LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

I. Structure and Bonding Studies

Several review articles dealing with this area have appeared in 1974. Stucky has examined the structure and bonding of Group I organometallic complexes [1]. Langer and co-workers have discussed magnetic resonance studies on chelated alkali metal compounds as a probe to determine structural information [2]. They have also described the nature of the electrical

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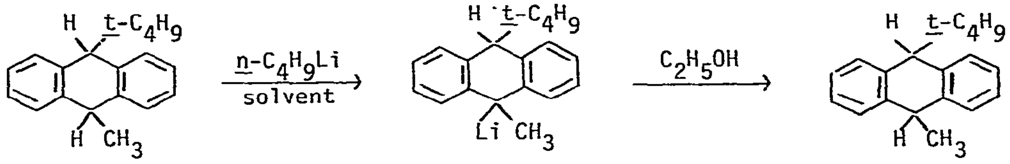
* Lithium, Annual Survey covering the year 1973
see J. Organometal. Chem., 95(1975)1-137.

conductance of N-chelated aryl and aralkyl lithium compounds complexed with polyamines [3]. Mann has reviewed the use of ^{13}C NMR chemical shifts and coupling constants of organometallics including organolithiums [4]. Wakefield has published a book on organolithiums which includes sections on their crystal structures and association in solution, their preparations, and their use in both organic and organometallic synthesis [5]. Finally, Wittig has published a summary of some of the research performed throughout his career [6]; the chemistry described encompasses virtually all the areas included in this survey

Several papers have appeared concerning ion pairing of carbanions. The extent of ionic association in the excited states of fluorenyl carbanions has been studied as a function of solvent and cation by spectrofluorimetry [7]. Two types of ion pairs, contact and separated, present in the ground state are also present in the first excited state. However, the amount of separated ion pairs in the latter state is generally higher than in the ground state. For example, in tetrahydropyran, fluorenyllithium exists as 70% contact and 30% separated ion pairs in the ground state but only as separated ion pairs in the excited state.

The stereospecificity of protonation of 9-lithium 10-t-butyl-9-methyl-9, 10-dihydroanthracene (I) is a function of the nature of ion pairing which, in turn, depends upon the solvent [8]. Thus, in ether or THF, I exists as contact and solvent separated ion pairs; protonation with ethanol affords mostly the cis hydrocarbon. In contrast, in the presence of hexamethylphosphoramide (HMPA), I exists as a loosely associated ion pair protonation of which gives mostly the trans hydrocarbon. It is suggested that the protonation stereoselectivity of the structured ion pairs is metal-cation directed while that of the loose ion pairs is controlled by product development.

Using conductometric methods, dimsyllithium and dimsylsodium in dimethyl sulfoxide (DMSO) have been found to exist partially as ion pairs, the constants being 370 and 127 M^{-1}, respectively [9]. Similarly, the ion pairing constants



(cis or trans)

(I)

(either cis or trans)

for lithium, sodium, potassium, and cesium t-butoxides in DMSO are 10^8, 10^6, 270, and 200 M^{-1}, respectively.

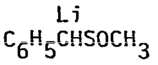
Certain complexes of fluorenyllithium were synthesized and isolated and their visible absorption spectra both as solids and in solutions were compared [10]. Thus, the 1:1 complex of this carbanion with TMEDA and the 1:2 complex with THF exhibited little change in the λ_{max} between solid and solution other than a slight hypsochromic shift probably due to tighter contact ion pairs in the solid. In contrast, the spectra of the solid 1:1 complex with pentamethyl-diethylenetriamine exhibited a substantial bathochromic shift presumably because of coordination of the metal with the three amine nitrogen atoms.

It has been determined by variable temperature proton NMR studies that solutions of lithiotrimethylstannane (and the corresponding potassium salt) exist as an equilibrium mixture of contact and solvent separated ion pairs [11].

$$M, Sn(CH_3)_3 \rightleftharpoons M||Sn(CH_3)_3$$

The equilibria lies to the right in HMPA and to the left in THF.

The extent of ion-pairing of a lithiosulfoxide has been shown to dictate the relative amounts of two diastereoisomers obtained upon methylation by methyl iodide [12]. Thus, methylation of II in THF and in THF-HMPA gives the diastereoisomers in ratios of 19:1 and 9:1, respectively.

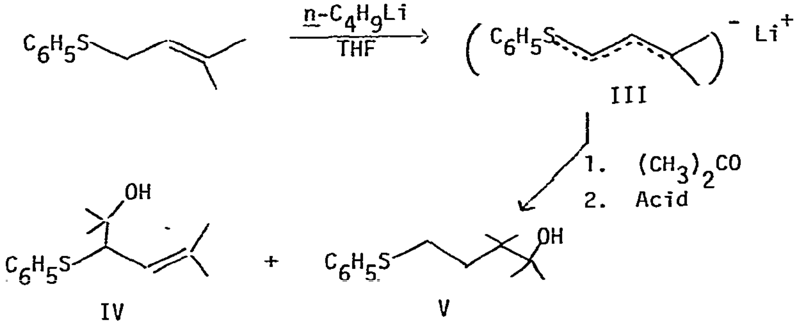


$$C_6H_5\overset{Li}{C}HSOCH_3$$

II

It is suggested that reactions of the intimate or solvated ion pair of II are stereoselective while those in the presence of HMPA or cryptates are not. A temperature effect is also noted.

In a similar study involving lithiosulfide III, it has been shown that the regioselectivity of alkylations and of reaction with acetone depends on the presence of the solvating species [13]. For example, treatment of III with acetone in THF in the absence of an additional solvating species gave IV and V in yields of 25% and 75%, respectively. In contrast, repetition of the experiment in the presence of the macrobicyclic diaminopolyether [2,2,2] gave only IV. The results are interpreted in terms of the type of ion pair present.



Ion pairs were also studied by NMR. Thus, the ^7Li NMR spectra of the lithium salts of cyclopentadiene, indene, 1-phenylpropene, fluorene, 1,3-diphenylpropene, triphenylmethane, and cyclononatetraene have been obtained in ether, THF, DME, diglyme, and HMPA [14]. Ranges of about 8.0 ppm upfield in the ^7Li shifts were observed. The data is explained in terms of the location of the lithium cation with respect to the anion of an ion pair and the type of ion pair present.

Similarly, the line widths in the ^6Li, ^7Li, and other alkali cations of the nmr spectra of solutions of the alkali salts of biphenyl and fluorenone have been reported as a function of solvent and temperature [15]. Expressions for the relaxation times are presented for static and dynamic ion pair models to describe the variation in ion pair structure with temperature. It is shown how, in combination with shift data, a numerical analysis of the line widths can often give detailed information about the structure of the ion pair..

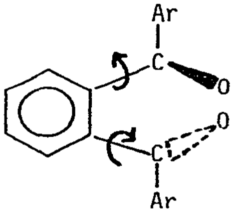
Nuclear magnetic resonance continued to be employed to study other aspects of organolithium chemistry. First, a method has been reported where the ^{7}Li chemical shifts of a variety of such compounds were determined relative to an internal proton lock instead of to the more usual external lithium salt [16]. This method provides the basis for a general standard of comparison by which all ^{7}Li data may be correlated since previously, relative positions of resonance were a function of the choice of standard and its concentration. Also, this new method precludes errors in the chemical shifts due to magnetic susceptibility factors.

Additional papers have been published by T. L. Brown and co-workers dealing with NMR investigations of exchange processes in lithium-containing compounds. Thus, the kinetics of ^{7}Li exchange between methyllithium, ethyllithium, lithiomethyltrimethylsilane and the corresponding $LiAlR_4$ compounds were determined in ether [17]. The rate-determining steps in the exchanges were found to be dissociation of the organolithium tetramers which were promoted by electron release and/or increased steric requirement of the R group. The exchange was rapid on the NMR time scale ($>\sim 10^3 sec^{-1}$) at -90°. Also studied were the 220 MHz ^{1}H NMR spectra of methyllithium/lithium bromide (10/1 ratio) in ether at various temperatures to ascertain the rate and energetics of the exchange of methyl groups between $Li_4(CH_3)_4$ and $Li_4(CH_3)_3Br$ tetramers [18]. Though the two species exhibited distinct resonances at low temperatures, methyl group exchange between the two tetramers occurred at -32° to 0°. It is suggested that the rate-determining step is dissociation of $Li_4(CH_3)_3Br$ to $Li_2(CH_3)_2$ and Li_2CH_3Br. This dissociation obeys the equation $\ln k_2 = 36.0 - 8303T$ and is slower than dissociation of the methyllithium tetramer

Methyllithium tetramer in THF containing ^{7}Li and ^{13}C in abundances of 92.6% and 25%, respectively was studied by heteronuclear double resonance experiments

[19]. It was shown that $^1J(^7Li-^{13}C)$ is positive; this result is consistent with the dominance of the coupling mechanism by the Fermi contact interaction.

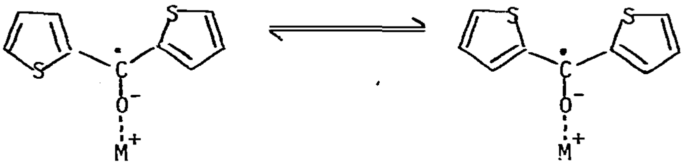
Alkali metal and proton hyperfine splitting constants of o-dimesitylbenzene alkali metal complexes have been studied in various solvents [20]. The coupling constants are positive and are in agreement with the structure below where the mesityl groups are rotated in a conrotatory mode.



The ^{13}C NMR spectra of a variety of saturated and unsaturated organolithium reagents in THF were obtained and the chemical shifts of each carbon atom were compared to the corresponding hydrocarbons [21]. Another paper described similar NMR spectra for lithiotrimethylstannane enriched to 7 mole % in ^{13}C in THF [22]. The electon-mediated reduced nuclear spin-spin coupling constants $^1K(Sn-C)$ and $^2K(Sn-H)$ are negative and positive, respectively. The former constant represents the first observation of a negative reduced coupling constant between any pair of directly bound Group IV elements. This is attributed to the presence of a lone pair of electrons on the tin atom.

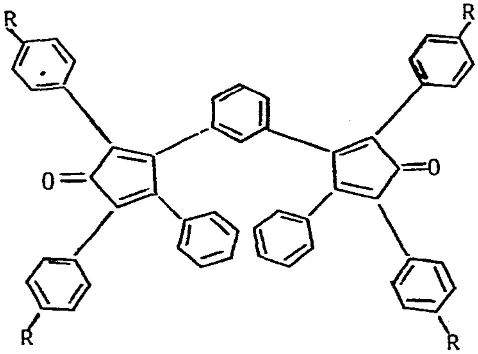
Respective mixtures of methyllithium with $LiMn(CO)_5$ and $LiCs(CO)_4$ in ether at -50° gave ^7Li NMR spectra containing only resonances due to the pure compounds [23]. Thus, no mixed tetrameric species of the type $Li_4(CH_3)_nX_{4-n}$ are formed. The infrared spectra of $LiMn(CO)_5$ in ether in the CO stretching region indicated the presence of ion-paired species of C_3v symmetry.

ESR has been employed to determine the ratio of the cis-trans (VI) and trans-trans (VII) conformers of 2,2'-dithienyl ketyl and its lithium, sodium, potassium, and cesium complexes [24]. The amount of VII increased with increasing size of the cation at -50° in DME. Thus, the ratio of VII to VI is about 1.5 and about 4.1 for lithium and cesium, respectively. The trend is ascribed to steric interaction between the cation and the atoms adjacent to the binding site.



VI VII

EPR triplet powder spectra of the alkali metal ketyls of bistetracyclones bridged by phenyl rings at meta positions (VIII) have been obtained [25]. The spectra can be interpreted in terms of electron-electron dipolar coupling between the unpaired spins of randomly oriented molecules.



VIII

Using ESR and NMR spectroscopy on lithium-nitrobenzene radical anion-HMPA, a technique has been presented that determines the hydrogen bonding energy of a proton donor to a radical anion acceptor [26]. The technique consists of a thermochemical cycle.

The first two crystal structures of hexameric lithium derivatives have been determined. First, cyclohexyllithium·2 benzene (Figure 1) was found to have a geometry of lithium atoms in a near octahedral configuration [27]. There are six triangular lithium atom faces which have two short (2.397(6)Å) and one long (2.968(9)Å) distances. The shorter of these is the closest known Li-Li atom contact reported. It is suggested that interaction between the α- and β-hydrogens of the cyclohexyl rings with the lithium atoms determines the orientation of the cyclohexyl rings.

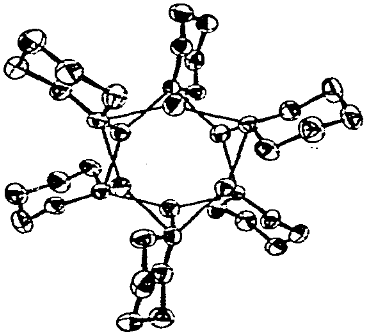


Figure 1

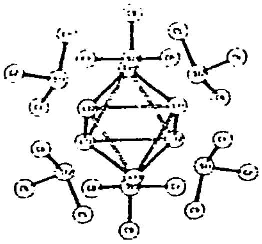


Figure 2

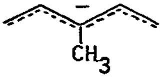
The crystal structure of hexameric trimethylsilyllithium has also been obtained (Figure 2) [28]. The framework of the molecule is best represented as a chair-form six-membered lithium ring of approximate D_{3d} symmetry with each face occupied by a bridging trimethylsilyl group. There apparently is significant lithium-lithium interaction only between adjacent lithium atoms.

Several papers were published which dealt with the structures of allyllithiums. The geometry-optimized structure of allyllithium-bis(dimethyl ether) was calculated using the INDO approximation [29]. The analysis suggested the presence not only of a substantial π-type three-center bond between the metal and the carbanion but also σ-type bonding from the carbon s-orbitals and the lithium s and p_z orbitals. Negative charge densities are found on the lithium and ether oxygen atoms as a result of the transfer of 0.43 electrons from the allyl π-system and 0.39 electrons from the allyl σ-bonds to the solvated lithium atom. Appropriate bond distances and charge densities are listed which are in agreement with those calculated using the CNDO/2 approximation for allyllithium solvated by two molecules of ammonia [30]. CNDO/2 calculations were also employed to determine the equilibrium geometry of unsolvated allyllithium which is predicted to have a non-planar bridge structure [30].

CNDO/2 calculations were performed on nine isomeric pairs of substituted allyl anions to assess the effect of substituents on their relative stabilities [31]. Examples of substituents employed included methyl, vinyl, fluoro, trifluoromethyl, methoxy, and others. It was determined that electron-withdrawing substituents decrease the proton affinities of the anions with the trans-substituted anion being more stable. However, the cis-anion was found to be more stable when the only substituent on the anion is an alkyl group.

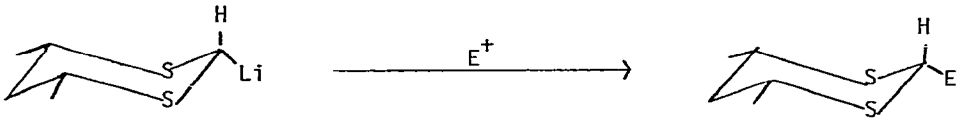
The π-charge distribution in allyl, 1,3-diheteroallyl, and 1- and 3-heteroallyl anions bearing acceptor substituents at C_1 have been calculated using a simple Hückel MO model [32]. INDO calculations and ^{7}Li and ^{1}H NMR, IR, and UV spectroscopy on 3-butenyllithium have indicated a perturbation of the π-system of the butenyl moiety by the lithium aggregate [33]. Such a direct observation of a lithium-olefin interaction supports earlier postulations of a similar interaction for ethylenation reactions in ether.

Conformational isomers of several acylic pentadienyllithiums have been directly observed by proton-decoupled ^{13}C NMR spectroscopy [34]. In conjunction with pmr spectroscopy, it is concluded that the principal conformation of these compounds is the W conformer like IX with substantial amounts of the sickle conformer present in some cases.



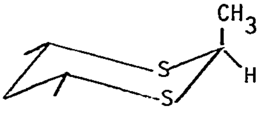
IX

Conformationally locked (anancomeric) 2-lithio-1,3-dithianes have been studied for comparison with anancomeric cyclohexyllithium derivatives [35]. Thus, treatment of X with a variety of electrophiles affords exclusively or nearly exclusively equatorial products (XI). That there exists a large preference for lithium in the equatorial position (>6kcal/mole) was further demonstrate by lithiation and deuteration by DCl of XII and XIII to mostly afford XIV. The preference for such stereoselectivity is ascribed to a stereoelectronic rather than a simple steric effect and is largely thermodynamically controlled.

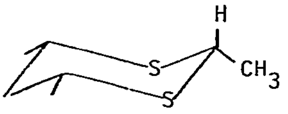


X

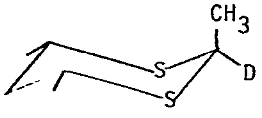
XI



XII



XIII



XIV

Two other studies involving calculations deserve mention. First, the NDDO method has been found superior to the CNDO/2 method in accounting for the effect of nitrogen lone pairs on the stability of π-delocalized and σ-delocalized carbanions derived from 14 azabenzenes [37]. For example, the deprotonization energies of toluene and the three isomeric picolines calculated by the former method follow the same trend as the negative logarithms of hydrogen exchange rates; this is not the case for deprotonization energies calculated by the CNDO/2 method. Second, ab initio molecular orbital calculations have been obtained for the lithium pyrazine ion pair [37]. The lowest energy conformation consists of the lithium occupying a position in the plane of the pyrazine ring along the C_2 axis passing through the nitrogen atoms.

The enthalpy differences between o- and p-lithioanisoles in di-n-butyl ether and TMEDA have been determined by adding their solutions to ethanol in a calorimeter [38]. For example, the values for the o- and p-isomers in the ether were -54.5±0.2 and -62.8 kcal/mole, respectively; slightly less negative numbers were realized in TMEDA. The method provides a straight-forward procedure for determining relative enthalpies of isomeric organometallics and provides the first quantitative information about stabilization by a substituent bearing non-bonding electrons proximate to the carbon-lithium bond.

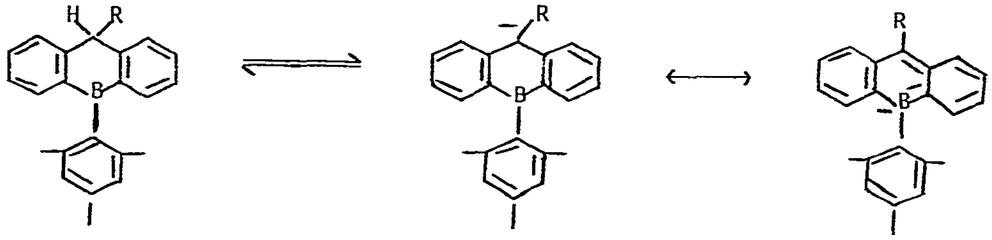
A previously developed direct calorimetric method has also been employed to study the effects of steric interactions on the heats of interaction of THF and substituted tetrahydrofuran bases with n-butyllithium and lithiomethyltrimethylsilane [39]. The data suggest that base coordination to hexamers of the above species may lead directly to solvated tetramers.

