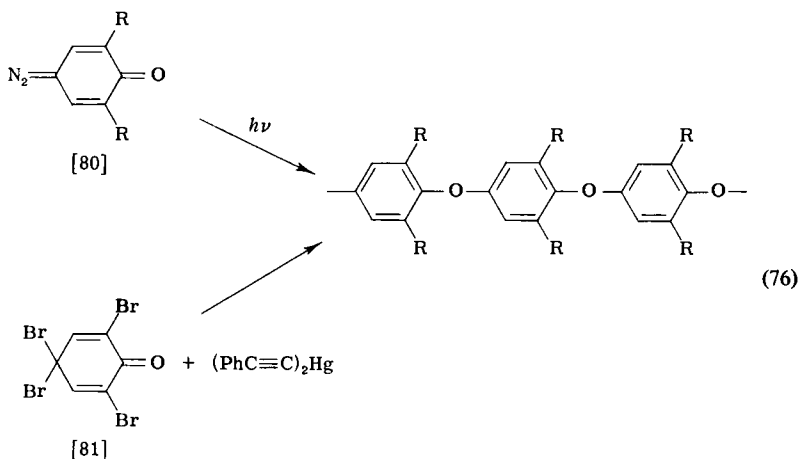
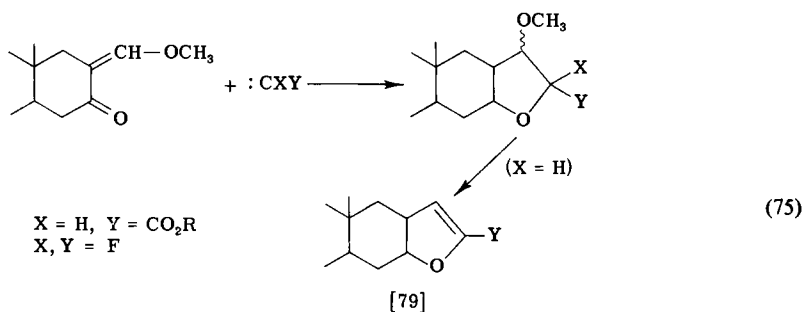


1,3-Dipolar addition involving the carbonyl oxygen was observed when ethyl trifluoroacetyldiazoacetate [75] was photolyzed in acetone (183, 184). The resulting 1,3-dioxole [76] was converted into a photodimer on further irradiation (184). The carbene derived from tetrachlorobenzene-1,2-diazooxide [29] also added ketones to give cyclic acetals in moderate yields (81). Intramolecular carbonyl addition of a diarylcarbene has been suggested as the key step in the photorearrangement of the quinoxaline-*N*-oxide [77] to the isobenzofuran [78] (185).



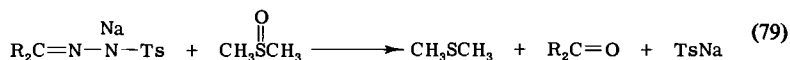
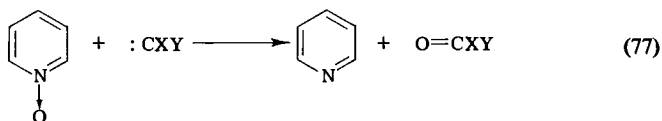


α -Methoxymethylene ketones accept ethoxycarbonylcarbenoid (186, 187) and difluorocarbene (188) by 1,4 addition. Subsequent elimination of methanol may lead to furans [79]. The formation of polyphenyl ethers from suitable precursors such as benzene-1,4-diazooxides [80] (189, 190) or 2,4,4,6-tetrabromocyclohexadienone [81] (191) can be viewed as a carbonyl addition of carbenacyclohexadienones although the mechanism of this reaction awaits further elucidation.



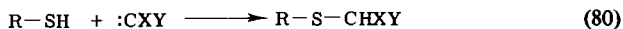
E. Amine Oxides and Sulfoxides

Deoxidation of pyridine-*N*-oxide occurred on treatment with PhHgCX_3 (192), 9-diazofluorene (193), and ethyl diazoacetate in the presence of cupric stearate (194). Carbonyl compounds derived from the hypothetical carbene intermediates, such as phosgene, fluorenone, and ethyl glyoxylate, have been isolated. A similar oxidation of dichlorocarbene was observed when ethyl trichloroacetate reacted with sodium methoxide in the presence of dimethyl sulfoxide (195). The products were dimethyl sulfide and dimethyl carbonate, Eq. (78). Tosylhydrazone salts of benzaldehyde, acetophenone, and benzophenone gave fair yields of the parent carbonyl compounds when decomposed in dimethyl sulfoxide (195), Eq. (79).



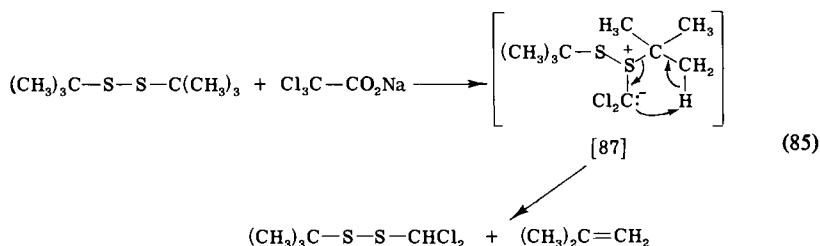
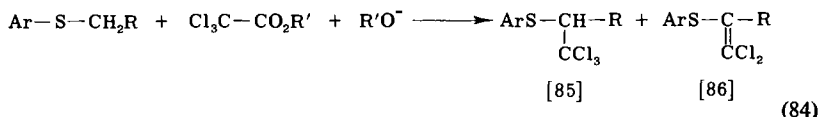
V. ORGANOSULFUR COMPOUNDS

“Insertion” of carbenes and carbenoids into the S—H bonds of thiols has been achieved by cuprous chloride-catalyzed decomposition of ethyl diazoacetate (124), photolysis of bis(phenylsulfonyl)diazomethane (132), and by dehydrohalogenation of chlorodifluoromethane (196).

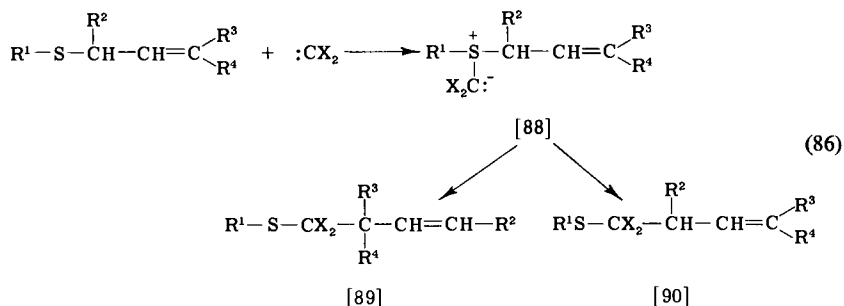


Dialkyl sulfides afforded stable sulfur ylides by adding carbenes with strongly electron-withdrawing substituents. Bis(phenylsulfonyl)carbene could be trapped with di-*n*-butyl sulfide and dimethyl sulfoxide to give the ylides [82] and [83], respectively (132). The photo-induced reaction of diazobiscarbonyl compounds with dimethyl sulfide, Eq. (82), also produced stable sulfur ylides which underwent Stevens-type rearrangement and Hoffmann-like elimination at temperatures above 200° (197). The benzophenone-sensitized photolysis of diazo compounds in dimethyl sulfide did not result in the formation of sulfur ylides, indicating that only singlet carbenes are capable of attack on sulfur. Competition experiments showed that bis(methoxycarbonyl)carbene reacts with dimethyl sulfide four times

yield (200). The role of dichlorocarbene in the formation of [85] and [86] is not easily rationalized because the last step obviously involves trichloromethide ion. Sulfides inhibit the addition of dichlorocarbene to olefins but are recovered in high yield (200). The reaction of *t*-butyl disulfide with dichlorocarbene afforded *t*-butyl dichloromethyl sulfide in 80% yield (201). It is reasonable to formulate this carbene-disulfide reaction as formation of the ylide [87], followed by a cyclic elimination process, Eq. (85).



Sulfur ylides [88], derived from allylic sulfides, are distinguished from those mentioned above by facile rearrangement. Eq. (86). When dichlorocarbene was the attacking species, only part of the rearrangement proceeded with allylic inversion (202), whereas inversion was virtually complete in the cuprous halide-catalyzed reaction of diazomethane (160) and in the photolytic reaction of dimethyl diazomalonate (203) with allylic sulfides. In direct photolysis, attack of bis(methoxycarbonyl)carbene on sulfur appeared to be 4–5 times faster than addition to the C=C bond. In the benzophenone-photosensitized reaction, on the other hand, the addition products were favored. Copper salt or copper powder catalysis yielded exclusively products of allylic rearrangement (203). Because of geometric limitations, cyclic sulfides, such as dihydro-2*H*-thiopyran, cannot undergo the rearrangement observed for the open-chain analogs. They react by addition to the double bond and by insertion into allylic C—H bonds (204). Table IV records the product ratios of [89] and [90] in allylic sulfide-dichlorocarbene reactions.

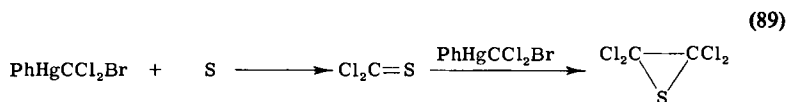
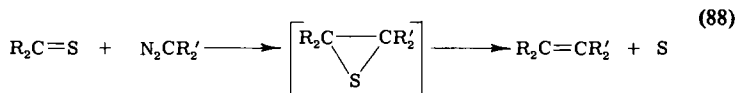
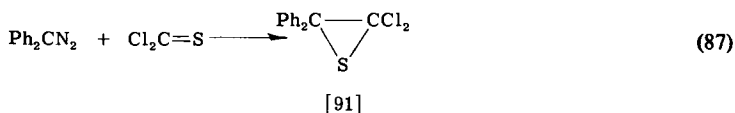


The reaction of diazoalkanes with thiophosgene and with thioketones was reported by Staudinger and Siegwart (205) nearly 40 years ago; e.g., diphenyldiazomethane with thiophosgene gave 2,2-dichloro-3,3-diphenylthiirane [91] in 68% yield. Other examples of such reactions have been described (206); ethyl diazoacetate (207), diazo ketone [45] Eq. (36) (208), and thiocarbonyl fluoride (209) produced olefins which are thought to arise by elimination of sulfur from intermediate thiiranes, Eq. (88). Inter-

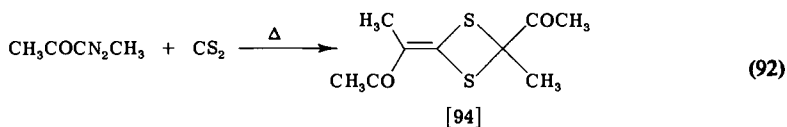
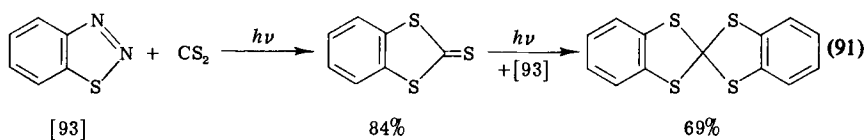
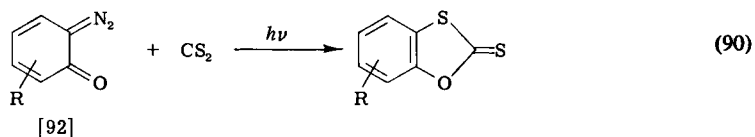
TABLE IV
Product Ratios in Allylsulfide-Dichlorocarbene Reactions (202)

Carbene precursor	R ¹	R ²	R ³	R ⁴	[89] / [90]
Cl ₃ C-CO ₂ R + R ₂ Na	Ph	H	CH ₃	H	9
	Ph	CH ₃	H	H	1.8
	<i>n</i> -C ₄ H ₉	H	CH ₃	H	25
	<i>n</i> -C ₄ H ₉	CH ₃	H	H	3.7
	Ph	H	CH ₃	CH ₃	0.64
	Ph	H	Ph	H	2

action of diazoalkanes with sulfur also afforded thiiranes (210, 211). In all of these reactions, however, it is not clear whether the diazoalkane or the carbene derived from it is the reacting species. Conditions (low temperature, no irradiation) were frequently not those which would release the carbenes. The reactions of phenyl (bromodichloromethyl)mercury with thiophosgene thiobenzophenone, and sulfur, Eq. (89), also appeared to proceed under slightly milder conditions than those employed in dichlorocarbene transfer to olefins (212).

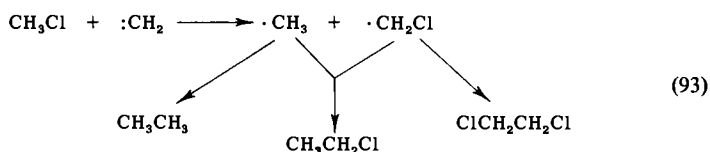


1,3-Dipolar addition of carbenes derived from benzene-1,2-diazooxides [92] (81) and their thio analog [93] (213) to carbon disulfide proceeded in fair to excellent yields. However, the compound obtained from the thermal decomposition of 3-diazobutan-2-one in CS_2 (214) was shown by X-ray analysis to be a 2-methylene-1,3-dithiacyclobutane [94] (215).

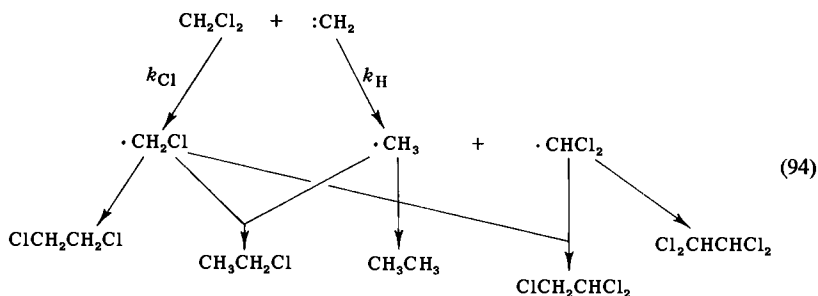


VI. ORGANIC HALIDES

The gas-phase reactions of methylene with methyl chloride (216–218) and methylene chloride (216, 219) take place predominantly by chlorine and hydrogen abstraction. In the case of methyl chloride, both abstraction processes give rise to the same intermediates, methyl and chloromethyl radicals. At pressures above 50 mm the products were ethane (30%), ethyl chloride (43%), and 1,2-dichloroethane (27%), formed by radical recombination. At lower pressures, elimination of hydrogen chloride from "hot" haloalkane molecules gave rise to ethylene and vinyl chloride. Addition of oxygen suppressed product formation completely, indicating that direct insertion was a negligible process (216).

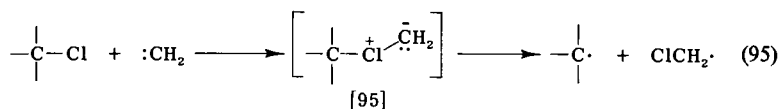


In the case of methylene chloride, hydrogen and chlorine abstraction are distinguishable. Abstraction of chlorine by CH_2 should generate chloromethyl radicals only, and 1,2-dichloroethane would be the sole product. Hydrogen abstraction leads to ethane and a variety of chlorinated ethanes, Eq. (94). From the product analysis it was concluded that $\sim 20\%$ of the reaction proceeded by hydrogen abstraction (216, 219). A similar figure was derived from the methylene–ethyl chloride system (220) where all the fourteen products of radical recombination have been identified.

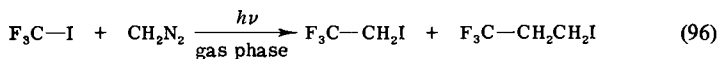


Methylene was generated in these experiments by the photolysis of ketene, and was a mixture of both triplet and singlet species. By studying the effect of added carbon monoxide (removes triplet CH_2 preferentially),

nitrogen (increases portion of triplet CH_2 by collisionally induced spin inversion), and of the wavelength of the incident light, it was concluded that chlorine abstraction was largely due to singlet methylene, whereas triplet methylene preferred hydrogen abstraction. A lower limit of $k_{\text{Cl}}/k_{\text{H}} \geq 16$ was set for the singlet; for the triplet, an upper limit of $k_{\text{Cl}}/k_{\text{H}} \leq 0.14$ was derived (220). Chlorine abstraction by singlet CH_2 and hydrogen abstraction by triplet CH_2 proceed with rate constants of comparable magnitude (220a). These conclusions were fully confirmed by studies of the gas-phase reactions of methylene with 1- and 2-chloropropane (221). Insertion of singlet methylene into C—H bonds plays an important part in the overall reaction of the higher chloroalkanes, but no C—Cl insertion was detected. Chlorine abstraction by singlet methylene may proceed via ylide [95] which undergoes homolytic fission at the original C—Cl bond (221).

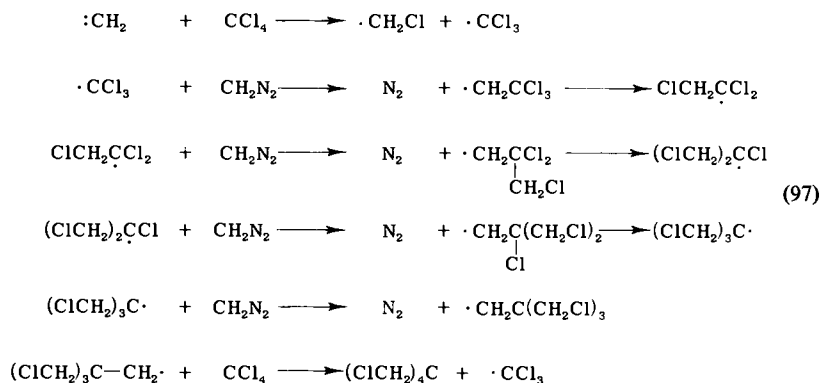


Little evidence is available on the mechanism of apparent C—Cl insertion by methylene in the liquid phase (222, 223). Different reactivities of various alkyl chlorides have been observed in competition experiments (223), but the dependence on structure is not clear. Few alkyl bromides have been studied (222, 224), but apparently they react very much like the chlorides. Haloalkyl radicals were generated by the abstraction reactions of methylene from CH_2Br_2 or CH_2BrCl ; methylene insertion was judged to be negligible (224). The carbon—fluorine bond, however, proved to be inert toward attack by methylene; only products of C—H insertion were obtained from CH_3F (225), CH_2F_2 (226), and CH_3CHF_2 (227). Trifluoroiodomethane reacted exclusively at the carbon—iodine bond (228).

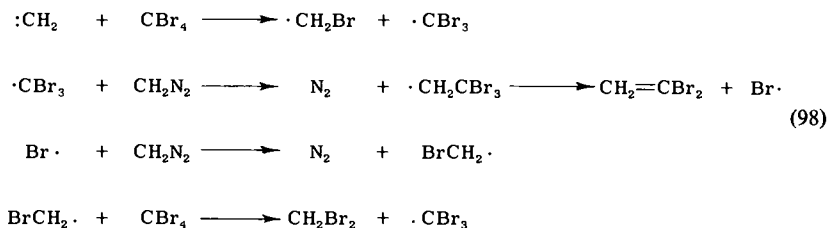


The reaction of diazomethane with polyhalomethanes in the liquid phase proceeds by a radical chain mechanism, Eq. (97), which is initiated by halogen abstraction. The fast migration of chlorine in the intermediate radicals is thought to prevent chain transfer at an early stage, and to make

$C(CH_2Cl)_4$ the major product from CCl_4 (229). The formation of compounds such as X_3C-CH_2Cl and $X_2C(CH_2Cl)_2$ was favored only at very low concentrations of diazomethane (230). The high quantum yield and the inhibiting effect of radical scavengers provide further support for the chain mechanism.

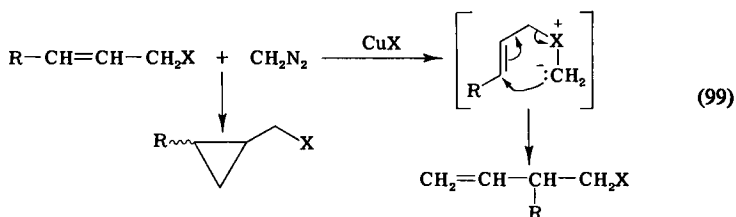


All tetrahalomethanes and haloforms containing at most one bromine atom react according to Eqs. (97). The radical intermediates derived from CBr_4 , CBr_2Cl_2 , $CHBr_3$, and CHI_3 , however, will eliminate $Br\cdot$ (or $I\cdot$) rather than rearrange (231). Methylene bromide and 1,1-dibromoethylene were the major products obtained from carbon tetrabromide and diazomethane.

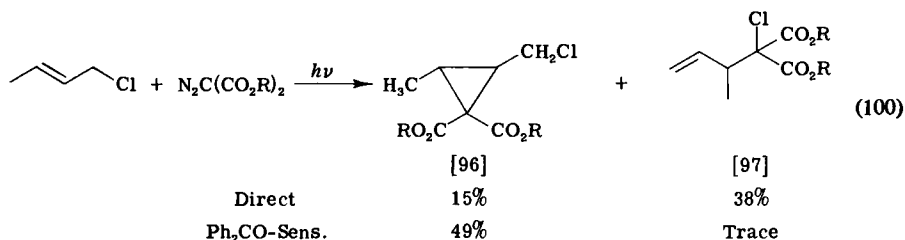


The carbenoid generated by cuprous halide-catalyzed decomposition of diazomethane does not attack the carbon-halogen bond except in allylic halides (232). Cyclopropanation of the $C=C$ bond of allylic halides was accompanied by apparent insertion of CH_2 into the allyl-halogen bond.

Allylic inversion was demonstrated in several cases, and suggests an ylide mechanism analogous to Eq. (58). The higher yields of 4-halobutenes from allyl bromide as compared to allyl chloride are in accord with the proposed mechanism.

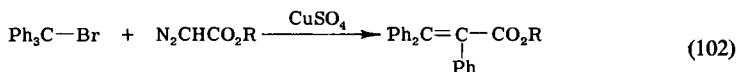
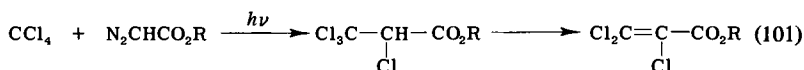


The direct photolysis of dimethyl diazomalonate in the presence of γ -methylallyl chloride also proceeded with allylic inversion to give α -methylallyl chloromalonate [97] and the cyclopropane [96] (233). Relative rates indicate that singlet bis(methoxycarbonyl)carbene attacks bromine and sulfur atoms about two times faster than it attacks chlorine in an allylic position. The benzophenone-sensitized photolysis of dimethyl diazomalonate resulted in addition and only a trace of insertion.



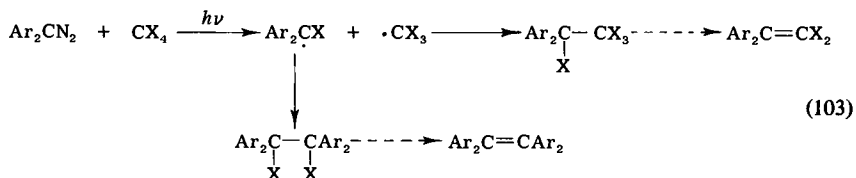
Ethoxycarbonylcarbene has been reported to give mixtures of isomers which result from insertion into allyl-halogen bonds with and without allylic inversion (234). Addition of ethoxycarbonylcarbene to the double bond competed effectively with insertion into the C-Cl bond of allyl chloride (235) and 2,3-dichloropropene (236), whereas no cyclopropanes have been obtained from allyl bromide and allyl iodide (235, 236). A duality of ylide and halogen abstraction mechanisms appears likely since ethoxycarbonylcarbene also "inserts" into the C-X bonds of polyhalo-

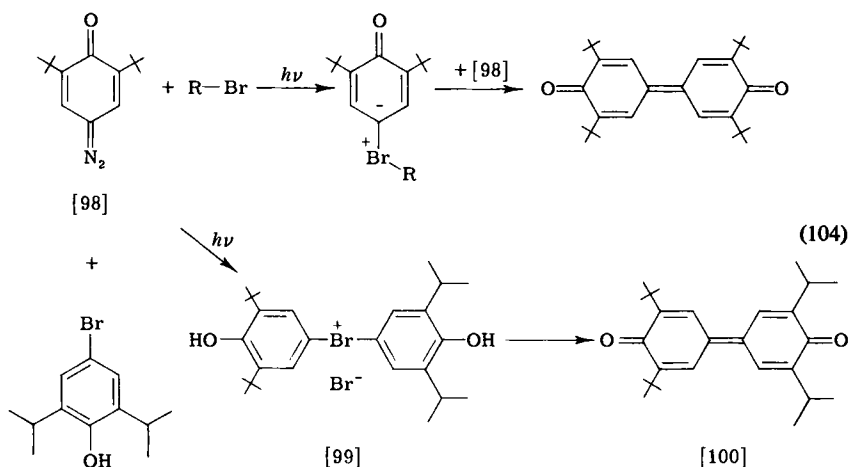
methanes (237), triarylmethyl- (238), and benzhydryl halides (239). "Insertion" was frequently followed by dehydrohalogenation, and ethyl haloacetates (indicative of halogen abstraction) were encountered as by-products.



Ando *et al.* (293a) argued against a radical chain mechanism of reaction (101) since they obtained different products from the radical-initiated decomposition of ethyl diazoacetate in CCl_4 , CHCl_3 , and CH_2Cl_2 . On the other hand, Roth *et al.* (239b) observed chemically induced dynamic nuclear polarization of unusually large relaxation time (ca. 70 sec) when ethyl diazoacetate was photolyzed in CCl_4 or CDCl_3 . They assumed that products are still being formed after the irradiation is discontinued, by way of a radical chain mechanism.

Halogen abstraction and combination of the radicals thus produced appears to be the major path of diarylcarbene reactions with polyhalomethanes (240, 241), Eq. (103). On the other hand, ylide formation plays an important part in the formation of diphenoquinones by photolysis of benzene-1,4-diazooxides [98] in the presence of halogen compounds (242). The isolation of the bromonium salt [99] lends support to the ylide mechanism, [99] being converted into the diphenoquinone [100] by triethylamine. Since halogen abstraction can be viewed as proceeding through an ylide intermediate, Eq. (95), the stability of the ylide and the reaction paths available to it will determine the course of carbene reactions with organic halides.





Both monofluorocarbene and difluorocarbene (produced by hot ^{18}F atom reactions with various precursors) reacted in direct insertion with hydrogen halides to form CH_2FX and CHF_2X , respectively (242a). Competitive studies showed rapidly decreasing reactivity toward CF_2 in the order $\text{HI} > \text{HBr} > \text{HCl}$.

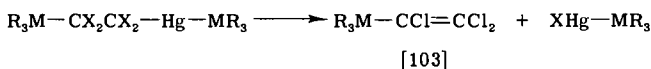
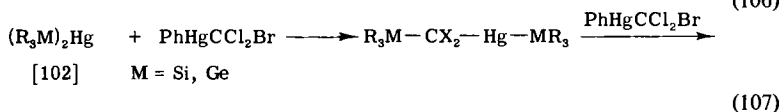
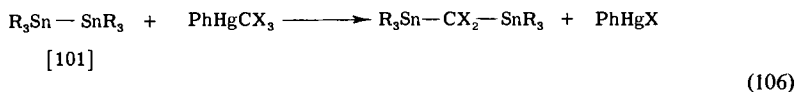
VII. ORGANOMETALLIC COMPOUNDS

Many reactions of metal halides with diazoalkanes have been reported which result in methylene transfer to the metal-halogen bond but do not involve carbene intermediates (Chapter 3). The synthesis of aryl(tri-halo-methyl)mercury compounds by reaction of arylmercury halides with haloform and base (243, 244) proceeds by nucleophilic displacement of halide by trihalomethide ion rather than by insertion of dihalocarbene into the $\text{Hg}-\text{X}$ bond (244). However, dichlorocarbene generated from ethyl trichloroacetate was found to insert into the $\text{C}-\text{Hg}$ bond of several dialkylmercury compounds (245, 246). $\beta\text{-C}-\text{H}$ insertion competed efficiently with $\text{C}-\text{Hg}$ insertion when secondary or tertiary β -hydrogens were available.

