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Preface

This book was prepared with the idea of collecting some of the multitudinous new literature on carbanions and presenting it along with the fundamentals of carbanion chemistry. Some 400 papers from the period 1976 to 1982 have been assimilated into the book along with about an equal number of references (many to reviews) from the earlier literature.

The material is organized under the headings *Structures* (with emphasis on the results of X-ray studies since they unambiguously show the molecular geometry), *Preparations*, and *Reactions*. Reactions, the largest topic, is divided into reactions with electrophiles, eliminations, oxidations, and rearrangements. Under these headings, carbanions without resonance stabilization (σ carbanions) are generally discussed first, and are further subdivided into sp^3 (alkyl) followed by sp^2 (vinyl and aryl) followed by sp (acetylenic); resonance-stabilized (π) hydrocarbon anions such as allyl and benzyl follow; lastly, heteroatom-containing π carbanions such as enolates are considered. Some references to carbanion equivalents are included at the end.

Tucson, Arizona U.S.A.
May 1983

Robert B. Bates
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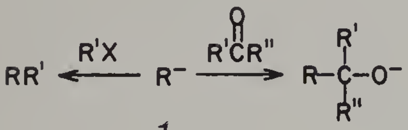
I. Introduction

Carbanions (*1*) are among the most important synthetic organic intermediates, largely because of their ability to form carbon-carbon bonds in high yield by reaction with a great variety of electrophiles, e.g., alkyl halides and ketones:



1

R = alkyl
X = halogen

Improved methods permitting the preparation of many new types of carbanions paired with many different metals (and even without counterions!) have been responsible for the spectacular growth of this area since Cram's book appeared in 1965 [1]. The Journal of Organometallic Chemistry *weekly* includes many new organometallics, and annually provides surveys of the literature on the organometallics of selected metals.

This book will be limited to relatively "free" carbanions, i.e., those paired with group IA and IIA metals, aluminium, zinc, cadmium, quaternary ammonium ions, and those studied in the gas phase in the absence of counterions. Earlier books in this series discuss organic synthesis by means of transition metal complexes [2, 3].

II. Structures

1. Non-delocalized (σ)

a. sp^3

That the charge-bearing carbon atom in simple alkyl anions is sp^3 rather than sp^2 hybridized has been amply demonstrated in the gas phase by photoelectron spectroscopy (methyl carbanion without counterion or solvent [4]), in solution by NMR spectroscopy [5, 6], and in crystals by X-ray studies (monomeric $EtMgBr \cdot 2\ Et_2O$ [7], dimeric bicyclo[1.1.0]butan-1-yllithium · TMEDA [8], tetrameric MeLi [9] and EtLi [10], and hexameric cyclohexyllithium · 1/3 benzene [11]).

The state of aggregation (monomeric, dimeric, tetrameric, hexameric, or polymeric) depends on the carbanion structure, cation, temperature, and solvent; coordinating solvents such as ethers and tertiary amines tend to break down the larger aggregates into more reactive [12] smaller ones [13, 14]. That these particular aggregates (with structures given below) should represent energy minima is supported by MO calculations [15].

The organometallic bond may be from a carbon to one metal atom (*2*, simple σ bond), to two metal atoms (*3*, "3-center 2-electron" bond), or to three metal atoms (*4*, "4-center 2-electron" bond); *3* and *4* are considered to contain alkyl groups "bridging" between metal atoms. Electron density at the expected position amidst the four atoms has been observed in a high-quality X-ray study [10]. Carbon-metal bond lengths involving bridging carbons are longer than those for 2-center bonds, as can be seen from the entries for K, Rb, Mg, and Al in Table 1. 4-Center bonds are not noticeably different in length than 3-center bonds (see Li entries). Since C—M bonds involving sp^3, sp^2, and sp hybridized carbon atoms differ very little in length, they have been lumped together in Table 1.

2

3

4

M = metal

As can be seen in Table 1, the smaller elements (especially Li) are particularly prone to form stable compounds containing bridging alkyl groups.
Monomers — Crystalline $EtMgBr \cdot 2\ Et_2O$ [7] and $Me_2Mg \cdot TMEDA$ [36]

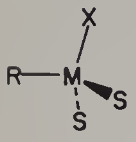
Table 1. Carbon-Metal Bond Lengths (Å) in Organometallics from X-ray Studies

Metal	Calculated[a]	Observed			
		σ (2-center)	σ (3-center)	σ (4-center)	π (shortest only[b])
Li	2.00	2.19[14a]	2.21–2.28[8,16]	2.18–2.41[9,10,11,17,18]	2.13–2.34[19–27,27a]
Na	2.34	2.49[28]	—	—	2.64–2.83[29,30]
K	2.80	2.55[28]	—	3.22[31]	3.04–3.16[32,33]
Rb	2.93	2.98[28]	—	3.36[34]	—
Cs	3.12	—	—	3.53[34]	—
Be	1.66	—	1.93[35]	—	—
Mg	2.13	2.09–2.20[7,36–40]	2.22–2.26[40–42]	—	2.26–2.50[40,43]
Ca	2.51				
Sr	2.68				
Ba	2.75				
Al	2.02	1.95–1.99[44,45]	2.24[44]		2.10[45]

[a] Values calculated by adding the covalent radius of carbon (0.77 Å) to the covalent radius of the metal[46]

[b] Only the shortest metal-carbon distance in each π structure is listed

illustrate this group. They both have tetrahedral arrangements of four groups around their magnesium atoms as depicted for the former (*5*) and the latter (*6*), with all bond distances around magnesium being close to calculations from covalent radii.



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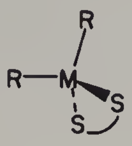
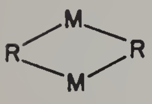


6

S = solvent

Dimers — Crystalline bicyclo[1.1.0]butan-1-yllithium · TMEDA [8] and trimethylaluminium [44]; menthyllithium [12] and trimethylaluminium [13] in hydrocarbon solvents illustrate the simplest type. These dimers are held together by two 3-center bonds (*3*) arranged as in *7*; a metal-metal bond is not usually drawn because most of the bond strength is calculated to come from carbon-metal bonding [15]. In the trimethylaluminium dimer, there are two non-bridging methyl groups on each aluminium atom.

8a, a different type of dimer with bridging *halogens*, is observed for EtMgBr · Et_3N [37] and EtMgBr · *i*-Pr_2O [38]. *8b*, with a chair-shaped six-membered ring, represents a further type of dimer; it is exemplified by 2-lithio-2-methyl-1,3-dithiane · TMEDA (X = sulfur covalently bond to the negatively charged carbon) [27a].



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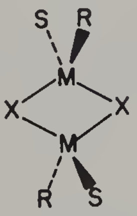
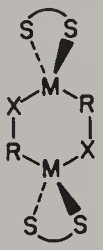
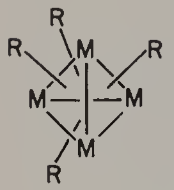


8a

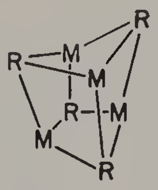


8b

Tetramers — Crystalline MeLi [9], EtLi [10], and MeLi · 1/2 TMEDA [17]; *n*- and *t*-BuLi [13] and Li_3MgMe_5 [13] in hydrocarbon solvents, and MeLi, *n*-BuLi [47], and Li_4Et_3OEt [48] in Et_2O; EtLi in the gas phase [49]. These are held together by four 4-center bonds (*4*), giving structures *9a* which consist of a tetrahedron of metal atoms with a bridging alkyl group at the center of each face. Direct metal-metal bonds are drawn in *9a* only to aid in visualizing the structure; representation *9b*, in which the atoms strongly bonded to one another are connected, shows that this structure can be thought of as a cube (*9c*) in which 4 non-adjacent corners have been pulled together. Donor atoms such as O, N, S, and P can coordinate with the metal atoms at the tetrahedron corners without disrupting the tetrameric structure [14, 50]; not surprisingly, for steric reasons *t*-butyllithium$_4$ is not solvated appreciably [14]. In the Li_3MgMe_5 structure, there is a methyl group attached at the magnesium corner of the tetrahedron [13]. Li_4Et_3OEt presumably has OEt replacing an Et on a face [48]. The stability of these tetramers is illustrated by their survival in the presence of the strongly chelating ligand TMEDA, which in $(MeLi)_4(TMEDA)_2$ crystals forms not rings but linear bridges between tetramers via N—Li bonds [17].



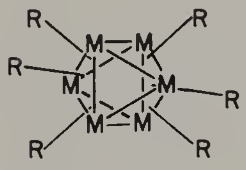
9a



9b

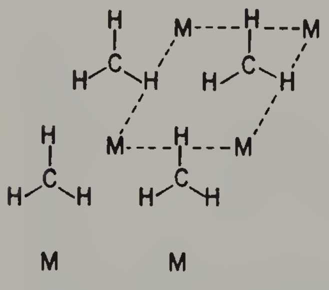
9c

Hexamers — Crystalline $\text{cyclohexyllithium}_6 \cdot \text{benzene}_2$ [11]; EtLi and *n*-BuLi in hydrocarbon solvents [13]; EtLi in the gas phase [49]. The X-ray study of the former shows these structures to be of type *10*, with a core consisting of a distorted octahedron of metal atoms. Note that two opposite triangular M_3 faces (near and far in *10*) bear no alkyl groups; in the X-ray study the Li—Li distances in these triangles were 3.0 Å, whereas the other Li—Li distances were only 2.4 Å (compared to 2.4—2.6 Å in tetramers [9, 10, 17], 2.7 Å in a dimer [8], and 2.5 Å in Li metal [46]). These bond lengths help to show that the hexamers are held together by six 4-center bonds (*4*); again, the direct metal-metal bonds are drawn for visualization only, and solvation of the metal atoms at the corners can occur [14].



10

Polymers — Crystalline MeK [31], MeRb and MeCs [34], Me_2Be [35], Me_2Mg [41], and Et_2Mg [42]. The first three are insoluble substances consisting of alternating sheets of alkali metal cations and methyl anions, arranged as in *11* (viewed ⊥ to sheets). Metal atoms in all sheets are directly above one another, but carbanions in every other carbanion layer are displaced so that carbons are very close to the hydrogens of the layer above and below.



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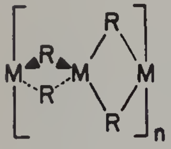
The carbons are believed to be sp^3 hybridized from IR and weak X-ray evidence; a neutron diffraction study would be helpful. 4-Center bonds (*4*) are thus apparently used.

The alkaline earth alkyls in this class [35, 41, 42] are linear polymers of the type *12*, with a line of metal atoms held together by alkyl groups bridging *via* 3-center bonds as in certain dimers (*7*). The alkyl groups are arranged approximately tetrahedrally about the metal atoms.



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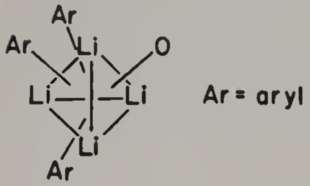
b. sp^2 and sp

Other carbanions in which the negative charge is not delocalized by resonance over several atoms are the vinyl and aryl anions, with an electron pair localized in an sp^2 orbital, and cyanide ion and the acetylenic anions, with an electron pair localized in an sp orbital. $\Phi MgBr \cdot 2\,Et_2O$ [39] and $\cdot\, 2\,THF$ [51] are monomeric in the solid state, with structures like $EtMgBr \cdot 2\,Et_2O$ (*5*) [39]. Crystalline phenyllithium · TMEDA has a dimeric structure similar to that of the sp^3 dimers *4* [16]; presumably the same type of dimer is present in phenyllithium in ether solution [47]. An X-ray study shows (2,6-dimethoxyphenyllithium)$_6 \cdot Li_2O$ to consist of two approximately tetrahedral Li_4 clusters with aryl groups at three faces connected *via* an oxide ion at the fourth; one such cluster is depicted in *13* [18]. The C—Li bond lengths in this aryllithium dimer and tetramer are similar to those in the alkyllithiums. X-ray studies on ethynylsodium, -potassium, and -rubidium, and 1-propynylsodium and -potassium show metal-carbon distances involving σ-bonding to an sp orbital; there is also some interaction (at a greater distance) between the metal atom and an acetylenic π bond as shown in *14* [28].



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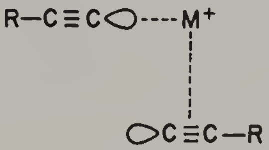

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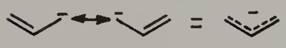
The configurational stabilities of lithium and magnesium salts of alkyl anions (sp^3, *optical* isomerization at the charge-bearing carbon) and vinyl anions (sp^2, *geometric* isomerization about the double bond) have been examined in a few cases, with the general finding of low barriers in the former [5] and high [52, 53] but not insurmountable [54] barriers in the latter. Cyclopropyl anions, which are in between sp^2 and sp^3 in hybridization, have high barriers to inversion [55, 56]. The barriers are generally much higher in nonpolar solvents [53]. Some studies of the exchange rates between the various aggregated forms have been made [13].

2. Delocalized (π)

a. Hydrocarbon Anions

Delocalization of negative charge over two or more atoms through resonance as in allyl anion *15* has an enormous stabilizing effect, especially in the gas phase without a counterion [57]. Many X-ray studies on metal salts of such carbanions show them to consist of contact ion pairs, with the carbons in the π systems sp^2 hybridized and coplanar or roughly coplanar, and the metal atoms usually positioned above one or several of the most negatively charged carbons; examples are cyclopentadienylsodium · TMEDA (*16*) [29], cyclopentadienylmagnesium bromide · TMEDA [43], $[Me_5CpAlMeCl]_2$ [45], hexatriene dianion dilithium · 2 TMEDA (*17*) [19], benzyllithium · triethylenediamine *18* [20], 1,3,5,7-tetramethylcyclooctatetraene dianion dipotassium · 2 diglyme *19* [32], indenyllithium · TMEDA [21], bis(indenyl)magnesium [40]. naphthalene dianion dilithium · 2 TMEDA [22], acenaphthene dianion dilithium · 2 TMEDA [23], fluorenyllithium · 2 quinuclidine [24], fluorenylpotassium · TMEDA [33], anthracene dianion dilithium · 2 TMEDA [25], triphenylmethyllithium · TMEDA [26], triphenylmethylsodium · TMEDA [30], *20* [27], and phthalocyanine dianion dipotassium · 2 diglyme and · 2(18-crown-6) [58]. The shortest carbon-metal distances (Table 1) in these π-carbanions are greater than for 2-center bonds, and about the same as for 3- and 4-center bonds. The π-carbanions have longer distances than the 3-center bond examples with Mg [40], but the shortest C—Li distance observed so far is in a π case: 2.13 Å in acenaphthene dianion dilithium · 2 TMEDA [23].



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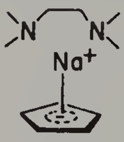

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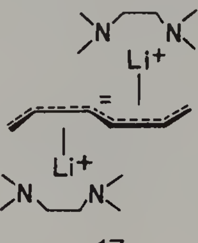

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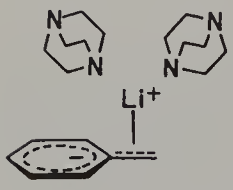

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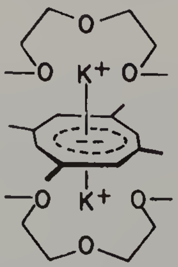

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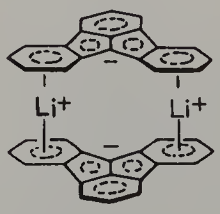

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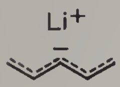
UV-visible [59, 60], infrared-Raman [61], and NMR [62–64] studies indicate that in solution contact ion pairs again predominate for metal salts of π-carbanions, except for highly delocalized carbanions (e.g., fluorenyl) which exist as solvent separated ion pairs in strongly cation-solvating solvents like DMSO. The behavior of the carbanion in solvent separated ion pairs is (as expected) cation independent, but in contact ion pairs the geometry, solubility, and reactivity of the carbanion are often very cation dependent. For example, whereas pentadienyllithium (*21*) is mostly W-shaped in THF solution and gives largely reaction products with *trans* double bonds, pentadienylpotassium (*22*) is U-shaped (giving better coordination to the large cation) and gives products with *cis* double bonds [65]. A dimeric cyclohexadienyllithium derivative has been shown by ^{7}Li and ^{13}C NMR to have the "triple ion"-containing sandwich structure *23* [64].



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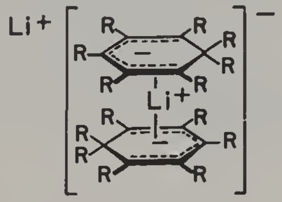


23

Certain allylmagnesium compounds apparently prefer covalent σ structures to ion-paired π structures, at least under some conditions [67].

Rotation barriers in allyl and pentadienyl anions in solution are 10–25Kcal/mole, depending on substituents and conditions [67–69]; rotations about the *inner* C—C bonds in pentadienyl anions equilibrate the U, sickle, and W shapes and are generally faster than rotations about the outer C—C bonds. Alkyl substituents on C-1 of an allyl or pentadienyl group in solution prefer the *cis* position (*24*) [70, 71], presumably because of their hyperconjugative resemblence to butadiene dianion (*25*) [72–74]. The latter dianion has not conclusively been demonstrated to prefer the *cis* shape shown, but many substances with isoelectronic π systems (e.g., *26*, X = halogen) *have*, and dianion *15* has been shown to have this sort of shape in solution [72] as well as in the solid state [19]. The greater stability of the *cis* isomer in all of these cases is presumably due to favorable 1,4 overlap in the HOMO [75, 76]. Surprisingly, in the gas phase without counterions, the *trans* forms of 1-alkylallyl anions appear to be more stable [77].

24

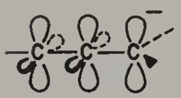
25

26

Rotation barriers in these π anions (and in their heteroatom-containing analogs discussed in the next section [78]) are higher as the alkali metal size increases [68, 78, 79]; this may be due to the greater ability of the smaller cations to form a σ bond at one carbon long enough to permit rotation about resulting C—C single bonds [79, 80]. Traces of oxygen efficiently catalyze bond rotation in allyl anions, probably by electron transfer to allyl radicals, in which the barriers are much reduced [71].

Monoanions of type (*27*) with two sp carbons in line with an sp^2 carbon form very readily from allenes and non-terminal acetylenes [81].

Some highly lithiated polymeric species of unknown structure have been prepared which presumably contain some combination of σ and π carbon-lithium bonds [82–84]. An example is C_3Li_4, prepared by perlithiating methylacetylene. It is possible that it contains structure *28*, with two σ and two π C—Li bonds and an arrangement of three sp hybridized carbons in a line which is found in "sesquiacetylenic" dianions [85]. By observing their thermal interconversions at 220 °C, the stability order $(C_2Li_2)_n > (C_3Li_4)_n > > (C_2Li_4)_n > (CLi_4)_n$ has been established [84]. It would be helpful to have X-ray results on some of these substances to clarify their structures.



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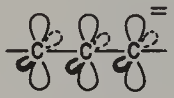

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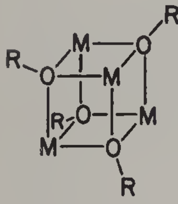
b. Heteroatom-containing Carbanions

Enolate ions (*29*) are the most important members of this large class. Although the negative charge is largely on oxygen with resulting high rotation barriers about the adjacent carbon-carbon ~double bond, NMR studies show that *some* negative charge resides on the α-carbon [86–88]. It has been calculated that while monomeric π-bonded allyllithium is more stable than σ-bonded by 16 Kcal/mole, lithium enaminate *30* is only 4 Kcal/mole more stable π-bonded than σ-bonded (Li to N) and lithium enolate (*29*) is 7 Kcal/mole more stable σ-bonded with the lithium coordinated to oxygen and 176° away from the nearest carbon [89]. It should be noted, however, that enolates are often aggregated, especially in non-polar solvents (see below), and these calculations for monomeric species thus may not be completely relevant. The higher carbon-carbon bond orders in *30* and especially *29* are evidenced by higher rotation barriers about these bonds: ~11 Kcal/mole in *15*, ~18 Kcal/mole in *30*, ~21 Kcal/mole in *29* [90].

29

30

The X-ray studies on salts of heteroatom-containing π-carbanions include lithium 3,3-dimethyl-1-buten-2-olate · THF and lithium cyclopentenolate · THF (*31*) [90a, 90b], dipotassium squarate · H_2O (*32*) [91] and its tetrathio analog [92], diammonium croconate (*33*) [93], several metal enolates of β-diketones (e.g. *34* [94]; also [95, 96]), and benzophenone dianion dilithium · TMEDA · THF (*35*) [97]. These studies generally reveal highly symmetrical highly delocalized π systems with almost all of the negative charge on oxygen or sulfur, and the cations coordinating with oxygen or sulfur only. This coordination is most often with unshared (n) electron pairs on the heteroatoms rather than with the π system; e.g., lithium acetylacetonate (*34*) has the linear polymeric structure depicted, with lithiums alternately approximating tetrahedral and square planar coordination to four oxygens *via* n-electrons. In the simple enolate tetramers *31*, which resemble the alkyllithium tetramers *9*, the fourth coordination position of lithium is occupied by a THF molecule in each case, and the bond lengths are similar to those found in enol ethers [90a]. In dianion *35*, on the other hand, there is considerable negative charge on carbon (there are two negative charges and only one oxygen), and while one Li^+ is in the plane n-coordinated with oxygen, the other lies above the π cloud in the location shown, giving a shortest C—Li distance of 2.24 Å. The C—O bond in this substance is 1.41 Å long, as expected from its lowered bond order compared to benzophenone.



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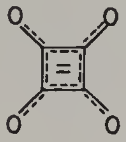

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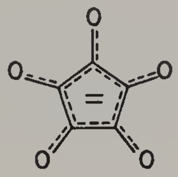

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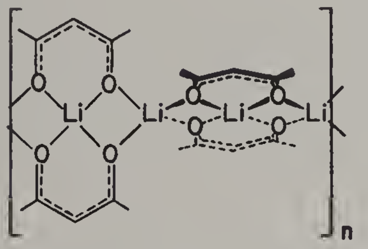

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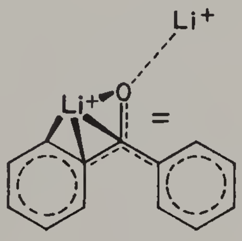

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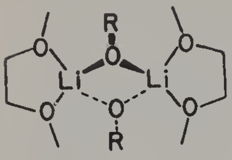
Simple enolates and phenolates may be free ions in highly ionizing solvents, but they are ion paired in other solvents and aggregated, especially in nonpolar solvents [86]. The lithium enolate of isobutyrophenone has been shown to be tetrameric in dioxolane solution, no doubt with structure *31* [98]. In 1,2-dimethoxyethane, there is 15% tetramer and 85% of a dimeric structure, presumably *36*, analogous to the alkylmetal dimers *7*. Added LiCl converts both tetramer *31* and dimer *36* into a structure like *31* but with Cl replacing OR at one corner. Addition of a cryptand with a strong affinity for Li^+ gives a monomeric enolate ion with much more negative charge on carbon as evidenced by an upfield shift in the ^{13}C NMR of 8 ppm for the charge-bearing carbon atom. *Potassium* enolates are probably *not* tetrameric [90b].

Alkali metal enolates form equimolar complexes with alkali metal alkoxides [99].



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It has been deduced from NMR studies that α-lithiosulfoxides (*37*) have an sp^2 hybridized charge-bearing carbon atom, suggesting resonance stabilization of the type shown [100].