II. Kinetics and Mechanisms

Brook has reviewed the rearrangements of organosilicon compounds where the migration terminus is oxygen [40] and Chen has reviewed molecular rearrangements in lithium aluminum hydride reductions [41].

Many interesting papers in this section have appeared in the last year stemming from ionization or metalation reactions by organolithiums. Thus, the relative and actual rates of exchange of deuterated cubane were determined using lithium cyclohexylamide in cyclohexylamine and found to be 1.20 and 6.78±0.48 sec^{-1}, respectively [42]. The corresponding values for benzene under the same conditions were 1.0 and 5.53±0.05 sec^{-1}, respectively. That cubane is 1,000 times more acidic than the reported value for cyclopropane is ascribed to the altered hybridization at the anionic carbon atom to an orbital with significantly enhanced s-character.

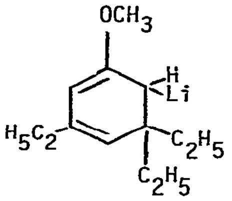
Lithium cyclohexylamide in cyclohexylamine was also employed to obtain the equilibrium acidities of 9-mesityl-9,10-dihydro-9-boraanthracene (XV) and its 10-phenyl derivative [43]. After correction for Lewis adduct formation with the amine, the pka of both compounds was found to be 15.8 (relative to 9-phenylfluorene whose pka = 18.49). The completely aromatic canonical form XVII is thought to contribute to the resonance hybrid.



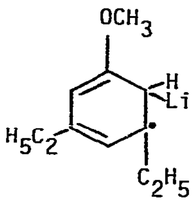
R = H or C_6H_5

XV XVI XVII

In contrast to an earlier proposal, metalation of 3,5-diethylanisole by ^{14}C labeled ethyllithium demonstrated that adduct XVIII is not an intermediate in the reaction [44]. Negative CIDNP results also eliminated XIX as an intermediate. Steric factors in metalations were studied on various 3-alkyl and 3,5-dialkylanisoles and other aromatics with n- and t-butyllithium and their TMEDA complexes. The results have been correlated with the concept that the steric requirement of the organolithium is related to the oligomer size where n-butyllithium > t-butyllithium in hydrocarbons > n-butyllithium in ether > n-butyllithium·TMEDA in hydrocarbons.

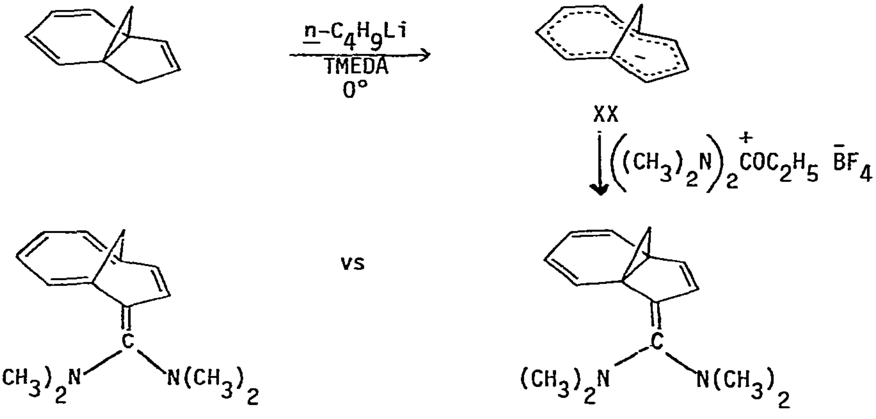


XVIII



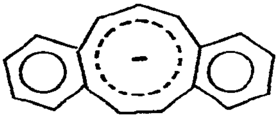
XIX

It has been found that the stable ten π-electron bicyclo[4·3·1]decatetraenyl anion XX can be prepared at low temperature by n-butyllithium [45]. Treatment of XX with bis(dimethylamino)ethoxycarbonium tetrafluoroborate, though, gave the closed norcaradiene XXI rather than the desired bridged nonafulvene XXII.

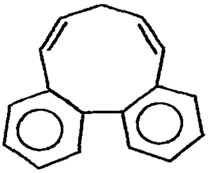


XXII XXI

Treatment of the dibenzannelated 1,2:5,6-dibenzocyclononatetraene with n-butyllithium in cyclohexane at -20° was found to instantaneously give a red solution of the non-benzenoid aromatic anion XXIII [46]. This is to be contrasted with the previously reported rather slow related conversion of the 3,4:5,6 isomer (XXIV). The authors conclude that XXIV undergoes such slow ionization because of its biphenyl backbone, not because of the annelation of the benzene rings.

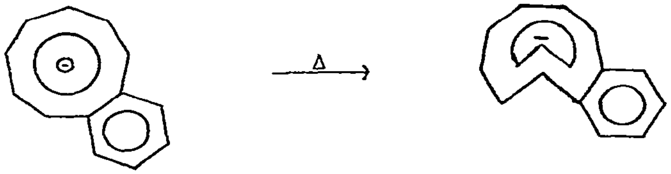


XXIII



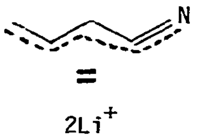
XXIV

It has been determined that the related monobenzo system (XXV) is thermally labile [47]. Thus, at 56° in ammonia, XXV undergoes unidirectional isomerization [$k = (2.56 \pm 0.22) \times 10^{-5}\ \mathrm{sec}^{-1}$, $\Delta G^{\ddagger} = 26.2$ kcal/mole] to give the trans-isomer XXVI. The isomerization is surprising in light of the fact that the parent cyclononatetraenyl anion prefers to isomerize from trans to cis. The reaction of XXV to XXVI is rationalized in terms of diminution of peri H-H interactions.

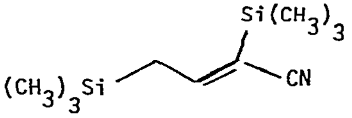


XXV XXVI

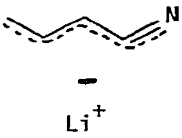
Attempts were made to prepare dianion XXVII by metalation of 3-butenenitrile with n-butyl- and methyllithium at low temperature [48]. Though subsequent reaction of the carbanion with chlorotrimethylsilane or benzyl bromide afforded bis-products, e.g., XXVIII, NMR indicated that only monometalation to give XXIX had occurred. Thus, products like XXVIII arose via sequential metalation and alkylation.



XXVII

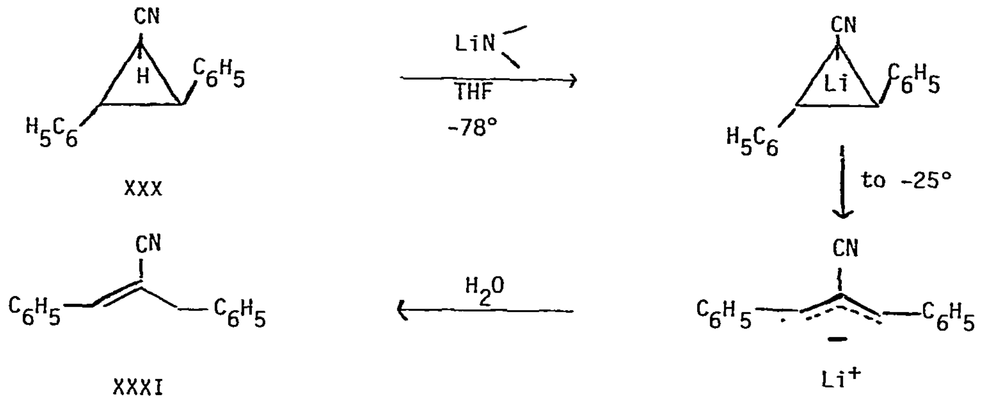


XXVIII



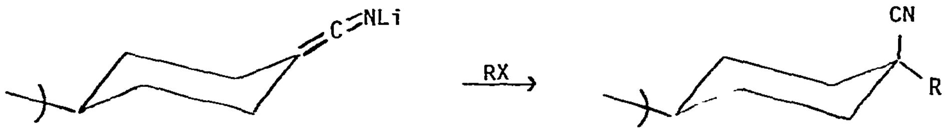
XXIX

Several other papers dealt with cyclic carbonitriles or compounds isomeric with them. Thus, four different cyclopropanenitriles were converted to their lithio salts by strong bases in THF at -78° [49]. Though the carbanions were stable at this temperature, three of the salts underwent thermal opening at >-25° apparently by conrotatory orbital symmetry control. The process is illustrated by the conversion of XXX to XXXI, a reaction also effected by a photochemical process. The latter reaction represents the first example of a photochemical opening of a cyclopropyl anion to an allyl anion.

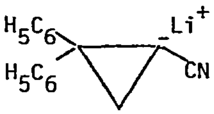

XXX

XXXI

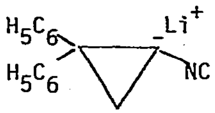
Alkylation of lithionitrile XXXII and related compounds as well as addition of hydrogen bromide to 1-chloro-4-phenylcyclohexane are used as examples to illustrate the recently described rule that exocyclic double bonds of cyclohexanones and methylenecyclohexanes are attacked at the ring trigonal atom from the equitorial and axial sides by electrophiles and nucleophiles, respectively [50]. Such selectivities are ascribed to different electron densities on the two faces of the plane containing the trigonal atom due to the interaction of the p-orbital of that trigonal atom with the symmetric β-carbon-carbon bonds.


XXXII

In contrast to lithiocyanocyclopropane XXXIII which is incapable of maintaining its configuration in aprotic solvents, the corresponding lithioisocyanocyclopropane XXXIV retains its configuration to a high degree in THF at -72° to -52° [51]. The data suggests that the cyano group is better able to delocalize an adjacent negative charge than is the isocyano group. Stabilization of such a charge by the latter group probably occurs via an inductive effect.

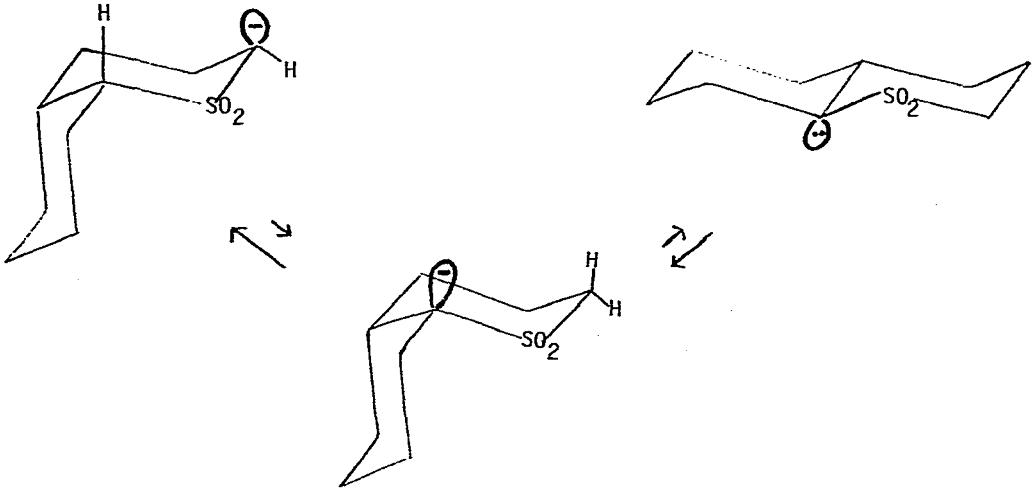


XXXIII



XXXIV

The interaction of strong bases with sulfones and sulfoxides continues to be studied. Three *cis*-fused bicyclic sulfones were treated with *n*-butyllithium in benzene to give *cis*-*trans* isomerization of the ring fusion [52]. The process presumably proceeds via intramolecular proton transfer. A portion of the proces for one example follows.



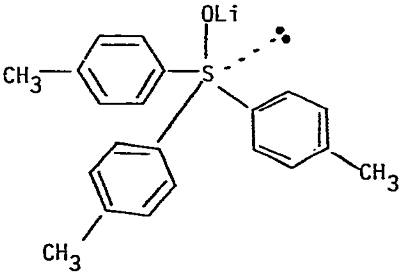
Reaction of various sulfoxides with methyllithium, n-butyllithium, and t-butyllithium has been studied to determine the relative extent of α-ionization versus carbon-sulfur bond cleavage; the latter process affords a new sulfoxide [53].

$$RSOCH_2R_1 + R_2Li \longrightarrow \overset{Li}{RSOCHR_1} \quad vs \quad RSOR_2 \text{ or } R_2SOCH_2R_1$$

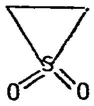
XXXV XXXVI

It was found that α-ionization is best effected by methyllithium or lithium diisopropylamide and that the cleavage reactions occur with inversion of configuration at sulfur. Such inversion processes are extremely facile even at -78° and are thought to be SN_2-like rather than involving a hypervalent sulfur intermediate (e.g., a sulfurane).

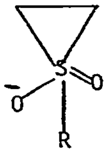
Other workers, though, suggest the presence of such hypervalent intermediates in similar reactions. Thus, sulfurane XXXVII is proposed in the reaction of excess p-tolylithium with p-tolyl sulfoxide to afford p-tolyl sulfide and other products [54]. Similarly, it is suggested that reaction of episulfones like XXXVIII with organolithiums involve intermediates such as XXXIX which decompose to olefin and lithium alkylsulfinate [55].



XXXVII

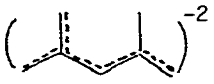


XXXVIII

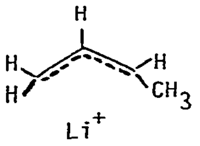


XXXIX

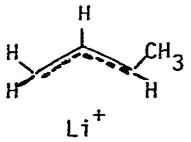
Many papers describing chemistry of allyl anions appeared in 1974. A variety of monoolefins, and unconjugated dienes were treated with excess n-butyllithium in TMEDA to study allylic di- and trimetalation [56]. That the new anionic compounds shown were formed was established by NMR and by alkylation The work demonstrates that aromatic or homoaromatic stabilization is not necessary to form highly lithiated systems.



Crotyllithium has been readily prepared from 1-butene, Z-2-butene, or E-2-butene and t-butyllithium using a reaction period of only 15 min [57]. At 35° in TMEDA, the Z-isomer (XL) of this ionic species predominates over the E-isomer (XLI) by a ratio of about 85:15. Alkylation of this mixture with n-butyl bromide gave 46% Z-2-octene, 8% E-2-octene, and 46% 3-methyl-1-heptene.



XL



XLI

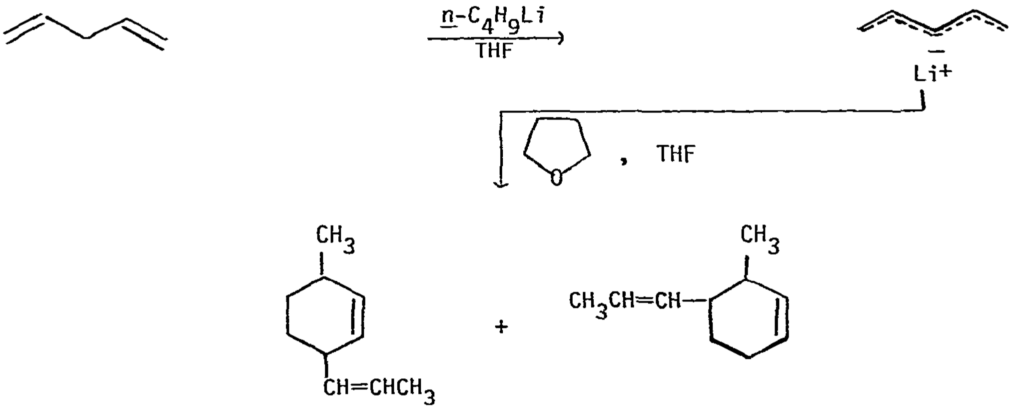
Crotyllithium has also been prepared from either Z or E-XLII and methyl- or n-butyllithium to afford a 3:2 trans:cis mixture of the organometallic [58]. A possible mechanism of the isomerization between Z- and E-crotyltrimethyltin via XL and XLI is discussed.

$CH_3CH{=}CHCH_2Sn(CH_3)_3$

XLII

(Z or E)

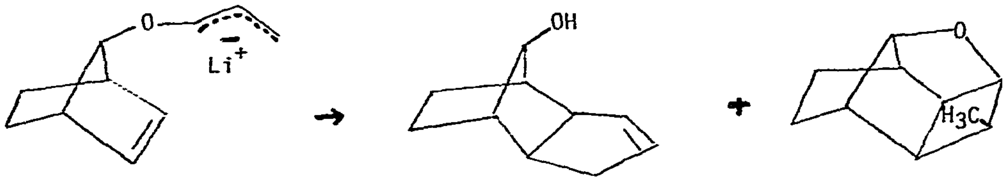
A paper appeared that describes stepwise cycloadditions of pentadienyllithiums to 1,3-dienes in the presence of furan or toluene both in the presence and in the absence of added 1,3-pentadiene [59]. For example, 1,4-pentadiene affords XLIII, XLIV, and other products. The furan and toluene presumably act as proton donors to the initial pentadienyllithiums as well as to 1:1 adducts of the latter with 1,4-pentadiene.



XLIII XLIV

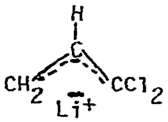
Allyl anion XLV was observed to undergo an intramolecular cyclization reaction to afford XLVI and XLVII in a ratio of 3:7 in 55% yield [60]. The corresponding O-benzyl ether behaved similarly. A two-step mechanism is proposed.

Two papers described the ambident nucleophilicity of gem-dichloroallyllithium XLVIII [61,62]. Reactions of XLVIII with aldehydes and ketones are governed by electronic effects of the carbonyl compound; for example, acetone and perfluoroacetone give XLIX and L in high yields, respectively [62]. The

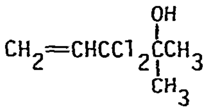


XLV XLVI XLVII

authors speculate that such selectivities might be explained using Pearson's HSAB approach. XLVIII also gives products like XLIX with chlorotrimethylsilane methyl iodide, and water, products like L with bromotrimethylstannane, and both types of products with chlorotrimethylgermane [61].

