LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1975

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CONTENTS

1. REVIEWS AND BOOKS

A book of interest to organolithium chemists dealing with physical-organic aspects of carbanions discusses kinetic and thermodynamic acidities of active-

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see J. Organometal. Chem., 98(1975) 1-115.

hydrogen compounds, stereochemistry, various tautomeric systems, classical and non-classical carbanions, rearrangements, and reactions with organometallic compounds [1]. Another book describes the chemistry of sulfur ylides including their synthesis, structures, and reactions; various experimental procedures are included [2]. Two other books discuss the chemistry of organoboranes including lithium boronate complexes [3, 4].

Reviews devoted either wholly or in part to organolithium chemistry included the following:

-The hard soft acid base theory applied to organic chemistry [5].

-A survey of equilibrium acidities of carbon-hydrogen bonds [6].

-Electron transfer processes and stereochemistry [7].

-Stereochemistry of addition reactions of organolithiums and other organometallics to ketones [8].

-Substitution reactions at saturated carbon via radical intermediates [9].

-Reactivities in SN_2 processes as a function of dissociated and associated alkali nucleophiles [10].

-Dipole inversion of amines via metalated nitrosamines [11].

-Chemistry of cyclooctatetraene [12].

-Dimetalation and reactions of carboxylic acids and related compounds [13].

-Some preparations and reactions of functionally substituted cyclopropanes [14].

-Heterocycles possessing eight π-electrons [15].

-Preparations of α-methylene lactones [16, 17].

-A survey of the ylides of nitrogen, phosphorus, and sulphur [18].

-Condensations of bis-Wittig reagents with dicarbonyls to afford ring compounds [19].

-Ylides in inorganic chemistry [20].

-Perfluorooganometallic reagents [21].

-Trends in organosulfur chemistry [22].

-Silicon, phosphorus, and sulfur in organic synthesis [23, 24].

-Mechanistic study of the Bamford-Stevens reaction [25].

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-Substitution reactions of lithium cuprates and other organocopper reagents [27].

-Preparation and synthetic applications of α-haloenolates [28].

-Methanetetraboronic and triboronic esters [29].

-Transistion metal carbyne complexes [30].

-Steric control in transition metal coordination [31].

-Displacement of alkali metals by mercury and the dissociation of ion pairs [32].

-Skeletal transformations of organopolysilanes [33].

-Preparations and reactions of acetylenic arsenic compounds [34].

-Various aspects of carboranes [35, 36].

2. STRUCTURE AND BONDING

Molecular structures of several organolithium reagents were described in 1975. Thus, the lithium atom of indenyllithium tetramethylethylenediamine (TMEDA) was found to reside over but not at the center of the five-member ring of the indenyl group (Fig. 1) [37]. The lithium was said to be over a node in the highest occupied molecular orbital of the carbanion and is coordinated to bidentate diamine molecule. The proton nmr spectra of this compound were determined in various solvents and the degree of solvent-separated ion pairing was established. The current results are related to earlier ones concerned with similar organolithium amine complexes.

The molecular structure of bis[(tetramethylethylenediamine) lithium(I)]-anthracenide, shown in Fig. 2, consists of an anthracene molecule coordinated to two lithium atoms each of which is coordinated in a bidentate manner to an

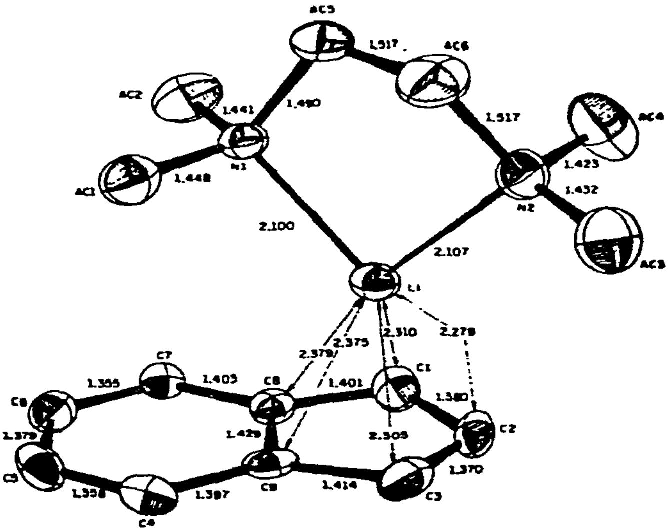


Figure 1.

amine group [38]. The two lithium atoms are located over the central six-membered ring and on the opposite side of the molecule over one of the outer rings, respectively. Though a substantial nonplanar geometry is observed in the anthracene portions of the molecule, such distortion from planarity is less than that seen in a related naphthalene compound.

Next, the molecular structure of $\Delta^{9,9'}$-bifluorenyl bis(lithiumtetramethylethylenediamine) (Fig. 3) was found to consist of a bifluorene molecule bonded to two lithium atoms each of which is also coordinated to an amine molecule [39]. Each lithium atom was determined to lie on a bisector of the C_9-C_9' bond; the fluorenyl ring deviates slightly from planarity. As above, each lithium atom is in a position corresponding to a nodal surface of the HOMO of the dianion.

Finally, dilithiohexatriene has been found to prefer the same Z,Z-shape in the crystalline form as in solution [40]. The structure of the species ion-paired with lithium·TMEDA is shown in Fig. 4. The authors speculate on the reasons for the stability of the conformation observed.

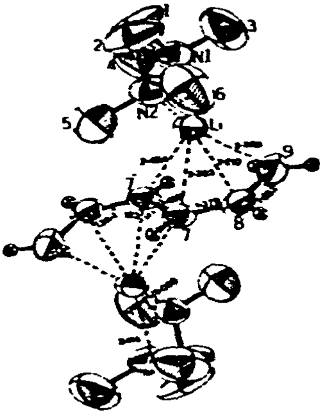
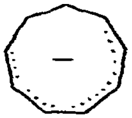
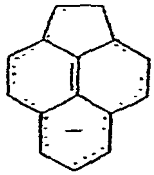


Figure 4.

Nuclear magnetic resonance has been employed in certain cases to garner structural information about several organolithium reagents. Thus, the pmr spectra of dilithiohomocyclooctatetraene(I) suggests that the C_1-C_8 bonds are not coplanar; instead, some twist is present about each of the C-C bonds in the ring [41]. The spectra rule out both a norcaradiene-like structure and an angle-strainless conformation. The proton-decoupled ^{13}C nmr spectra suggest the presence of a molecule with a symmetry plane perpendicular to the ring. The proton chemical shifts are compared with those of the corresponding potassium compounds.



I



II

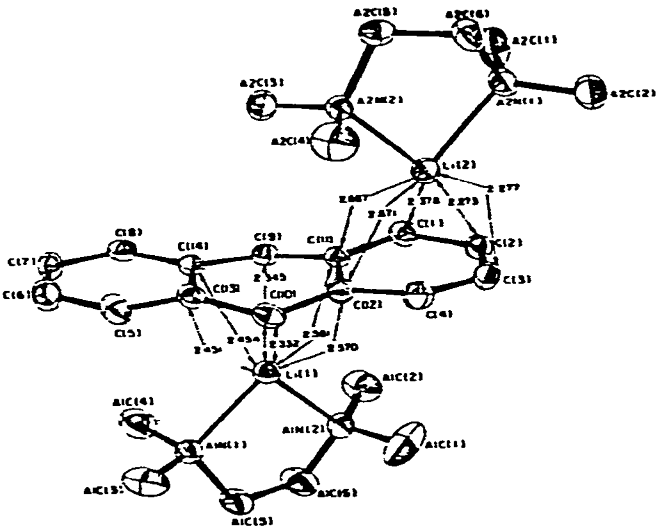


Figure 2.

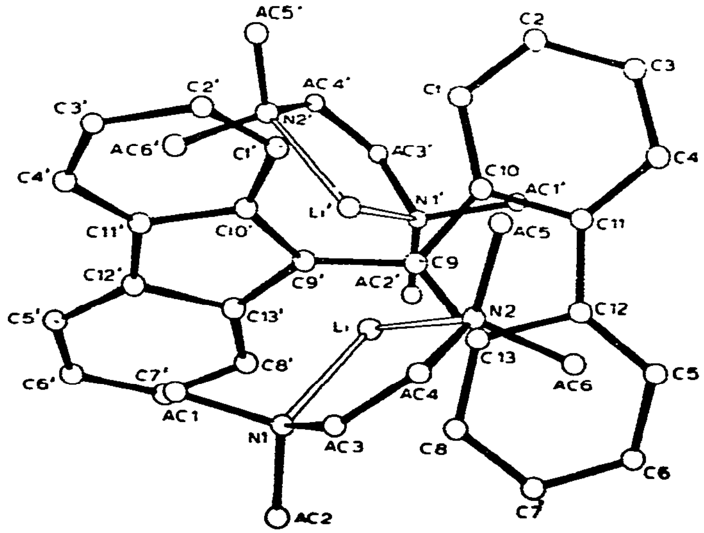
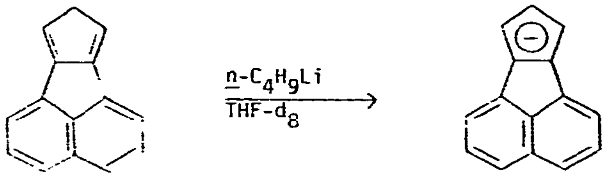


Figure 3.

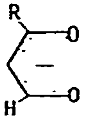
The pmr spectrum of lithiocyclopenta[cd]phenalene(II) exhibits symmetrical spin-systems and a narrow chemical shift range; the data are taken as evidence that II has a delocalized structure with C_{2v}-symmetry [42]. A variable-β SCF-MO calculation on the anion shows that an appreciable charge is also found on the phenalenyl skeleton.

Metalation of the new acidic hydrocarbon, 8H-cyclopent[a]acenaphthylene(III) by n-butyllithium has afforded anion IV, the pmr of which suggests the negative charge resides on both the cyclopentadienide and naphthalene moieties [43]. The predicted π-electron densities and π-bond orders are shown in the paper.

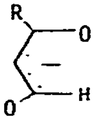


III IV

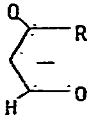
Pmr has been employed to study the conformational stability of enolate anions of several β-ketoaldehydes as a function of the cation, the solvent, and β-alkyl substituents [44]. Of the four possible conformations shown below, lithium enolates were present only as U in aprotic solvents but as U, S-trans, and W in protic solvents. In contrast, sodium enolates were present as U, S-trans, and W in aprotic solvents but only as S-trans and W in protic ones. Finally, in the case of potassium enolates, the U-form was absent in both aprotic and protic solvents. The association parameters of the configuration transitions were determined and the mechanisms of the above are discussed.



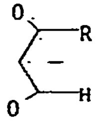
U



S-trans

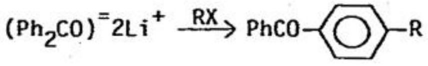


S-cis



W

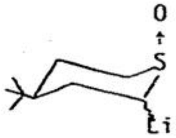
Electron density distributions in various dilithiobenzophenones have been calculated from their pmr spectra in order to justify formation of *p*-substituted products like V in certain alkylation reactions [45].



V

The pmr spectra of α-lithiosulfoxides VI and VII have been obtained in an effort to provide direct experimental evidence concerning their structure [46]. Though some of the data are difficult to explain using the hypothesis of pyramidal carbanions, the authors indicate that such structures can not be completely excluded at this time.

VI

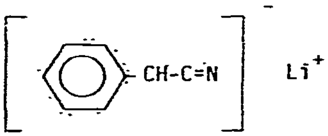


VII

A third paper in a series describing the pmr spectra of picolyl-type carbanions has appeared [47]. Specifically, the current work is concerned with the 2-lithio salts of 2-methyl-, 2,4-dimethyl-, and 2,6-dimethylquinoline where the methylene proton signals appear as doublets at 25° thus indicating magnetic nonequivalence. These results are explained by the carbanions having near sp^2-configurations at the α-carbons.

Also described have been the pmr spectra of several 1-allylcarbazoles in which the side-chains are shown to possess the Z-configuration [48], and of lithium 9-(2-methoxy-1-naphthyl)fluorenide which demonstrate that this anion has a near planar structure [49]. Finally the ^{7}Li nmr spectra of lithium tetramethylboron and related aluminum, gallium, and thallium compounds exhibit chemical shifts that are a function of lithium solvation and ion pairing [50].

Turning to other kinds of spectroscopy, nitrile infrared bands of various lithiated acetonitriles found in the region 2050-2071 cm^{-1} have been assigned to structures like VIII and IX [51]. The latter structure is apparently present both in solution and in the solid state. A plot of ν(CN) versus SCF $P^{\pi'}_{CN}$ is shown.

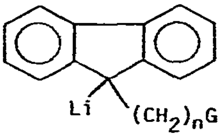


VIII

$[CH_2\text{-}C{=}N]^- Li^+$

IX

The electronic spectra of lithium 9-substituted fluorenyl salts like X in which the substituents contain methoxy and dimethylamino groups have been described [52]. The spectra showed that the relative amounts of contact ion pairs varied as a function of the heteroatom and the length of the 9-side chain and was ascribed to association between such heteroatom and the counter ions.



X $(G{=}OCH_3 \text{ or } N(CH_3)_2)$

Ion cyclotron resonance (ICR) techniques have been employed to study alkali ion complexes with π- and n-donor bases [53, 54]. Using a thermionic source in an ICR cell, association of an alkali ion and various organic halides affords chemically activated species which eliminate HX to give an alkene or ketene with the alkali ion remaining bound to either HX or the organic material. For example, XI and XII have been observed in the interaction of lithium cation with acetyl bromide and i-propyl chloride, respectively [53]. The binding energies of the lithium cation to a large number of organic molecules have been determined [54].

$[CH_3CH{=}C{=}O]Li^+$

XI

$HClLi^+$

XII

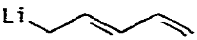
Pulse radiolysis continues to be used in connection with organolithiums. Thus, the benzyl carbanion was formed by electron irradiation of dibenzylmercury in the presence of lithium perchlorate and tetrabutylammonium perchlorate, respectively and the absolute rate constants for the subsequent reactions with methyl and t-butyl alcohols were determined [55]. In connection with earlier data, the ion paired species were found to be more reactive towards protonation than the free carbanion. The authors discuss the effect of ion pairing upon the absorption spectrum of the benzyl carbanion associated with lithium, sodium, and tetrabutylammonium cations.

Also, solutions of alkali methylamides in methylamine have been subjected to pulse radiolysis to give three distinct species: e_S^-, (M^+, e_S^-), and M^- [56]. Comparisons are made between the spectra, extinction coefficients, and yields with those observed previously.

Two papers described certain physical properties of solvated electrons prepared from dissolution of alkali metals in HMPA [57, 58]. (See the warning about HMPA on page 29 of this survey.) Discussed are conductivities, esr spectra density measurements, electrical properties of frozen solutions, and electron emission from the surfaces of the solutions.

Turning attention to quantum mechanical aspects, the results of ab initio SCF-LCAO-MO calculations on methyl, ethyl, vinyl, and ethynyl anions have been reported [59]. Special attention was directed towards discussion of ionization potentials and proton affinities, the electronic structure and molecular geometry of carbanions, electron density functions of ethylene and acetylene, and the vinyl anion. Several three-dimensional perspective plots are shown.

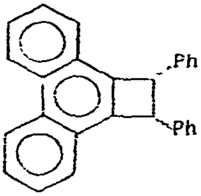
Ab initio SCF calculations have also been performed on pentadienyllithium XIII [60]. Computations with STO/3G atomic orbitals suggest, in agreement with pmr and ^{13}C nmr spectroscopy, that XIII is most stable in the W-form as shown below. The authors also conclude that a non-planar structure is favored in the covalent form of this lithium salt.



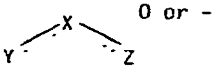
XIII

Two papers have been concerned with the thiomethyl anion, $\overline{C}H_2SH$ [61, 62]. Basis sets both with and without d-orbitals were used and the data were compared to the deprotonation of ethane in one case [61] and to the oxomethyl anion, $\overline{C}H_2OH$, in the other [62]. Both papers conclude that the α-carbanion-stabilizing ability of sulfur occurs by polarization rather than by d-orbital participation.

In connection with the stereochemistry of retroelectrocyclic reactions, the cleavages of cis- and trans-XIV by biphenyl anion radicals were studied [63]. The trans-isomer was found to undergo reaction at a faster rate in an order that may be considered diagnostic for conrotation. This mode is clearly predicted by INDO/MO calculations. In contrast, the HOMO method predicts disrotation while the OCD method allows neither dis- nor conrotatory cleavage.



XIV



XV

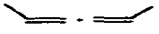
Another paper discusses the results of CNDO computations concerned with ring closures of nine different examples of the heteroacylic unit XV [64]. Three types of ring closures were revealed:

a. Thermal conrotation allowed, disrotation forbidden; e.g., X=NH, Y=CH_2, Z=CH_2.

b. All variations allowed; e.g., X=NH, Y=CH_2, Z=NH.

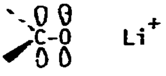
c. Thermal ring closures forbidden, photochemical closures allowed; e.g., X=CH, Y=NH, Z=O.

The authors recommend that the simplest current procedure for such systems be the construction of an orbital correlation diagram with the aid of the extended Hückel or CNDO/INDO approximations.

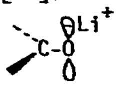
A quantum chemical study of the protonation of the anion radical of  covering both the site and the stereochemistry of the reaction has been described [65]. Provided higher order perturbation terms (induction energy) are included in the calculations, they predict, in agreement with experimental evidence, that the central carbon atom is protonated to afford a planar allyl radical.

INDO calculations on the monohomocyclooctatetraene anion radical have led to the conclusion that the eight-membered ring of this molecule is planar, the best angle between this ring and the plane of the fused cyclopropyl ring is 83.5°, and that there is a high π-bond order accompanied by a 10-20% reduction in σ-bond order between the two base carbon atoms of the latter ring [66]. Based on these results, the latter bond can not be considered to be opened in this species.

SCF-MO calculations have been performed on the lithium-formaldehyde ion pair [67] and the acetaldehyde enolate anion [68]. In the first case, structure XVI is predicted to be more stable than XVII though XVII also corresponds to an energy minimum [67]. In the second case, an all-planar structure compatible with XVIII has been found to be the minimum point on the rotation-inversion surface; this structure is ascribed to the effect of the conjugative stabilization present in this conformation [68].



XVI



XVII

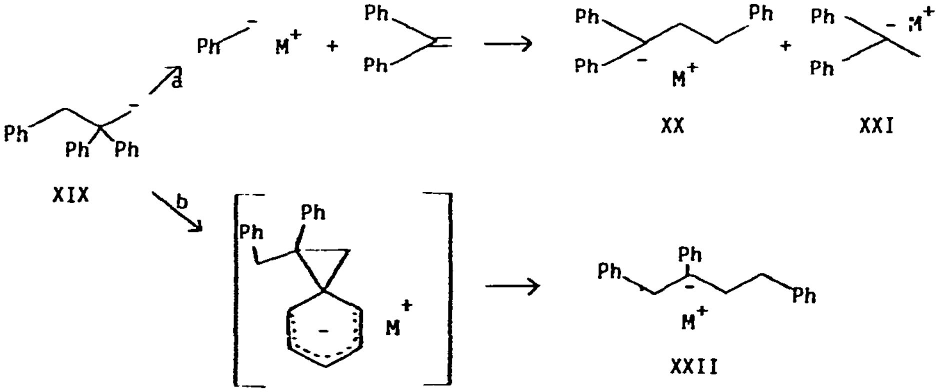
$\overline{C}H_2\text{-}CHO \leftrightarrow CH_2\text{=}CH\overline{O}$

XVIII

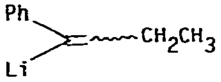
Two papers discussed the stereochemical courses of certain nucleophilic and electrophilic reactions in terms of the orbital distortion technique [69, 70]. The first one discusses five postulates and rules of the technique and applies them to the axial attack observed in addition of cyanide to cyclohexenone, axial protonation in metal-ammonia reductions of enones, axial halogenation of cyclohexanone enols, and others [69]. The second paper discusses the *cis*-stereochemistry of allylic nucleophilic displacement processes [70].

Finally, ab initio SCF-MO calculations have been performed on the structure and stability of the silylmethyl anion [71]. It was determined that although the SiH_3 group hardly affects the geometry of the carbanion, this group stabilizes the anion by 50 kcal/mole more than does a methyl group but 75 kcal/mole less than does a nitro group.

Ion pairing phenomena continue to be studied. Thus, the rearrangement of XIX to XX and XXI or to XXII has been further investigated in terms of metallic cation effects, solvent, temperature, and the presence or absence of 18-crown-6 [72]. Path a arising from migration of a benzyl group is observed under conditions favoring loose or separated ion pairs while path b arising from migration of a phenyl group is observed under conditions favoring tight or contact-ion pairs.

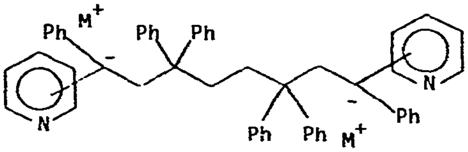


E- and Z-1-Lithio-1-phenyl-1-butenes (XXIII) have been prepared with retention of configuration by reaction of Z- and E-1-bromo-1-phenyl-1-butenes with *n*-butyllithium in THF at -78°, respectively [73]. The compounds are configurationally stable at 25-35° in hexane in the presence of less but not more than one equivalent of THF. The rate of isomerization of Z-XXIII, studied as a function of various donor solvents at 22°, has been found to be in the order TMEDA>DME>THF>ethyl ether and is thus explained in terms of ion pair intermediates. The pmr spectra of Z- and E-XXIII support these conclusions.



XXIII

The extent of ion pairing in 2-,3-, and 4-pyridyl derivatives XXIV has been studied by UV-visible spectroscopy and by conductance measurements [74]. The results indicate that such ion pairs of the lithium, sodium, and cesium salts of the 2- and 4-isomers in various ethereal solvents are tighter than the corresponding ones from the 3-isomer or related phenylated compounds. Moreover, it is demonstrated that the 4-pyridyl isomer exists in a tighter ion pair than the corresponding 2-isomer. The results are interpreted in terms of strong coulombic attractions between the nitrogen atom in the 2- and 4-isomers and the cation.

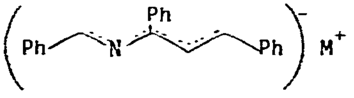


XXIV

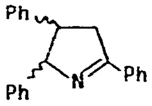
Ion pairing from alkali metal reductions of naphthalene in methyl-, ethyl-, and n-butylamine has been studied as a function of the metal and solvent [75]. For example, the lithium naphthalene anion radical in butylamine is a separated ion pair while the corresponding sodium salt is a contact ion pair. The most reactive species in this study were solvent separated ions while the free ions were the most stable.

Three papers were concerned with anionic polymerization of dienes [76, 77, 78]. The studies were concerned with stereospecificity, ion pairing, and the propagation mechanism as a function of the solvent, alkali cation, and temperature. In general, the stereospecificity decreased as the size of the alkali counter ion increased and the growing ion pairs separated or dissociated.

The anion of 1,3,5-triphenyl-4-aza-1,3-pentadiene (XXV) has been studied in terms of its stereochemistry and its ability to undergo electrocyclization to afford 2,4,5-triphenyl-1-pyrrolines (XXVI) [79]. Thus, quenching of XXV at -78° or -15° with acetic acid gave four geometrical isomers of the parent diene and led the authors to conclude that the anion exists in both W and sickle forms. Such anions electrocyclize at 0° in a nonstereospecific manner to give a 1:1 mixture of <u>cis</u>- and <u>trans</u>-XXVI.