37

III. Preparations

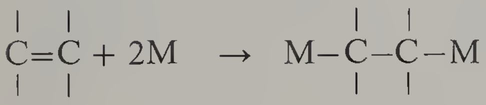
The major methods for preparing carbanions are shown in reactions (3-1) to (3-5). *Unstabilized* carbanions (e.g., simple alkyl, aryl, and vinyl anions) are usually prepared from the corresponding halide by reaction with a metal (3-1a) or an organometallic reagent (3-1b). *Resonance* and *inductively-stabilized* carbanions are more often made from an appropriate precursor RH, with the proton being abstracted by a metal (3-2a) or a basic metal salt (3-2b). Certain alkenes add metals to give dicarbanions (3-3a), and metal salts to give monocarbanions (3-3b). The metal can sometimes be changed in an organometallic by reaction with the desired metal (3-4a) or one of its salts (3-4b). Carbanion rearrangements (3-5), useful for preparing certain carbanions, are discussed in Chapter VIII and the other methods are described in the present chapter in the order indicated below.

$$\mathrm{RX} + 2\,\mathrm{M} \rightarrow \mathrm{RM} + \mathrm{MX} \tag{3-1a}$$

$$\mathrm{RX} + \mathrm{R'M} \rightarrow \mathrm{RM} + \mathrm{R'X} \tag{3-1b}$$

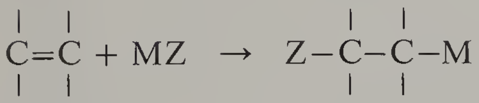
$$\mathrm{RH} + \mathrm{M} \rightarrow \mathrm{RM} + 1/2\,\mathrm{H_2} \tag{3-2a}$$

$$\mathrm{RH} + \mathrm{MZ} \rightarrow \mathrm{RM} + \mathrm{HZ} \tag{3-2b}$$



$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + 2\mathrm{M} \rightarrow \mathrm{M}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{M}$$

(3-3a)



$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}} + \mathrm{MZ} \rightarrow \mathrm{Z}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{M}$$

(3-3b)

$$\mathrm{RM'} + \mathrm{M} \rightarrow \mathrm{RM} + \mathrm{M'} \tag{3-4a}$$

$$\mathrm{RM'} + \mathrm{MZ} \rightarrow \mathrm{RM} + \mathrm{M'Z} \tag{3-4b}$$

$$\mathrm{R'M} \rightarrow \mathrm{RM} \tag{3-5}$$

1. From Alkyl Halides

a. With Metals (3-1a)

Magnesium, lithium, zinc, sodium and potassium metals all readily reduce organic halides to metal salts of carbanions. The first three are the most commonly used, since sodium and potassium generally give more coupling products (Wurtz reaction) than carbanion.

Grignard reagent preparations (3-6) are the best known examples of this general type of reaction (X = Cl, Br, or I). Ethers are usually required as solvents. Diethyl ether is most often employed, but for more sluggish reactions the better coordinating tetrahydrofuran or the much higher boiling di-*n*-butyl ether and glymes are utilized. Reactivity of RX decreases in the order RI > RBr > RCl, and alkyl halides are more reactive than aryl halides.

$$RX + Mg \longrightarrow RMgX \tag{3-6}$$

Grignard reagent preparations are sometimes difficult to get started: often a small amount of iodine, 1,2-dibromoethane, or some other very reactive alkyl halide is added to initiate reaction [101]. Ultrasounds have recently been reported to initiate Grignard reactions, even in wet commercial grade THF [102]. Magnesium metal formed *in situ* from $MgCl_2$ and K ("Rieke" Mg) enables facile low temperature preparation of even aryl Grignard reagents [103].

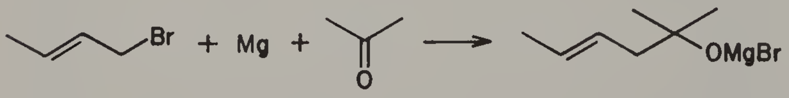
Intermolecular [104] and intramolecular [105] trapping experiments as well as CIDNP results [106] indicate that Grignard reagents are formed through alkyl radical intermediates.

The "Schlenk" equilibrium (3-7) [107] can be driven to the right by adding dioxane, which precipitates MgX_2 and leaves a solution of dialkyl- or diarylmagnesium [108].

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2 \tag{3-7}$$

Attempts to prepare allylic and benzylic Grignard reagents in the usual way leads to Wurtz type coupling products (3-8) [109, 110], but by careful control of reaction conditions allylic and benzylic Grignard reagents have been successfully prepared [111]. Coupling can sometimes be avoided by preparing the Grignard reagent in the presence of the desired electrophile (the "Barbier" reaction (3-9) [112]), or by using "Rieke" magnesium [113].

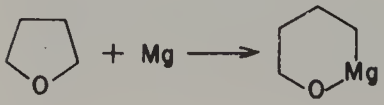
(3-8)



(3-9)

Grignard-like reagents can also be prepared from compounds other than alkyl halides. For example, reaction of dimethyl sulfate and magnesium yields such a reagent (3-10) [114]. Also, at elevated temperatures THF is reported to react with "Rieke" magnesium to give insertion into the carbon oxygen bond (3-11) [115].

$$Me_2SO_4 + Mg \longrightarrow MeMgOSO_3Me \tag{3-10}$$



(3-11)

Calcium [116], strontium [117] and barium [117] are of much less importance than magnesium. They react similarly (e.g., (3-12)) but give greater amounts of coupling, which is minimized by running the reactions below room temperature.

$$\phi I + Ca \longrightarrow \phi CaI \qquad (3\text{-}12)$$

Lithium reacts readily with alkyl and aryl halides without ether solvents but both alkanes and ethers are commonly employed as solvents [118]. Organolithiums are generally created from the chloride or bromide, as alkyl iodides tend to give more coupling products [119]. Trace impurities of sodium in the lithium are necessary for the formation of organolithium reagents [120], and for the preparation of *t*-butyllithium, a copper powder coating on the lithium has been recommended [54].

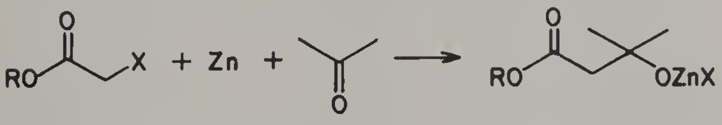
Preparation of allyl- and benzyllithium by this route leads to coupling [110], but allyllithium is readily produced by reduction of allyl phenyl ether with lithium metal (3-13) [121]. Organolithiums can be prepared by analogous reduction of alkyl phenyl sulfides [122, 123]; α-lithioethers have been made in this way using Li naphthalenide (3-14) [124].

(3-13)

(3-14)

Amyl- and phenylsodium are made by slow addition of the corresponding chloride to sodium dispersion at low temperatures (to reduce coupling) [125]; phenylpotassium is made similarly in quantitative yield [126]. Sodium and potassium also reduce aryl alkyl ethers to the corresponding alkylalkali [127, 128].

The Reformatsky reaction of an α-haloester with zinc forms an intermediate organozinc reagent which reacts in situ with an electrophile (3-15) [129]. This reaction has recently been shown to proceed analogously starting with α-halocarboxylate salts [130]. The yields in the Reformatsky reaction are generally better with bromides than with chlorides. Allylic halides can be employed [131]. Alkyl- and arylzinc compounds, with reactivities comparable to Grignard reagents, can be synthesized from "Rieke" zinc and the corresponding alkyl or aryl halide [132].



(3-15)

b. With Organometallics (3-1b)

Metal-halogen interchanges are used primarily to prepare organolithium compounds from alkyl and aryl halides; they often give better yields than reactions of the halides with lithium metal due to less side reactions [133]. In general the rates decrease in the series I > Br > Cl ≫ F. The reactions are equilibrium processes favoring the more stable carbanion [134]. They are performed at or below room temperature in hydrocarbon solvents or (more rapidly) in ethers [135]. Concerted mechanisms have been postulated due to the observed second order kinetics and salt effect [134]. CIDNP experiments on the reaction of alkyllithiums with alkyl and aryl halides indicate the presence of radical intermediates [136, 137].

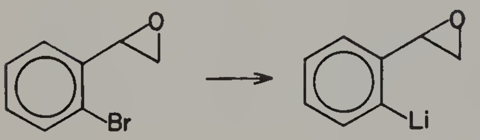
This method is used frequently to prepare vinyllithiums (3-16 to 3-18) and aryllithiums (3-19, 3-20) from alkyllithiums; each of these reactions used *n*- or *t*-butyllithium in THF or Et_2O at —70 to —100 °C. Reactions (3-18 to 3-20) show that carbanions can be prepared by this method even in the presence of functional groups which readily react with carbanions at room temperature. In (3-18), when the chloride was used instead of the bromide, the Si—O bond was cleaved.

(3-16) [138, 139]

(3-17) [140]

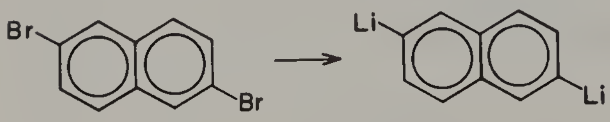
(3-18) [141]

(3-19) [142, 143]

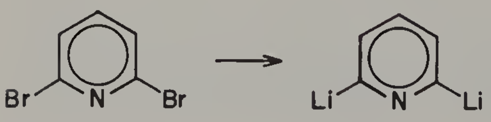


(3-20) [144]

Many dicarbanions have been made this way as well (3-21, 3-22).



(3-21) [145]



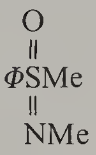
(3-22) [146]

2. From Alkanes by Proton Abstraction (3-2)

a. Acidities of CH Protons

Deprotonation is the method used most often for the preparation of resonance- and inductively-stabilized carbanions; it is thus important to know the acidities of substances containing various types of CH bonds [147]. Several thermodynamic acidity scales have been offered, such as Cram's MSAD scale (McEwen-Streitwieser-Applequist-Dessy) [1], which includes measurements made in various solvents, and Bordwell's scale (Table 2) of values in DMSO. Such scales provide a basis for choosing an appropriate base for a particular CH acid. For example, from the last two entries in Table 2, if kinetics permit, it should be possible to abstract a proton from dimethyl sulfide with an alkyllithium; this has been shown to be the case [162].

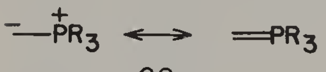
Table 2. Bordwell's Acidities of Carbon Acids in DMSO

Acid	pKa	ref
$\Phi CH(CN)_2$	4.2	148
ΦCO_2H	11.0	149
$CH_2(CN)_2$	11.1	148
$MeCH(CN)_2$	12.4	150
$(MeCO)_2CH_2$	13.3	148
$CH_2CH_2SO_2CH_2SO_2CH_2$	15.5	148
$(MeO_2C)_2CH_2$	15.7	149
$EtNO_2$	16.7	150
$MeNO_2$	17.2	150
cyclopentadiene	18.0	151
ΦOH	18.2	152
indene	20.1	153
p-nitrotoluene	20.5	149
thiourea	21.1	149
ΦCH_2CN	21.9	149
fluorene	22.6	149
$(\Phi S)_3CH$	22.5	154
$\Phi COEt$	24.4	150
$\Phi COMe$	24.7	150
$MeCONH_2$	25.5	150
cyclohexanone	26.4	149
Me_2CO	26.5	155
urea	26.9	149
$\Phi C{\equiv}CH$	28.7	156
ΦSO_2Me	29.0	150
MeOH	29.0	152
$(\Phi_2P)_2CH_2$	29.9	154
$MeCO_2Et$	30–31^{b}	157
Φ_3CH	30.6	151
$(\Phi S)_2CH_2$	30.8	154
ΦSO_2Et	31.0	150
Me_2SO_2	31.1	155
$CH_2CH_2SCH_2SCH_2$	31.1^{a}	158
MeCN	31.3	155
H_2O	31.4	152
Φ_2CH_2	32.1	151
Me_3COH	32.2	152
 $\Phi\overset{O}{\underset{NMe}{S}}Me$	33^{b}	159
Me_2SO	35.1	155
H_2	36^{a,b}	160
NH_3	41^{b}	151
ΦMe	42^{b}	161
propene	43^{a}	158
pyrrolidine	44^{b}	151
ΦSMe	49^{b}	149
CH_4	55^{b}	151

[a] Solvent other than DMSO
[b] Estimated

Aromaticity can be important in stabilizing carbanions, as illustrated by the very low pKa of cyclopentadiene; its conjugate base, cyclopentadienyl anion, has been estimated to have 24–27 Kcal/mole of aromatic stabilization [151]. Homoaromaticity appears not to be very important in homocyclopentadienyl anions [163, 164], but does help to stabilize homocyclooctatetraene dianions, which form easily and exhibit large ring currents [165, 166]; calculations indicate that it should not be as important in anions as in cations [167].

From Table 2, an ordering of the ability of groups to stabilize a negative charge on an adjacent carbon atom can be obtained: $-NO_2 > -(C{=}O)R > -(C{=}O)OR > -CN \sim -(SO_2)R > -(SO)R > -\Phi > -SR$. The most strongly stabilizing groups act primarily by resonance; all on this list do except for —SR, which stabilizes by polarization [158] and possibly $-(SO_2)R$ and —(SO)R (the latter has an sp^2 hybridized S, which suggests a contribution from resonance stabilization [168]. Ylides (38) [169, 170] are stabilized partly through resonance and partly through inductive effects. Certain groups such as —O(C=O)R stabilize partly through inductive effects and partly through chelation (3-23) [171].



$$^{-}\!-\overset{+}{P}R_3 \longleftrightarrow\ =PR_3$$

38

(3-23)

α-Alkyl groups destabilize simple alkyl, nitrile, and sulfone anions, but stabilize enolates and nitroates; these are complex blends of hyperconjugative, steric, and polarizability effects [150] but can be rationalized at least partially on the basis that in enolates and nitroates, the negative charge is very heavily on oxygen rather than carbon, and in enolates and nitroates the methyl group is essentially on a double bond; methyl groups are known to stabilize double bonds.

Almost any type of non-metal atom bonded to a carbon atom will make a proton attached to that carbon acidic enough to be abstracted by very strong bases such as butyllithium to give an essentially σ carbanion. Examples in which the metallation is selective enough to be useful include the following groupings attached to the CH: $-SiR_3$ [172, 173], —NRCH=NR [174], —NR(C=O)OAr [175, 176], $-NR(P{=}O)NR_2$ [177], $-\overset{+}{N}\equiv C^-$ [178, 179], $-PAr_2$ [180], $-\overset{+}{P}R_3$ [169, 170], $-(P{=}S)Me\Phi$ [181], —O(C=O)Ar [176, 182, 183], $-\overset{+}{S}R_2$ [184, 185], $-S(C{=}S)NR_2$ [186], —(S=NTs)R [187, 188], and $-Se\Phi$ [189, 190].

That two stabilizing groups are better than one is evident from the acidities in Table 2. The many combinations of two such activating groupings which have been successfully employed to make σ carbanions include: 2-$SiMe_3$ [191], $-SiMe_3$ and —OMe [192], $-SiMe_3$ and $-S\Phi$ [193], $-SiMe_3$ and $-Se\Phi$ [194], $-SiMe_3$ and —Cl [195, 196], 2-$P\Phi_2$ [154], $-(P{=}O)\Phi_2$ and $-NR_2$ [197], $-(P{=}O)\Phi_2$ and —OR [198], $-(P{=}O)\Phi_2$ and $-S\Phi$ [199],

—(P=O)(OEt)$_2$ and —Cl [200], 2—OR [201], 2—SR [154, 158, 201, 202], —SR and —S(O$_2$)— [203], —S(O)— and —Cl [204], and 2—Cl [205].

A few cases of three such stabilizing groups are known: 3—SiMe$_3$ [191], 3—SΦ [154, 206] and 3—Cl [207].

From the table it is evident that carbanions increase in stability with an increase in the amount of s character at the carbanion center such that sp > sp^2 > sp^3. Equilibrium acidity measurements indicate the following expanded order for various types of sp^2 and sp^3 groupings: phenyl > vinyl > cyclopropyl > methyl > ethyl > isopropyl > *t*-butyl [208]. Cyclopropanes owe their enhanced acidity to the increase in s character in their CH bonds relative to simple alkanes [209].

Heteroatom-containing groupings can control which proton is removed from an alkene (3-24) [171]. Examples are known where Y = —NR$_2$ [210, 211], —$\overset{+}{N}\equiv C^-$ [212], —OR [213], —SR [214], and —Cl [171].

(3-24)

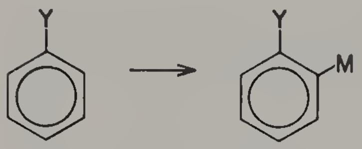
Activation of a CH bond in an aromatic ring by a heteroatom, leading to ortho-metallation, has become increasingly important for the preparation of substituted arenes [171]. If the heteroatom is in the aromatic ring (3-25, Y = NR, O, or S) [215—217] it stabilizes largely through its inductive effect. Two heteroatoms are better than one (3-26) [216], and polymetallation is possible (3-27); furan and thiophene give only the dimetallation product shown, whereas N-methylpyrrole gives also the 2,4-dimetallation product. Pyridines usually undergo addition faster than metallation, so metallated pyridines are made in other ways such as from the corresponding aryl halide by halogen exchange (3-1 b).

(3-25)

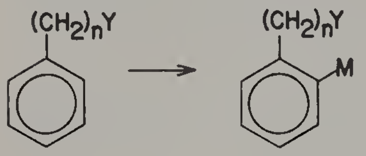
(3-26)

(3-27)

Alternatively, the heteroatom can be attached directly to the ring (3-28) [171, 218—222], again acting by induction and perhaps partly through complexation with the metal. Virtually any non-metal atom possessing an unshared pair of electrons (including halogens) will direct the metallation *ortho*. Or, the heteroatom can be further out in the chain, as in (3-29) [171, 218–220, 223–234], in which case complexation with the metal rather than an inductive effect controls the reaction. Among groupings used to activate for and direct metallation to an ortho position on an aromatic ring, amides and sulfonamides are better than methoxy, carboxy, and N,N-dimethylamino [218–220].



(3-28)



(3-29)

The *rate* of ionization (kinetic acidity) can play an important role in deprotonations since kinetic acidities only roughly parallel thermodynamic acidities. Kinetic acidities measured by a variety of techniques have recently been compiled for many C—H acids [235]. Carbon acids ionize much more slowly than oxygen and nitrogen acids of comparable thermodynamic acidity, presumably because C—H bonds are not so favorably polarized for attack by base as are OH and NH bonds. Among carbon acids, α-protons in nitriles ionized faster than expected, and α-protons in nitro compounds ionized slower.

In the generation of enolates from ketones, weaker bases, aprotic solvents, lower temperatures and excess base favor kinetic deprotonations, while strong bases, protic solvents and excess carbonyl precursor favor the equilibrium products [236]. Generally the more highly substituted enolate is the equilibrium product whereas kinetic control favors deprotonation at the less hindered site, yielding the less substituted enolate [236, 237].

Among alkyllithiums, lesser aggregation is probably responsible for *sec*-BuLi reacting 24 times faster than *n*-BuLi; menthyllithium, which exists in dimeric form, is still faster [12].

Development of high-pressure mass spectrometry, flowing afterglow and ion cyclotron resonance spectroscopy has permitted the measurement of gas phase acidities of C—H acids *without cations or solvents* [238]. Comparison with solution acidities shows the stabilizing effects in carbanions of counterion effects [239] and solvation energies [240] to be on the order of 50–90 Kcal/mole. Rather than as pKa's, gas phase acidities are usually expressed in terms of proton affinity of the anion in Kcal/mole (Table 3). They can be calculated by summing the energy required for *homolytic* dissociation of the acid, the electron affinity of the resulting radical, and the ionization potential of a hydrogen atom (313.6 Kcal/mole). Comparing Tables 2 and 3, some striking differences become apparent. Delocalization plays an extra important role in the gas phase, where toluene is more acidic than water, and fluorene (charge delocalized over more atoms) is more acidic than cyclopentadiene. In the gas phase, *t*-butanol is more acidic than methanol, reversing the trend found in solution. As in solution acidities, the role of alkyl substituents is complicated, although generally α-alkyl groups stabilize negative charge in the gas phase; apparently alkyl groups can stabilize a charge of either sign by polarizing as needed.

Table 3. Gas Phase Acidities of Carbon Acids

Acid	ΔH°, Kcal/mole	ref
CF_3CO_2H	322.7	241
HCl	333.6	241
$CH_2(CN)_2$	336.0	241
ΦCO_2H	338.8	241
$(MeCO)_2CH_2$	343.7	241
succinimide	345.4	241
$(EtO_2C)_2CH_2$	348.3	241
$MeCO_2H$	348.5	241
ΦOH	349.8	241
ΦCH_2CN	351.9	241
H_2S	352.0	241
p-nitrotoluene	353.1	241
fluorene	353.3	241
cyclopentadiene	355.5	241
Me_2CHNO_2	356.6	241
$EtNO_2$	357.3	241
$MeNO_2$	357.6	241
Φ_2CH_2	364.5	242
Me_2SO_2	366.4	241
MeCHO	367.0	241
Me_2CO	370.0	241
$MeCO_2Me$	371.0	242
HF	371.5	242
Me_3COH	373.3	242
$MeCONMe_2$	373.5	242
MeCN	373.5	241
Me_2SO	374.6	241
$HC{\equiv}CH$	375.4	242
CF_3H	375.6	242
EtOH	376.1	242
Φ-*i*-Pr	377.5	242
ΦEt	378.3	242
ΦMe	379.0	242
MeOH	379.2	242
propene	390.8	243
H_2O	390.8	244
benzene	397.0	244
NH_3	399.6	244
H_2	400.6	244
CH_4	416.6	244

Since most of the calculations which have been done on carbanion stabilities do not include solvent and cation effects, they generally agree better with gas phase acidity measurements than with solution phase acidities [245–248]; these calculations include many delocalized dicarbanions [248].

b. Base-solvent Systems

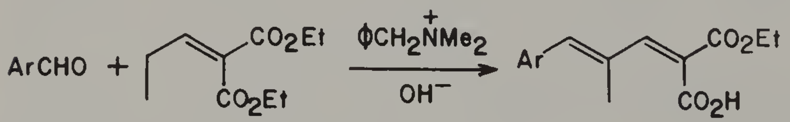
That a great variety of base-solvent systems have been used to abstract protons in carbanion-generating reactions is not surprising in view of the tremendous range of acidities of C—H compounds. The range of pKa's of such compounds is even larger than the 4 to 55 indicated in Table 2, for $CH(NO_2)_3$ is more acidic than any compound in Table 2, and other alkanes are somewhat less acidic than methane. As can be seen from Table 2, hydroxide and *t*-butoxide are strong enough in DMSO to abstract the most acidic proton from most of the compounds in Table 2. Stronger bases like alkyllithiums are required to abstract an allylic proton from propene or a benzylic proton from toluene to produce an allyl or benzyl anion in *high* concentration, but weaker bases like KO-*t*-Bu will pull off such protons to provide *low* concentrations of such anions for double bond isomerizations or deuterium exchange reactions.

The *counterion* makes some difference, as indicated by a factor of 10^3 in the rates of alkene isomerization in DMSO with KO-*t*-Bu being faster than LiO-*t*-Bu; the latter is probably more covalent [249].

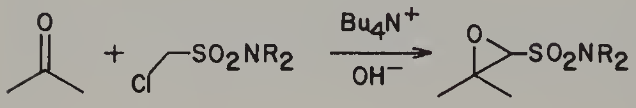
The *solvent* can have an enormous effect on the reaction, especially when the comparison is between a hydroxylic solvent and one of the non-hydroxylic solvents (e.g., DMSO) which increase basicity by efficiently solvating cations but not anions. Thus KO-*t*-Bu in DMSO is 10^{14} more basic alcohol-free than in the presence of 5% of *t*-BuOH [250]! Such solvents, with their rate factors for a KO-*t*-Bu catalyzed alkene isomerization relative to diglyme, include DMSO (1580), hexamethylphosphoramide (HMPA, 465) N-methylpyrrolidone (NMP, 300), and dimethylformamide (DMF, rate about the same as NMP) [249]. Thus DMSO is kinetically fast, but its relatively high thermodynamic acidity renders it unsuitable for very strong bases such as metal amides; HMPA is the solvent of choice for these bases. Among the less active solvents which have been used are alcohols, water, ethers, and hydrocarbons.