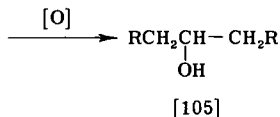
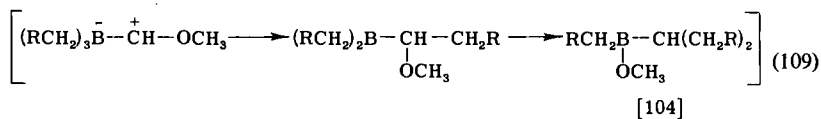
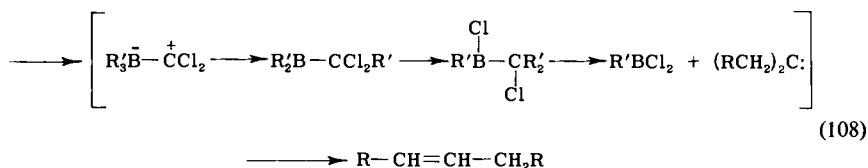
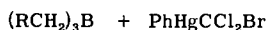


The first (and so far only) case of dihalocarbene insertion into a metal-metal bond to give a stable $\text{M}-\text{CX}_2-\text{M}$ system was observed when

hexaorganoditin compounds [101] were treated with PhHgCX_3 (247). The action of $\text{PhHgCCl}_2\text{Br}$ on bis(trialkylsilyl)mercury and bis(trialkylgermyl)mercury compounds [102] provided a novel route to trichlorovinylsilanes and -germanes [103] (248). A reasonable mechanism for the formation of [103] is given in Eq. (107).



Although dihalocarbenes are known as electrophilic reagents, trialkylboranes reacted with PhHgCX_3 (and, less efficiently, with $\text{Cl}_3\text{C}-\text{CO}_2\text{Na}$) to give olefins, probably as shown in Eq. (108) (249). Triarylboranes afforded trichlorovinylarenes in a reaction analogous to Eq. (107). Dichloromethyl methyl ether and methyllithium, the carbenoid equivalent of methoxycarbene, converted trialkylboranes into methoxydialkylboranes [104] which were oxidized to alcohols [105] (250).



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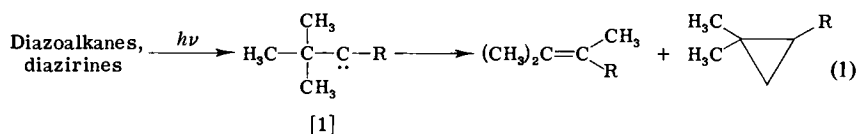
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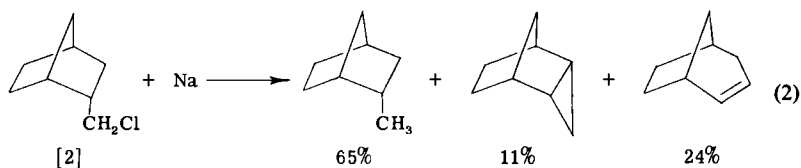
Rearrangements

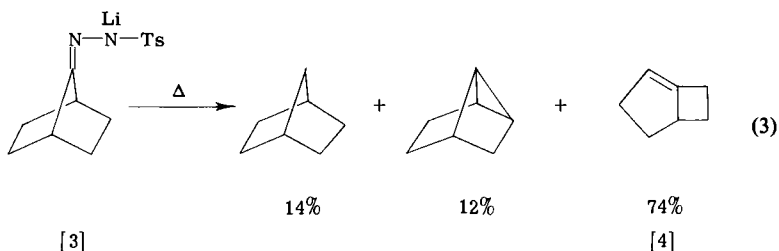
I. 1,2 SHIFTS IN ALKYL CARBENES

THE INTRAMOLECULAR INSERTION reactions discussed in Chapter 7, Section IV, include 1,2 shifts of hydrogen which do not lead to a reorganization of the structural framework. Intramolecular C—H insertion of alkylcarbenes of type **[1]** is accompanied by methyl migration, particularly when the carbenes are generated by photolysis of diazoalkanes or diazirines [cf. Tables IX and XI and Eq. (55) in Chapter 7].

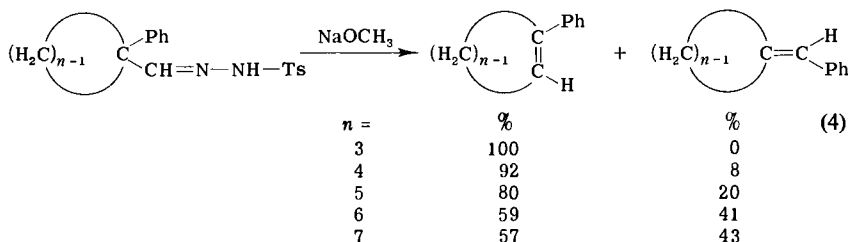


Alkyl migration is promoted by ring strain and by β -substituents such as aryl and alkoxy. Cyclopropylcarbenes undergo rearrangement and fragmentation exclusively; these reactions are treated in Section III of this chapter. Cyclobutylcarbene afforded 37% of cyclopentene together with products of intramolecular C—H insertion **[1]** (cf. Chapter 7, Section IV, Table XIII). Treatment of *endo*-2-chloromethylnorbornane **[2]** with sodium in an attempt to generate the corresponding carbene (carbenoid) by α -elimination led to considerable ring expansion, Eq. (2), (2). This reaction was not observed with the *exo* isomer of **[2]**, and only to the extent of 7% in the photolysis of the corresponding tosylhydrazone sodium salt (*2a*). Pyrolysis of the lithium salt of norbornan-7-one tosylhydrazone **[3]** gave bicyclo[3.2.0]-hept-1-ene **[4]** as the major product (3).

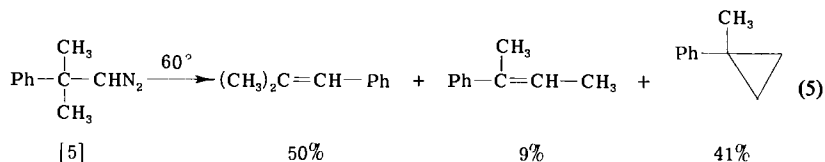




The promoting effect of β -phenyl groups on alkyl migration is obvious from the reactions of 1-phenylcycloalkylcarbenes, Eq. (4) (4, 5), compared to the behavior of cycloalkylcarbenes which undergo less than 2% of rearrangement when $n \geq 5$ (Chapter 7, Table XIII).

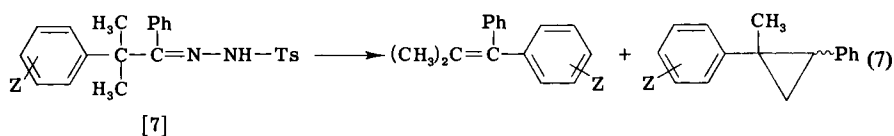
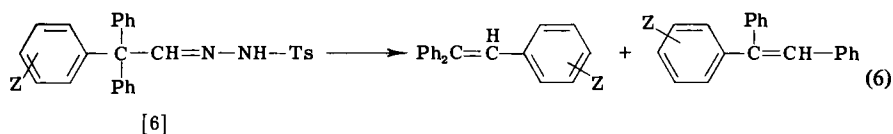


Equation (4) shows that 1,2 shift of phenyl competes efficiently with ring expansion. Early examples of phenyl migration were provided by the thermolysis of 2,2,2-triphenyldiazoethane which gave triphenylethylene as the sole product (6), and by the thermolysis of 2-methyl-2-phenyl-1-diazo-propane [5] (7). Lewis acid-catalyzed decomposition of [5] (which may involve a Lewis acid-carbene complex) led to a substantially higher fraction of methyl migration (8).

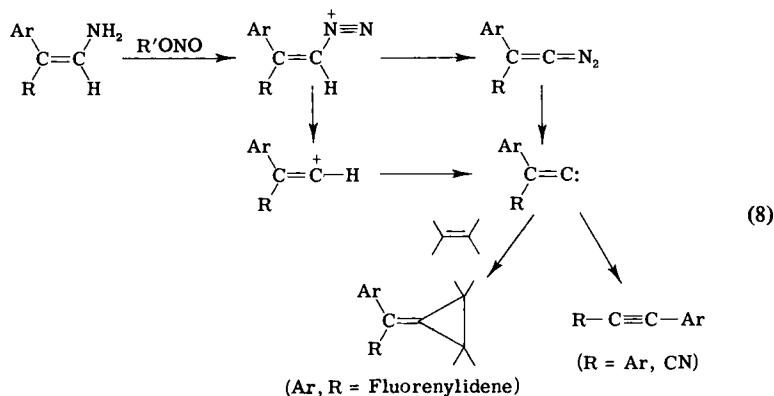


Relative migratory aptitudes of substituted phenyl groups were determined by thermal decomposition of the tosylhydrazones of triarylacetaldehydes [6] (9), and of α -arylisobutyrophenones [7] (10). In the former case, product analysis (oxidation followed by VPC of the methyl benzoates) gave migratory aptitudes which correlated linearly with σ^+

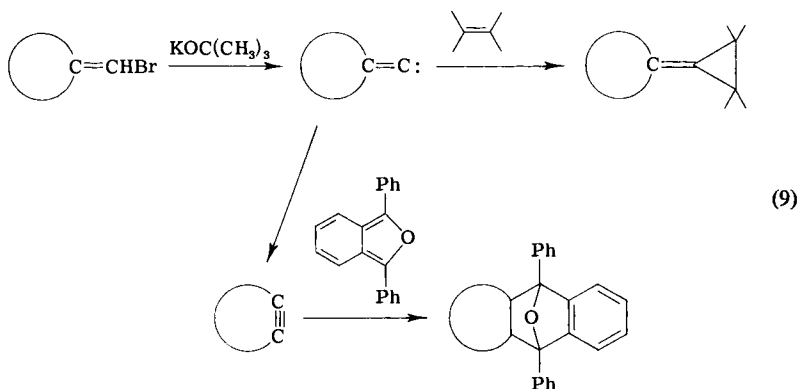
constants, $\rho = -0.28$. In reaction (7), the rate of cyclopropane formation was considered to be independent of the nature of the aryl group. Again a relationship of the data with σ^+ existed, exhibiting $\rho = -0.68$. Despite the divergent ρ values, both studies indicate a stabilization of the transition state of aryl migration by donor substituents. On the basis of migratory aptitudes, carbene intermediates have been excluded in certain base-induced rearrangements such as the formation of triphenylethylene from 2,2,2-triphenylethyl phenyl sulfone (11).



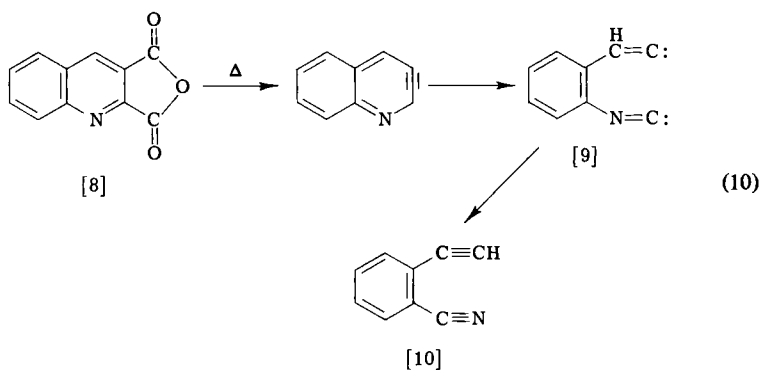
The formation of diarylacetylenes by dehydrohalogenation of 2,2-diarylvinyllalides (Fritsch-Buttenberg-Wiechell rearrangement; Chapter 3, Section III) has been recognized as a carbanion rearrangement. Nitrosation of 2,2-diarylvinyllamines, however, leads to the same products, and must proceed by either a cationic or a carbenoid path (12, 13). A carbene intermediate appears likely in view of the addition to olefins observed in such cases, where rearrangement would lead to excessively strained products (12).



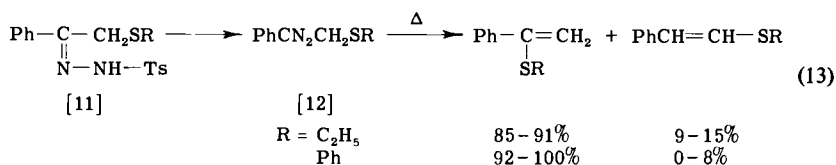
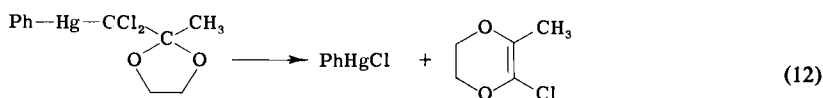
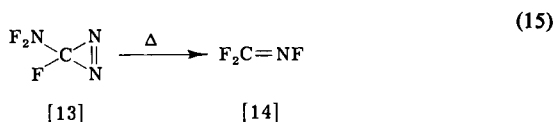
No definite mechanistic conclusions have been reached so far concerning the rearrangement of 2,2-dialkylvinyl halides on dehydrohalogenation (14). This reaction not only afforded dialkylacetylenes but also produced strained small-ring cycloalkynes which have been trapped in fair yield by 1,3-diphenylisobenzofuran, Eq. (9). Competitive addition to olefins suggests a carbenoid intermediate.



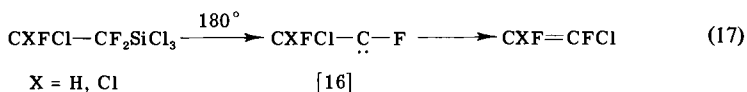
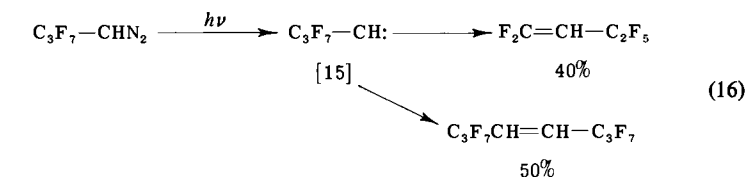
The gas-phase pyrolysis of quinoline-2,3-dicarboxylic acid anhydride [8] proceeded smoothly to yield (2-cyanophenyl)acetylene [10] (15). Since the related pyrolysis of phthalic anhydride produces benzyne, it was suggested that, in the case of [8], 2-quinolyne fragments to the carbenoid isonitrile [9] which subsequently rearranges to [10].



β -Alkoxyalkylcarbenes did not undergo alkoxy shift; rather, they displayed alkyl and hydrogen migrations promoted by the alkoxy group

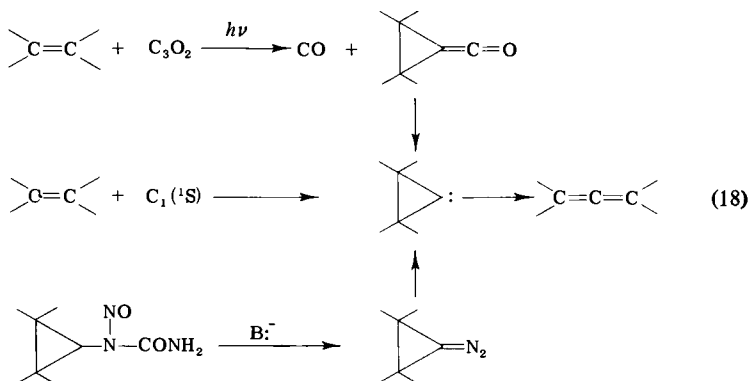
$$\begin{array}{ccc}
 (C_2H_5O)_2CH-CHN_2 & \longrightarrow & (C_2H_5O)_2C=CH_2 + C_2H_5OCH=CHOC_2H_5 \\
 & & \text{cis + trans} \\
 \begin{array}{cc}
 h\nu & 34\% \\
 \Delta, 160^\circ & 68\%
 \end{array} & & \begin{array}{cc}
 & 66\% \\
 & 32\%
 \end{array}
 \end{array} \quad (11)$$

$$\begin{array}{c} \text{CF}_3\text{CHN}_2 \xrightarrow[0.1 \text{ atm}]{h\nu} \text{CF}_3\text{CH} \cdot \xrightarrow{\text{CF}_3\text{CHN}_2} \text{F}_2\text{C}=\text{CHF} \quad 30\% \\ \downarrow \\ \text{CF}_3\text{CH}=\text{CHCF}_3 \quad 50\% \end{array} \quad (14)$$


In perfluoropropylcarbene [15], migration of a perfluoroalkyl group, rather than of fluorine, took place (19). Chlorine shift was preferred to fluorine shift in carbenes [16] which were generated by thermolysis of the appropriate alkyltrichlorosilanes (21).

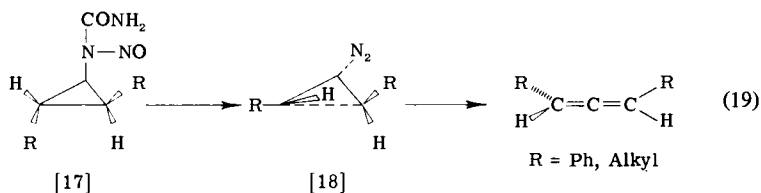


II. CYCLOPROPYLIDENE–ALLENE REARRANGEMENT

Cyclopropylidenes (carbenacyclopropanes) may be generated by decomposition of diazocyclopropanes, by addition of atomic carbon to olefins, and by photolysis of carbon suboxide in the presence of olefins. The studies with C_1 reveal that only singlet cyclopropylidenes rearrange to allenes (Chapter 8, Section I,B); this is in accord with theoretical expectation (22, 22a). The carbon suboxide reaction probably involves addition of C_2O to the olefin, followed by spontaneous decomposition of the highly energetic ketene thus produced (Chapter 2, Section III). Photolysis of C_3O_2 –alkene systems gave small amounts of acetylenes in addition to allenes (23), but the proportion of acetylenes decreased with increasing pressure and increasing molecular weight of the alkene.

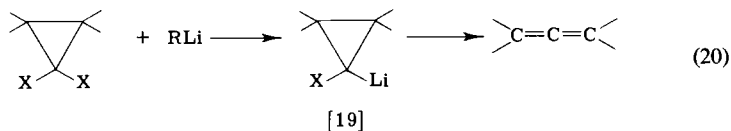


The conversion of *N*-nitroso-*N*-cyclopropylureas into allenes has been studied extensively by W. M. Jones and his co-workers. Both the diazo-cyclopropane and cyclopropylidene intermediates have been trapped by addition to alkenes, electrophilic alkenes (diethyl fumarate) reacting with the diazo compound, and nucleophilic alkenes accepting the carbene (24–26). When the decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea was performed in the presence of varying amounts of cyclohexene, a curved plot of the spiropentane to allene ratio vs. the concentration of alkene was obtained (26). The original conclusion was that both the diazocyclopropane and the cyclopropylidene were precursors to the allene. Later it was shown, however, that the curved plot resulted from a medium effect, and two distinct allene precursors were not required (27). The decomposition of optically active *N*-nitroso-*N*-(*trans*-2,3-diphenylcyclopropyl)urea [17] gave 1,3-diphenylallene exhibiting a high degree of rotation (28). Correlation of the absolute configurations of reactant and products (29) revealed that the rotation in [18] proceeded in a clockwise manner to avoid phenyl–phenyl interaction. The rotation of 1,3-diphenylallene decreased with increasing polarity of the solvent (27). The same kind of steric control by repulsion of the *trans* groups was observed in the conversion of (+)-2,3-dimethylcyclopropanecarboxylic acid to (+)-1,3-dimethylallene (30). Optically active 3,4-heptadiene and 5,6-nonadiene were prepared by the same route (31).

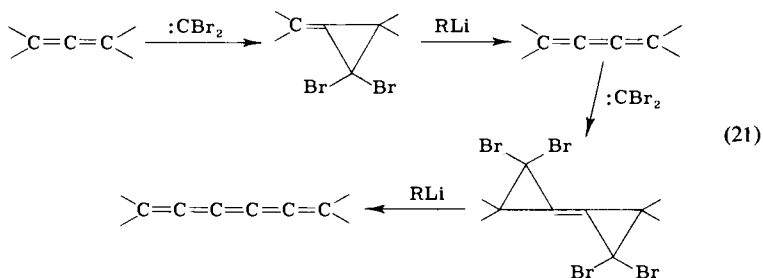


A very popular carbenoid modification of the cyclopropylidene–allene rearrangement is α -elimination of halogen from *gem*-dihalocyclopropanes by means of magnesium in ether (32–34), Grignard reagents (35), sodium on alumina (32), and, most efficiently, lithium alkyls (36, 37). A one-step olefine-to-allene conversion involves treatment of excess olefin with one equivalent of carbon tetrabromide and two equivalents of methyllithium in ether at -65° (38). The allenes produced by reaction between 1,1-dichlorocyclopropanes and allyllithium reagents showed chemically induced dynamic nuclear polarization (CIDNP) (39). The radical reaction which causes CIDNP is halogen–metal interchange. The fact that CIDNP was

observed in the allenes places the proton relaxation time (a few seconds) as an upper limit on the lifetime of 1-halocyclopropyllithium intermediates [19].

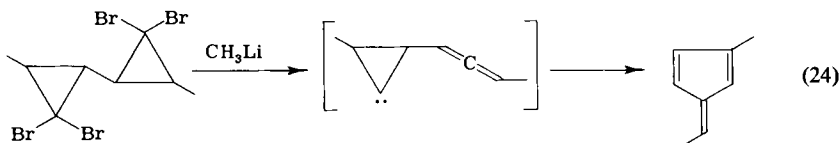
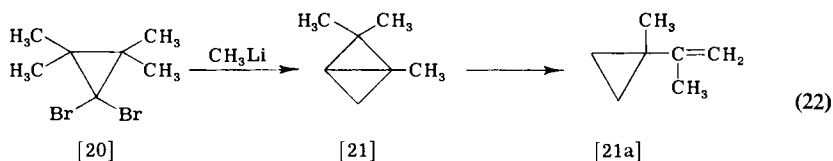


Reaction (20) has been brought about by Cr(II) sulfate, but competing reduction to monohalocyclopropanes and cyclopropanes occurred in some cases (40). By utilizing chromous (+)tartrate, asymmetric induction in the synthesis of cyclic allenes was achieved. Butyllithium in the presence of (–)spartein as a bidentate ligand served the same purpose even better (40). The ready access to the starting materials and the excellent yields of reaction (20) encouraged many synthetic applications. Cyclic allenes from cycloalkenes were hydrated to cycloalkanones by 88% sulfuric acid (41). Allenic alcohols made from allylic alcohols (42) were converted into α,β -unsaturated ketones by 20% phosphoric acid (43). *S*(+)-4-Methyl-1,2-hexadiene was prepared from *S*(+)-3-methyl-1-pentene (44). Both enantiomers of optically active *trans*-cyclooctene were converted to 1,2-cyclononadiene having a high optical purity (44a). 1,2,6,7-Cyclodecatetraene was obtained from 1,5-cyclooctadiene (44b). Application of reaction (20) to allenes afforded butatrienes (45, 46), e.g., 1,2,3-cyclodecatriene in 93% yield (47). At least one case of further conversion to an elusive hexapentaene has been reported (45).

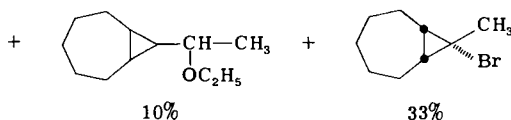
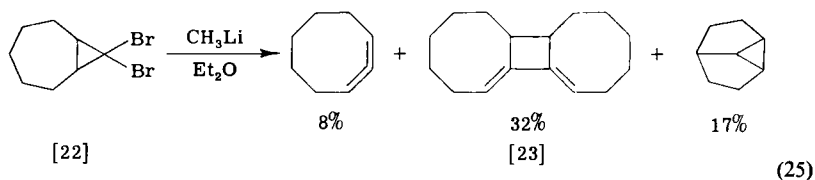


There are also some notable failures of reaction (20). The dibromocarbene adducts of tetraalkyl-substituted olefins, e.g. [20], gave bicyclobutanes, not allenes, as the major products (37, 37a). Acidic surfaces or

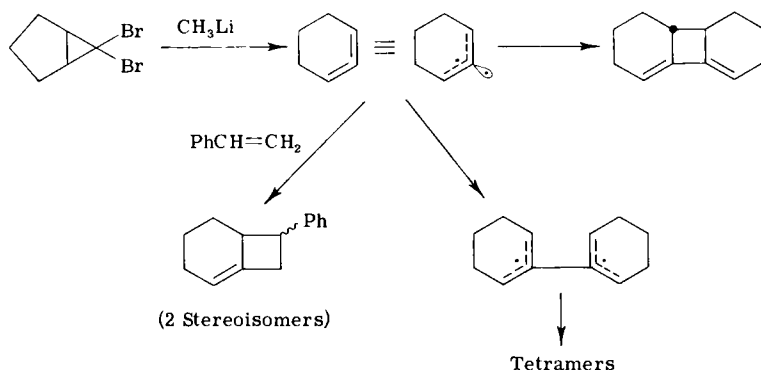
impurities cause isomerization of [21] to mainly olefin [21a]. Reactions of 1,1-dibromo-2-vinylcyclopropanes with methyllithium yielded cyclopentadienes as the main products, together with small amounts of allenic compounds (48), Eq. (23). With suitable reactants, derived from 1,3-dienes, the products were fulvenes, Eq. (24).



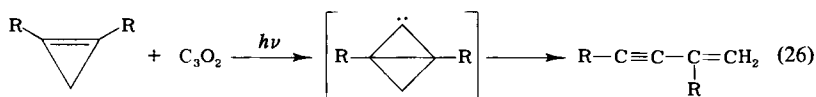
Ring size imposes restrictions on the formation of cyclic allenes. 1,2-Cyclononadiene is a fairly stable compound, but attempts to prepare 1,2-cyclooctadiene from 8,8-dibromobicyclo[5.1.0]octane **[22]** failed (49). Although the desired allene was detected by IR and catalytic hydrogenation in ~8 % yield immediately after quenching the reaction mixture, the major product was its dimer **[23]**. The carbenoid intermediate also reacted by intramolecular C—H insertion, attack on the solvent, and displacement with methyllithium.



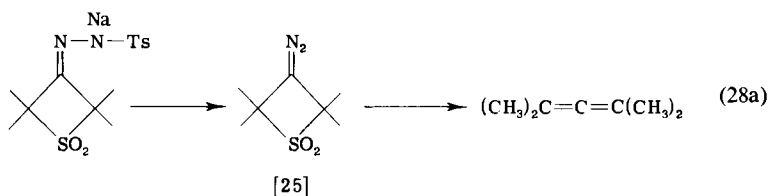
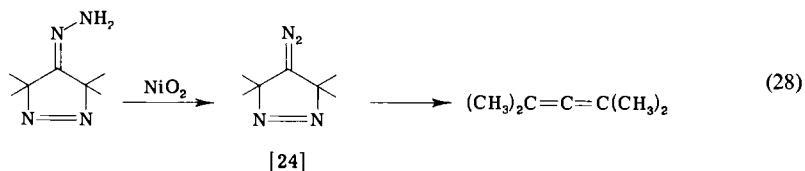
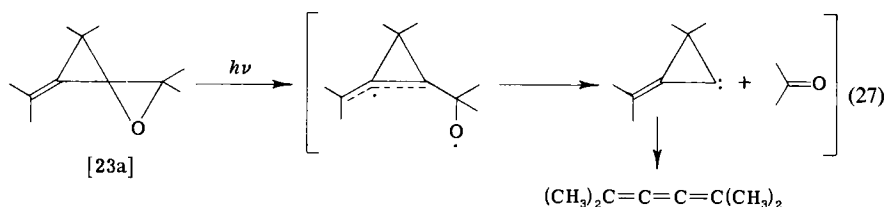
No indication of an allene was obtained in the reaction of 7,7-dibromonorcarane with methyllithium, the products being derived by intramolecular and intermolecular C—H insertion, and by apparent dimerization of the carbenoid (50, 51). In contrast, the reaction of 6,6-dibromobicyclo[3.1.0]hexane with methyllithium in ether gave no products derived from a carbenoid. The major products were a dimer and two stereo-isomeric tetramers of the hypothetical 1,2-cyclohexadiene which was also trapped by addition to styrene (51*a*). Analogous intramolecular C—H



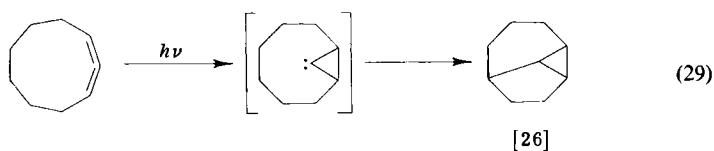
insertion of carbenabicyclobutanes would provide a simple route to tetrahedranes. However, the photolysis of carbon suboxide in the presence of 1,2-dimethylcyclopropene (52) and cyclopropene (53) produced alkenynes as the major products; tetrahedranes have not been detected. Experiments with cyclopropene-3,3- d_2 , however, resulted in a deuterium distribution among the acetylenes which is consistent with a tetrahedrane intermediate (53*a*).