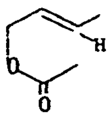


XXV

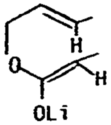


XXVI

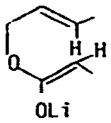
In connection with a study of the Claisen rearrangement of allyl ester enolates, it has been found that certain enolates can be generated stereoselectively as a function of solvent [80]. For example, treatment of <u>cis</u>-XXVII with lithium diisopropylamide (LDIPA) at -78° in THF gives the Z-enolate XXVIII; in contrast, use of THF-HMPA (77/23) under the same conditions affords the corresponding E-enolate XXIX. Similar results were observed with <u>trans</u>-XXVII.



XXVII

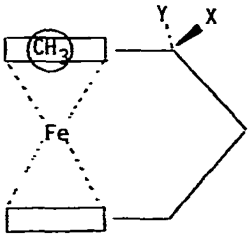


XXVIII



XXIX

Finally, treatment of XXX (X=CN, Y=H) with *n*-butyllithium in ether gave anion XXX (X=CN, Y=Li) which easily racemized to XXXI (X=CN, Y=Li) since methylation afforded a mixture of XXX (X=CN, Y=CH_3) and XXXI (X=CN, Y=CH_3 [81]. These results are contrasted with secondary and tertiary carbonium ions in similar molecules which are configurationally stable.



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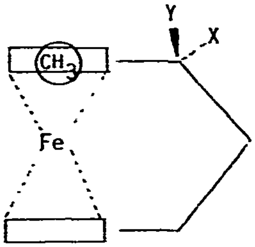
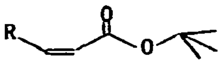


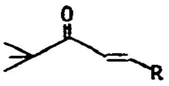
XXXI

3. KINETICS AND MECHANISM

Two potential tests to ascertain the presence of anion radicals in addition reactions of various nucleophiles to certain α,β-unsaturated carbonyl compounds have been reported [82, 83]. The first test, a successful one, involved the use of *cis*-enones XXXII (R=*t*-C_4H_9 and Ph) which are known to undergo rapid electron exchange with their corresponding anion radicals to afford the corresponding *trans*-enones. Thus, reaction of an excess of XXXII with lithium dimethylcuprate and other anion radical producing nucleophiles gave recovered isomerized enones (*trans*-XXXII). In contrast, use of methyllithium and related reagents afforded unisomerized recovered enones. The second test involved enones like XXXIII (R contains an olefin, phenyl, or cyclopropyl) and was devised to trap intermediate anion radicals by cyclization. Such cyclizations, though, either failed or were too slow to detect the presence of such intermediates.

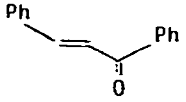


XXXII

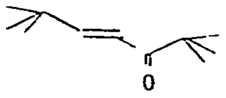


XXXIII

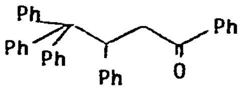
The preceeding papers [82, 83] as well as one dealing with the reaction of tritylithium with enones [84] discuss additions of nucleophiles to such unsaturated compounds in terms of the oxidation and reduction potentials of the carbanions and the enones, respectively. Thus, two-step anion radical processes rather than direct addition of nucleophiles can be anticipated only when E_{red}-E_{ox} is less negative than -0.4 volts. The prediction has been nicely demonstrated in the reactions of trityllithium with XXXIV (E_{red}-$E_{ox}$$\simeq$-0.1V) and XXXV ($E_{red}$-$E_{ox}$$\simeq$-0.9V) to give XXXVI and mostly XXXVII, respectively [84]. Incidentally, the latter reaction was much slower than the former one. Other examples are included.



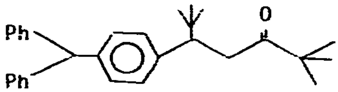
XXXIV



XXXV



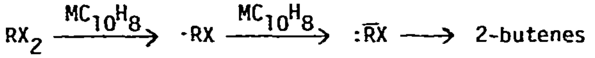
XXXVI



XXXVII

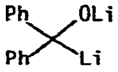
The kinetics of the cis,trans-isomerization of cis-stilbene, effected by alkali anthracenides, have been studied and a mechanism proposed for the transformation [85]. The authors conclude that the process proceeds via both the cis- and the trans-stilbene dianions and that hindrance to rotation of the cis- to the trans-dianion is a function of the cation where the tighter the association, the slower the rotation. In another study, the lithium salts of the tetraphenylethylene anion radical and dianion were studied by spectroscopy and by conductometric and flash-photolytic methods [86]. It was found that the lithium anion radical behaves similarly to that of the related sodium anion radical and forms loose ion pairs in THF. In contrast, the lithium salt of the dianion was found to be quite different from that of the corresponding disodio salt; for example, the former salt is more dissociated, has only a slightly exothermic ΔH and a small entropy loss, and exhibits a strong absorption band at 385 nm. The band is absent in the sodium salt and is ascribed to a charge transfer transistion.

Dehalogenation of meso- and dl-2,3-dihalobutanes by lithium and sodium naphthalene has been studied at various concentrations of the organometallic to determine the cis,trans-product distributions [87]. Since the systems exhibited CIDNP at magnetic fields of 60 G, the authors proposed the pathway for the reactions shown (Eq. 1). The results were compared to similar reactions effected by tributyltin and chromium (II) species.



$$RX_2 \xrightarrow{MC_{10}H_8} \cdot RX \xrightarrow{MC_{10}H_8} :\bar{R}X \longrightarrow \text{2-butenes} \qquad (1)$$

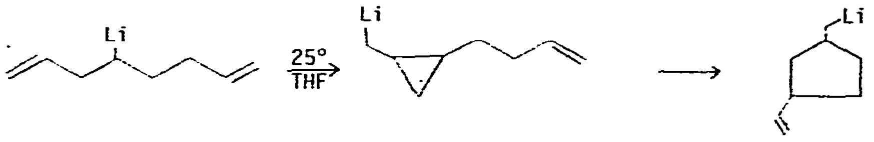
The mechanism of alkylation of the lithium ketyls of benzophenone and fluorenone has been studied by magnetochemical kinetic measurements as a function of concentration and the reactivity of the alkyl halide [88]. For example, magnetochemical zero-order kinetics are observed for reaction of these ketyls at concentrations of 1M with n-butyl bromide and benzyl chloride and are ascribed to 1,2-dianions like XXXVIII. In contrast, more reactive alkyl halides were found to follow first-order kinetics.



XXXVIII

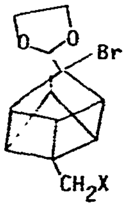
Finally, the thermodynamic parameters of the anionic polymerization of 3-methoxypropanal effected by the lithium ketyl of benzophenone in THF have been described and include ΔH_{SS} = -4.8 ± 0.2 kcal/mole, ΔS_{SS} = -22.4 ± 1.3 cal/mole-degree, and $(T_c)_{SS}$ = -59°C [89].

Next, a variety of papers have described additional investigations in the area of rearrangements of organolithium reagents. First, reagent XXXIX, though stable at -78° in THF, rearranges at 25° via XL to afford XLI (34%) [90] That XL is an intermediate was demonstrated by appropriate deuterium labeling.

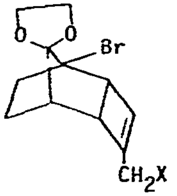


XXXIX XL XLI

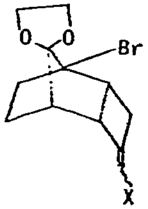
Base induced homoallylic rearrangements of highly strained homocubane and cubane systems having carbanionic centers adjacent to the bridgehead position have been studied [91]. Homocubanes XLII (X=CN or SO_2Ph) with LDIPA in THF thus afforded mixtures of XLIII and XLIV. Interestingly, when X=CO_2CH_3, the rearrangement failed though the α-carbanion had been formed as evidenced by trapping experiments with deuterium oxide and carbon dioxide. Related cubane derivatives including an ester underwent similar γ-homoallylic rearrangements the mechanism of which is discussed.



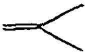
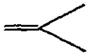
XLII

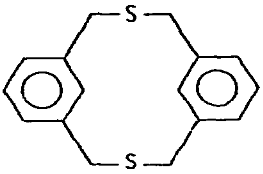


XLIII

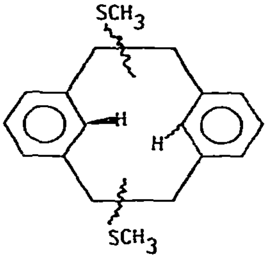


XLIV

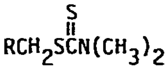
The Wittig rearrangement has been applied to several sulfur-containing systems. Thus, treatment of dithia[3,3]cyclophane XLV with either n-butyllithium or LDIPA in THF at 0° followed by methyl iodide afforded a mixture of *anti* : *syn* isomers of XLVI (94%); five other examples are shown [92]. Similarly, treatment of XLVII (R=Ph or ) with LDIPA at -60° in THF-HMPA followed by methyl iodide gave XLVIII (R=Ph or ) in nearly quantitative yield [93]. Solvent HMPA is necessary since the rearrangement is not observed in its absence.



XLV

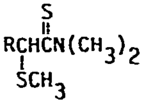


XLVI



$RCH_2S\overset{\overset{S}{\|}}{C}N(CH_3)_2$

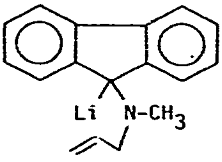
XLVII



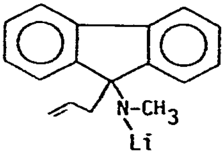
$R\underset{\underset{SCH_3}{|}}{C}H\overset{\overset{S}{\|}}{C}N(CH_3)_2$

XLVIII

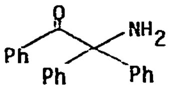
A dyotropic rearrangement of lithio derivative XLIX, prepared by metalation of the corresponding active-hydrogen compound, has been observed to give L provided the reaction mixture was refluxed in THF for seven hours [94]. The authors compare this rearrangement to one on a related ether. In a different study, action of alkali amides in liquid ammonia on amine LI surprisingly results in C-N migration of a benzoyl group to afford anion LII [95]. Presumably, the driving force in this reaction is the higher thermodynamic stability of the nitrogen anion of LII compared to that of LI.



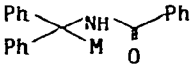
XLIX



L

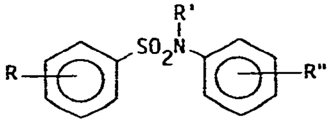


LI

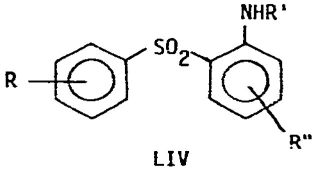


LII

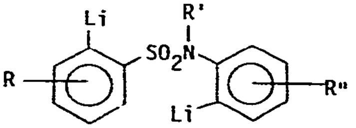
Two papers discussed examples and the mechanism of the rearrangement of sulfonamides to aminosulfones effected by organolithium reagents [96, 97]. Approximately one dozen examples are shown and are illustrated by the conversion of LIII to LIV. The rearrangements are preceeded by formation of dicarbanions like LV.



LIII

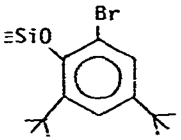


LIV

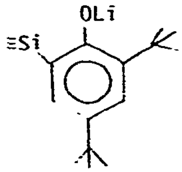


LV

Several o-bromophenoxysilanes have been found to undergo rearrangement by n-butyllithium to give o-hydroxyphenylsilanes as illustrated by the conversion of LVI to LVII [98]. The reaction including its mechanism is discussed in relation to previously described 1,2- and 1,3-migrations of organosilyl groups.



LVI



LVII

4-Chloro-1-p-biphenylylbutane has been reacted with lithium, potassium, cesium, and cesium-potassium-sodio alloy to afford LVIII [99]. When the metal was lithium, LVIII was reasonably stable since methanolysis gave LIX and LX in a ratio of about 3:1; the latter compound arises from spiro anion LXI. In contrast, use of the other metals gave mostly LXI and anion LXII. No evidence was found to indicate that LXI reverts back to LVIII.

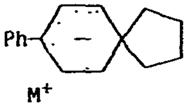
$p\text{-}PhC_6H_4(CH_2)_4M$

LVIII

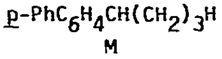
$p\text{-}PhC_6H_4(CH_2)_3CH_3$

LIX

LX



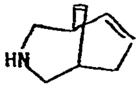
LXI



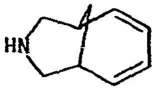
$p\text{-}PhC_6H_4\underset{M}{C}H(CH_2)_3H$

LXII

Treatment of amine LXIII with methyllithium at 30° in ether or n-pentane has been reported to give rearranged amine LXIV (90%) after only one min. [100]. In fact, above 30°, the sample exploded. The reaction represents a novel example of a suprafacial 1,3-sigmatropic rearrangement.



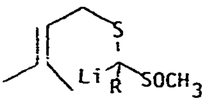
LXIII



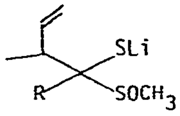
LXIV

Two papers described 2,3-sigmatropic rearrangements of LXV (R=CH_3 or H) [101, 102]. Though the salts were stable at -65°, they readily rearranged at

0° to 10° to afford LXVI (R=CH_3 or H) which were trapped by various electrophiles

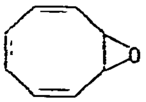


LXV

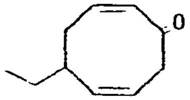


LXVI

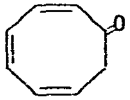
Finally, the isomerization of cyclooctatetraene oxide (LXVII) by organometallics and metal salts was studied as a function of the metallic cation and solvent [103]. For example, reaction of LXVII with ethyllithium in ether gave LXVIII (70%) and LXIX (6%). In petroleum ether and in the presence of HMPA, the yield of LXVIII dropped to 15% and 0%, respectively. The results are rationalized by the intermediacy of homotropylium cation intermediates.



LXVII



LXVIII



LXIX

Two papers in 1975 were concerned with the kinetics of anionic polymerization [104, 105]. The kinetics of the polymerization of styrene effected by ethyllithium in DME-benzene were thus studied and the rate constants for ion pairs, free ions, and triple ions (LXX) were determined [104]. The authors suggest that the latter ions are a solvent-separated intermolecular type which are more reactive than the free ions. The kinetics of the reaction of tetrameric oligobutadienyllithium (LXXI) with 1,3-butadiene suggest the reaction is induced by mono- and dimeric forms of the dissociation products of LXXI [105].

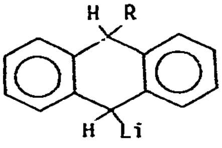
$\cdots\cdots S^-,Li^+,S^-\cdots$

LXX

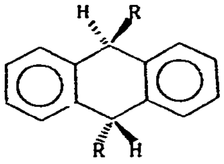
$[R\text{-}(C_4H_6)_m\text{-}Li]_4$

LXXI

The stereochemistry of the reactions of various lithiated anthracenes with electrophiles continues to be studied [106, 107, 108]. Thus, alkylation of 9-alkyl-10-lithio-9,10-dihydroanthracenes (LXXII) has been studied as a function of both the 9-alkyl group and the alkyl halide [106, 107]. The amount of trans-product (LXXIII) increases as the size of either the 9-alkyl group or the alkylating agent is increased. The reactions are said to be under kinetic control since, for example, cis-9-ethyl-10-isopropyl-9,10-dihydroanthracene is more stable than its trans-isomer. The carbanion is postulated to exist as an equilibrium mixture of ions and ion-pairs with the dihydro ring in a flattened boat conformation and the 9-alkyl group in a preferred axial orientation. In another study, a variety of stereoselective reactions have likewise been effected on lithium and sodium anthracenilide to afford cis-isomers [108].

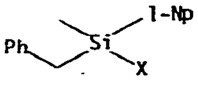


LXXII

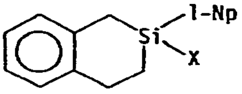


LXXIII

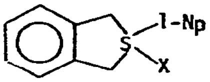
Kinetic studies have been reported for the coupling reactions of 1-naphthyl methoxy-, fluoro-, and chlorosilanes LXXIV, LXXV, and LXXVI with n-butyllithium and two Grignard reagents [109]. The rates observed were a function of ring strain since they increased in the order LXXIV<LXXV<LXXVI.



LXXIV

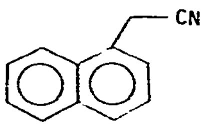


LXXV

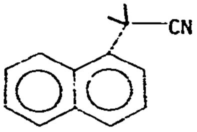


LXXVI

Metalation and methylation of certain nitriles has been found to give disubstituted nitriles, ketones, or N-methylketimines by using controlled amounts of methyllithium and methyl iodide [110]. In certain cases, a new displacement of cyanide ion from saturated carbon has been realized. Thus, treatment of LXXVII with four equivalents of methyllithium and two of methyl iodide presumably afforded LXXVIII which was converted to its anion radical by the former reagent; subsequent expulsion of cyanide ion would account for the observed product, 1-isopropylnaphthalene.

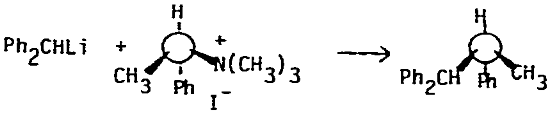


LXXVII



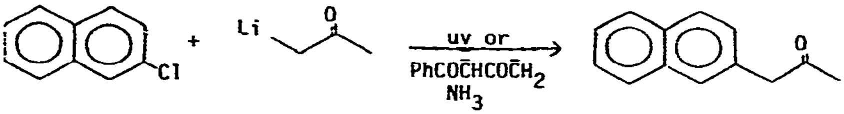
LXXVIII

Stereospecific coupling reactions of charge-delocalized organolithium reagents with chiral trimethylammonium quaternary salts have been reported to occur by a polar process; chemical evidence for an electron transfer mode was not found [111]. An example is shown (Eq. 2).



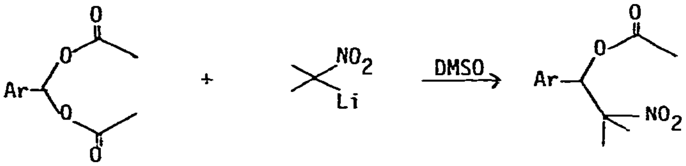
(2)

Two papers were concerned with the $S_{RN}1$ mechanism in nucleophilic substitution reactions [112, 113]. First, it has been determined that reaction of 2-chloroquinoline with lithioacetone is subject to photostimulation with near uv irradiation and to entrainment by 10 mole % of dilithiobenzoylacetone (Eq. 3); the reaction thus proceeds via the $S_{RN}1$ pathway [112]. In contrast,



(3)

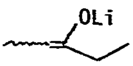
reaction of lithium 2-nitropropane with a variety of benzylidene acetates (Eq. 4), originally thought to proceed by this same mechanism, has instead been found to occur by an ionic chain mechanism since it is not catalyzed by light, inhibited by oxygen or *p*-dinitrobenzene, and does not require the presence of a nitro group in the benzylidene acetate [113]. Experiments are described which confirm the non-radical chain process.



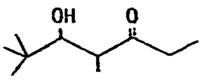
(4)

Concerning addition reactions, *t*-butyl- and *i*-propyllithium have been found to add regiospecifically to 1-octene to give 1-lithio derivatives [114]. These results are contrasted with those obtained with various organoaluminum and magnesium compounds which afford substantial or exclusive 2-metallo derivatives. Another paper has compared reactions of several ketones, benzaldehyde, and ethyl benzoate with *i*-butyllithium and *i*-butylmagnesium bromide [115]. While the former reagent gives addition products almost exclusively, the latter one gives large amounts of reduction products.

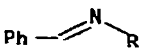
The stereochemistry of the reactions of *cis*- and *trans*-LXXIX with pivalaldehyde to afford differing amounts of *erythro*- and *threo*-LXXX have been studied as a function of the geometry of the enolate [116]. The results are ascribed to the approach of the aldehyde from the side of the double bond with the least electronic repulsion. Also, in a different reaction, crotyllithium has been found to add to imines like LXXXI (R=Ph and alkyl) to predominately afford *threo*-amines regardless of the size of the R group [117]. The results



LXXIX



LXXX

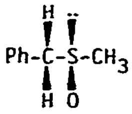


LXXXI

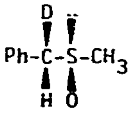
are contrasted to those realized with crotylmagnesium, zinc, and aluminum reagents where the amount of threo-isomer increases with the size of the R group

In other areas of interest, lithium vapor has been reacted with certain partially chlorinated or brominated propanes at 800-1000° followed by deuterolysis with D_2O [118]. The results indicate the presence of perlithiated ethane, ethylene, propane, propylene, methylacetylene, and allene before the D_2O quench. Though the highest yields of C_3Li_8 were obtained from monohalopropanes, extension of the reaction to monohalobutanes gave no perlithiobutanes; instead, D_2O quenching gave only monodeuterobutanes and fragmentation products were observed.

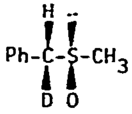
Abstraction of the diastereotropic hydrogens of benzyl methyl sulfoxide (LXXXII) by methyllithium has been reinvestigated in terms of the source of the metalating agent and the presence or absence of inorganic lithium salts [119]. For example, metalation of LXXXII by commercial samples of this base prepared by two different companies from methyl chloride and methyl bromide followed by addition of D_2O gave LXXXIII and LXXXIV in ratios of 15:1 and 3.1:1, respectively. The above ratios were also found to change when the reactions were run in the presence of various amounts of soluble lithium salts. Similar results were realized with benzyl ethyl sulfoxide.


$\mathrm{Ph{-}\overset{H}{\underset{H}{C}}{-}\overset{\cdot\cdot}{\underset{O}{S}}{-}CH_3}$

LXXXII

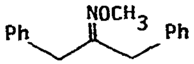

$\mathrm{Ph{-}\overset{D}{\underset{H}{C}}{-}\overset{\cdot\cdot}{\underset{O}{S}}{-}CH_3}$

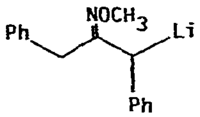
LXXXIII

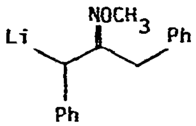

$\mathrm{Ph{-}\overset{H}{\underset{D}{C}}{-}\overset{\cdot\cdot}{\underset{O}{S}}{-}CH_3}$

LXXXIV

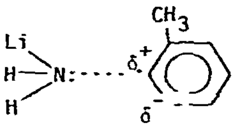
Regioselective metalation has been demonstrated in reactions of LXXXV with LDIPA at -60° to afford LXXXVI [120]. The authors ascribe such selectivity to the presence of a six π-electron system with a configuration which permits nonbonded interaction between the α-carbon and oxygen; such a system is not possible in the isomeric LXXXVII.

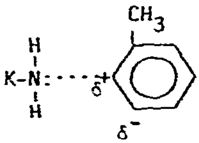

LXXXV


LXXXVI

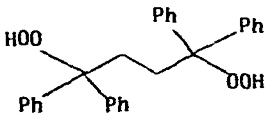

LXXXVII

The decreasing ratios of *o*- to *m*-toluidine in the reactions of *o*-chlorotoluene with alkali metal amides in ammonia as the metal is changed from lithium to sodium to potassium have been ascribed to the abilities of the metal to control the geometry of the transistion states, e.g., LXXXVIII and LXXXIX, and to the relative selectivities of the alkali amides [121]. It is suggested that with lithium and potassium, the amido nitrogen atoms are closer to sp^3 and sp, respectively. In the latter case, increased steric hindrance decreases the amount of *o*-product.