Base-solvent systems will now be illustrated, starting with some relatively weak bases and finishing with the most powerful ones.

Classical base-catalyzed aldol condensations often employ hydroxide in water or alcohols to generate low concentrations of enolate ions [251]. Quaternary ammonium hydroxides have recently found use as bases in phase transfer systems [252, 253], permitting such reactions as Stobbe (3-30) [254] and Darzens condensations (3-31) [255] under simple, convenient conditions.



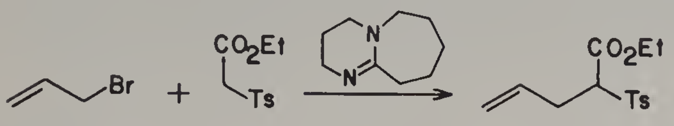
(3-30)



(3-31)

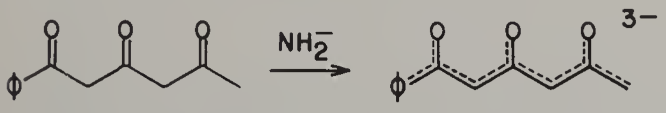
Alkoxides are widely used to generate carbanions in high concentration in malonic, cyanoacetic and acetoacetic ester syntheses, and Dieckmann, Stobbe and Darzens ester condensations. Especially useful is potassium *t*-butoxide [256]; being tertiary, it is a stronger base than primary and secondary alkoxides, and also is incapable of hydride transfer reactions which can lower yields significantly when these other alkoxides are used. Potassium *t*-butoxide in DMSO will readily deprotonate ketones, partially deprotonate esters, and can be used to generate allylic and benzylic carbanions in very low but often useful concentrations.

There are a variety of non-nucleophilic hindered amines capable of generating carbanions in low concentration. 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU) is one of the most popular, being used in the alkylation and acylation of active methylenes (3-32) [257, 258].

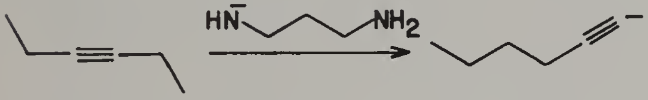


(3-32)

Lithium, sodium and potassium amides in liquid ammonia are powerful bases capable of generating dicarbanions from *β*-diketones [259] and higher carbanions from higher ketones (3-33) [260]. Such bases have been used for isomerizing alkynes (3-34) [261], and for deuterium exchange of hydrocarbons [262]. Lithium diisopropylamide (LDA), generated in situ from *n*-butyllithium and diisopropylamine, is the most common hindered amide used to prepare enolates in high concentration. Lithium 2,2,6,6-tetramethylpiperidide (LiTMP), lithium dicyclohexylamide and lithium hexamethyldisilamide are more sterically hindered and often can be employed when LDA fails [263]. The lithium amidine salt of 3,3,6,9,9-pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene has proven useful in the preparation of lithium enolates where other hindered amides failed (3-35) [264].



(3-33)



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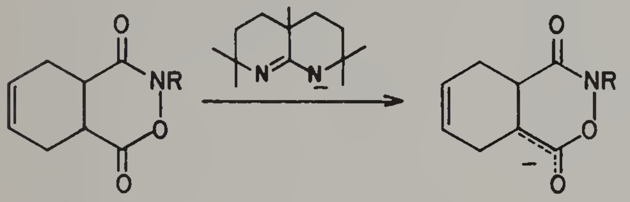


(3-35)

Sodium and potassium hydride are used for generating enolate anions for alkylations and for Dieckmann condensations [265, 266]. Sodium hydride in DMSO produces the dimsyl anion which is a convenient base [267].

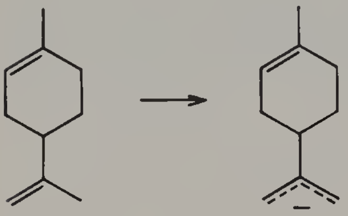
The alkali metals themselves are sometimes used for the metallation of very acidic hydrocarbons such as cyclopentadiene and terminal acetylenes [268]; with many compounds such as aldehydes and ketones, reduction (see next section) becomes the main reaction. Sodium and potassium on charcoal, graphite and alumina have recently been employed in the metallation and alkylation of ketones, nitriles and esters [269–271].

Deprotonation of very weakly acidic C—H acids is usually accomplished by metallation with organolithium and organosodium compounds [272–274]. Direct metallation of acidic C—H bonds is often impossible with these organometallics due to their ready addition to groups such 'as carbonyls.

Metallations can be carried out in hydrocarbon solvents, but activating solvents such as ethers or tertiary amines which help peptize the organometallic reagent are usually used. For example, *n*-butyllithium/THF allowed preparation of pentadienyllithium from 1,4-pentadiene (3-36); no reaction occurred in hexane [275].

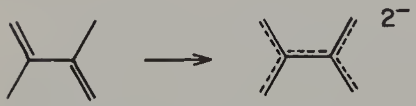

(3-36)

Tetramethylethylenediamine (TMEDA) has an even more dramatic effect in activating alkyllithiums and alkylsodiums [276–278], though its "bite" is apparently too small for a potassium ion [33]. *n*-Butyllithium/TMEDA smoothly metallates propene and isobutylene [279], even dimetallating the latter [72, 280]. This base system when given a choice among allyl anions yields predominantly the least substituted one (3-37) [281].


(3-37)

It has been demonstrated that the *kinetic* product in metallation of certain substituted olefins and alkylbenzenes with organosodiums and potassiums is metallated at an sp^2 carbon; this rearranges to the thermodynamically more stable (resonance-stabilized) allyl or benzyl anion [282, 283].

Activation of alkyllithiums can also be achieved by addition of alkoxides, especially potassium *t*-butoxide [284–288]. This base system is less nucleophilic than *n*-butyllithium/TMEDA, allowing preparation of carbanions from *conjugated* dienes (3-38) [288]. The much less soluble potassium salt usually precipitates from solution, and the lithium *t*-butoxide may be removed by filtration or decantation. The insolubility of the potassium salt can be an advantage in preserving stereochemistry, as has been done with crotyl anions [289].



(3-38)

Trimethylsilylmethylpotassium has been found to be a superior metallating agent which is similar in behavior to the potassium *t*-butoxide/*n*-butyllithium base system [287, 290].

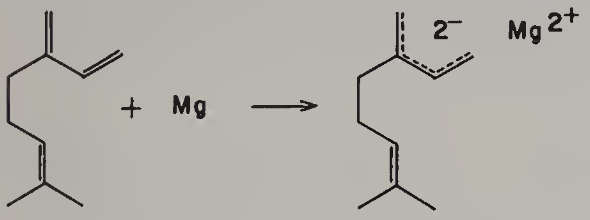
These organometallic reagents being very reactive and highly aggregated pose problems in finding appropriate solvents. Diethyl ether, tetrahydrofuran, HMPA, and TMEDA are all commonly used but all do eventually react with organometallics such as *n*-butyllithium [177, 210, 291–293].

Because metallating agents react very readily with air and water, many methods have been devised for the determination of the concentration of the base. The newer methods titrate the organometallic with a diprotic C—H acid which gives a visible end point when one equivalent of base has been added and the highly colored dianion starts to form [294, 295].

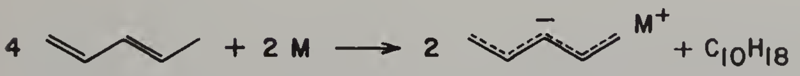
3. From Unsaturated Compounds

a. By Reduction (3-3a)

Many types of unsaturated compounds have been two-electron reduced with active metals or electrochemically to form dicarbanions (3-3a). The anion radical from one-electron transfer is a presumed (or in some cases, demonstrated) intermediate. Simple alkenes do not have sufficiently stable dianions to undergo this reaction, but many of their conjugated derivatives do. For example, cyclooctatetraene (antiaromatic) with any of the alkali metals yields cyclooctatetraene dianion (aromatic) [296, 297]. Benzene (aromatic) does *not* yield its antiaromatic dianion, and naphthalene reduces only to its anion radical (its dianion may be prepared by a deprotonation route [22]), but anthracene and most other polycyclic aromatics readily reduce to the corresponding dianions [298]. 1,3-Dienes are reduced by magnesium to butadiene dianions (e.g., 3-39), which have found use in terpene synthesis [299–302]. When 1,3-pentadiene is reduced with alkali metals, the anion radical dimerizes to give a bis-allyl anion which abstracts protons from two 1,3-pentadiene molecules, yielding two pentadienyl anions and a mixture of $C_{10}H_{18}$ dienes (3-40); this reaction provides an economical route to certain pentadienyl anions from 1,3-dienes and an alkali metal [303].

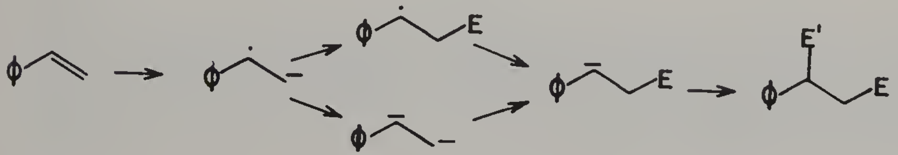


(3-39)



(3-40)

Electrochemical methods have been used to "reductively acylate" olefin derivatives such as α,β-unsaturated esters [304, 305] and styrenes (e.g., 3-41) [306] via the corresponding anion radicals and perhaps dianions to various acyl and diacyl derivatives. E can be —CHO (from DMF) or —(CO)R (from Ac_2O or RCN).



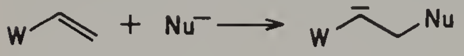
(3-41)

There are several examples of the reduction of σ bonds as in (3-42) [132] to give stabilized carbanions; such reactions probably occur by cleavage of the carbon-carbon bond in the intermediate anion radical to give anion and radical, followed by reduction of the latter to give a second anion.

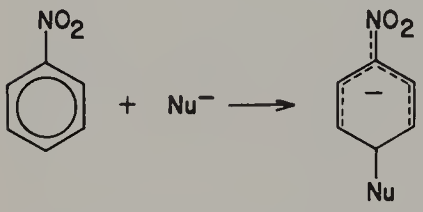
$$(\phi_2CH)_2 + 2\,K \longrightarrow 2\,\phi_2CHK \tag{3-42}$$

b. By Addition (3-3b)

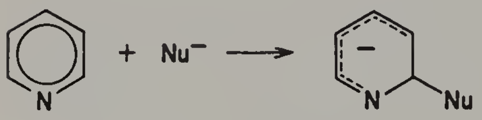
The Michael (3-43) [307], Meisenheimer (3-44) [308], and Chichibabin reactions (3-45) [309] are common examples of this method of carbanion generation, which is only successful for stabilized carbanions.



(3-43)



(3-44)

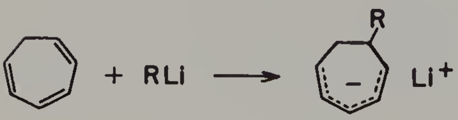


(3-45)

This method has been applied to formation of enaminates (3-46) [310, 312], benzylic anions (3-47) [313], and pentadienyl anions (3-48) [314]. Anionic polymerization proceeds through a propagation step of this type [315].

(3-46)

(3-47)



(3-48)

Enolate anions resulting from the conjugate addition of organocuprates to α,β-unsaturated carbonyls are recognized as valuable intermediates in natural product synthesis [316, 317].

4. From Other Organometallics by Changing the Metal

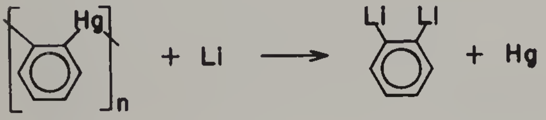
a. With Metals (3-4a)

The most common transmetallation reactions involve organotin and mercury compounds, but analogous reactions for silicon and lead are known. Metal-metal exchange is used especially when halide — free carbanions are wanted. Reactions of type (3-4a) are slow and reversible, and M must be more electronegative than M′ for the reaction to proceed [318]. For example, reduction of an organomercurial with an alkali metal [319] can be used to obtain unstabilized (3-49 [320]), stabilized (3-50 [321] and 3-51 [322]), and dicarbanions (3-52 [323]).

$$sec\text{-}Bu_2Hg + Li \longrightarrow 2\ sec\text{-}BuLi + Hg \tag{3-49}$$

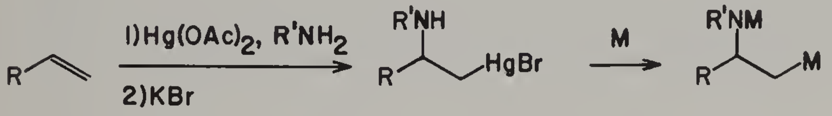
$$(Me_3SiCH_2)_2Hg + K \longrightarrow 2\ Me_3SiCH_2K + Hg \tag{3-50}$$

$$(\phi CH_2)_2Hg + Li \longrightarrow 2\ \phi CH_2Li + Hg \tag{3-51}$$



(3-52)

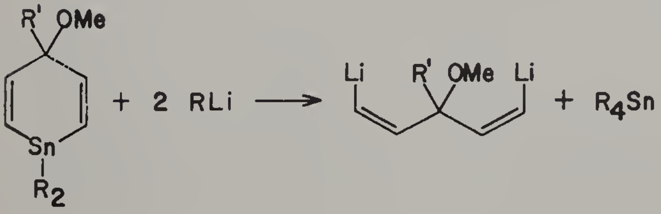
This reaction has recently been used in the conversion of primary alkenes to carbanions through mercurated intermediates (3-53) [324, 325]. Alcohols could be used in place of primary amines.



(3-53)

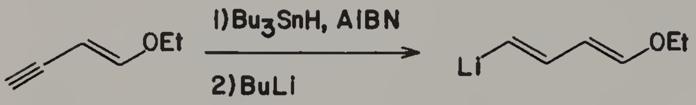
b. With Metal Salts (3-4b)

Transmetallation of organotin compounds with organolithiums is a useful example of (3-4b). This reaction is an equilibrium which is driven by formation of the more stable carbanion or by precipitation of one of the products [326]. Vinyllithium [327], many substituted allyllithiums [328–330], and dicarbanions (3-54) [331] have been made by this route.



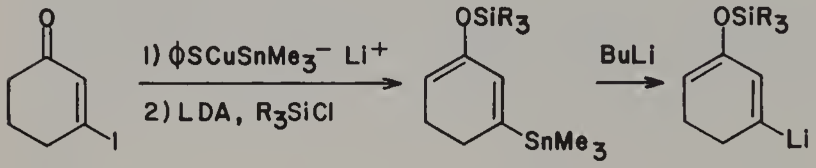
(3-54)

Alkenyllithiums are conveniently derived from alkenyltin reagents which are readily made by hydrostannation of substituted alkynes (3-55) [332–334].



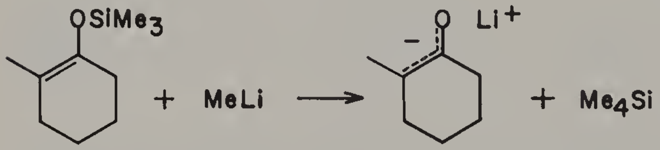
(3-55)

Alkenyltin compounds are recognized in organic synthesis as latent carbanion equivalents (3-56) [335].



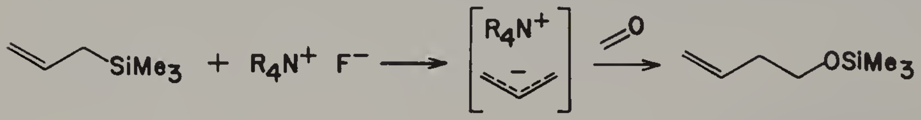
(3-56)

This same type of reaction is employed for regiospecific generation of enolate anions from the corresponding trimethylsilyl vinyl ether and methyllithium (3-57) [336].



(3-57)

Allyl anions with quaternary ammonium counterions can be generated and reacted *in situ* with aldehydes and ketones (3-58) [337–339]. This reaction is initiated by the formation of Me_3SiF, and made possible by the great stability of the Si—F bond. The allyl anion does not build up in very high concentration, but is trapped as it adds to aldehydes and ketones.



(3-58)

IV. Reactions of σ Carbanions with Electrophiles

These reactions, summarized in Table 4, have been divided into substitutions (4-1 to 4-21) and additions (4-22 to 4-31). In the former, a leaving group Y^- usually departs as a bond is formed between R and some non-metallic (4-1 to 4-20) or metallic (4-21) element. Virtually all of the elements except the noble gases can be bonded to carbon in this way. Y^- is most often a halide ion, but many other groupings such as sulfonates, sulfates, and alkoxides have been used. The additions to double and triple bonds form a bond between R and C, N, O, or S, with the resulting anion usually picking up a proton as in (4-22 to 4-24). It should be noted that all of these reactions are limited in scope in that certain other groupings which react readily with carbanions cannot be present, and many have other limitations. In some cases, R′ can be an aromatic group or a hydrogen, and in others, it cannot.

1. Substitution Reactions of Alkyl (sp^3) Anions

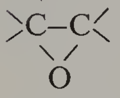
Abstraction of a proton by an organometallic (reaction 4-1) is an extremely important reaction, as such substances as the butyllithiums are among the most readily available very strong bases and thus are used to generate many other anions, as described in Chapter III. The reaction can also be used to make specifically deuterated hydrocarbons; e.g., the most convenient way to generate CH_3D is to add D_2O (slowly!) in an ether to CH_3Li or CH_3MgI in ether.

Alkylboranes can be produced by (4-2), usually as an intermediate step in converting a carbanion to the corresponding alcohol. Either a dialkoxyfluoroborane [340] or a trialkoxyborane [341] can be used. Reactions of more complicated carbanions with alkylboranes may be followed by rearrangement of an alkyl group from boron to carbon [342, 343].

One of the most important carbon-carbon bond-forming reactions consists of a carbanion coupling with an alkyl halide (4-3). The use of copper-lithium reagents R_2CuLi, readily prepared from the alkyllithium and cuprous chloride, bromide, or iodide, gives high yields of many unsymmetrical alkanes in cases where the yield directly from the alkyllithium or alkylsodium (Wurtz reaction) is low [344].

A variety of heterocuprates RCuYLi have been used to make more efficient use of R groups; $Y = S\Phi_2$ gives a relatively stable reagent [345]. The mechanism may be simple S_N2, or, especially with very basic carbanions,

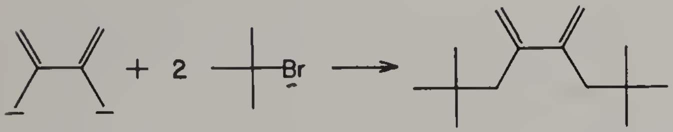
Table 4. Reactions of Carbanions R^- with Electrophiles

Substitutions			Additions		
	R^-			R^-	
YH[a]	$\rightarrow RH$	4-1	$\mathrm{C{=}CW}$[b]	$\rightarrow \mathrm{RC{-}CHW}$	4-22
$YB(OR')_2$	$\rightarrow RB(OR')_2$	4-2			
YR'	$\rightarrow RR'$	4-3	$\mathrm{{-}C{\equiv}C{-}}$	$\rightarrow \mathrm{RC{=}CH}$	4-23
$\mathrm{C{=}C{-}CY}$	$\rightarrow \mathrm{RC{-}C{=}C}$	4-4	$\mathrm{C{=}N}$	$\rightarrow \mathrm{RC{-}NH}$	4-24
$\mathrm{{-}C{\equiv}C{-}CY}$	$\rightarrow \mathrm{RC{=}C{=}C}$	4-5	$\mathrm{C{=}N^+}$	$\rightarrow \mathrm{RC{-}N}$	4-25
			$\mathrm{{-}C{\equiv}N}$	$\rightarrow \mathrm{RC{=}NH}$	4-26
	$\rightarrow \mathrm{RC{-}COH}$	4-6	$\mathrm{C{=}O}$	$\rightarrow \mathrm{RC{-}OH}$	4-27
$\mathrm{YC{=}C}$	$\rightarrow \mathrm{RC{=}C}$	4-7	$\mathrm{O{=}C{=}O}$	$\rightarrow RCO_2H$	4-28
			$\mathrm{C{\equiv}O}$	$\rightarrow \mathrm{R_2C{=}O}$	4-29
$\mathrm{C{=}C{=}CY}$	$\rightarrow \mathrm{RC{-}C{\equiv}C{-}}$	4-8	$\mathrm{S{=}CSR'}$	$\rightarrow \mathrm{RSCHSR'}$	4-30
YAr	$\rightarrow RAr$	4-9	$\mathrm{S{=}C{=}S}$	$\rightarrow RCS_2H$	4-31
$\mathrm{YC{=}O}$	$\rightarrow \mathrm{RC{=}O}$	4-10			
$\mathrm{YC{\equiv}N}$	$\rightarrow \mathrm{RC{\equiv}N}$	4-11			
$YSiR'_3$	$\rightarrow RSiR'_3$	4-12			
YNR'_2	$\rightarrow RNR'_2$	4-13			
YNO_2	$\rightarrow RNO_2$	4-14			
YPR'_2	$\rightarrow RPR'_2$	4-15			
O_2	→ (see Chapter VIII)	4-16			
S_8	$\rightarrow RS^-$	4-17			
YSR'	$\rightarrow RSR'$	4-18			
YSO_2R'	$\rightarrow RSO_2R'$	4-19			
YX	$\rightarrow RX$	4-20			
YM	$\rightarrow RM$	4-21			

[a] Y = leaving group, most often halide
[b] W = carbanion-stabilizing group

may involve single electron transfer (SET) from the carbanion to the alkyl halide, giving an alkyl radical and an anion radical which very rapidly decomposes into a halide ion and an alkyl radical; the alkyl radicals can join as desired or give disproportionation or symmetrical coupling products. Bordwell has noted that "the more strongly basic the carbanion, the greater the likelihood that it will react by an electron-transfer pathway rather than an S_N2 pathway" [346]. The reactions of Grignard reagents with alkyl halides are also promoted by the addition of cuprous halides and amines or phosphates [347, 348].

Surprisingly, even tertiary halides like *t*-butyl bromide can be reacted with some carbanions, e.g., as in (4-32), to give coupling products [349a–e]; very likely this sort of reaction goes by an electron transfer mechanism (probably $S_{RN}1$).



(4-32) [349]

Heteroatoms are often included in carbanions to guide an alkylation (or other reaction) to a desired position and then removed. Some of the heteroatom-containing groupings are readily replaced by hydrogen (e.g., S by Raney nickel desulfurization [350] or with other reducing agents [351]), hydrolyzed to carbonyl compounds (e.g., dithioacetals to aldehydes and ketones [202, 352, 353] or 1,1,1-trihalides to acids [207]), or eliminated to give alkenes (e.g., —SeΦ [194, 354] and —SΦ [193] by oxidizing and warming, or —S(C=S)NR_2 by reacting with methyl iodide followed by LiF/Li_2CO_3 [186]).