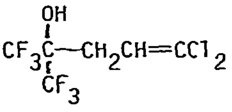


XLVIII



$CH_2{=}CHCCl_2C(OH)(CH_3)CH_3$

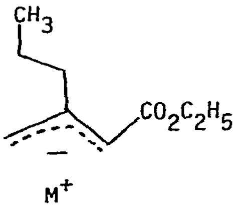
XLIX



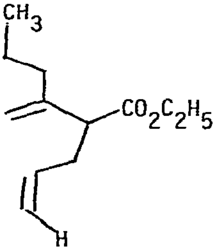
$CF_3C(OH)(CF_3){-}CH_2CH{=}CCl_2$

L

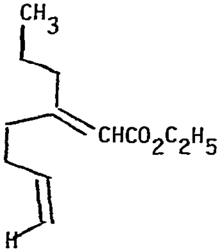
The regioselectivity in the alkylation of dienolate LI was studied as a function of the metal cation and various allyl halides [62]. Though alkylation of LI (M=Li) with allyl bromide gave mostly the expected α-product LII, reaction of LI (M=Cu) with this halide afforded LII and the γ-product LIII in a ratio of 44:56. . The use of more complicated allyl halides led to α-products. Interestingly, γ-products from the copper enolate (LI, M=Cu) appear to arise from SN_2' rather than SN_2 substitutions as evidenced from deuteration studies.



LI

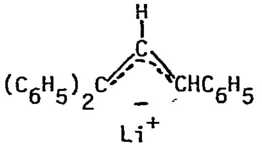


LII

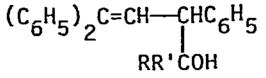


LIII

Aldol-type condensations of allyl anion LIV and related compounds were investigated with a variety of aldehydes and ketones [64]. Though LIV appears to be more nucleophilic at C_1 towards alkyl halides, only alcohols like LV arising from attack at C_3 were obtained in this study.



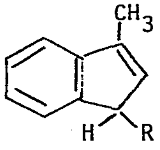
LIV



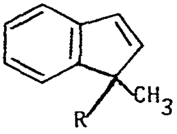
$$(C_6H_5)_2C{=}CH{-}\underset{RR'COH}{\underset{|}{C}}HC_6H_5$$

LV

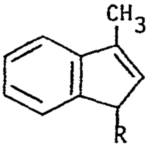
Similarly, indenyllithium underwent alkylations with various alkyl halides to give 1-alkylindenes in good yields [65]. Though alkylations of methylindenyllithiums gave mixtures of LVI and LVII, methylation of certain alkylindenyllithiums gave LVIII in good yields.



LVI

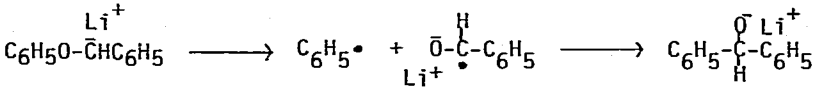


LVII



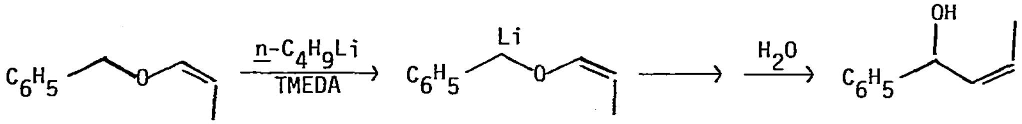
LVIII

A variety of workers continued to investigate rearrangements effected by bases. Thus, detailed study of the mechanism of 1,2-aryl shifts of several α-lithiobenzyl ethers has been described [66]. The following observations led the authors to suggest the mechanism shown with LIX: 1) no aldehydic products could be trapped; 2) no products arising from aryne intermediates could be isolated; and 3) the NMR signals from LIX were obliterated in the 4.0 - 8.0 ppm region during the first minute of reaction.



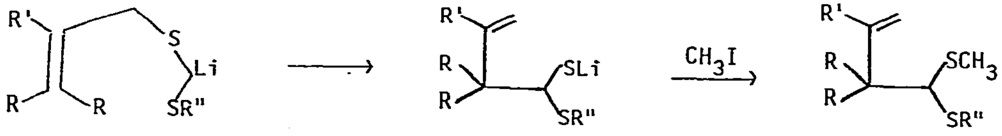
LIX

A new, stereospecific vinyl migration in the Wittig rearrangement has been reported to give divinyl- and benzylvinylcarbinols in excellent yields [67]. For example, the lithio salt of ether LX rearranged to LXII with preservation of the geometry of the migrating vinyl group; LXI was also trapped with deuterium oxide and chlorotrimethylsilane. Some but not all allyl vinyl ethers studied also underwent the rearrangement. On the other hand, though benzyl vinyl sulfid underwent metalation, the lithio carbanion did not rearrange. The rearrangement are thought to involve fragmentation to vinyllithiums and carbonyls which recomb to give products.



LX LXI LXII

Allylic sulfides with lithium diisopropylamide were found to give carbanions (e.g., LXIII) which undergo a [2,3] sigmatropic rearrangement to afford, after methylation, β,γ-unsaturated dithioacetals (e.g., LXIV) [68].

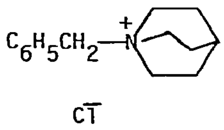


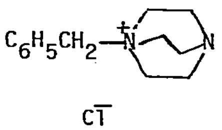
LXIII LXIV

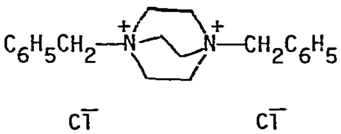
MINDO/3 calculations for a pericyclic mechanism for the Steven's rearrangement indicate the reaction could occur by a concerted pericyclic path [69].

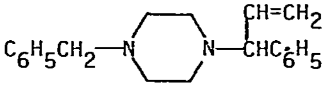
Though the calculations do not allow a distinction between the above and a radical pair mechanism, they do suggest that the Woodward-Hoffmann rules may break down for very exothermic reactions.

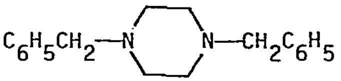
Base promoted reactions of bicyclic mono- and diquaternary ammonium salts LXV-LXVII to give products arising from the Steven's rearrangement (e.g., LXVIII), elimination (e.g., LXIX), or displacement are controlled by the acidifying influence of the quaternary nitrogen atom [70]. The novel vinyl Steven's rearrangement leading to LXVIII was also observed on benzylvinyldimethylammonium hydroxide to give LXX in low yield.

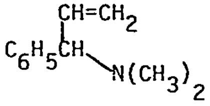

LXV


LXVI

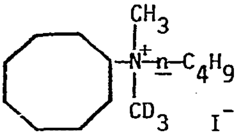

LXVII


LXVIII

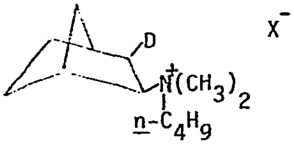

LXIX


LXX

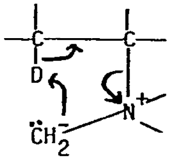
Two papers described the differences in reaction of quaternary ammonium salts with alkali amides in ammonia versus *n*-butyllithium in pentane. First, salt LXXI with either potassium amide or lithium amide gave *cis*:*trans*-cyclooctene in a ratio of 32:68 [71]. Most of the deuterium had been completely exchanged prior to elimination. In contrast, LXXI with *n*-butyllithium gave *cis*:*trans*-cyclooctene in a ratio of 70:30; less than a statistical loss of deuterium was realized before elimination. Thus, the N-ylide is formed reversibly with alkali amides and irreversibly with *n*-butyllithium. Second, salt LXXII with lithium amide in ammonia gave undeuterated norbornene and dimethylbutylamine. The latter contained 6.7% deuterium and the reaction proceeded by a *syn*-elimination [72]. This salt with *n*-butyllithium gave the same products except the amine contained 99% deuterium; this reaction proceeded by the *syn*-α'β-mechanism shown (LXXIII).



LXXI



LXXII

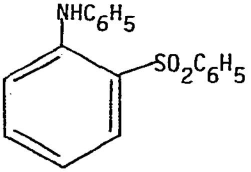


LXXIII

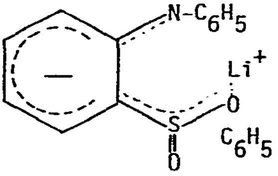
Though the sulfonamide-aminosulfone rearrangement has long been known to be effected by sulfuric acid, it has now also been effected by organolithiums in ether or THF [73]. Thus, LXXIV has been converted to LXXV, apparently via LXXVI.

$(C_6H_5)_2NSO_2C_6H_5$

LXXIV

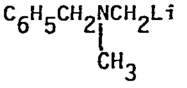


LXXV



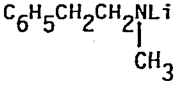
LXXVI

Another example of the rare rearrangement of tertiary amines analogous to the Wittig reaction of ethers has been discovered [74]. Thus, carbanion LXXVII at 20° rearranged to lithio salt LXXVIII in at least 83% yield. LXXVII was prepared from stannane LXXIX and *n*-butyllithium, a process used to synthesize several other α-lithiomethylamines.



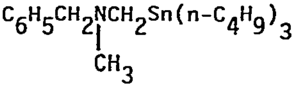
$C_6H_5CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}CH_2Li$

LXXVII



$C_6H_5CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}Li$

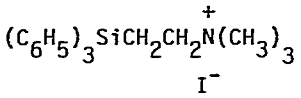
LXXVIII



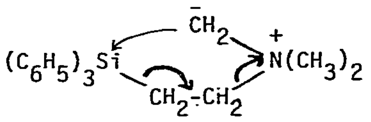
$C_6H_5CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}CH_2Sn(n\text{-}C_4H_9)_3$

LXXIX

A new rearrangement of dialkylmethyl(2-triphenylsilyethyl)ammonium ylides has been reported [75]. Thus, treatment of LXXX with n-butyllithium below -15° gave a transient red colored mixture which, upon work-up, gave silylamine LXXXI in good yield. The reaction which presumably involves LXXXII represents a fourth reaction of quaternary ammonium salts with strong bases and stands beside the Steven's, the Sommelet-Hauser, and the Hofmann reactions.


$(C_6H_5)_3SiCH_2CH_2\overset{+}{N}(CH_3)_3\ I^-$

$(C_6H_5)_3SiCH_2N(CH_3)_2$

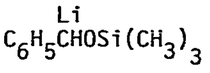


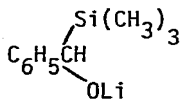
LXXX

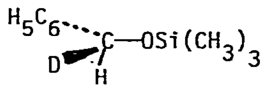
LXXXI

LXXXII

Several other descriptions of rearrangements involving silicon and germanium also were published in 1974. Wittig-type rearrangements of alkoxysilanes and germanes where silicon and germanium are the migrating atoms have been discussed in a full paper; for example, LXXXIII is rapidly convented to LXXXIV [76]. This rearrangement which proceeds because of equilibration of LXXXIII and LXXXIV is contrasted with the Brook rearrangement which involves the reverse conversion of neutral α-silylcarbinols to neutral alkoxysilanes effected by catalytic amounts of base. Alkoxysilane LXXXV undergoes stereospecific rearrangement with 99% inversion at the benzyl carbon atom [77]. The reaction exhibits $^{k_H}/_{k_D} = 24 \pm 4$, the highest value reported for a metalation reaction.


$C_6H_5\overset{Li}{C}HOSi(CH_3)_3$





LXXXIII

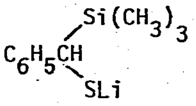
LXXXIV

LXXXV

The first examples of similar 1,2-anionic rearrangements of silicon and germanium from sulfur to carbon have also been described [78]. For example, LXXXVI is converted to LXXXVII by stoichiometric amounts of strong bases. The reverse conversion of LXXXVIII to LXXXVI is effected by a radical initiator.

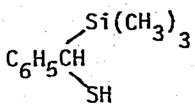
$C_6H_5CH_2SSi(CH_3)_3$

LXXXVI



$C_6H_5CH(Si(CH_3)_3)SLi$

LXXXVII



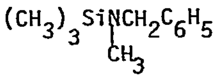
$C_6H_5CH(Si(CH_3)_3)SH$

LXXXVIII

Finally, aminomethylsilanes like LXXXIX have been rearranged to methylaminosilanes like XC in high yields by catalytic amounts of n-butyllithium [79]. A mechanism is proposed.

$(CH_3)_3SiCH_2NHCH_2C_6H_5$

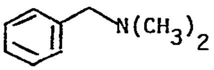
LXXXIX



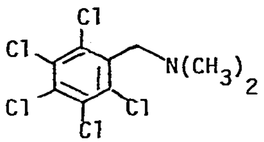
$(CH_3)_3SiN(CH_3)CH_2C_6H_5$

XC

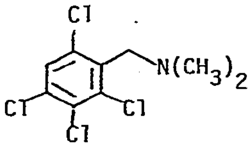
A few miscellaneous papers deserve mention. In contrast to the well-known directed ortho-metalations of amines like XCI, metal-halogen exchange of XCII by n-butyllithium at low temperatures followed by addition of water gives XCIII and XCIV [80]. Since no product from an o-lithio derivative is observed, coordination of the metal cation with the amine nitrogen atom seems unimportant.



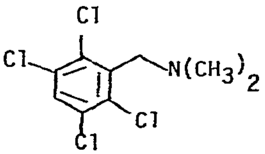
XCI



XCII



XCIII



XCIV

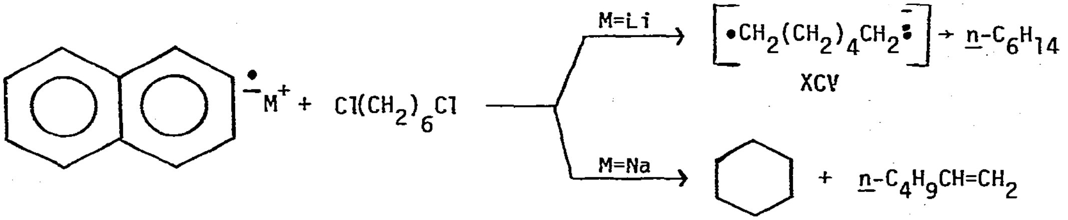
A remarkable solvent effect has been found in the interaction of aryl bromides with primary aliphatic organolithiums [81]. Thus, such reactions in ether give metal-halogen exchange to afford aryllithium reagents. Similar reactions in THF though give Wurtz-Fittig products (ArR) in yields of 52-87%.

The latter reactions are thought to occur via metal-halogen exchange followed by SN_2-like reactions.

The cyclization of 4,6-dihalononanes by alkyllithiums, the lithium radical anions of naphthalene and biphenyl, and lithium amalgam to afford cyclopropanes has been studied [82,83]. The cyclizations normally occur in a stereoconvergent manner indicating that the halogens are cleaved in a non-concerted mode. The less thermodynamically stable cis-1,2-di-n-propylcyclopane is formed predominately in most cases. It is thought that "π-cyclopropane" does not participate as an intermediate in these reactions.

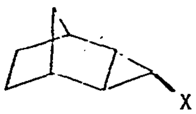
Second order rate constants for the exchange of phenyl radicals between phenyllithium and ^{14}C-labeled bromobenzene were found to increase in the following solvent order: phenetole < ether < dioxane < THF [84]. A linear correlation between the enthalpy and the entropy of phenyllithium solvation in these solvents was found.

The interaction of 1,6-dihalohexanes with lithium or sodium naphthalene radical anion have been shown to give hexane, cyclohexane, cyclohexene, and significant amounts of C_{12}-hydrocarbons [85]. The latter type of compounds are not significant in similar reactions of 1,4- and 1,5-dihaloalkanes. Metallic cations are important since hexane is the dominate reaction product when M=Li; in contrast, cyclohexane and 1-hexene predominate when M=Na. It is suggested that at least part of the hexane arises via radical anion XCV.

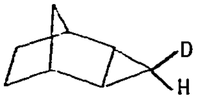


Another paper presented evidence that nearly all dimer formed from the reaction of benzyl and benzhydryl halides with naphthalene radical anions (M=Li, K) involves a carbanion precursor as previously suggested by Garst [86]. This was established by comparing the amounts of dimers in the presence and absence of the carbanion trap, *t*-butyl alcohol.

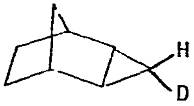
The reactions of the *anti*-halo compounds XCVI with lithium, *n*-butyllithium, and lithium naphthalene radical anion followed by quenching with deuterium oxide or *t*-butyl alcohol-O-d have been found to give XCVII and XCVIII [87]. The ratio of XCVII to XCVIII is 1.70 with lithium (X=Cl) and >100:1 with lithium naphthalene radical anion (X=Cl). Only XCVIII is formed with *n*-butyllithium (X=Br). Since the *anti*-lithium reagent once formed is configurationally stable, the authors conclude that the stereoselectivity is governed primarily by a radical pre-equilibrium where the *anti*-radical is less stable than the *syn*-radical.



XCVI
(X=Cl, Br)

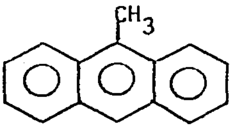


XCVII

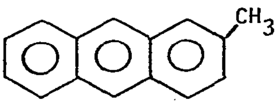


XCVIII

Despite previous reports, it has been found that alkylation of anthracene by methyllithium can be effected photochemically [88]. A variety of products are formed including XCIX and C. In contrast, thermal addition of methyllithium to anthracene gives mostly XCIX. Possible mechanisms including electron transfer-alkyl transfer versus direct addition of methyl carbanion are discussed.



XCIX



C

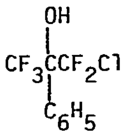
Finally, three papers have described the reaction of organolithiums with di-t-butyl peroxide. Ethyllithium with this peroxide has been found to afford lithium t-butoxide, ethyl t-butyl ether, ethane, ethylene, and butane [89]. The product distribution can be quantitatively related to the known values for the relative rates of the combination and disproportionation reactions of the t-butoxy and ethyl radicals. The ethyl t-butyl ether is thought to arise from cross-combination of these radicals in a solvent cage. Electron-donor additives have been found to accelerate the reaction of n-butyllithium with this peroxide in heptane [90]. The accelerating effect decreased in the order THF > ether > $(n\text{-}C_4H_9)_2O$ > $(i\text{-}C_3H_7)_2O$ > phenetole. The above reaction is not affected by various lithium alkoxides [91].

III. Lithium Carbenoids and Other Halogen-Substituted Organolithiums

The first description of the successful trapping of a halodifluoromethide ion other than by protonation has been reported [92]. Thus, treatment of ester CI with lithium chloride in the presence of various ketones gave species like CII. Experiments are presented to suggest products like CII arise from CIII and not from difluorocarbene.