Less conventional approaches to cyclopropylidenes include photolysis (2537 Å) of the strained oxaspiropentane [23*a*] which, among other products, gave tetramethylbutatriene (54). Diazo compounds [24] and [25], generated from suitable precursors, decomposed with extrusion of N_2 and SO_2 , respectively, in addition to the loss of diazo nitrogen (55). Whether these reactions proceed in two steps or in a concerted fashion is not known, but all attempts to trap intermediates have been unsuccessful.



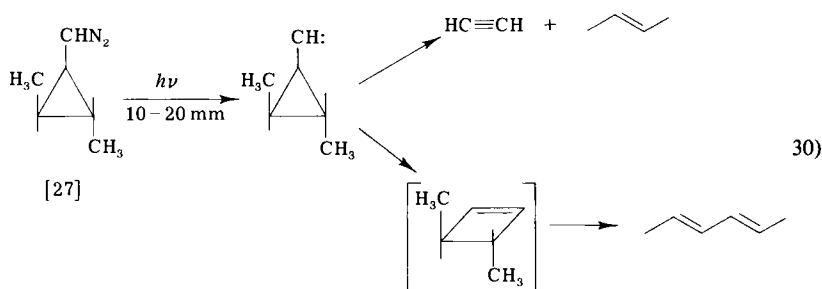
It appears that the cyclopropylidene-allene rearrangement can be reversed photochemically. Irradiation of 1,2-cyclononadiene gave tri-cyclo[4.3.0.0^{2,9}]nonane [26], $\phi = 0.17$ (56). The formation of [26] is rationalized in terms of allene-cyclopropylidene rearrangement followed by intramolecular C—H insertion. Alternative diradical mechanisms are unattractive on thermodynamic grounds. A similar, though less efficient ($\phi = 0.005$), reaction converted 1,2-hexadiene into bicyclo[3.1.0]hexane.



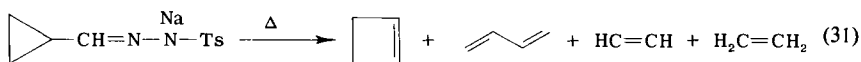
III. REARRANGEMENT AND FRAGMENTATION OF CYCLOPROPYLCARBENES

Cyclopropylcarbenes, generated from diazomethylcyclopropanes, rearrange to cyclobutenes and butadienes and decompose to alkenes and alkynes. Probably not all of these reactions are independent. Gas-phase

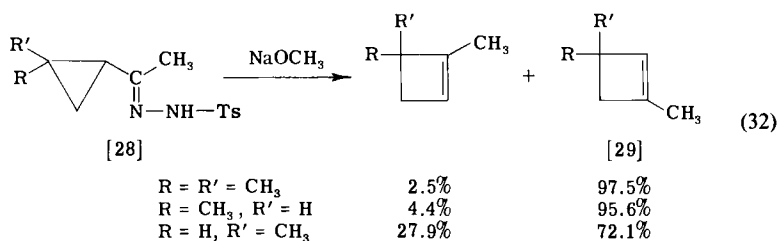
photolysis of cyclopropyldiazomethane (57) and *trans*-2,3-dimethylcyclopropyldiazomethane [27] (58) produced little, if any, cyclobutenes. A high degree of stereospecificity was observed when the photolysis of [27] was carried out at low pressures, *trans*-2-butene and *trans,trans*-2,4-hexadiene being the major products. The results suggest that the singlet carbene rearranges in a concerted fashion to *trans*-3,4-dimethylcyclobutene which then undergoes a thermal conrotatory ring opening. Deexcitation of the carbene by added nitrogen reduced the overall ring scission yield and the stereospecificity (58).



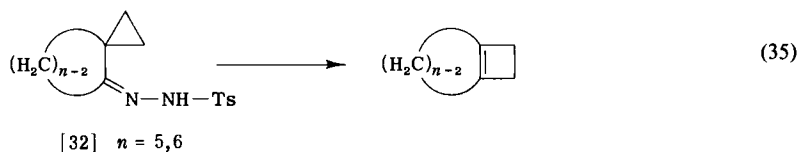
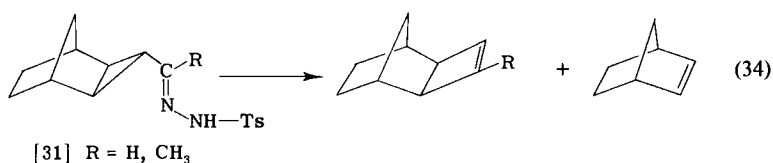
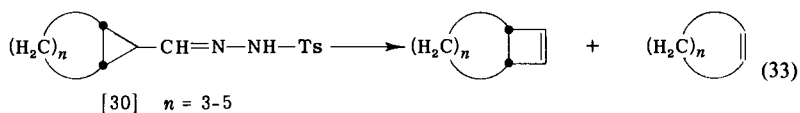
With cyclopropanecarboxaldehyde tosylhydrazone as the carbene precursor, cyclobutene was the major product (83–85%) under strictly aprotic conditions and with a small excess of sodium methoxide (59, 60). The relative yield of butadiene increased with a large excess of base, whereas fragmentation remained below 10%. Bicyclobutane, first observed among the reaction products by Frey (61), was not produced under aprotic conditions, and was shown to arise from poorly solvated cyclopropylcarbonium (or diazonium) ions rather than from cyclopropylcarbene (62, 63).



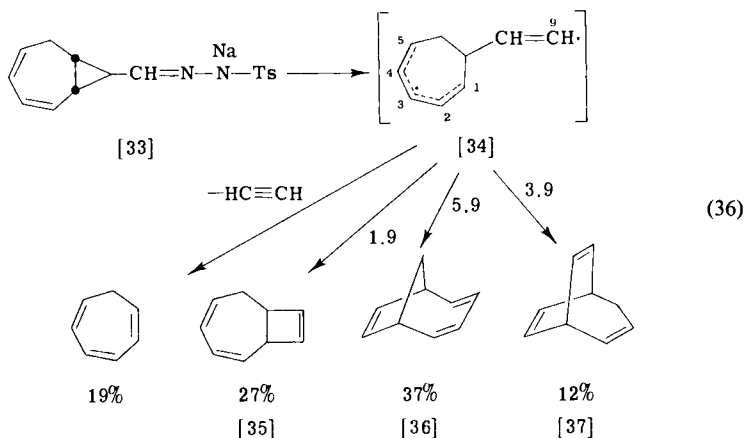
Various substituted cyclobutenes were obtained in fair to excellent yields by the tosylhydrazone procedure: 1-methylcyclobutene (92%) (59), 1-phenylcyclobutene (78%) (60), 1,2-diphenylcyclobutene (76%) (64), 3,3-dimethylcyclobutene (65), and 1-cyclopropylcyclobutene (41%) (65, 66). In all three cases of unsymmetrically substituted cyclopropyl ketones [28] which were studied, the predominant product [29] was formed by migration of the less substituted bond of the cyclopropane ring (65).



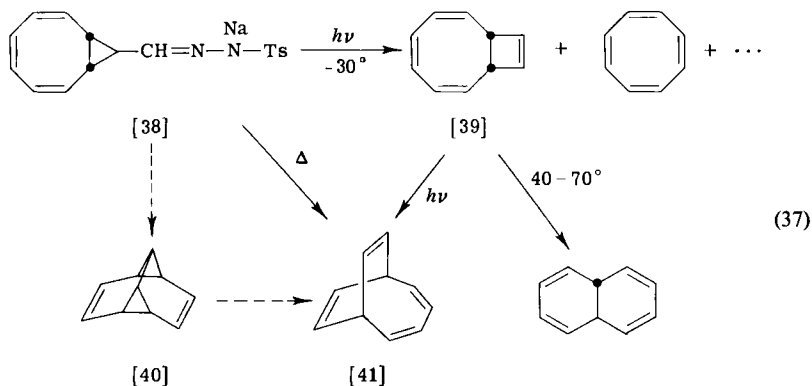
Bicyclo[*n*.1.0]alkylcarbenes generated from the tosylhydrazones [30] reacted with ~70% rearrangement and ~30% fragmentation (67). Similar ratios were observed with tricyclic precursors [31] (68). Spiro[2.*n*]-alkanone tosylhydrazones [32], *n* = 5, 6, rearranged smoothly (69), but an azine was the only product isolated from the decomposition of [32], *n* = 4 (70).



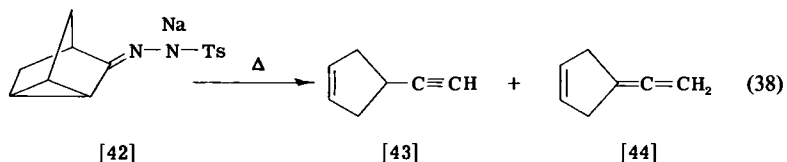
More complex product mixtures were obtained from tosylhydrazones of the bicyclo[5.1.0]octa-2,4-diene and bicyclo[6.1.0]nona-2,4,6-triene series. Thus [33] afforded cycloheptatriene plus three C₉H₁₀ hydrocarbons, [35]–[37] (71). Product [35], which was expected from cyclopropylcarbene rearrangement, could be pyrolyzed to *cis*-8,9-dihydroindene but did not produce [36] and [37]. The diradical [34] was therefore considered to be a plausible intermediate of the fragmentation and rearrangement processes.



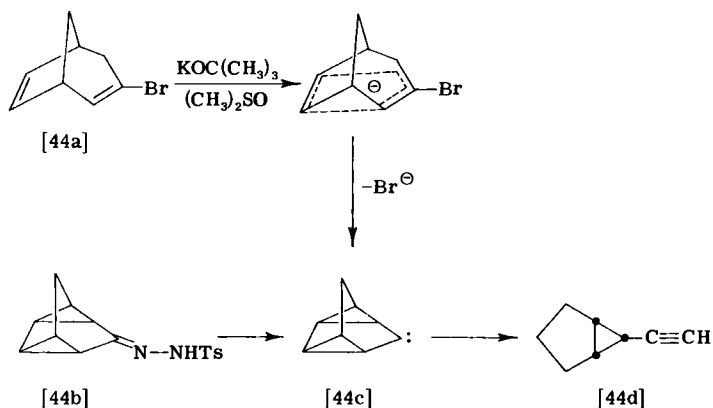
Thermal decomposition of bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde tosylhydrazone **[38]** gave cyclooctatetraene, dihydronaphthalene, and **[41]**, but not the expected **[39]** (72, 72a). Photolysis of **[38]** at -30° and workup below 0° , however, led to the isolation of **[39]** which isomerized to *trans*-9,10-dihydronaphthalene at $40-70^\circ$ (73). Irradiation of **[39]** afforded **[41]**. Since **[41]** was also obtained in the thermolysis of **[38]**, other routes to **[41]** should be available, e.g., by way of **[40]**. Deuterated **[38]** afforded **[41]** with deuterium scrambling over the 3,4,7,8, and 9,10 positions (74). Compound **[40]** was postulated as an intermediate in the degenerate rearrangement of **[41]**.



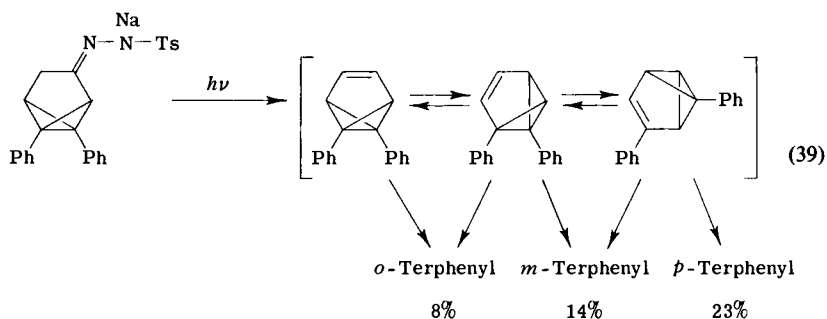
Several geometrically constrained cyclopropylcarbenes prefer fragmentation to rearrangement. The sodium salt of nortricyclanone tosylhydrazone [42] yielded 3-cyclopentenylacetylene [43] and the allene [44]; the latter arises by base-catalyzed rearrangement of [43] (75, 76). The reaction of nortricyclyl chloride with sodium did not give [43] and [44]; apparently it proceeds by a carbanion route rather than by a carbene mechanism (77).



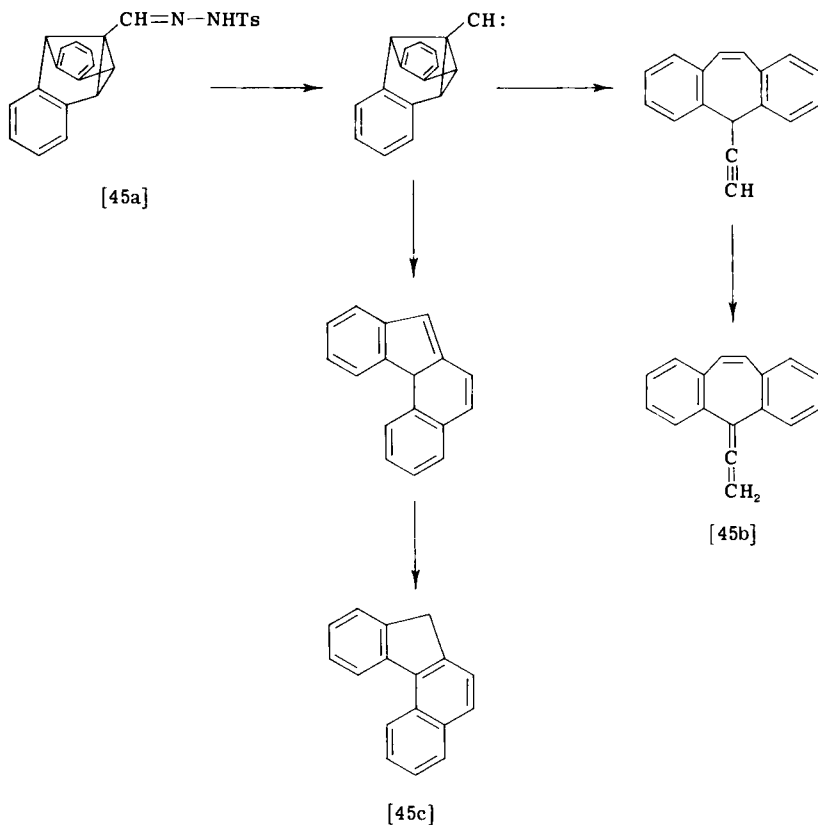
The base-induced elimination of HBr from 3-bromobicyclo[3.2.1]octa-2,6-diene [44a] and the alkaline pyrolysis of the quadricyclic tosylhydrazone [44b] both produced 6-ethynylbicyclo[3.1.0]hex-2-ene [44d]. A common carbene intermediate [44c] appears likely (77a).



Analogous fragmentation, plus some hydrogen shift, was observed with the tosylhydrazones of bicyclo[3.1.0]hexan-2-ones (78), including sabina ketone, dihydroumbellulone, and 2-caranone (79). Hydrogen shift predominated over fragmentation in the photolysis of the sodium salt of 5,6-diphenyltricyclo[3.1.0.0^{4,6}]hexan-2-one tosylhydrazone [45]. The isomer distribution of the terphenyl products suggests rapid rearrangement of a benzvalene intermediate (80).

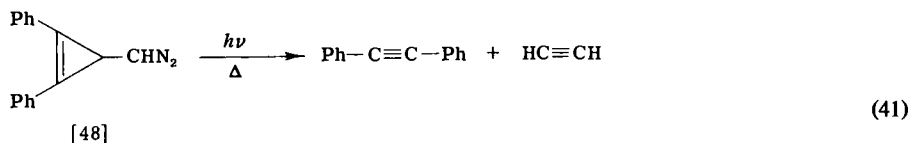
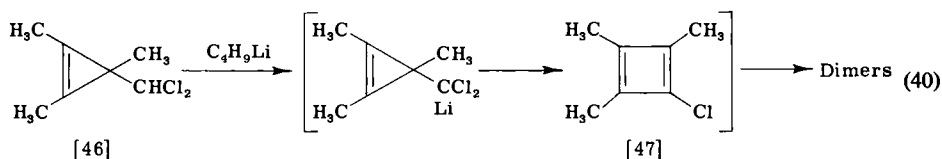


The decomposition of dibenzosemibullvalene-1-carboxaldehyde tosylhydrazone [45a] afforded 3,4-benzofluorene [45c] and the allene [45b] in a 2 : 1 ratio (80a). As a result of D-labeling and D-incorporation studies, an unprecedented 1,3 aryl shift leading to [45c] has been suggested.



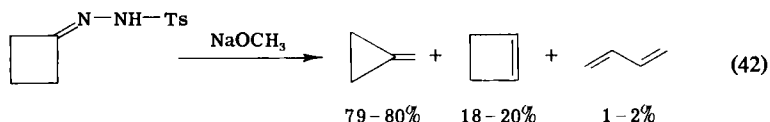
Attempts to generate cyclopropylcarbene by insertion of carbon (^1S) atoms into C—H bonds of cyclopropane led to methylene cyclopropane as the major product (81). The product distribution of this solid-phase reaction differed not only from that observed in the decomposition of cyclopropyldiazomethane, but also from that obtained in C^{11} reactions with liquid and gaseous cyclopropane (57). The reasons for this unusual phase dependence are not yet understood.

Cyclopropenylcarbenes, when rearranging in analogy to cyclopropylcarbenes, should produce cyclobutadienes. Treatment of 3-dichloromethyl-1,2,3-trimethylcyclopropane [46] with butyllithium at -20° did afford dimers of 1-chloro-2,3,4-trimethylcyclobutadiene [47] in 85% yield (4 stereoisomers) (82). Since 3,4-dichloro-1,2,3-trimethylcyclobutene was inert toward butyllithium under these conditions, a carbenoid rearrangement appears most likely. In contrast, photolysis and thermolysis of 1,2-diphenylcyclopropenyldiazomethane [48] led exclusively to fragmentation (83).



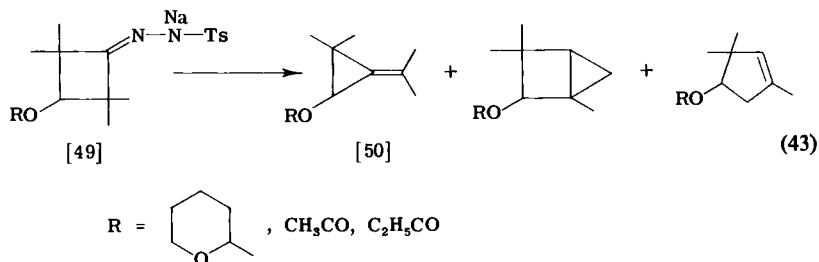
IV. CYCLOBUTYLIDENE-METHYLENECYCLOPROPANE REARRANGEMENT

The tosylhydrazones of cyclobutanone (59) and of 2,2,4,4-tetramethylcyclobutanone (84) afforded methylenecyclopropanes as the major products when pyrolyzed in the presence of excess sodium methoxide.

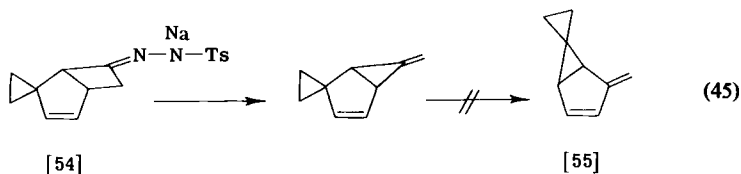
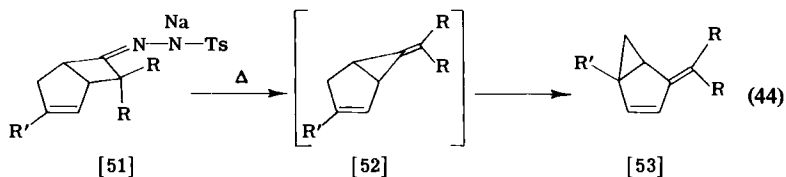


Because structure [50], $R = C_2H_5CO$, had been incorrectly assigned to the sex attractant of the female American cockroach (*Periplaneta Americana* L.), many attempts were made to synthesize [50] by cyclobutylidene-methylenecyclopropane rearrangement (85–87). Moderate

yields of [50], $R = C_2H_5CO$ and CH_3CO , were obtained by dry pyrolysis of the corresponding sodium salts [49] with copper powder (87). Under these conditions, [50] was accompanied by bicyclo[2.1.0]pentane and cyclopentene derivatives. Pyrolysis and photolysis of [49] in solution were less successful, giving bicyclopentanes (85), cyclobutenes (86), hexatrienes (86), and much azine (85), but not [50].

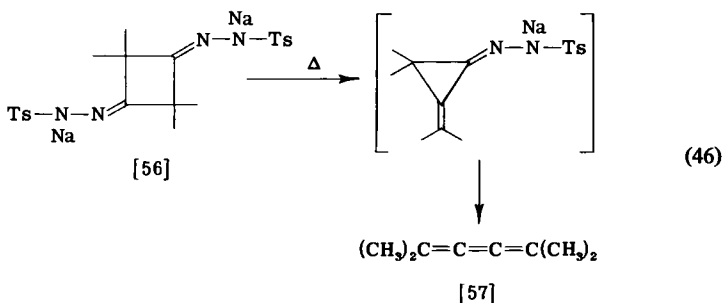


Homofulvenes [53] were among the hydrocarbon products formed in the thermal decomposition of the sodium salts of the tosylhydrazones of bicyclo[3.2.0]hept-2-en-6-ones [51] (88). Homofulvene formation may be rationalized by ring contraction of the carbene followed by a valence isomerization of [52] which releases ring strain and profits from the conjugation in [53]. A methylenecyclopropane was obtained from [54], the strain in the spirocyclopentane system of [55] presumably offsetting the homofulvene stabilization (88).

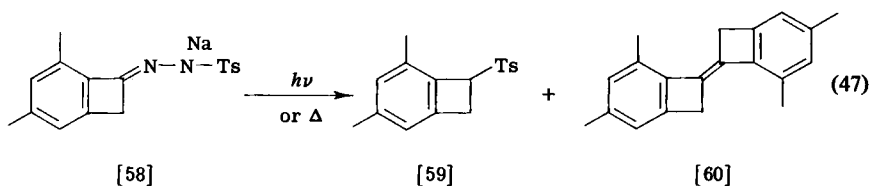


Carefully controlled thermolysis of the disodium salt of tetramethylcyclobutane-1,3-dione ditosylhydrazone [56] gave tetramethylbutatriene [57] (89, 90). Ring contraction of the cyclobutylidene is combined with

cyclopropylidene-allene rearrangement. In contrast, photolysis of [56] in the presence of methanol afforded 2,4,4-trimethyl-3-pentenal and its dimethyl acetal, presumably via carbonium ions (91).

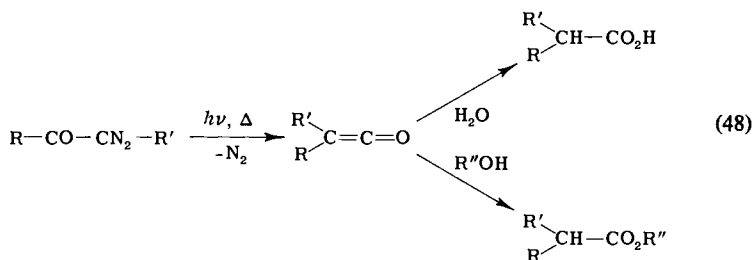


As might be expected, the tosylhydrazone of 4,6-dimethylbenzocyclobutenone [58] was not capable of ring contraction to a methylenebenzocyclopropene. The products were sulfone [59] and dimer [60] (92).



V. WOLFF REARRANGEMENT OF DIAZO KETONES

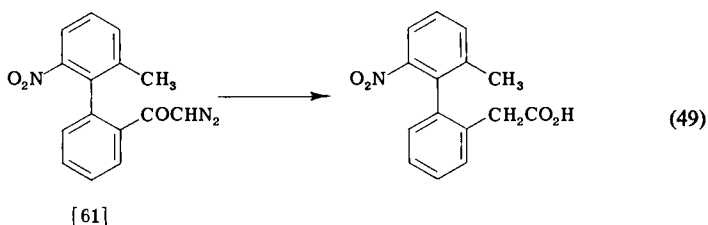
When decomposing dicarbonyl diazo compounds in aqueous solution, Wolff (93) isolated products formed with rearrangement of the carbon skeleton. Later he realized that his reaction was analogous to the Curtius degradation of carbonyl azides. The products were rationalized by assuming a ketene intermediate (94) after Schroeter (95) had obtained diphenylketene from the thermolysis of phenylbenzoyldiazomethane. The Wolff rearrangement did not attract much attention until an efficient synthesis of diazo ketones, RCOCHN_2 , from acid chlorides and diazo-methane was developed (96, 97). More recently, ready access to diazo ketones, $\text{RCOCN}_2\text{R}'$, was provided by the tosylhydrazone and tosyl azide procedures (98). Availability of the starting materials triggered an avalanche of mechanistic and preparative work which has been summarized in several review articles (98–103). Much special information may be obtained from these reviews which has not been incorporated in this section.



A. Mechanism of the Wolff Rearrangement

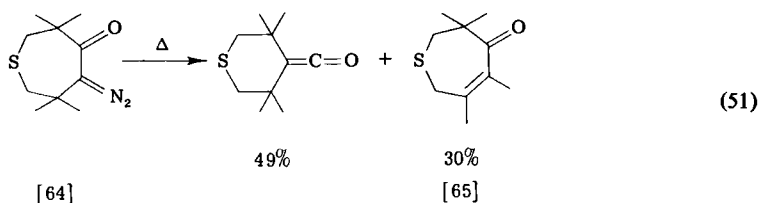
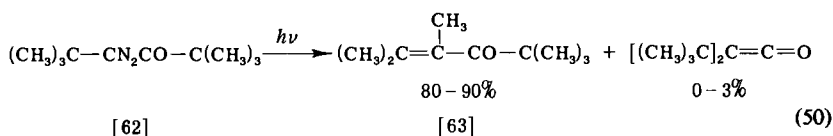
Does the Wolff rearrangement proceed by a concerted process, with migration and loss of nitrogen occurring simultaneously? Or does it involve an intermediate? If so, what is the structure of the intermediate? Despite the wealth of data which have been gathered, no definitive answers to these questions are available as yet.

Studies with optically active diazo ketones have demonstrated predominant or complete retention of configuration of the migrating group (104–108). Homologization of *cis*,*trans* pairs of 2-phenylcyclohexanecarboxylic acid (109) and cyclohexene-3,4-dicarboxylic acid (110) led to the same result. Even diazo ketone [61], the optical activity of which depends on hindered rotation about the bond connecting the two phenyl rings, afforded an optically active homologous acid (111). These observations are consistent with both a concerted mechanism and an electron-deficient intermediate.