Some S_N2' type reactions (4-4) of carbanions with allyls attached to good leaving groups employ as leaving groups halogen [355], N-ethyl-4,6-dimethyl-2-oxidopyridinium [356], and 2-oxidopyridine [357]. The first two of these leaving groups gave virtually complete S_N2' rearrangement (γ-alkylation), but the last required heavy α-substitution or the S_N2 product predominated. A further sequence for γ-alkylating allyl alcohols *via* a copper complex has been shown to involve *anti* γ-alkylation [358]; if 2-O^--benzothiazole is the leaving group, only the *trans*-1,2-disubstituted alkene is formed [359]. The conversion of a propargyl acetal to an allenyl ether by a Grignard reagent catalyzed by cuprous bromide (4-5) [360] is at least formally related to the above, as is a reaction of type 4-8 involving an organoaluminate and allenyl bromide with a cuprous chloride catalyst [361].

The reaction of alkyl carbanions with epoxides (reaction 4-6) can be considered either as an addition or as an intramolecular substitution. The mechanism is ordinarily intramolecular S_N2, with substitution occurring with inversion of configuration at the less hindered carbon atom [362]. Alkyllithiums or Grignard reagents are usually used, but cuprates react similarly [363]. Episulfides sometimes react analogously, though attack can occur at sulfur [364].

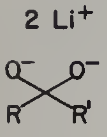
Vinyl halides (reaction 4-7) are notoriously sluggish in nucleophilic displacement reactions, since their structures are not conducive to S_N1 and S_N2 mechanisms, and the addition-elimination mechanisms is slow unless some additional grouping is present to stabilize the intermediate carbanion, as in the case $R_2CuLi + R'IC{=}CH(C{=}O)R' \rightarrow RR'C{=}CH(C{=}O)R'$ [365]. In the absence of such a grouping, a transition metal catalyst containing copper [366], nickel [367], or palladium [368, 369] may serve to break the vinyl-iodine or vinyl-bromine bond and give a good yield of coupled product from a Grignard reagent or alkyllithium. Such reactions generally go with retention of configuration at the double bond. Other possible mechanisms by which vinyl halides may react include halogen exchange to give a vinyl anion and an alkyl halide, which could then react in an S_N2 fashion to give the same coupling product, and elimination to the alkyne followed by nucleophilic addition to the alkyne.

Aryl halides (reaction 4-9) behave toward organometallics very much like the vinyl halides just discussed. S_N1 and S_N2 are disfavored, but addition-elimination involves a resonance-stabilized pentadienyl anion intermediate *39*, and can go very rapidly if a carbanion-stabilizing group such as nitro is present *ortho* or *para* to the halogen. The elimination-addition mechanism now involves a benzyne intermediate *40*, and the R group may go into the *ortho* positions as well as the position to which the halogen was attached. Again, a transition metal catalyst containing palladium may bring about the desired coupling by breaking the carbon-halogen bond [370]. The reaction of methyllithium with iodobenzene to give toluene probably involves halogen exchange followed by displacement [371].

39

40

Acylation of a carbanion (reaction 4-10) can proceed readily by an addition followed by elimination of Y^-, but is complicated by addition of further carbanion to the product (probably a ketone; this is a good route to tertiary alcohols of the type $R_2R'COH$ [372]). This further reaction has been avoided in several ways. When an organolithium reagent RLi reacts with a lithium carboxylate, $R'CO_2Li$, the resulting insoluble salt *41* can be quenched by adding to aqueous acid to produce the ketone $RR'C{=}O$ [373]. Reaction of a Grignard reagent with an anhydride can also give an insoluble precipitate (*42*) which hydrolyzes to the ketone [374]; closely related is the addition product *43* from the S-2-pyridyl thioate, which does not require recycling of R'COOH recovered in the anhydride reaction [375]. Similarly, the N-methyl-N-2-pyridyl formate gives the aldehyde *via 44* [376]. In HMPA, Grignard reagents are acylated by esters to give ketones if the enolate of the ketone is formed fast enough [377]. Grignard reagents and organolithiums react with tertiary amides to give ketones [378] and aldehydes (from DMF) [379]. An acid chloride can be used directly for acylation if the Grignard reagent or organolithium is first converted to the less reactive cadmium [380, 381], manganese [382], copper [345], or rhodium [383] reagent. $Me_3SiCH_2^-$ with esters gives ketones if two equivalents of the base are used; the ketone is converted to its enolate faster than it suffers nucleophilic attack [384]. (4-10) is not limited to ketone preparation: Formates can give aldehydes, and carbonates can give esters [181].



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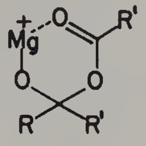

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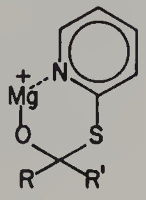

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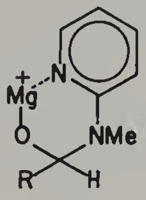


44

The reaction of carbanions with TsCN (4-11) has been used to prepare nitriles [385].

Silylation with, for example, chlorotrimethylsilane, often proceeds quantitatively and has been used to characterize carbanions (4-12) [172, 386]. Again, however, SET can occur with strongly basic anions to lower the yield [387].

Tertiary amines not easily made by nucleophilic substitution can be synthesized from alkyllithiums or Grignard reagents by reaction with N,N-dialkyl-O-arenesulfonylhydroxylamines (4-13) [388]. Aromatic nitro compounds have been made from aryllithiums and alkyl nitrates (4-14) [389]. Trialkylphosphines can be made as in 4-15 by reaction with dialkylchlorophosphines [390].

The reactions of carbanions with oxygen (4-16) and other oxidizing agents are discussed in Chapter VII. Carbanions react with elemental sulfur to give mercaptides (4-17) [391], and with disulfides (4-18, Y = R'S— [392]), sulfenyl chlorides (4-18, Y = Cl— [393]), or thiocyanates (4-18, Y = N≡C— [394]) to give mixed sulfides RSR′. With phenyl arenesulfonates, alkyl aryl (or diaryl) sulfones are formed (4-19) [395].

Reaction (4-20) of carbanions with halogen-containing species (X_2 [228, 396], TsCl [397], NXS [398], CH_2X_2 [399], CX_4 [400], or C_2X_6 [399]) is sometimes used for replacing an acidic hydrogen by halogen; often, however, the halide RX is more readily prepared than the carbanion R^- and it is the reverse reaction (3-1) which is practical. Oxidative coupling (Chapter VII) competes with halogenation in many cases and may predominate.

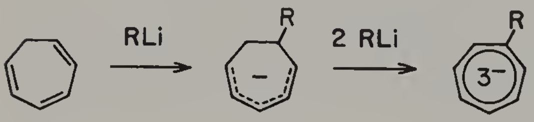
Reaction (4-21) can be used to attach alkyl groups to any metal, since the most active (alkali) metal can initially be associated with the carbanion, and the reaction favors the organometallic containing the less active metal [401]. This sort of reaction can be used to take advantage of the varied reactivity of carbanions coordinated to transition metals [2]; e.g., (4-33) is a useful synthetic procedure [201, 402].

$$\mathrm{RMgX} \xrightarrow[\text{2) R'I}]{\text{1) Fe(CO)}_5} \mathrm{R(CO)R'} \qquad (4\text{-}33)$$

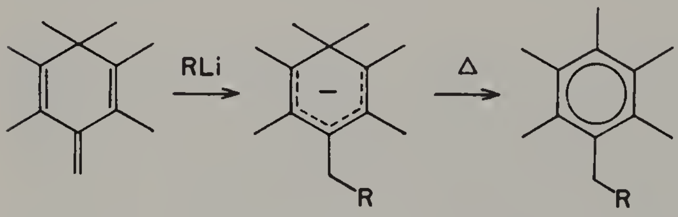
2. Addition Reactions of Alkyl (sp^3) Anions

The addition of alkyl anions to alkenes (reaction 4-22) is greatly facilitated by the presence of a carbanion-stabilizing group (W) on the double bond, though one is not essential as shown by the anionic polymerization of ethylene catalyzed by alkyllithiums [403]. Other simple alkenes without carbanion-stabilizing groups fail in this reaction, however, presumably because they lack ethylene's unique combination of an unhindered carbon for attack and a primary carbon at the other end for a relatively stable carbanion. Many alkenes containing carbanion-stabilizing groups, e.g. $CH_2{=}CHCN$, can be anionically polymerized by catalytic amounts of bases; if the 1:1 adduct is desired, the alkene is added slowly to the alkyllithium.

The carbanion-stabilizing group W can stabilize through induction, resonance, or a combination. Examples of the former are ΦSi—, ΦS— [404], ΦSe—, and Φ_2As— [405]. For resonance stabilization, even a second carbon-carbon double bond (conjugated with the first) will aid greatly, by giving an allyl carbanion intermediate; thus butadiene is readily anionically polymerized [403] or telomerized [406] by organometallics. Some other synthetically useful additions to various conjugated diene systems are shown in reactions (4-34) [407], (4-35) [408], and (4-36) [409].



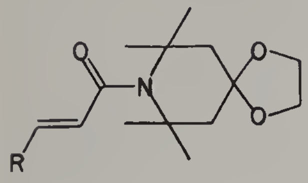
(4-34)



(4-35)

(4-36)

One of the most important types of carbanion-stabilizing groups W is a carbonyl group, which gives a (resonance-stabilized) enolate ion intermediate. While 1,2-addition of alkyllithiums or Grignard reagents to α,β-unsaturated carbonyl compounds usually predominates over 1,4-addition, when lithium dialkylcuprates (or sometimes simply catalytic amounts of a cuprous halide) are used, 1,4-addition (4-24) is usually favored [410–412]. Lithiodithioacetals add 1,2 kinetically and 1,4 thermodynamically [413, 414]. A mixed cuprate such as LiCu(R)SΦ, prepared from copper(I) thiophenoxide and an alkyllithium [365], or addition of a trialkylphosphine [412], saves alkyl groups when desired [345]. Of the methyl-copper species, $Me_5Cu_3Li_2$ was found most selective for 1,4-addition [415]. Ways of favoring 1,4-addition without employing copper are to use zinc [416] or to use an α,β-unsaturated carbonyl compound to which 1,2-addition is sterically difficult, e.g., *45* or *46* [417].



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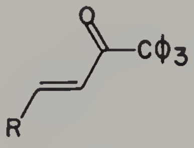
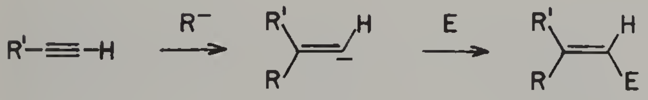


46

The many other groupings W which promote addition of metal alkyls to alkenes through resonance include C=N— [418, 419], —C≡N ("cyanoethylation" if acrylonitrile itself is used (4-37)) [420], and, in the presence of copper salts and with accompanying reduction to —NH$_2$, —NO$_2$ [421].

(4-37)

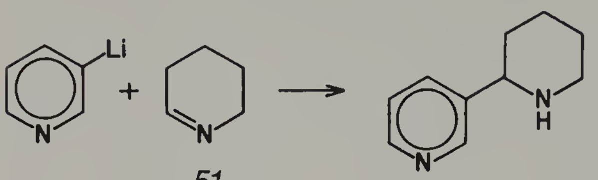
Metal alkyls add to acetylenes (4-23) somewhat more readily than they do to alkenes since the intermediate carbanion has its charge on an sp^2 hybridized carbon atom; carbanion-stabilizing groups are not necessary, but make the addition faster [54, 398, 422]. Even terminal alkynes may be used with cuprous catalysts, with the carbanion adding *syn* to the non-terminal carbon to give an intermediate vinyl copper reagent *47* which can be reacted with electrophiles E stereospecifically to give trisubstituted alkenes *48* [398]. Though initial additions are *syn*, in some cases the intermediate vinyl anions can be isomerized to provide the other stereoisomer [54]. Alkyllithiums and Grignard reagents react with acetylenic sulfones of type *49* to give acetylenes of type *50*, presumbably *via* an addition-elimination mechanism [423].



47 *48*

49 *50*

Many imines are not very stable, but some, e.g. *51*, are sufficiently so that they can be reacted with metal alkyls (4-24) [424–426]. Additions of this type often compete successfully with α-metallation of γ-substituted pyridines, e.g. *52* [231, 427]. Iminium salts, e.g. *53*, can similarly be used to make tertiary amines (4-25, 4-38, 4-39).



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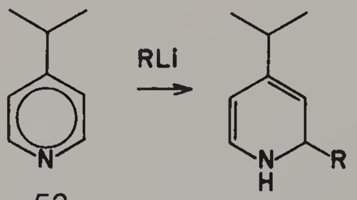

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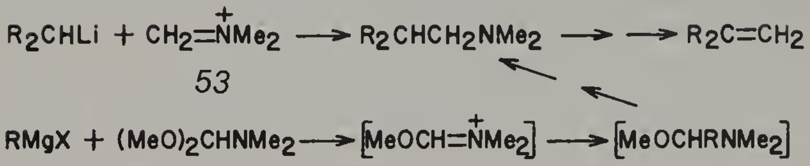
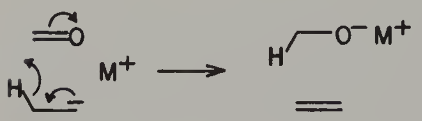


$$R_2CHLi + \underset{\textit{53}}{CH_2{=}\overset{+}{N}Me_2} \longrightarrow R_2CHCH_2NMe_2 \longrightarrow \longrightarrow R_2C{=}CH_2$$ (4-38) [428]

$$RMgX + (MeO)_2CHNMe_2 \longrightarrow [MeOCH{=}\overset{+}{N}Me_2] \longrightarrow [MeOCHRNMe_2]$$ (4-39) [429]

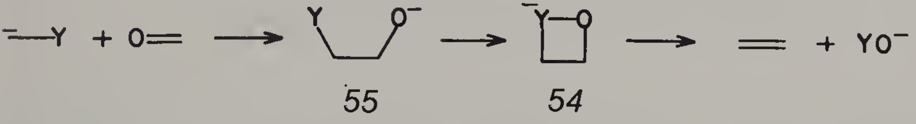
Organometallics add to nitriles (4-26) almost as rapidly as to ketones; the imine formed by addition of one mole is not usually stable, but may be hydrolyzed in good yield to the ketone in many cases [430]. In some cases, a second mole of carbanion adds, giving on hydrolysis a tertiary alkyl amine $R_2R'CNH_2$ [430, 431].

The reaction of a carbanion with an aldehyde or ketone to give a 1°, 2°, or 3° alcohol (4-27) is one of the most widely used carbon-carbon bond-forming reactions [432, 433]. Though often thought of as a simple ionic addition, recent evidence indicates that in at least some cases it proceeds by an SET mechanism involving as intermediates R· and the ketone anion radical [434]. Occasional side reactions are enolate ion formation, which usually results in recovered ketone (and can also involve SET [434]), and reduction of the ketone to the corresponding alcohol (4-40); this side reaction may also go by an SET mechanism, at least when a good electron acceptor like a diaryl ketone is used [435]. Considerable progress has been made in the synthesis of optically active 2° alcohols from achiral alkyllithiums and aldehydes using chiral TMEDA analogs [436]. The Barbier reaction, in which an alkyl halide is reacted with Li (much better than Mg) in the presence of an aldehyde or ketone, often proceeds better than the two-step route [102]. There is evidence that in at least some cases the Barbier reaction may not go *via* an organometallic reagent at all, but may follow a radical pathway [437].



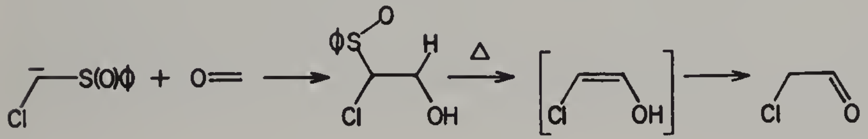
(4-40)

The additions of heteroatom-containing carbanions to aldehydes and ketones are often followed by useful secondary reactions. The secondary reaction is an olefin-forming elimination in the case of the Wittig (4-41, $Y = \text{—}P\Phi_3^+$) [169, 170, 438], Horner-Emmons (4-41, $Y = \text{—}(P{=}O)(OR)_2$) [191, 197, 439–442], Peterson (4-41, $Y = \text{—}SiMe_3$) [191, 216, 443–445], and related reactions (4-41, $Y = \text{—}(C{=}O)\Phi$ [446], $Y = \text{—}Sn\Phi_3$ [447], $Y = \text{—}S(C{=}O)OR$ [448, 449]). These reactions, which have the decided advantage over many other olefin syntheses of giving the double bond in a single known position, probably proceed *via* 4-membered ring intermediates of type *54*. These reactions are versatile enough to permit the synthesis of alkenes possessing —OR [198, 393], $\text{—}NR_2$ [197], $\text{—}SiMe_3$ [444], $\text{—}CO_2H$ [441, 442], —CN [393], and $\text{—}SO_2R$ [446] groupings.



(4-41)

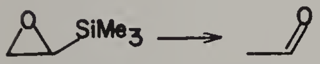
The addition of anion *55* to an aldehyde followed by pyrolysis leads to a different sort of olefin-forming elimination (4-42) [204].



(4-42)

Certain groupings Y in *55* are γ-eliminated to form epoxides (4-43). Examples are $Y = \text{—}SMe_2^+$ [184]; Y = —Cl, in which case an additional activating $\text{—}SiMe_3$ group permits acidic hydrolysis to an aldehyde or ketone (4-44) [195, 196]; or $Y = \text{—}(S{=}NTs)\Phi$ [187], in which case additional reagent can ring expand the epoxide to an oxetane (4-45) [188].

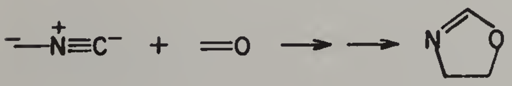
(4-43)



(4-44)

(4-45)

The products of addition of α-metallated isocyanides to aldehydes and ketones are readily cyclized to dihydrooxazoles (4-46) [179].



(4-46)

A standard preparation of carboxylic acids involves reaction of an organometallic with CO_2 (4-28) [450]. If a second equivalent of organometallic is present, it may add to the resulting carboxylate anion to give a dianion of type *41*, which will give ketone upon workup [372].

Alkyllithiums react with CO (4-29) to give symmetrical ketones and other products [451, 452].

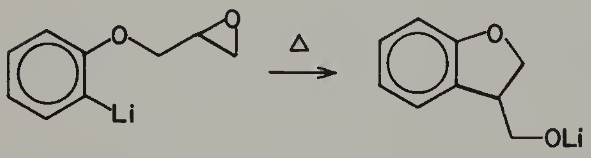
While carbanions add to the carbon atom of ester carbonyl groups, leading to substitution (4-10) followed by further addition (4-27), the direction of addition to thioester thiocarbonyl groups is reversed (4-30) [352]. Their addition to carbon disulfide (4-31), however, is analogous to their addition to carbon dioxide [453].

3. Vinyl (sp^2), Aryl (sp^2), and Acetylenic (sp) Anions

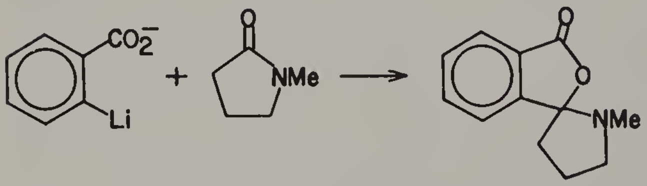
These anions undergo most of the reactions described above for alkyl anions (sp^3); examples are (4-47) to (4-55). In the reactions of vinyl anions, the configuration about the double bond is retained if the temperature is kept sufficiently low. With vinyl anions as with alkyl anions, the lithium dialkylcopper reagent is often prepared when the lithium reagent reacts unsatisfactorily, e.g., to get 1,4-additions to α,β-unsaturated carbonyl compounds [454]. Acyl anions are not stable under ordinary conditions [455], though they are probably the first intermediates in the reactions of carbanions with carbon monoxide (4-29) [452]; fortunately many acyl anion equivalents have been devised (Chapter IX).

$$CH_2{=}CHMgCl + MeCHBrCH_2OMgCl \xrightarrow{CuBr} CH_2{=}CHCHMeCH_2OMgCl \qquad (4\text{-}47)\ [456]$$

$$R_2C{=}CHCuR' + NBS \longrightarrow R_2C{=}CHBr \qquad (4\text{-}48)\ [457]$$



(4-49) [458]

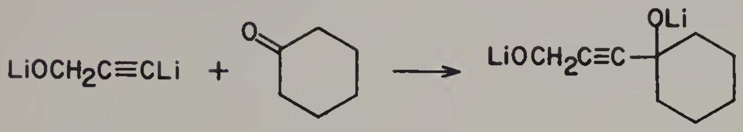


(4-50) [459]

$$R_2C(OAc)C{\equiv}CLi + R'_3B \longrightarrow R_2C{=}C{=}C(R')BR'_2 \xrightarrow{H_2O} R_2CHC{\equiv}CR' \qquad (4\text{-}51)\ [460]$$

$$RC{\equiv}CZnCl + ArI \xrightarrow{Pd(P\phi_3)_4} RC{\equiv}CAr \qquad (4\text{-}52)\ [370]$$

$$RC\equiv CLi + NCS \longrightarrow RC\equiv CCl$$ (4-53) [461]



(4-54) [462]

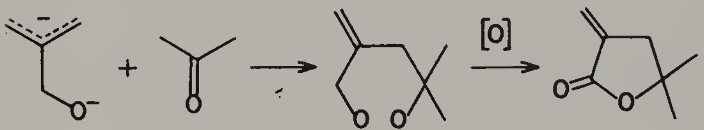
$$RC\equiv CLi + R'CO_2Et \longrightarrow RC\equiv C(CO)R' + (RC\equiv C)_2R'COH$$ (4-55) [463]

V. Reactions of π Carbanions with Electrophiles

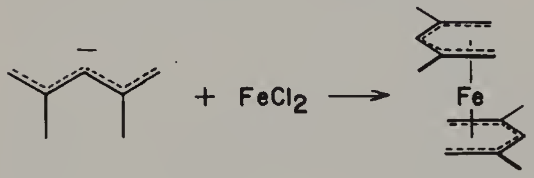
1. Hydrocarbon π Anions

π type carbanions undergo most of the reactions decribed in the last chapter for alkyl anions; (5-1) to (5-4) are examples with no regiochemical problems.

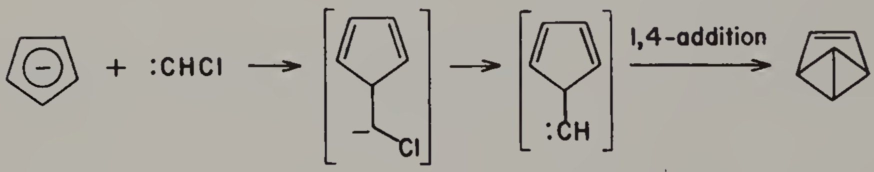
$$CH_2{=}CHCH_2MgCl \; + \; ClRC{=}NR' \longrightarrow (CH_2{=}CHCH_2)_2RCNHR'$$ (5-1) [464]



(5-2) [465]

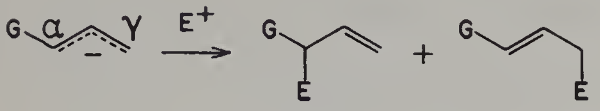


(5-3) [466]



(5-4) [467]

The main complication which arises with π anions is the site of reaction in unsymmetrical cases; e.g., substituted allyl anion *56* gives *57* by α-attack or *58* by γ-attack. In rate-controlled reactions with electrophiles, attack occurs primarily at the carbon of higher electron density, though steric and other factors no doubt contribute as well. When grouping G stabilizes an α-carbanion (as in *59*) more than it does a double bond (as in *60*), the electron density will be higher at the α-carbon and α-attack to give *57* will predominate; this is the case with G = —(C=O)— [468, 469] unless Cu^+ is the counterion [470], 2-benzothiazole [418], —CN [471], $—NO_2$ [472], —S— [473], —S(O)— [474], $—S(O_2)—$ [474, 475], and —Cl [476, 477]. When the reverse is true of grouping G, γ-attack to give *58* wins out, as with G = —R (usually) [289], vinyl (usually) [478, 479], —Ar [480], —NR_2 [481, 482], and —O— [474].