$ClF_2CCO_2CH_3$

CI



$CF_3C(OH)(C_6H_5)CF_2Cl$

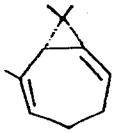
CII

$LiCF_2Cl$

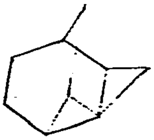
CIII

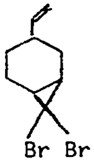
An improved procedure for the preparation of gem-dichlorocyclopropanes from alkenes in yields of 75-96% has been described [93]. The procedure involves mixing chloroform, the alkene, and a sterically bulky base like the lithium or potassium salts of triethylcarbinol.

A variety of novel ring systems have been prepared using carbenoid reagents. The first example of a bicyclo[5.1.0]octadiene CIV (and its monoolefin) was prepared by reaction of vinyl chloride CV with n-butyllithium at -60° [94]. Ring CVI was prepared from a carbenoid derived from CVII and methyllithium at -48° to -50° [95].


CIV

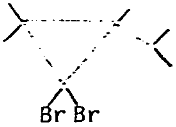
CV


CVI

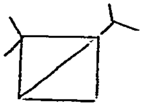


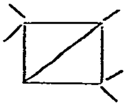
CVII

The reaction of dibromocyclopropane CVIII with methyllithium at -40°, 10°, and 36° has been found to afford mostly CIX arising from insertion of the cyclopropylidene into a primary carbon-hydrogen bond [96]. Though such reactions usually involve insertion into tertiary carbon-hydrogen bonds, the product that would arise from this route, CX, was not found in this study.



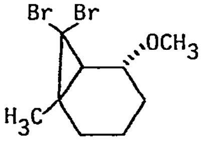
CVIII


CIX

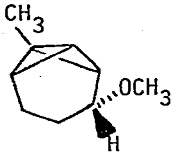

CX

On the other hand, reactions of the carbenoid derived from CXI substantiated the quantitative preference for insertion into a secondary rather than a primary carbon hydrogen bond [97]. Product CXII was subsequently reduced by lithium/ethylenediamine to give CXIII. Similar compounds were obtained in the conversion of CXIV to CXV and related compounds [98].

CXI CXII CXIII

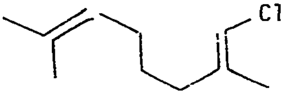


CXIV

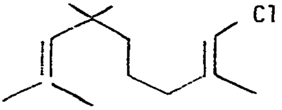


CXV

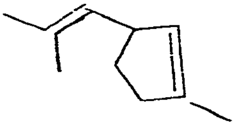
The action of n-butyllithium on vinyl chlorides CXVI and CXVII lead to cyclopentenes CXVIII and CXIX in good yields, respectively [99].



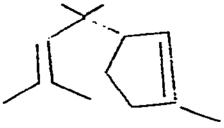
CXVI



CXVII



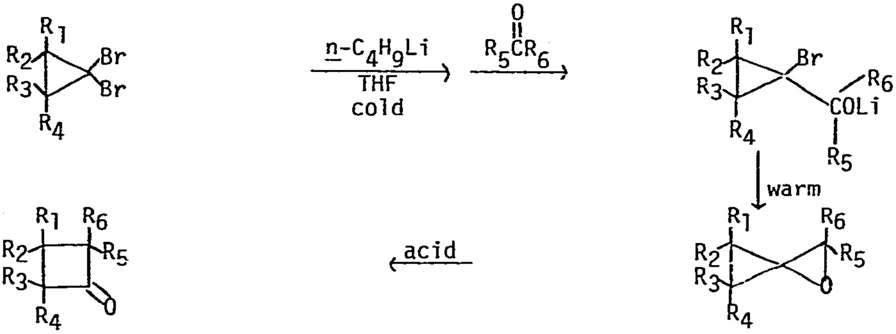
CXVIII



CXIX

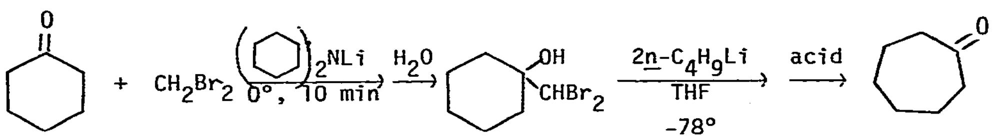
Two papers have described a new method of converting dibromocyclopropanes to cyclobutanones via oxaspiropentanes [100,101]. The process is illustrated below where the carbenoids are prepared and ketones added at < -90°; warming the mixtures gives CXX which can be isolated in some cases with basic work-up

[100] or isomerized to cyclobutanones with either acid or silicon dioxide. A wide variety of specific examples are listed.



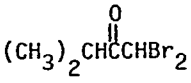
CXX

A practical synthesis of polyhalomethyllithium carbonyl adducts like CXXI has been described [102]. The procedure involves the <u>in situ</u> preparation of the carbenoid reagent in the presence of the carbonyl and avoids the problems of preformed carbenes. An example is shown below. Carbenoid precursors studied have included CH_2X_2 (X=Cl, Br, and I) and CHX_3 (X=Cl and Br); most of the adducts were formed in > 86% yield. A separate paper described the conversion of adducts like CXXI to ketones [103]. The overall process thus represents a highly effective method of effecting ring enlargements of one carbon atom.



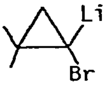
CXXI

Carbenoids have been reacted with electrophiles other than aldehydes and ketones. Thus, reaction of lithiodichloro- or dibromomethane with esters gives α,α-dihaloketones like CXXII in good to excellent yields [104]. Carbonation followed by treatment with diazomethane and reaction with N-methyl-N-phenylformamide of cyclopropyl derivative CXXIII give CXXIV and CXXV, respectively [105].

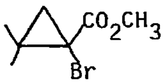


$(CH_3)_2CH\overset{O}{\overset{\|}{C}}CHBr_2$

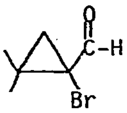
CXXII



CXXIII

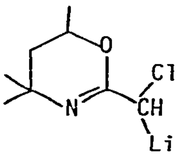


CXXIV

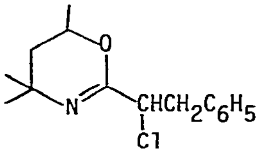


CXXV

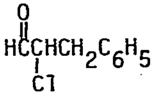
Carbenoids alpha to oxazines and oxazolines have been prepared, then alkylated to eventually afford α-chloroaldehydes or α-chloroacids [106,107]. For example, benzylation of CXXVI affords CXXVII which can be converted to either CXXVIII or CXXIX depending on the choice of subsequent reagents [106]. The use of optically active oxazolines CXXX and CXXXI afford optically active α-methoxy- and α-chloro acids, respectively [107].



CXXVI

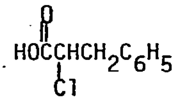


CXXVII



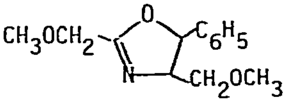
$H\overset{O}{\overset{\|}{C}}\underset{Cl}{\underset{|}{C}}HCH_2C_6H_5$

CXXVIII

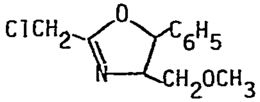


$HO\overset{O}{\overset{\|}{C}}\underset{Cl}{\underset{|}{C}}HCH_2C_6H_5$

CXXIX



CXXX

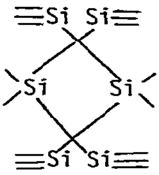


CXXXI

The preparation of new 1,3-dimetallacyclobutanes using carbenoid CXXXII has been described [108]. For example, treatment of CXXXII with dichlorodimethylsilane gives CXXXIII in a yield of 36%. Other examples are mentioned and a mechanism for their formation is postulated.

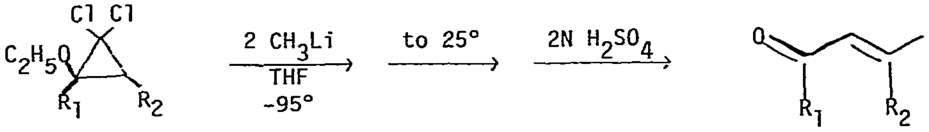
$[(CH_3)_3Si]_2CBrLi$

CXXXII



CXXXIII

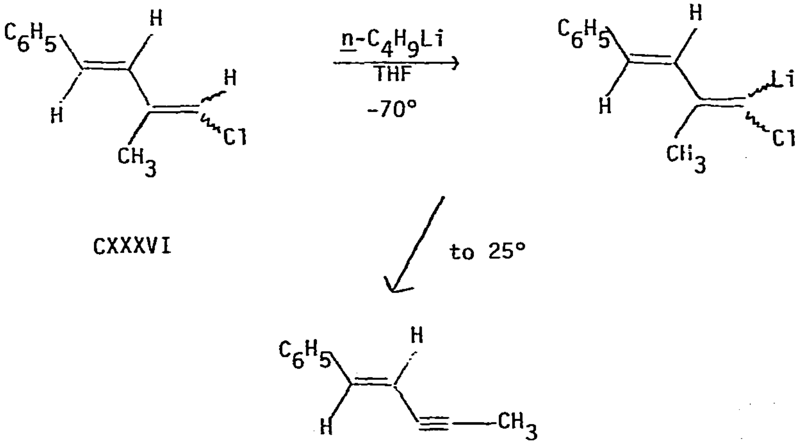
β-Methyl substituted α, β-unsaturated ketones (CXXXIV) may now be prepared in fair to good yields by a new one-carbon homologation involving cyclopropane CXXXV [109]. Several specific examples are listed in the paper.



CXXXV

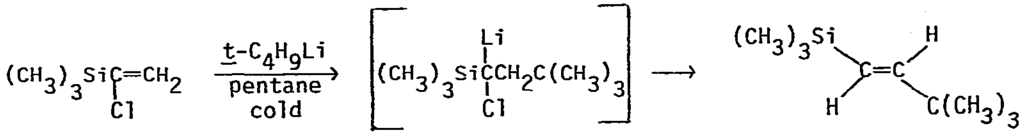
CXXXIV

A new synthesis of alkenylacetylenes from α, β-unsaturated ketones has been described [110]. The method is illustrated by the conversion of CXXXVI to CXXXVII.



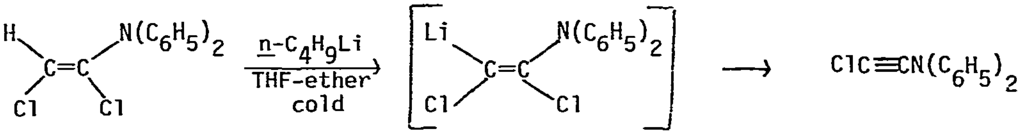
CXXXVII

Vinylsilanes may now be prepared by a new synthesis involving the interaction of organolithiums with α-chlorovinyltrimethylsilane (CXXXVIII) [111]. The reactions presumably proceed via CXXXIX as illustrated in the preparation of CXL.



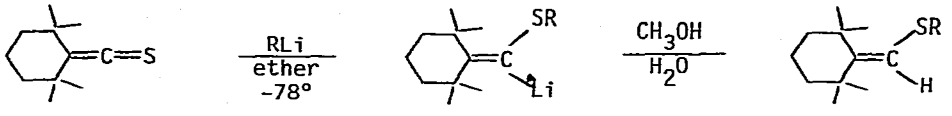
CXXXVIII CXXXIX CXL

Halogenated ynamines have been synthesized from polychlorinated enamines [112]. For example, CXLI is converted to CXLII in low yield.

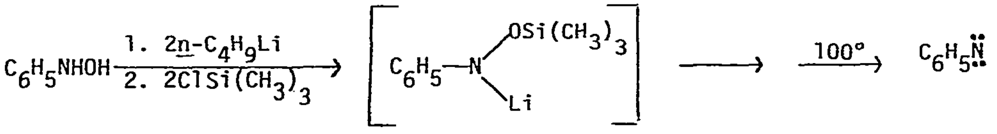


CXLI CXLII

Finally, two other papers deserve brief mention. First, phenyl- and methyllithium have been added to dialkylthioketenes like CXLIII to afford carbenoids like CXLIV [113]. Protonation of CXLIV gives thioethers (CXLV). Other reactions of CXLIV including trapping with certain electrophiles and thermolysis to afford carbenes are discussed. Second, α-deoxysilylation of hydroxylamine derivatives offers a new method of generating nitrenes perhaps via nitrenoid CXLVI [114].



CXLIII CXLIV CXLV



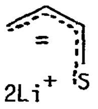
CXLVI

IV. Metalations (Hydrogen-Lithium Exchange Reactions)

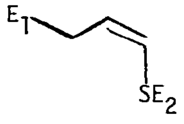
Several reviews have been concerned with metalations of organic compounds. Thus, the mechanistic aspects of chelating tertiary amines with respect to their effect on the reactivity and properties of organolithiums have been summarized [115]. The synthetic aspects of the metalations of aromatics, alkylbenzenes, ethers, sulfides, and other compounds by n-butyllithium-tertiary diamine complexes have been described [116,117]. Metalation by organolithiums of elastomers prepared by anionic initiators [118], and polymetalation by similar reagents of acetylenes, aromatics, and arylacetylenes have been discussed [119]. Directed metalations of a variety of substituted aromatics have been reviewed [120]. A review of the chemistry of carbon suboxide contains portions dealing with interaction of this compound with organolithiums [121]. A paper concerned with the preparation of olefins with organic phosphonate carbanions contains information on the synthesis of the latter using a variety of basic reagents [122]. The types of compounds that can be prepared to date from cyclopropylides via cyclopropanation and epoxides have been summarized [123] The use of carbanions of allylic sulfoxides to prepare allylic alcohols, and in regioselective alkylations has been discussed [124]. 1,3-Anionic cycloadditions of organolithiums [125] and recent advances in the chemistry of a variety of allylic organometallics including organolithiums [126] have been described. The chemistry of α-metalated isocyanides [127] and synthesis of carbocyclic spiro compounds via intramolecular alkylations have been discussed [128]. Finally, the determination of acidity constants [129] and O-organometal hydroxylamine and oxime derivatives [130] have been reviewed.

A. At sp^3 Carbon

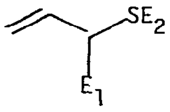
Several papers have used carbanions as synthons of various functional groups. Thus, allyl mercaptan has been converted to its dilithio salt CXLVII which is treated successively with two different electrophiles E_1 and E_2 to give a mixture of CXLVIII and CXLIX in a ratio of 67:30 to 80:20 [131]. Though E_2 has usually been methyl iodide, E_1 can be alkyl halides, epoxides, aldehydes, ketones, and others. Treatment of CXLVIII and CXLIX with methyl



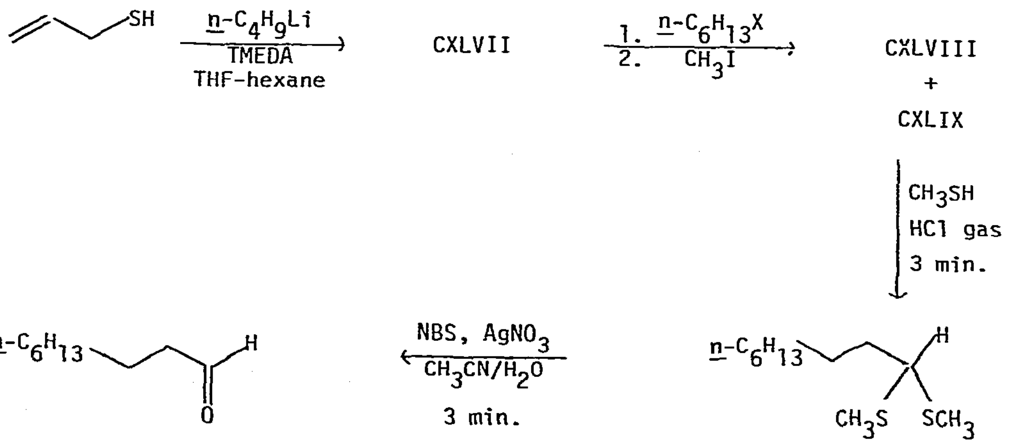
CXLVII



CXLVIII

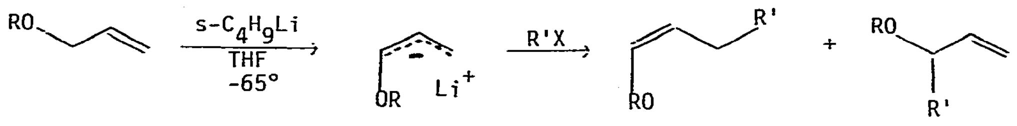


CXLIX



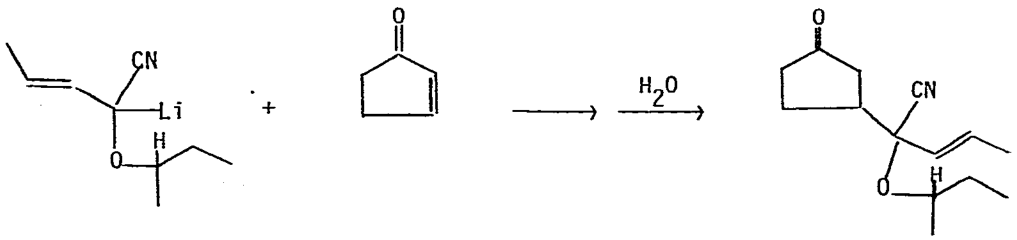
mercaptan followed by hydrolysis with NBS and silver nitrate gives aldehydes in yields of 65-95%. The entire procedure is illustrated for the preparation of nonanal.

Related metalated allylic ethers CL serve as homoenolate anion equivalents [132,133,134]. Such carbanions react with alkyl halides like n-hexyl iodide predominately γ to oxygen to afford CLI and CLII; the ratio of these species is a function of R, more γ-product (CLI) being formed when R=t-butyl (γ:α = 89:11) than when R=THP (γ:α = 54:46) [132]. The latter result has been independently confirmed [133]. Even higher ratios of γ:α (i.e., CLI:CLII) have been found by alkylation of the carbanion of certain allyl silyl ethers [134]. Thus, methylation of CL (R=$Si(C_2H_5)_3$) gives γ:α = 97:3.



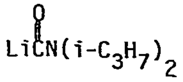
CL CLI CLII

Conjugate additions of acyl carbanion equivalents via protected cyanohydrin have been described [135]. The procedure is illustrated by the conversion of CLIII to CLIV.

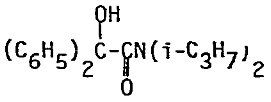


CLIII CLIV

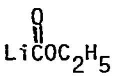
Direct formation of the carbonyl anion of diisopropylformamide (CLV) has been achieved at -78°; CLV was trapped with benzophenone to give CLVI in 92% yield [136]. The work demonstrates that a carbonyl anion can be formed by proton abstraction. In a different study, evidence has been found using radio-gas-liquid chromatography that the carbonyl anion of ethyl formate (CLVII) is an intermediate in the reaction of this ester with certain dilithio salts of carboxylic acids [137].