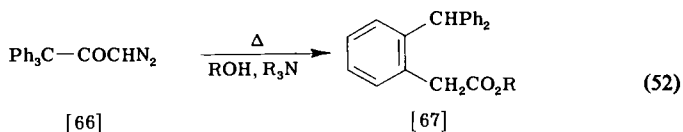


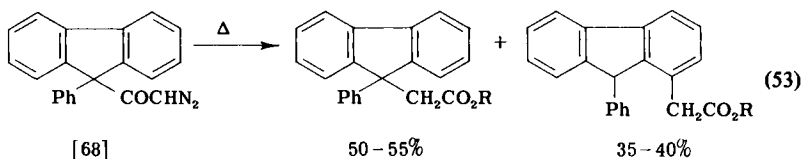
Support for a concerted mechanism of the Wolff rearrangement comes from stereochemical considerations. Studies of hindered internal rotation about the C—C bond in diazo ketones by NMR spectroscopy (112) have shown that diazo ketones exist as an equilibrium mixture of *cis* and *trans* forms. A *cis* relationship of diazo and carbonyl group is highly preferred in diazo ketones of the type R—COCHN₂. The electronic spectra of these

diazo ketones could be satisfactorily interpreted in terms of energy levels calculated for each pair of conformers on the basis of the EHT method (113). The *cis* form presents the desirable feature of the migrating group being *trans* to the leaving group. Consideration of models of [62] shows that the *cis* form would be virtually nonexistent owing to the large steric interaction of the *t*-butyl groups. In fact, decomposition of [62] produced little, if any, ketene. Methyl shift with formation of an unsaturated ketone [63] was the major reaction (114). In contrast, [64] decomposed spontaneously at room temperature to give ketene and acid in a combined yield of 49% plus 30% of an unsaturated ketone [65] (115). The conformation of the seven-membered ring in [64] is such that the diazo function and carbonyl group are skew to each other. The difference in behavior of [62] and [64] is in accord with a conformational control of the Wolff rearrangement.



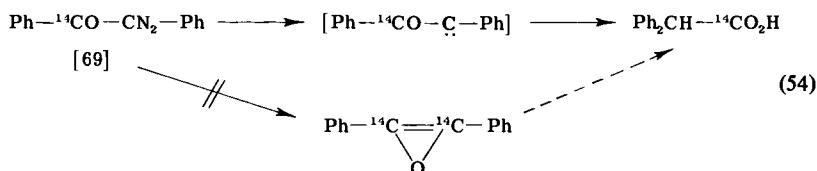
The "abnormal" rearrangement of triaryldiazoacetones has been interpreted in a similar manner (116). Thermolysis of [66] afforded the abnormal product [67], whereas [68] produced both normal and abnormal products. Photolysis of both [66] and [68] led to normal products only. It was concluded that steric factors were important in the thermal reaction, impeding normal rearrangement of [66].



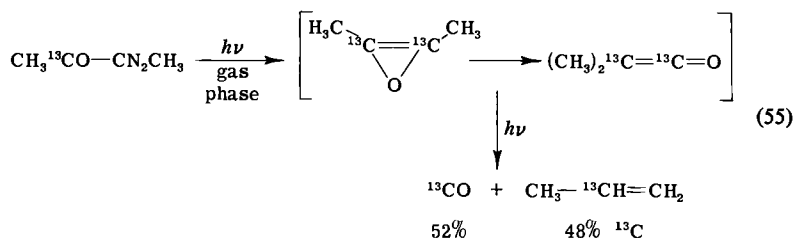


Kinetic studies, however, do not support a concerted mechanism. Electron-releasing substituents on the migrating aryl group strongly retarded the thermolysis of diazoacetophenones (117) and phenylbenzoyldiazomethanes (118, 119, 119a). The opposite effect would be expected if the migrating aryl group participated in the extrusion of nitrogen. Furthermore, no kinetic isotope effect was observed in the Wolff rearrangement of carbonyl- ^{14}C - and phenyl-1- ^{14}C -labeled diazoacetophenone (120).

Eventual intermediates of the Wolff rearrangement may have carbonylcarbene and/or oxirene structure. The latter possibility has been tested by labeling of the carbonyl carbon. Homologization of benzoic acid-1- ^{13}C led to quantitative incorporation of the ^{13}C label in the carboxyl group of the resulting phenylacetic acid (121). More conclusively, a study with phenylbenzoyldiazomethane- ^{14}C [69] demonstrated the absence of an oxirene, or other symmetrical intermediate, in the rearrangement (122).

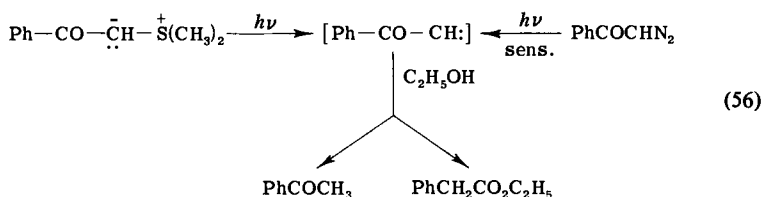


A recent reinvestigation of the Wolff rearrangement in the gas phase led to divergent results (123). The ketenes formed from ^{13}C -labeled diazo ketones subsequently underwent photolysis to yield carbon monoxide and olefins. Both products contained comparable amounts of ^{13}C when a symmetrical oxirene could be formed. Appreciable scrambling was found even with diazoacetone-2- ^{13}C . The cause of the discrepancy with earlier work in the liquid phase is not clear.



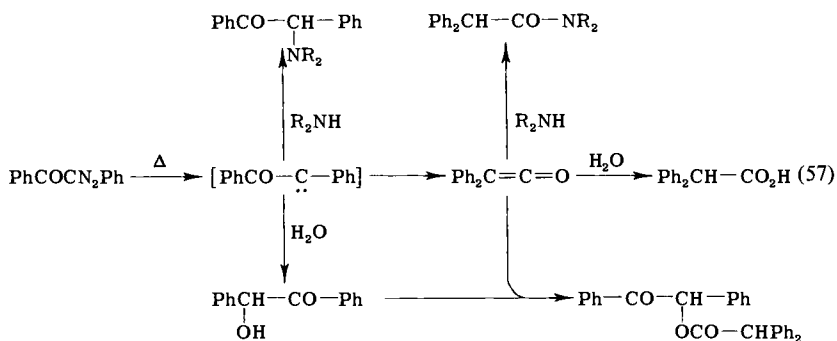
The product pattern obtained by oxidation of di-*tert*-butylacetylene and cyclodecyne with *m*-chloroperbenzoic acid was consistent with the intervention of a ketocarbene (123a). There is no rigorous evidence, however, that an oxirene precedes the ketocarbene in these reactions.

Obvious ways of supporting a carbonylcarbene intermediate are: (i) generating the intermediate from different precursors, and (ii) diverting the intermediate to reactions other than rearrangement. α -Ketodiazirines undergo Wolff rearrangement (124), but previous rearrangement to the diazo ketone cannot be definitely excluded. More conclusively, the intermediate generated from dimethylsulfoniumphenacylide [70] by photolysis behaved very much like that produced by photosensitized decomposition of diazoacetophenone (125).

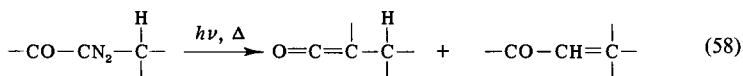


Equation (56) shows also partitioning of the intermediate between abstraction and rearrangement processes. However, the intervention of triplet species (sensitized photolysis of diazoacetophenone leads to more abstraction than direct photolysis) (126), the effect of substituents and of solvent (126, 127), and the possibility of radical chain reactions (128) are complicating factors in identifying the intermediate. Extraneous nucleophiles seem to be better suited for this purpose. The thermal Wolff rearrangement of phenylbenzoyldiazomethane in the presence of amines yielded diphenylacetamides and 1,2-diphenylethylamines, Eq. (57). The rate constants of the unimolecular reaction were found independent of the concentration and basicity of the amine by Jugelt and Schmidt (119),

whereas Bartz and Regitz (119a) observed a linear increase with the concentration of arylamines. Thermolysis in dioxane–water mixtures gave diphenylacetic acid and the benzoin ester of diphenylacetic acid. Although in this case the rate increased with increasing dielectric constant of the mixture, no deuterium solvent isotope effect was apparent (119). This observation excludes direct reaction of the diazo ketone with acid and supports the mechanism outlined in Eq. (57).

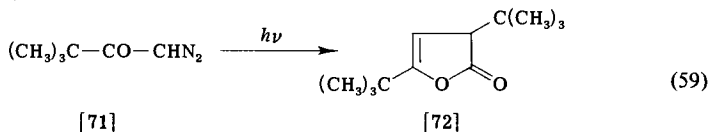


Diazo ketones containing C—H bonds adjacent to the diazo group were found to undergo hydrogen shift in competition with Wolff rearrangement (129). Although hydrogen shift is a familiar reaction of alkylcarbenes and may be mentioned in favor of a divalent carbon intermediate, the increase in rearrangement at higher temperatures lends itself also to an interpretation in terms of conformational control (112).

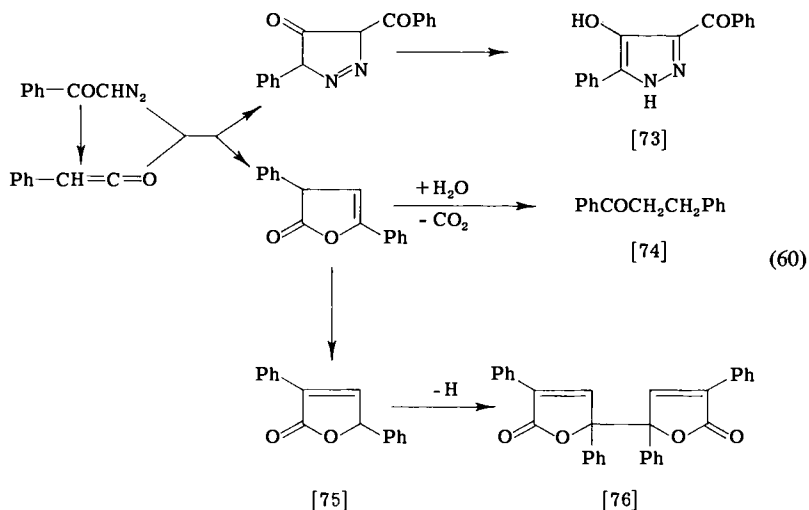


B. Products Derived from Ketenes

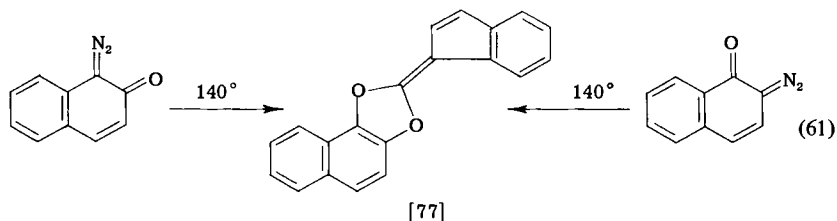
Ketenes originating from a Wolff rearrangement can give rise to a large variety of products. Reactions with water, alcohols, amines, etc., to give carboxylic acid derivatives deserve no further comment. In the absence of such nucleophiles, ketenes react with excess diazo ketone to form butenolides, e.g., [72] from 3,3-dimethyl-1-diazobutan-2-one [71] (130). Analogous products have been obtained from steroid-derived diazo ketones (131).



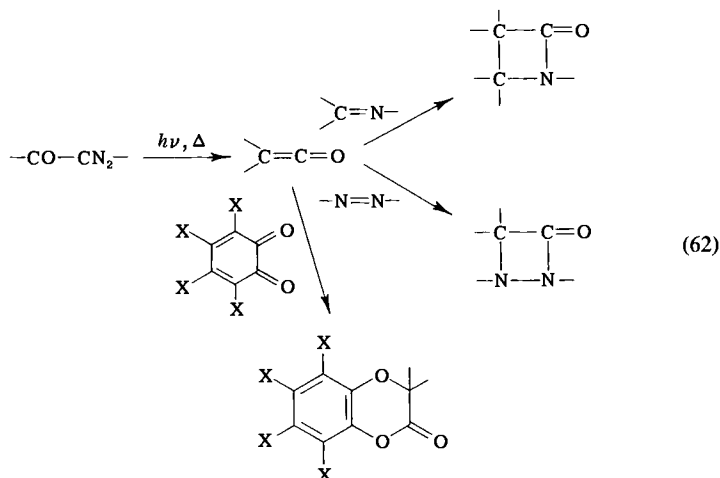
Thermolysis of diazoacetophenone at 140° afforded the butenolide [75] in only 4% yield; the major product (24%) was a "dimer" [76] derived from [75] by oxidation (132). Decomposition of diazoacetophenone at 50° , induced by silver benzoate-triethylamine catalyst, gave 3-benzoyl-4-hydroxy-5-phenylpyrazole [73] and β -phenylpropiophenone [74] (133). The formation of [73] indicates that the reaction of ketenes with diazo ketones under mild conditions may proceed without loss of nitrogen.



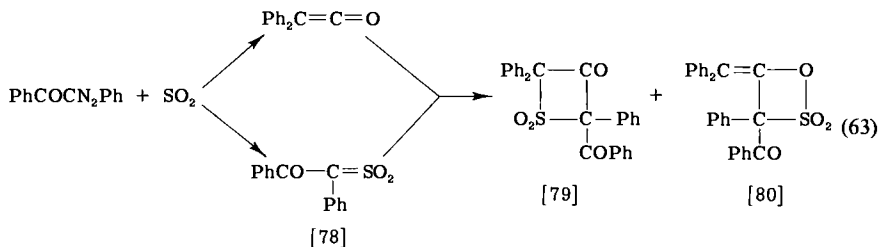
Arene-1,2-diazooxides afforded ketene acetals on decomposition in inert solvents. The product obtained by pyrolysis of both 1,2- and 2,1-naphthalenediazooxide was assigned structure [77] (134), and a large variety of related compounds were prepared (135). When ketenes and diazooxides were brought together at low temperatures, adducts still containing nitrogen were produced which formed ketene acetals on heating (136).



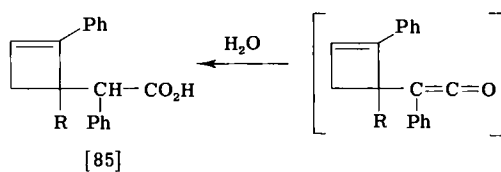
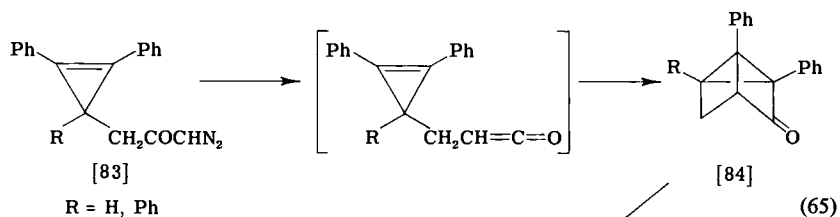
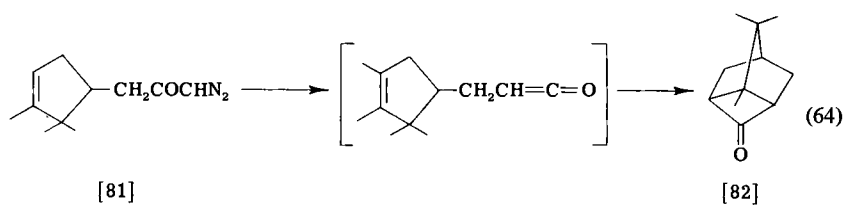
Ketenes generated by Wolff rearrangement have also been trapped by addition to azomethines, with formation of β -lactams (137), by addition to azo compounds (138), and by addition to *o*-quinones (139).



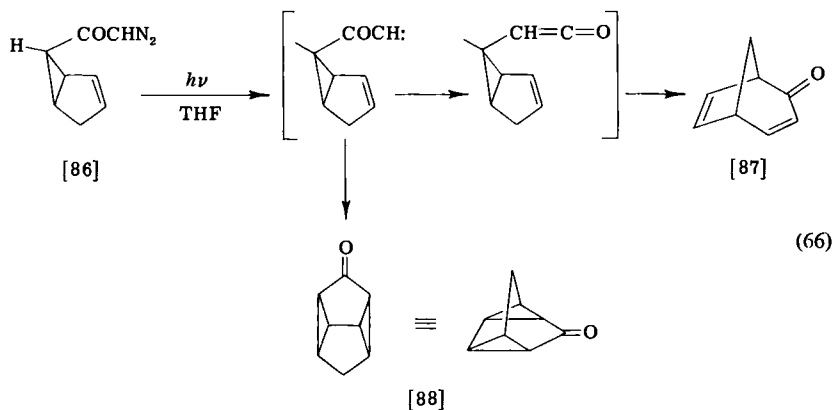
The reaction of phenylbenzoyldiazomethane with sulfur dioxide gave the four-membered cyclic sulfones [79] and [80] together with benzil and diphenylacetic acid (140). Most probably, [79] and [80] arise by cycloaddition of the ketosulfene [78] to diphenylketene. Formation of the ketosulfene may involve trapping of the carbonylcarbene, since photolysis at -5° to -20° afforded good yields of [79] and [80]. The thermal reaction of phenylbenzoyldiazomethane with SO_2 was slow even at $+80^\circ$.



Intramolecular cycloaddition of the ketene intermediate led to 6,7,7-trimethyltricyclo[3.2.1.0^{3,6}]octan-4-one [82] as the major product of the decomposition of diazo ketone [81], even in boiling dioxane-water (141). A more complex sequence of cycloaddition and reopening of the intermediate [84] has been proposed to account for the formation of acid [85] from diazo ketone [83]. Under suitable conditions, [84] has been isolated (142).



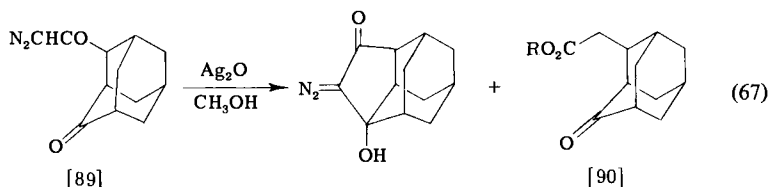
Photolysis of diazo ketone **[86]** resulted in the formation of bicyclo-[3.2.1]octa-3,6-dien-2-one **[87]** and tetracyclo[3.3.0.0^{4,6}.0^{2,8}]octan-3-one **[88]** (143). Whereas **[88]** arises by intramolecular carbene addition, **[87]** originates by Cope rearrangement of the ketene produced in the Wolff reaction.



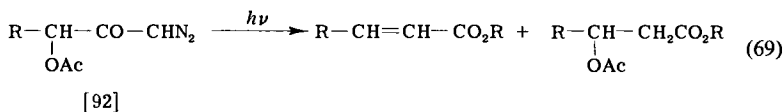
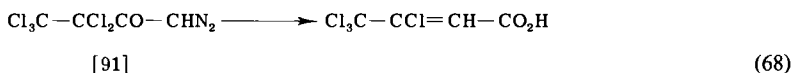
C. Scope and Limitations

Wolff rearrangement may be initiated by photolysis, pyrolysis, and silver (ion) catalysis. Decomposition of diazo ketones in the presence of copper and copper salts leads to addition and insertion reactions of carbonylcarbenes (Chapter 7, Section IV,D,2; Chapter 8, Sections IV and VI,E.). Only a few cases of Wolff rearrangement catalyzed by copper compounds have been recorded (144–147). Photolysis of diazo ketones, introduced by Horner (148), appears to be the most generally applicable method. Photolysis was often successful when other methods failed, e.g., in the synthesis of strained cyclic systems by ring contraction (see below). Thermolysis sometimes results in displacement of the diazo group by nucleophiles without rearrangement (94, 119); cf. Eq. (57). Elevated temperatures favor Wolff rearrangement. The most efficient thermal procedures involve decomposition of diazo ketones in refluxing aniline (94, 149) or refluxing benzyl alcohol (150).

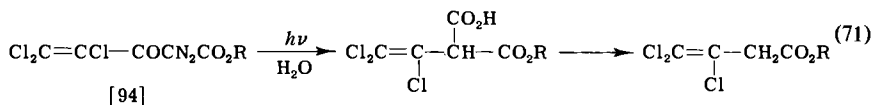
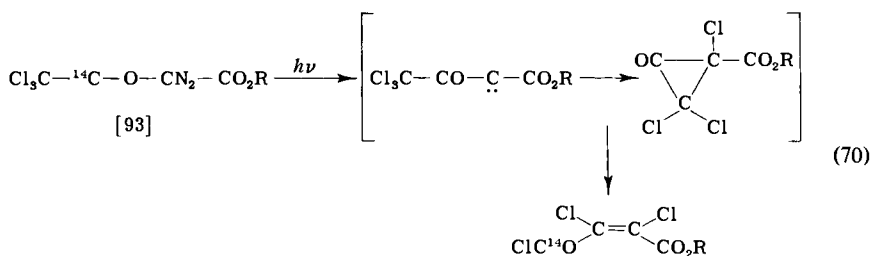
Silver catalysis, although conveniently carried out, is most liable to failure. Cyclic diazo ketones of medium size ($n = 7-12$) afforded cycloalkenones when treated with Ag_2O , whereas photolysis and thermolysis in aniline led to Wolff rearrangement (151). Ketol formation and intramolecular C—H insertion were other side reactions in the Ag_2O procedure (152), and even aldol condensation was observed with diazo ketone [89] (153). Photolysis of [89] produced the ester [90] exclusively.



The presence of functional groups within the diazo ketone molecule may lead to side reactions and restrict the application of the Wolff rearrangement. Elimination of hydrogen halide accompanied the rearrangement of α -halodiazo ketones, e.g., [91] (154). Similarly, α -acetoxydiazo ketones [92] yielded α,β -unsaturated acids and esters as the major products (155).

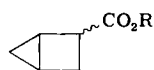


Halogen in a more remote position did not interfere with the Wolff rearrangement (156). 3,3,3-Trifluoro- and 3,3,3-trichloro-1-diazopropan-2-one were converted into the ester $CX_3CH_2CO_2R$ in 40 and 74% yield, respectively (157). $CF_3COCN_2CF_3$ required 300° for thermal decomposition, but afforded 75% of an rearranged anilide (158). In contrast to these findings, fluorinated diazo ketones $CF_3(CF_2)_x(CH_2)_nCOCHN_2$ failed to undergo Wolff rearrangement unless $n \geq 2$ (159). Ethyl trichloroacetyldiazoacetate [93] reacted abnormally by C—Cl insertion; the course of the reaction was elucidated by ^{14}C labeling (160), Eq. (70). Ethyl trichloroacryloyldiazoacetate, on the other hand, displayed normal rearrangement (161).

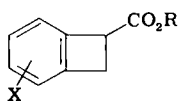


Unless the double bond is unreactive as in [94], α,β -unsaturation created problems in both the preparation and decomposition of diazo ketones (162, 163). Multiple bonds not conjugated with the carbonyl group had little effect (162). Cyclopropyl- (164) and indolyldiazo ketones (165) rearranged smoothly. Successful homologization of *N*-phthaloyl- α -amino acids (166, 167) and of *N*-trifluoroacetylaspartic acid (168) has been reported.

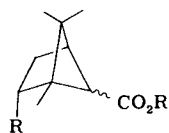
Ring size imposes few restrictions on the Wolff rearrangement. Strained cyclic systems which have been prepared by ring contraction of diazo ketones include cyclobutanes (169), oxetanes (170), bicyclo[2.1.0]pentanes [95] (171), benzocyclobutenes [96] (172–174), bicyclo[2.1.1]hexanes [97]–[103] (175–184), bicyclo[3.1.1]heptanes [104] (185), bicyclo[2.2.1]heptanes [105] (186), *trans*-bicyclo[5.1.0]octanes [106] (187, 188), and homocubanes [107] (189). 2-Diazoacenaphthenone [108] is one of the few diazo ketones where Wolff rearrangement could not be achieved (190).



[95]

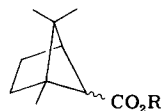
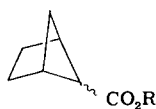
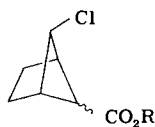
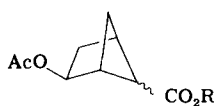
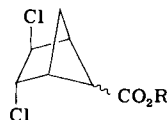
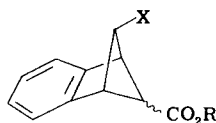
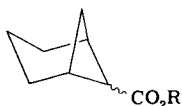


[96]

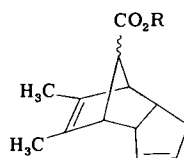


[97]

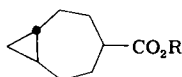
R = H (175-177)
R = OAc (178)

[98]
(179)[99]
(180)[100]
(181)[101]
(182)[102]
(183)[103]
(184)

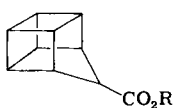
[104]



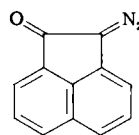
[105]



[106]

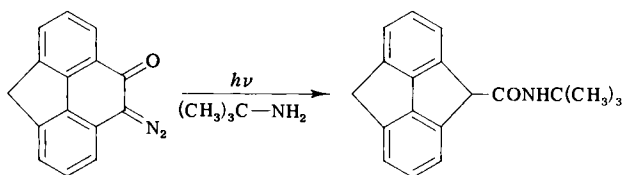


[107]



[108]

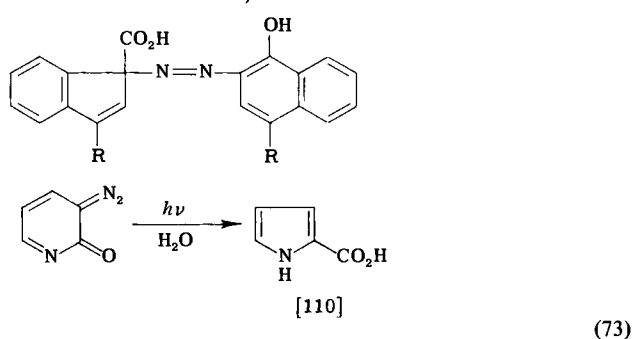
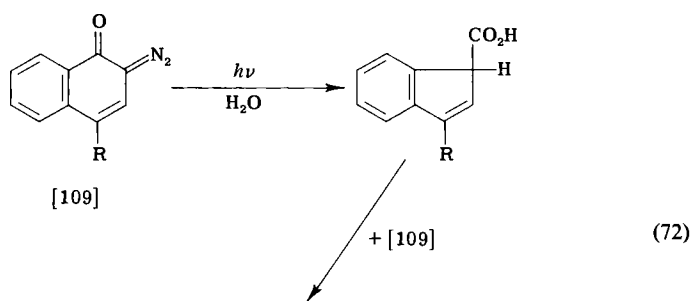
9-Diazo-10-keto-4,5-methylenephenanthrene **[108a]** is a “borderline” case where ring contraction to the amide **[108b]** has been achieved in 2% yield (190a). **[108b]** served as the precursor of a perturbed [12] annulene dianion.



[108a]

[108b]

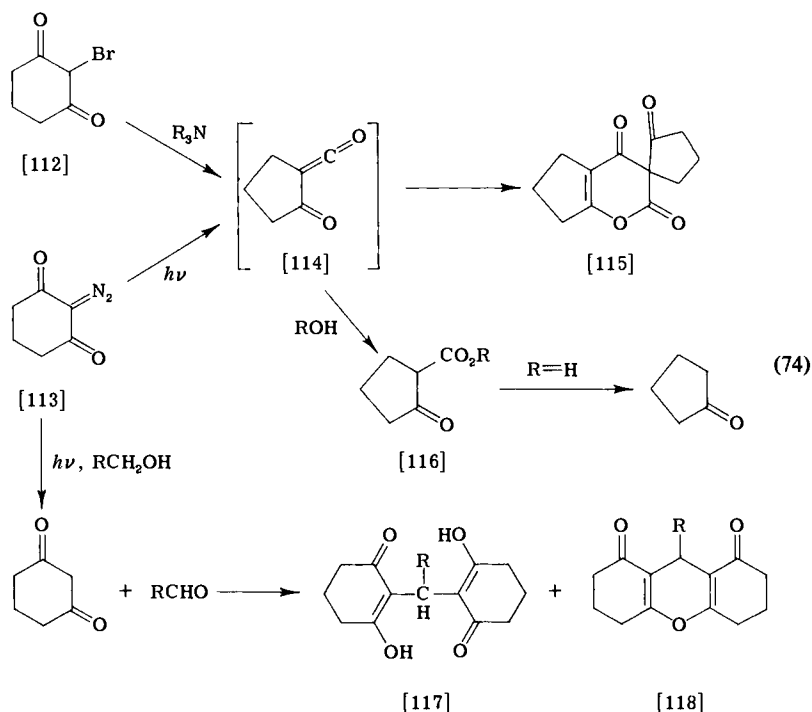
Steroid-derived diazo ketones have been utilized in the synthesis of A-norsteroids (191, 192), A-bisnorsteroids (191), and D-norsteroids (193–197). A-nor derivatives of triterpenes (oleananes) were prepared in an analogous fashion (198). Ring contraction of medium-sized rings (199) and paracyclophanes (200) proceeded without difficulty. The Wolff rearrangement of arenediazooxides is complicated by azo coupling between reactants and products (201, 202), e.g., Eq. (72). Careful control of the pH was essential in the synthesis of a large variety of polycyclic and heterocyclic compounds from arene diazooxides (201, 203–206), including pyrroles [110] (which involve the unusual migration of nitrogen) and tetrahydropentalenes [111].