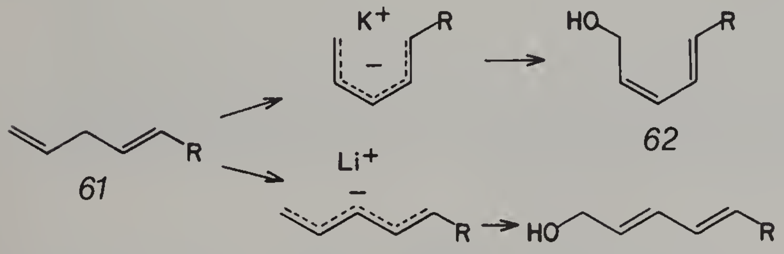
56 *57* *58*

59 *60*

The reactions of crotyl anion (*56*, G=Me) with electrophiles illustrate the regioselectivity obtained with alkyl groups and in addition the stereochemical results which can be obtained in the γ-alkylation product *58*. Equilibrated crotyllithium (85% *Z*) gives 46% α-butylation and 54% γ-butylation; 85% of the γ product is *Z* [483]. *Z*-Crotylpotassium, prepared at low temperatures from *Z*-2-butene, gives γ-boronation product which is almost 100% *Z*, while *E*-crotylpotassium from *E*-2-butene gives γ-boronation product which is essentially 100% *E* [289].

When prenyl *Grignard* reagents are used, the regiochemistry can be quite well controlled: In the absence of CuI, the γ-alkylation product predominates (92–98%), whereas addition of CuI gives mostly α-alkylation (97–99%) [484]. Interestingly, the α-attack observed when G = —(C=O)— can be converted to γ-attack by adding CuX [485].

The conversion of diene *61* to dienols *62* and *63* with high regio- and stereoselectivity *via* the sequence metallation — $B(OMe)_3$ — H_2O_2 (5-5 and 5-6) illustrates the reactions of pentadienyl anions with electrophiles [479].

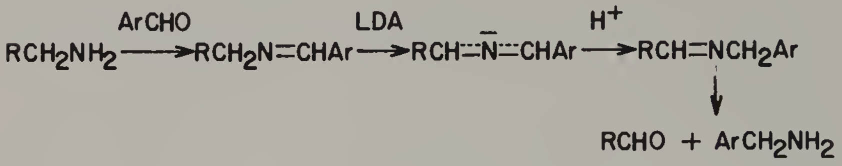


(5-5)

63

(5-6)

Allylic deprotonation of an alkene followed by protonation of the allyl anion may result in a double bond shift, as in the biomimetric transamination reaction (5-7) [486]. In many cases, the carbanion is not prepared in high concentration, as substances such as alkenes are equilibrated in kinetically strong but thermodynamically weak base-solvent systems such as KO-*t*-Bu — DMSO (e.g., 5-8) [487].



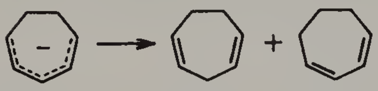
$$\mathrm{RCH_2NH_2} \xrightarrow{\mathrm{ArCHO}} \mathrm{RCH_2N{=}CHAr} \xrightarrow{\mathrm{LDA}} \mathrm{RCH{\cdots}\bar{N}{\cdots}CHAr} \xrightarrow{\mathrm{H^+}} \mathrm{RCH{=}NCH_2Ar} \tag{5-7}$$

$$\downarrow$$

$$\mathrm{RCHO} + \mathrm{ArCH_2NH_2}$$

(5-8)

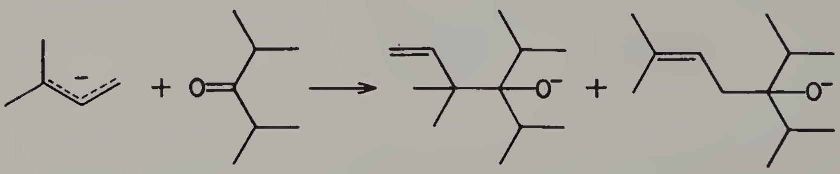
Protonations and other readily reversible reactions can lead eventually to the equilibrium mixture of products, usually different from the rate-controlled mixture. For example, in (5-9), rate-controlled protonation of cycloheptadienyl anion (*64*) gives 1:3 *65*:*66*, whereas equilibrium control gives 99+ % *66* [314]. The ratio of rate-controlled products depends on the protonating species and conditions; in principle one could find protonating agents and conditions which would give either *65* or *66* exclusively, and in less symmetric cases, one could induce chirality by using a suitable optically active protonating agent. Much less can be done to control the composition of the equilibrium mixture; it will generally vary some with temperature, but the temperature range over which equilibrium can be attained is usually rather restricted by competing reactions. With equilibrium or kinetic control, it may be possible to separate the desired isomer and recycle the undesired one to get more of the desired isomer. In the present case, for example, the unconjugated isomer *65* can be separated from the kinetic mixture and the conjugated isomer *66* recycled by deprotonating it with *n*-BuLi — KO-*t*-Bu [288] and again kinetically protonating it.



64 65 66

(5-9)

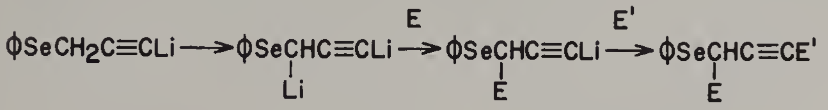
More surprisingly reversible to equilibrium are reactions of prenyl anion with ketones, e.g., (5-10): *67* is formed 4:1 over *68* at short reaction times, but after a long time only *68* is present [488].



67 68

(5-10)

A useful and usually reliable rule for reactions of di- and higher anions is that the first reaction with an electrophile will occur where the last proton came off (assuming the dianion was generated by removal of protons) [259], e.g., (5-11) [489, 490]. The vast majority of examples illustrating this rule involve anions with stabilization from heteroatoms, but the principle applies to hydrocarbon dianions as well. A serious problem with hydrocarbon dianions in this respect is that many of them have very low solubilities (especially dipotassium salts; dilithium salts are more soluble); many cannot be reacted selectively with one electrophile followed by another since the monoanion from initial reaction *is* soluble and reacts faster with electrophile than the dianion.



$$\phi SeCH_2C\equiv CLi \longrightarrow \phi Se\underset{Li}{C}HC\equiv CLi \xrightarrow{E} \phi Se\underset{E}{C}HC\equiv CLi \xrightarrow{E'} \phi Se\underset{E}{C}HC\equiv CE'$$

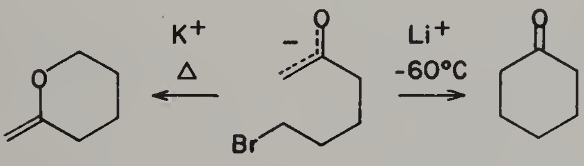
(5-11)

2. Enolate Anions

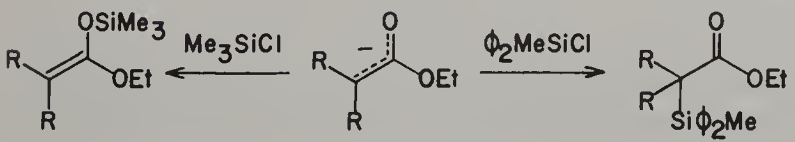
a. Substitutions

Enolates derived from esters will be included in this section with enolates from aldehydes and ketones.

As with unsymmetrical allyl anions, a question of regiochemistry arises when enolates are reacted with electrophiles; in this case, it is whether reaction will occur at carbon or oxygen. In most cases, the product of bond formation at carbon is desired, and in most cases, this can be achieved by employing conditions which favor it: (1) Li^+ rather than K^+ or Na^+ as the counterion, as lithium enolates tend to associate into dimers and tetramers in which the oxygen is sterically shielded from attack (if it is the monomeric Li enolate which reacts, this also must have a more shielded oxygen than do the other enolates) [86, 98, 491]; (2) A relatively non-polar solvent to favor aggregation and an S_N2 mechanism over S_N1 (e.g., THF rather than a solvent which strongly solvates cations preferentially like DMF, DMSO, and DME) [98, 492]; (3) Lower temperature to favor aggregation [98, 491]; (4) Avoidance of crown ethers and cryptands, which give relatively free anions [98]; (5) A "softer" electrophile, such as MeI (rather than Me_2SO_4) or $\Phi_2MeSiCl$ (rather than Me_3SiCl), which will prefer to react at the "softer" carbon atom rather



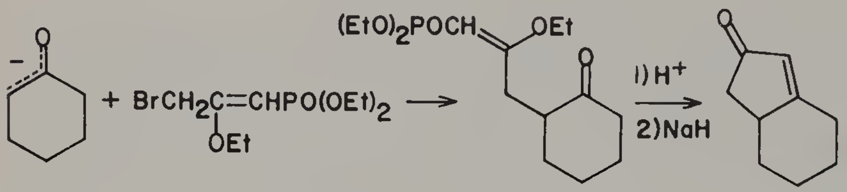
(5-12) [491]



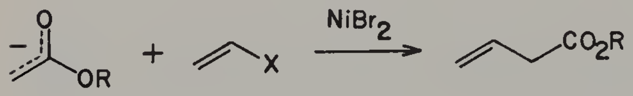
(5-13) [493]

than at the "harder" oxygen [98, 493]. Reactions (5-12) and (5-13) show how the product can be changed by varying some of these factors.

Polyalkylation of enolates can be a problem if proton exchange between the alkylation product and the enolate occurs very rapidly. This can sometimes be avoided by adding Bu_3SnCl or Et_3Al to generate the tin or aluminium enolate [494] or by adding triethanolamine borate [495]. Enolates of aldehydes can sometimes be alkylated directly, though rapid aldol condensation and polyalkylation can make the yield low [496, 497]. Indirect routes involving alkylation of the enamine [498] or enaminate (Section 5 below) may be preferable. Reactions (5-14) and (5-15) illustrate the alkylation and vinylation of enolates [499].

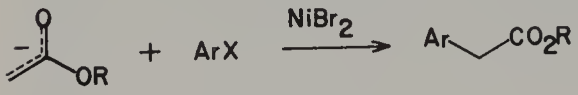


(5-14) [500]

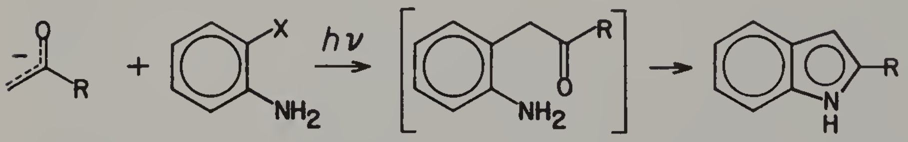


(5-15) [501]

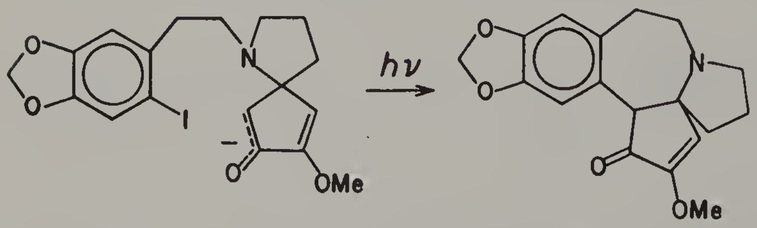
Arylation of enolates, like the vinylation shown in (5-15), does not occur without assistance in breaking the carbon-halogen bond. This may be done with the aid of a transition metal (5-16) or by an $S_{RN}1$ mechanism, in which case the anion radical of the aryl halide dissociates into halide anion and aryl radical (5-17, 5-18) [502–508].



(5-16) [501]

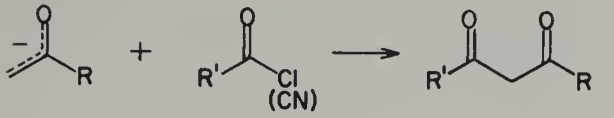


(5-17) [502, 503]

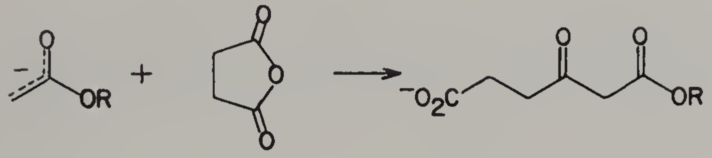


(5-18) [504]

Acylation of an enolate can be accomplished with an acyl chloride (5-19), an acyl cyanide (5-20), an anhydride (5-21), or even an ester (5-22). In the latter case, if the enolate is derived from an ester, the intermolecular reaction is called a Claisen condensation [512] (recently shown to occur even in the gas phase without a counterion [513]) and the intramolecular reaction is a Dieckmann condensation [265]. These two condensations (and a few of the other enolate reactions) are best and most easily run without preliminary generation of the enolate ion in high concentration. The enolate in (5-23) reacts analogously, but O-phosphorylation occurs in (5-24).

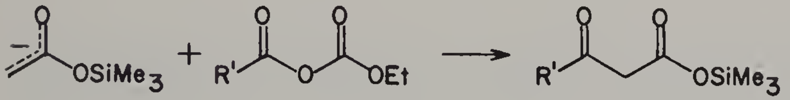


(5-19) [509]
(5-20) [510]

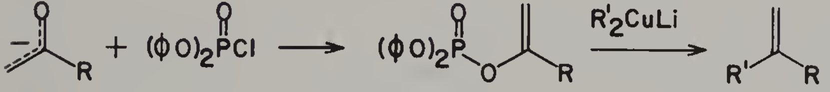


(5-21) [511]

(5-22) [512]



(5-23) [514]

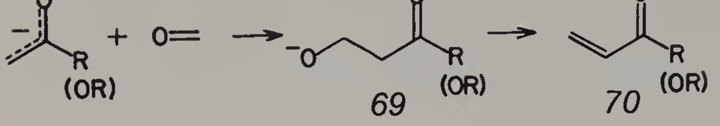


(5-24) [515]

b. Additions

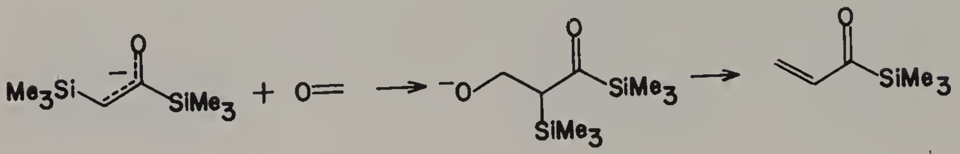
The addition of an enolate to an aldehyde or ketone carbonyl group (5-25) is the key step in the base-catalyzed aldol condensation, which is one of the most important carbon-carbon bond-forming reactions [516]. The intermediate β-alkoxylaldehyde or ketone (*69*) may be protonated, trapped with Me_3SiCl [517], or, under vigorous conditions, caused to eliminate water to give the α,β-unsaturated aldehyde or ketone (*70*). In cases where mixing the carbonyl components and adding base leads to the wrong aldol product, it may be possible to get the desired product using a preformed enolate [518] or enaminate [519]. This is necessary, for example, if an enolate from an ester is to be added to a ketone containing an α-hydrogen (5-26) [518]. Me_3SiOH may be eliminated instead of water, as in (5-27) [520]. Reaction (5-28) shows the use of an aldol condensation followed by the loss of carboxylate in a vinyl sulfone synthesis [521]. (5-29) shows an aldol followed by

γ-elimination of chloride to give α-epoxyester; this is the Darzens condensation [522].

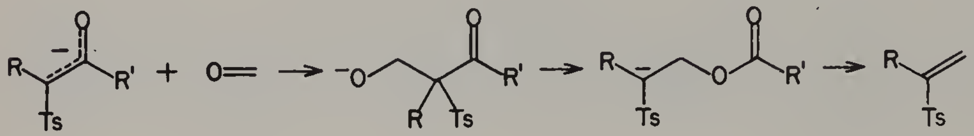


69 70

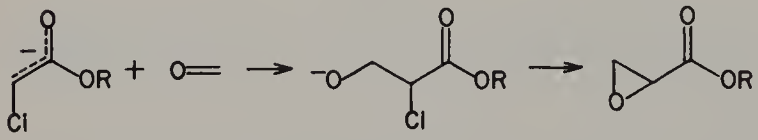
(5-25)
(5-26)



(5-27)

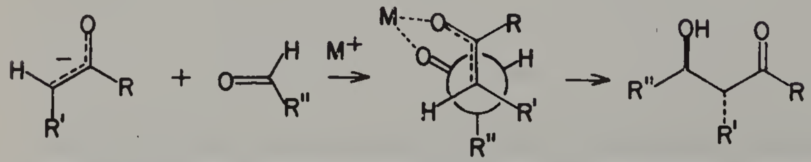


(5-28)



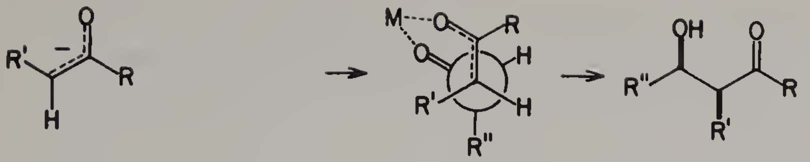
(5-29)

The stereochemistry of the aldol condensation has been extensively studied recently with a view to developing highly stereoselective aldol methods for synthesizing certain natural products, e.g., macrolide antibiotics [523]. With lithium [524] or boron [525] enolates, the favored kinetic products, obtained at low temperatures, are *threo*-β-hydroxyketone *71* from *E*-enolate *72 via* transition state *73* (5-30) and *erythro*-β-hydroxyketone *74* from *Z*-enolate *507 via* transition state *76* (5-31). The equilibrium product, especially favored by adding $ZnCl_2$, is *threo* (*71*), presumably because R′ and R″ are pseudo-equatorial in *77* [526]. With $(Et_2N)_3S^+$ as the cation, *erythro* product *74* is favored from *either* enolate *72* or *75* (avoiding the necessity of generating a specific enolate), presumably *via* transition states *78* (from *E*-enolate *72*) and *79* (from *Z*-enolate *75*) [517]. For unknown reasons, zirconium enolates give *erythro* products regardless of enolate geometry [527], aluminium *Z*-enolates give considerable *threo* product [528], and either crotyltin stereoisomer gives *erythro* alcohol *80* which can be converted into *erythro* β-hydroxycarbonyl derivatives *74* [529].



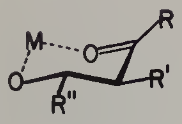
72 73 71

(5-30)

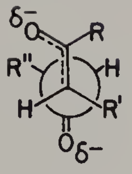


75 76 74

(5-31)



77



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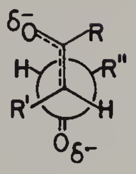

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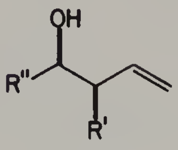
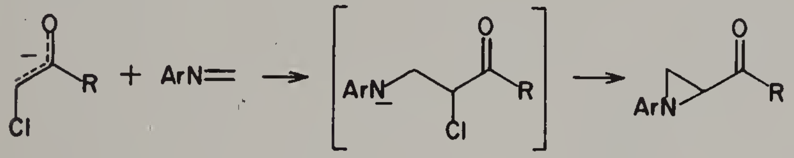
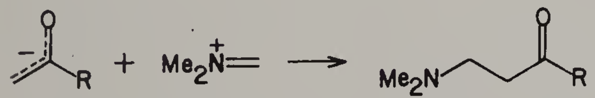


80

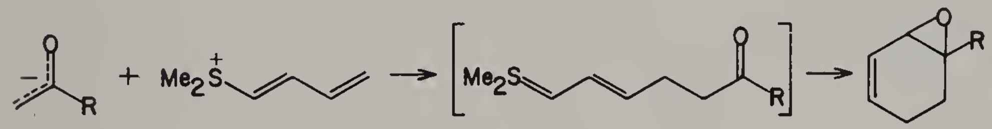
Reactions (5-32) to (5-36) show additions of enolate anions to carbon-nitrogen and activated carbon-carbon double bonds. (5-33) is the key step in the base-catalyzed Mannich reaction of secondary amines [535]; in the Mannich the iminium salt is prepared *in situ* by mixing the amine with the aldehyde.



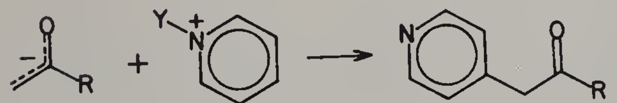
(5-32) [530]



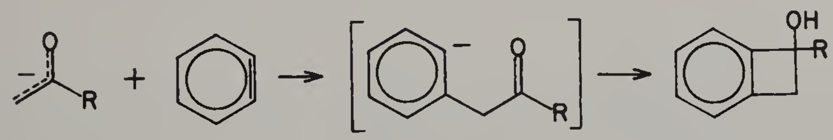
(5-33) [531]



(5-34) [532]



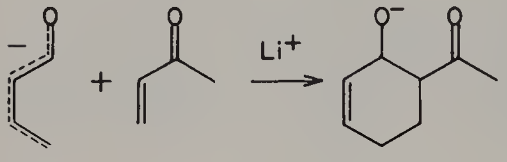
(5-35) [533]



(5-36) [534]

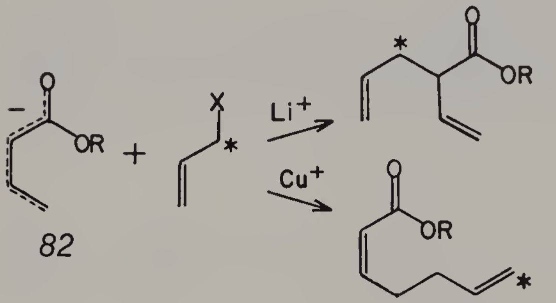
3. Other O-Stabilized Monoanions

The conjugation in enolates can be linearly extended by addition of a carbon-carbon double bond to give dienolate ions *81* and *82*, which usually react with electrophiles under kinetic control in the α-position. In (5-37), the observed γ-attack may indicate thermodynamic control. In (5-38), γ-attack is found when Cu^+ is the counterion, and α-attack when Li^+ is the counterion. If the conjugation is extended in a cross-conjugated manner to give ions *83* and *84*, reaction can occur on oxygen as in (5-39) or in the α-position as in (5-40) and (5-41). Anion *85*, with its conjugation extended by two carbon-carbon double bonds, has been used as an equivalent of 2-metallated-2-cyclohexenone (5-42).