$\mathrm{Li\overset{O}{\overset{\|}{C}}N(\textit{i}\text{-}C_3H_7)_2}$

CLV


$\mathrm{(C_6H_5)_2\overset{OH}{\overset{|}{C}}\text{-}\underset{O}{\underset{\|}{C}}N(\textit{i}\text{-}C_3H_7)_2}$

CLVI

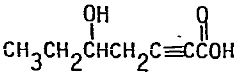

$\mathrm{Li\overset{O}{\overset{\|}{C}}OC_2H_5}$

CLVII

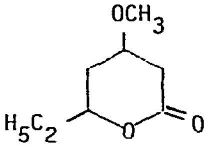
The dilithio salt of propiolic acid (CLVIII) acts as an acyl synthon [138]. Thus, reaction of CLVIII with epoxides affords δ-hydroxyacids like CLIX which are cyclized by acid to lactones like CLX.

$\mathrm{LiC{\equiv}CCO_2Li}$

CLVIII

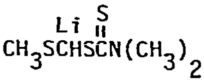

$\mathrm{CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_2C{\equiv}\overset{O}{\overset{\|}{C}}OH}$

CLIX

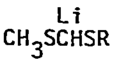


CLX

Lithiocarbamate CLXI has been shown to be a useful reagent for the synthesis of aldehydes [139]. It is suggested that CLXI is more stable than carbanions like CLXII, and that the thiol group is more easily removed in the former than in the latter.

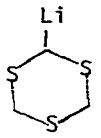

$\mathrm{CH_3S\overset{Li}{C}HS\overset{S}{\overset{\|}{C}}N(CH_3)_2}$

CLXI

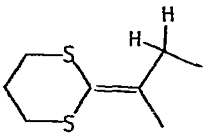

$\mathrm{CH_3S\overset{Li}{C}HSR}$

CLXII

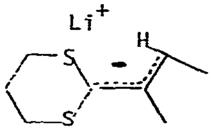
Several papers have described additional chemistry of lithium salts of tri- and dithianes. A full paper describes the preparation and reactions with electrophiles of lithio-1,3,5-trithianes like CLXIII [140]. Their use in the synthesis of aldehydes is demonstrated. Conversion of alkylidenedithianes like CLXIV to masked α,β-unsaturated acyl anions like CLXV may now be considered general since CLXV is conveniently prepared in high yields by treatment of CLXIV with either *n*-butyllithium or lithium diisopropylamide [141]. Alkylation of CLXV by RX followed by hydrolysis conveniently affords products like CLXVI.



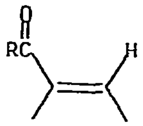
CLXIII



CLXIV

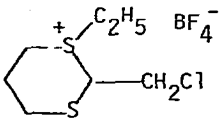


CLXV

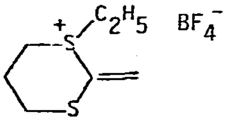


CLXVI

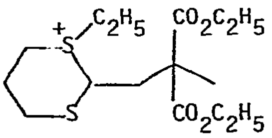
Treatment of salt CLXVII with lithium diisopropylamide gives CLXVIII which serves as a two-carbon Michael acceptor [142]. For example, reaction of CLXVIII with diethyl methylmalonate gives CLXIX which is converted to CLXX with 3% copper sulfate.



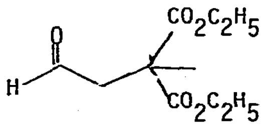
CLXVII



CLXVIII

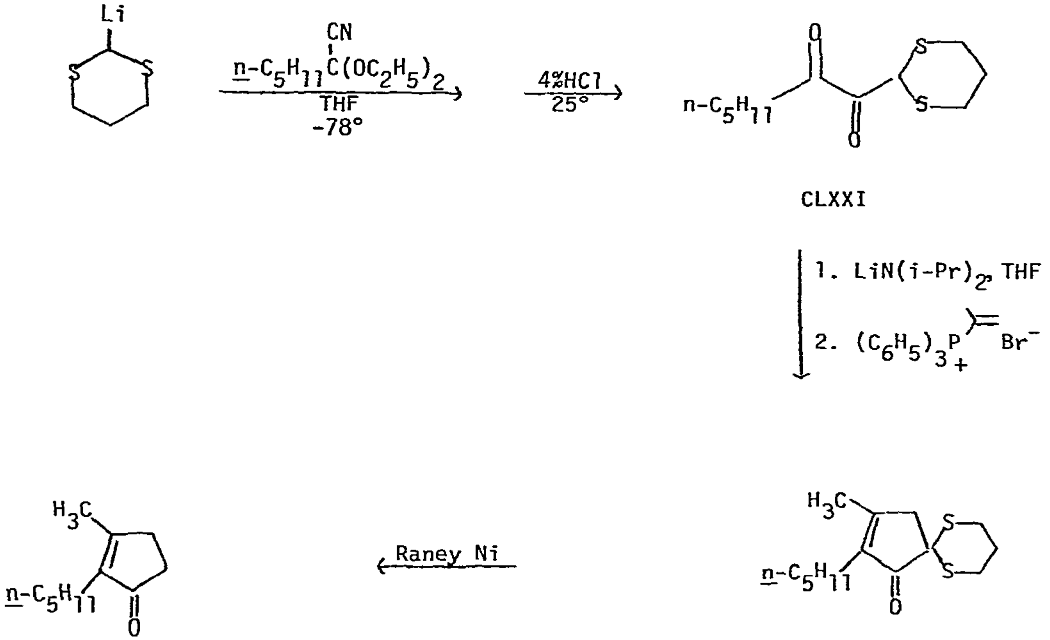


CLXIX



CLXX

A convenient preparation of α-oxoalkanoyl-1,3-dithianes (CLXXI) has been described [143]. These compounds, in turn, are used in a new synthetic route involving an intramolecular Wittig reaction to afford substituted cyclopentenones. The sequence is illustrated by the preparation of dihydrojasmone (CLXXII) in 70% yield.

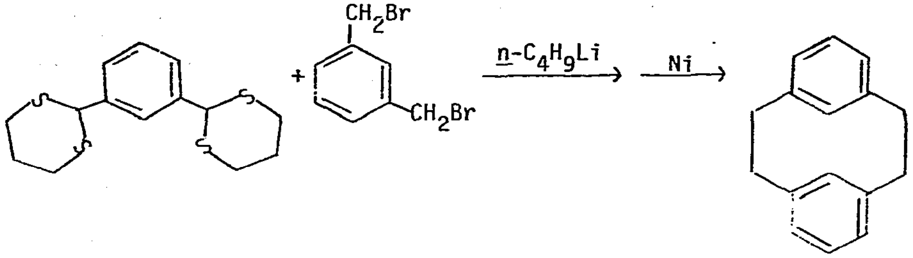


CLXXI

CLXXII

Finally, dithianes have been employed in the preparation of cyclophanes as illustrated for the conversion of CLXXIII to CLXXIV [144]. The method is particularly useful for the synthesis of cyclophanes with functionality in the aliphatic bridges.

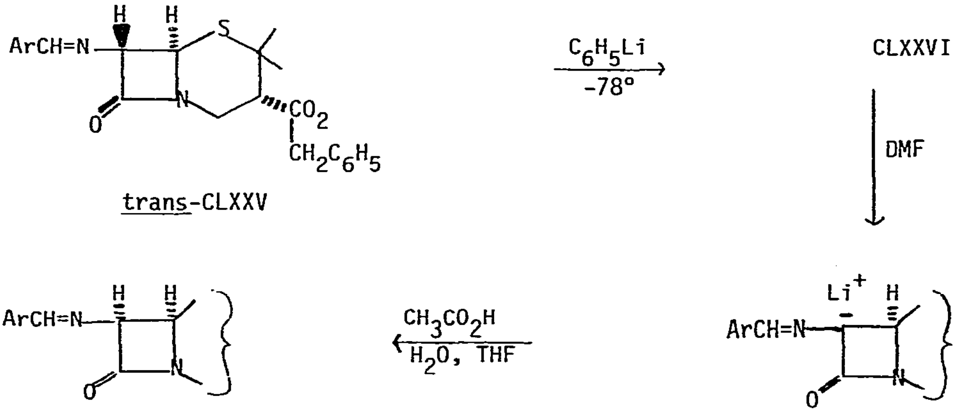
Lithiation of Schiff bases and enamines continues to provide a rich source of practical intermediates for synthetic purposes. Thus, epimerization of the p-nitrobenzaldehyde Schiff bases of 6α-aminopenicillins and 7α-aminocephalo-



CLXXIII

CLXXIV

sporins with phenyllithium followed by protonation with acetic acid under kinetically controlled conditions has enabled the completion of new total syntheses of penicillins and cephalosporins [145,146]. An example illustrates the conversion of the inactive trans-CLXXV to the active cis- isomer. The series is apparently successful because treatment of lithium salt CLXXVI with DMF affords an ion pair whose configurational memory is lost.

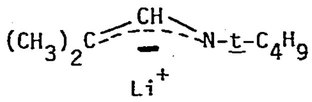


trans-CLXXV

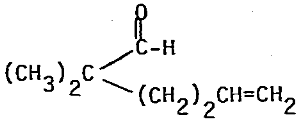
CLXXVI

cis-CLXXV

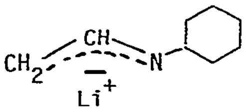
Two papers have described alkylations of Schiff bases to afford, after hydrolysis, mono-α-alkylated aldehydes [147,148]. For example, carbanion CLXXVI and 4-bromo-1-butene give CLXXVII while CLXXVIII and 1-bromo-4-chlorobutane afford CLXXIX.



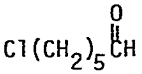
CLXXVI



CLXXVII



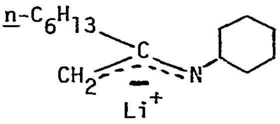
CLXXVIII



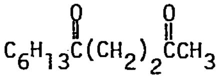
$Cl(CH_2)_5\overset{O}{\overset{\|}{C}}H$

CLXXIX

Other papers have described similar reactions leading to mono-α-alkylated ketones [149,150]. For example, treatment of CLXXX with 2,3-dichloro-1-propene affords, after hydrolysis, 1,4-diketone CLXXXI which is a precursor to dihydrojasmone (CLXXII) [149]. Use of optically active Schiff bases like CLXXXII in these transformations leads to optically active ketones; 2-methylcyclohexanone has thus been prepared with an optical purity of 26% [150].

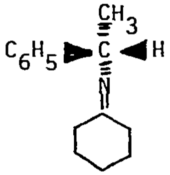


CLXXX



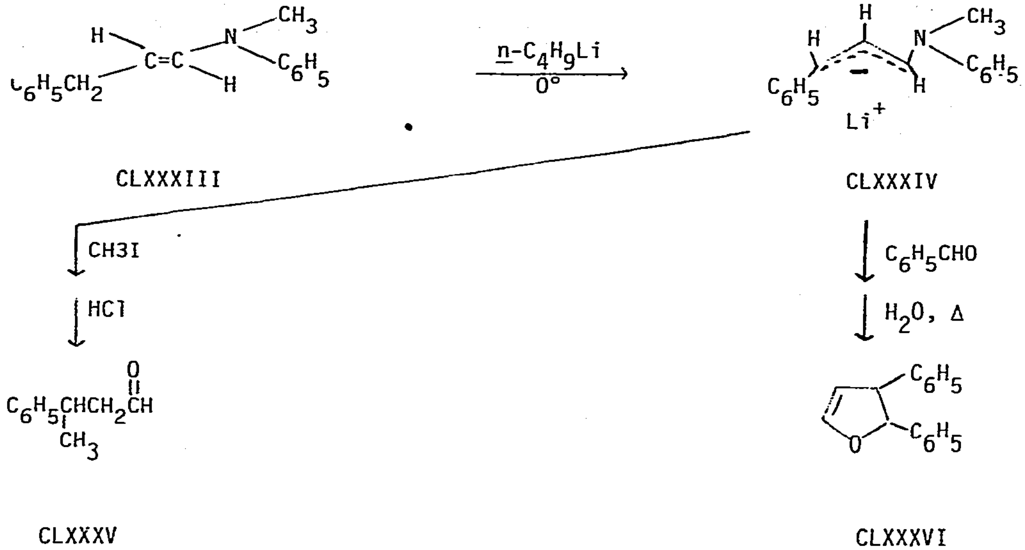
$C_6H_{13}\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}CH_3$

CLXXXI



CLXXXII

Metalated enamines are 3-oxocarbanion equivalents. For example, enamine CLXXXIII is converted to its lithium salt CLXXXIV which upon treatment with methyl iodide and benzaldehyde gives, after hydrolysis, CLXXXV and CLXXXVI, respectively [151]. Metalation of allyl amines like CLXXXVII afford similar intermediates which also have been alkylated and, in some cases, hydrolyzed to aldehydes [152,153]. Thus, butylation of the lithio salt of CLXXXVII gives mostly CLXXXVIII hydrolysis of which gives n-heptanal.

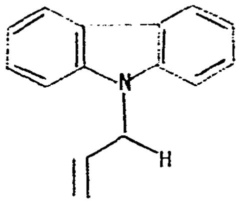


CLXXXIII

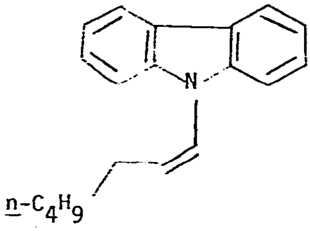
CLXXXIV

CLXXXV

CLXXXVI



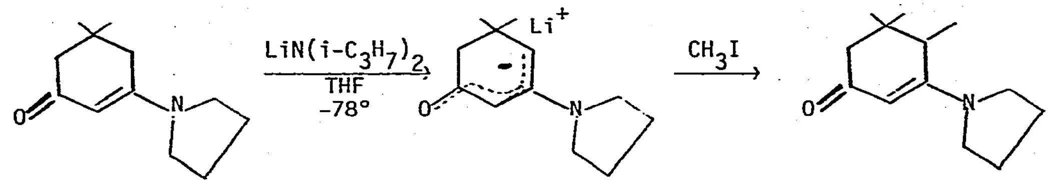
CLXXXVII



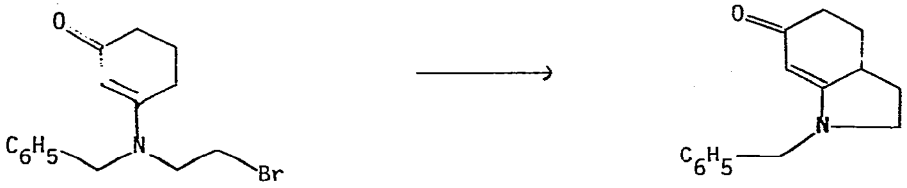
CLXXXVIII

Regioselective γ-alkylations are also realized on enaminoketones, esters, and nitriles [154]. Such reactions have been found to be insensitive to substitution at or near the γ-carbon atom; for example, CLXXXIX is converted via CXC to CXCI in good yield. Intramolecular alkylations are also conveniently realized as illustrated by the conversion of CXCII to CXCIII.

N-*t*-Butyl-3-methyleneaziridine has been lithiated and the resulting carbanion (CXCIV) trapped at low temperatures with methanol-O-d, methyl iodide, and chlorotrimethylsilane to give CXCV [155]. Upon warming to >-50°, CXCIV

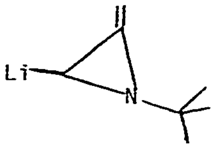


CLXXXIX CXC CXCI

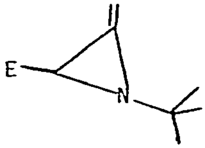


CXCII CXCIII

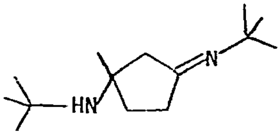
dimerizes to CXCVI. Lithio salts of enamines have also been reacted with an aldehyde [156] and a ketone [157] as a part of the total syntheses of maytansine and cembrene, respectively.



CXCIV

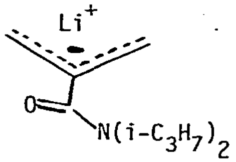


CXCV

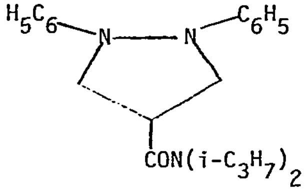


CXCVI

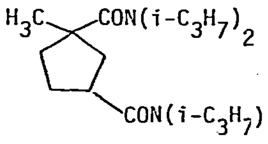
In connection with cycloaddition reactions of allyl anions, lithium salt CXCVII has been reacted with azobenzene to afford, after hydrolysis, heterocycle CXCVIII in 65% yield [158]. In the absence of azobenzene, CXCVII reacts with unmetalated starting material to afford cyclopentane derivative CXCIX in low yield. Similarly, allyl anion CC has been condensed with α, β-unsaturated esters to give CCI in good yield [159]. Though the cyclization leading to CXCVIII is thought to involve a two-step process, that leading to CCI is thought to be concerted.



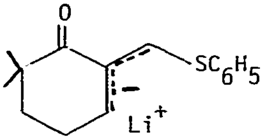
CXCVII



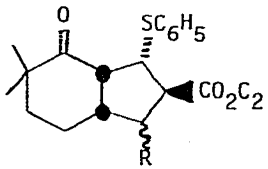
CXCVIII



CXCIX

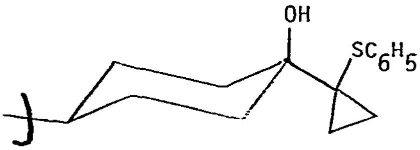


CC

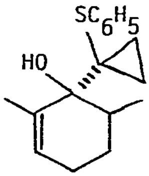


CCI

A large number of papers have appeared dealing with lithiation α to sulfur atoms. Thus, two new cyclopropyl phenyl sulfides, CCII and CCIII, have been prepared from lithiocyclopropyl phenyl sulfide and appropriate ketones [160]. Such compounds are useful in the spiroannelations involving the conversion of cyclopropyl to cyclobutyl systems.

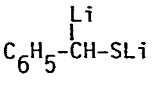


CCII

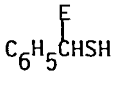


CCIII

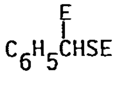
1,2-Dianions of mercaptans like CCIV, previously only prepared by reductive metalation of thioketones, have now been synthesized by metalation of benzyl mercaptan [161]. Dianion CCIV has been condensed with a variety of electrophiles to afford either CCV or CCVI depending on the stoichiometry.