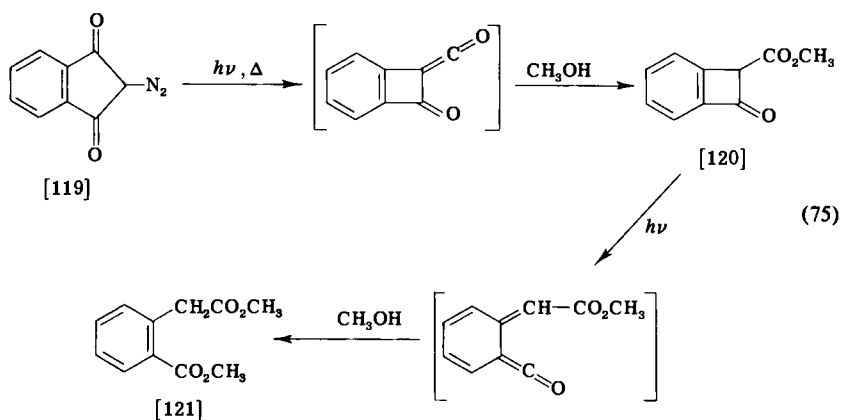
D. Rearrangement of 2-Diazo-1,3-dicarbonyl Compounds

Thermolysis of 2-diazocyclohexane-1,3-dione [113] (207), and of the 5,5-dimethyl (208, 209) and 4,5-diphenyl derivatives (210), gave dimers

[115] of the carbonylketene [114]. The latter, [114], has been trapped by addition to ketones, nitriles, azomethines, and isocyanates. Since dehydrohalogenation of 2-bromocyclohexane-1,3-dione [112] led to the same products, [114] is most likely involved in this reaction too, although its formation does not necessarily proceed by a carbene mechanism (211). Cyclopentanones, presumably arising by decarboxylation of keto acids [116], $R = H$, were most abundantly produced by photolysis of [113] in carbon tetrachloride (209, 210). Irradiation of [113] in alcohols afforded esters [116], $R = \text{alkyl}$, only in moderate yield. The major reaction was hydrogen abstraction to give cyclohexane-1,3-dione and aldehyde which then combined with formation of [117] and [118].

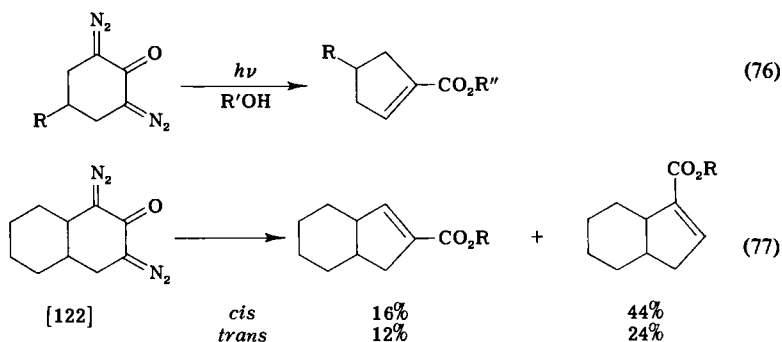


Photolysis of 2-diazoindan-1,3-dione [119] in methanol afforded dimethyl homophthalate [121] as the major product (212). Most probably, 2-methoxycarbonylbenzocyclobutenone [120] underwent photochemical conversion into [121]. Vacuum pyrolysis of [119] at 750° with subsequent introduction of methanol vapor gave [120] in 45–50% yield.



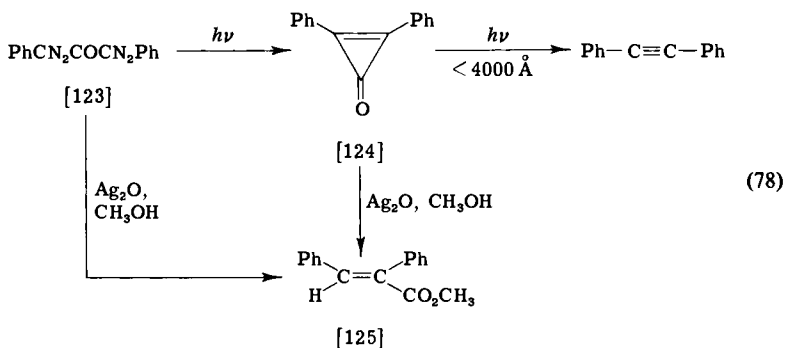
E. Rearrangement of α,α' -Bisdiazo Ketones

Irradiation of 1,3-bisdiazocyclohexan-2-one (213) and 5-*t*-butyl-1,3-bisdiazocyclohexan-2-one (214) in hydroxylic solvents produced cyclopentene-1-carboxylic acids and esters. *cis*- and *trans*-1,3-Bisdiazo-2-decalone [122] showed some directional selectivity, as shown in Eq. (77). The selectivity was independent of ring-junction stereochemistry, and has been attributed to the inductive effect promoting preferential loss of nitrogen from C_1 (215).



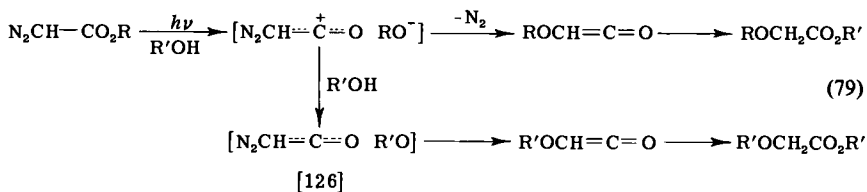
The course of reactions (76) and (77) has been interpreted as a Wolff rearrangement followed by 1,2 shift of hydrogen. Recent studies with 1,3-bisdiazo-1,3-diphenylpropan-2-one [123], however, lend support to a cyclopropene intermediate (216). When [123] was irradiated at 4360 Å in toluene, [124] was the major product. Decomposition of [123] by methanolic

silver oxide produced 11% of [124] and 36% of [125]; it was shown that, under the reaction conditions, [124] was partially converted into [125].

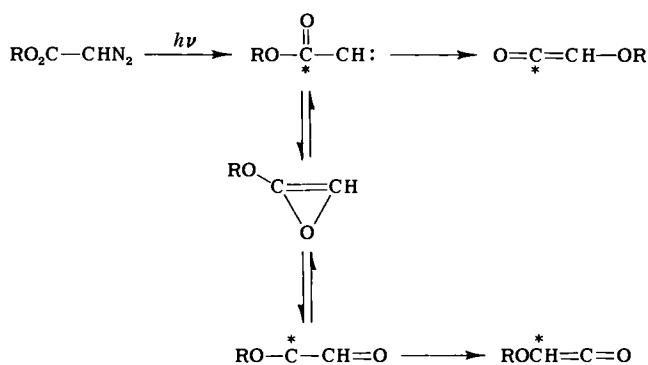


F. Rearrangement of Alkyl Diazoacetates

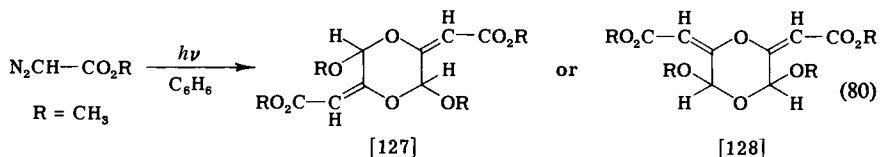
Alkyl diazoacetates have been used as carbene precursors for more than 80 years, but their ability to undergo alkoxy shift with formation of alkoxyketenes and products derived therefrom has been discovered only recently when diazoacetyl enzymes (!) were photolyzed (217). A rearrangement analogous to the Wolff rearrangement of diazo ketones was confirmed with ethyl diazoacetate (20–25%), phenyl diazoacetate (45–60%), and *N*-methyldiazoacetamide (30%) (218). The major competing reactions were insertion into the C–H and O–H bonds of the alcohols employed as solvents and ketene traps (218, 219) (cf. Chapter 11, Section IV,B). Rearrangement was accompanied by alkoxy exchange; the photo-induced exchange process apparently does not involve carbenes, nor does it occur in the starting materials. The formation of ions [126] by a light-induced heterolysis has been suggested (219).



Recent studies on the photolysis of ^{13}C -labeled methyl and ethyl diazoacetate indicated appreciable carbon scrambling which may be due to the intervention of an oxirene intermediate (219a).

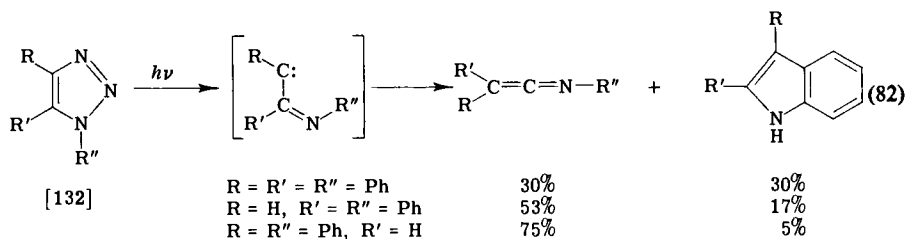
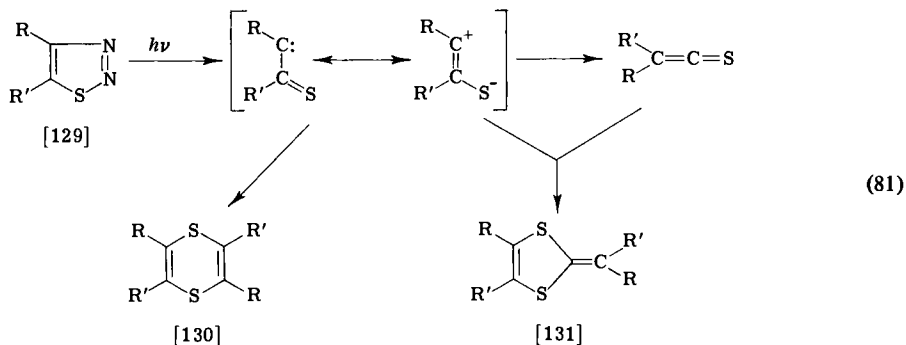


The isolation of the same products, although in different ratios, from the photolysis of diethyl mercurybisdiazoacetate (220) suggests that a "carbyne" intermediate may also undergo rearrangement followed by hydrogen abstraction. Compounds which are formally tetramers of methoxycarbonylcarbene have been obtained by photolysis of methyl diazoacetate in benzene (221). The structures assigned on the basis of spectral data, [127], and [128], contain units derived from methoxyketene.

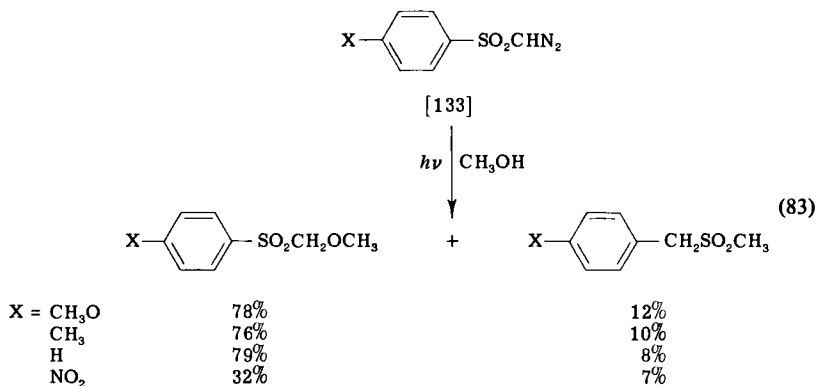


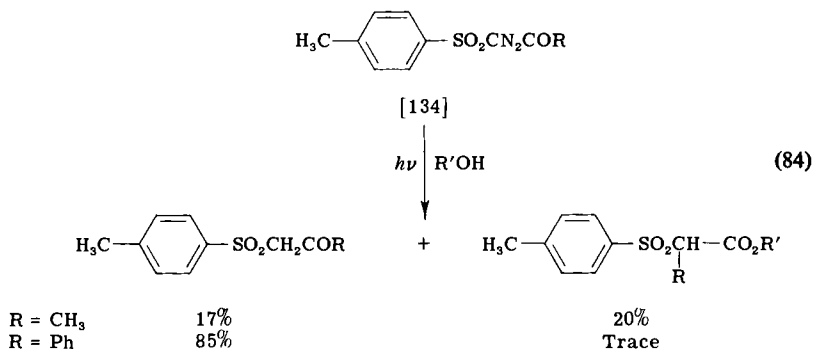
G. Hetero Analogs of Diazo Ketones

Replacement of the oxygen of diazo ketones by sulfur leads to 1,2,3-thiadiazoles [129]. Although they do not contain a diazo group, 1,2,3-thiadiazoles are readily decomposed by UV irradiation to give derivatives of 1,3-dithiacyclopentene [131] ("dithiafulvenes") (222). In some cases, 1,4-dithia-2,5-cyclohexadienes [130] were also obtained. The dithiafulvenes contain a rearranged fragment of the precursor [129], indicating some tendency of the hypothetical thiocarbonylcarbene intermediates to undergo Wolff rearrangement. The related 1,2,3-triazoles [132] also rearranged to ketenimines in competition with intramolecular C—H insertion, Eq. (82) (223).

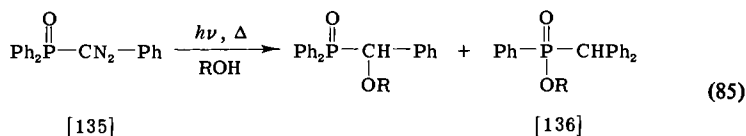


Diazo sulfones and diazophosphine oxides may also be considered as hetero analogs of diazo ketones, with sulfonyl and phosphonyl groups, respectively, in place of carbonyl. Diazo sulfones are very reluctant to undergo Wolff rearrangement; sulfene-derived products accounted for less than 12% with [133] (224). Compound [134], which has carbonyl and sulfonyl groups attached to the diazo function, showed migration of the carbonyl substituents only (225).





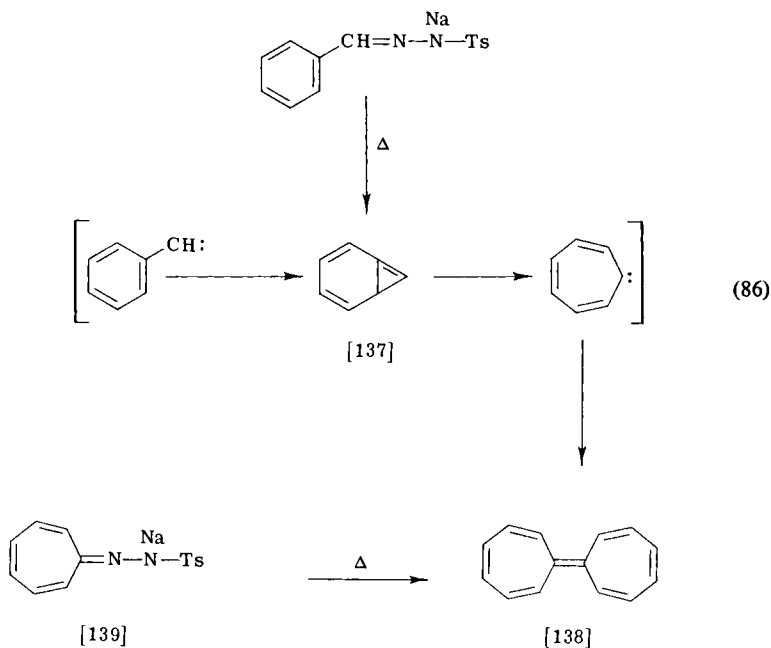
The diazophosphine oxide [135] reacted in dioxane-water (226), ethanol, and aniline (227) predominantly by apparent O—H and N—H insertion. Phenyl migration to give [136] occurred only to a minor extent.



VI. REARRANGEMENT OF ARYLCARBENES

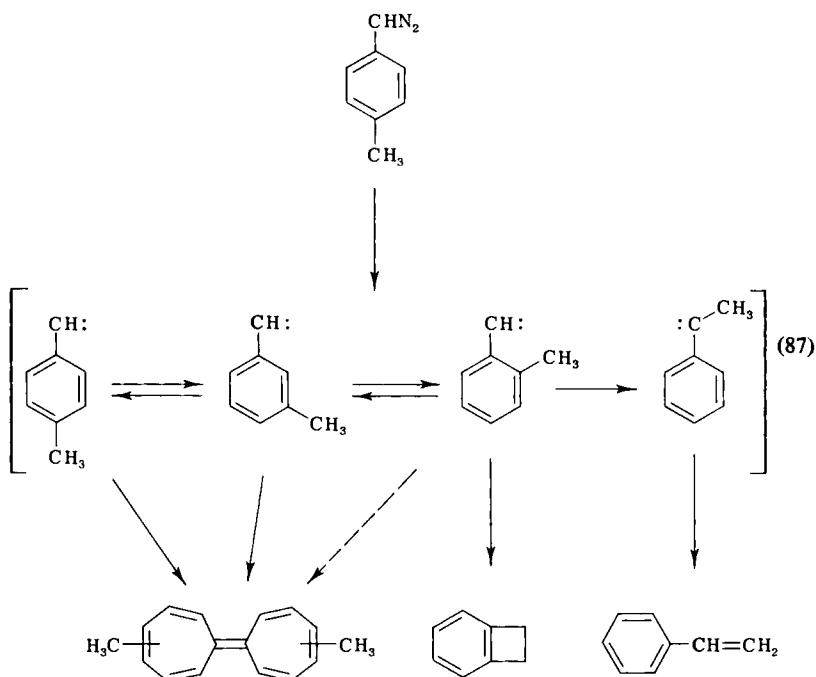
Although arylcarbenes show no tendency of rearrangement in solution, they behave differently when generated by flash pyrolysis in the gas phase. Thus, the sodium salt of benzaldehyde tosylhydrazone at 250° (40 mm) afforded ca 15% of stilbenes and 30% of heptafulvalene [138](228). Since heptafulvalene was also a major product from tropone tosylhydrazone [139] under similar conditions, these results suggest the rearrangement of phenylcarbene to cycloheptatrienyldiene, initiated by intramolecular carbene addition to give the highly strained cyclopropene [137]. Experiments carried out with mixtures of benzaldehyde and *p*-methylbenzal-

dehyde tosylhydrazones indicate that dimerization occurred in the gas phase and was complete before the monomer reached the end of the pyrolysis column (228).

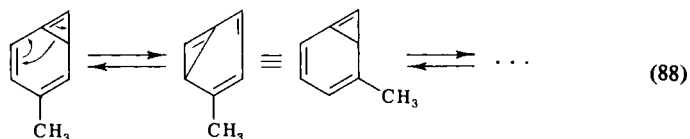


The behavior of the tolylcarbenes depended critically on the temperature. Pyrolysis of the corresponding diazoalkanes or tosylhydrazone salts at 225° produced largely dimers, at 350° dimethylheptafulvalene and benzocyclobutene were obtained, and pyrolysis at 420° led to benzocyclobutene and styrene in the ratio 0.8 (228, 229). Formation of the latter products suggests rearrangements of *m*- and *p*-tolylcarbene to *o*-tolylcarbene and further to phenylmethylcarbene.

At least two plausible mechanisms may be advanced to explain these changes. One requires that the conversion of phenylcarbene to cycloheptatrienyldiene [Eq. (86)] be reversible. Alternatively, a vinylcyclo-

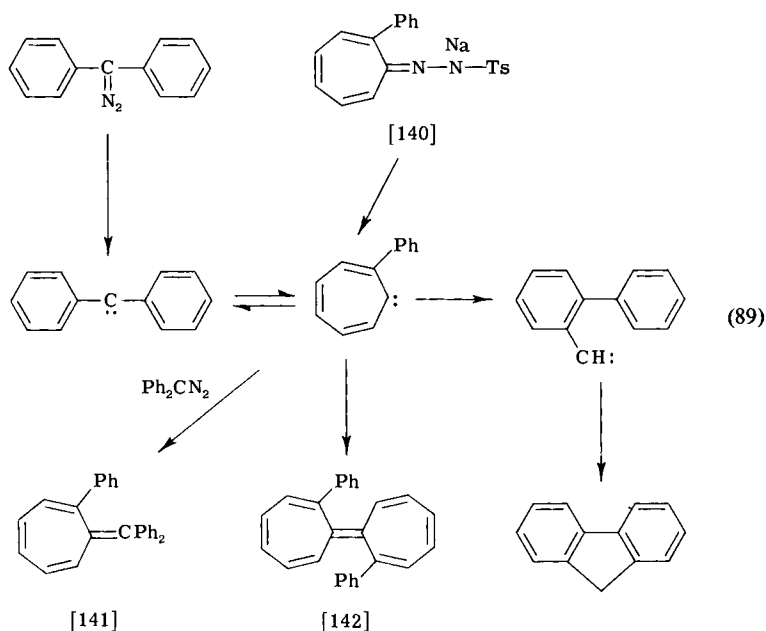


propene $\rightarrow$ vinylcyclopropene rearrangement of the intermediate [137] could be envisaged which would bypass the expanded carbene, Eq. (88).

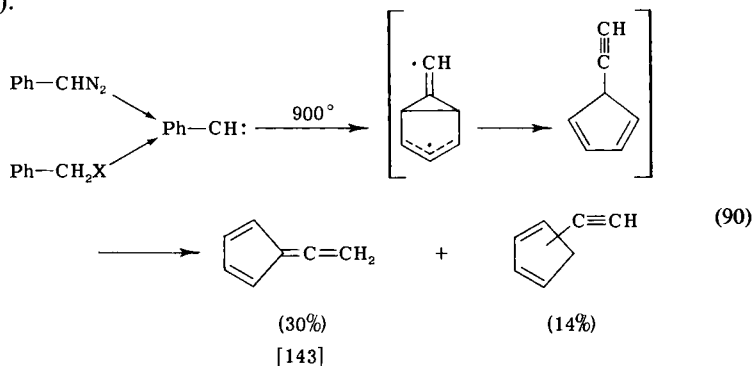


This question has been elaborated further in a study of pyrolytic diarylcarbene rearrangements (230, 231). Diphenyldiazomethane, at 350–375° and 1–3 mm, afforded fluorene, triphenylheptafulvene [141] and diphenylheptafulvalene [142] in the approximate ratio 3 : 3 : 1. The fluorene derived from *p*-methyldiphenyldiazomethane was exclusively 2-methylfluorene. Consequently, the mechanism of fluorene formation is multiple carbene rearrangement, followed by intramolecular insertion, Eq. (89). Fluorene was also obtained when the sodium salt of 2-phenyltropone

tosylhydrazone [140] was pyrolyzed. This result strongly supports a reversible interconversion of cyclohexatrienylenes and arylcarbenes.



At temperatures above 600° , phenylcarbene (generated from either phenyldiazomethane or benzyl halides) underwent ring contraction rather than ring expansion, producing 5-vinylidenecyclopentadiene (fulvenallene) [143] as the major product (231, 232). A tentative mechanism is shown in Eq. (90).



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CHAPTER 13

Silicon, Germanium, and Tin Structural Analogues of Carbenes¹

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I. INTRODUCTION

THE RECOGNITION THAT the chemistry of methylene, :CH_2 , is of great interest followed only some thirty years after the species was postulated as an intermediate in the pyrolysis of methane and in the pyrolysis and photolysis of diazomethane and ketene. The discovery of the distinctive reactions of methylene, insertion into C—H bonds and addition to π bonds, has had a great impact on many branches of chemistry. It is not surprising, then, that the divalent compounds of the other Group IV elements have elicited interest in recent years. These compounds are often called carbene analogs, but there is real danger in using this name. It is very easy to carry the structural analogy further and to succumb to the supposition that the divalent compounds of silicon, germanium, and tin will undergo reactions analogous to the reactions of carbenes. Indeed,

¹ United States Atomic Energy Commission Technical Report No. COO—1713—18.

The hospitality of the Department of Chemistry, Princeton University, to one of the authors (Peter P. Gaspar) during the preparation of this chapter is gratefully acknowledged.

much experimental work in this area has been carried out in order to test this hypothesis.

We should be careful to examine critically the experimental evidence for the chemical properties of the "carbene analogs." In the past there has been an unfortunate tendency on the part of a few investigators to rely on tenuous analogies and even wishful thinking. The temptations have been so great that none of us who are interested in the problem can claim total innocence in this regard. A comparison of the chemistry of tetravalent carbon and silicon reveals such gross differences that the pitfalls of casual analogies should be apparent.

The real danger is that the distinctive features of the chemistry of the divalent compounds of silicon, germanium, and tin will be overlooked because the interpretation of their reactions is colored by the expectation that their behavior will resemble that of carbenes. This actually happened in the early days of carbene chemistry when the possibility of a spin-paired s^2p^2 valence state for the carbon atom in methylene was interpreted as conferring considerable stability on the methylene molecule. This was a reasonable, if fallacious, analogy with the properties of the other known small molecules of first-row elements.

In this chapter no attempt is made to include every reaction which might proceed by way of a structural analog to a carbene. Instead, we concentrate on those reactions which in the light of present knowledge (May 1970) are most likely to involve, and illuminate the behavior of, such species. We list the reactions which are believed to produce the various species, discuss the available physical and spectroscopic evidence for their existence and structure, and present the transformations which the various molecules are believed to undergo. Our greatest emphasis is on a critical interpretation of the available experimental data.

Our hope is to convey our impression of what is known about these interesting species. Perhaps a realistic appraisal of the present state of our knowledge will promote further fruitful investigation and help free our imaginations from the shackles of our predispositions.

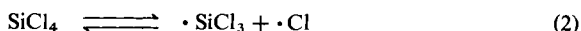
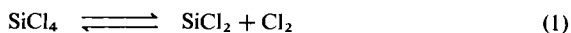
This chapter owes much to the previous reviews of Nefedov and Manakov (1), Timms (2), and Atwell and Weyenberg (3). Readers are therapeutically referred to these earlier reviews.

Nomenclature deserves a word, but no more. In this chapter, divalent silicon and germanium compounds are called silylenes and germylenes, or occasionally are given inorganic binary names such as silicon difluoride (3).

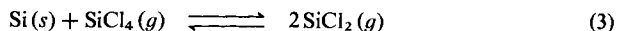
II. SILICON DICHLORIDE, :SiCl_2

A. Formation

As so often has occurred in the chemistry of reactive intermediates, spectroscopists were the first to recognize :SiCl_2 . The 2560 Å and 2450 Å emission bands observed when an electric discharge was passed through SiCl_4 vapor were attributed to :SiCl_2 in 1938. A vibrational analysis of the spectrum in terms of a triatomic molecule was successful (4). The bands had been observed even earlier and assigned to a silicon nitride or chloride of unspecified formula (5). It was also a spectroscopic experiment which suggested in 1951 that a thermolytic reaction gives rise to :SiCl_2 (6). When subjected to a temperature above 900°, SiCl_4 was found to give a species whose continuous absorption of ultraviolet radiation reaches a maximum at 3150 Å (6). To the absorbing molecule was assigned the structure :SiCl_2 because it was believed to be formed by a reaction less endothermic than that which yields the otherwise equally plausible absorber, SiCl_3 .



In 1953 the presence of SiCl_2 was used to explain vapor-pressure measurements on the heterogeneous system $\text{Si}(s) + \text{SiCl}_4(g)$ (7). The pressure increase in the temperature range 800–1300° seems to be due to equilibrium (3). This equilibrium accounts for the transport of silicon

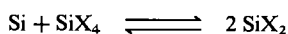


(8–10) across a temperature gradient by a gas stream containing SiCl_4 , a process first observed in 1876 (11). Equilibrium (3) has been thoroughly studied both in static (7, 12, 13) and flow (14, 15) systems. The reaction of Si and SiCl_4 has recently proved to be a convenient source of monomeric SiCl_2 for use in reaction studies (16), and one can expect to see it widely utilized in the future.