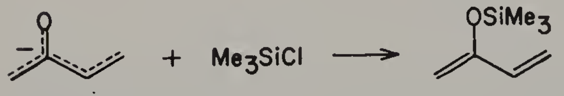
81

(5-37) [536]



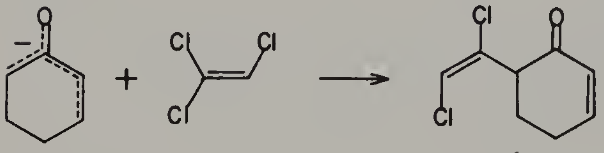
82

(5-38) [470]



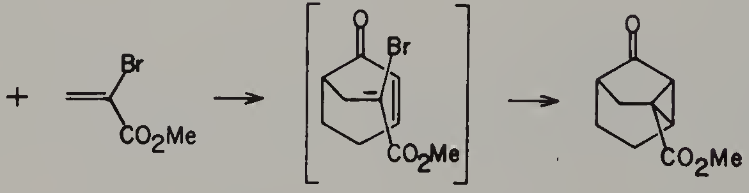
83

(5-39) [537]

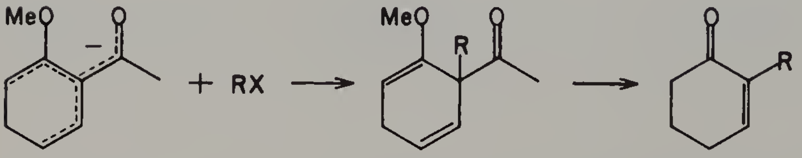


84

(5-40) [538]



(5-41) [539]



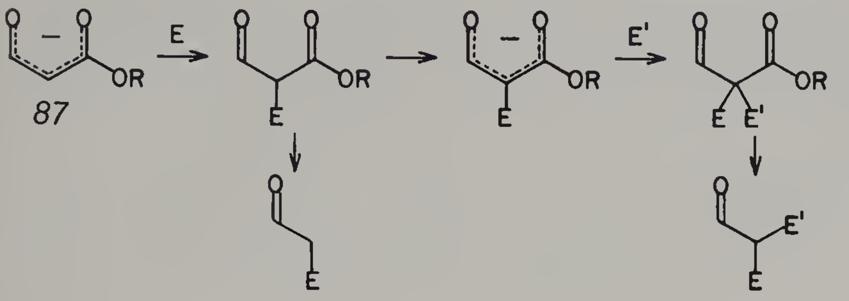
85

(5-42) [540]

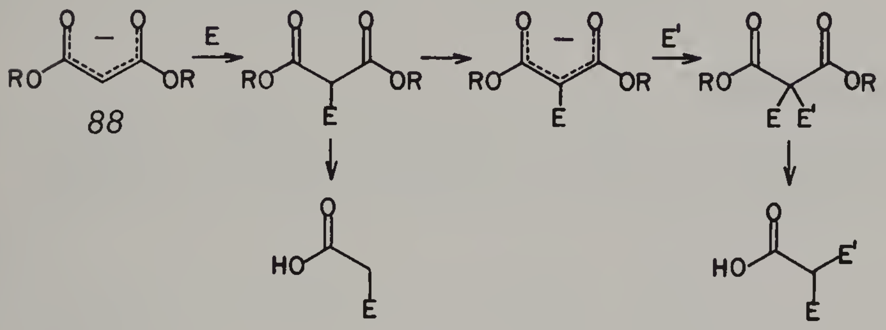
With two stabilizing oxygens arranged as in *86–88*, the anion is relatively easy to prepare and is easy to alkylate on carbon (5-43 to 5-45); (5-44) [542] is the acetoacetic ester synthesis and (5-45) [543] is the malonic ester synthesis.

Some recent variations of these syntheses using di- and trianions will be mentioned in the next section. Two alkene syntheses employing carbanion chemistry of this type are (5-46) and (5-47).

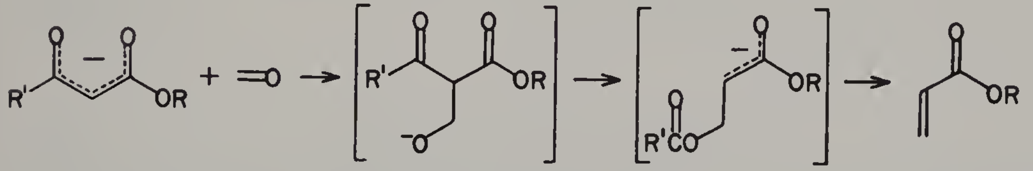
(5-43) [541]



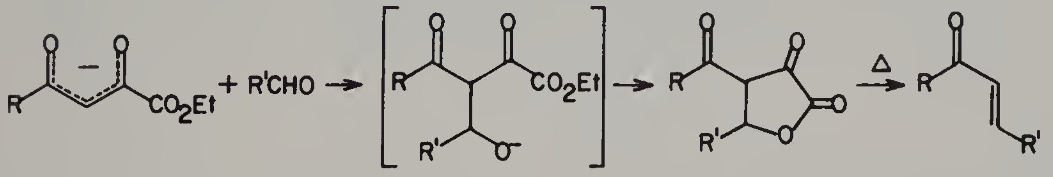
(5-44) [542]



(5-45) [543]

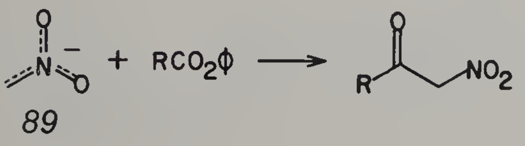


(5-46) [544]



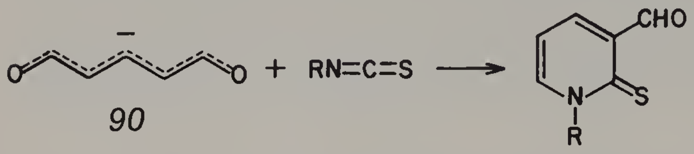
(5-47) [545]

Two stabilizing oxygens are also present in an anion *89* derived by abstraction of an α proton from a nitroalkane; these anions react with electrophiles on carbon in some cases, e.g. (5-48).



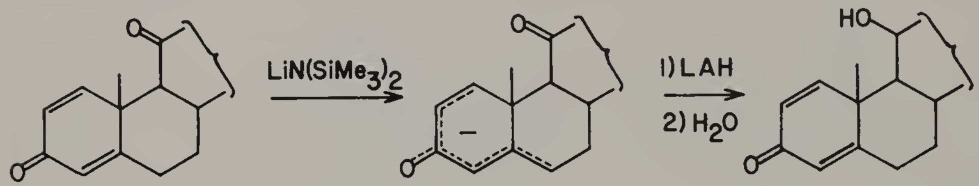
(5-48) [546]

Anion *90*, a higher vinylog of *86*, is available commercially with Bu_4N^+ as the counterion for use in synthesis; in at least some of its reactions, e.g. (5-49), initial attack on the α carbon is indicated.



(5-49) [547]

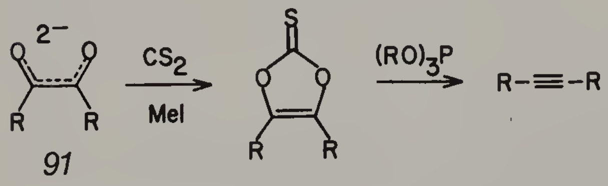
Various types of extended enolate ions have been used as protecting groups (e.g. 5-50) [548–550], with the carbonyl compound being liberated at the end by protonation of the enolate.



(5-50)

4. O-Stabilized Dianions

Many oxygen-stabilized dianions are synthetically useful, e.g. enediolate dianion *91* in the acetylene synthesis (5-51); initial attack is on oxygen in this case.

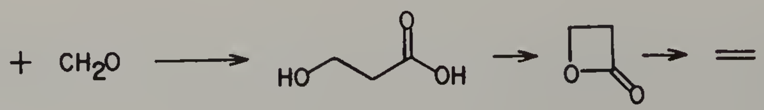


(5-51) [551]

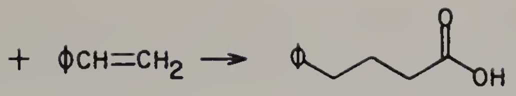
Reactions (5-52) to (5-56) of branched-chain dianions *92*, usually derived by removal of two protons from carboxylic acids, illustrate the usually valid principle that the first site of reaction of a dianion with an electrophile is the atom from which the last proton was removed [259], i.e., at the end carbon in these cases.

(5-52) [552]

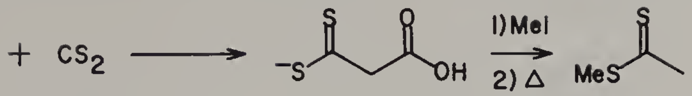
(5-53) [553]



(5-54) [554, 555]

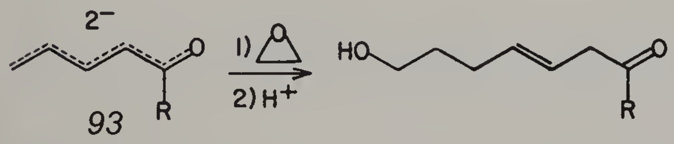


(5-55) [556]



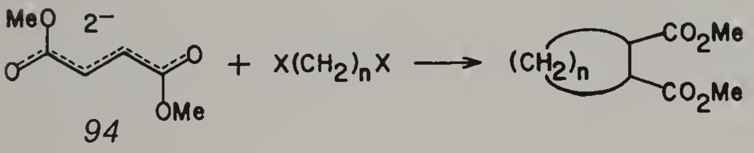
(5-56) [557]

The above dianions *91* and *92* have 4 atoms in a π system bearing the negative charges. Reactions (5-57) to (5-63) of some of the analogous 6-atom systems *93–98* are given below. (5-59) illustrates kinetic *vs.* thermodynamic control in a reversible addition. (5-60) shows that β-diketones and β-ketoesters can be reacted with electrophiles at the γ-position *via* the dianion *96*; this complements well the usual reactions of the monoanions at the α-position. *97* is the dianion (usually with Mg^{2+} as the counterion) of ethyl hydrogen malonate, which is superior to monoanion *88* from diethyl malonate for many "malonic ester" type syntheses because a hydrolysis step is avoided and a monoester is obtained upon decarboxylation.



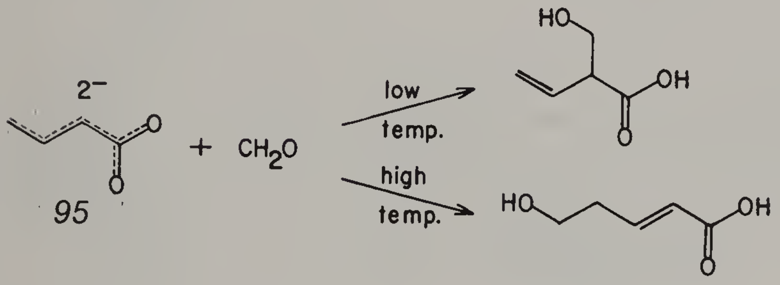
93

(5-57) [558]



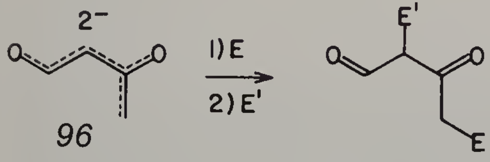
94

(5-58) [559]



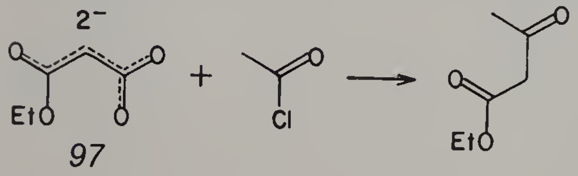
95

(5-59) [560, 561]



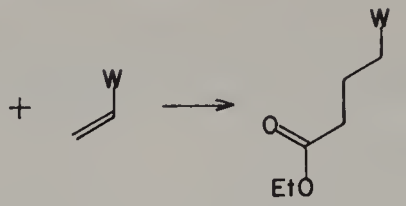
96

(5-60) [552, 562–564]

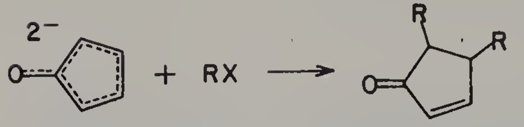


97

(5-61) [565]



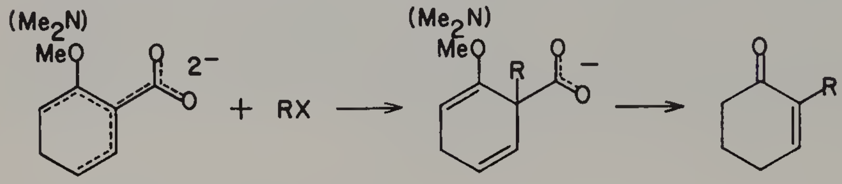
(5-62) [566]



98

(5-63) [567]

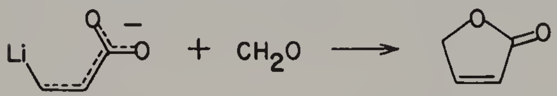
Dianions *99* with more extended π systems alkylate as shown (5-64); they have been used as synthetic equivalents of 2-metallated-2-cyclohexenone.



99

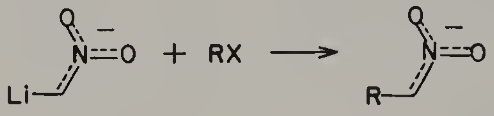
(5-64) [568, 569]

Dianions *100–102*, with the negative charges in separate systems, have found use in synthesis as shown in (5-65) to (5-67).



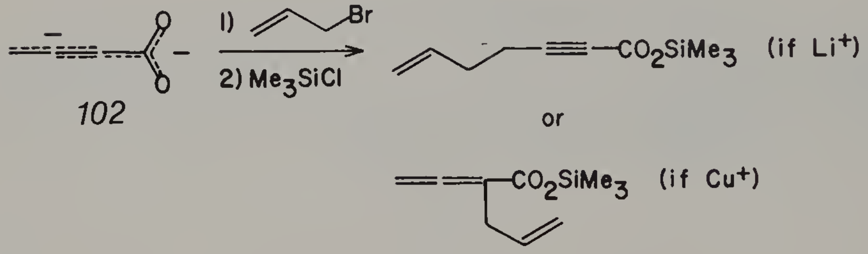
100

(5-65) [570]



101

(5-66) [571]

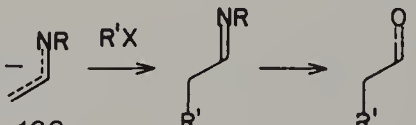


102

(5-67) [572]

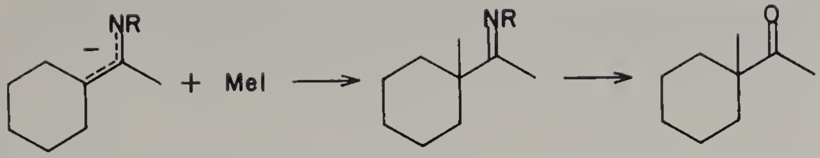
5. N-Stabilized Anions

Enaminate ions *103* alkylate readily on carbon as in (5-68) [310–312, 573–579]; some examples of this reaction are given in (5-69) to (5-71). These reactions are most often used when the corresponding enolate reaction is unsatisfactory.

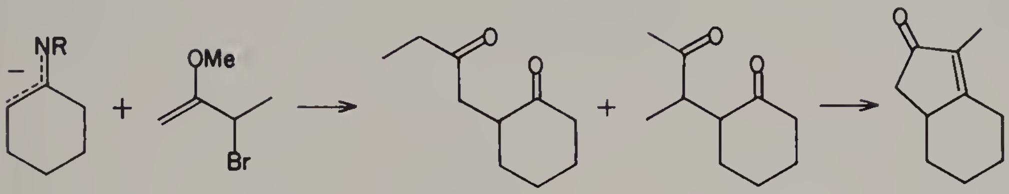


103

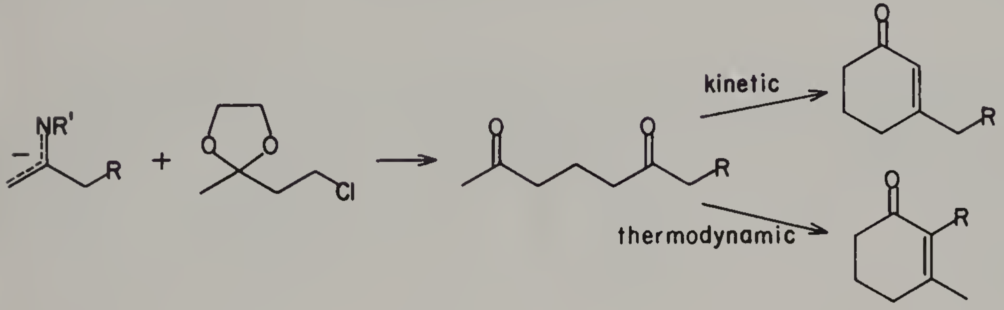
(5-68)



(5-69) [310]

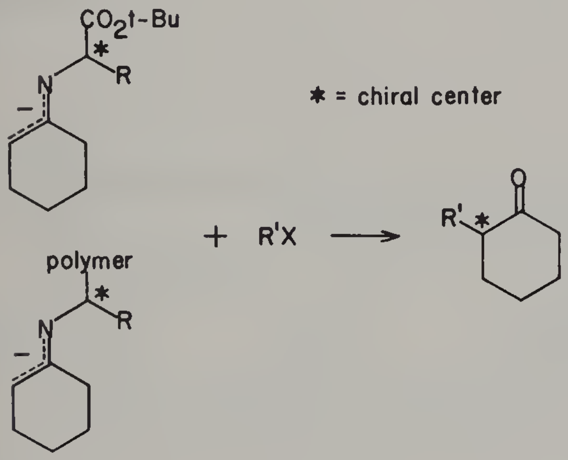


(5-70) [575]



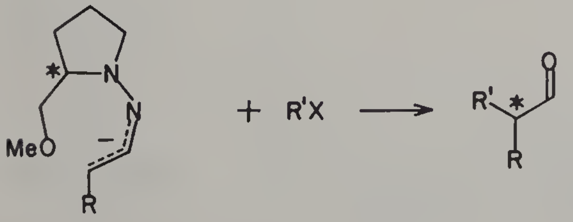
(5-71) [576]

These anions have been used in many asymmetric syntheses of α-alkylated ketones, e.g. (5-72) to (5-74). Many of the groupings on nitrogen contain a heteroatom which can chelate with the metal atom.



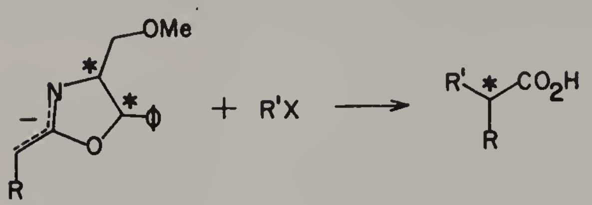
(5-72) [580]

(5-73) [581]

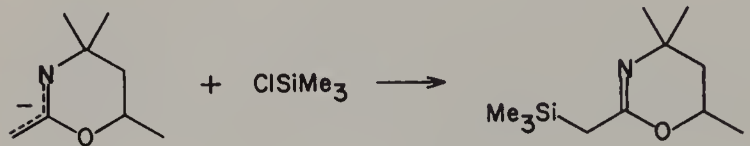


(5-74) [582]

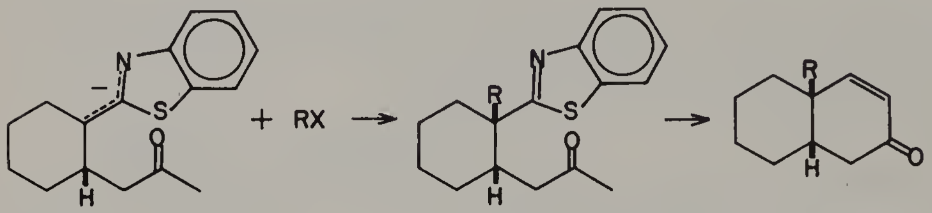
Anions from oxazolines, oxazines, and thiazoles have been used similarly to make carboxylic acids and derivatives, e.g. (5-75) to (5-77).



(5-75) [583]

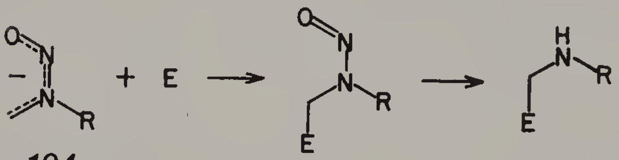


(5-76) [584]



(5-77) [418]

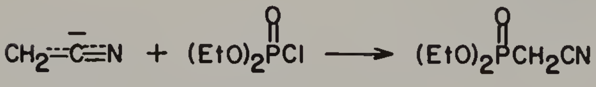
Anions *104* derived from N-nitrosoamines alkylate well on carbon and have been used as equivalents for α-metallated secondary amines (5-78).



104

(5-78) [585–589]

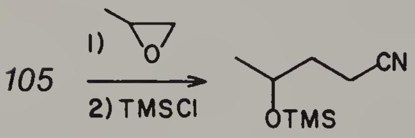
α-Metallated acetonitrile (*105*) and some of its derivatives have been used in syntheses as illustrated in (5-79) to (5-81).



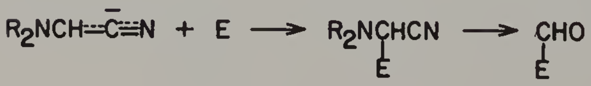
$$\mathrm{\overset{-}{CH_2{=}C{\equiv}N}} + \mathrm{(EtO)_2\overset{O}{\overset{\|}{P}}Cl} \longrightarrow \mathrm{(EtO)_2\overset{O}{\overset{\|}{P}}CH_2CN}$$

105

(5-79) [590]



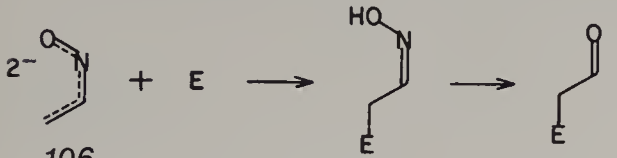
(5-80) [591]



$$\mathrm{R_2NCH{=}\overset{-}{C}{\equiv}N} + \mathrm{E} \longrightarrow \mathrm{R_2N\underset{E}{CH}CN} \longrightarrow \mathrm{\underset{E}{CHO}}$$

(5-81) [592]

The *cis*-dianions *106* derived regiospecifically from *syn*- or *anti*-oximes react with electrophiles on carbon, e.g. (5-82) to (5-84).



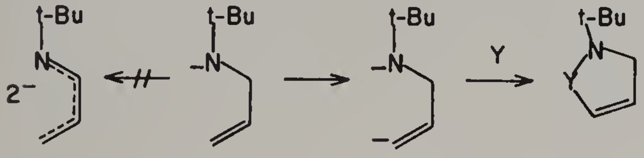
106

(5-82) [593–595]

(5-83) [596]

(5-84) [597]

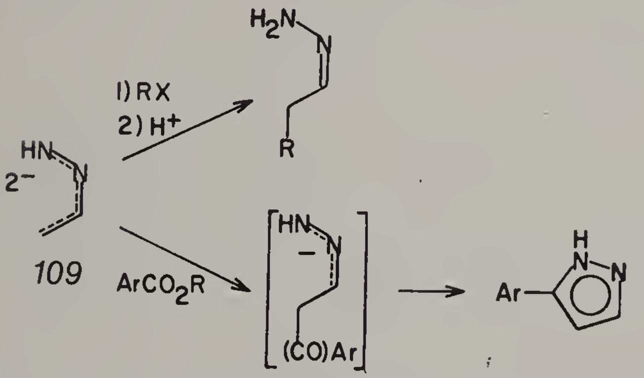
An attempted preparation of N-stabilized butadienedianion analog *107* gave instead dianion *108*, stabilized by chelation, as indicated in (5-85).



107 *108*

(5-85) [598]

On the other hand, dianions of type *109*, stabilized by two nitrogens, were easily prepared and reacted smoothly with electrophiles at the end carbon atom (5-86 and 5-87).

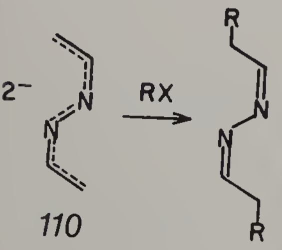


109

(5-86) [599]

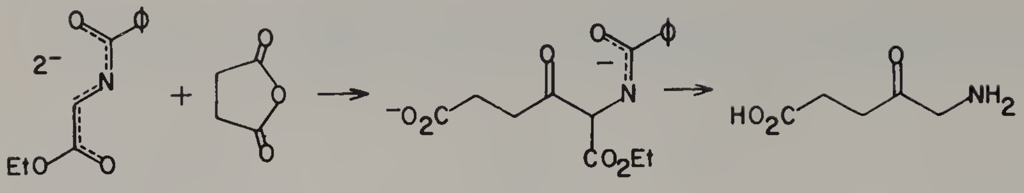
(5-87) [600]

Nitrogen-stabilized hexatrienedianion analogs *110* and *111* react with electrophiles on carbon as shown in (5-88) and (5-89).