$C_6H_5\text{-}\overset{\overset{Li}{|}}{C}H\text{-}SLi$

CCIV

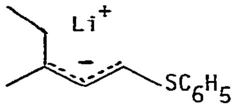

$C_6H_5\overset{\overset{E}{|}}{C}HSH$

CCV

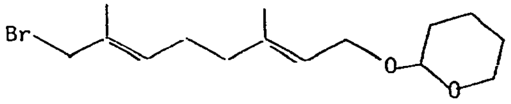

$C_6H_5\overset{\overset{E}{|}}{C}HSE$

CCVI

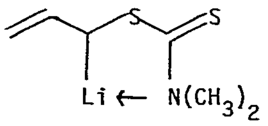
A key step in a stereoselective synthesis of dl-C_{17}-*Cecropia* juvenile normone involved the reaction of lithiosulfide CCVII with bromide CCVIII [162]. Lithioallyl dithiocarbamates (CCIX) have been alkylated to afford CCX which can be converted to α, β-unsaturated aldehydes [163,164]. Salt CCIX was also reacted with a variety of other electrophiles.[163].



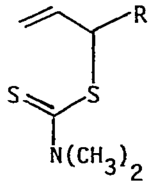
CCVII



CCVIII

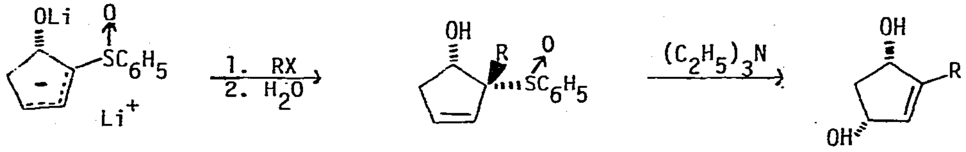


CCIX



CCX

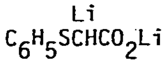
A general synthesis of 1-alkyl-1-cyclopentene-*cis*-3,5-diols, compounds useful in prostaglandin preparations, has been described [165]. The method involves regioselective alkylation of dianion CCXI followed by isomerization and cleavage with triethylamine to afford CCXII; a variety of alkyl halides have been employed.



CCXI CCXII

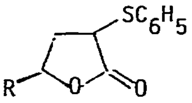
Other dilithio salts of sulfur containing compounds have also been used in synthesis. Thus, dilithio salt CCXIII has been reacted with various epoxides to give CCXIV which are converted to γ-substituted $\Delta^{\alpha,\beta}$-butenolides (CCXV) [16

Dialkali salts of β-keto sulfoxides like CCXVI have been alkylated with several alkyl halides as a route to ketones and aldols [167,168]. For example, benzylation of CCXVI followed by reductive elimination of the sulfoxide moiety with aluminum amalgam affords the methyl vinyl ketone homologue CCXVII in a yield of 75%.



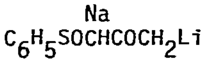
$C_6H_5S\overset{Li}{C}HCO_2Li$

CCXIII



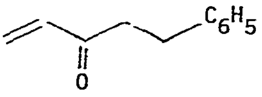
CCXIV

CCXV



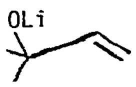
$C_6H_5SO\overset{Na}{C}HCOCH_2Li$

CCXVI

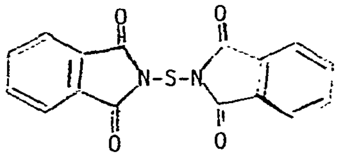


CCXVII

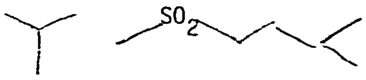
A new synthesis of allylic sulfones has been described which involves reaction of the lithio salt of allyl alcohols like CCXVIII with CCXIX to afford CCXX in good yields [169]. Elimination of the SO_2 moiety from such sulfones using potassium hydroxide and carbon tetrachloride or via dilithio salts provides a facile method for the preparation of polyolefins such as β-carotenes. Dianions of sulfones have also provided a novel, versatile method of preparing small ring systems as illustrated by the conversion of CCXXI to CCXXII [170].



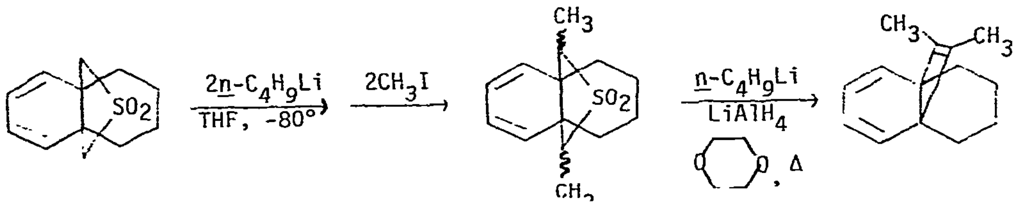
CCXVIII



CCXIX



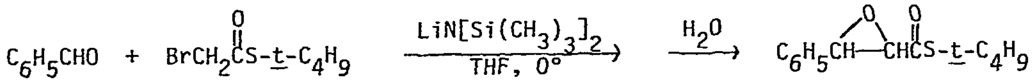
CCXX



CCXXI

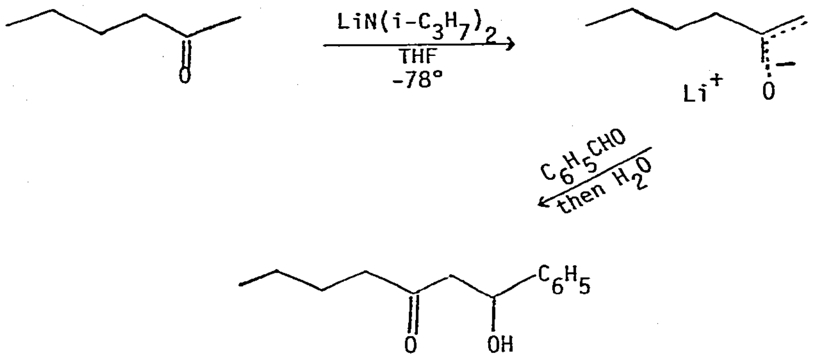
CCXXII

The first Darzens synthesis of glycidic thiol esters has been described [171]. The success of the method depends on the use of α-bromothiol esters, non-nucleophilic bases, and polar, aprotic solvents. An example follows.

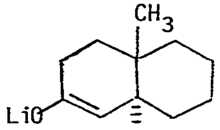


$$C_6H_5CHO + BrCH_2\overset{O}{\overset{\|}{C}}S\text{-}\underline{t}\text{-}C_4H_9 \xrightarrow[THF,\ 0°]{LiN[Si(CH_3)_3]_2} \xrightarrow{H_2O} C_6H_5\overset{O}{\overbrace{CH—CH}}\overset{O}{\overset{\|}{C}}S\text{-}\underline{t}\text{-}C_4H_9$$

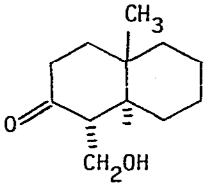
Several papers dealing with regiospecific reactions of ketone enolates have appeared in 1974. By employing highly reactive electrophiles such as aldehydes, methyl alkyl ketones have been caused to undergo aldol condensations via the kinetic lithium enolate [172]. An example is shown. Kinetic enolates from α, β-unsaturated ketones are similar.



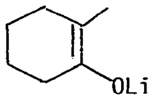
Other regiospecific ketone enolates generated by treatment of enol acetates or silyl ethers with organolithiums have been reacted with a variety of electrophiles. Thus, for example, treatment of CCXXIII with formaldehyde gives CCXXIV in high yield [173]. Compound CCXXIV and related ones are particularly useful for Michael condensations, annelations with β-ketoesters, chain extension with cuprates, and Diels-Alder reactions. Enolates like CCXXV have also been reacted with γ-iodotiglate esters and silanes to afford compounds like CCXXVI [174,175]. The γ-iodotiglate compounds serve as masked ketoalkyl groups. Finally, enolates like CCXXIII have been treated with α-silylketones like CCXXVII to eventually give ketones like CCXXVIII [176,177].



CCXXIII

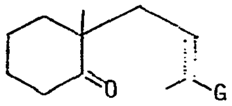


CCXXIV



CCXXV

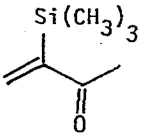
α-Lithio salts of esters continue to be studied. A new synthetic conversion of silylesters to α, β-unsaturated esters in high yields has been described [178]. Thus, CCXXIX with benzaldehyde gives ethyl cinnamate (E:Z = 3:1) in a



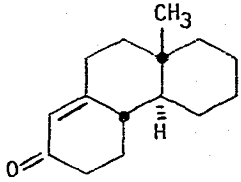
CCXXVI

(G = $Si(CH_3)_3$ or

$CO_2\text{-}\underline{t}\text{-}C_4H_9$)

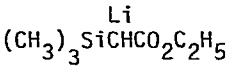


CCXXVII



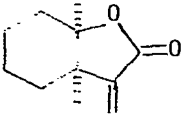
CCXXVIII

yield of 84%. The method is better in some cases than either the Wittig or the Emmons-Wadsworth-Horner procedures. A new route to α-methylene-γ-butrolactones (CCXXX) from α-methyllactones involving lithiation with triphenylmethyllithium and bromination with 1,2-dibromoethane gives bromolactones like CCXXXI which, upon treatment with base, give CCXXX in high yields [179]. A related procedure on *trans*-lactones involves treatment of the lithiolactone with diphenyl disulfide to afford CCXXXII [180]. Oxidation, then heating, of the latter gives *trans*-CCXXX. Finally, treatment of estrone methyl ether with lithium salt CCXXXIII unexpectedly affords heterocycle CCXXXIV [181].

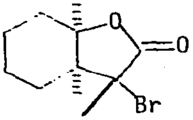


$(CH_3)_3Si\overset{Li}{C}HCO_2C_2H_5$

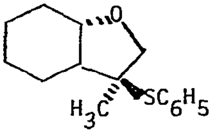
CCXXIX



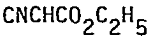
CCXXX



CCXXXI

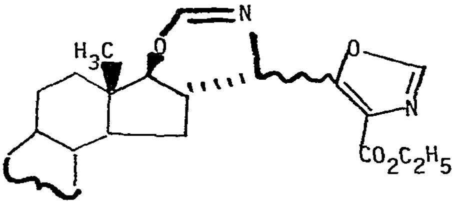


CCXXXII



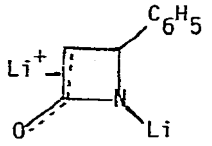
$CN\overset{Li}{C}HCO_2C_2H_5$

CCXXXIII

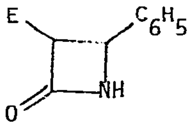


CCXXXIV

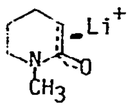
In the area of α-lithiocarboxamides, it has been found that N-unsubstituted β-lactams with n-butyllithium afford dianions like CCXXXV that undergo reaction with alkyl halides and ketones to afford species like CCXXXVI [182]. It should be noted that the acidity of the carbon-hydrogen bond of such lactams is not enhanced by an additional functional group like a Schiff base as in CLXXV. Lactam CCXXXVII has similarly been alkylated with a variety of alkyl halides and with chlorodimethylphenylsilane to afford CCXXXVIII [183]. The latter reagent is interesting since the C-silylation product obtained contrasts with related reactions of lactone enolates which afford O-silylation. Another α-metalated lactam has been used in the total synthesis of the alkaloid dl-vincamine [184]. N,N-Disubstituted acetamides and their α-alkyl and α,α-dialkyl derivatives are metalated by lithium diethylamide; alkylations with alkyl halides proceed on the α-carbon as expected [185].



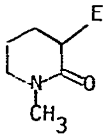
CCXXXV



CCXXXVI

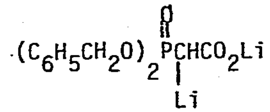


CCXXXVII



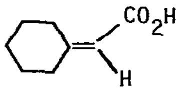
CCXXXVIII

Metalation of phosphorus-containing compounds has also been syntheticall useful. Thus, a new one-step carboxyvinylation of an aldehyde or ketone to give derived α, β-unsaturated acids has been described [186]. For example, treatment of dilithio salt CCXXXIX with cyclohexanone affords CCXL in good yield. An efficient one-pot procedure for the one-carbon homologation of ketones to α-allyl aldehydes has been reported [187]. The method involves treatment of salt CCXLI with a ketone to afford enamines like CCXLII which are reacted with allyl bromide; hydrolysis gives aldehyde CCXLIII.

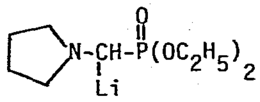


$(C_6H_5CH_2O)_2\overset{O}{\overset{\|}{P}}\underset{Li}{\underset{|}{C}}HCO_2Li$

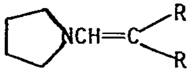
CCXXXIX



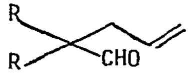
CCXL



CCXLI

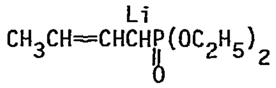


CCXLII



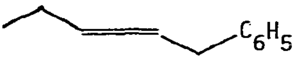
CCXLIII

A new method for the stereoselective synthesis of trans-olefins has been described which involves alkylation of salt CCXLIV and reductive cleavage of the resulting alkylated ester to afford, for example, CCXLV [188]. The cleavage of HMPA by organolithiums effected at lower temperatures and longer reaction periods than previously described gives rise to mixed secondary amines by attack of the organolithium on N-methylmethylene imine [189]. Dilithio salts of aminophosphonamides CCXLVI have been alkylated to give either straightforward products like CCXLVII or cyclic ones like CCXLVIII depending upon conditions [190].

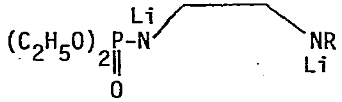


$CH_3CH{=}CH\overset{Li}{C}H\underset{O}{\underset{\|}{P}}(OC_2H_5)_2$

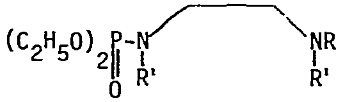
CCXLIV



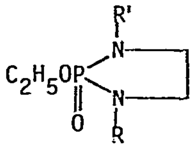
CCXLV



CCXLVI

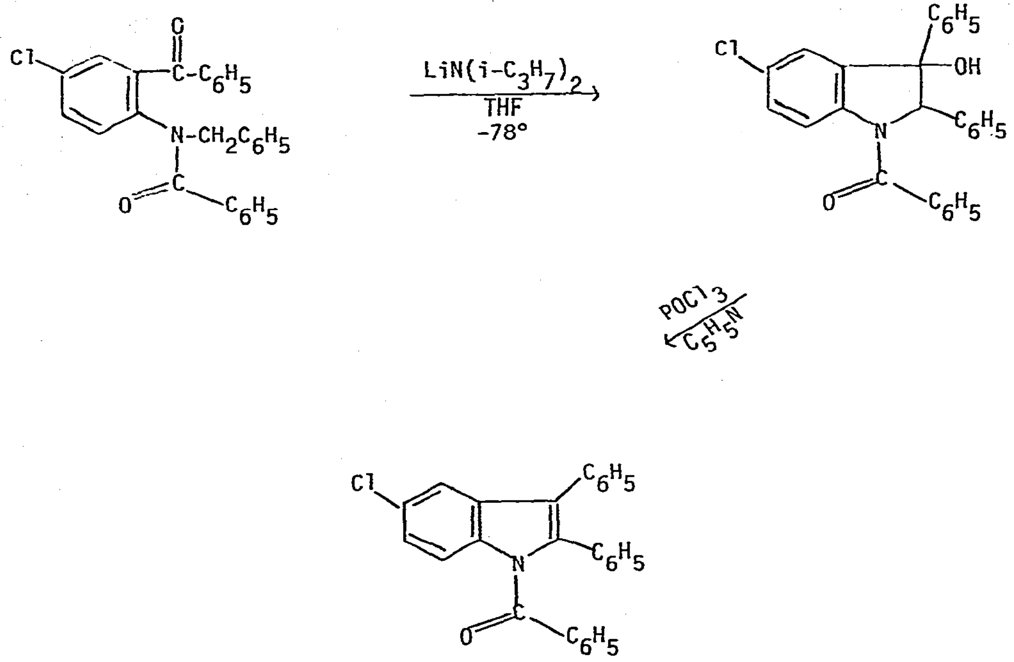


CCXLVII

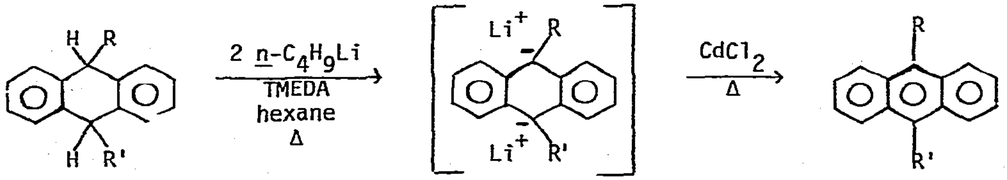


CCXLVIII

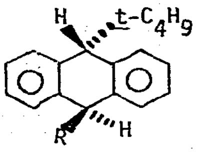
A new synthesis of 2-aryl- and 2-vinylindoles by means of an intramolecular addition of α-lithioamides has been described [191]. An example follows.



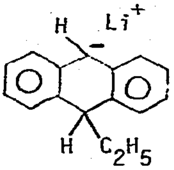
A new method to dehydrogenate ring systems has been demonstrated [192]. An example is shown on anthracene derivative CCXLIX. In another study, monometalation of CCXLIX (R=t-butyl, R'=CH_3) followed by alkylation with various species affords only trans-CCL [193]. In contrast, alkylation of CCLI with ethyl halides gives only cis-CCXLIX (R=R'=C_2H_5).