The currently accepted thermodynamic values for the silicon dihalides (12) are given in Table I. Monomeric SiCl_2 is also believed to result from the reduction of such chlorosilanes as SiCl_4 and SiHCl_3 with hydrogen at high temperatures (17, 18). The pyrolysis of higher silanes such as Si_2Cl_6

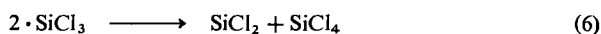
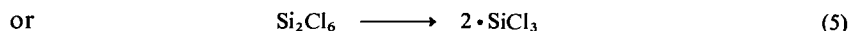
TABLE I (3, 12)

Heats of Formation of Silicon Dihalides and Calculated Heats of Reaction for



SiX_2	$\Delta H_f^\circ, 298$ (kcal/mole)	$\Delta H_R^\circ, 298$ (kcal/mole)
SiF_2	-139	108
SiCl_2	-39.5	82.6
SiBr_2	-10.0	79.8
SiI_2	+18.7	86.0

(19) also seems to be a source of SiCl_2 , either from an unsymmetrical cleavage or from disproportionation of trichlorosilyl radicals.

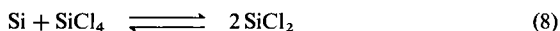


A substance whose analysis indicates it to be polymeric, $(\text{SiCl}_2)_x$, has been prepared by passing SiCl_4 vapor rapidly over silicon heated to 1250° (20). The polymeric substance (average molecular weight 1600–1700) was collected just outside the hot zone. A similar material was obtained by circulating SiCl_4 through an oven at the vapor pressure of the liquid. The product collected in the flask from which SiCl_4 vapor was continuously pumped (21).

B. Evidence for the Formation of SiCl_2

The spectroscopic evidence for the formation of SiCl_2 is plausible but not entirely conclusive. The emission bands first observed by Jevons (5) and then by Asundi *et al.* (4) were subjected to a vibrational analysis, but no rotational fine structure was resolved. Thus the conclusion that the emitting species is a triatomic molecule whose identity is SiCl_2 awaits confirmation from the analysis of a high-resolution spectrum. The absorption band assigned to SiCl_2 which was observed on pyrolysis of SiCl_4 (alone or in the presence of Si) shows no fine structure (6). The assignment of the spectrum to SiCl_2 rests on its nonidentity with the known SiCl spectrum, and the belief (based on enthalpies of reaction) that SiCl_4 is more likely to lose a chlorine molecule to give SiCl_2 than to lose a chlorine atom to give SiCl_3 .

In the vapor-pressure studies (7) on the system $\text{Si} + \text{SiCl}_4$ it is clear that there is an increase in the number of molecules present in the gas phase above 800° . The vapor pressure of SiCl_4 increases linearly with temperature *in the absence of solid Si* over the entire range studied, $100\text{--}1300^\circ$. There is however a positive deviation from linearity above 800° when solid silicon is present. Thus a chemical reaction is taking place which increases the number of molecules, and the reaction must involve silicon. Since the pressure change is reversible, a chemical equilibrium or equilibria are established. Three Eqs. (7)–(9), were considered likely. Other possible



equilibria would *decrease* the number of gas molecules (except $\text{Si} + \text{SiCl}_4 \rightleftharpoons 2 \text{ Si} + 2 \text{ Cl}_2$, which was not considered).

For each of the three equilibria (7) to (9), a function was derived relating the "excess pressure" in the system (over that for pure SiCl_4) to the pressure of SiCl_4 initially present. Only for equilibrium (8) do the data obey the function derived from the equilibrium. On this basis, SiCl_2 was considered to be the only reactive intermediate formed. The calculated equilibrium constant gave the expected linear function when its logarithm was plotted against $1/T$, and the slope of this plot gave the enthalpy of reaction listed in Table I.

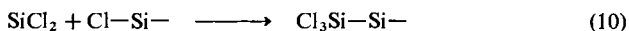
When a flow technique was used to study the reaction of SiCl_4 with heated solid Si, equilibrium (8) was *assumed* in the analysis of the data (15). It was noted that the incursion of additional equilibria would cause deviations from linearity in the plots of $\log K$ vs. $1/T$. Such deviations were not observed. The equilibrium constant $K = (p_{\text{SiCl}_2})^2 / (p_{\text{SiCl}_4})$ reaches unity at 1340° .

On the basis of the foregoing evidence, the formation of SiCl_2 seems quite certain. One could wish for a complete analysis of a high-resolution spectrum, as has been possible for HSiCl and HSiBr (*vide infra*), and for a mass spectrometric study of the system $\text{Si} + \text{SiCl}_4$. No doubt, such studies will confirm the conclusion that SiCl_2 is produced from $\text{Si} + \text{SiCl}_4$.

C. Reactions of SiCl_2

Insertion into boron–chlorine, carbon–chlorine, silicon–chlorine, and phosphorus–chlorine bonds appear to be the only well-documented re-

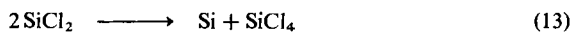
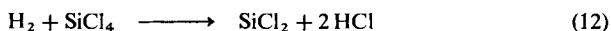
actions of silicon dichloride. As long ago as 1876, it was observed that higher chlorosilanes (e.g., Si_2Cl_6) are formed when a *rapid* gas stream containing SiCl_4 is passed over heated silicon (11). Si_2Cl_6 was later observed as a product, at 700° , of the reaction of SiCl_4 and Si which produces polymeric $(\text{SiCl}_2)_x$ at higher temperatures (21). Pyrolysis of Si_2Cl_6 at 400° produces SiCl_4 , Si_3Cl_8 , and $\text{Si}_4\text{Cl}_{10}$ (19). All these reactions can be understood if SiCl_2 is formed as an intermediate which undergoes an insertion reaction reminiscent of carbene chemistry.



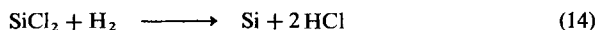
Schäfer was the first to suggest such an explanation, in 1951 (22). He pointed out that the vapor-pressure measurements indicate that, if a mixture of SiCl_2 and SiCl_4 is cooled *slowly*, then solid Si and SiCl_4 are formed by simple reversal of reaction (8). On the other hand, if the mixture is *suddenly* cooled, "aggregation" will occur:



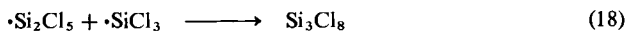
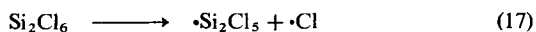
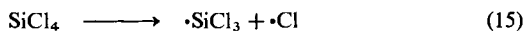
He also concluded that the reduction of SiCl_4 with hydrogen, first noted in 1927 (23), occurs via SiCl_2 as an intermediate,



This mechanism was placed on a firm footing when it was later shown that the yield of silicon goes through a maximum as a function of temperature (17). This is expected since reaction (12) is endothermic, whereas reaction (13) is exothermic, but would be difficult to understand if the reduction occurred in a single step. A second step alternative to (13) which yields the same overall stoichiometry is (17)



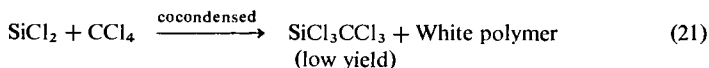
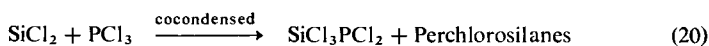
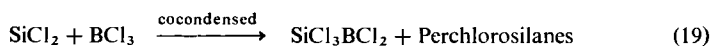
Another mechanism for the production of higher chlorosilanes had been suggested earlier for the reaction of SiCl_4 with Si (24) and was accepted for the pyrolysis of Si_2Cl_6 (19).



In light of the evidence for the presence of SiCl_2 and the absence of SiCl_3 under the reaction conditions, we may discount the radical hypothesis until such time as direct evidence in its favor is presented.

It is interesting to consider the implications of the insertion mechanism in view of the fact that the reaction $\text{Si} + \text{SiCl}_4 = 2 \text{SiCl}_2$ seems to be totally reversible. If no SiCl_2 is lost at the high temperatures ($800\text{--}1300^\circ$) at which the reversibility of this reaction has been established, then two possibilities are indicated. Either SiCl_2 does not insert into SiCl_4 at high temperatures, or insertion occurs but is also cleanly reversible at these temperatures. The latter conclusion is indicated by the low temperature ($\sim 350^\circ$) at which Si_2Cl_6 undergoes decomposition (19). If SiCl_2 inserts into SiCl_4 to form Si_2Cl_6 , then microscopic reversibility demands that the reverse reaction occur directly rather than by way of SiCl_3 , as previously suggested (19).

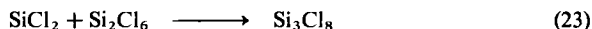
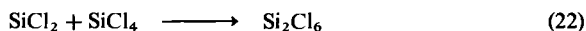
The recent experiments of Timms have thrown further light on the chemistry of SiCl_2 (16). Timms produces SiCl_2 at $\sim 1300^\circ$ by the reaction of SiCl_4 vapor with solid Si. The resulting mixture of $\sim 80\%$ SiCl_2 and 20% SiCl_4 is sprayed through a nozzle into a chamber maintained at a vacuum of 2×10^{-6} mm Hg. Under these conditions the SiCl_2 molecules undergo few collisions before striking a wall cooled by liquid nitrogen. Reactions of SiCl_2 are examined by cocondensing SiCl_2 and appropriate substrates sprayed into the reaction chamber through a second nozzle. Reactions (19)–(21) have been observed. When SiCl_2 is cocondensed with



benzene and acetylene, only polymers and perchlorosilanes are obtained as reaction products.

In the apparatus used by Timms, little reaction takes place in the gas phase. That one is indeed observing reactions of monomeric SiCl_2 is indicated by the copious quantities of perchlorosilanes obtained when SiCl_2 is cocondensed with SiCl_4 (25). Since these products are obtained from SiCl_2 in the gas phase, we may assume an identical mechanism for the reactions which occur on cocondensation. It is the reaction of SiCl_2 with the small amount of unchanged SiCl_4 always present which accounts

for the perchlorosilanes obtained in the reactions with BCl_3 and PCl_3 . The reactivity of SiCl_2 toward SiCl_4 is so much greater than toward other substrates in the gas phase that perchlorosilanes are the dominant products (25). Thus one can write with considerable confidence such reactions as



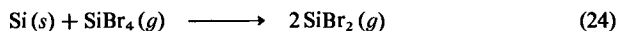
(22) and (23). Timms has stressed the instability of SiCl_2 below the temperatures required for its formation. At a pressure of 10^{-3} mm Hg the lifetime of SiCl_2 may be as short as several milliseconds (2).

It is to be hoped that in the near future the effluent of the high temperature nozzle will be subjected to spectroscopic and mass spectrometric scrutiny to prove conclusively that the reactions of monomeric SiCl_2 are being investigated.

While polymeric $(\text{SiCl}_2)_x$ is quite sensitive to oxygen (apparently explosive in contact with air) it shows no carbenelike reactions. It is soluble in organic solvents, including benzene, without undergoing reaction. The polymer is believed to contain rings (24, 26), although no definite proof of cyclic structure has been presented. Pyrolysis and chlorination of the polymer lead to complex mixtures of perchlorosilanes $\text{Si}_n\text{Cl}_{2n+2}$.

III. SILICON DIBROMIDE AND DIIODIDE, SiBr_2 AND SiI_2

The formation of silicon dibromide and silicon diiodide closely parallels that of the dichloride. At high temperatures a heterogeneous mixture of solid Si and SiBr_4 vapor behaves similarly to the system $\text{Si} + \text{SiCl}_4$ (12). SiBr_2 is believed to arise from the equilibrium (24). SiI_2 is formed from the

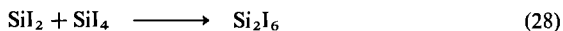


analogous system $\text{Si} + \text{SiI}_4$, but additional equilibria are also important (12):



Polymeric $(\text{SiBr}_2)_x$ (27, 28) and $(\text{SiI}_2)_x$ (29) have also been prepared, and their properties resemble those of $(\text{SiCl}_2)_x$. The only available information on the reactions of monomeric SiI_2 may come from the treatment

of solid Si with HI and with $H_2 + I_2$ (30). The products include SiI_4 , $SiHI_3$, and Si_2I_6 , the latter believed to arise by an insertion of monomeric SiI_2 :



The reactions of monomeric $SiBr_2$ and SiI_2 remain a fertile field for future investigation. The high-temperature nozzle method of Timms (2, 16) seems ideally suited for the study of these interesting molecules

IV. CHLOROSILYLENE AND BROMOSILYLENE: HSiCl AND HSiBr

While no chemistry has been reported for these species, Herzberg has presented unambiguous spectroscopic evidence for their formation by flash photolysis from SiH_3Cl and SiH_3Br , respectively (31). The molecular parameters are

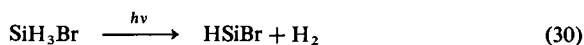
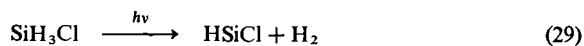
Ground-state HSiCl: $r(Si-H) = 1.56 \text{ \AA}$, $r(Si-Cl) = 2.064 \text{ \AA}$, $\angle HSiCl = 102.8^\circ$

Ground state HSiBr: $r(Si-H) = 1.56 \text{ \AA}$, $r(Si-Br) = 2.231 \text{ \AA}$, $\angle HSiBr = 102.9^\circ$

The analysis of the spectra is a lesson in rigor. The changes in the spectra in going from the chloro compound to the bromo compound suggested that a chlorine atom and bromine atom, respectively, is contained in the species responsible for the spectra. Since there is a spectral shift in going from SiH_3Cl to SiD_3Cl , the presence of hydrogen in the absorbing molecule was confirmed. That there is no intensity alternation in the rotational K fine structure suggested that there is only one hydrogen present in the species whose spectra were recorded. The typical symmetric top spectra indicated the presence of an atom in addition to hydrogen and halogen. This was proved to be silicon by isotope studies. The band structure of the spectra could have been due to molecules with structures $HXYCl$ and $HXYBr$, if the $XYCl$ and $XYBr$ portions of the molecules were linear. For the absorbing molecules to have structures $HXYCl$ and $HXYBr$, however, X and Y would have to be atoms of the mass of carbon or nitrogen in order for the molecules to have the moments of inertia deduced from the spectra. Even so the bond distances $r(X-Y)$ and $r(Y-Cl)$ or $r(Y-Br)$ would have to be unacceptably small in $HXYCl$ and $HXYBr$. Therefore the absorbing molecules must have the structures $HXCl$ and $HXBr$. If X were carbon or nitrogen, $r(X-Cl)$ and $r(X-Br)$ would have to be unreasonably large. Therefore X must be a heavier

atom. From the band structure alone, X could be Al, Si, P, or S but, since there is no evidence for an Al, P, or S impurity, X must be Si. Thus the transients were unambiguously identified as HSiCl and HSiBr.

The other product of photolysis is believed to be a hydrogen molecule, since the photon carried insufficient energy to produce two hydrogen atoms.



V. SILICON DIFLUORIDE, SiF₂

It is truly unfortunate that SiF₂, the best characterized structural analog to carbenes, is also the least prone to undergo reaction in monomeric form; Thompson and Margrave have published a review of the chemistry of silicon difluoride (32).

A. Detection and Spectroscopy

The relative inertness of silicon difluoride has allowed its structure to be determined by spectroscopic techniques. As in the case of SiCl₂, molecular spectroscopy preceded the chemical investigation of SiF₂. As early as 1927, ultraviolet emission bands from SiF₂ were observed in an arc discharge through SiF₄, although a rotational analysis was carried out for F—Si—Si—F (33). By 1958 the 2200 Å to 2500 Å emission spectrum of SiF₂ was recognized and properly assigned by analogy with the strikingly similar CF₂ bands which occur in the same spectral region (34). A vibrational analysis for a bent molecule gave good agreement with observed spacings, and a singlet ground electronic state was assigned to SiF₂ by analogy with CF₂. By 1961 vibrational-rotational subbands had been resolved in the emission spectrum, and rotational analysis led to the assignment of a value $124 \pm 2^\circ$ to the F—Si—F bond angle and 1.49 ± 0.07 Å to the Si—F bond lengths (35). Later reports of the microwave (36, 37) and ultraviolet absorption (38) spectra of SiF₂ have added to our structural knowledge. The microwave spectrum indicates that the bond angle in the ground state is $100^\circ 59'$ and the bond lengths are 1.591 Å. The low-resolution ultraviolet absorption spectrum (38) has been analyzed entirely in terms of bending vibrational modes of SiF₂. Infrared spectra have also been reported for SiF₂ in the gas phase (39) and in solid matrices (40, 41).

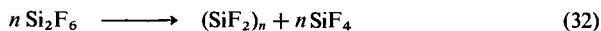
Their analyses ($\angle \text{FSiF} = 100^\circ 53'$ (gas), $97.5 \pm 1^\circ$ (solid), $r(\text{Si}-\text{F}) = 1.5947 \text{ \AA}$) are in excellent agreement with the results of microwave spectroscopy. However, the gas-phase infrared spectrum was not well resolved, and several extra peaks in the matrix isolation spectra remain to be explained. Nevertheless, the geometry and vibrational frequencies of silicon difluoride (42) are known more precisely than those for any carbene or other carbene analog; Herzberg has discussed some uncertainty which remains concerning the vibrational frequencies (42).

B. Preparation

It was discovered some years ago that a polymer of SiF_2 can be prepared by reaction of SiF_4 vapor with solid Si at low pressure and high temperatures (43).



The same polymer has been obtained from the pyrolysis of Si_2F_6 at 700° (44).



It is interesting to trace the development of the comprehensive investigation of the properties of SiF_2 carried out by Margrave and co-workers at Rice. Using equilibrium pressures of SiF_2 estimated from the yields of polymeric products in reaction (31), an estimate of the heat of formation of SiF_2 was published in 1962 (45). The third law calculation gave a value of $-148 \pm 4 \text{ kcal/mole}$ (45) which can be compared to a previous estimate of $-118 \pm 10 \text{ kcal/mole}$ (46), and the presently accepted value of -139 kcal/mole (47).

While transpiration studies on the evaporation of Si in a stream of SiF_4 vapor indicated the formation of a gaseous polymer of SiF_2 (47), mass spectrometric studies on the reaction of calcium fluoride with silicon at high temperatures indicated that monomeric SiF_2 was a reaction product (48). Despite indications that monomeric SiF_2 was not the sole precursor of the SiF_2^+ ion (48), the mass spectrometric experiments clearly indicated the feasibility of producing gaseous monomeric SiF_2 .

Gaseous monomeric SiF_2 can be conveniently prepared by passing a stream of SiF_4 vapor through a tube containing small pieces of pure silicon heated to 1150° (49, 50). At the downstream end of the heated tube an optimal pressure of 0.1 to 0.2 mmHg is maintained. The product is a 2 : 1

mixture of SiF₂ and SiF₄ from a reaction identical to that known to yield SiCl₂:



C. Reactions of SiF₂

It became immediately apparent that SiF₂ is quite unreactive in the gas phase. Its half-life at 0.1 mmHg (together with 0.05 mmHg SiF₄) is 150 sec and is unaffected by the presence of nitrogen, boron trifluoride, and carbon monoxide (49). The presence of 1 mmHg of oxygen reduces the half-life to 6 sec, but reaction reportedly occurs on the walls of the reaction flask. No gaseous polymers are formed during decay of SiF₂ in SiF₄, as monitored mass spectrometrically, but a polymer film appears on the walls of the container. Thus SiF₂ appears to be extraordinarily stable in the gas phase, in marked contrast with SiCl₂ and all known carbenes.

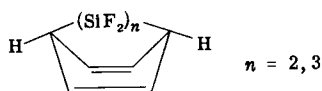
When silicon difluoride vapor is condensed, irreversible polymerization occurs as well as reactions with cocondensed substrates. Margrave (32) and Timms (51) have pointed out that the reactions of silicon difluoride with cocondensed substrates must all be regarded as secondary reactions of intermediate (SiF₂)_x polymers. In the absence of a cocondensate, silicon difluoride forms a reddish yellow deposit which becomes a white, rubbery, polymeric solid at room temperature. Destructive distillation of the polymer gives all the perfluorosilanes from SiF₄ to at least Si₁₄F₃₀ (47, 49).

It was concluded, by electron spin resonance spectroscopy (ESR) in a matrix-isolation experiment, that monomeric silicon difluoride has a singlet electronic ground state, invisible to ESR (52). A broad ESR spectrum was obtained when a mixture of SiF₂ and SiF₄ was condensed without dilution at 77°K. Under these conditions, silicon difluoride would be expected to polymerize and the ESR signal was attributed to the dimer (SiF₂)₂. When the mixture of SiF₂ and SiF₄ was diluted 50 : 1 with argon prior to condensation, no signal was observed. It was believed that monomeric silicon difluoride was protected from polymerization by the inert matrix. Thus the lack of an ESR spectrum was attributed to the diamagnetic behavior of the singlet ground state. No ESR signal was detected in the gas phase, in accord with the assignment of a singlet ground state to the silicon difluoride monomer.

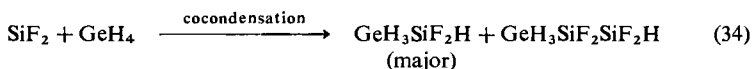
Since the reported chemistry of "SiF₂" is principally due to the reactions of the polymeric species (SiF₂)_x, it is of only indirect interest to the study of divalent silicon species. A brief summary, however, seems appropriate.

When a 2 : 1 mixture of SiF_2 and SiF_4 is cocondensed with BF_3 , a series of compounds is formed with empirical formulae $\text{BSi}_n\text{F}_{2n+3}$ (53). The compounds are apparently all members of the homologous series $\text{SiF}_3(\text{SiF}_2)_n\text{BF}_2$. Three facts taken together indicate that dimerization of silicon difluoride precedes the reaction with boron trifluoride: (1) None of the products contain only one silicon atom; (2) SiF_3BF_2 is no less stable than the observed reaction products; (3) SiF_2 and BF_3 do not react in the gas phase.

Cocondensation of silicon difluoride with benzene also leads to products invariably containing more than one silicon atom (54). The lowest members of the homologous series of products, $\text{C}_6\text{H}_6(\text{SiF}_2)_n$, have been assigned the interesting structures:

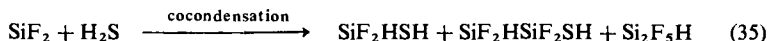


Ethylene and silicon difluoride under the cocondensation conditions also give cyclic products containing at least two silicon atoms linked together (55). In contrast, cocondensation of silicon difluoride and perfluorobenzene produces compounds containing isolated silicon atoms (54). Perfluorophenylsilane, $\text{C}_6\text{F}_5\text{SiF}_3$, and the positional isomers of $\text{C}_6\text{F}_4(\text{SiF}_3)_2$ (in ratio ortho : meta : para = 1 : 6 : 9) are formed, and spectacular intermittent blue light flashes are observed during cocondensation. The suggestion by Margrave that monomeric SiF_2 may be the attacking species in the reaction with perfluorobenzene is of doubtful validity but should be tested by means of experiments in the gas phase. Although a product containing a single silicon atom is obtained from silicon difluoride and germane, Eq. (34), Timms has suggested that it is



due to attack by germane on the Si—Si chain of $(\text{SiF}_2)_n$ polymer, “breaking off units containing one, two or more silicon atoms” (51).

Recently the possibility that monomeric SiF_2 may undergo direct reactions with substrates other than itself has been revived by Margrave in his interpretation of the cocondensation of silicon difluoride and hydrogen sulfide (56), Eq. (35). There seems to be no evidence, however,

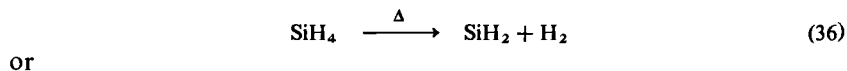


which supports a mechanism for a reaction of SiF₂ which excludes a dimerization step. It is, of course, very disappointing that the careful investigation of the properties of the best characterized divalent silicon compound has yielded little information which provides a comparison between the reactions of carbenes and divalent silicon compounds. It is clear that SiF₂ is considerably less reactive than CF₂ toward the substrates investigated. In light of the instability associated with silicon-silicon π bonds and the relatively low silicon-silicon bond strength, the tendency for silicon difluoride to polymerize rather than undergo reactions with other molecules is remarkable. It is very likely that characteristic reactions of silicon difluoride other than polymerization will be found in the near future.

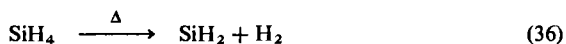
VI. SILYLENE (3), SiH₂

A. Formation

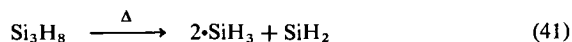
The simplest divalent silicon compound silylene SiH₂ has a long and controversial history which parallels that of methylene. The existence of SiH₂ was first postulated in pyrolysis studies on silane (57). Evidence for the formation of silylene has been somewhat indirect. A dilemma not yet entirely solved presented itself in the decision between two plausible primary steps in silane pyrolysis:



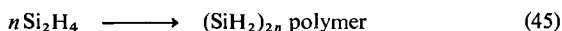
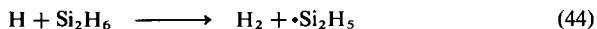
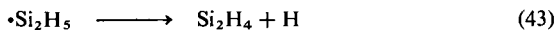
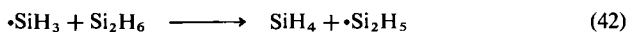
Only hydrogen and silicon were obtained as products of static pyrolysis at 380–490°. The mechanism which was written to accommodate this result postulated SiH₂ as an intermediate (57):



In 1936 (57) the step producing silylene was preferred because a polymer (SiH₂)_x of the proposed intermediate was known from the action of an electric discharge (58, 59) on silane. Later, in 1939, the formation of both silyl radicals and silylene was suggested by Emeléus as primary steps in the pyrolysis of higher silanes (60):



The silane, hydrogen, and polymeric $(\text{SiH}_2)_x$ obtained from disilane pyrolysis were explained by the mechanism in Eqs. (40) and (42)–(45). The



silylene formed from trisilane was believed to lose hydrogen as in Eq. (38) (60). This mechanism was suggested as an analogy to the pyrolysis of ethane which was believed to yield methyl radicals.

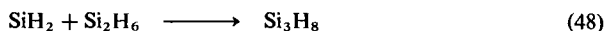
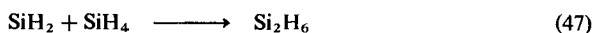
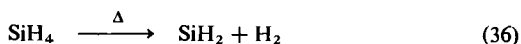
A considerable amount of information about the thermal decomposition of various silanes has become available from kinetic studies. The nature of the primary steps is still a hotly contested question, however. The existing data have not lent themselves to a resolution of the relative importance of silylene and silyl radicals as primary products of pyrolysis.

In his extensive investigations of the chemistry of silanes, Stokland established that the thermal decomposition of disilane is unimolecular, that chain reactions play no important role, and that rather little polymerization of added ethylene takes place (61). An activation energy of 48.9 kcal/mole for disilane pyrolysis was reported (61). Comparison of this value and the activation energy for pyrolysis of monosilane, 51.9 kcal/mole, with the estimates of Si—H and Si—Si bond energies, 75.1 and 52 ± 1 kcal/mole respectively (62, 63), led Stokland to conclude that pyrolysis of silane yields SiH_2 and H_2 , Eq. (36), while pyrolysis of disilane may yield either silyl radicals, as in Eq. (40), or silylene as shown in Eq. (46) (61).²

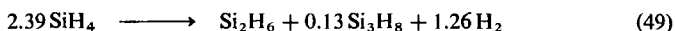


² Estimates of bond energies in silicon compounds vary chaotically. Pauling (62a) gives 42.2 and 70.4 kcal/mole, respectively, for the Si—Si and Si—H bond energies. Hess and co-workers (62b) give bond energies of 77 and 48 kcal/mole, respectively, for Si—H and Si—Si and point out that, for silicon compounds, bond energies cannot be equated with bond dissociation energies, which are given as 94 kcal/mole for Si—H in SiH_4 and 81 kcal/mole for Si—Si in Si_2H_6 .

The pyrolysis of silanes has continued to be a popular area of investigation, partially, one must surmise, because so few firm conclusions have been drawn. Purnell and Walsh published a careful kinetic study of silane pyrolysis in a static system in 1966 (64). From the initial stoichiometry, the initial reaction order (1.5), the effect of added gases, and from thermochemical considerations, Purnell and Walsh concluded that the mechanism in Eqs. (36), (47), and (48) is operative. In the initial stages of the reaction,

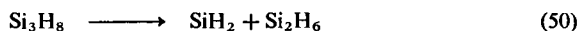


only gaseous products are formed according to the overall stoichiometry in Eq. (49).