110

(5-88) [599]

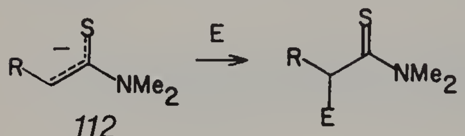


111

(5-89) [601]

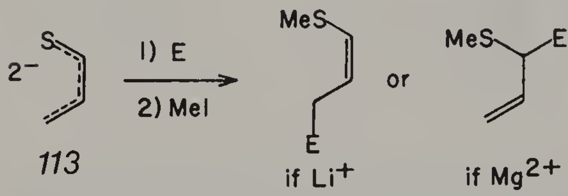
6. S-Stabilized Anions

Some analogous S-containing carbanions *112–115* react with electrophiles on carbon as shown in (5-90) to (5-93).



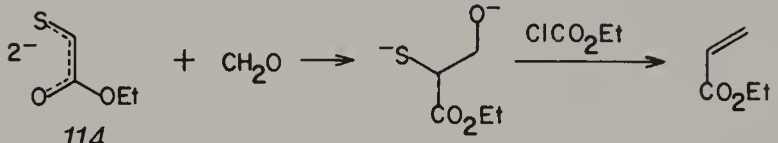
112

(5-90) [602]



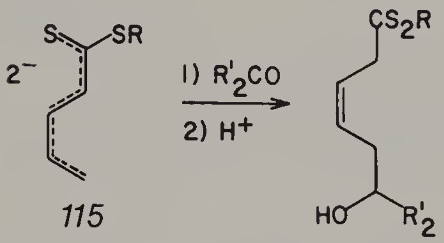
113

(5-91) [603]



114

(5-92) [604]



115

(5-93) [605]

VI. Eliminations

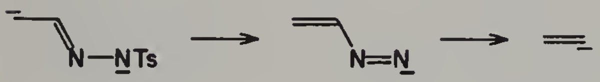
Eliminations of various leaving groups Y from carbanions are useful routes to carbenes (from α-elimination, (6-1)), alkenes and alkynes (from β-elimination, (6-2a) and (6-2b)) cyclopropanes (from γ-elimination, (6-3)), and vinyl anions (from the Shapiro reaction, (6-4)). Many of these reactions proceed rapidly at room temperature but are slow at dry ice temperatures, thus permitting carbanions containing good leaving groups to be used in substitution and addition reactions at low temperatures [205, 207]. Leaving groups can be halide, RO^-, R_2N^-, or even R^-, H^-, and O^{2-}. Cycloeliminations of carbanions (6-5) are also known.

$$R_2\bar{C}Y \longrightarrow R_2C: \qquad (6\text{-}1)\ [606]$$

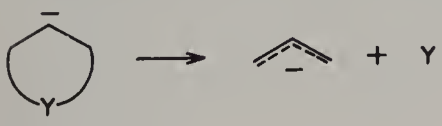
(6-2a)

(6-2b)

(6-3)



(6-4)



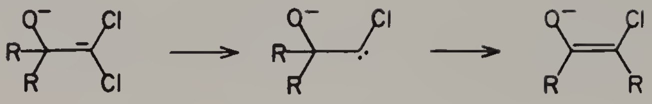
(6-5)

1. α-Eliminations

Examples are (6-6), from the Reimer-Tiemann reaction, and (6-7), which can be avoided at low temperatures. Reaction (6-8) may also go by α-elimination as shown.

$Cl_3C^- \longrightarrow Cl_2C:$ (6-6) [606]

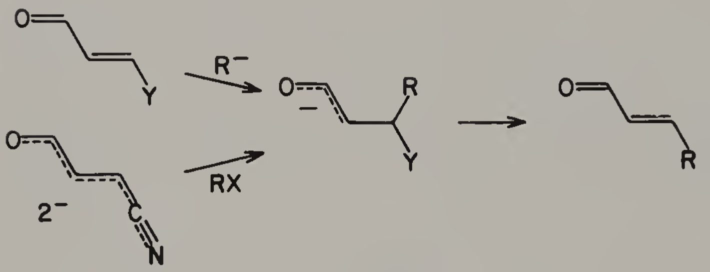
$EtOCH_2^- \longrightarrow CH_2:$ (6-7) [607]



(6-8) [205]

2. β-Eliminations

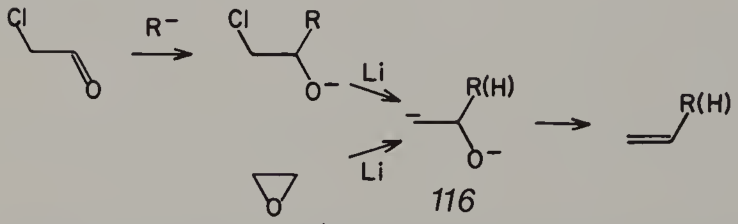
Reaction (6-2a) is a key step in the formation of alkenes by the ElcB mechanism [608, 609]; e.g., the base-catalyzed aldol condensation (5-25) often involves as a last step the elimination of a β-OH from an enolate ion to give an α,β-unsaturated carbonyl compound (*70*). This is also a key step in several sequences in which the enolate ion is generated in different ways, e.g., by addition as in (6-9) and by alkylation of a dianion as in (6-10). The former sequence can be carried out with retention of configuration at the double bond [610]. The latter sequence takes advantage of the rare combination of good leaving group ability and α-carbanion stabilizing ability possessed by the CN grouping.



(6-9) [610] (Y = OAc),

(6-10) [612] (Y = CN)

RO⁻ [183] and R_2N^- [210] are known as leaving groups in reactions of type (6-2a). When it is desired to avoid elimination but these groups leave too rapidly, dianions *116* and *117* have been used successfully [613]. It should be noted that when *lithium* is used as the counterion, *116* will eliminate Li_2O at 25 °C; this has been profitably used in the conversions of α-haloketones (6-11) and epoxides (6-12) into alkenes.



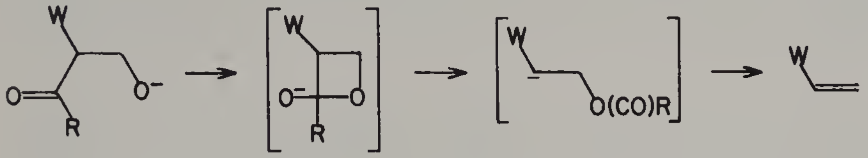
116

(6-11) [614]

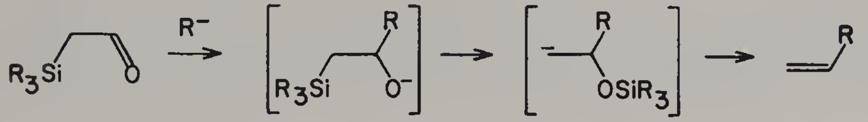
(6-12) [615]

117

A type of reaction which probably involves β-elimination of RCO_2^- is (5-46), which presumably proceeds as shown in (6-13) (W = CO_2R). The very useful olefin-forming eliminations of R_3SiO^- [520], e.g. (6-14), probably also involve β-elimination, possibly in some cases as depicted.

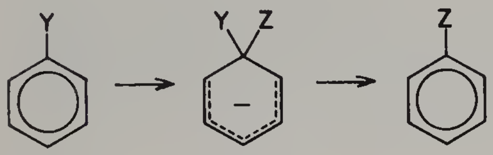


(6-13) [544]



(6-14) [616]

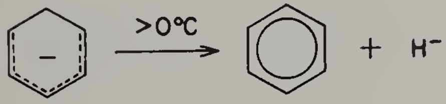
The last step in a nucleophilic aromatic substitution by the addition-elimination mechanism (6-15) can be considered as a β-elimination of Y^-; the commonest leaving groups are halides. Groupings in the *o*- and *p*-positions of *118* which stabilize the intermediate cyclohexadienyl anion *119* are required for the reaction to proceed well.



118 *119*

(6-15) [617]

Many carbanions have been observed to lose β-hydride, either by simply ejecting metal hydride (6-16) or by transferring hydride to an acceptor such as a trialkylborane [618, 619] or ketone (6-17). Cyclohexadienyllithium, which gives the highly stable substance benzene when hydride is lost, eliminates rapidly at 0 °C, but ethyllithium decomposes to lithium hydride and ethylene at 100 °C and ethylpotassium gives potassium hydride and ethylene with a half-life of 1 day at 25 °C [125]. The reduction of ketones (6-17) by Grignard reagents [620] and alkyllithiums [621], which can be an annoying side reaction during addition, especially with Grignard reagents, apparently involves hydride transfer from a simple alkyl carbanion. Reactions (6-18) and (6-19), which occur when the hydrocarbons are metallated, probably have as key steps the ejection of hydride from an intermediate di- or possibly trianion.



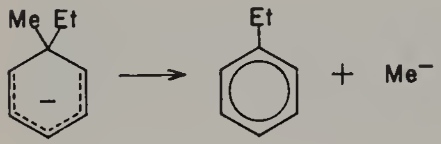
(6-16) [275]

(6-17) [620, 621]

(6-18) [622]

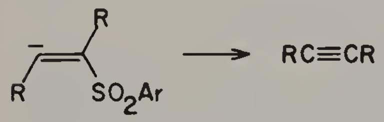
(6-19) [623]

Ejection of a β-alkyl group from a carbanion is not usually as facile as hydride elimination, but in the case of cyclohexadienyl anions in which there is no good alternative (6-20) it is observed on heating; as expected, the more stable carbanion (methyl) is ejected in the example shown. *n*-Butylpotassium gives some ethylene and ethylpotassium on standing at 25 °C [125].



(6-20) [624]

The elimination of HX from vinyl halides with strong base has long been a good way to prepare alkynes; (6-2b) may be a key step in many of these reactions. Other leaving groups, e.g., $ArSO_2^-$, can be used as well (6-21) [423]. An intriguing alkyne synthesis of unknown mechanism in which three hydrides are eliminated is (6-22) [625].

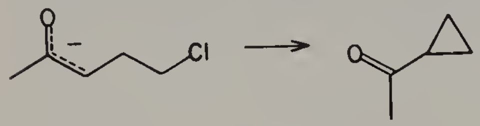


(6-21)

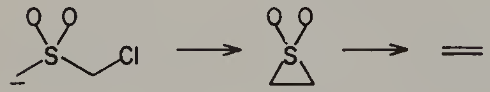
(6-22)

3. γ-Eliminations

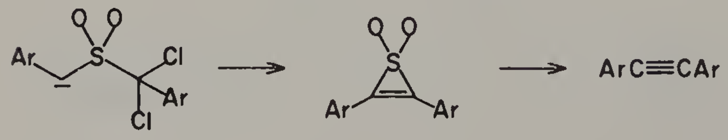
Reactions (6-23) to (6-25) show the use of (6-3) to make 3-membered rings; the latter two are termed Ramberg-Bäcklund reactions.



(6-23) [626]



(6-24) [627]

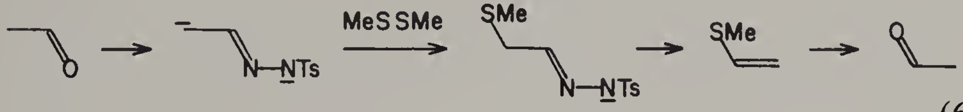


(6-25) [628]

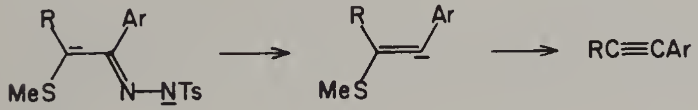
4. δ-Eliminations

The most useful type of reaction which is formally in this category is the Shapiro reaction (6-4) [629]. The vinyl anion can be reacted usefully with a variety of electrophiles [630–634], e.g., as in (6-26). This reaction has been used for carbonyl transposition as in (6-27) and for the synthesis of arylacetylenes (6-28).

(6-26) [634]



(6-27) [635]



(6-28) [636]

5. Cycloeliminations

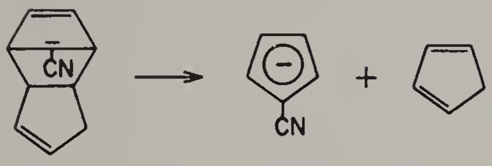
Cyclopentyl type anions *120–124* (unlike the corresponding cyclohexyl anions) undergo rapid ring-openings to allyl type anions *125–129* and ethylene or ethylene analogs (6-29) to (6-33).

120 *125*

(6-29) [293]

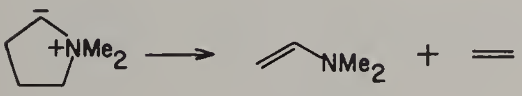
121 *126*

(6-30) [637]



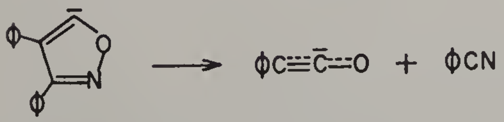
122 *127*

(6-31) [638]



123 *128*

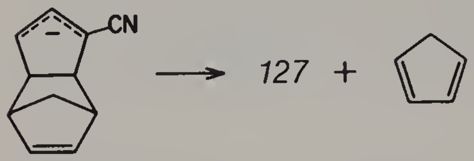
(6-32) [639]



124 *129*

(6-33) [640]

π-cyclopentenyl anion *130* undergoes a different type of reverse [4+2] cycloaddition to give the same products observed from isomeric anion *122* (6-34).



130

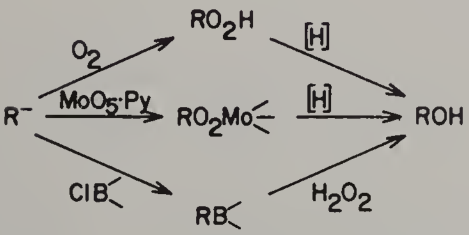
(6-34) [638]

VII. Oxidations

One-electron oxidation of monocarbanions leads to carbon radicals and two-electron oxidation gives carbonium ions [641]. In most of the oxidations below, the mechanism is not known (e.g., do oxidative coupling products arise from radical dimerization, combination of a cation with an anion, or nucleophilic displacement involving R^- and RY?), though progress is being made on some of the mechanisms [642, 643]. Again, the parallelism between base strength and ease of oxidation of carbanions should be noted [346].

1. Oxidations to Hydroperoxides, Alcohols, and Ketones

The reaction of O_2 with carbanions followed by quenching with protons (7-1) can give hydroperoxides in good yield in favorable cases [644, 645]. As some hydroperoxides are potentially explosive, they are usually reacted further without isolation; e.g., if the alcohol is desired, they can be reduced with a reagent such as sodium sulfite [646] or a trialkyl phosphite [647]. Alcohols can also be prepared *via* hydroperoxy molybdenum complexes (7-2) and alkylboranes (7-3). Oxygen can catalyze rotations about carbon-carbon bonds in allyl anions through reversible one-electron transfer [71].

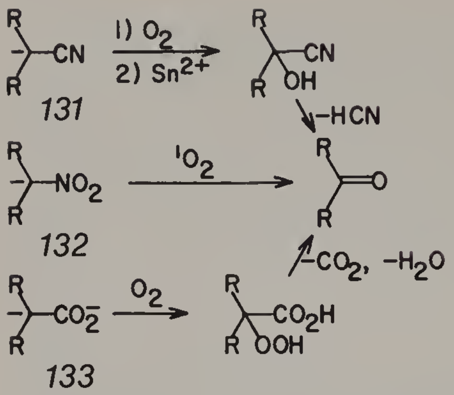


(7-1)

(7-2) [648]

(7-3) [340, 341]

Ketones can be prepared from special carbanion types *131–133* by elimination reactions which follow the oxygenation (7-4 to 7-6).



131 (7-4) [649]

132 (7-5) [650]

133 (7-6) [651]

2. Oxidative Couplings

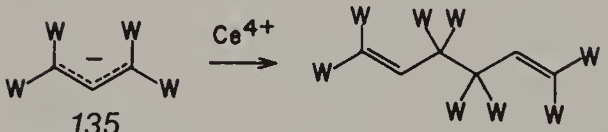
The simple coupling reaction (7-7) works well only in certain cases. One of the most useful is the Eglinton reaction (7-8), which consists of the oxidation of acetylenic anions with ferric ion and goes very well indeed. Resonance-stabilized carbanions *134–136*, often containing carbanion-stabilizing groups W, have been oxidatively coupled with a variety of oxidizing agents to give products such as 1,2-dinitro compounds (7-9), 1,4-diketones (7-10), 1,4-diimines (7-11), and 1,5-dienes (7-12 and 7-13). Useful mixed couplings have been reported [655].

$$R^- \xrightarrow{[O]} RR \qquad (7\text{-}7)$$

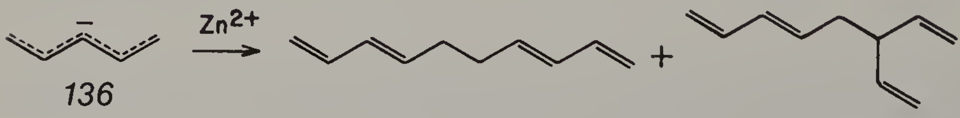
$$RC{\equiv}C^- \xrightarrow{Fe^{3+}} RC{\equiv}CC{\equiv}CR \qquad (7\text{-}8)\ [652]$$

134

W	[O]	
$-NO_2$	I_2	(7-9) [653]
$-(C{=}O)R$	Cu^{2+}	(7-10) [654, 655]
$-(C{=}NR)R$	Cu^+	(7-11) [656]



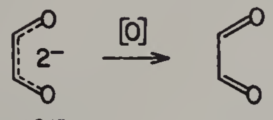
135 (7-12) [657]



136 (7-13) [658]

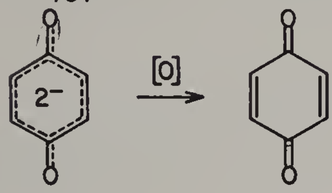
3. Dianion Oxidations

Oxidation of dianions *137—144* leads to the products shown in (7-14) to (7-22); all are two-electron oxidation products except for *145–147*, which presumably arise by dimerization of the anion radical formed by one-electron oxidation of dianions *140–142*. The first two oxidations (7-14 and 7-15) are very important in biological systems. All of these 2-electron oxidations can represent the second step in a general dehydrogenation process in which the first step consists of abstracting two protons, and the second, two electrons [661–666].



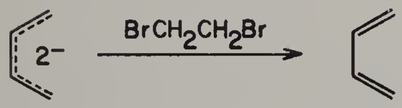
137

(7-14)



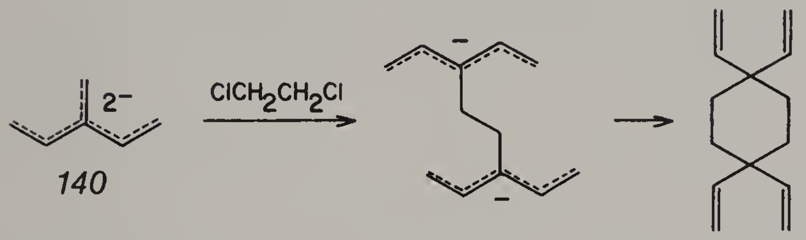
138

(7-15)



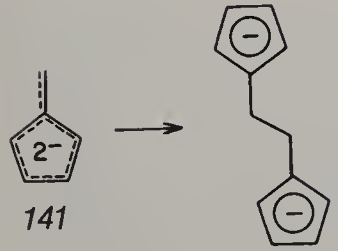
139

(7-16) [73]



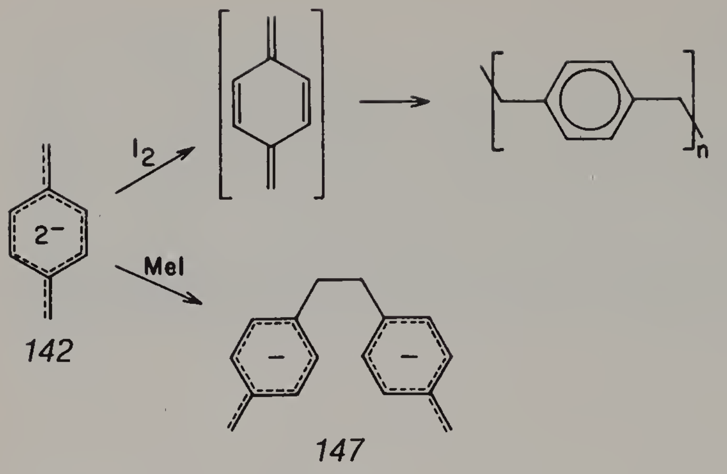
145

(7-17) [659]



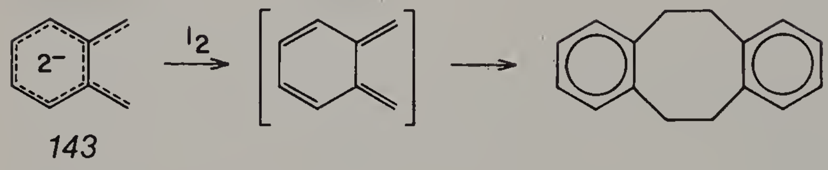
146

(7-18) [660]

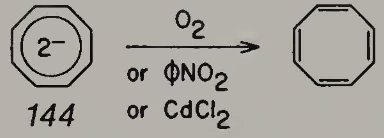


(7-19) [661]

(7-20) [661]

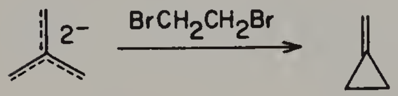


(7-21) [661]

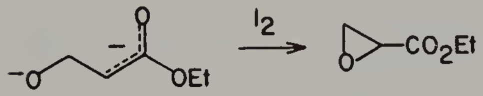


(7-22) [622, 662]

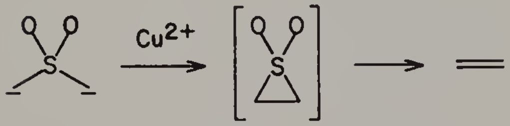
When the product of two-electron oxidation would be a diradical, the isolated products can usually be thought of as arising from intra- or intermolecular coupling of this diradical (7-23 to 7-27).



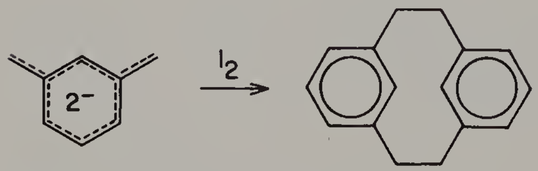
(7-23) [73]



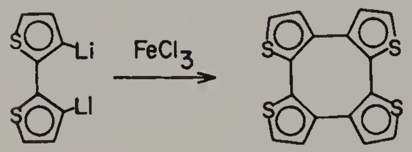
(7-24) [518]



(7-25) [667]



(7-26) [661]



(7-27) [668]

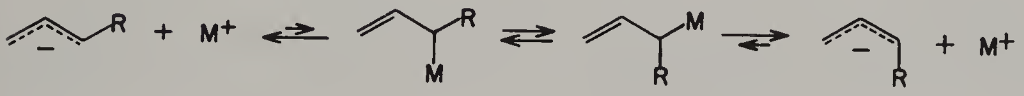
VIII. Rearrangements

The various types of simple intramolecular rearrangements described in Sections 2 to 5 below are often combined in complex sequences, some examples of which are given in Section 6.