LXXXVIII


LXXXIX

Finally, the interaction of molecular oxygen with the dialkali derivatives of the dimer of 1,1-diphenylethylene has been studied to determine the peroxidation mechanism of anionic polymers [122]. Compound XC was found to be the major product from reactions which were little affected by the choice of alkali cation.

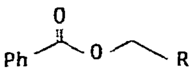

XC

4. METALATIONS (LITHIUM-HYDROGEN EXCHANGE REACTIONS)

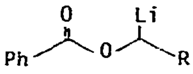
A. AT sp^3 CARBON

Warnings to users of HMPA have been published describing its toxic effects on laboratory animals [123, 124, 125]. For example, daily inhalation of 400 and 4000 ppb of HMPA for eight months caused nasal tumors in rats which, in some cases, filled the nasal cavity and penetrated into the brain. Other effects are described.

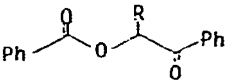
A full paper appeared in 1975 describing the interaction of certain benzoate esters (XCI; e.g., R=Ph, $CH=CH_2$) with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) at -78° to afford dipole stabilized carbanions XCII which self-condensed with unmetalated esters to give XCIII [126]. In contrast, benzoate esters derived from strictly aliphatic alcohols gave only o-metalation; benzophenone behaved similarly to afford XCIV.



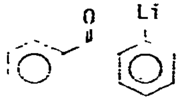
XCI



XCII

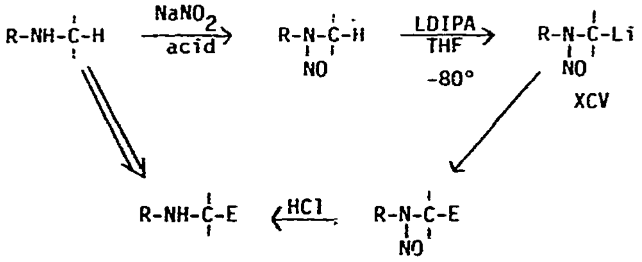


XCIII



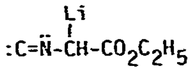
XCIV

The preparation and subsequent reactions of a variety of highly nucleophilic lithiomethylnitrosamines like XCV have been described in a full paper [127]. Since the nitroso group is readily removed from the resulting products, the procedure represents a method for effecting electrophilic substitution at the methyl group of secondary methylamines (Eq. 5). Electrophiles studied included alkyl halides, aldehydes, ketones, and acid halides.



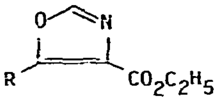
(5)

Additional syntheses using α-metalated isocyanides have been reported [128, 129]. Thus, lithio derivative XCVI and others react with acid halides and other carboxylic acid derivatives to afford oxazoles like XCVII [128]. Similar reactions with various alkylating agents give higher homologues in which the isocyano group can be converted to amines by mild acid hydrolysis [129]. The sequence of reactions thus represents a route to higher amino acids.



$$:C{=}\ddot{N}{-}\overset{\overset{\displaystyle Li}{|}}{C}H{-}CO_2C_2H_5$$

XCVI

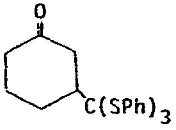


XCVII

A large number of papers discussed additional chemistry of carbanions stabilized by sulfur. Thus, XCVIII, which is equivalent to $RO\bar{C}O$, has been shown to enter into conjugate additions with nine α,β-unsaturated ketones to afford compounds like XCIX (65-95%) [130].

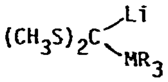
$(PhS)_3CLi$

XCVIII

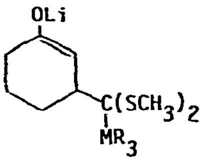


XCIX

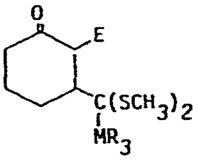
Lithiated silyl- and stannyl systems C also conjugatively add to cyclic enones to give compounds like CI which, after addition of water or alkyl halides, give CII (60-78%) [131]. The preparation and some chemistry of dianion CIII is discussed.



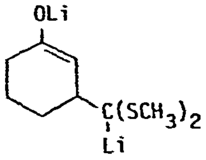
C



CI

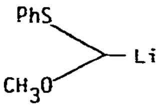


CII

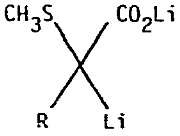


CIII

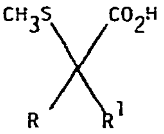
Lithium reagent CIV, prepared by metalation of methoxymethyl phenyl thioether by n-butyllithium at -30°, adds to γ-butyrolactones and provides a valuable route to α-alkoxy or α-methylene δ-lactones [132].



CIV



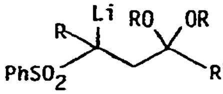
CV



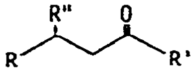
CVI

Dilithio salts of thiocarboxylic acids (CV) have been found to be latent vinyl, oxiranyl, and acyl carbanion equivalents [133, 134, 135]. Thus, species like CVI, derived from alkylation of CV, have been converted to ketones by N-chlorosuccinimide [133, 135]. Olefins have been obtained by LAH reduction of CVI, conversion to benzoate esters, and reduction by lithium/ammonia [134]. Finally, oxiranes are obtained by treatment of CVI with trimethyloxonium fluoroborate, then base [134].

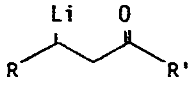
Four papers described the use of sulfone acetals as carbanion synthons. For example, alkylation of CVII and related compounds followed by reductive cleavage of the sulfone and hydrolysis of the acetal gave CVIII; CVII was thus acting as synthon CIX [136]. In contrast, alkylation of CVII followed by hydrolysis of the acetal and elimination of the sulfone gave α,β-unsaturated ketone CX; in this case, CVII was acting as synthon CXI [136, 137]. Similar reactions of CVII with esters [138] and terminal epoxides [139] ultimately gave 1,4-diketones and δ-lactols (CXII), respectively. Many specific examples are illustrated for these processes in the respective papers.



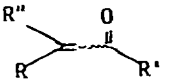
CVII



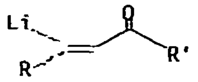
CVIII



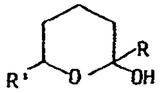
CIX



CX

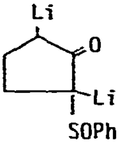


CXI

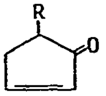


CXII

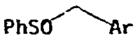
Ketosulfoxides and related compounds continue to be studied. Thus, dilithio salt CXIII has been alkylated by several alkyl halides followed by pyrolytic elimination of the sulfoxide moiety to afford the thermodynamically less stable olefin CXIV in fair yields [140].



CXIII



CXIV

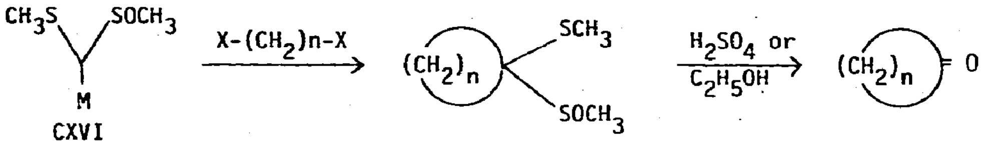


CXV

A convenient one-pot olefin synthesis has been described involving alkylation and in situ elimination of several sulfoxides including CXV and others substituted on the α-carbon with phenylthio-, phenylsulfinyl-, and cyano groups [141]. In another paper dealing with the elimination from β-sulfinyl esters, the authors conclude that dipole effects as well as steric interactions, proton acidity, and olefin stability must be considered when accounting for the regioselectivity of such reactions [142].

In connection with a study of the silicon-Pummerer rearrangement, it has been found that α-lithiosulfoxides can be conveniently silylated at -78° provided the anion is added to excess chlorotrimethylsilane [143]. Diastereomeric silylsulfoxides were obtained in certain cases.

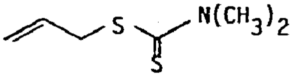
A general synthesis of cyclic ketones from lithio- or potassiosulfoxide CXVI and α, ω-dihalo- or α, ω-ditosyloxyalkanes has been described and is illustrated in Eq. 6 [144]. Yields of cyclopropanone to cyclohexanone generally were greater than 78%.



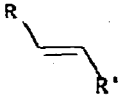
CXVI

(6)

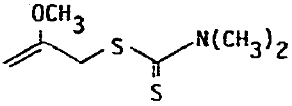
Additional chemistry of lithiated dithiocarbamates continues to be described. Thus, CXVII and related species are vinyl synthons since alkylation, [3,3]-sigmatropic rearrangement, alkylation, and reduction afford disubstituted olefins like CXVIII [145, 146]. The method has been used to synthesize certain alkenol sex pheromones [145], α-curcumene [146], and nuciferal [146]. The new, related compound, CXIX, is an acetonyl synthon since reaction with alkyl halides, aldehydes, ketones, and epoxides followed by hydrolysis and reduction gives α-substituted acetones [147]. Finally, thiocarbamoylsulfenylation of compounds similar to CXVII by CXX has been shown to ultimately lead to α,β-unsaturated aldehydes in fair yields [148].



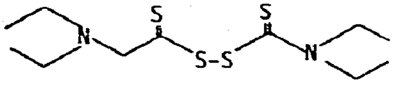
CXVII



CXVIII

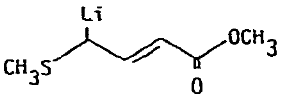


CXIX

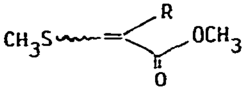


CXX

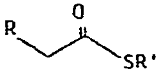
Lithio-γ-methylthiocrotonic esters like CXXI have been found to undergo alkylation and Michael-type condensations at their α-carbon atoms to afford compounds like CXXII; subsequent transformations are discussed [149]. In another study, thio esters (CXXIII) have now been metalated by LDIPA and condensed with aldehydes and ketones to give β-hydroxy derivatives in fair to excellent yields [150].



CXXI

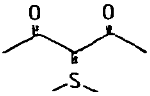


CXXII

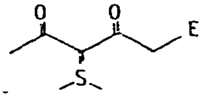


CXXIII

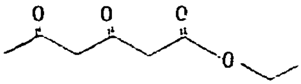
Finally, bis-carbonyl-stabilized sulfonium ylide CXXIV has been lithiated at a terminal methyl group, then condensed with several types of electrophiles to afford CXXV; in some cases, the sulfur moiety has been removed [151]. For example, reaction of lithio-CXXIV with ethyl chloroacetate, then zinc-acetic acid gives CXXVI in good yield.



CXXIV

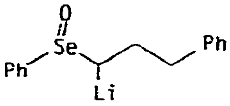


CXXV

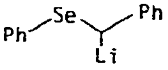


CXXVI

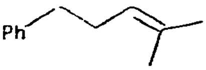
Turning attention to organoselenium chemistry connected with organolithium reagents, a full paper appeared which describes the scope and limitations of the transformation of ketones to enones by selenenylation and subsequent syn-elimination [152]. Detailed procedures are given for the conversion of ketones and esters to their α-seleno derivatives mostly via lithium enolates. In other papers, the preparation of several α-lithioselenoxides and selenides like CXXVII and CXXVIII, respectively by metalation have been described [153, 154, 155]. Subsequent reactions with alkyl halides and aldehydes, ketones, or epoxides followed by elimination affords olefins or dienes and allylic alcohols in good to excellent yields, respectively. Finally, β-hydroxyselenides prepared by the above methods have been converted to olefins by methanesulfonyl chloride in the presence of triethylamine [155]; for example, CXXVII and acetone ultimately give CXXIX (73%).



CXXVII

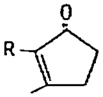


CXXVIII

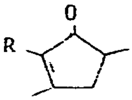


CXXIX

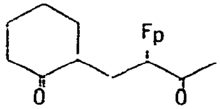
Additional work on the metalation of simple ketones has resulted in the description of regiospecific methylation of cyclopentenone derivatives [156]. Thus, methylation of four kinetic enolates prepared by addition of CXXX to LDIPA-HMPA at -77° gave only the corresponding 5-methyl derivatives CXXXI (56-74%). Other lithium enolates of ketones have been found to conjugatively add to methyl vinyl ketone coordinated to η^5-$C_5H_5Fe(CO)_2$ (Fp), a powerful acceptor of nucleophiles, without complication of polymerization [157]. For example, cyclohexanone lithium enolate reacts with the complex to afford CXXXII (45%); other examples are included.



CXXX

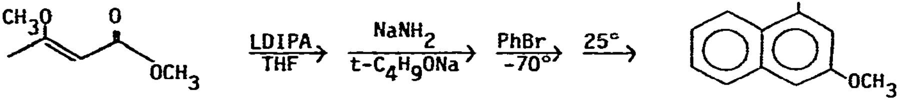


CXXXI



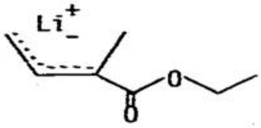
CXXXII

Regiospecific generation of an enolate and subsequent trapping with formaldehyde has been employed as part of a synthesis of (±)-prostaglandin $F_{2\alpha}$ [158]. Several dienolate anions have been reacted with benzynes to give substituted naphthalenes and naphthols [159]. An example is shown in Eq. 7. The sodio lithio salt of methyl acetoacetate has been alkylated with cyclopentenylmethyl bromide as part of a synthesis of certain neurotoxins in the 2,7-*epi*-histrionicotoxin series [160].

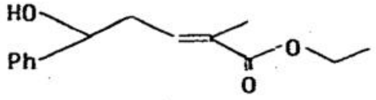


(7)

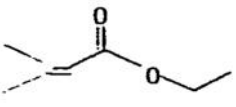
In contrast to earlier regioselective α-alkylations of ester dienolates, certain aldol reactions of such lithiated species having methyl groups at both the α- and β-carbon atoms have been found to afford γ-condensation products [161]. For example, CXXXIII and benzaldehyde give CXXXIV (75%). Additional examples of previously described α-alkylation were carried out on CXXXV in connection with a new approach to the preparation of simple cyclopentenones [162]. The product esters were simply converted to diazoketones which were then cyclized to desired products.



CXXXIII

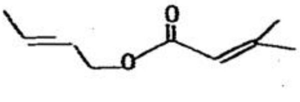


CXXXIV

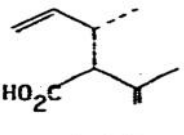


CXXXV

Treatment of trans-crotyl senecioate (CXXXVI) with LiTMP followed by chlorotrimethylsilane, heating, and hydrolysis gave (2S), (3S)-acid CXXXVII (95%) [163]. It is concluded that the dienolate anion has the E-configuration The corresponding (2S), (3R)-acid obtained from cis-CXXXVI was employed in a preparation of dl-botryodiplodin.

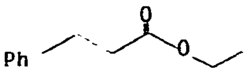


CXXXVI

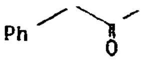


CXXXVII

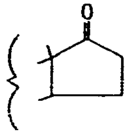
New 1,2-(alkylative) carbonyl transpositions of esters and ketones have now been described [164]. For example, ester CXXXVIII is converted in high yield to ketone CXXXIX by sulfenylation, LAH reduction, elimination, and hydrolysis. Similarly, steroidal ketone CXL is converted to CXLI. Other examples are listed [164] including the use of the method in the preparation of acorenone B [165]. Incidentally, the first step of the above sequence, sulfenylation, has been employed in the synthesis of pheromones of the honey bee from ester enolates [166].



CXXXVIII



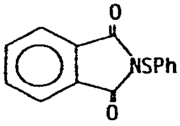
CXXXIX



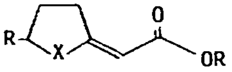
CXL

CXLI

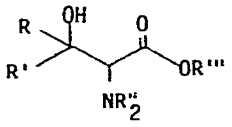
Several other condensations of ester enolates deserve mention. γ-Butyrolactone has been bis-sulfenylated by CXLII in the presence of LDIPA as part of a route to 3-substituted 2-buten-4-olides [167]. The selenation of the lithium enolates of four enamino, enol ether, and thioenol ether esters (CXLIII) followed by elimination affords pyrrole, furan, or thiophene derivatives (71-95%), respectively [168]. Alkylation of silylated ester enolates and silylation of lactone and amide enolates have been found to give C-silylated systems in good yields [169]. Finally, a series of α-amino or alkoxy-β-hydroxyesters (CXLIV) have been prepared in good to excellent yields by condensation of corresponding lithium enolates with various aldehydes and ketones [170].



CXLII

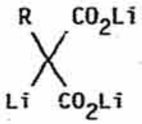


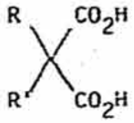
CXLIII

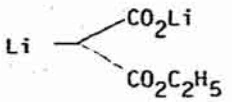


CXLIV

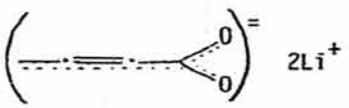
Two new alternatives to the classic malonic ester synthesis involving multiple anions of carboxylic acids have been described. First, phenyl- and methylmalonic acids have been trilithiated by n-butyllithium to afford CXLV, alkylation and hydrolysis of which leads directly to dialkyl derivatives CXLVI (74-88%) [171]. Similarly, alkylation of CXLVII, prepared from ethyl malonate and lithium isopropylcyclohexylamine, followed by hydrolysis and decarboxylation affords monoalkylated derivatives of ethyl acetate; ten different examples are shown [172].

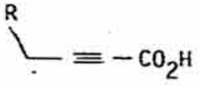

CXLV

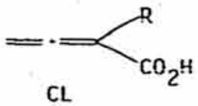

CXLVI


CXLVII

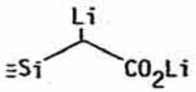
Dilithio-2-butynoic acid (CXLVIII), prepared by metalation of the parent acid, has been alkylated and condensed with cinnamaldehyde to give mixtures of γ- and α-condensation products CXLIX and CL, respectively [173, 174]. The ratios of CXLIX to CL were 2.2:1 and 1:1, respectively.

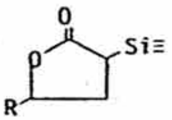

CXLVIII

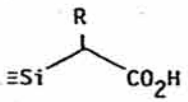

CXLIX


CL

A method has been described to prepare α-trimethylsilyl derivatives of acids and esters without the formation of isomeric O-silylated derivatives [175]. Thus, trimethylsilylacetic acid has been dimetalated with LDIPA to afford CLI. Condensations of CLI with epoxides, aldehydes (ketones), and alkyl halides give α-silyllactones like CLII, α,β-unsaturated acids (83-90%), and alkylated derivatives CLIII (60-98%), respectively.


CLI

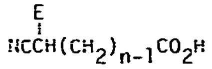

CLII


CLIII

Two of three methods employed in the synthesis of the insect juvenile hormone analog, ethyl 3,3,11-trimethyl-2,4-dodecadienoate involved addition of dilithioacetic acid and dilithio-3-methyl-2-butenoic acid to appropriate carbonyl compounds [176]. The third method similarly utilized addition of propynyllithium to 3,7-dimethyl-1-octanal. In a different study, several ω-cyanocarboxylic acids (CLIV) were metalated alpha to the nitrile group by lithium amide in liquid ammonia; subsequent condensations with imines and benzophenone gave species like CLV [177].

$NC(CH_2)_nCO_2H$

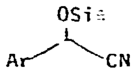
CLIV



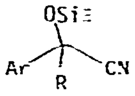
$NC\overset{E}{C}H(CH_2)_{n-1}CO_2H$

CLV

Four silylated cyanohydrins (CLVI) have been metalated by LDIPA, then alkylated to afford CLVII [178]. Subsequent hydrolysis gave the corresponding phenones generally in good to excellent yields.

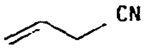


CLVI

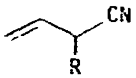


CLVII

Despite earlier suggestions that metalation and alkylation of 3-butenenitrile (CLVIII) affords only α,α-dialkyl derivatives [110], other workers have effected <u>mono</u>alkylations on CLVIII to give CLIX (72-98%) by employing allylic, propargylic, and other "active" alkyl halides at -78° [179]. In a different study, alkylations of mono- and dialkylacetonitriles (CLX) with haloacetals afford β- or γ-cyanoacetals (67-84%) which have been hydrolyzed to the corresponding aldehydes (88-96%) [180].



CLVIII

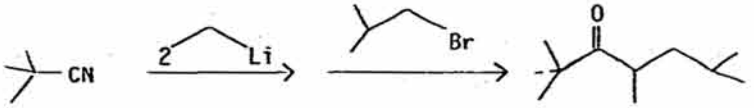


CLIX

CLX

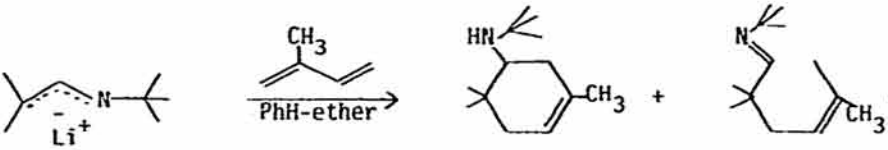
Reaction of several nitriles without α-hydrogen atoms has been reported to give lithioimides which undergo subsequent *in situ* metalation [181].

Alkylation and hydrolysis affords highly branched ketones as illustrated in Eq. 8.



(8)

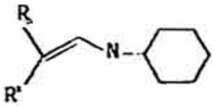
Metalation of other organonitrogen compounds continues to be studied. Thus, lithiated aldimine CLXI has been cycloalkenylated with isoprene to afford CLXII and CLXIII (Eq. 9) in yields of 53% and 45%, respectively [182]. Related reactions were applied to the synthesis of certain terpenoids.



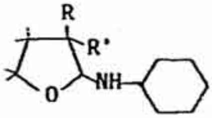
(9)

CLXI CLXII CLXIII

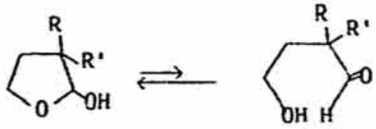
Several other lithiated aldimines like CLXIV have been condensed with epoxides to give either α-aminofurans (CLXV) (73-87%) or γ-hydroxyaldehydes (CLXVI) (62-72%) depending upon the work-up conditions [183].



CLXIV

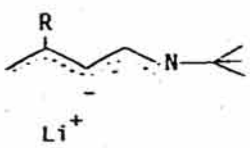


CLXV

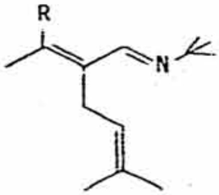


CLXVI

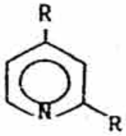
The first reports of lithiation of α,β-unsaturated aldimines appeared in 1975 [184, 185]. In one case, alkylation of CLXVII with prenyl chloride gave α- or α,α-dialkylation; the former products were isomerized to CLXVIII in high yields [184]. In contrast, the use of chlorotrimethylsilane gave only γ-alkylation (100%). Secondly, reaction of CLXVII with nitriles (R'CN) afforded a new synthesis of 2-alkyl or 2-arylpyridines (CLXIX) [185].



CLXVII

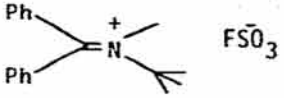


CLXVIII

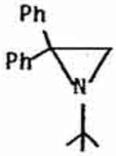


CLXIX

The deprotonation of iminium salt CLXX and others has been studied as a route to aziridines (CLXXI) via azomethine ylides using a variety of basic reagents [186]. For example, LiTMP and sodium hexamethyldisilazane gave CLXXI: CLXX in ratios of about 0.7 and 22, respectively. The authors conclude that the method does not appear to constitute a general route to aziridines.