CCXLIX

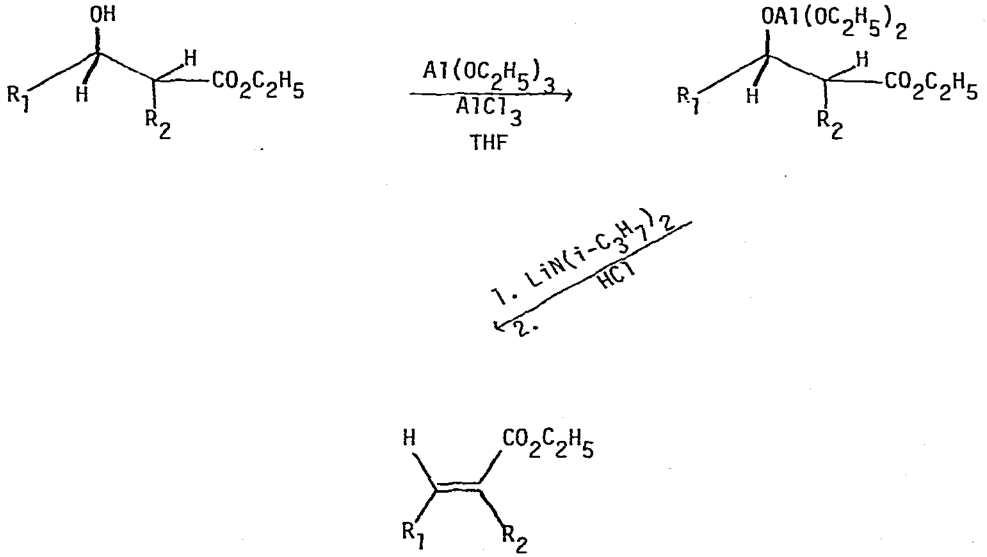


CCL

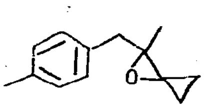


CCLI

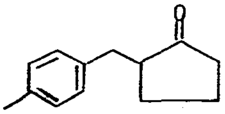
A highly stereoselective, completely regiospecific method has been reported for dehydration of β-hydroxyesters [194]. An example is shown.



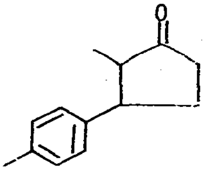
Treatment of epoxide CCLII with lithium diisopropylamide, chlorotrimethylsilane, and acid gives cyclopentanone CCLIII [195]. In contrast, use of lithiu pyrrolidine in the reaction sequence affords cyclopentanone CCLIV. These results represent the first example in base induced epoxide ring openings where kinetic versus thermodynamic control determines the orientation.



CCLII

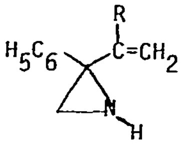


CCLIII

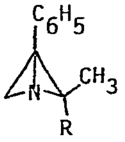


CCLIV

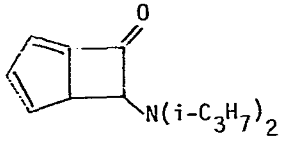
A new preparation of certain N-unsubstituted 2-vinylaziridines CCLV (R=H or CH_3) has been achieved by treatment of 2-methyl-substituted 1-azabicyclobutanes CCLVI with lithium diisopropylamide [196]. The first example of a small ring dehydroannulene (CCLVII) has been achieved by treatment of ketone CCLVIII with this same base [197].



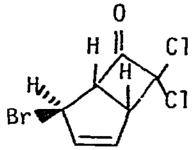
CCLV



CCLVI



CCLVII

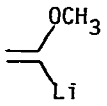


CCLVIII

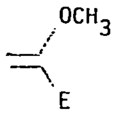
B. At sp^2 and sp Carbon and at Nitrogen

Metalation of methyl vinyl ether and related compounds gives compounds like CCLIX that are acyl anion equivalents [198]. Reactions of CCLIX with aldehydes, ketones, and alkyl halides give substituted ethers like CCLX that are converted by methanolic hydrochloric acid to ketones like CCLXI.

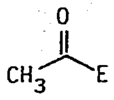
1,4-Dihalo-1,3-butadiynes (CCLXII) have been prepared by treatment of 1,4-dilithio-1,3-butadiyne with molecular chlorine in Freon-11 at -80°, liquid bromine at -55°, and molecular iodine in ether at -55° [199]. Two papers have



CCLIX



CCLX

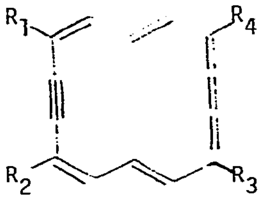


CCLXI

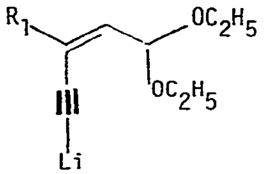
described the synthesis of [14]-annulene derivatives (CCLXIII) using lithioacetylenes [200,201]. The syntheses are begun by condensing species like CCLXIV with CCLXV.

$X-C\equiv C-C\equiv C-X$

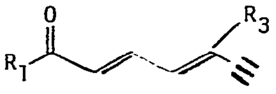
CCLXII



CCLXIII

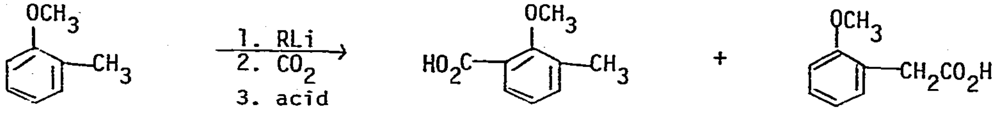


CCLXIV

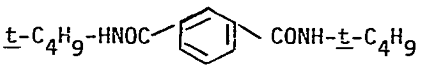


CCLXV

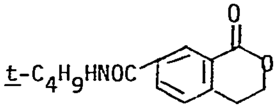
o-Methylanisole has been reacted with n- and t-butyllithium and the reaction mixtures carbonated to measure the relative amounts of o- versus α-metalation [202]. Since the amount of o-metalation is higher with t-butyllithium, the authors conclude that the relative oligomer size of the metalating agent is more important than steric hindrance to coordination with the anisole oxygen atom.



Other authors believe that steric effects of the m-carboxamide substituents of CCLXVI are responsible for lithiation occurring at the 4- rather than at the 2-position of this molecule [203]. Treatment of the resulting organolithium with ethylene oxide gives CCLXVII.

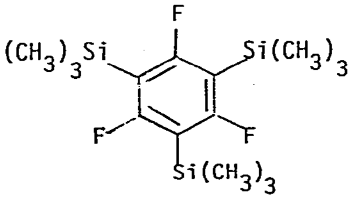


CCLXVI

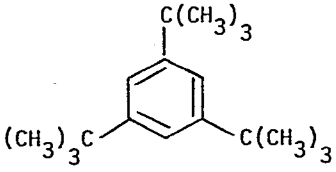


CCLXVII

Two papers have described the interaction of 1,3,5-trifluorobenzene with n- and t-butyllithium [204,205]. Though n-butyllithium affords metalation as evidenced by trapping with chlorotrimethylsilane to give CCLXVIII, t-butyllithium affords CCLXVIII only at low temperatures (-115°). At higher temperatures (-78°) t-butyllithium enters into a substitution type reaction giving CCLXIX in good yield.

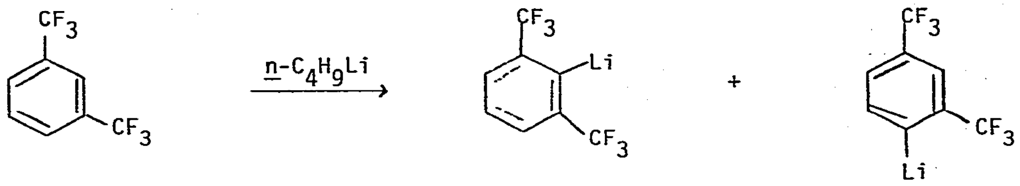


CCLXVIII

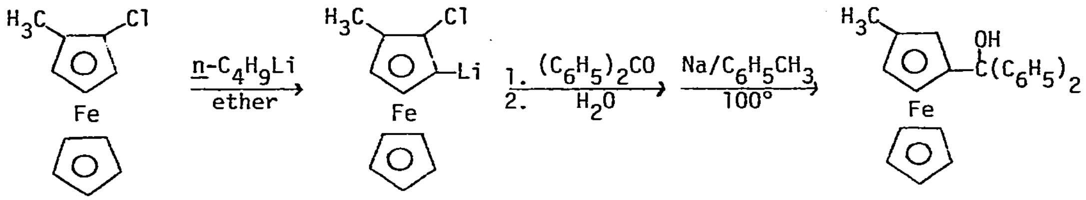


CCLXIX

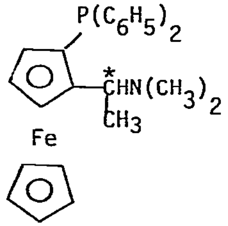
In contrast to previous reports, lithiation of m-di(trifluoromethyl)benzene affords only the 2- and 4-lithio derivatives as evidenced by carbonation [206]. None of the previously described 5-lithio isomer could be isolated.



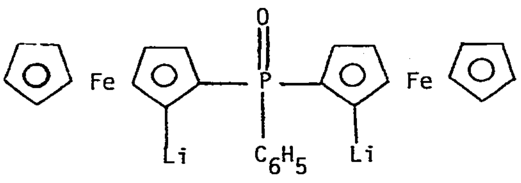
The first application of sequential directed metalation followed by removal of the directing group to give 1,3-disubstituted ferrocenes has been reported [207]. An example is shown.



Two phosphorus substituted ferrocenes have also been described. Chiral ferrocene CCLXX has been prepared by treatment of the corresponding lithio ferrocene by chlorodiphenylphosphine; CCLXX is useful as a chiral ligand in asymmetric catalytic hydrosilylation of ketones [208]. Diferrocenyl phenyl phosphine oxide has also been dimetalated by n-butyllithium to give CCLXXI which undergoes condensation with a variety of electrophiles [209].

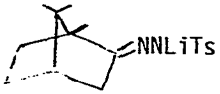


CCLXX



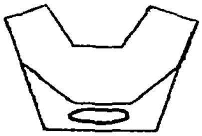
CCLXXI

Finally, decomposition of tosylhydrazones by organolithiums continues to be fruitful. The first case of effecting vinyl deuteration from a tosylhydrazone has been described (CCLXXII to CCLXXIII) which apparently proceeds via a previously unrecognized mechanism [210]. Decomposition of the tosylhydrazone of fluorenone has now been shown to proceed via a carbanion intermediate [211]. The smallest paracyclophane to date (CCLXXIV) has been prepared by decomposition of CCLXXV; pmr of CCLXXIV reveals a ring current despite the high degree of strain [212].

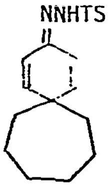


CCLXXII

CCLXXIII



CCLXXIV

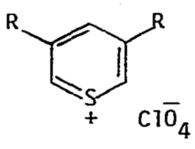


CCLXXV

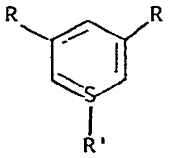
Decomposition of tosylhydrazones has also given rise to tetracyclo-[4.2.0.0^{2,4}.0^{3,5}]oct-7-ene [213], bicyclo[2.2.1]hepta-2,5-dien-7-spirocyclobutane [214], benzobullvalene [215], and five new bicyclic methylenecyclopropane [216].

V. Heterocycles

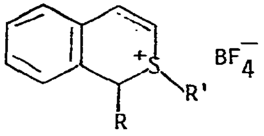
Reinvestigation of the reactions of phenyllithium with thiopyrylium salts like CCLXXVI (R=H) has demonstrated that such reactions give oligomeric materials rather than stable thiabenzenes like CCLXXVII (R=H, R'=phenyl) [217]. In fact, extensive degradation of the sulfur-containing ring system occurs giving sulfide intermediates. On the other hand, in agreement with earlier workers, deprotonation of salts CCLXXVIII with the lithium or sodium salts of DMSO give thianaphthalenes (CCLXXIX) some of which are stable in solution to 40° [218]. Such thianaphthalenes have been found to be pyramidal at sulfur [219]. A full paper describing the synthesis of 1-methyl-3,5-diphenylthiabenzen (CCLXXVII, R=phenyl, R'=methyl) from salt CCLXXX and *t*-butyllithium, and the related synthesis of CCLXXIX (R=phenyl, R'=methyl) has appeared [220]. Use of the latter method has resulted in the first example of a selenabenzene (CCLXXXI) [221].



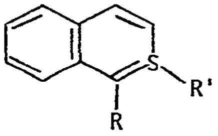
CCLXXVI



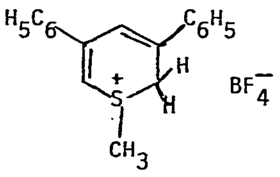
CCLXXVII



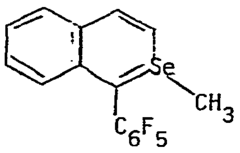
CCLXXVIII



CCLXXIX

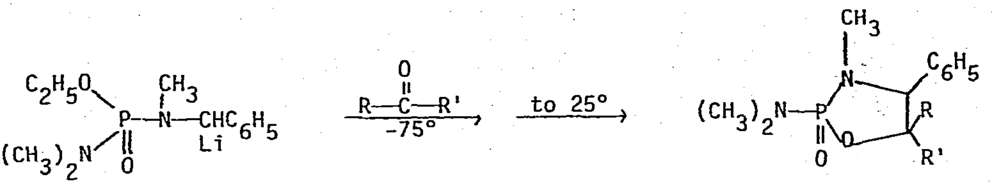


CCLXXX

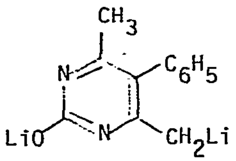


CCLXXXI

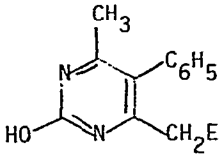
A new, direct synthesis of oxazaphospholidines has been described; an example is shown [222].



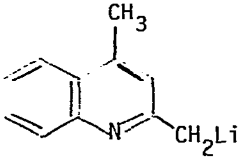
Metalation of side chains of various heterocyclics continued to find use in synthesis. Dianions like CCLXXXII of certain pyrimidines and related compounds have been condensed with alkyl halides, ketones, and other electrophiles to give compounds like CCLXXXIII [223]. Selective metalations of dimethylated quinolines and pyridines have been found to be strongly affected by choice of solvent [224]. Thus, CCLXXXIV solvated by THF or by ether is formed by a kinetically and a thermodynamically controlled process, respectively. The opposite is realized with CCLXXXV.



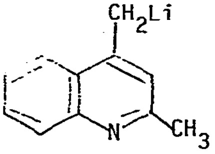
CCLXXXII



CCLXXXIII

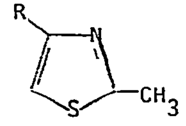


CCLXXXIV

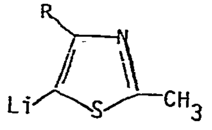


CCLXXXV

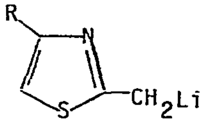
Temperature and substituent effects have been found to be important in the metalation of 2-methyl-4-substituted-1,3-thiazoles and related compounds [225,226]. Thus, metalation of CCLXXXVI (R=phenyl) at -78° proceeds predominately on the ring to give CCLXXXVII while similar reaction of CCLXXXVI (R=methyl) occurs at the 2-methyl group to give CCLXXXVIII. Though the latter compound (R=CH_3) is stable at -78°, it couples with unmetalated heterocycle at 25°. Interestingly, initial metalation of CCLXXXVI (R=phenyl) at higher temperatures gives mostly CCLXXXVIII.



CCLXXXVI

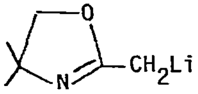


CCLXXXVII

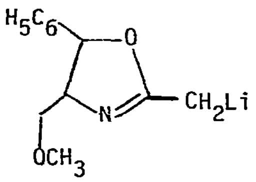


CCLXXXVIII

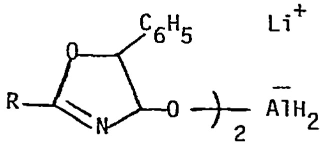
Lithio-2,4,4-trimethyl-2-oxazoline (CCLXXXIX) continues to be alkylated, then decomposed with aqueous acids or alcoholic sulfuric acid to give carboxylic acids or esters, respectively [227]. Use of 1,4-diiodopentane in the sequence has been shown to be highly stereospecific leading to mostly *cis*-2-methylcyclopentane carboxylic acid [228]. The use of the lithium salt of chiral oxazoline CCXC leads to optically active carboxylic acids [229,230]. Either R or S dialkylacetic acids can thus be prepared depending on the order of addition of RX and R'X. Treatment of CCXC with racemic *sec*-alkyl iodides gives 30-40% stereoselective alkylation of the S-enantiomer of the halide and allows recovery of R-enriched halide [231]. Thus, CCXC is capable of chiral recognition. Treatment of CCXC with aldehydes followed by water or by methyl iodide then water affords optically active β-hydroxy- or β-methoxyacids, respectively [232]. The use of benzaldehyde or phenyl ketones in the latter reactions gives cinnamic acids. Finally, treatment of CCXC with lithium aluminum hydride gives ate complex CCXCI which is a new chiral reducing agent of ketones [233]. Alcohols obtained by such reductions have exhibited optical purities ranging from 0.5-65%.



CCLXXXIX

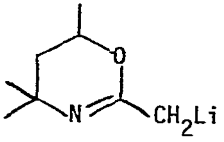


CCXC

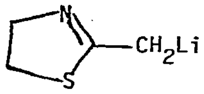


CCXCI

Reactions of the lithium salts CCLXXXIX, CCXCII, and CCXCIII with epoxides give the γ-hydroxyl derivatives of the heterocycles which, on treatment with mineral acid, afford butyrolactones in high yields [234,235]. Reaction of CCXCII with esters and nitriles gives keto derivatives of the oxazine that are resistant to reduction by sodium borohydride; such compounds thus do not serve as precursors to aldehydes [236].

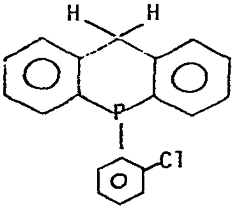


CCXCII

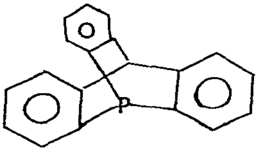


CCXCIII

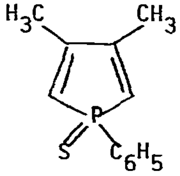
Metalation and aryne formation of phosphine CCXCIV has resulted in the first reported formation of a phosphatriptycene (CCXCV) [237]. Metalation of phosphole sulfide CCXCVI and subsequent condensation with electrophiles have been described [238]. Products arising from reaction at the methyl group of CCXCVI are obtained with aldehydes and ketones while ring 2-substituted compounds are realized with esters and carbon dioxide.



CCXCIV

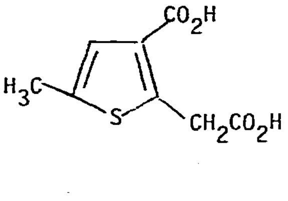


CCXCV

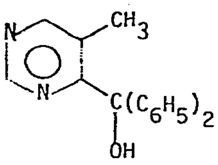


CCXCVI

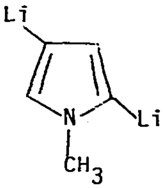
In contrast to previous results, 2,5-dimethylthiophene has been caused to undergo both ring and side-chain metalation by lithium diisopropylamide as evidenced by carbonation to give CCXCVII in low yield [239]. Similarly, 5-methylpyrimidine has been ring metalated and condensed with benzophenone to afford CCXCVIII. Even pyridine, quinoline, and isoquinoline apparently are metalated by the above base at low temperature. Evidence has also been presented that 2,3-dialkylpyrazines can be ring-metalated [240], and that N-methylpyrrole can be α, β'-ring-dimetalated to give CCXCIX by organolithiums [241].