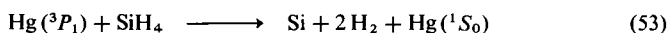
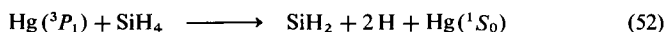
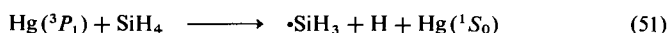
Since products are formed which are less stable than silane, it was felt that only initial rate measurements could be easily interpreted. The same energy of activation, 55.9 ± 0.5 kcal/mole, was found for the formation of hydrogen and disilane. Thus both products must arise by way of the same rate-determining step, believed to be Eq. (36). The decomposition of silane was shown to be homogeneous by varying the surface-to-volume ratio without affecting the reaction rate. The presence of added gasses, ethane, sulfur hexafluoride, or carbon dioxide, during silane pyrolysis did not lead to new products, but the apparent order of reaction changed. It was suggested that the rate-determining step is a unimolecular decomposition outside of its first-order pressure region. This step was identified with Eq. (36). A thermochemical argument supported the suggestion made earlier by Stokland (63) that formation of silyl radicals by reaction (37) would require an activation energy greater than that observed experimentally. As pointed out by Purnell and Walsh (64), the thermochemical arguments unfortunately rest on values for bond energies whose uncertainties are larger than the differences expected for various mechanisms. Stokland had also suggested insertion by silylene as the explanation for the formation of higher silanes in pyrolyses of silane (63) and disilane (65).

Recent reinvestigations of the pyrolysis of disilane and trisilane have been interpreted as proceeding via unsymmetrical cleavage to silylene and silane or disilane, respectively (66), as in Eqs. (46) and (50). However,

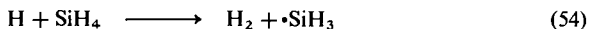


unanimity has not been reached concerning the mechanism of silane pyrolysis. It has once again been suggested, on the basis of isotopic scrambling in the pyrolysis of silane-deuterosilane mixtures, that the primary process in thermal decomposition of silane is the scission of a single silicon-hydrogen bond as shown in Eq. (37) (67).

Silylene has also been involved in the interpretation of photolysis experiments. In 1935 Emeléus could not decide whether a silyl radical or silylene was the primary product of silane photolysis (68). In 1964 Niki and Mains invoked several primary reactions to account for the quantum yield of hydrogen in the mercury-sensitized photolysis of silane (69). Disilane is the other principal volatile product.

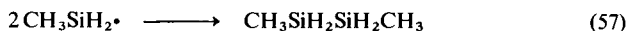
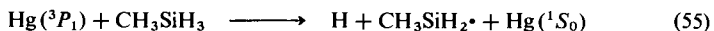


The first process (51) would give a maximum yield of unity for the formation of hydrogen by secondary processes such as



Some combination of the three primary processes above, Eqs. (51)–(53), is required to explain the observed quantum yield of hydrogen, 1.8.

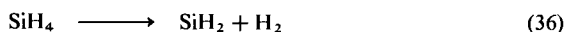
Gunning and co-workers have found that mercury-sensitized photolysis of silane is extremely complex, apparently producing silylene and silicon atoms as shown by Eqs. (52) and (53). The principal volatile product, in addition to hydrogen, was disilane (70). It is curious that the photolysis of silane takes a different course from that of alkyl silanes, which react cleanly by a scission of a single silicon-hydrogen bond, giving hydrogen and substituted disilanes in unit quantum yield (70):



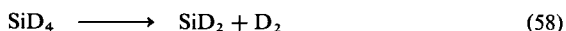
All the methylsilanes, CH_3SiH_3 , $(\text{CH}_3)_2\text{SiH}_2$, and $(\text{CH}_3)_3\text{SiH}$, follow this mechanism, with quantum yields for hydrogen formation between 0.7 and 1.0. In striking contrast, silane yields hydrogen with a primary quantum yield of ~ 3 , which requires a more complex mechanism whose details are not entirely clear.

It has been suggested that the decomposition of silane by an electric discharge in a flow system also produces silylene (71). The evidence is the

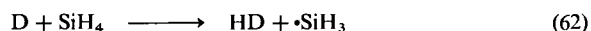
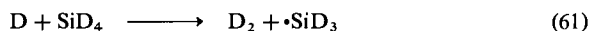
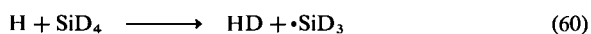
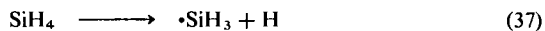
predominance of H_2 and D_2 over HD in the decomposition of mixtures of silane and perdeuterosilane. This suggests the elimination of molecular hydrogen:



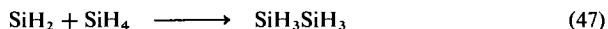
and



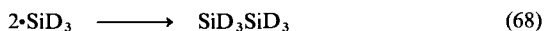
rather than loss of hydrogen atoms, which would lead to scramblings:



Both mechanisms can account for the formation of disilane:



or

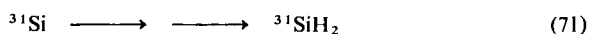
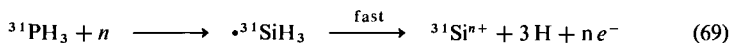


The distribution of products as determined by mass spectrometry was in somewhat better accord with the mechanism involving silylene than with that involving silyl radicals. Similar results were obtained on vacuum-ultraviolet photolysis. It appears, however, that the electric discharge decomposition of silane is more complex than simple loss of a hydrogen molecule to form silylene. This is indicated by the observation of emission from excited states of silicon atoms on passage of silane through a microwave-sustained plasma discharge (72). The vigorous action of an electric discharge on silane may well produce a variety of charged and neutral species.

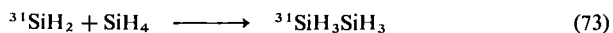
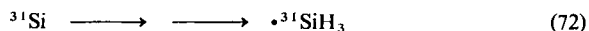
The reactions of recoiling silicon atoms with mixtures of phosphine and various silanes also seem to involve silylene, in this case $^{31}\text{SiH}_2$, as a

reactive intermediate. When a phosphorus-containing compound is bombarded with fast neutrons (whose energy is above ~ 7 MeV), phosphorus atoms are transmuted into silicon atoms by the nuclear transformation $^{31}\text{P}(n, p)^{31}\text{Si}$. The tremendous amount of energy released by the nuclear reaction, $\sim 10^5$ eV/atom, suffices to rupture the chemical bonds in the precursor molecule. Thus a nuclear reaction can serve as a convenient source of reactive free atoms (73). Most of the initial kinetic energy of the recoiling atoms is lost before chemical reactions capture them, and the nuclear recoil technique is complementary to thermal and photochemical methods for studying reactive species. The small number of atoms produced per experiment, typically 10^8 to 10^{10} , is compensated in the case of silicon by the short half-life of the particular isotope ^{31}Si , 2.65 h. Roughly 7,000 disintegrations per second take place among 10^8 atoms of ^{31}Si , and this is an ample number for accurate measurement by detectors of radioactive decay such as a gas-filled proportional counter. The reactions of recoiling silicon atoms have been investigated in the gas phase by determining the reaction products from various substrates and the effects on product distributions of such parameters as the structure of the substrate, the total pressure of the reaction mixture, and the pressure of moderators and scavengers present (73). The microscopic quantities of radioactive reaction products render chemical methods of structure determination difficult. The products are conveniently identified and their yields determined by a combination of vapor chromatography and flow counting (73).³

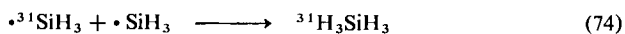
When phosphine-silane mixtures are bombarded with fast neutrons, high yields of radioactive silane and disilane are produced (74). While one can invoke mechanisms, (69)–(74), for the formation of disilane involving either silylene or silyl radicals,



or

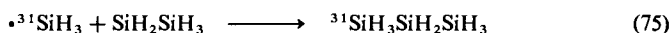
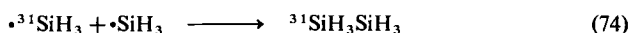


or

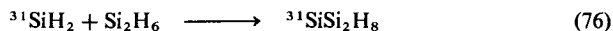


³ For a lucid presentation of the principles of hot-atom chemistry, see Wolf (73a) and Wolfgang (73b).

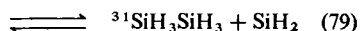
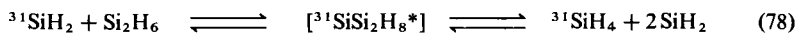
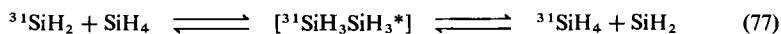
radioactive silylene seems to be the important intermediate. The incursion of radioactive silyl radicals in the reaction mechanism is rendered unlikely by the failure of nitric oxide and ethylene to act as scavengers (75). Also, if coupling of silyl radicals were the source of the disilane, one would need to invoke radiation damage to the starting materials as the origin of the nonradioactive silyl radicals. There is no evidence for such radiation damage. If radiation damage to silane produced silyl radicals, then one would expect both silyl radicals and disilyl radicals Si₂H₅ from radiation damage to disilane. Thus one might expect large quantities of radioactive disilane and trisilane from the fast-neutron irradiation of phosphine-disilane mixtures due to coupling of radicals:



Actually, the major product is radioactive trisilane, less than 10% as much disilane being produced (76). Insertion by silylene seems to be the dominant product-forming reaction:



The small amounts of radioactive silane and disilane also formed can be explained by decomposition of vibrationally excited adducts:



The decomposition of disilane and trisilane has been discussed above.

B. Spectroscopy and Theory

The absorption spectrum of silylene in its ground state has been observed in the flash photolysis of phenylsilane and silane. The spectrum, consisting of innumerable fine lines grouped in seven bands in the wavelength region 4800–6500 Å, resembles the red bands of methylene (77). The structural parameters for the upper and lower electronic states involved in the observed transition are given in Table II and compared with the latest values for methylene (78).

The similarity in structure between silylene and methylene in their two lowest singlet electronic states is striking. While the ground state of methylene is a triplet, silylene is believed to possess a singlet ground

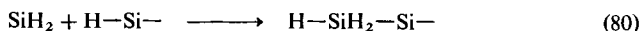
TABLE II (77, 78, 79)
Structural Parameters for Silylene and Methylene

Species	Electronic state	Bond length	Bond angle	Relative energy
SiH ₂	¹ A ₁	$r_0(\text{Si-H}) = 1.521 \text{ \AA}$	$\angle \text{HSiH} = 92.1^\circ$	0
	¹ B ₁	$r_0(\text{Si-H}) = 1.48_5 \text{ \AA}$	$\angle \text{HSiH} = 122^\circ$	15,540 cm ⁻¹
CH ₂	¹ A ₁	$r_0(\text{C-H}) = 1.11_1 \text{ \AA}$	$\angle \text{HCH} = 102.4^\circ$	—
	¹ B ₁	$r_0(\text{C-H}) = 1.05_3 \text{ \AA}$	$\angle \text{HCH} = 140 \pm 15^\circ$	—
SiH ₂ (calculated)	¹ A ₁	—	$\angle \text{HSiH} = 95.4^\circ$	0
	¹ B ₁	—	$\angle \text{HSiH} = 146.2^\circ$	20,460 cm ⁻¹
	³ B ₁	—	$\angle \text{HSiH} = 137.8^\circ$	16,180 cm ⁻¹

electronic state (79). The excellent agreement with the structural parameters and energies predicted by Jordan on the basis of semiempirical valence bond calculations speaks highly for the value of the calculation. It should be noted that in contrast with Jordan's work all elaborate calculations on methylene have been carried out after experimental spectroscopic values have become available (80, 81).

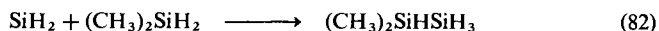
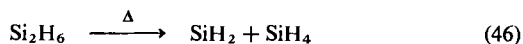
C. Reactions of SiH₂

The first reaction of silylene to be recognized was insertion into silicon-hydrogen bonds (63). It was postulated on the basis of the observation that higher silanes are generally found in the decomposition of silane, disilane, and trisilane and on the belief that silylene is the principal intermediate formed. Stokland's recognition of the insertion reaction of

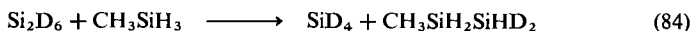


silylene preceded by some six years the discovery of indiscriminate insertion by methylene into carbon-hydrogen bonds (82). Insertion by silylene into silicon-hydrogen bonds to form higher silanes has also been postulated by Gunning *et al.* (70) and by Purnell and Walsh (64). These workers made no attempt, however, to determine experimentally whether silylene was indeed the precursor of the higher silanes. The first conclusive evidence for the occurrence of the insertion reaction came from experiments involving dimethylsilylene, (CH₃)₂Si (*vide infra*).

Recent experiments have placed the insertion reaction on a firm basis. Scavenger experiments have indicated that ³¹SiH₂ is the intermediate whose reactions form higher silanes after the recoil of silicon atoms in silane and disilane (74–76). The formation of higher silanes in the copyrolysis of disilane and alkyl silanes is also interpreted as demonstrating the occurrence of the insertion reaction, since silylene is believed to be the active intermediate (83).



The validity of this mechanism is supported by the finding that no hydrogen is formed in early stages of disilane pyrolysis and by the result of the labeling experiment shown below.



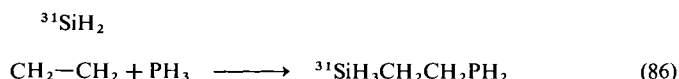
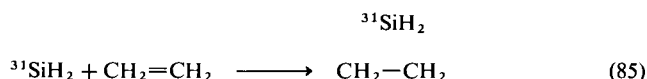
Had cleavage of Si₂D₆ to SiD₃ taken place, one would have expected SiD₃H and CH₃SiH₂SiD₃ as products.

There is, however, a certain chicken *versus* egg element in arguments about silane decomposition mechanisms, based on product studies. If silyl radicals were to undergo the efficient disproportionation to silylene and silane (70) shown in Eq. (84a)

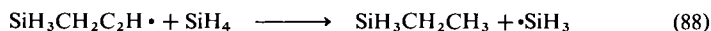
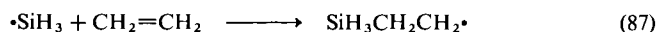


then products of silylene reactions would be observed, regardless of whether SiH₂ or SiH₃ is formed initially. If the disproportionation reaction (equation 84a) were reversible the situation would be even more complex.

Two other reactions of silylene seem likely based on available experimental data. Addition of silylene to olefins has been postulated to account for the formation of a product tenuously identified as ³¹SiH₃-CH₂CH₂PH₂, which was obtained from the reaction of recoiling silicon atoms with phosphine-ethylene mixtures (75). This product should be contrasted with the formation of ethylsilane under conditions where silyl radicals are believed to undergo addition to ethylene (84). Ethylsilane is only a very minor product from the recoil experiments (75).

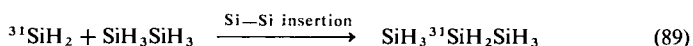
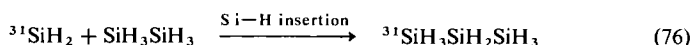


but

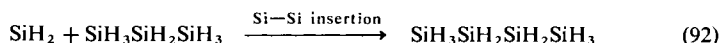
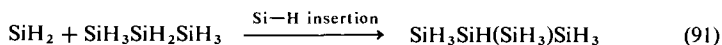
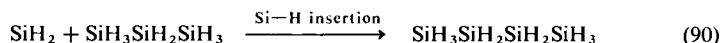


Both insertion into silicon-hydrogen bonds and addition to π bonds are reactions of silylene quite analogous to the reactions of methylene. The instability of silacyclopropanes has thus far prevented the isolation of the primary adducts. It is interesting to note that carbon-hydrogen bonds appear to be inert toward silylene (76, 85).

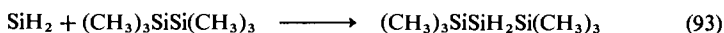
A novel reaction of silylene seems to be insertion into silicon-silicon bonds. The occurrence of silicon-silicon insertion is suggested by the unusually high reactivity of disilane toward silylene (76) and by the high ratio of *normal*-tetrasilane to *iso*-tetrasilane formed from the reaction of silylene and trisilane (83). Disilane has been found to be five times as reactive as silane toward silylene in recoil-atom experiments. A reactivity ratio of 3 : 2 would be expected if the number of silicon-hydrogen bonds per molecule were the sole determining factor. Likewise, a 3 : 1 ratio of *normal*-tetrasilane to *iso*-tetrasilane would be expected from insertion by silylene into the silicon-hydrogen bonds of trisilane on statistical grounds. The ratio obtained experimentally was 4.4–5.2 : 1 (83). Both these results can be understood if silicon-silicon insertion is competitive with silicon-hydrogen insertion:



and

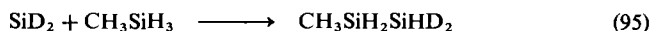
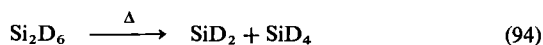


Confirmation of these reactions awaits degradation studies on labeled products, or the finding of an unambiguous reaction product such as



It has been suggested that the silicon-hydrogen bonds of disilane may be weaker than those in silane (86). One must consider, therefore, the possibility that the nonstatistical product ratios obtained in reactions (76) and (89)–(92) may be due to differential rates of insertion of silylene into *silicon-hydrogen* bonds.

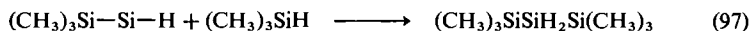
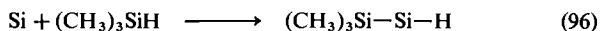
Apparently, silylene does not insert into carbon-silicon bonds (83, 87). This is evident from the reaction, already presented as overall equation (85).



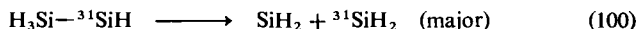
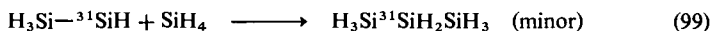
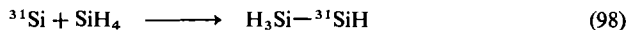
Had insertion into the silicon-carbon bond taken place, the product would have been $\text{CH}_3\text{SiD}_2\text{SiH}_3$. Silylene does not insert into carbon-hydrogen bonds (85).

VII. SILICON ATOMS, Si

The reactions of recoiling silicon atoms are under active investigation (74–76, 88–90). Skell has shown that thermally evaporated silicon atoms are unreactive toward carbon-hydrogen bonds but undergo insertion into silicon-hydrogen bonds to form a divalent silicon species which undergoes further insertion (91) (*vide infra*):

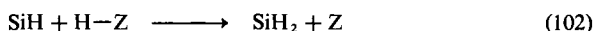
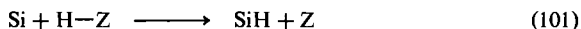


Although there is very little information about the primary reactions of silicon atoms generated by nuclear recoil, insertion into silicon-hydrogen bonds may explain the formation of a small amount of radioactive trisilane from the reaction of recoiling silicon atoms with silane (76).



The sole evidence for these reactions attributed to silicon atoms are the structures of the starting materials and products. As in the case of the reactions attributed to silylene, it is highly desirable to obtain more direct evidence for the structures of the reactive intermediates and for the reactions they undergo.

Alternatively, one can rationalize the formation of silylene from reactions of recoiling silicon atoms with phosphine-silane mixtures by a series of successive hydrogen abstractions (85):

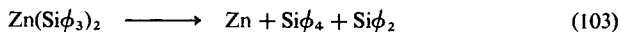


It is not possible to decide at this time whether path (98)–(100) is the source of silylene in the recoil experiments or if instead the source is path (101)–(102). The species Si–H is known spectroscopically (92), but its chemistry has not been explored. All the nuclear recoil experiments mentioned in this section have employed the nuclear transformation $^{31}\text{P}(n, p)^{31}\text{Si}$. The reactions of silicon atoms recoiling from the nuclear reaction $^{30}\text{Si}(n, \gamma)^{31}\text{Si}$ are also under investigation (88–90), but uncertainties in the charge state and energy of the recoiling atom, and increased radiation damage, render interpretations of the experimental data somewhat insecure.

VIII. ALKYL- AND ARYLSILYLENES, RSiH AND RR'Si

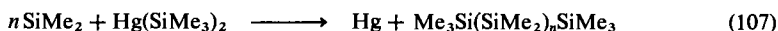
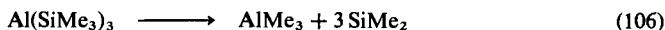
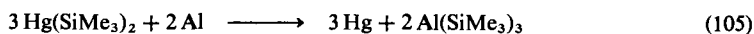
The formation of alkyl- and dialkylsilylenes as reactive intermediates has long been postulated (1–3). Generally these divalent silicon intermediates have been invoked to explain products which can be regarded as adducts to π bonds, polymers, or insertion products of a silylene. Little direct evidence for the intermediacy of such divalent silicon compounds has been presented, however.

Wiberg and co-workers have suggested that diphenyl silicon, $\phi_2\text{Si}$, is formed on thermolysis of di(triphenylsilyl)zinc, $\text{Zn}(\text{Si}\phi_3)_2$ (93). Tetraphenylsilane and a polymer whose composition indicated it to be $(\text{Si}\phi_2)_x$ were among the products for which the reaction sequence (103)–(104), was proposed. In a similar thermolysis of di(trimethylsilyl)mercury,



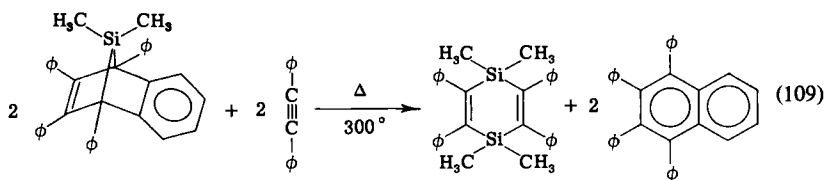
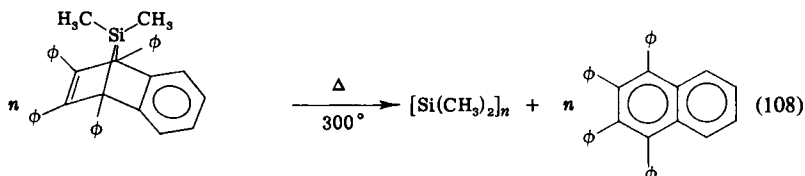
$\text{Hg}(\text{SiMe}_3)_2$, in the presence of aluminum, the formation of dimethyl

silicon, $\text{Si}(\text{CH}_3)_2$, was postulated to account for the production of higher silanes and the failure to isolate tri(trimethylsilyl)aluminum.



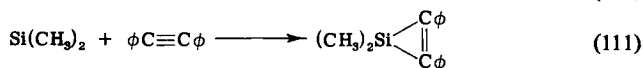
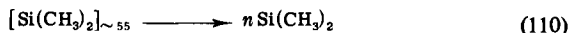
These mechanisms, based solely on the products formed, are exceedingly speculative, and cannot be accepted without further evidence.

Gilman and co-workers found indications in 1964 that dimethylsilylene can be extruded from the bicyclic compound shown below (94).

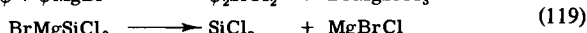
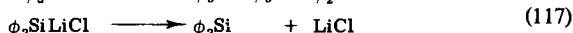


The structure of the adduct with diphenylacetylene was taken as evidence for the intermediacy of dimethylsilylene. Although the conclusion may be correct, it would be gratifying to have some kinetic information, e.g., whether the decomposition is unimolecular as required by the proposed mechanism. It should also be established that the rate of decomposition of the bicyclic starting material is independent of the concentration of the trapping reagent.

The product of reaction (109), which is considered to be a dimer of an adduct of dimethylsilylene, is the same compound as that reported earlier by Volpin and co-workers for the pyrolysis of a polymer, $[\text{Si}(\text{CH}_3)_2]_{55}$, in the presence of diphenylacetylene (95-97). A silacyclopropene structure was initially proposed before the product was shown to be dimeric (98).

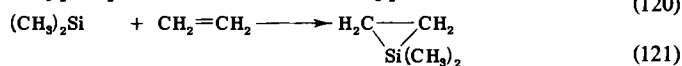
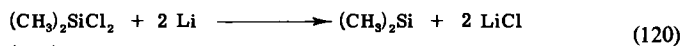


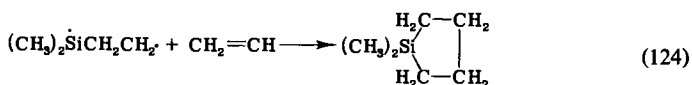
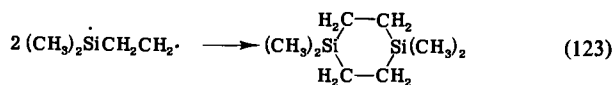
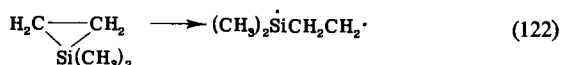
Even earlier, several organometallic reactions were interpreted as producing divalent silicon intermediates (99, 100):



One must level the same criticism at these mechanistic proposals as was accorded to those of Wiberg (*vide supra*). Although these reactions are plausible, there is no compelling evidence for the incursion of divalent silicon compounds as reaction intermediates. Not even the structures of the products demand such an explanation. No attempt was made to rule out ionic reactions as the sources of the polymeric products.

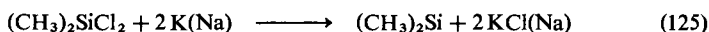
Treatment of diphenyldichlorosilane, $\phi_2\text{SiCl}_2$, with lithium in the presence of olefins did not lead to products indicative of the intermediacy of diphenylsilylene (101). However, in another laboratory, treatment of dichlorodimethylsilane with lithium in the presence of ethylene gave products attributed to the reactions of dimethylsilylene (102):



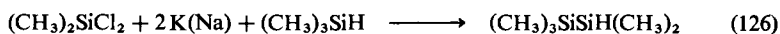


Similar products have been obtained from pyrolysis of cyclic polymers, $[\text{Si}(\text{CH}_3)_2]_n$, in the presence of olefins (103). Unfortunately, there is no evidence for the participation of divalent silicon species in these reactions other than the structures of the products themselves.

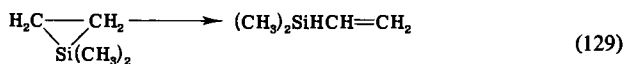
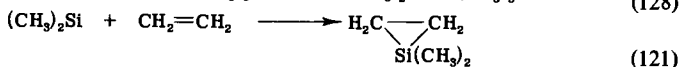
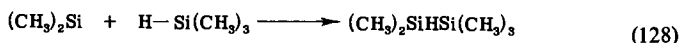
The first convincing demonstration of the formation of dimethylsilylene comes from the work of Skell, in which sodium-potassium vapor reacted with dimethyldichlorosilane in the gas phase at 260–280° (104).



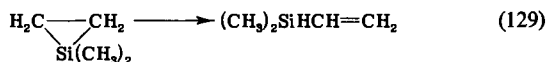
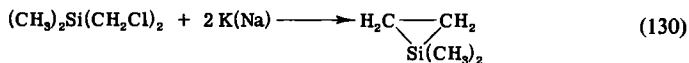
Identification of the intermediate depends on the products formed in the presence of trimethylsilane and ethylene, respectively:



These products are rationalized by insertion of dimethylsilylene into the silicon-hydrogen bond of trimethylsilane, and by addition of dimethylsilylene to ethylene followed by rearrangement, respectively.

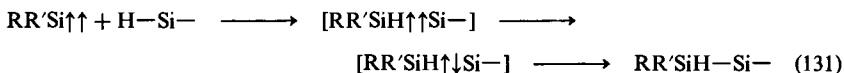


That vinyltrimethylsilane arises by rearrangement (129) was rendered quite likely by performing a related reaction which would be expected to give a silacyclop propane and which gave the same product.