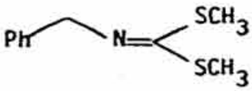


CLXX

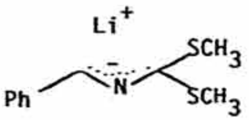


CLXXI

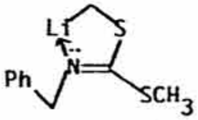
Certain dialkyl N-alkyliminocarbonates like CLXXII have been reacted with basic reagents to give either CLXXIII or CLXXIV depending upon the metallic cation [187]. Thus, potassium *t*-butoxide and LDIPA afford CLXXIII and CLXXIV, respectively as evidenced by subsequent alkylation and aldol-type condensations. That lithium cations favor the formation of CLXXIV is ascribed to chelation as shown.



CLXXII

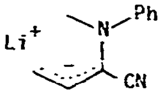


CLXXIII

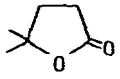


CLXXIV

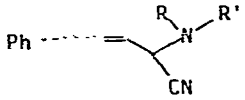
Lithiocyanoenamine CLXXV, a 3-carboxycarbanion equivalent, has been prepared by metalation, then reacted with aldehydes or ketones like acetone to give, upon hydrolysis, lactones like CLXXVI [188]. Similar chemistry is described for butenenitrile CLXXVII.



CLXXV

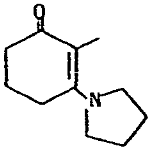


CLXXVI

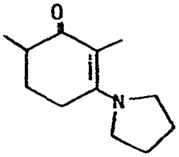


CLXXVII

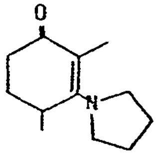
In connection with a study of the enamino ketone variant of the Robinson annelation reaction, CLXXVIII has been converted by metalation with LDIPA, then methyl iodide to either CLXXIX or CLXXX depending upon the amount of LDIPA employed [189]. Thus, use of an excess of this base exclusively gives the kinetically favored cross-conjugated enolate which leads to CLXXIX. In contrast, use of a slight deficiency of the base allows equilibration to the thermodynamically favored enolate which gives rise to CLXXX.



CLXXVIII



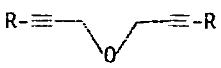
CLXXIX



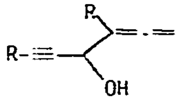
CLXXX

Finally, some experimental details have now been published describing the conversion of certain lactims to their 3-alkylated derivatives [190].

Two papers described metalations of ethers alpha to oxygen atoms. For example, metalation of unsaturated ethers like CLXXXI (R=H, CH_3, or Si≡) with _n_-butyllithium·TMEDA gave CLXXXII (10-64%) [191].

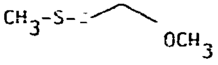


CLXXXI

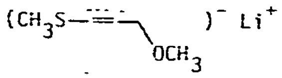


CLXXXII

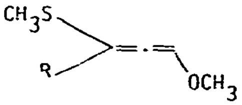
In agreement with earlier observations, metalation of CLXXXIII gives CLXXXIV which reacts as an allenic carbanion [192]. Thus, reaction of CLXXXIV with five different alkyl halides afforded CLXXXV (54-94%) which were hydrolyzed either to α-thiomethyl-α,β-unsaturated aldehydes (aqueous acid) or to β-ketoacetals (aqueous mercuric ion) [192]. Other condensations are described.



CLXXXIII

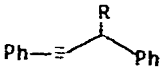


CLXXXIV

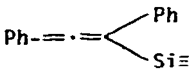


CLXXXV

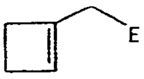
Considering hydrocarbons, 1,3-diphenylpropyne has been metalated by several strong bases and the anion reacted with alkylating agents to give either CLXXXVI or CLXXXVII depending upon the hardness or softness of the alkylating agent [193]. Thus, alkyl iodides afford only CLXXXVI while chlorotrimethylsilane gives only CLXXXVII. Methylenecyclobutane has also been metalated; subsequent condensations with a variety of electrophiles affords mixtures of CLXXXVIII and CLXXXIX [194]. The relative amounts of the two products varied as a function of solvent, temperature, and alkylating agent; for example, benzyl chloride in hexane at -78° gave only CLXXXIX while the use of benzyl bromide in hexane at 25° afforded a 50:50 mixture of the products.



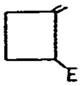
CLXXXVI



CLXXXVII

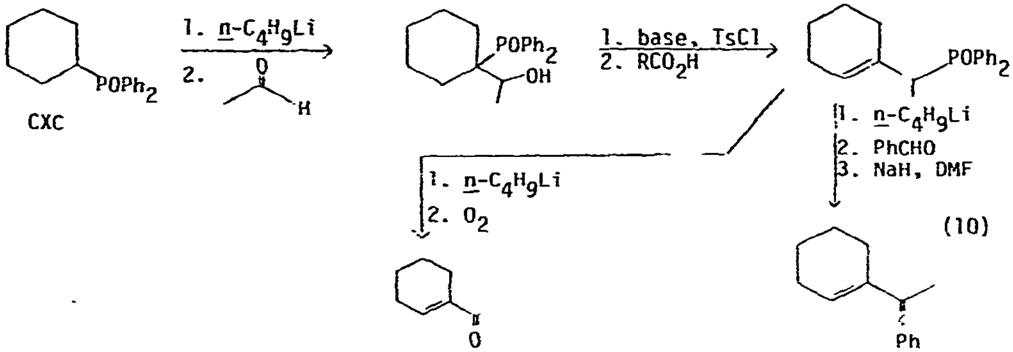


CLXXXVIII



CLXXXIX

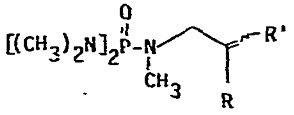
In the area of phosphorous-containing molecules, the diphenylphosphinoyl group activates α-hydrogens towards metalation as illustrated by the conversion of CXC to various compounds (Eq. 10) [195].



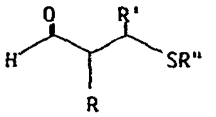
CXC

(10)

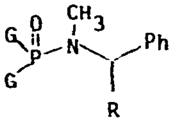
Four allylic phosphoramides CXCI have been metalated by n-butyllithium at -50° and the resulting anions then condensed with various disulfides to ultimately afford CXCII; such anions thus act as 3-lithiopropanal synthons [196]. In another study, the ease of metalation of phosphoramides and phosphonates CXCIII ($G=OC_2H_5$, $N(CH_3)_2$ and various combinations) and the stabilities of the resulting carbanions have been found to be a function of G, nitrogen substituents giving more stable carbanions than oxygen ones [197].



CXCI

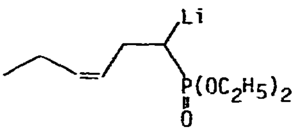


CXCII

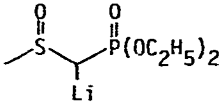


CXCIII

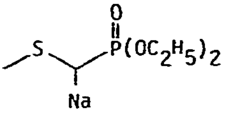
Lithiophosphonate ester CXCIV has been condensed with methyl levulinate ethylene ketal as part of a three-step synthesis of cis-jasmone [198]. Condensation of lithio salt CXCV with aldehydes and ketones has resulted in a new synthesis of α,β-unsaturated sulfoxides (50-84%) [199]. Similar reactions were obtained on sodio salt CXCVI to give α,β-unsaturated sulfides (41-66%).



CXCIV

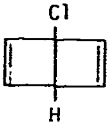


CXCV



CXCVI

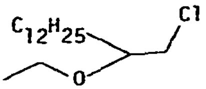
Finally, dehydrohalogenations were involved in the following. Reaction of bicyclic CXCVII with lithium dimethylamide gives N,N-dimethylaniline (100%) [200]. Formation of this product as well as trapping experiments led the authors to conclude that the reaction proceeds via butalene (CXCVIII).



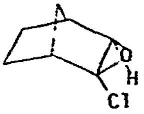
CXCVII

CXCVIII

Chloroether CXCIX has been reacted with excess n-butyllithium to give 1-tetradecyne apparently via a 1-chloroalkene which undergoes dehydrochlorination to the acetylene [201]. α-Chloroepoxide CC predominately affords CCI upon treatment with lithium diethylamide [202]. The formation of CCI is ascribed to transannular insertion of an α-keto carbene followed by an α-elimination of chloride ion. The results obtained with the related bicyclooctene are also discussed.



CXCIX

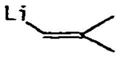


CC

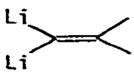
CCI

B. AT sp^2 AND sp CARBON AND AT NITROGEN

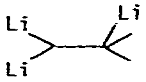
Several alkenes have been reacted with excess lithium vapor to afford polylithiated alkanes and alkenes; the products arise from substitution of lithium for hydrogen and addition of the metal across double bonds [203]. For example, isobutylene with lithium gas at 850° gives CCII-CCIV.



CCII

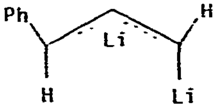


CCIII



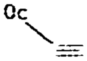
CCIV

Allylbenzene has been dimetalated by *n*-butyllithium·TMEDA to afford CCV; deuteration experiments suggest the second metalation occurred by abstraction of a terminal rather than a benzylic hydrogen atom [204]. In a different study, metalation of allenes followed by alkylation has been found to constitute a simple route to mono-, di-, or trisubstituted allenic compounds [205]. For example, CCVI and CCVII are obtained (87:13) (68%) by octylation of 1-lithio-1,2-propadiene. The lithiated allenes can also be formed from bromoallenes and lithium metal or *n*-butyllithium.



CCV

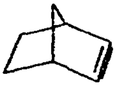
CCVI



CCVII

Dehydrochlorinations effected by organolithium reagents were discussed in several papers. Thus, reaction of 2-chlorobicyclo[2.2.1]heptene (CCVIII) with *n*-butyllithium apparently proceeds via norbornyne (CCIX) as evidenced by labeling and trapping experiments [206]. In contrast, formation of CCX in a similar reaction of CCVIII with methyllithium has been suggested to occur via a direct coupling reaction rather than by norbornyne or by an addition-α-elimination pathway [207].

CCVIII

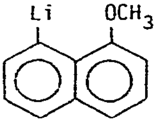


CCIX

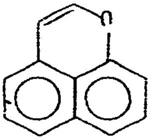
CCX

Treatment of *gem*-dichloroalkenes with ethyl- or *n*-butyllithium has been shown to afford lithium acetylides that have been directly alkylated or hydrolyzed [208]. Finally, benzyne has been prepared from chlorobenzene and LiTMP as evidenced by trapping experiments with four different dienes [209].

Considering aromatic compounds, directed metalations of ethers continue to be studied in connection with synthesis. Thus, several methoxy- and hydroxynaphthaldehydes have been prepared from species like CCXI and appropriate electrophiles [210]. Similarly, CCXI has been employed in a three-step preparation of naphtho[1,8-bc]pyran (CCXII) [211].

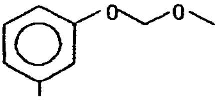


CCXI

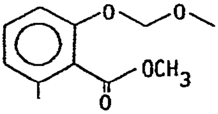


CCXII

The use of methoxymethyl rather than methoxy side-chains in such metalations has been found to constitute a convenient source of certain salicylaldehydes [212]. Moreover, this group promotes metalations that are faster and more regioselective than those described earlier. For example, CCXIII, *t*-butyllithium, carbon dioxide, and diazomethane rapidly gives CCXIV (90-95%) that is at least 99.5% isomerically pure [213].

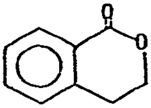


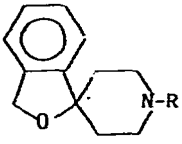
CCXIII

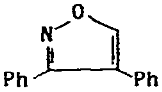


CCXIV

o-Lithiation of aromatic amides has been employed in a simplified preparation of isocoumarin (CCXV) [214] and in the synthesis of a variety of spiro piperidines like CCXVI [215]. Finally, metalation of 3,4-diphenylisoxazole (CCXVII) has been found to constitute a source of lithium phenylethynolate (CCXVIII); condensation of the latter material with aldehydes and ketones affords β-lactones (51-79%) [216].


CCXV

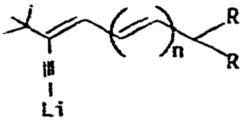

CCXVI

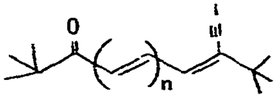

CCXVII

$(Ph\text{-}C{\equiv}C\text{-}O)^-Li^+$

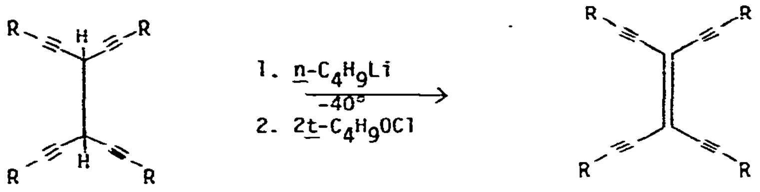
CCXVIII

Turning attention to acetylenes, five papers described the preparation of a variety of dehydroannulenes by condensation of lithioacetylides like CCXIX and related o-disubstituted aromatic compounds with α,β-unsaturated carbonyl systems like CCXX. Those prepared included benzo[c]-7,10,14-tri-t-butyl-1,8-didehydro[14]annulene [217], dibenzo[c;j]-7,14-di-t-butyl-1,8-bisdehydro[14]annulene [218], benzo[c]-naphtho[1,2-j]-7,14-di-t-butyl-1,8-bisdehydroannulene [218], 3,7,12,16-tetra-t-butyl-1,8,10-tridehydro[16]annulene [219], an annulenoannulene consisting of two 18 π-electron systems [220], and 3,9,14,20-tetra-t-butyl-1,10,12-trisdehydro[20]annulene [221].


CCXIX


CCXX

Tetraethynylethylenes (CCXXI, R=Ph, t-C_4H_9, $Si(CH_3)_3$, and CH_3) have now been obtained (36-45%) by lithiation of the corresponding ethanes followed by treatment with t-butylhypochlorite (Eq. 11) [222]. This method of preparation seems better than the previously described dimerization of 1,4-pentadiyne units or of diethynylcarbenes.

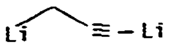


CCXXI

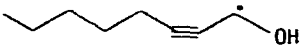
(11)

A convenient preparation of monolithium acetylide in the absence of nitrogenous complexing agents has been achieved by adding n-butyllithium to a THF solution of acetylene at -78° [223]. Subsequent condensations with aldehydes and ketones have afforded the corresponding carbinols (66-98%). Similar alkylations with long-chain alkyl halides (83-93%) have also been reported [224].

Reaction of propyne with two equivalents of n-butyllithium complexed with TMEDA or DABCO has been found to give dilithio salt CCXXII which reacts regiospecifically with electrophiles [225]. For example, butylation of CCXXII followed by addition of formaldehyde affords CCXXIII (80%); other reactions are shown.



CCXXII



CCXXIII

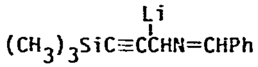
Several other metalated acetylene derivatives also deserve mention. Thus, dilithiopropiolic acid (CCXXIV) has been condensed with epoxides to afford 5-hydroxy derivatives which, depending upon subsequent reactions, have been cyclized to four different types of 5,6-dihydro-2H-pyran-2-ones [226]. Propargyl alcohol has been metalated by lithium amide in liquid ammonia to presumably give CCXV; alkylation affords only C-alkyl derivatives even in the presence of excess lithium amide and alkyl halides [227]. Finally, several 2-substituted propargylamines have been synthesized by reactions of protected lithium acetylene CCXVI with alkyl halides and methyl acrylate [228].

$LiC{\equiv}CCO_2Li$

CCXXIV

$LiC{\equiv}CCH_2OLi$

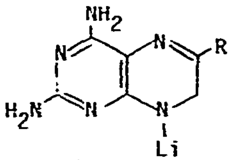
CCXV



$(CH_3)_3SiC{\equiv}C\overset{Li}{C}HN{=}CHPh$

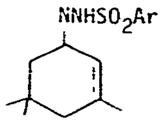
CCXVI

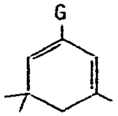
In the area of organonitrogen compounds, a variety of N^8-alkyl derivatives of 2,4-diamino-7,8-dihydropteridines have been prepared by alkylation of lithium salt CCXVII [229]. This salt was prepared by metalation of the parent heterocycle by n-butyllithium in DMSO.

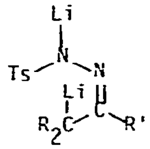


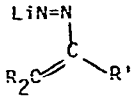
CCXVII

Certain intermediates in the reactions of sulfonylhydrazones with organolithium reagents have now been trapped. Thus, for example, in the reaction of CCXVIII with n-butyllithium in TMEDA solvent, vinyl anion CCXIX has been converted to CCXX (98%) by deuterium oxide [230]. This useful preparation of vinyl deuterated species is also illustrated in four other examples. Similarly, vinyl anions derived from eight tosylhydrazones have been alkylated to give substituted olefins; for example, propiophenone tosylhydrazone, butyllithium, and methyl iodide afford cis- and trans-2-phenyl-2-butene (>95%) [231]. The latter paper also describes the trapping of dianion CCXXI and vinyl diimide anion CCXXII. Control of the regiospecificity in the overall conversion of such hydrazones to olefins has now been ascribed to the configuration of the carbon-nitrogen double bond where the α-hydrogen syn to the tosyl group is removed regardless of its relative acidity [231]. A third paper in this area describes the conversions of the tosylhydrazones of a variety of cycloalkanones containing from seven to 15 carbon atoms to cycloalkenes [232].


CCXVIII (G= =O)

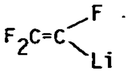

CCXIX (G=Li)
CCXX (G=D)

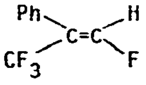

CCCXXI

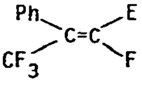

CCXXII

5. LITHIUM CARBENOIDS AND OTHER HALOGEN-SUBSTITUTED ORGANOLITHIUMS

Trifluorovinyllithium (CCXXIII) has been prepared from chlorotrifluoroethylene and n-butyllithium at -135°; subsequent condensations with several aldehydes and ketones afford the expected alcohols (83-88%) [233]. Another study revealed that similar fluorinated vinylic lithium carbenoids maintain their stereochemical integrity both during their formation and their reactions [234]. Thus, for example, Z-CCXXIV, LiTMP, and various electrophiles gave CCXXV exclusively. Four other examples are cited including lithio-(E)-pentafluoropropene, a system that was previously said to undergo isomerization.


CCXXIII


CCXXIV


CCXXV

Pairs of carbon tetrachloride and chloroform, fluorotrichloromethane and dichlorofluoromethane, and two others have been treated with methyllithium in the presence of 2-methyl-2-pentene as part of a study of the stereoselectivity of diastereogenic carbon-carbon bond formations [235]. Significant discrepancies in the outcome of both carbene- and carbenoid-convergent reactions have been revealed.

In a study of matrix reactions of carbon tetrachloride and the main alkali metals, infrared spectroscopy has been employed to identify both the previously described CCXXVI and the new species CCXXVII [236]. Results obtained with certain other tetrahalomethanes are also discussed.

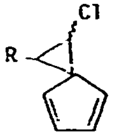
$MCCl_3$

CCXXVI

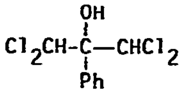
$X^{-}\cdots M^{+}\cdots CCl_2$

CCXXVII

Dichloromethyllithium has been reacted with six fulvenes to afford spiro derivatives like CCXXVIII [237]. The novel spirocyclization has also been realized in four cases with dibromomethyllithium. In another study, dichloromethyllithium has been condensed with a variety of acid chlorides to afford ketones, carbinols, or epoxides depending upon the substrate and the reaction conditions [238]. Thus, benzoyl chloride gives CCXXIX and CCXXX at low and high temperatures, respectively while, in contrast, 2,4,6-trimethylbenzoyl chloride affords ketone CCXXXI. Other examples are listed.

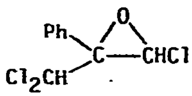


CCXXVIII

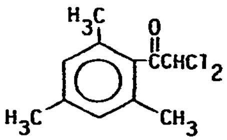


$$Cl_2CH-\overset{OH}{\underset{Ph}{C}}-CHCl_2$$

CCXXIX

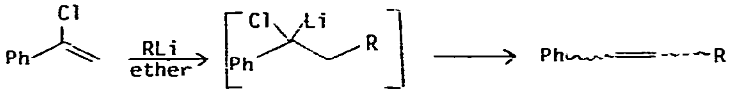


CCXXX



CCXXXI

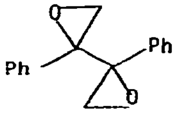
An interesting synthesis of alkenylbenzenes from α-chlorostyrene and four different organolithium reagents has been reported; the reactions presumably proceed via carbenoids CCXXXII (R=n-C_4H_9, t-C_4H_9, Ph, and CH_3) as shown in Eq. 12 [239].



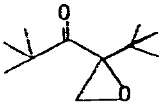
(12)

CCXXXII

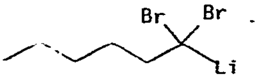
About a dozen bis-epoxides have been obtained from reactions of dibromomethyllithium and dicarbonyl compounds; for example, benzil gives CCXXXIII (31%) [240]. In contrast, sterically hindered carbonyl compounds like bipivaloyl give only monoepoxides like CCXXXIV. In a different investigation, dibromomethyllithium and five of its homologues have been found to decompose above -70° to afford α-bromoalkenes or dimeric products; for example, CCXXXV gives 1-bromo-1-hexene (28%) [241]. These carbenoids were also reacted with a variety of alkyl halides, aldehydes, ketones, and esters.



CCXXXIII

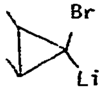


CCXXXIV

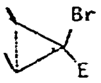


CCXXXV

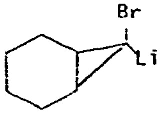
Several papers discussed α-bromocyclopropyllithiums. Thus, a variety of gem-dibromocyclopropanes and α-bromocyclopropylstannanes were treated at -90° to -100° with n-butyllithium to give configurationally stable carbenoids like CCXXXVI which were hydrolyzed or treated with several organometallic halides to afford products like CCXXXVII [242]. An interesting isomerization of syn-7-bromo-anti-7-lithionorcarane (CCXXXVIII) to anti-7-bromo-syn-7-lithionorcarane which apparently proceeds via halogen-metal exchange with parent dibromo compound is discussed. Another paper describes the conversion of syn-7-bromo-anti-7-trimethylstannylnorcarane to the syn-7-anti-7-lithio system by n-butyllithium at -95° [243].



CCXXXVI

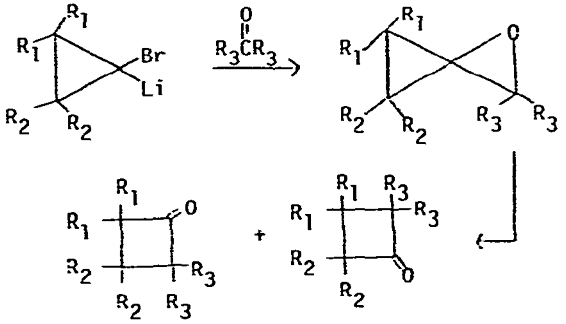


CCXXXVII



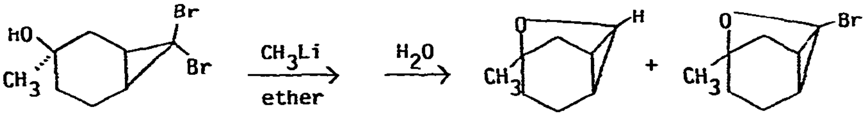
CCXXXVIII

Other 1-lithiocyclopropyl bromides have been stereoselectively alkylated [244] and reacted with aldehydes and ketones to give bromohydrins [245]. Certain of the latter condensations have been employed in the synthesis of cyclobutanones as illustrated in Eq. 13.