1. Intermolecular Rearrangements

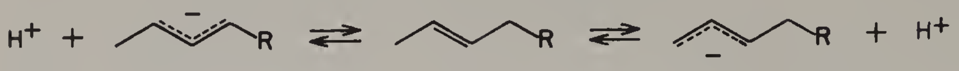
The equilibrium (8-1) in which the counterion M^+ becomes more and less tightly associated with the carbanion R^- can account for stereochemical changes in the carbon species present: (a) σ carbanions, in which the tight structure R—M is favored, can have the configurations at their carbons inverted *via* the loose form R^-; this is most easily detected by racemization in a case where the charge-bearing sp^3 hybridized carbon is the only chiral center (Chapter II, section 1, part b); (b) π carbanions, in which the loose form is favored, can undergo rotations about partial double bonds which essentially become single bonds in the tight form (8-2); if R = vinyl, this could represent a change from W- to U-shaped pentadienyl anion. Rotations can of course occur about partial double bonds in the delocalized carbanion itself, independent of M^+, but this seems less likely than the above. π anions have been geometrically isomerized photochemically as well as thermally [669].

$$R^- + M^+ \rightleftharpoons RM \tag{8-1}$$

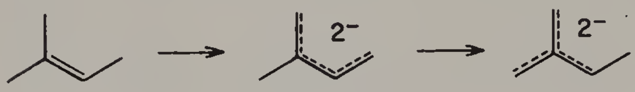


(8-2)

More drastic rearrangement of a π carbanion can occur through the equilibrium (8-1) if M = H; the proton can come off a different allylic carbon, causing a shift of the allyl anion system down the chain in addition to any stereochemical changes (8-3). This sequence is a vital part of base-catalyzed alkene isomerizations, which are generally run under conditions where the alkenes are much more stable than the allyl anions, and the *alkenes* are thus equilibrated rather than the allyl anions [487, 670, 671]. Sometimes, however, the *anions* themselves are equilibrated, as when the kinetic dimetallation product *148* is converted to the thermodynamically more stable isomer *149* on standing at 25 °C (8-4) [672]; for other examples, see [282, 283].



(8-3)



(8-4)

148 *149*

Acetylenes and allenes can similarly be equilibrated efficiently by base (8-5). Again, the bases used are usually not sufficiently strong to provide high concentrations of the anions, *unless* R or R′ = H, in which case the final step consists of abstraction of the terminal acetylenic proton to give the acetylenic anion, e.g., (8-6).

$$RCH_2C{\equiv}CR' \rightleftarrows RCH{=\!=}\overline{C}{\equiv}CR' \rightleftarrows RCH{=}C{=}CHR' \rightleftarrows RC{\equiv}\overline{C}{=\!=}CHR' \rightleftarrows RC{\equiv}CCH_2R'$$

(8-5) [673]

$$Me(CH_2)_nC{\equiv}CR \longrightarrow {}^{-}C{\equiv}C(CH_2)_{n+1}R$$

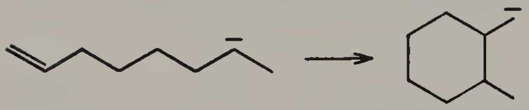
(8-6) [673, 674]

2. Intramolecular Additions

5-Membered rings are kinetically favored over 6; e.g., reaction (8-7) is faster than (8-8) by a factor of 2800 [675]. The preference for an anion of the type *150* to form a 5- rather than a 6-membered ring is borne out in other systems [73, 676, 677].

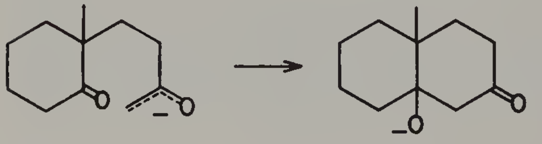
(8-7)

150



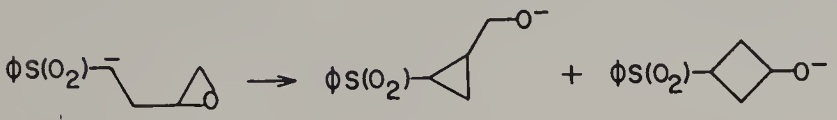
(8-8)

The most important intramolecular additions are probably ring-forming aldol condensations, e.g. (8-9). These are usually equilibrium-controlled reactions in which only 5- and 6-membered rings are observed.



(8-9) [678]

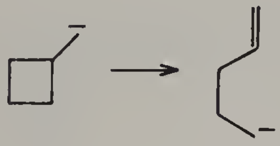
Reaction (8-10) shows the formation of cyclopropane and cyclobutane rings by intramolecular additions; in this case the energy to make such thermodynamically unfavored ring sizes is provided by the opening of an epoxide and the shift of charge from carbon to oxygen. Li^+ at room temperature favored the former product and Mg^{2+} at —70 °C the latter.



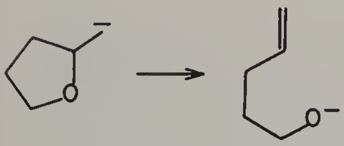
(8-10) [679]

3. Intramolecular Eliminations

These reactions are simply the reverse of the reactions in Section 2 [680]. The driving force is often relief of ring strain (8-11), or leaving group stabilization as in (8-12) and reverse aldols (8-9), or both.

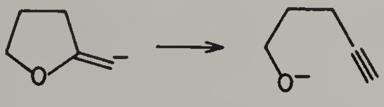


(8-11) [681]

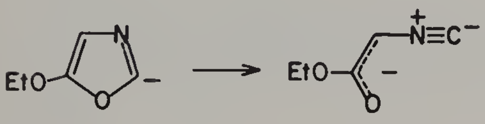


(8-12) [682]

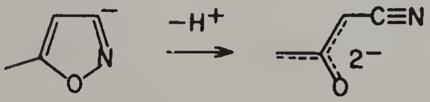
Vinyl (8-13) and heteroaromatic (8-14 and 8-15) anions can also undergo ring opening, even though an aromatic ring is destroyed in the process in the latter cases. Benzylic-type anions (8-16 and 8-17) also undergo cleavage of the aromatic ring [688].



(8-13) [683]

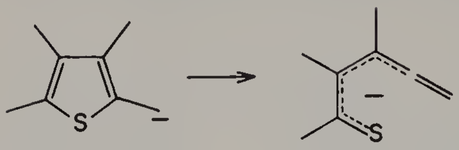


(8-14) [684]



(8-15) [685]

(8-16) [686]



(8-17) [687]

4. Sigmatropic Carbanion Rearrangements

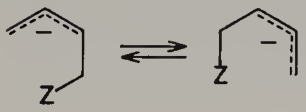
In sharp contrast to carbonium ions, carbanions undergo [1,2]sigmatropic shifts very rarely if ever, in accordance with the Woodward-Hoffmann rules [689]. 1,2-Aryl shifts occur, but by addition-elimination rather than concertedly (see Section 6). Stevens (8-18, 8-19) and Wittig (8-20) rearrangements involve 1,2-alkyl shifts but probably proceed by diradical mechanisms [692, 695].

$$Me_3\overset{+}{N}CH_2^- \longrightarrow Me_2NEt \qquad (8\text{-}18)\ [690\text{–}692]$$

$$Me_2\overset{+}{S}\bar{C}HR \longrightarrow MeSCHRMe \qquad (8\text{-}19)$$

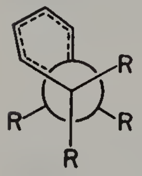
$$MeO\bar{C}HR \longrightarrow {}^-OCHRMe \qquad (8\text{-}20)\ [693\text{–}695]$$

Suprafacial [1,4]proton shifts in allyl anions (8-21) are permitted thermally but have not been observed due to the thermal instability of allyl anions.



(8-21)

On the other hand, some thermal antarafacial [1,6]sigmatropic proton shifts in pentadienyl anions (8-22) occur just above room temperature [696, 697] *via* a coiled transition state (*151*). Steric hindrance (R's = alkyl in *151*) slows the rearrangement; each R = Me up to two (the maximum tried) increases the activation energy by several Kcal/mole. The photochemical suprafacial counterpart of this reaction was found in (8-23) [696].



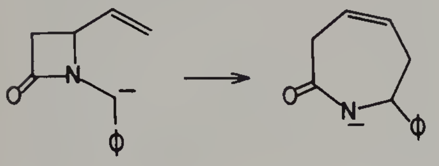
151

(8-22)

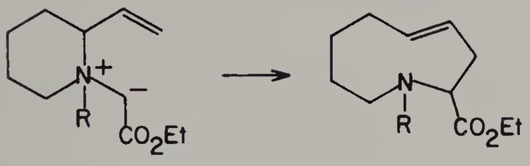
(8-23)

Efforts to observe thermal [1,8]sigmatropic proton shifts in heptatrienyl anions failed.

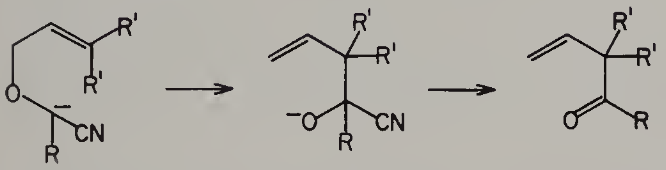
Many [2,3]sigmatropic rearrangements of heteroatom-containing carbanions are known [698–703]. The usual driving force for these reactions is the transfer of charge from carbon to a heteroatom, which can be N (8-24, 8-25), O (8-26, 8-27), or S (8-28). (8-26) is a β,γ-unsaturated ketone preparation, and (8-27) provides a means of getting only *ortho* substitution in the acylation of an alkylbenzene.



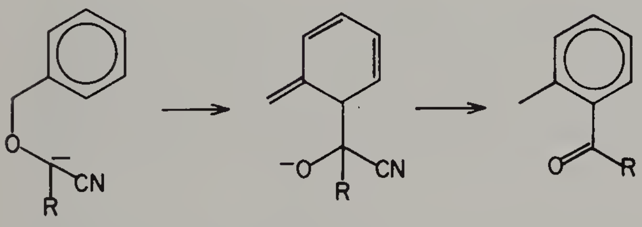
(8-24) [698]



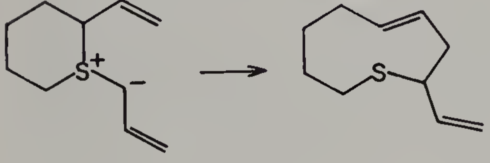
(8-25) [699]



(8-26) [700]

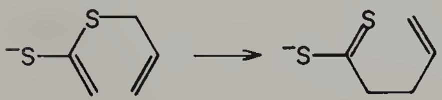


(8-27) [701]



(8-28) [703]

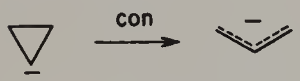
A [3,3]sigmatropic rearrangement (8-29) in which a thioenolate anion rearranges has been observed [704]; the driving force is presumably the transferring of partial negative charge from carbon to the much more electronegative sulfur.



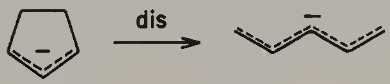
(8-29)

5. Electrocyclic Carbanion Rearrangements

In the all-carbon unsubstituted systems, the thermal equilibria in the cyclopropyl ⇆ allyl (8-30), cyclopentenyl ⇆ pentadienyl (8-31), and cycloheptadienyl ⇆ heptatrienyl (8-32) anion rearrangements probably lie in the directions shown; this has only been actually demonstrated in the last case, where the energy barrier is especially low and the reaction proceeds rapidly just above —30 °C [314, 705, 706]. The last two examples require the open system to be coiled rather than extended as shown, but the rotation barriers about the inner carbon-carbon bonds in pentadienyl [79] and heptatrienyl [314] anions are known to be low enough that this is no problem. In the first two cases, the open anions have not been observed to close; cyclopropyl anion can be prepared and reacted without opening [55, 56], whereas cyclopentenyl anion has resisted preparation.



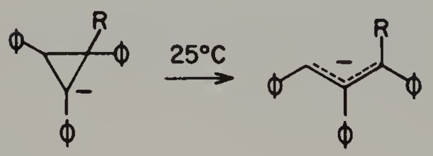
(8-30)



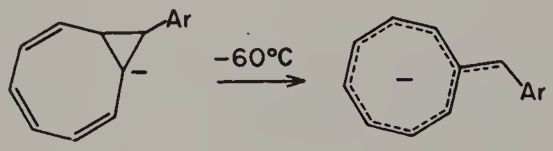
(8-31)

(8-32)

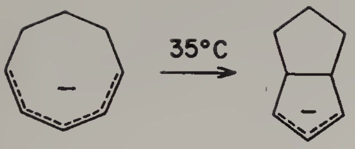
These reactions have all been observed in systems containing substituents (8-33 to 8-35) and heteroatoms (8-36 to 8-39) which can change the position of equilibrium [707]. The cyclopropyl anions in (8-33) and (8-34) were not observed at 25 °C but opened rapidly to the allyl anions. Putting a pentadienyl system in an 8-membered ring as in (8-35) strains it considerably (none of the shapes with the π system planar is unstrained) with the result that it closes to the cyclopentenyl system at 35 °C with a half life of 90 minutes. The positions of the electrocyclic equilibria in (8-36) and (8-37) are not known since under the reaction conditions the closed anions go on to the further products depicted. Reactions (8-38) and (8-39) are useful for preparing the dienolate and trienolate anions with the shapes shown; the charges are largely on oxygen in the products, driving the equilibria in the direction shown and causing high rotation barriers about the C2–C3 bonds which prevent equilibration with the fully extended shapes.



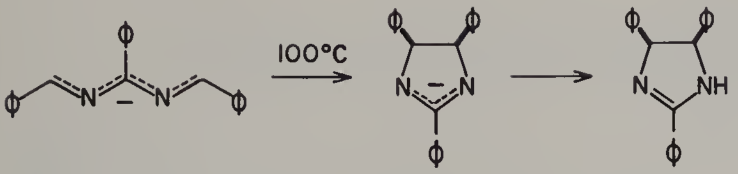
(8-33) [708]



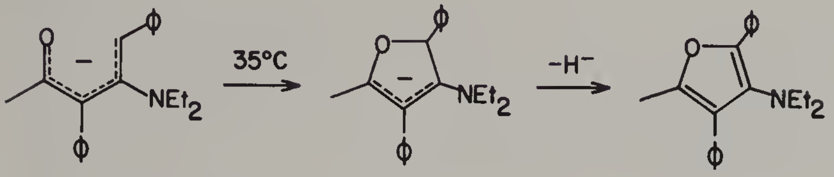
(8-34) [709]



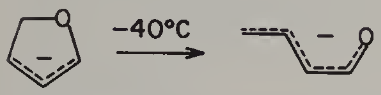
(8-35) [710]



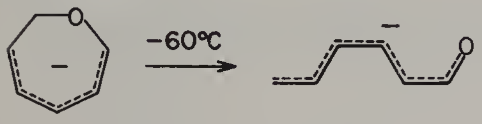
(8-36) [711]



(8-37) [712]

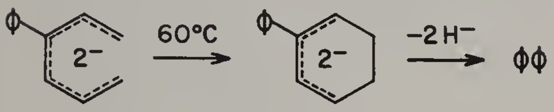


(8-38) [713, 293]



(8-39) [714]

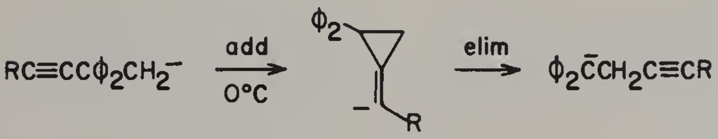
A dianion electrocyclization is apparently involved in (8-40).



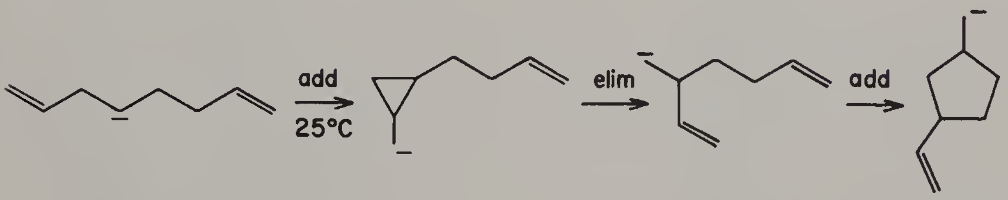
(8-40) [715]

6. Complex Intramolecular Rearrangements

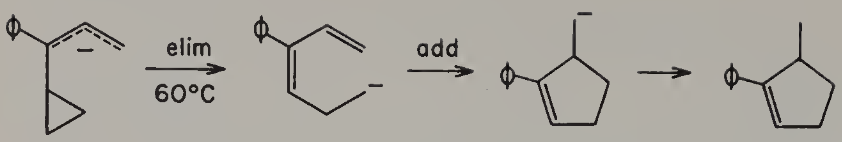
Some sequences combining additions and eliminations are shown in (8-41) to (8-45).



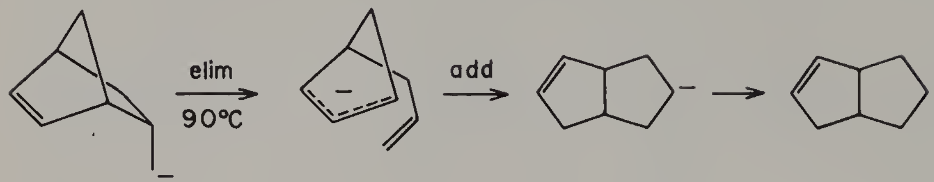
(8-41) [716]



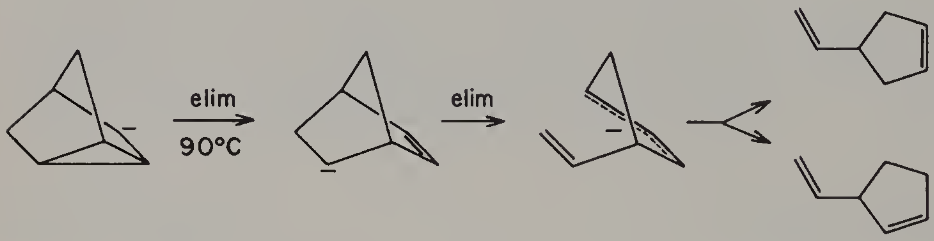
(8-42) [717]



(8-43) [715]

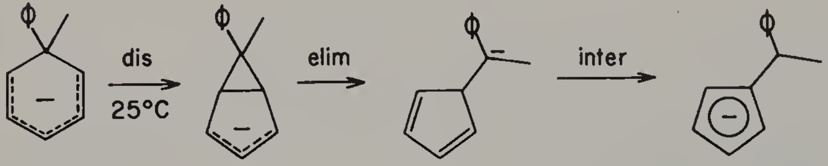


(8-44) [718]

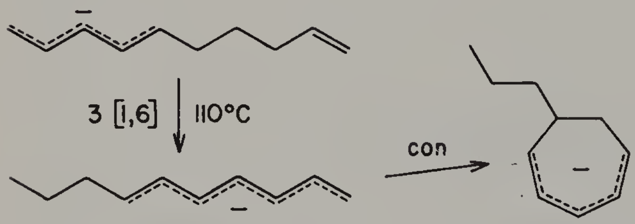


(8-45) [719]

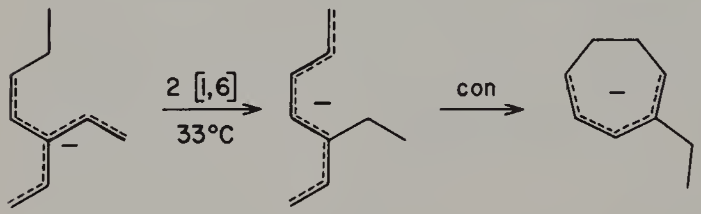
Combinations including electrocyclic and/or sigmatropic rearrangements as well as other types are shown in (8-46) to (8-48).



(8-46) [720]



(8-47) [696]

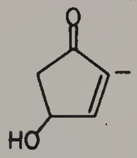
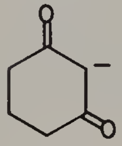
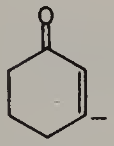
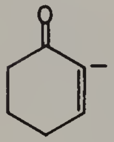


(8-48) [721]

IX. Carbanion Equivalents

When a carbanion is inherently unstable or reacts in the wrong way, it may well prove possible to use a several step route involving a “carbanion equivalent” to accomplish the desired synthetic goal. Acyl anions, for example, lose CO at 25 °C, but hundreds of acyl anion equivalents have been devised which serve the same purpose. The carbanion equivalents with reference numbers below 722 are mentioned in the text and can be located in the text from the reference number.

C_1	$NH_2CH_2^-$	178, 571, 722
	$RNHCH_2^-$	585–589
	$\Phi_3\overset{+}{P}CH_2^-$	191, 216, 443–449, 723, 724
	$ROCH_2^-$	192
	XCH_2^-	725, 726
	$H(C{=}O)^-$	193, 194, 206, 727–732
	$HO(C{=}O)^-$	207, 728, 733
C_2	RCH_2^-	351, 734
	$HOCH_2CH_2^-$	613
	$H(C{=}O)CH_2^-$	141, 454, 542, 727, 735
	$NCCH_2^-$	543
	$HO(C{=}O)CH_2^-$	552–557, 565, 566
	$HO(C{=}O)\bar{C}HNH_2$	736
	$HO\bar{C}HR$	182
	$R(C{=}O)^-$	183, 199, 202, 210, 343, 352, 455, 571, 592, 727, 728, 737–749
C_3	$HOCH_2CH_2CH_2^-$	750
	$H(C{=}O)CH_2CH_2^-$	751—753
	$HO(C{=}O)CH_2CH_2^-$	754, 755
	$RNHCH_2CH_2^-$	613
	$CH_2{=}CHCH_2^-$	756, 757
	$R(C{=}O)CH_2^-$	418, 542, 576, 758
	$CH_2{=}CH\bar{C}HOH$	759, 760
	$RCH{=}CH^-$	761, 762
	$HOCH_2CH{=}CH^-$	763
	$H(C{=}O)CH{=}CH^-$	764, 765
	$CH_2{=}\bar{C}COOH$	354, 766–770

C_4	$R(C{=}O)CH_2CH_2^-$	771
	$R(C{=}O)CH{=}CH^-$	771, 772
	$CH_2{=}CH\bar{C}{=}CH_2$	773
	$R(C{=}O)\bar{C}{=}CH_2$	774
	$H(C{=}O)CH_2CH_2(C{=}O)^-$	775
C_5	$CH_2{=}CH(C{=}O)CH_2CH_2^-$	550
	$HOCH_2RC{=}CHCH_2^-$	757
	$^-CH_2(C{=}O)CH{=}CHCH_2^-$	776
	$CH_2{=}C(CH_2^-)CH{=}CH_2$	773
	$H(C{=}O)CH_2CH_2(C{=}O)CH_2^-$	777
	$H(C{=}O)CH_2CH_2CH{=}CH^-$	778
		779
	$H(C{=}O)CH_2CH_2CH_2(C{=}O)^-$	775
	$R(C{=}O)CH_2CH_2(C{=}O)^-$	780
C_6	$HO(C{=}O)CH_2CH_2CH_2CH_2CH_2^-$	781, 782
	$HO(C{=}O)CH_2CH_2CH_2(C{=}O)CH_2^-$	781, 782
		783
		784
		540, 568, 569, 785

X. Summary

Carbanions owe their importance as intermediates in synthesis to the great variety of bond-forming reactions which they undergo which lead to bonds from carbon to every element except the noble gases. Unlike many carbonium ions, most carbanions do not undergo rearrangements but in many cases react in substitution and addition reactions in high yield. Changing the cation and solvent can greatly affect the reaction, even without employing transition metals which add a further dimension to their reactivity.

Much further work on the structures of carbanion salts and on the mechanisms of their reactions is necessary before their utility in synthesis can be fully exploited.

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