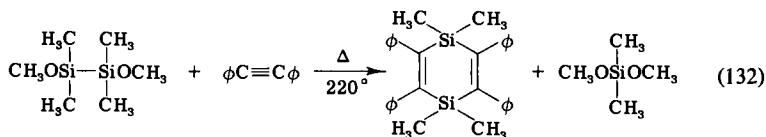
Although the products obtained by Skell are persuasive evidence for reactions of dimethylsilylene, one cannot exclude organometallic intermediates such as $(\text{CH}_3)_2\text{SiKCl}$ on the basis of the products formed.

Skell has written that insertion into a silicon-hydrogen bond by dimethylsilylene establishes a singlet electronic state for the reacting species. This point of view cannot be rigorously defended because the detailed mechanism for insertion is not known and a triplet silylene could give an "insertion product" by an abstraction-recombination mechanism.

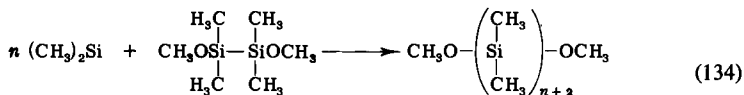
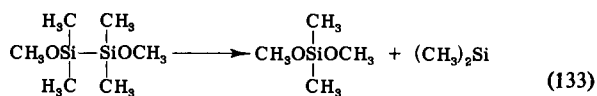


Such a process as (131) could be quite efficient depending on the time required for spin inversion. Even in carbene chemistry the time scale for spin inversion has not been established.

Recently a new method has been discovered for carrying out reactions which appear to involve dialkylsilylene intermediates. By pyrolyzing alkoxydisilanes in the presence of diphenylacetylene, Atwell and Weyenberg have obtained the product which is regarded as a dimer of the dimethylsilylene adduct (105).



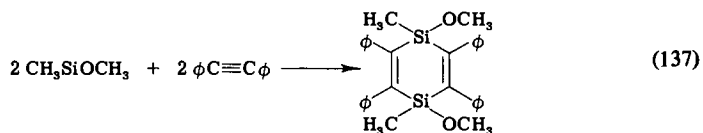
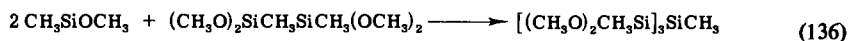
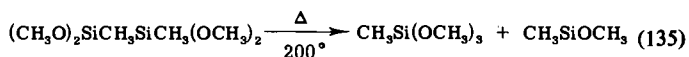
The primary step is believed to be formation of dimethylsilylene which can undergo reaction with the starting disilane.



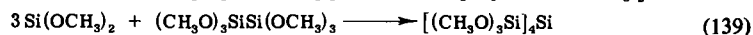
This mechanism has been supported by kinetic studies (106). The decomposition of $\text{CH}_3\text{OSi}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{OCH}_3$ has been shown to be

unimolecular in benzene solution, and the rate of decomposition is not accelerated by the presence of trapping reagents such as diphenylacetylene. Pyrolysis in the inlet of a mass spectrometer is said to give dimethylsilylene, detected by the molecular ion. Thus one can regard this mechanism as well established.

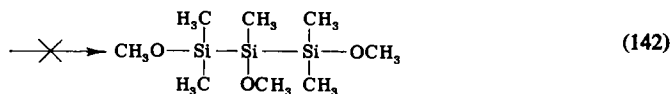
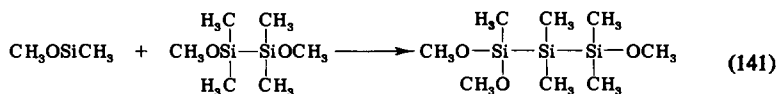
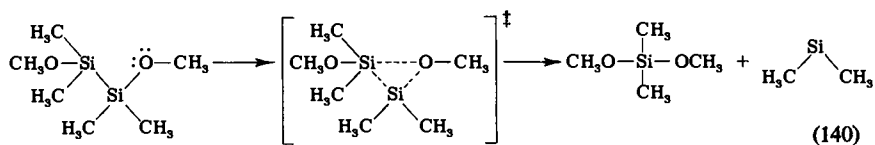
Trapping experiments with diphenylacetylene have also indicated that other divalent silicon intermediates can be formed similarly.



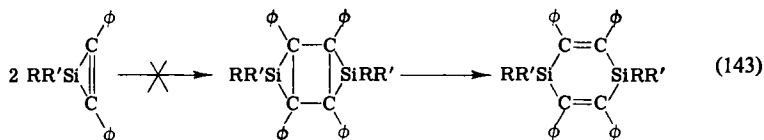
Hexamethoxydisilane also undergoes facile pyrolysis, but no adduct with diphenylacetylene is obtained, apparently because reaction of dimethoxysilylene with the starting disilane is extremely rapid.



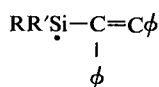
A three-membered transition state has been postulated for the cleavage, but no activation parameters in support of this geometry are given.



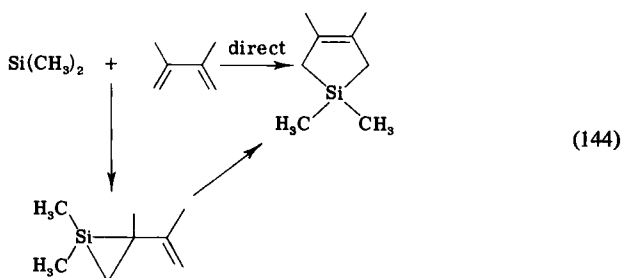
Reaction (141)–(142) has been interpreted as establishing that silylenes insert into silicon–oxygen bonds of alkoxydisilanes (3). It is curious that dimethylsilylene is comparatively unreactive toward $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ in view of the hypothesis that O–Si insertion is favored over Si–Si insertion. An ingenious experiment indicated that the cyclic compounds which arise in reactions such as (132) and (137) cannot be products of silacyclopentene cycloadditions (3).



The cyclic products probably are dimers of open-chain species of formula



Dimethylsilylene generated by pyrolysis of alkoxydisilanes has also been added to dimethylbutadiene (106). The product may be due to a direct 1,4 addition, or may arise by rearrangement of a vinylsilacyclopentane. The “direct” route itself may consist of several steps.

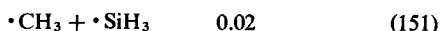
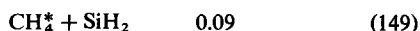
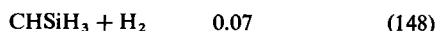
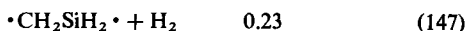
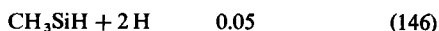
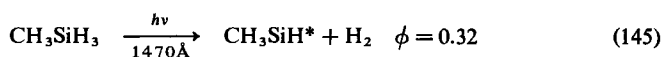


While addition of alkylsilylenes to conjugated dienes is feasible, simple olefins are not sufficiently reactive to compete with the alkoxydisilanes for the silylene. An order of reactivity toward dimethylsilylene has been deduced by Atwell and Weyenberg (3).



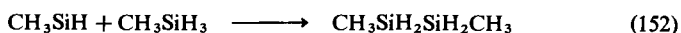
A. Methylsilylene, CH₃SiH

Product studies supplemented by labeling experiments, quantum yield measurements, scavenger experiments, and exact determination of stoichiometry have led Gunning and co-workers to conclude that vacuum ultraviolet photolysis of methylsilane produces methylsilylene (107, 108). The reaction is analogous to the vacuum-ultraviolet photolysis of silane in which silylene has been detected spectroscopically (*vide supra*), but apparently the methylsilane photolysis is quite complicated. The following primary steps occur, with the quantum yields given summing nicely to unity (108).



$$\text{Total } \phi = 1.04$$

The final products obtained, H₂, CH₃SiH₂SiH₂CH₃, CH₃SiH₂SiH₃, CH₄, CH₃CH₃, CH₃SiH₂CH₃, and SiH₄, listed in order of decreasing yield, are in accord with the primary steps listed above, followed by insertion reactions into silicon-hydrogen bonds by SiH₂ and CH₃SiH. Radical coupling reactions are also assumed to occur.



Methylsilylene was not scavenged by either nitric oxide or ethylene (107, 108), in agreement with earlier studies on silylene (75).

Pyrolysis of methylsilane at 520° gives a 77% yield of 1,2-dimethyldisilane, a remarkably clean reaction which may also involve methylsilylene as the active intermediate (109).

IX. SILICON MONOXIDE AND SILICON MONOSULFIDE, SiO AND SiS

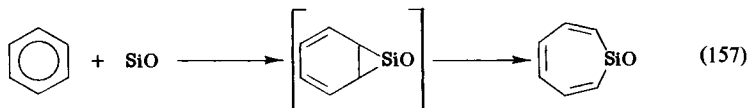
It has long been known that monomeric silicon monoxide, SiO, can be produced in the gas phase by heating silicon and silicon dioxide together (110).



When condensed, silicon monoxide forms a polymer whose chemistry depends on the mode of quenching (111). Spectroscopic studies on silicon monoxide monomer have been carried out in the gas phase (112–115), and its dissociation energy ($D_0^\circ = 182.8 \pm 3$ kcal/mole) and ionization potential (11.6 ± 0.2 volts) have been determined mass spectrometrically (116). No chemistry of the monomer has been reported. However, the cocondensation of silicon monoxide and potentially reactive substrates is being investigated at the present time (117).

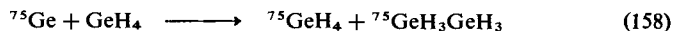
The preparation of silicon monosulfide, SiS, as a polymeric solid has been described, and the ultraviolet emission spectrum of the gaseous monomer has been observed and analyzed, but no chemistry has been reported (118).

Both SiO and SiS have great potential interest as divalent silicon species. One may anticipate such reactions as



X. GERMANIUM ATOMS, Ge

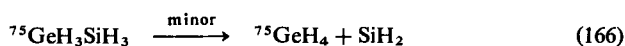
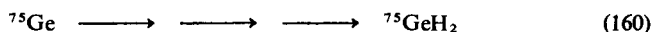
Only recently has investigation of the chemistry of germanium atoms been undertaken. Reactions of germanium atoms recoiling from the nuclear transformation $^{76}\text{Ge}(n, 2n)^{75}\text{Ge}$ (half-life of $^{75}\text{Ge} = 82$ min) with germane give radioactive germane and digermane (119):



From germane-silane mixtures an additional product is obtained:



The products suggest the formation of germylene, GeH_2 , which then undergoes reactions similar to those of silylene, but this mechanism is entirely speculative, and further experiments are required for its elucidation.



XI. GERMYLENE GeH_2

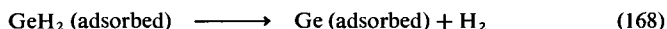
As in the case of silylene, SiH_2 , germylene, GeH_2 , has often been invoked as a reactive intermediate. With the exception of the postulated insertion into silicon-hydrogen and germanium-hydrogen bonds presented above, little is known about the chemistry of germylene.

The pyrolysis of germane, GeH_4 , was first thought to yield only germanium and hydrogen when carried out in a static system at 283–374° (120). A surface-catalyzed decomposition was postulated with a rate proportional to the one-third power of the germane concentration. This postulated mechanism required a three-body surface collision. On careful reinvestigation of the kinetics of germane pyrolysis, Taylor and co-workers found that the reaction is of first order at pressures above 100 mm Hg but decreases to zeroth order at lower pressures (121). It was concluded that there are concurrent gas-phase first-order and surface-catalyzed zeroth-order reactions occurring with activation energies of 51.4 and 41.2 kcal/mole, respectively.

Taylor and co-workers offered a mechanism for the first-order homogeneous decomposition of germane which produces germylene (122).

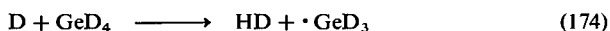
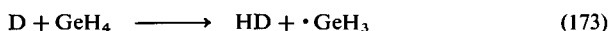
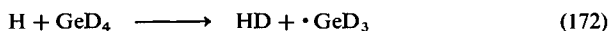
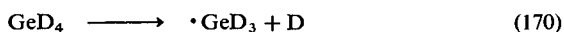
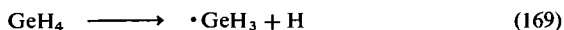


The subsequent fate of the germylene was not determined. Reaction with hydrogen to re-form germane was ruled out by lack of isotopic scrambling in the recovered germanes from the copyrolysis of GeH_4 and GeD_4 . It was speculated that the germylene molecules may diffuse to the walls, where catalyzed decomposition could occur.



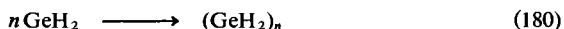
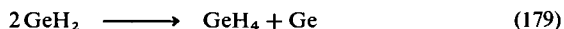
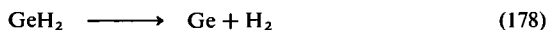
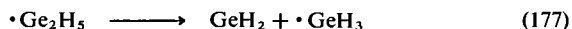
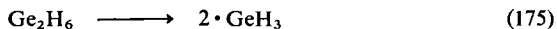
Actually this mechanism seems very unlikely to be correct on the basis of the data given by Taylor and co-workers (121, 122). When a mixture of GeD_4 and GeH_4 was decomposed, most of the resulting hydrogen was HD, although no HD but only H_2 came from the decomposition of GeH_4 in the presence of D_2 .

While Taylor and co-workers explained the formation of HD by exchange reactions of molecular hydrogen catalyzed by intermediate radicals, the mechanism (169)–(174) seems preferable. Isotopic scrambling



in the wall reaction is also incompatible with a simple cleavage of germane into germylene and hydrogen.

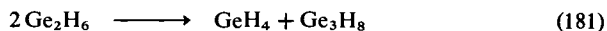
Emeléus and Jellinck have suggested that the pyrolysis of digermane is homogeneous and of first order at 195–222° (123), with an activation energy of 33.7 kcal/mole. Germane, hydrogen, and a polymeric substance were reaction products. To account for the reduced yield of germane and the formation of polymer in the copyrolysis of digermane and propylene, a mechanism, (175)–(180), was written which incorporated germanium-



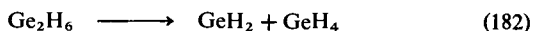
germanium bond scission as the primary step. No direct evidence for the incursion of germylene or the occurrence of other unusual steps was given.

Timms and co-workers suggested in 1964 that the production of germylene by pyrolysis of germane accounts for the formation of various mixed germanium-silicon hydrides when germane and a silane are subjected to copyrolysis (124). Pyrolysis of higher germanes has also been alleged to give germylene, but the evidence seems to consist of the formation of polymeric $(\text{GeH}_2)_x$ (125).

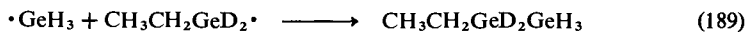
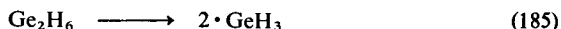
Recently, pyrolysis of digermane at $230\text{--}240^\circ$ has been shown to yield germane and trigermane, with no hydrogen formed below 250° (87).



When digermane, Ge_2H_6 , and deuterated ethylgermane, $\text{CH}_3\text{CH}_2\text{GeD}_3$, are copyrolyzed at 280° , a temperature at which the ethylgermane is stable, the products are germane, trigermane, and ethyldigermanes. These products are consistent with the intermediacy of germylene, which undergoes germanium-hydrogen bond insertion to give the observed products.



Since no monodeutero germane or diethyldigermane was produced, the mechanism (185)–(189) seems definitely to have been ruled out. The



labeling experiment establishes the mechanism of digermane pyrolysis as definitely giving germylene, and insertion by germylene into germanium-hydrogen bonds seems to occur also. This seeming analogy with the chemistry of silicon hydrides should not, however, be carried too far. While pyrolysis of methylsilane leads to predominant silicon-hydrogen bond fission, methylgermane pyrolysis leads principally to carbon-germanium bond cleavage (109).

XII. DIALKYL AND DIARYL GERMYLENES, R_2Ge

No firm evidence exists at this time for the formation or reactions of these species. When ethylene is passed through a solution of dimethyldichlorogermane, $(CH_3)_2GeCl_2$, in the presence of lithium, products are formed which have been rationalized by the postulation of a dimethylgermylene, $Ge(CH_3)_2$, intermediate (102). Photolysis of a polymeric diphenylgermylmercury compound yields a polymer which was attributed to the intermediacy of diphenylgermylene (126), but no mechanistic studies are reported.

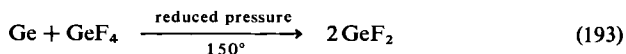


XIII. GERMANIUM DIHALIDES, GeX_2

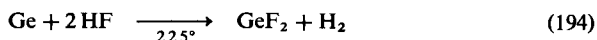
A. Formation and Reactions

Germanium dihalides are stable in the solid state. The solids do not seem to contain germanium-germanium bonds (2), and they act as sources of the germanium dihalide moiety in chemical reactions.

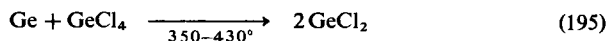
Germanium difluoride has been prepared by Bartlett and Yu by reaction of germanium and germanium tetrafluoride, a reaction similar to the one which forms silicon difluoride (127).



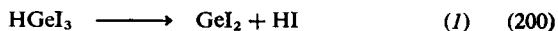
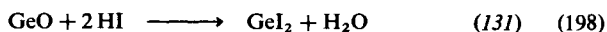
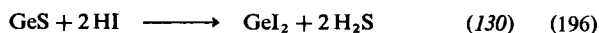
Muetterties has obtained germanium difluoride from germanium and anhydrous hydrogen fluoride (128).



Dennis and Hunter prepared germanium dichloride as follows (129):



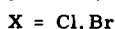
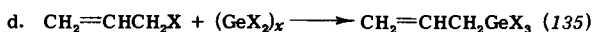
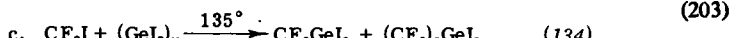
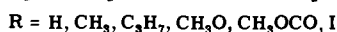
Several preparations of germanium diiodide have been reported:



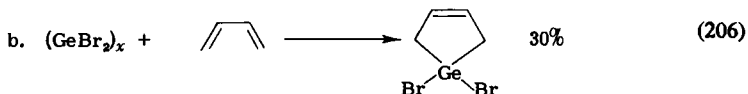
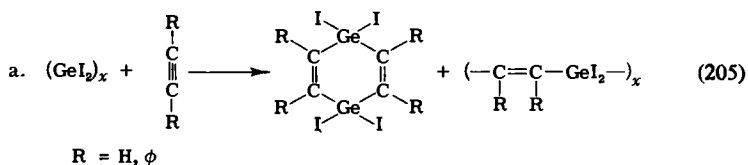
The following direct reactions of the solid germanium dihalides have been reported. In no case has the role of the germanium dihalide monomer in the operative reaction mechanisms been determined.

1. Reactions with alkyl and aryl halides.

1. Reactions with alkyl and aryl halides

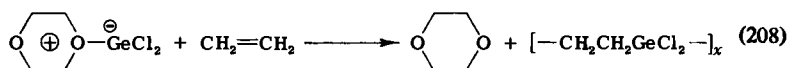
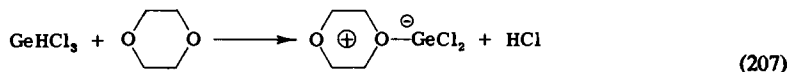


2. Reactions with alkynes (96, 136–138) and dienes (1).



At first, addition of germanium diiodide to diphenylacetylene was believed to give a germacyclopropene.

Ether adducts of germaform, GeHCl_3 , are believed to be complexes of monomeric germanium dichloride. The ether complexes behave toward reactive substrates similarly to polymeric germanium dichloride. It is not clear, however, whether dissociation to monomeric germanium dichloride occurs in the reactions of either the ether complex or the polymer (135, 139, 140).



B. Spectroscopy

Preliminary studies have been made recently of the spectra of gaseous monomeric germanium halides. Chemiluminescent emission from a flame of germanium tetrachloride burning in potassium vapor consists of a group of closely spaced diffuse bands in the region 4100–4900 Å (141); it has been attributed to a nonlinear triatomic molecule on the basis of a vibrational analysis. The emitter is believed to be germanium dichloride (141).

A poorly resolved electronic absorption spectrum for monomeric germanium dichloride in the region 3140–3300 Å has been reported on vaporization of liquid polymeric germanium dichloride or from reaction of germanium tetrachloride with germanium (142). Again the structure of the emitter was assigned on the basis of a successful vibrational analysis for a triatomic molecule.

The chemiluminescent emission from germanium dichloride previously observed was attributed to an excited triplet with the help of an extended Hückel molecular orbital calculation (142). A region of continuous emission from 3125 and 3341 Å observed when a microwave discharge is passed through germanium tetrachloride was attributed to emission from the upper singlet state, also observed in absorption studies (142). The separations of energy levels found by spectroscopic experiments of various Group IV dihalides are given in Table III (142). The data come from several sources (142).

TABLE III (142)
Energy Level Separations for Group IV Dichlorides Estimated
from Spectroscopic Data

Species	$^1A_1-^1B_1$	$^1A_1-^3B_1$
CCl ₂	17,700 cm ⁻¹ (band system)	—
SiCl ₂	29,952 } (two-band system) 28,952 }	22,900 cm ⁻¹ (continuum)
GeCl ₂	30,969 (bands) 29,900–32,000 (continuum) }	22,700 (bands)
SnCl ₂	31,055 (continuum)	22,237 (bands)
PbCl ₂	31,000 (continuum)	—

The increase in the $^1A_1-^1B_1$ separation with decreasing covalency of the metal-chlorine bonds is explained by a decreased interaction between an s orbital on the metal and $3p$ orbitals on the chlorines (138). The highest occupied orbital in the ground singlet electronic states of these dichlorides can be thought of as arising from overlap between an s orbital on the central atom and chlorine $3p$ orbitals, with some contribution from a p orbital on the central atom. Since the $3p$ orbitals on chlorine are occupied, there is an antibonding interaction between the electrons in the highest occupied molecular orbital in the molecule and the "localized" chlorine $3p$ electrons. This repulsion effectively raises the energy of the ground state and reduces the transition energy to an excited state. In the transition an electron is promoted from the highest occupied molecular orbital of the ground state to an orbital which consists largely of a p orbital on the central atom. As one goes down the periodic table from carbon to silicon, etc., the antibonding interaction between the highest occupied orbital in the ground state, and the chlorine $3p$ orbitals decreases. Thus the energy of the ground state is lowered relative to the first excited singlet, and the transition energy is increased.

The assignment of bands in Table III is somewhat speculative, so one should await confirmation of the assignments by further spectroscopic experiments before the structural implications can be fully explored. The large errors involved in the extended Hückel calculations cause particular concern about assignments based on such calculations.

No chemistry involving triplets of any dihalide of a Group IV element has been reported, with the exception of difluoromethylene CF_2 ⁴.

A poorly resolved absorption spectrum has been reported for germanium difluoride (143), obtained from the vapor in equilibrium with liquid germanium difluoride polymer at 150° , and from the products of reaction of germanium tetrafluoride vapor with germanium metal at $\sim 250^\circ$. A vibrational analysis for a bent triatomic molecule was successful. The transition energy between ground and excited singlet electronic states is given as $43,843 \pm 10 \text{ cm}^{-1}$. A large increase in bond angle is postulated in going to the excited state. An absorption spectrum has also been obtained for tin difluoride ($\text{O}-\text{O}$ energy of $40,741 \text{ cm}^{-1}$) and for lead difluoride (144).

⁴Two reactions of triplet difluoromethylene have been reported, self annihilation and addition to oxygen $^3\text{CF}_2 + ^3\text{O}_2 \rightarrow \text{CF}_2\text{O}$. See T. Johnston and J. Heicklen, *J. Chem. Phys.* **47**, 475 (1967).

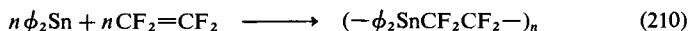
XIV. GERMANIUM MONOXIDE AND MONOSULFIDE, GeO AND GeS

Germanium monoxide has been prepared as an amorphous sublimate by reaction of germanium metal with carbon dioxide and with germanium dioxide (145). Thermochemical evaporation studies and mass spectroscopy have yielded values for the dissociation energy (156.2 ± 1.9 kcal/mole) and ionization potential (11.5 ± 0.2 volts) (116). Monomeric GeO has been observed spectroscopically (146). Germanium monosulfide has been produced as black crystals from the reaction of germanium metal with hydrogen sulfide (147). No chemistry of monomeric germanium monoxide or monosulfide has been reported.

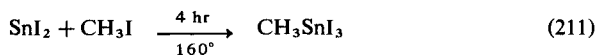
XV. DIVALENT TIN COMPOUNDS

Divalent tin halides are, of course, well-known stable compounds. Divalent alkyl- and aryltin compounds can also be prepared, but they are polymeric materials containing tin-tin bonds. Their preparation and properties have been reviewed (148).

Upon photolysis, polymeric diphenyltin reacts with tetrafluoroethylene to give a polymer which is a 1 : 1 adduct (149). While this can be formulated as an addition reaction of monomeric diphenyltin, there is no evidence which demands this interpretation.



A reaction which was formulated as an insertion by tin diiodide was reported many years ago, but there was no evidence for participation by the monomer (150).



XVI. CONCLUSION

We see that a rich variety of reactions has been reported for divalent compounds of silicon, germanium, and tin. Reactions analogous to the insertion and addition reactions of carbenes have been claimed for *all* these divalent silicon, germanium, and tin compounds. Quite often it is *assumed* that a mechanism is operative analogously to one involving a

carbene, because analogous products are formed. The discovery of products that *might* have arisen by insertion or addition has all too often been interpreted as proving both that a divalent intermediate has been formed *and* that the intermediate undergoes addition or insertion, as any well-behaved carbene analog should do.

Unfortunately, there are serious problems with such logic. If one wants to learn about the *chemistry* of the divalent silicon, germanium, and tin compounds, one must produce them under conditions such that their formation can be verified by means other than the nature of the reaction products. On the other hand, if one wishes to use chemical tests for the formation of these divalent species, then one must unambiguously demonstrate that the diagnostic reactions really demand the divalent intermediates.

As usual, nature strives to retain her sphinxlike ambiguity. The divalent species such as silicon difluoride which are well characterized as monomeric divalent species show little tendency to undergo reactions other than with themselves. On the other hand, species like silicon dichloride and silylene, which seem to undergo the addition and insertion reactions ascribed to them by analogy with carbenes, are difficult to detect under reaction conditions.

Among the many careful mechanistic studies cited, a few should be singled out as providing the most substantial proof for the formation of monomeric divalent silicon and germanium intermediates. The work of Atwell and Weyenberg in solution (3, 105, 106), and that of Gunning, Strausz, and co-workers (107, 108), Purnell and Walsh (62), Skell and Goldstein (104), Ring and co-workers (66, 67, 71, 87), and Bowrey and Purnell (83) in the gas phase all supplemented product studies with other means such as kinetic analysis, labeling, and scavenger studies. Thus the suggested mechanisms for the formation and reactions of divalent species were buttressed. Nevertheless, direct monitoring of the reaction kinetics of a divalent silicon or germanium species has been possible thus far only for the disappointingly unreactive silicon difluoride by Margrave and co-workers.

One can state the situation fairly by pointing out that, indeed, reactions have been found which resemble those of carbenes and which may involve divalent silicon, germanium, and tin intermediates. These insertion and addition reactions should be carefully investigated using fast spectroscopic methods to ascertain the intermediacy of the postulated divalent intermediates. On the other hand, much remains to be done to find the reactions

of these divalent intermediates which differ from those of carbenes. Virtually all recent attempts to study the chemistry of divalent silicon and germanium have been limited to reaction substrates analogous to those employed in carbene chemistry. The futility of such a line of attack is indicated clearly by the recognition in recent years that a host of organo-metallic compounds mimic carbenes in the transfer of a methylene moiety. Surely it will be found in silicon and germanium chemistry that a subtle gradation between the reactions of divalent and tetravalent species exists, and that the very terms "divalent" and "tetravalent" are archaic notations for limiting ideal cases of chemical behavior. It is now evident that silicon, germanium, and even tin compounds can be made to behave like carbenes. The forced similarities do exist, but it is now time to broaden the scope of our interests and look at the distinctive features of the chemistry of higher divalent Group IV compounds. These distinctive features remain to be discovered.

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