(13)

The 6-oxatricyclo[3,2,1,0^{2,7}]octane ring system may have been prepared via a carbenoid since treatment of CCXXXIX with excess methyllithium affords the products shown in Eq. 14; CCXL is of particular interest [246].



(14)

CCXXXIX

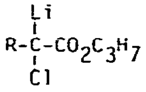
CCXL

Turning to α-haloenolates, a variety of isopropyl α,α-dichloro esters (CCXLI) have been reacted with lithium diethylamide in benzene/HMPA or lithium metal in THF to afford carbenoids like CCXLII [247, 248, 249]. Subsequent condensations with alkyl halides, aldehydes, ketones, and acid chlorides are described. Carbenoids derived from methyl chloroacetate and chloroacetonitrile and a variety of bases including lithiohexamethyldisilazane have been reacted with benzalacetophenone to give α-epoxyalkenes like CCXLIII (G=CO_2CH_3 or CN) [250]. The lithium enolates of several mono- and dichloroketones prepared by lithium-chlorine exchange have been hydrolyzed and condensed with aldehydes and acetic anhydride [251].

$RCHCl_2CO_2C_3H_7$

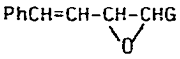
CCXLI

(R=H or alkyl)



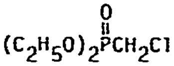
$R-\overset{Li}{\underset{Cl}{C}}-CO_2C_3H_7$

CCXLII



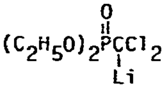
CCXLIII

Treatment of CCXLIV with n-butyllithium and carbon tetrachloride has afforded carbenoid CCXLV which has been alkylated with several alkyl halides to give 1,1-dichloroalkanephosphonates [252]. Use of CCXLVI in Wittig-Horner types of reactions to afford twelve 1,1-dichloroalkenes (62-90%) has been described [253]. Several related α-aryl-α-chlorocarbenoids of phosphonate esters (CXLVI) have been prepared similarly and their reactions with alkyl halides and aldehydes are discussed [254].



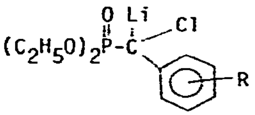
$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}CH_2Cl$

CCXLIV



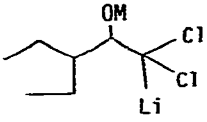
$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}\underset{Li}{C}Cl_2$

CCXLV

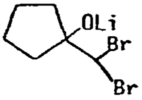


CCXLVI

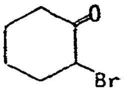
Unstable lithium β-alkoxycarbenoids like CCXLVII (M=Li) have been prepared from the corresponding halohydrin and n-butyllithium or lithium piperidide which ultimately afford either α-chloroketones or aldol lithium enolates [255]. One interesting aspect is the conversion of species like CCXLVIII to "homologues" like CCXLIX using the latter base. In another study, CCXLVII (M= Si≡), stable to -80°, decomposes above that temperature to initially give CCL and CCLI arising from α- and β-elimination, respectively [256]. The mode of elimination can be controlled as a function of steric hindrance.



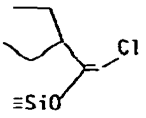
CCXLVII



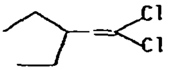
CCXLVIII



CCXLIX

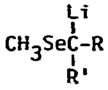


CCL

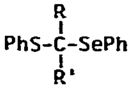


CCLI

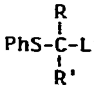
Finally, α-seleno- and α-sulfocarbenoids deserve mention in this section. Thus, species like CCLII have been reacted with a variety of aldehydes and ketones as part of a general preparation of epoxides [257]. Epoxides are also the ultimate products in the reactions of CCLIII with n-butyllithium and aldehydes and ketones; the transformations proceed via carbenoid CCLIV [258].


$CH_3Se\overset{\overset{Li}{|}}{\underset{\underset{R'}{|}}{C}}-R$

CCLII


$PhS-\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{C}}-SePh$

CCLIII


$PhS-\overset{\overset{R}{|}}{\underset{\underset{R'}{|}}{C}}-Li$

CCLIV

6. ADDITION AND SUBSTITUTION REACTIONS

Several organometallic reagents have been heterophilically added to thio-benzophenone (CCLV) and phenanthraquinone; for example, the former compound and vinyllithium gives CCLVI (40%) [259]. That such reactions with Z- and E-1-propenyl organometallics proceed with retention of configuration is suggestive that the mechanism does not involve a free 1-propenyl radical; the authors favor direct nucleophilic addition of RLi reagents to CCLV. Carbophilic rather than heterophilic additions have been obtained with several other carbonyl-containing compounds.

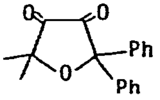
$Ph_2C{=}S$

CCLV

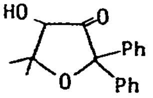
$Ph_2CHSCH{=}CH_2$

CCLVI

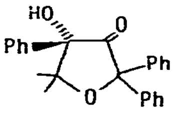
The first example of a 1,2-reduction of a carbonyl by an organolithium has now been reported [260]. Thus, reaction of α-dione CCLVII with *t*-butyllithium gave only CCLVIII (46%). Interestingly, the use of phenyllithium afforded addition products CCLIX and CCLX depending on the stoichiometry while methyllithium gave only CCLX.



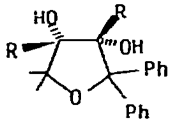
CCLVII



CCLVIII

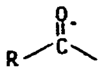


CCLIX

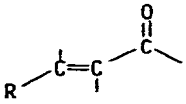


CCLX

A new 1,3-alkylative carbonyl transposition has been described which involves the overall conversion of CCLXI to CCLXII [261]. The method involves addition of vinyllithiums to CCLXI, quenching with benzenesulfenyl chloride, sulfenylation with diphenyldisulfide, and hydrolysis; [2,3]-sigmatropic rearrangements are involved in the process.



CCLXI



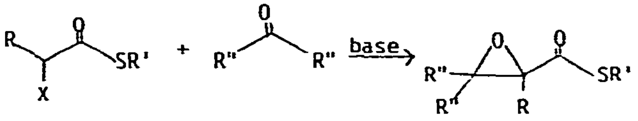
CCLXII

In an attempt to add a butyl group to the carbonyls of 4-t-butylcyclohexanone and 2-methylcyclopentanone from the more hindered side, the above ketones were complexed with trialkyl, aryl, and chloroaluminums and treated with n-butyllithium [262]. However, the relative amounts of isomeric alcohols obtained were about the same as those realized with n-butyllithium and the noncomplexed ketones. The reactions in the presence of the aluminum species did not occur via ate complexes like CCLXIII.

$LiAlR_3\text{n-}C_4H_9$

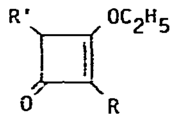
CCLXIII

A full paper describing the Darzens synthesis of glycidic thiol esters has appeared [263]. The reaction, illustrated in Eq. 15, is successful with R=hydrogen or methyl, X=chlorine or bromine, and R'=t-butyl or benzyl provided nonnucleophilic bases such as lithium hexamethyldisilazane or sodium hydride are employed in polar aprotic solvents.

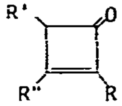


(15)

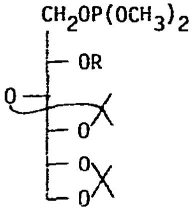
Other papers concerned with addition to carbonyls have included the conversion of cyclobutanedione enol ethers CCLXIV to cyclobutenones CCLXV [264], the use of secoalkylation in a synthesis of grandisol [265], carbonyl addition reactions as part of a preparation of an aromatic bis(propellane) [266] and in the synthesis of 9-isopropylidene-9,10-dihydroanthracene [267], and the preparation of certain phosphorus-containing carbohydrates like CCLXVI [268]. Finally, the interaction of prenyllithium (CCLXVII) with diethyl ketone and isobutyraldehyde have been found to give mixtures of isomeric alcohols CCLXVIII and CCLXIX [269]. In contrast, similar reactions with the corresponding Grignard reagent affords only CCLXVIII.



CCLXIV

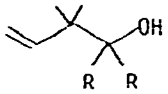


CCLXV

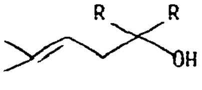


CCLXVI

CCLXVII

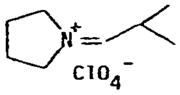


CCLXVIII

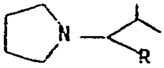


CCLXIX

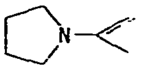
Considering imines, nitriles, and related compounds, iminium salts without α-hydrogens like CCLXX have been reacted with organolithium reagents to afford tertiary amines like CCLXXI [270]. Those salts with α-hydrogens do not undergo satisfactory addition but instead are deprotonated to afford enamines like CCLXXII.



CCLXX

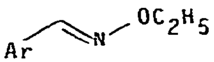


CCLXXI

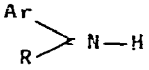


CCLXXII

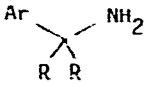
Reaction of O-ethylarylaldoximes (CCLXXIII) with various organometallics has been found to give five different products (CCLXXIV-CCLXXVIII) depending upon the metal and solvent [271]. For example, allyllithium in THF affords CCLXXVI and CCLXXVIII in low yields. In contrast, allylmagnesium bromide and the corresponding organozinc compound give CCLXXVIII and CCLXXVI in high yields, respectively. Similar results have been obtained with alkyl O-alkylbenzohydroximates [272].



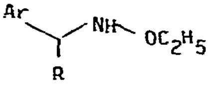
CCLXXIII



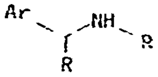
CCLXXIV



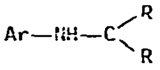
CCLXXV



CCLXXVI

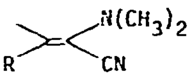


CCLXXVII

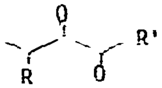


CCLXXVIII

Addition of organolithiums (R' = CH_3, Ph, and $\underline{n}$-C_4H_9) to several α-cyanoenamines (CCLXXIX) represents a novel, general method for preparing α-diketones like CCLXXX [273]. The α-cyanoenamines are prepared from readily available carboxamides.

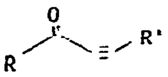


CCLXXIX

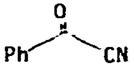


CCLXXX

α-Ynones (CCLXXXI) have been obtained from the reaction of phenylpropiolonitrile with phenyllithium and lithium phenylacetylide [274]. The use of other lithium reagents though, affords the cleavage products phenylacetylene and appropriate nitriles. A better, more general preparation of CCLXXXI has been achieved by treating lithium acetylides with benzoylcyanide (CCLXXXII) [275].

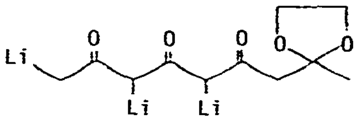


CCLXXXI

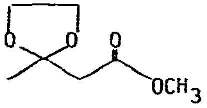


CCLXXXII

Other acylations have been employed as part of the syntheses of 6-hydroxymusizin and barakol. Thus, trilithio salt CCLXXXIII has been acylated by ester CCLXXXIV in good yields [276]. Similar chemistry has been applied to the syntheses of emodin and eleutherinol.

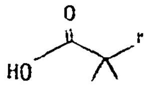


CCLXXXIII

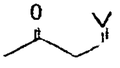


CCLXXXIV

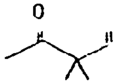
The formation of β,γ-enone from reaction of methyllithium and β,γ-carboxylic acids has now been extended to acylic acids [277]. Thus, using more vigorous conditions than described earlier, acid CCLXXXV has been converted to CCLXXXVI in THF-ether; unrearranged CCLXXXVII is obtained in ether alone.



CCLXXXV



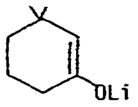
CCLXXXVI



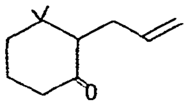
CCLXXXVII

In a thorough study of the reactions of organolithium and Grignard reagents with lithium carboxylates, it has been demonstrated that the former reagents afford ketones (79-89%) with all carboxylates studied except lithium acetate [278]. In contrast, Grignard reagents give mixtures of carbinols and ketones, the relative percentages of which vary as a function of both the carboxylate and the organometallic.

In the case of nucleophilic substitution reactions, β,β-disubstituted enolate CCLXXXVIII has been shown to undergo alkylation with allyl bromide with no loss of regiospecificity to give CCLXXXIX (70%) [279]. This chemistry is part of a total synthesis of (±)-diumycinol.

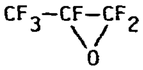


CCLXXXVIII

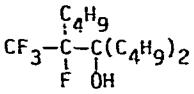


CCLXXXIX

n-Butyllithium has been found to attack CCXC at the central carbon atom in ethyl ether and at the terminal carbon atom in hexane to give CCXCI and CCXCII, respectively [280]. Such differences in products are ascribed to chelation effects. Several other organolithium reagents in ether were also found to attack the central carbon atom of CCXC.

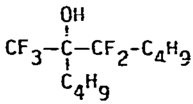


CCXC



$CF_3-\underset{F}{\overset{C_4H_9}{C}}-\underset{OH}{C}(C_4H_9)_2$

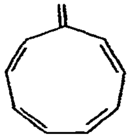
CCXCI



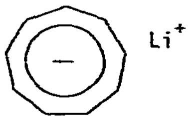
$CF_3-\underset{C_4H_9}{\overset{OH}{C}}-CF_2-C_4H_9$

CCXCII

Finally, nonafulvene (CCXCIII) has been prepared by reaction of CCXCIV with acetoxybromomethane followed by elimination of acetic acid [281]. Attempts to prepare triafulvene and calicene have been unsuccessful however [282].

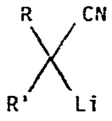


CCXCIII

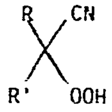


CCXCIV

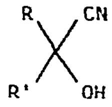
Several papers in 1975 discussed oxidations of organolithium reagents. Thus, treatment of secondary nitrile anions CCXCV with molecular oxygen affords α-hydroperoxynitriles CCXCVI which are reduced to cyanohydrins CCXCVII with stannous chloride [283]. The net process represents the conversion of nitriles to ketones.



CCXCV

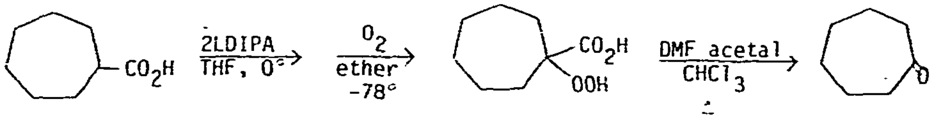


CCXCVI



CCXCVII

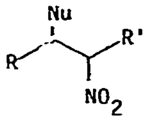
A variety of carboxylic acids and their derivatives likewise have been converted to α-hydroxy or α-hydroperoxy compounds. Both mono- and dilithioamides with molecular oxygen thus afford α-hydroxyamides in good to excellent yields [284, 285]. Dilithio salts of acids and lithium enolates of esters behave similarly [286, 287, 288]. In one study, it has been found that intermediate α-hydroperoxycarboxylic acids can be conveniently converted to ketones by means of either p-toluenesulfonic acid or DMF dimethylacetal [287]. The process is illustrated in Eq. 16.



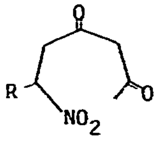
(16)

Several lithiated mono- and disubstituted ethyl acetates have been electrolyzed in an undivided cell with a platinum anode and mercury cathode to afford substituted succinate esters [289]. Yields of product ranged from 0-100% depending upon solvent, temperature, and the alkyl or aryl substituent. Several β-diketone and β-ketoester dianions have also been dimerized by cuprous chloride [290].

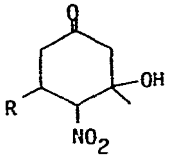
Considering additions to carbon-carbon bonds, a variety of organolithium reagents (NuLi) have been added to nitroolefins to afford synthetically useful intermediates like CCXCVIII which have been converted to ketones, indoles, diamines, and isoquinolines [291, 292]. Dilithio salts derived from β-diketones have been shown to give either open chains CCXCIX or cyclohexanones CCC depending upon the reaction conditions employed [293].



CCXCVIII

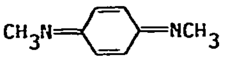


CCXCIX

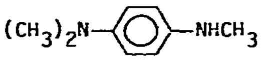


CCC

Reaction of diimine CCCI with methyllithium has been found to give predominately 1,6-addition product CCCII accompanied by small amounts of 1,4-adduct and reduction product.[294].

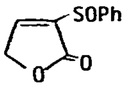


CCCI

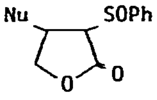


CCCII

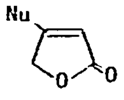
Michael additions on α-phenylsulfinyl-$\Delta^{\alpha,\beta}$-butenolide (CCCIII) by enolates of a ketone, an ester, and a β-ketoester afford CCCIV (30-83%); two of the adducts have been converted to β-substituted $\Delta^{\alpha,\beta}$-butenolides CCCV [295]. Sulfinyl system CCCIII is a more efficient Michael acceptor than the corresponding phenylthio compound.



CCCIII

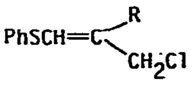


CCCIV



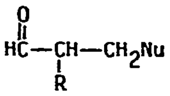
CCCV

Thiophenoxy systems like CCCVI have been found to act as synthons of α,β-unsaturated aldehydes in a Michael sense since organic lithium reagents react to give ultimately CCCVII [296].



$PhSCH{=}C(R)CH_2Cl$

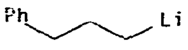
CCCVI



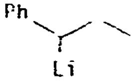
$HC(=O)\text{—}CH(R)\text{—}CH_2Nu$

CCCVII

Organolithiums have also been added to "unactivated" olefins. Thus, decomposition of THF by benzyllithium gives ethylene which reacts further to afford CCCVIII [297]. Further reaction of CCCVIII with ethylene is precluded by an intramolecular 1,3-proton shift to give the more stable CCCIX. When phenyllithium is used in THF, two molecules of ethylene react before the proton migration is observed. The results in THF are contrasted with those in ether where higher molecular weight telomers are obtained.

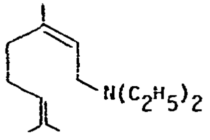


CCCVIII

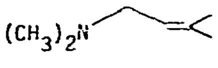


CCCIX

As part of a syntheses of (±)-linalool and (±)-2-hydroxydihydrolinalool, isoprene has been telomerized by n-butyllithium and diethylamine to afford CCCX (75%) [298]. In a similar reaction between isoprene and dimethylamine effected by alkali metals, the ratio of 4,1- (CCCXI) to 1,4-addition (CCCXII) product varied with the alkali metal, the ratio being highest with lithium [299]. Isoprene has also been polymerized by lithium diethylamide in the presence of a variety of ethers or triethylamine [300].



CCCX

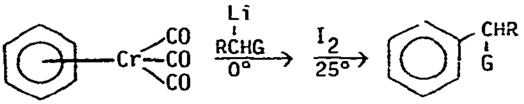


CCCXI

CCCXII

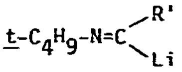
Other polymerization reactions all initiated by n-butyllithium have been described. These involved stereoregulation in polymerizations of methyl α-ethylacrylate [301], reactivities and other studies in the copolymerization of methyl methacrylate with a variety of other methacrylates [302, 303, 304], and anionic polymerization of vinyl chloride [305].

Finally, under a miscellaneous category, additional carbanions including some alpha to nitriles, sulfur, cyanohydrins, esters, and ketones as well as a few non-resonance stabilized ones have been reacted with π-benzenechromium tricarbonyl to afford phenyl substituted derivatives (Eq. 17) [306].



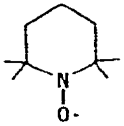
(17)

A new approach to the synthesis of partially mixed trialkylcarbinols has been discussed which involves interaction of previously described lithiated aldimines CCCXIII with dialkylchloroboranes, followed by thioglycolic acid, hydrogen peroxide, and base [307, 308]. In an unrelated study, it has been determined that 2,2,6,6-tetramethylpiperidine nitroxyl (CCCXIV) may be rapidly and quantitatively destroyed merely by treatment with n-butyllithium [309].



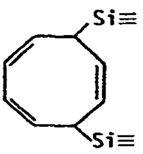
$\underline{t}\text{-}C_4H_9\text{-}N{=}C(R')(Li)$

CCCXIII



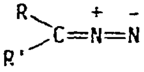
CCCXIV

A variety of carbanions have been silylated. Thus, the product from dilithiocyclooctatetraene and chlorotrimethylsilane has now been identified as CCCXV [310]. Methods for effecting C-silylation of ketones, aldehydes, nitriles, acid anhydrides, and esters by means of lithium, chlorotrimethylsilane, and THF at 0-10° have been described [311, 312]. Finally, 1-,.2-, and 9-trimethylsilylanthracenes as well as the 1,3-, and 9,10-bis-adducts have been prepared from appropriate lithiated anthracenes [313].

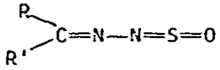


CCCXV

Two diazoalkanes (CCCXVI, R=Ph, R'=H and R=R'=Ph) have been prepared by addition of *n*-butyllithium to CCCXVII; the reaction apparently proceeds via elimination of a sulfenate anion [314].

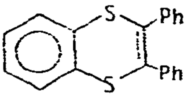


CCCXVI

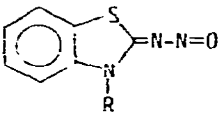


CCCXVII

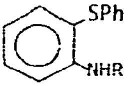
The major product in the reaction of phenyllithium with carbon disulfide has been identified as CCCXVIII [315]. A full paper describing the reaction of organolithium reagents with dihydrobenzothiazoles CCCXIX to give CCCXX has appeared [316]. Finally, *n*-butyl and phenyl sulfides have been prepared by reaction of the corresponding lithium reagents with CCCXXI [317].



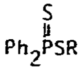
CCCXVIII



CCCXIX



CCCXX



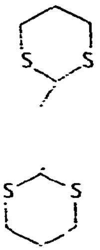
$\mathrm{Ph_2\overset{\overset{S}{\|}}{P}SR}$

CCCXXI

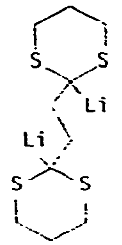
7. HETEROCYCLES

2-Lithio-1,3-dithianes continue to be extensively studied. Thus, a full paper describing their preparation, alkylations, acylations, and certain hydroxyalkylations has now appeared [318]. Extensive experimental details are included.

*Bis*dithiane CCCXXII has been converted to dilithio derivative CCCXXIII, then doubly alkylated to ultimately afford 1,4-diketones CCCXXIV (R=aliphatic) [319]. However, higher yields (43-79%) of CCCXXIV are generally obtained by carrying out sequential single metalation-alkylation reactions.



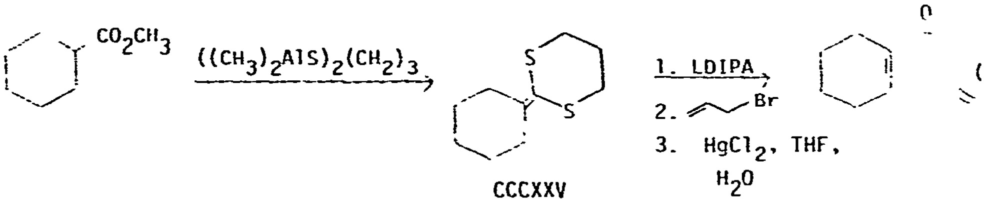
CCCXXII



CCCXXIII

CCCXXIV

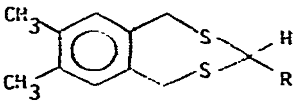
A variety of ketene thioacetals like CCCXXV have been prepared, metalated, then alkylated to afford ketones [320]. Since the ketene thioacetals are prepared from esters, the sequence represents a novel conversion of the latter to unsaturated aldehydes or ketones as illustrated in Eq. 18.



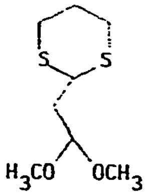
CCCXXV

(18

Other dithianes that have been metalated, then alkylated include CCCXXVI ($R=H$ or CH_3) derived from 1,2-dimethyl-4,5-bis(mercaptomethyl)benzene [321], and CCCXXVII [322]. The latter system has been investigated as part of the synthesis of a key prostaglandin intermediate.

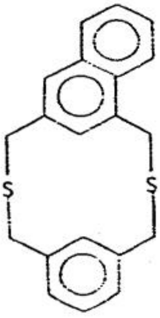


CCCXXVI



CCCXXVII

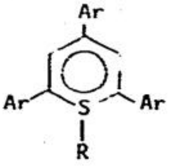
Studies on other heterocyclics containing two sulfur atoms have included the Wittig rearrangement of CCCXXVIII in connection with the preparation of the first monobenzannelated trans-15,16-dihydropyrene [323] and metalations of CCCXXIX which occur at vinylic rather than at allylic positions [324]. Such regioselectivity in the latter case is ascribed to the lack of aromaticity associated with 10-π-electron delocalization through sulfur atoms in this system.



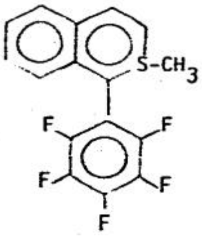
CCCXXVIII

CCCXXIX

Turning to ring systems containing one sulfur atom, a full paper has appeared describing the preparation of a variety of thiabenzene systems like CCCXXX, CCCXXXI, and others [325]. Similarities between these species and acyclic sulfonium ylides are discussed.

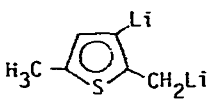


CCCXXX

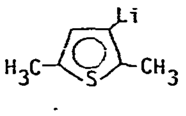


CCCXXXI

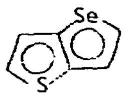
Metalation of 2,5-dimethylthiophene has been effected by ethyllithium·TMEDA to afford mostly CCCXXXII and small amounts of CCCXXXIII as evidenced by carbonation [326]. The former compound had earlier been said to be the 3,5-methyl dilithio isomer. Metalation of CCCXXXIV has been found to give mixtures of products arising from respective lithiation of both rings [327].



CCCXXXII

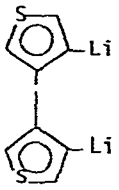


CCCXXXIII

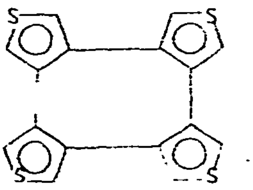


CCCXXXIV

Two papers have described the synthesis of heterocyclic cyclopolyaromatics containing similar [328] and different [329] kinds of nuclei. For example, CCCXXXV and cupric chloride affords CCCXXXVI (23%) [328]. Several other examples involving nitrogen, oxygen, and sulfur-containing heterocycles are described.

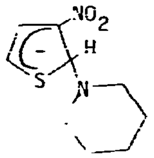


CCCXXXV

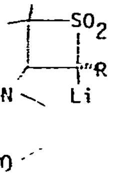


CCCXXXVI

2- and 3-Nitrothiophenes have been found to form Meisenheimer-type complexes like CCCXXXVII with lithium piperidide and other nucleophiles [330]. Finally, a general stereospecific synthesis of <u>cis</u>-3-amino-2(4)-R-thietane 1,1-dioxides via CCCXXXVIII has been discussed [331].

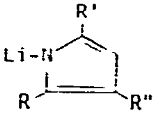


CCCXXXVII

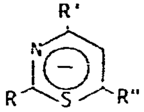


CCCXXXVIII

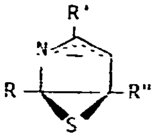
Considering ring systems with two different kinds of heteroatoms, the conversion of 2H-, 4H-, and 6H-1,3-thiazines to pyrrole anions CCCXXXIX by means of organolithium reagents at low temperatures apparently proceeds via 1,3-thiazine anions CCCXL which are energy rich 8-π-electron systems [332]. Extrusion of sulfur is said to occur from intermediate CCCXLI.



CCCXXXIX

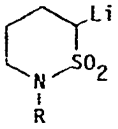


CCCXL

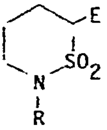


CCCXLI

N-methyl and N-phenylbutanesultam have now been α-metalated to afford CCCXLII and condensed with benzyl chloride, aldehydes, ketones, methyl benzoate, and benzonitrile to give CCCXLIII [333].



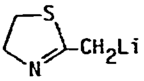
CCCXLII

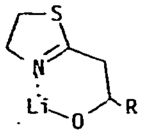


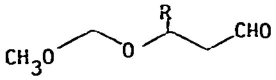
CCCXLIII

Metalated 2-methyl-2-thiazoline (CCCXLIV) has been alkylated then converted, after reduction, to aldehydes using neutral hydrolysis conditions [334]. Di- and trialkylation may also be effected to ultimately afford di- and trialkylated aldehydes, respectively. Treatment of CCCXLIV with aldehydes gives

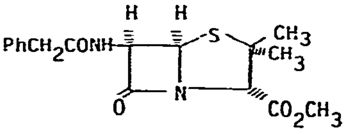
CCCXLV which have been trapped with chloromethyl methyl ether [335]. Subsequent reduction and hydrolysis gives aldehydes CCCXLVI which enter into Wittig condensations to ultimately afford homoallylic alcohols.

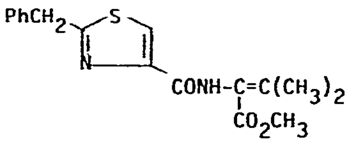

CCCXLIV


CCCXLV

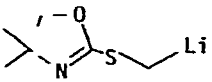

CCCXLVI

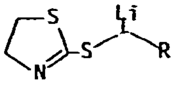
Rather than the expected alkyl-oxygen cleavage of the methyl ester of Penicillin G (CCCXLVII) upon treatment with lithium *t*-butylmercaptide, a novel-base promoted rearrangement has been observed to give thiazole CCCXLVIII [336]. Possible pathways to the thiazole product are suggested.


CCCXLVII

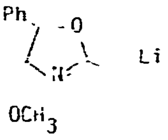

CCCXLVIII

Condensations of lithiated systems CCCXLIX [337] and CCCL [338] with aldehydes and ketones have been found to constitute convenient syntheses of thiiranes. Treatment of the latter with phosphines or phosphites affords olefins. The use of several other lithiated sulfur-containing molecules in thiirane preparations are described [338].

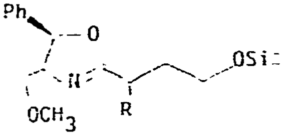

CCCXLIX


CCCL
(R=H or Ph)

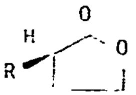
Chiral oxazolines continued to be studied. Thus, treatment of CCCLI with ethylene oxide, chlorotrimethylsilane, LDIPA, and alkyl halides (RX) gave CCCLII the hydrolysis of which afforded (R)-γ-butyrolactones CCCLIII (58-92%) [339]. The optical purity of CCCLIII ranged from 64.2% to 73.3%. Lithium aluminum hydride reduction of two of the lactones (R=n-C_3H_7 and allyl) gave the corresponding 2-alkylated (R)-1,4-butanediols (90-92%).



CCCLI

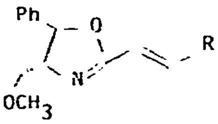


CCCLII

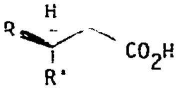


CCCLIII

α,β-Unsaturated oxazolines CCCLIV have been found to undergo conjugate additions with several organolithium reagents to afford, after hydrolysis, 3-substituted carboxylic acids (CCCLV) in high enantiomeric purity [340]. The addition reactions represent the first examples of chiral oxazolines acting as electrophiles.

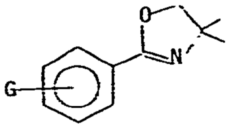


CCCLIV

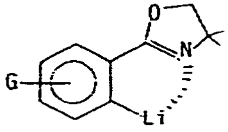


CCCLV

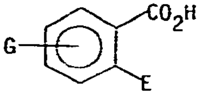
A variety of substituted aryloxazolines CCCLVI have been o-lithiated to afford CCCLVII, then condensed with electrophiles and hydrolyzed to give substituted benzoic acids CCCLVIII [341, 342, 343]. The sequence represents a convenient source of o-substituted carbonyl-containing derivatives.



CCCLVI

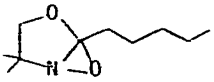


CCCLVII

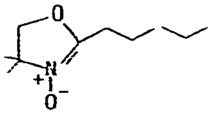


CCCLVIII

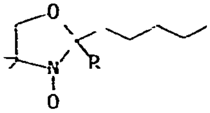
Finally, oxidation of oxazolines by m-chloroperbenzoic acid to oxaziridines CCCLIX, isomerization to nitrones CCCLX, addition of vinyllithium or certain Grignard reagents, and oxidation has been found to constitute a new, facile synthesis of doxyl spin labels CCCLXI [344].



CCCLIX

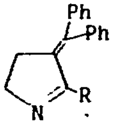


CCCLX

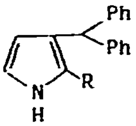


CCCLXI

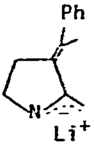
Not surprisingly, heterocycles containing only one nitrogen atom continued to be interacted with organolithium reagents. Thus, treatment of benzylidenes CCCLXII (R=H, CH_3, Ph) with strong basic reagents has been found to afford pyrroles CCCLXIII [345]. When R=CH_3, anion CCCLXIV was trapped with aldehydes and ketones at low temperatures.



CCCLXII

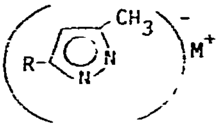


CCCLXIII

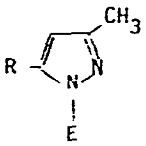


CCCLXIV

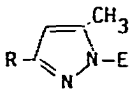
Alkali metal derivatives of three pyrazoles CCCLXIVa have been alkylated in DME and in a liquid-solid suspension in hydrocarbons to afford CCCLXIVb and CCCLXIVc [346]. The ratio of the products is determined both by the size of the alkali metal and by the presence of a coordination center.



CCCLXIVa



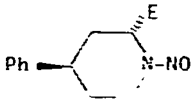
CCCLXIVb



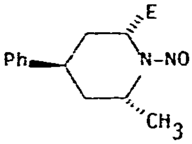
CCCLXIVc

Lithio-N-nitroso-4-phenylpiperidine (CCCLXIVd) has been reacted with electrophiles to give only the axial substitution product CCCLXIVe [347]. Subsequent lithiation and methylation of the latter similarly affords only axial product CCCLXIVf despite the fact that this isomer is the least thermodynamically stable one. A rationale is proposed to explain the results.

CCCLXIVd

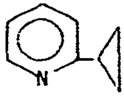


CCCLXIVe

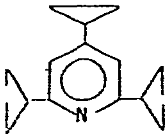


CCCLXIVf

Pyridine, quinoline, pyrimidine, and other related heterocycles have been treated with cyclopropyllithium to afford mostly 2-substituted products like CCCLXIVg [348]. As many as three cyclopropyl groups have been so placed on some of these hetereocycles to give species like CCCLXIVh.

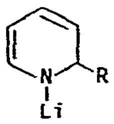


CCCLXIVg

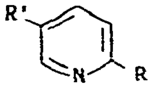


CCCLXIVh

Reaction of certain organolithium adducts of pyridine (CCCLXIVi) with disulfides has been found to afford 5-thiosubstituted pyridines (CCCLXIVj, R'=SPh and others) [349]. Similar results were found with epoxides to give alcohols like CCCLXIVj (R'=CH_2CH_2OH) [350]. Reactions of CCCLXIVi with other electrophiles are discussed.

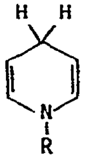


CCCLXIVi

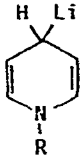


CCCLXIVj

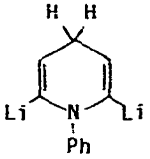
Attempted metalation of dihydropyridine CCCLXV (R=SO_2Ph) with organolithium reagents failed presumably because of the antiaromaticity of the product CCCLXVI [351]. Interestingly, metalation of CCCLXV (R=Ph) afforded CCCLXVII as evidenced by deuteration. Certain sulfonamides with α-hydrogens were also studied.



CCCLXV



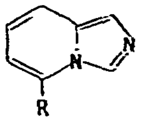
CCCLXVI



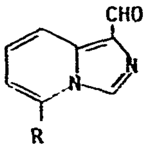
CCCLXVII

3-Picoline has now been conveniently metalated by LDIPA in THF-HMPA, then condensed with electrophiles to provide an improved synthetic route to 3-substituted pyridines [352].

In the area of larger nitrogenous heterocycles, imidazo[1,5-a]pyridines CCCLXVIII have been metalated, then formylated with DMF to give CCCLXIX [353].

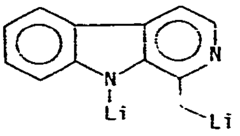


CCCLXVIII

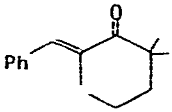


CCCLXIX

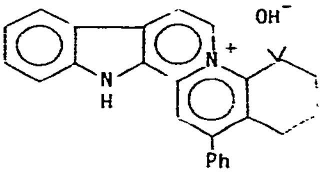
Condensation of dilithioharman (CCCLXX) with α,β-unsaturated ketone CCCLXXI has been found to afford quinolizinium salt CCCLXXII [354]. Other lithiomethylated heterocycles behave similarly in such cyclizations which previously were effected only by acid.



CCCLXX

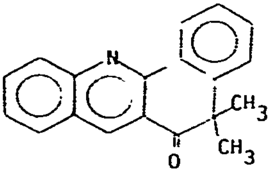


CCCLXXI

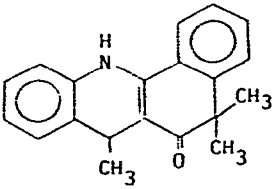


CCCLXXII

Finally, heterocycle CCCLXXIII has been conjugatively methylated by lithium dimethyl copper to give CCCLXXIV [355]. Similar results on other related hetereocycles have been described [356].

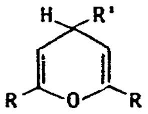


CCCLXXIII

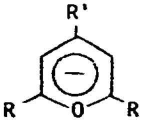


CCCLXXIV

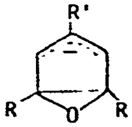
Under the topic of miscellaneous heterocycles, several pyrans (CCCLXXV) have been metalated to apparently afford CCCLXXVI which gives CCCLXXVII [357]. The latter compound then reacts with n-butyllithium to yield CCCLXXVIII or a cyclopentadiene derivative which has been trapped.



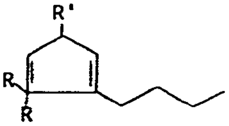
CCCLXXV



CCCLXXVI

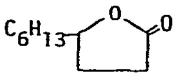


CCCLXXVII

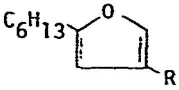


CCCLXXVIII

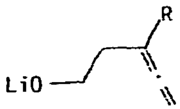
Metalation, alkylation, and selenenylation of five γ-lactones followed by elimination and reduction has afforded a general synthesis of furans [358]. The process is illustrated by the conversion of CCCLXXIX to CCCLXXX.



CCCLXXIX



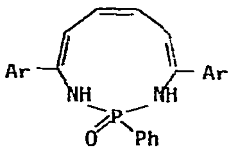
CCCLXXX



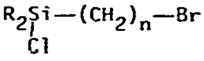
CCCLXXXI

Reaction of 3-chloro-2-methyl-4,5-dihydrofuran with methyl- and butyllithium affords CCCLXXXI via a chloroallene [359]. Results with other substituted dihydrofurans are discussed.

Upon dimetalation, 1-phenyl-3-phospholene has been converted directly to CCCLXXXII by treatment with aromatic nitriles [360]. Cyclic acylsilanes have now been conveniently prepared by dialkylating lithiodithiane by CCCLXXXIII to afford CCCLXXXIV and then hydrolyzing [361].

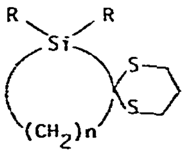


CCCLXXXII



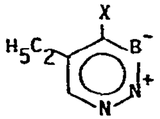
$R_2\underset{\mathrm{Cl}}{\mathrm{Si}}-(CH_2)_n-Br$

CCCLXXXIII



CCCLXXXIV

Certain halogenated borazaropyridines like CCCLXXXV have been subjected to halogen-metal exchange and the intermediate lithio compounds reacted with electrophiles to offer a new route to substituted derivatives of this heterocycle [362].



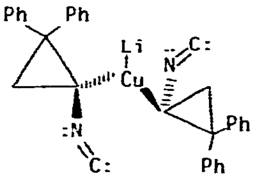
CCCLXXXV

Finally, condensations of the multiple lithium salts of certain phenylhydrazones and oximes with acid chlorides, aldehydes, and diethyl oxalate has afforded a variety of 4-acylpyrazoles [363], 2-pyrazolines [364], and bis-isoxazoles, bipyrazoles, and pyridazones [365].

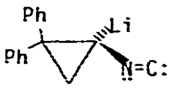
8. COPPER-LITHIUM REAGENTS AND THEIR REACTIONS

A convenient precursor for the preparation of lithium organocuprates, $(CH_3)_2SCuBr$, has been described which is easily prepared from dimethylsulfide and pulverized copper(I) bromide [366]. The crystalline complex is readily soluble in ethers containing dimethylsulfide and is conveniently separated from reaction products as illustrated in several conjugate addition reactions involving two different lithium organocuprates.

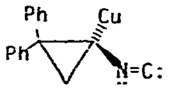
Stable, chiral, copper reagent CCCLXXXVI has been prepared from the corresponding organolithium compound (CCCLXXXVII) and has been found to be intermediate in stability between CCCLXXXVII and CCCLXXXVIII [367].



CCCLXXXVI

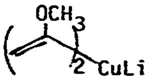


CCCLXXXVII

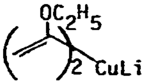


CCCLXXXVIII

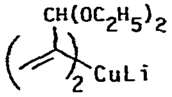
Other new lithium organocuprates recently described include α-methoxycuprate CCCLXXXIX [368], α-ethoxycuprate CCCXC [369], homocuprate CCCXCI [370] and acetylenic isopropenyl cuprate CCCXCII [370]. Each of these species was found to undergo conjugate addition reactions with various enones.



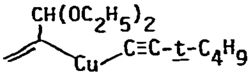
CCCLXXXIX



CCCXC

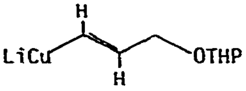


CCCXCI

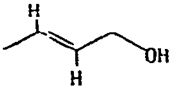


CCCXCII

Also newly prepared was cuprate CCCXCIII which has been conjugatively added to enones [371]. This reagent represents a convenient method for the nucleophilic introduction of CCCXCIV, a reagent useful in the preparation of medium-large rings.

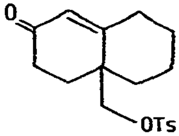


CCCXCIII

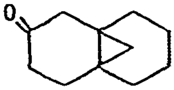


CCCXCIV

Two papers discussed the mechanistic aspects of the conjugate additions of lithium dimethylcuprate to CCCXCV to afford CCCXCVI [372, 373]. The first suggested that the process occurred by a two electron transfer since no esr signal due to an unpaired electron could be observed [372]. In connection with work on related acetates and tetrahydropyranates, the other paper suggested the reaction proceeded via single electron transfer to give an anion radical which could either undergo a 1,2-elimination or a methyl radical transfer depending upon the ability of acetate, tosylate, or tetrahydropyranate to leave [373].

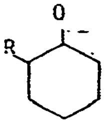


CCCXCV

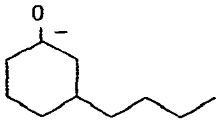


CCCXCVI

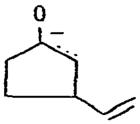
The relative rates of alkylation versus equilibration of lithium dialkylcuprate derived enolate ions CCCXCVII from 2,6-dibromocyclohexanones, CCCXCVIII from cyclohexenones, and CCCXCIX from 2-cyclopentenones have been studied [374]. Though such alkylations are faster than equilibrations with highly reactive alkyl halides, only CCCXCVIII reacts faster with *n*-alkyl iodides than it equilibrates. This paper also describes the preparation of the new reagent, lithium methyl(vinyl)cuprate.



CCCXCVII

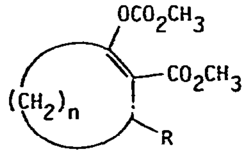


CCCXCVIII

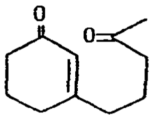


CCCXCIX

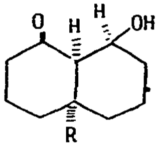
Similarly derived enolate ions have been condensed with methyl chloroformate to afford carbonates like CD [375] and with keto-α,β-unsaturated ketones like CDI to give cyclic products like CDII [376]. The former systems (CD) ultimately can lead to β-alkylalkanedioic acids while the latter reactions represent a new reaction, namely a combination of conjugate addition with directed intramolecular aldol condensation. Enolates have also been similarly trapped with aldehydes [377] and acid chlorides [378].



CD



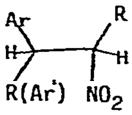
CDI



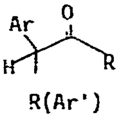
CDII

Organocuprates have been employed in total syntheses of certain prostaglandins [379, 380, 381], in the preparation of prostanoic acid [382], and in the synthesis of juvenile hormone analogs [383]. The first three papers utilized conjugate addition reactions on 2-cyclopentenones; in one case, the enolate ion was trapped with formaldehyde [381]. The latter two papers used conjugate additions on 1-cyclopentenecarboxaldehyde and acetylenic esters and amides, respectively. A similar conjugate addition has been employed in a synthesis of d,l-muscone [384].

Organocuprates have been conjugatively added to other systems besides α,β-unsaturated carbonyl compounds. Thus, the use of nitrostyrenes has afforded nitroalkanes CDIII which are easily converted to ketones CDIV [385]. The method is equivalent to α-alkylation or α-arylation by using R_2CuLi or Ar_2CuLi, respectively.

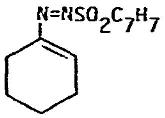


CDIII

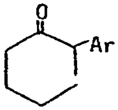


CDIV

The synthetic equivalent of α-arylation of ketones has also been achieved by the addition of lithium diphenylcuprate or phenylcopper to toluenesulfonylazocycloalkenes like CDV [386]. Carbonyl exchange with acetone and boron trifluoride etherate affords ketones like CDVI.

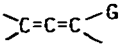


CDV

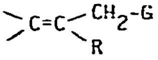


CDVI

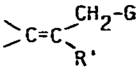
Allenes substituted on C-1 with phosphine oxides, sulfones, or sulfoxides (CDVII) undergo attack at C-2 by a variety of lithium organocuprates (RR'CuLi) to give CDVIII and/or CDIX depending on the cuprate [387]. Intermediate organometallics have been trapped with various electrophiles. In another study, it was determined that such addition reactions occur *trans* to the group on C-3 [388].



CDVII

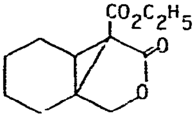


CDVIII



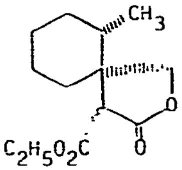
CDIX

Finally, cyclopropyl systems CDX and CDXI have been found to afford CDXII [389] and CDXIII [390], respectively with lithium dimethylcuprate. Other examples are cited.

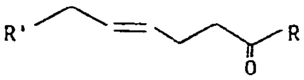


CDX

CDXI

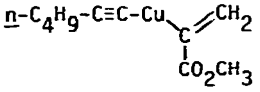


CDXII



CDXIII

Certain organocuprates have been found to add in a 1,2-fashion to a variety of α,β-unsaturated ketones and aldehydes. Thus, CDXIV so adds to 14 unsaturated systems to afford alcohols mostly in fair to excellent yields [391]. Similarly, the alkynyl groups of dilithium trialkynylcuprates like CDXV are transferred to the carbonyl carbon of seven cyclic enones (85-94%) provided 20% HMPA is employed as a co-solvent [392].



$\underline{n}\text{-}C_4H_9\text{-}C{\equiv}C\text{-}Cu\text{-}C(=CH_2)CO_2CH_3$

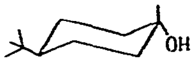
CDXIV

$(CH_3CH_2CH_2C{\equiv}C)_3CuLi_2$

CDXV

A combination of methyllithium-lithium dimethylcuprate has been determined to be a highly effective agent for the conversion of unhindered, conformationally biased cyclohexanones to methyl carbinols in which the methyl group is found nearly exclusively in equitorial positions [393]. For example, *t*-butylcyclohexanone is converted to CDXVI (94%) and CDXVII (6%). The authors speculate that the structure of the organometallic reagent is $(CH_3)_3CuLi_2$ or $(CH_3)_4CuLi_3$.

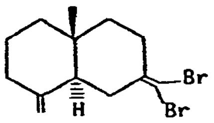
CDXVI



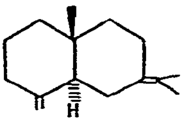
CDXVII

Finally, a variety of both aliphatic and aromatic aldehydes have been found to undergo 1,2-addition to afford secondary alcohols [394]. For example, lithium dimethylcuprate with benzaldehyde, heptaldehyde, and others gave the corresponding methyl carbinols (>90%).

Carbon-carbon bond formation via alkyl halides or related compounds and lithium organocuprates continued to be studied. Thus, several vinylidene bromides like CDXVIII have been converted to isopropylidene systems like CDXIX (82-95%) [395]. Since the dibromides are conveniently prepared from ketones and triphenylphosphine-carbon tetrabromide, the overall process is an isopropylidenation of ketones.



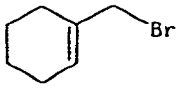
CDXVIII



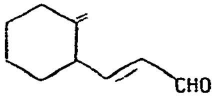
CDXIX

Copper reagent CDXX prepared from the corresponding lithium compound has been found to add in an SN_2' fashion to allylic bromides like CDXXI to afford, upon hydrolysis, aldehydes like CDXXII [396]. Compound CDXX thus acts as a synthon of CDXXIII. Results with other alkylthiocopper reagents are discussed.

CDXX



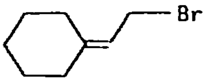
CDXXI



CDXXII

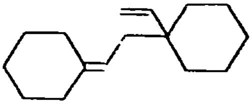
CDXXIII

Several lithium dialkylamides have been reacted with cuprous iodide to give a complex capable of effecting direct conversion of allylic halides to 1,5-dienes with preservation of stereochemistry [397]. The process is illustrated by the conversion of CDXXIV by lithium pyrrolidide and cuprous iodide to CDXXV (55%), CDXXVI (43%), and CDXXVII (2%).

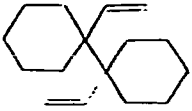


CDXXIV

CDXXV



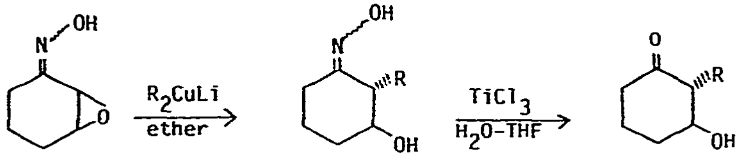
CDXXVI



CDXXVII

Seven ketone lithium enolates have been dimerized to the corresponding 1,4-diketones by cupric chloride [398]. For example, lithioacetophenone is converted to 1,4-diphenylbutan-1,4-dione (83%). Cross-coupling reactions have also been effected between certain ketones or between ketones and esters.

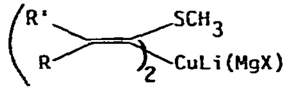
α-Alkylated β-hydroxyketones have been obtained by reaction of lithium dimethyl- and dibutylcuprate to α,β-epoxy oximes [399]. The sequence is shown for the conversion of CDXXVIII to CDXXIX (Eq. 19).



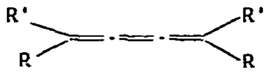
(19)

CDXXVIII CDXXIX

Reaction of seven different alkylthiovinylcuprates (CDXXX) with methyl iodide has been determined to give stereospecifically cis-cumulenes CDXXXI [400]. In another paper, a mechanistic scheme is proposed to account for the formation of allenes from the reactions of lithium diorganocuprates with propargylic acetates [401].

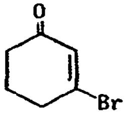


CDXXX

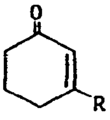


CDXXXI

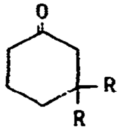
The reaction of β-bromo-α,β-unsaturated ketones like CDXXXII with four different organocuprates conveniently affords β-alkyl systems CDXXXIII (70-95%) [402]. The use of three equivalents of the organometallic reagent on the starting ketones gives β,β-dialkyl compounds like CDXXXIV.



CDXXXII

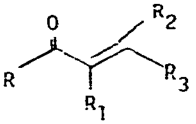


CDXXXIII

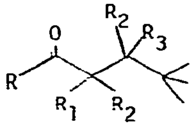


CDXXXIV

Alkylations of α-bromoketones by lithium organocuprates continue to be studied. Thus, while α,α'-dibromosystems afford either mono- or dialkylation depending upon conditions [403], monobromo systems regiospecifically give monoalkylated products at the site originally occupied by the bromine atom [404]. On the other hand, treatment of α-bromoketones possessing β-hydrogens with lithium di-t-butylcuprate apparently gives dehydrohalogenated intermediates like CDXXXV since subsequent alkylations afford products like CDXXXVI which contain the t-butyl group [405].



CDXXXV

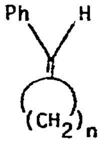


CDXXXVI

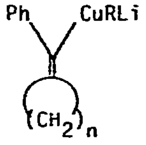
With respect to miscellaneous cuprate chemistry, α,β-epoxysilanes have been found to react with cuprates both regio- and stereospecifically to afford olefins via β-hydroxysilanes [406]. The ring opening of a substituted aziridine by lithium dibutylcuprate has been described as a key step in the preparation of (±)-perhydrohistrionicotoxin [407]. Reaction of ω-halogenated internal acetylenes like CDXXXVII with three cuprates affords, among other products, cyclic alkenes like CDXXXVIII [408]. The reactions apparently proceed via a metal-halogen exchange to give ω-cuprates cyclization of which yields species like CDXXXIX.

$PhC{\equiv}C(CH_2)_nX$

CDXXXVII



CDXXXVIII

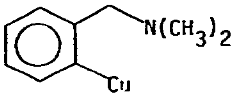


CDXXXIX

A large number of α,β-unsaturated ketones and esters have been converted to the corresponding saturated systems by CDXL and a related sodium complex [409]. Reduction of enones as a side reaction from the thermal decomposition of various cuprates to form copper hydrides has been discussed [410]. Finally, the chemistry of CDXLI and related compounds, prepared from the corresponding lithium reagents, has been described [411, 412].

$2LiAlH(OCH_3)_3 \cdot CuBr$

CDXL



CDXLI

Turning to the area of boronate complexes, reaction of lithiodimethyl sulfide with trialkylboranes gives CDXLII which, upon treatment with alkylating agents like methyl iodide, affords homologated organoboranes like CDXLIII [413]. Specific examples are described including the conversion of aryl- and vinylboranes to benzyl- and allylboranes, respectively.

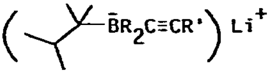
$(CH_3SCH_2\bar{B}R_3)Li^+$

CDXLII

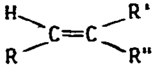
R_2BCH_2R

CDXLIII

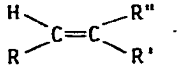
Alkylation of CDXLIV with a variety of electrophiles (R"X) has led to olefins CDXLV and CDXLVI in a ratio of about 9:1, respectively [414]. Interestingly, the alkyl group (R) migrating from the boron and the one introduced by alkylation (R") are cis to one another in the major product.



CDXLIV



CDXLV

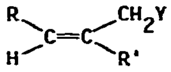


CDXLVI

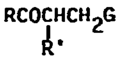
The use of propargyl bromide and iodoacetonitrile in similar reactions on CDXLVII has been found to give CDXLVIII or CDXLIX upon hydrolysis or oxidation, respectively [415].

$(R_3\bar{B}C{\equiv}CR')Li^+$

CDXLVII



CDXLVIII



$RCO\underset{R'}{\underset{|}{C}}HCH_2G$

CDXLIX

Acylation of lithium borate systems with acid chlorides has been found to give ketones. Thus, aryltrialkyl systems like CDL afford only mono- or diaryl ketones while strictly aliphatic systems like CDLI give aliphatic or monoaryl ketones depending upon the choice of acid chloride (R"COCl) [416, 417].

$(Ph\bar{B}R_3)Li^+$ CDL

$(R_4\bar{B})Li^+$ CDLI

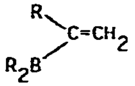
Alkylation of acetylenicborate CDLII with a tosylate ester has been employed in a facile synthesis of propylure [418]. Treatment of another acetylenic system, CDLIII, with ethylene oxide affords either (Z)- or (E)-3-methyl-3-octen-1-ol depending on whether the reactions are run in dichloromethane or THF, respectively [419].

$[(\underline{n}\text{-}C_3H_7)_3\bar{B}\text{-}C{\equiv}CSi(CH_3)_3]Li^+$ CDLII

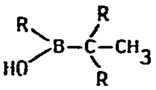
$[(\underline{n}\text{-}C_4H_9)_3\bar{B}\text{-}C{\equiv}C\text{-}CH_3]Li^+$ CDLIII

Protonolysis of ethynyltrialkylborates at -78° affords the Markovnikov organoborane as illustrated by the conversion of CDLIV to CDLV [420]. Subsequent oxidation of the latter gives ketones. Similar reactions of ethenyltrialkylborates lead to the formation of Markovnikov alcohols. Such products are obtained as a result of the migration of an alkyl group from boron to carbon. In contrast, protonolysis of CDLIV and other alkynyl systems at temperatures greater than -78° afford species like CDLVI arising from double alkyl migration [421]. The ultimate products in the latter conversions are tertiary alcohols.

$(R_3\bar{B}C{\equiv}CH)Li^+$ CDLIV



CDLV



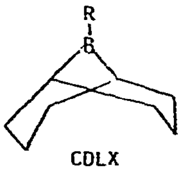
CDLVI

Dialkynylborates like CDLVII have been reacted with iodine to afford symmetrical diynes like CDLVIII in high yields [422] while di-, tri-, and tetrasubstituted ethylenes have been obtained by interacting bisborates CDLIX with cyanogen bromide [423]. The use of iodine on CDLIX gives symmetrical acetylenes [424].

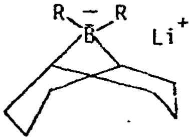
$[R_2\bar{B}(C\equiv CR')_2]Li^+$ $R'C\equiv C-C\equiv C-R'$ $(R_3\bar{B}-C\equiv C-\bar{B}R_3)2Li^+$

CDLVII CDLVIII CDLIX

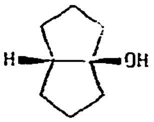
In contrast to the oxidation of organoboranes like CDLX, that of corresponding borates CDLXI has been found to give mostly bicyclic alcohol CDLXII and cyclooctanone [425]. This new sequence provides a convenient route to the bicyclo[3.3.0]octane system.



CDLX



CDLXI



CDLXII

In regard to other types of ate complexes, several lithium alanates, prepared by reaction of alkenyllithiums with trialkylaluminums, have been added to substituted cyclopentenones as part of the synthesis of prostaglandins and congeners [426]. Interaction of several lithium methyl ate complexes of beryllium with lithium aluminum hydride and alane have been studied as a source of complex metal hydrides of berylium [427]. Among such hydrides so prepared were CDLXIII—CDLXV.

$LiBeH_3$ Li_2BeH_4 Li_3BeH_5

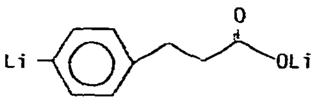
CDLXIII CDLXIV CDLXV

Finally, lithium tetraphenyl- and tetramethylniccolate [428] and lithium tetramethyllaurate [429] have now been synthesized.

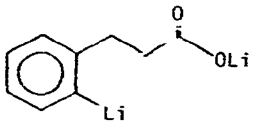
9. LITHIUM-HALOGEN EXCHANGE REACTIONS

Certain carbanions prepared by lithium-halogen exchange which have a tendency to abstract hydrogen atoms from solvent so rapidly that they can not be reacted with electrophiles have now been successfully trapped [430]. The tecnnique involves preparing the organometallic in the presence of the co-reagent and is illustrated by the conversion of haloaromatics to tritiated and trimethylsilylated systems.

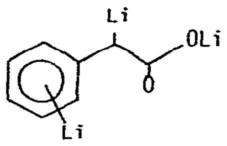
Additional evidence has been provided that the prior formation of lithium carboxylates offers ample protection against attack by organolithium reagents provided the temperature is maintained at -100° [431]. Thus, o- and p-bromophenylpropanoic acids have been converted to dianions like CDLXVI and CDLXVII. The former species has been trapped with electrophiles while the latter one cyclizes to indanones. The chemistry of similar anions derived from bromophenylacetic acids including CDLXVIII as well as that of certain anions prepared from carboxamides is discussed.



CDLXVI

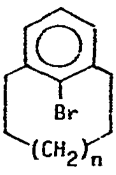


CDLXVII

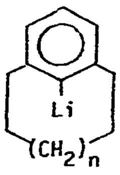


CDLXVIII

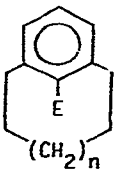
Several metacyclophanes (CDLXIX) have been converted to the corresponding lithium reagents CDLXX then condensed with electrophiles to afford CDLXXI [432]. The electrophiles employed included alkylating agents, aldehydes and ketones, oxygen, and others.



CDLXIX

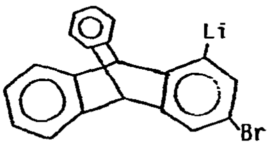


CDLXX

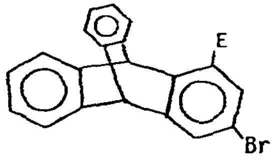


CDLXXI

Of the two bromine atoms of 1,3-dibromotriptycene, only that at the 1-position has been found to undergo halogen-metal exchange with n-butyllithium to afford CDLXXII [433]. Subsequent condensations with acetone and carbon dioxide gave 1-substituted products CDLXXIII.

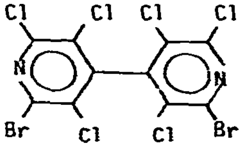


CDLXXII

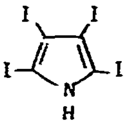


CDLXXIII

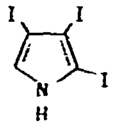
Treatment of bipyridine CDLXXIV with n-butyllithium affords lithium-bromine but not lithium-chlorine exchange [434]. Various hypotheses are discussed concerning the site of such reactions on halogenated pyridines and it is concluded that the fact that metal-halogen exchange and nucleophilic substitution occur at the same position of these molecules in many cases is largely fortuitous. In another study, the action of n-butyllithium·TMEDA on tetraiodopyrrole (CDLXXV) followed by hydrolysis has been shown to give a mixture of di- and triiodopyrroles; product CDLXXVI predominates (63%) [435].



CDLXXIV

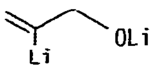


CDLXXV

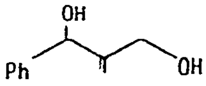


CDLXXVI

Dilithio system CDLXXVII, a potentially useful intermediate, has been conveniently generated from the corresponding bromoalcohol and t-butyllithium [436]. Condensations of CDLXXVII with aldehydes and ketones affords 1,3-glycols; for example, benzaldehyde gives CDLXXVIII.

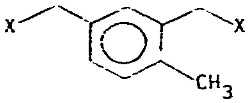


CDLXXVII

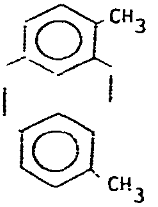


CDLXXVIII

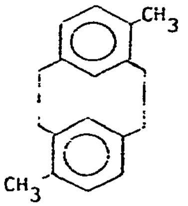
In contrast to earlier results, it has been demonstrated that coupling of CDLXXIX (X=Br) by basic reagents like phenyllithium affords a mixture of CDLXXX and CDLXXXI which seems uniform by glc and 60 MHz proton nmr [437]. Earlier workers indicated that coupling of CDLXXIX (X=Cl) gave CDLXXX only.



CDLXXIX

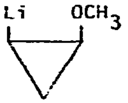


CDLXXX

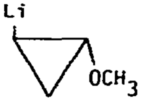


CDLXXXI

New cyclopropyllithium reagents, CDLXXXII and CDLXXXIII, have been prepared from the corresponding bromocyclopropanes and *t*-butyllithium [438]. Reaction of these species with aldehydes and ketones has ultimately led to *trans*-β,γ-unsaturated aldehydes.

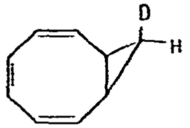


CDLXXXII



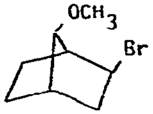
CDLXXXIII

A stereospecific synthesis of bicyclo[6.1.0]nonatriene-*syn*-9-d (CDLXXXIV) has been described involving the reaction of the *syn*-9-bromo compound, *n*-butyllithium, and deuterium oxide [439]. The epimerization of CDLXXXIV was studied and a mechanism proposed for the transformation.

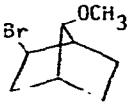


CDLXXXIV

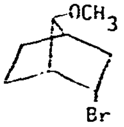
Interaction of n-butyllithium with isomeric bromides CDLXXXV, CDLXXXVI, and CDLXXXVII has been studied in terms of investigating intramolecular coordination between lithium and oxygen [440]. Though the first compound reacts very rapidly, the other two failed to so react after 2.5 hours presumably because such coordination was absent.



CDLXXXV



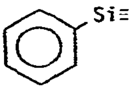
CDLXXXVI



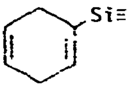
CDLXXXVII

10. REDUCTIONS AND RADICAL ANIONS

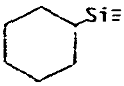
A large number of aryltrimethylsilanes have been reduced by lithium-ethanol-ammonia (Birch reduction) and by lithium-ethylamine (Benkeser reduction [441, 442]. For example, CDLXXXVIII is converted to CDLXXXIX and XD by these reducing agents, respectively. Some of the reductions resulted in the cleavage of trimethylsilyl groups, particularly those at allylic or benzylic positions.



CDLXXXVIII

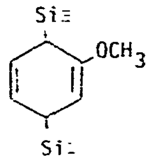


CDLXXXIX

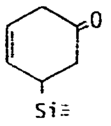


XD

Several aromatic ethers have been reduced by lithium in THF in the presence of chlorotrimethylsilane as illustrated by the conversion of anisole to XDI; hydrolysis gave XDII [443]. A tetracyclic aromatic methyl ether has been reduced under Birch conditions to a cyclohexenone as part of a study directed towards the total synthesis of (±)-shionone [444].

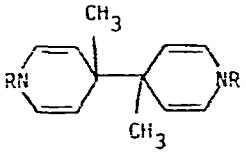


XDI

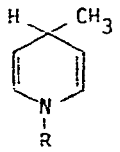


XDII

Lithium-ammonia reduction of 4-picoline followed by addition of an electrophile affords 4,4'-bipyridyls XDIII (R=H, CH_3, C_3H_7, carbomethoxy) (92-100%) [445]. In contrast, dihydropyridines XDIV are obtained with lithium-ethanol-ammonia.

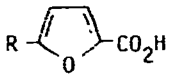


XDIII

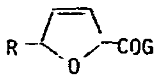


XDIV

2-Furoic acid and nine 5-substituted 2-furoic acids XDV have been reduced to dihydro compounds XDVI by lithium-alcohol-ammonia [446, 447]. Ring cleavages and trapping experiments are discussed.



XDV



XDVI
(G=OH, OCH_3)

Interaction of ethylene with lithium, biphenyl, and naphthalene in DME gives vinyllithium, 1,4-dilithiobutane, 1,6-dilithiohexane, 3-butenyllithium, n-butyllithium, and possibly lithium hydride as evidenced by various trapping experiments [448]. The author proposes that XDVII and XDVIII may be intermediates

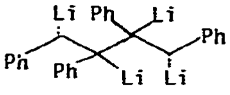
$Li\text{-}CH_2\text{-}CH_2^{\cdot}$

XDVII

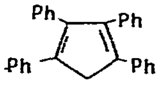
$Li\text{-}CH_2\text{-}CH_2\text{-}Li$

XDVIII

Reduction of *cis,cis*-1,2,3,4-tetraphenylbutadiene by lithium in THF affords tetralithium species XDIX which is apparently quite stable [449]. Deuterolysis yields the tetradeuterated *dl*- and *meso*-saturated butane derivatives (86%). The anion radicals of D and DI have been prepared similarly; the latter species dimerize to diallenic hydrocarbons (82-90%) [450,451].



XDIX

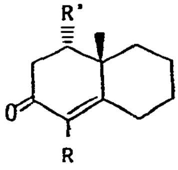


D

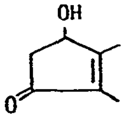
$RC{\equiv}CCH{=}CH_2$

DI

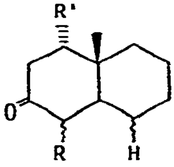
Lithium-ammonia reductions of DII and DIII to afford DIV and DV, respectively have been studied in terms of the stereochemistry of the products [452, 453]. With the former compounds, the resulting *cis*-fused decalones constituted 13-35% of the product mixtures, percentages higher than expected. In the case of DIII, the stereochemistry observed was a function of the acidity of the alcohol co-reagent.



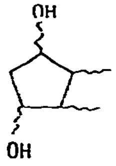
DII



DIII

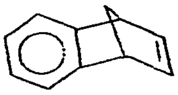


DIV

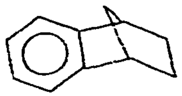


DV

Several benzobicyclic olefins have been reduced by lithium-*t*-butyl alcohol-ammonia as illustrated by the conversion of DVI to DVII [454]. The olefin to be reduced must be in constrained proximity to the aromatic ring in order for the reaction to be successful.

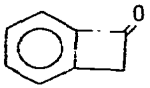


DVI

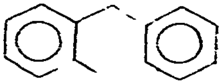


DVII

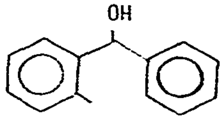
The synthesis of hydrocarbons by phenylation-reduction continued to be studied. Thus, a large number of ketones have been treated with phenyllithium and the resulting alkoxides then reduced by lithium to give the hydrocarbons after introduction of ammonia [455, 456]. The process is illustrated by the conversion of DVIII to DIX (93%). Interestingly, quenching of the latter reaction with sodium benzoate instead of ammonium chloride affords alcohol DX (86%). In another study, it has been found that benzylic alcohols can be converted to the corresponding hydrocarbons (88-100%) by lithium-ammonia-ammonium chloride [457].



DVIII

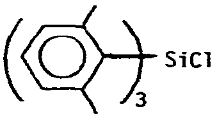


DIX

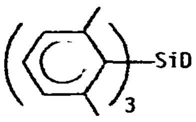


DX

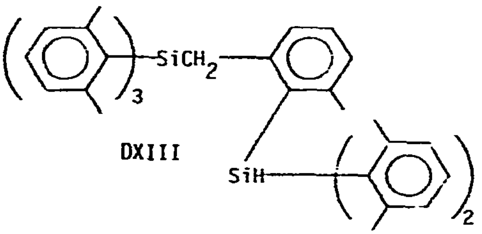
tris-(2,6-Xylyl)chlorosilane (DXI) has been reacted with lithium metal in THF followed by deuterium oxide to give DXII (41%) and DXIII (42%) [458]. The latter product apparently arises from the coupling of DXI with the novel rearranged intermediate DXIV. The presence of benzosilacyclobutene DXV is also discussed.



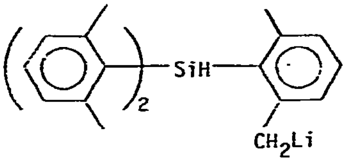
DXI



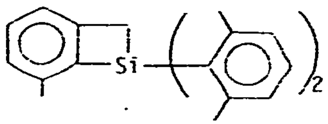
DXII



DXIII

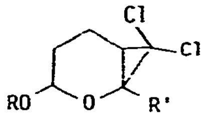


DXIV

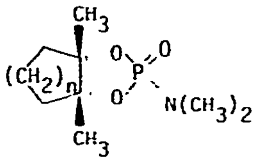


DXV

Several substituted dichloronorcaranes (DXVI) have been converted to their corresponding unchlorinated cyclopropanes by lithium-ammonia [459]. Cyclic phosphate derivatives DXVII have similarly been converted to alkenes by lithium-ammonia, sodium-naphthalene, or sodium in xylene [460].

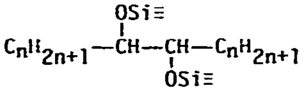


DXVI



DXVII

vic-bis[Trimethylsiloxy]alkanes DXVIII have been prepared by dimerizing aldehydes by lithium in the presence of chlorotrimethylsilane [461]. In DXVIII, n = 3-8 and the yields ranged from 45-63%.



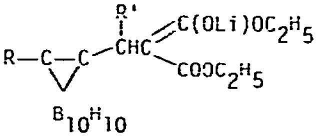
$$C_nH_{2n+1}-\overset{\text{OSi}\equiv}{\text{CH}}-\underset{\text{OSi}\equiv}{\text{CH}}-C_nH_{2n+1}$$

DXVIII

Crotonic acid and several aliphatic nitriles have been metalated by lithium naphthalenide [462] and lithium anthracenylide [463], respectively. Dilithiocrotonate was condensed with several aldehydes to give α- and γ-adducts. Finally, in a different study, methoxytrityl ether derivatives can now be deblocked conveniently by lithium or sodium naphthalenide [464].

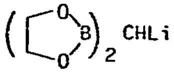
11. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

Several lithium o-carboranes have been found to add in a 1,4-fashion to benzylidene- and ethylidenemalonic esters to afford species like DXIX [465]. These results are to be contrasted with earlier ones on similar esters derived from monocarboxylic acids where 1,2-addition was observed. Certain lithium carboranes have been alkylated to reveal a new rearrangement in the B-alkyl-1,2-dicarbaundecaborate series [466], and have been silylated free of oligomerization side reactions in hydrocarbons [467]. Iridium containing carboranes have also been prepared from lithium carboranes [468, 469].

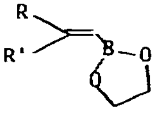


DXIX

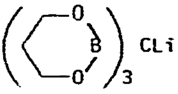
A simple aldehyde homologation has been described which involves the reaction of DXX with aldehydes or ketones (RCOR') to give, upon oxidation, RCH(R')CHO; the reactions apparently proceed via DXXI [470]. The new dioxyborylmethide system, DXXII, has now been synthesized and characterized [471].



DXX



DXXI



DXXII

Lithium dimethylamide has been reacted with a variety of boranes containing nitrogen like DXXIII to afford tris-(trialkylamino)boranes and lithium hydride [472]. Other products are described and mechanisms are proposed. In an unrelated study, the product of the reaction of trimesitylboron with excess lithium has now been ascribed to a dianion rather than to polymeric species [473].

$[(CH_3)_2N]_2BH$

DXXIII

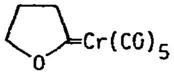
The first optically active titanium organometallics have now been described; in some cases, the only chiral element in such molecules is an asymmetric titanium atom [474]. The effectiveness of certain reduced cyclopentadienyltitanium systems as hydrogenation-catalysts has been increased by a factor of 25-120 by first attaching such molecules before reduction to a styrene-divinylbenzene copolymer [475]. In a different study, additional examples of titanium complexes containing (h^7-C_7H_7) rings have been presented which also possess cyclopentadiene, indenyl, and other ring systems [476]. Reaction of titanium and zirconium tetrachlorides with LDIPA has given the corresponding tetrakis systems DXXIV; similar reaction of the former tetrahalide with lithium hexamethyldisilazane affords DXXV [477]. Interaction of n-butyllithium with MX_3 where M=Ti, Zr, Hf, and Nb and X=S and Se yields DXXVI; structures DXXVI have been confirmed by optical, ir, chemical, and x-ray methods [478]. Finally, conductivity measurements and transference experiments have been obtained on several lithium alkyltitanates [479].

$[(i\text{-}C_3H_7)_2N]_4M$	$ClTi[N(Si\equiv)_2]_3$	Li_3MX_3
DXXIV	DXXV	DXXVI

Simple methylene complexes of tantalum like DXXVII, prepared using thallium or lithium cyclopentadienides, have been isolated and characterized [480]. Spectroscopic studies including nmr and x-ray determinations have been described [480, 481]. The crystal structure of tantalum complex DXXVIII where L is a diamine has also been reported [482].

$Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$	$\{[(CH_3)_3CCH_2]_3Ta\equiv CC(CH_3)_3\}\ LiL$
DXXVII	DXXVIII

Treatment of lithio derivatives of bis-benzenechromium with DMF and dimethylacetamide have given bis-(benzaldehyde)chromium and benzene(acetophenone)-chromium, respectively [483]. Lithiation and subsequent condensation of pentacarbonylchromium species DXXIX with acetaldehyde has been employed to synthesize α-methylene-γ-butyrolactone [484].

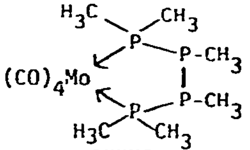


DXXIX

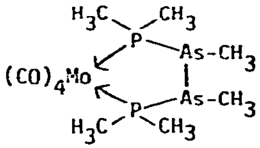
Reactions of DXXX with methyldichlorophosphine and arsine have been found to afford DXXXI and DXXXII, respectively [485].

$Mo(CO)_4[(CH_3)_2PLi]_2$

DXXX

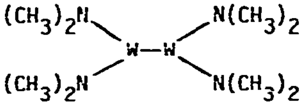


DXXXI



DXXXII

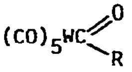
Tungsten-tungsten triple bonds have been reported in DXXXIII and related compounds; DXXXIII was prepared by reaction of tungsten tetrachloride with lithium dimethylamide [486, 487]. Alkyl- and aryl- pentacarbonyltungsten anions DXXXIV (R=alkyl or aryl) have been synthesized by reaction of $((CO)_5WBr)^-$ with alkyl- and aryllithiums, respectively [488]. Such compounds have also been prepared by photolysis of DXXXV.



DXXXIII

$(CO)_5\bar{W}R$

DXXXIV



DXXXV

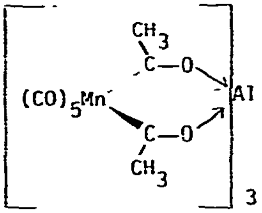
Two new complexes of manganese have been described. Thus, delithiation of DXXXVI has unexpectedly given trinuclear compound DXXXVII [489] while condensation of acetylpentacarbonylmanganese with methyllithium, then aluminum chloride has afforded the first example of a "metallo-acac" anion DXXXVIII [490]. The crystal structures of both products have been determined.

$C_5H_5(CO)_2MnP(C_6H_5)Li_2$

DXXXVI

$[C_5H_5(CO)_2MnPC_6H_5]_3$

DXXXVII



DXXXVIII

The first iron carbonyl compound to contain two methyl groups (DXXXIX) σ-bonded to the iron has been prepared by reaction of methyllithium with DXL and by reaction of methyl iodide with DXLI [491].

$Fe(CH_3)_2(CO)_2[P(CH_3)_3]$

DXXXIX

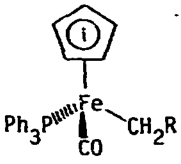
$FeI(CH_3)(CO)_2[P(CH_3)_3]$

DXL

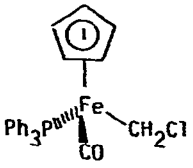
$Na[Fe(CH_3)(CO)_2[P(CH_3)_3]]$

DXLI

Optically pure chiral iron alkyls DXLII have been prepared by reaction of organolithiums or Grignard reagents with resolved DXLIII [492].

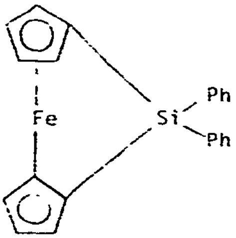


DXLII

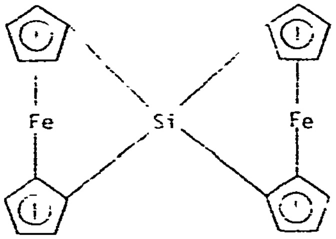


DXLIII

Reactions of 1,1'-dilithioferrocene with dichlorodiphenylsilane and tetrachlorosilane have afforded DXLIV (23%) and DXLV (7%), respectively [493]. Such compounds represent the first examples of [1] ferrocenophanes.



DXLIV



DXLV

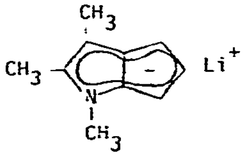
(Ferrocenylmethyl)diphenylphospine oxide (DXLVI) and sulfide DXLVII have been di- and monometalated, respectively on the alpha carbon atoms to give lithium reagents that have been alkylated [494]. In unrelated studies, reaction of iron(II) chloride with DXLVIII has given bis-[1,2,3-trimethylpyrrolo(b)] ferrocene [495] while reaction with 1-substituted borabenzene derivatives has afforded bis-(borabenzene)iron complexes DXLIX [496].

$FcCH_2P(O)Ph_2$

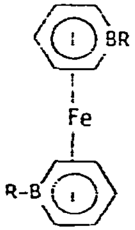
DXLVI

$FcCH_2P(S)Ph_2$

DXLVII



DXLVIII



DXLIX

Reaction of certain nickel-olefin complexes with lithium metal has been found to give crystalline adducts; for example, bis(1,5-cyclooctadiene)nickel and lithium affords DL [497]. Similar interaction of nickel carbonyl has now been shown to give DLI [498]. The role of nickel catalysts in the cross coupling of aryl halides with organolithiums and Grignard reagents [499] and of nickelole intermediates in alkyne oligomerizations has been discussed [500].

$[(COD)_2NiLi_2 \cdot 4THF]$

DL

$[Ni_5(CO)_{12}]^{=}2M^{+}$

DLI

Vinyl halides have been alkylated in high yields at the site of the halide atom by a variety of alkyllithiums and Grignard reagents in the presence of *tetrakis*(triphenylphosphine)palladium [501]. Olefins themselves complexed with certain palladium compounds react with organosodium reagents to afford products arising from allylic alkylation [502]. A number of beta-secondary and tertiary aminomercurials have been converted to the corresponding amines by lithium in the presence of aniline or butylamine [503].

Several new σ-bonded organouranium complexes like DLII have been prepared by reaction of halo-*tris*(cyclopentadienyl)uranium compounds and organolithium and sodium reagents [504]. Similar syntheses of lanthanide complexes DLIII (Ln=Gd, Er, and Yb) have also been reported [505, 506].

$(\eta^5\text{-}C_5H_5)_3UR$

DLII

$(\eta^5\text{-}C_5H_5)_2LnR$

DLIII

In the area of organolithiums applied to organosilicon systems, three papers have described the preparation of the highly hindered tri-*t*-butylsilane (DLIV) by reaction of *t*-butyllithium with various chloro- and fluorosilanes; yields of DLIV as high as 80% have been reported [507, 508, 509]. Some reduction of the halosilanes by the *t*-butyllithium is discussed as are the preparations of other hindered silanes like DLV.

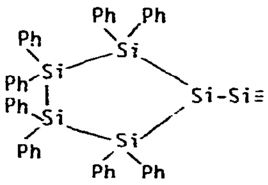
$(\underline{t}\text{-}C_4H_9)_3SiH$

DLIV

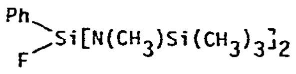
$(\underline{t}\text{-}C_4H_9)_2SiHCH_3$

DLV

Other new organosilicons similarly prepared include cyclosilane DLVI which contains a silicon side-chain [510], silicon-nitrogen-fluorine compounds like DLVII and related ones [511], and two chiral ferrocenylnaphthyl bifunctional silanes DLVIII and DLIX [512].

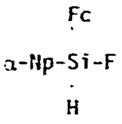


DLVI



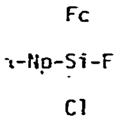
$Ph(F)Si[N(CH_3)Si(CH_3)_3]_2$

DLVII



$\alpha\text{-}Np\text{-}Si(Fc)(H)\text{-}F$

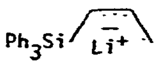
DLVIII



$\alpha\text{-}Np\text{-}Si(Fc)(Cl)\text{-}F$

DLIX

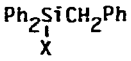
Allylsilyllithium reagents like DLX have been prepared by metalation, then reacted with various electrophiles to generally afford both α- and γ-products [513]. The use of methyl iodide and chlorotrimethylsilane, though, afford only γ-products like DLXI. Other metalations have been achieved on the methylene groups of chloro- and methoxysilanes DLXII [514].



DLX

$Ph_3SiCH{=}CHCH_2E$

DLXI



$Ph_2Si(X)CH_2Ph$

DLXII

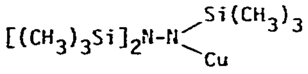
Specific lithium enolates of several cyclic ketones have been prepared by lithium amide cleavage of trimethylsilyl enol ethers in ammonia; subsequent regiospecific alkylations are obtainable since proton transfer under these conditions constitutes an insignificant side reaction [515]. Reaction of DLXIII with t-butyllithium at -95° has been shown to proceed via DLXIV [516]. Copper reagent DLXV, prepared from the corresponding lithium compound, has been found to react with five substituted iodobenzenes to ultimately give substituted phenylhydrazines (45-55%) [517].

$(CH_3)_2SiH(CF_2)_6SiH(CH_3)_2$

DLXIII

$Li(CF_2)_6Li$

DLXIV



$[(CH_3)_3Si]_2N\text{-}N\begin{matrix}Si(CH_3)_3\\Cu\end{matrix}$

DLXV

Triphenylsilyllithium has been reacted with several chiral chloro- and menthoxygermanes to give triphenylsilylgermanes and threo-digermanes, respectively [518]. The latter products arise from metalation of the methoxygermanes. Finally, treatment of uranium (IV) chloride with trimethylsilylmethyllithium has afforded DLXVI [519]. Other organolithiums behave similarly to give additional examples of the first alkyluranium compounds with more than one metal to carbon σ-bond. Similar chemistry of manganese and cobalt is described.

$Li_2U[CH_2Si(CH_3)_3]_6(tmeda)_7$

DLXVI

Seven different organogallium compounds of the type R_3Ga, R_2GaCl, and $RGaCl_2$ have been prepared by reaction of gallium chloride and alkyllithiums [520]. Aminogallanes like DLXVII [521] and tris(aryl)thallium (III) reagents like DLXVIII [522] have been prepared similarly.

$Ga[N(CH_3)_2]_3$

DLXVII

Ph_3Tl

DLXVIII

Group four systems of the periodic table other than those of silicon appropriate for this discussion include the preparation, x-ray, and proton nmr studies on alkali metal germanes [523], the reaction of DLXIX with various peroxides resulting in cleavages of oxygen-oxygen bonds [524], and the preparation of DLXX, a reagent useful for the conversion of aldehydes or ketones to nucleophilic olefins [525]. Other tin compounds recently prepared include DLXXI [526], DLXXII and DLXXIII [527], DLXXIV [528], and bis(dimethylamido)tin (II) [529].

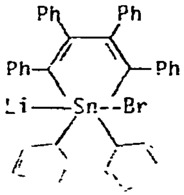
$[(CH_3)_3SiCH_2]_3MLi$

DLXIX

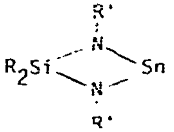
(M=Ge, Sn)

$Ph_3P{=}CHCH_2Sn(CH_3)_3$

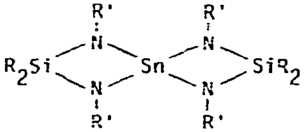
DLXX



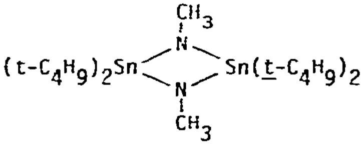
DLXXI



DLXXII



DLXXIII

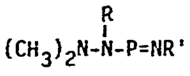


DLXXIV

With respect to group five atoms, reaction of N,N-dichlorocyclohexylamine with DLXXV or a related sodio salt affords trans-azocyclohexane (52-68%) either free (in THF) or complexed with chromium pentacarbonyl [530]. Treatment of lithio-1,2,2-trisubstituted hydrazines with dialkylaminophosphorusdichlorides leads to DLXXVI and DLXXVII [531]. Octamethylcyclotetraphosphazene has been converted to a tetraanion by methyllithium and then condensed with monohalides of silicon, germanium, and tin [532].

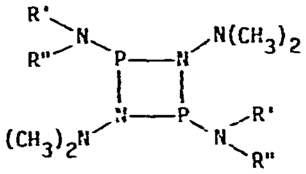
$(CO)_5Cr[C(OLi)(\underline{n}\text{-}C_4H_9)]$

DLXXV



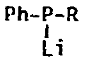
$(CH_3)_2N\text{-}\overset{R}{N}\text{-}P{=}NR'$

DLXXVI



DLXXVII

Polyphosphine dianion salts, $M_2(PPh)_n$, have been investigated by ^{31}P nmr spectroscopy; the authors conclude that $(PPh)_3^{2-}$ is acyclic with only two P-P bonds [533]. Nucleophilic substitution versus metalation of optically active diphenylmethylphosphine has been studied as a function of the organolithium and the medium [534, 535]. The substitution observed proceeds via inversion of configuration at the phosphorus atom. Lithiodiphenylphosphine has been found capable of debrominating 1,2-dibromoalkenes to acetylenes; lithiodiphenylarsine behaves similarly [536]. Related lithiophosphines DLXXVIII cleave THF to give alkyl-4-hydroxyphosphines which have been subsequently cyclized to phospholanium salts [537]. Tetrahydrofuran is similarly cleaved by DLXXIX and the related sulfur compound in the presence of lithium [538].



$Ph\text{-}\underset{\underset{Li}{|}}{P}\text{-}R$

DLXXVIII

$Ph_2P(O)Cl$

DLXXIX

The first stabilized arsinidene, DLXXX, an arsenic analog of a nitrene, has been synthesized by reaction of DLXXXI with N,N-dichlorocyclohexylamine [539].

$PhAs[Cr(CO)_5]_2$

DLXXX

$(OC)_5CrAs(Ph)Li_2$

DLXXXI

Finally, considering the chalcogen family, diimides like DLXXXII and DLXXXIII have been prepared by reaction of organolithiums with sulfinylamines (RNSO) and isocyanates, respectively [540]. The preparations and chemistry of tellurium compounds DLXXXIV and DLXXXV have been described [541]. In a different study, phenyllithium telluride has been alkylated by a variety of alkyl halides to give alkylphenyltelluridides (62-81%) [542].

$R{-}N{=}S{=}N{-}Si(CH_3)_3$

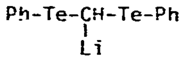
DLXXXII

$R{-}N{=}C{=}N{-}Si(CH_3)_3$

DLXXXIII

$Ph{-}Te{-}CH_2Li$

DLXXXIV



$Ph{-}Te{-}\underset{\displaystyle Li}{\underset{|}{C}H}{-}Te{-}Ph$

DLXXXV

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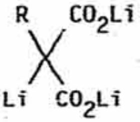
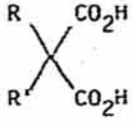
decarboxylation affords monoalkylated derivatives of ethyl acetate; ten different examples are shown [172].



CXLV



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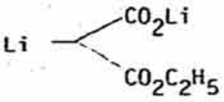
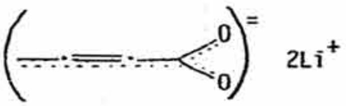
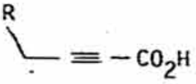


CXLVII

Dilithio-2-butynoic acid (CXLVIII), prepared by metalation of the parent acid, has been alkylated and condensed with cinnamaldehyde to give mixtures of γ- and α-condensation products CXLIX and CL, respectively [173, 174]. The ratios of CXLIX to CL were 2.2:1 and 1:1, respectively.



CXLVIII



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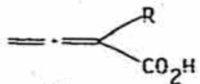
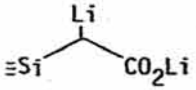
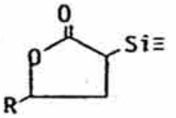


CL

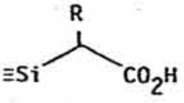
A method has been described to prepare α-trimethylsilyl derivatives of acids and esters without the formation of isomeric O-silylated derivatives [175]. Thus, trimethylsilylacetic acid has been dimetalated with LDIPA to afford CLI. Condensations of CLI with epoxides, aldehydes (ketones), and alkyl halides give α-silyllactones like CLII, α,β-unsaturated acids (83-90%), and alkylated derivatives CLIII (60-98%), respectively.



CLI



CLII



CLIII

Two of three methods employed in the synthesis of the insect juvenile hormone analog, ethyl 3,3,11-trimethyl-2,4-dodecadienoate involved addition of dilithioacetic acid and dilithio-3-methyl-2-butenoic acid to appropriate car-