CCXCVII

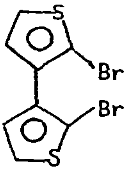


CCXCVIII

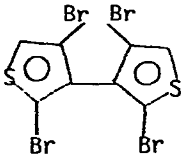


CCXCIX

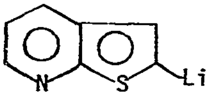
A variety of lithiated derivatives of thiophenes have been prepared either by metal-halogen exchange or by metalation and the compounds condensed with electrophiles. Thus, dibromo compound CCC [242] and tetrabromo derivative CCCI [243] have been converted to the corresponding dilithiated compounds. A route to 2-substituted thieno-[2,3-b]pyridines is now available via CCCII [244]. α, α'-Diiodothieno-[2,3-b]thiophenes (CCCIII) are readily synthesized from the corresponding lithiated derivatives and iodine [245]. Thiophene derivatives CCCIV [246] and CCCV [247] have likewise been dimetalated and reacted with a variety of electrophiles.



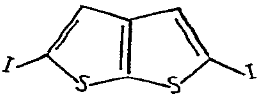
CCC



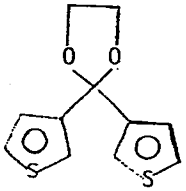
CCCI



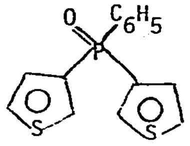
CCCII



CCCIII

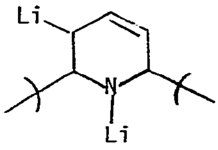


CCCIV

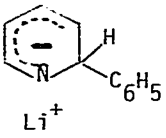


CCCV

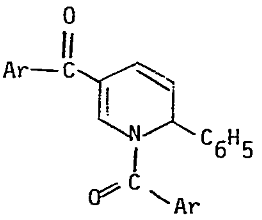
Several papers have been concerned with addition or addition-elimination reactions of pyridines and pyrimidines. Excess *t*-butyllithium adds to pyridine to afford CCCVI which decomposes to 2,6-di-*t*-butylpyridine and various reduced derivatives [248]. Treatment of CCCVII, derived from pyridine and phenyllithium, with *p*-ethoxybenzoyl chloride gives CCCVIII and represents a non-Friedel crafts method of acylating this heterocycle [249]. The linear linkage of as many as six different arenes has been achieved by coupling certain organolithiums with nitrogenous heterocycles [250,251]. The method is illustrated by the preparation of CCCIX.



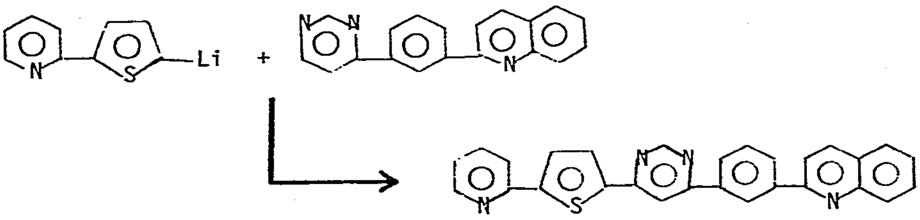
CCCVI



CCCVII

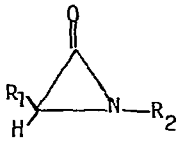


CCCVIII

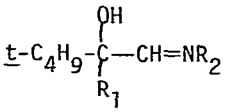


CCCIX

The first substantiated reaction of α-lactams with an organometallic has been reported [252]. Thus, treatment of CCCX (R_1=*t*-butyl, R_2=adamantyl) with *t*-butyllithium at 25° gives ring-opened product CCCXI. In contrast, reaction of this same α-lactam with various organolithiums (R'Li) at -78° gives α-aminoketones CCCXII in good yields [253].

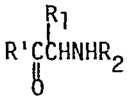


CCCX



$\underline{t}\text{-}C_4H_9\text{-}\overset{OH}{\underset{R_1}{C}}\text{—}CH{=}NR_2$

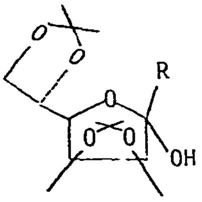
CCCXI



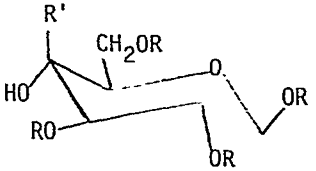
$R'\underset{O}{\underset{\|}{C}}\overset{R_1}{C}HNHR_2$

CCCXII

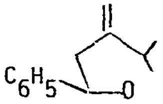
Organolithiums have been added to sugar lactones to afford sugar lactols like CCCXIII [254] and to oxo sugars to give alcohols like CCCXIV [255]. The latter reactions are stereospecific-attack of the nucleophile occurs from an axial direction. Methyllithium has been added to an oxocyclopentanone to give an alcohol which is dehydrated to afford the novel methylidenedihydrofuran (CCCXV) [256].



CCCXIII



CCCXIV

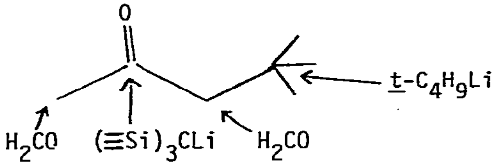


CCCXV

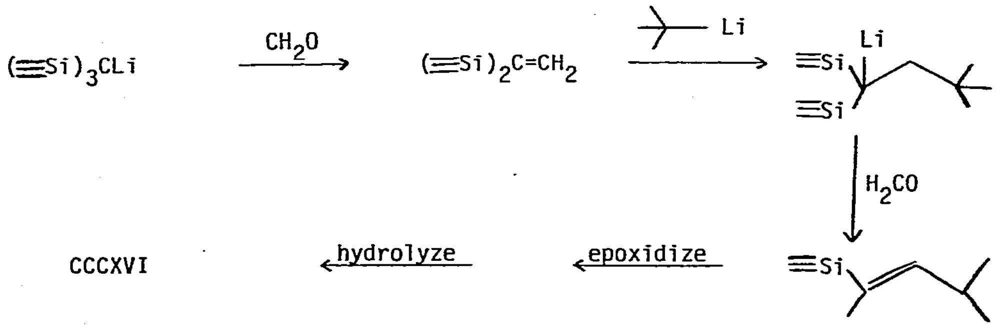
VI. Addition and Substitution Reactions

Reviews in this area include a discussion of carbanion additions and cyclizations involving anionic σ complexes [257] and base-catalyzed carbon-carbon addition of hydrocarbons and related compounds [258]. The use of organoalkalies complexed with tertiary amines as polymerization initiators [259], and as initiators for the telomerization of ethylene with aromatic hydrocarbons and olefins [260] have been described. Reactions of prochiral carbonyl compounds with organolithiums complexed with diamines to give optically active alcohols have been reviewed [261].

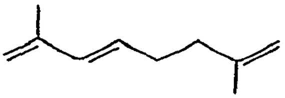
A novel building block system for the preparation of ketones from vinyl silanes has been described [262]. Several routes are presented and the process is illustrated by the preparation of CCCXVI from the components indicated (≡Si is $(CH_3)_3Si$).



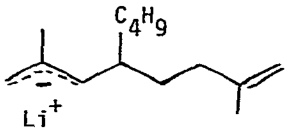
CCCXVI



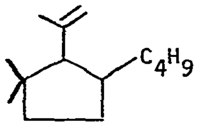
Synthetically useful addition of n-butyllithium to unconjugated triene CCCXVII followed by cyclization of intermediate CCCXVIII has given cyclopentane CCCXIX; CCCXVIII has been trapped by formaldehyde [263]. The use of the conjugated triene, 2,7-dimethyl-2,4,6-octatriene, in this reaction gives a substituted cycloheptadiene. Allyl- and *n*-butyllithium have also been added to conjugated enynes to afford terminal acetylenes [264].



CCCXVII

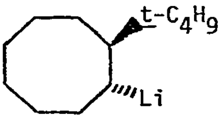


CCCXVIII

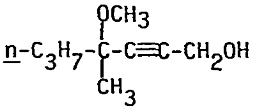


CCCXIX

t-Butyllithium has been shown to add to *trans*-cyclooctene to afford CCCXX and *cis*-cyclooctene in yields of 89% and 10%, respectively [265]. *cis*-Cyclooctene fails to react with *t*-butyllithium under the same reaction conditions. *n*-Butyllithium has now been shown to add to propargylic alcohols [266]. Such additions to methoxy derivatives like CCCXXI afford allenes like CCCXXII. Treatment of azulene derivatives like CCCXXIII with lithium acetylide give abnormal 4- and 6-substituted products (CCCXXIV and CCCXXV) where the chlorine substituent is lost [267].

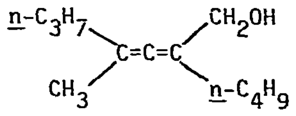


CCCXX

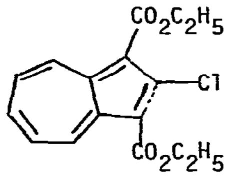


$n\text{-}C_3H_7\text{-}\overset{OCH_3}{\underset{CH_3}{C}}\text{-}C{\equiv}C\text{-}CH_2OH$

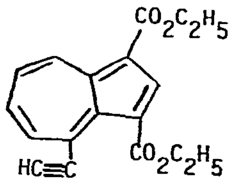
CCCXXI



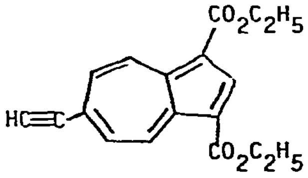
CCCXXII



CCCXXIII

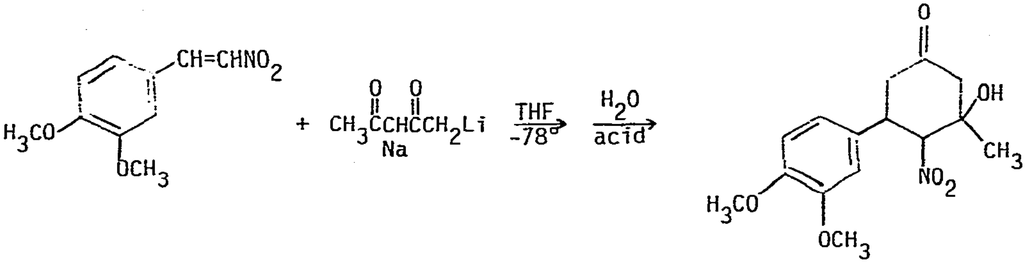


CCCXXIV

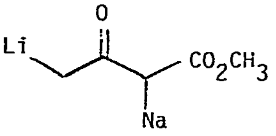


CCCXXV

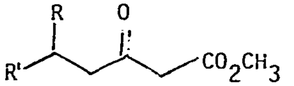
A new synthesis of cyclohexanones from dianions of β-diketones and nitroolefins has been described [268]. An example follows.



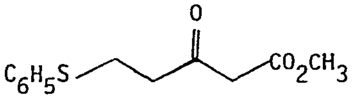
Lithiosodio salts of methyl acetoacetate (CCCXXVI) have been added to carbonyls to give compounds like CCCXXVII which are useful in annelation reactions [269], and alkylated wtih alkyl halides to give the expected terminal alkyl derivatives [270]. Alkylation of CCCXXVI with iodomethylthiophenol to give CCCXXVIII followed by oxidative elimination affords 3-oxo-4-pentenoate, a useful annelating reagent in the preparation of terpenes and alkaloids [271]. Treatment of CCCXXVI with an equivalent of methyllithium interestingly gives acetylacetone [272].



CCCXXVI

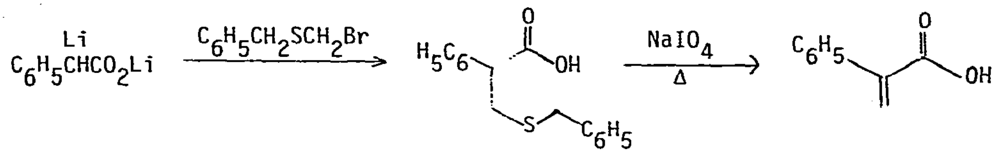


CCCXXVII

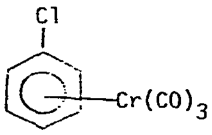


CCCXXVIII

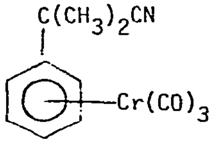
Bromomethylsulfides have been used as formaldehyde equivalents to prepare α-methylene derivatives of ketones and carboxylic acids [273]. An example is illustrated with dilithiophenylacetic acid.



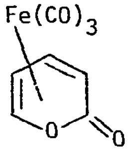
As part of a study to develop new techniques to activate aryl rings towards nucleophilic aromatic substitution, various organolithiums have been reacted with certain chromium tricarbonyl complexes of substituted benzenes [274,275]. The process is illustrated by the conversion of CCCXXIX to CCCXXX; the chromium moiety can be removed with iodine. Similar reactions on the iron tricarbonyl complex of α-pyrone (CCCXXXI) with organolithiums (RLi) give intermediates like CCCXXXII which, upon acylation, afford CCCXXXIII [276].



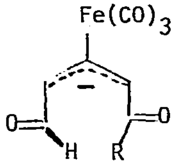
CCCXXIX



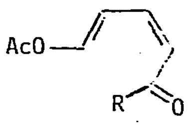
CCCXXX



CCCXXXI

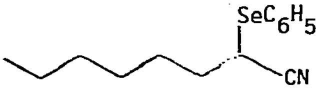


CCCXXXII

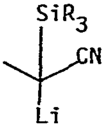


CCCXXXIII

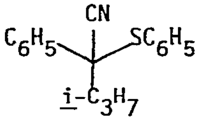
Two new methods of preparing α,β-unsaturated nitriles have been reported. Sulfenylation and selenylation of α-lithionitriles give compounds like CCCXXXIV which, upon treatment with hydrogen peroxide, give final product [277]. Treatment of lithio-α-silylpropionitriles (CCCXXXV) with esters also affords α, β-unsaturated nitriles [278]. Finally, oxidative decyanation of secondary nitriles like CCCXXXVI with NBS results in the replacement of the cyanide and thiophenyl moieties by a carbonyl group [279].



CCCXXXIV



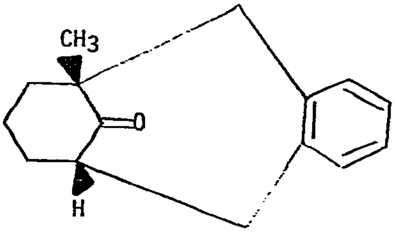
CCCXXXV



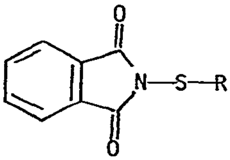
CCCXXXVI

Phenols may now be prepared from aryl chlorides or bromides in yields of 34-80% by adding them to a mixture of lithium/borane/THF followed by oxidation with basic hydrogen peroxide; the use of pre-formed aryllithiums results in diminished yields of the phenols [280]. Two papers have described alkylations of organolithiums that are more efficient than those of the corresponding lithium organocuprates. Thus, alkylations of primary halides with vinyllithiums proceed in high yield with retention of configuration of the organometallic [281]. Also, allyl- and benzyllithium undergo crossed-Wurtz reactions with cycloalkyl halides in excellent yield [282].

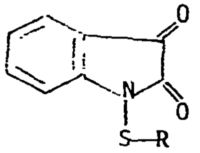
Regiospecially generated enolate CCXXV and others have been dialkylated with various 1,4-dichloro systems in the presence of methyllithium to give compounds like CCCXXXVII [283]. Reaction of organolithium reagents with CCCXXXVIII-CCCXL provides new methods of preparing unsymmetrical sulfides [284,285,286].



CCCXXXVII



CCCXXXVIII

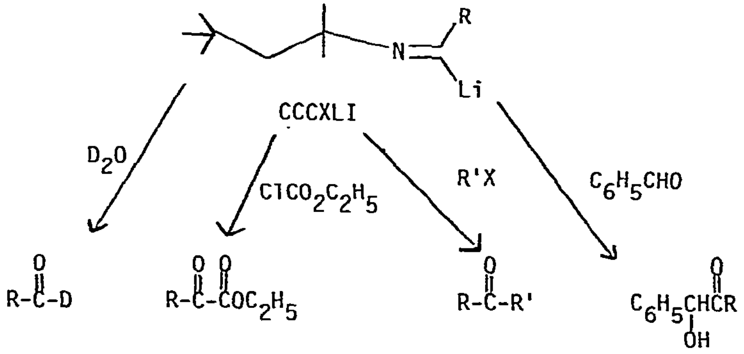


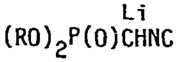
CCCXXXIX

$$\left((C_6H_5)_2C{=}N{-}S{-}\right)_2$$

CCCXL

The interaction of isocyanides without α-hydrogens with organolithiums to afford metallo aldimines like CCCXLI have been described; such compounds are masked acyl carbanions [287]. Some of the chemistry of CCCXLI is shown in the following chart. Related compounds have been employed in the preparation of optically active α-amino acids [288], of cyclobutanones [289], and in the synthesis of nitriles [290]. Another metalated isocyanide system, CCCXLII, has been prepared by reaction of the parent isocyanide (which has α-hydrogens) with n-butyllithium [291]. Some of the chemistry of this species has been described.

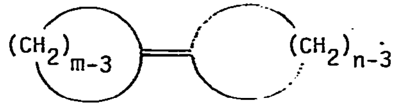




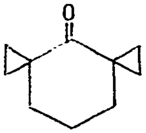
$$(RO)_2P(O)\overset{Li}{C}HNC$$

CCCXLII

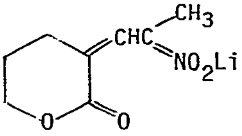
A route leading to the synthesis of either symmetrical or unsymmetrical cycloalkylidenecycloalkanes (CCCXLIII) from dilithio salts of cycloalkane carboxylic acids and substituted cycloalkanones like CCCXLIV has been described [292]. Lithium salts of esters and lactones have been reacted with nitroenamin to give aci-nitroalkylidine derivatives like CCCXLV [293]. α-Lithioesters have also been employed in the preparation of C_7-amide side-chains of cephalosporins [294].



CCCXLIII



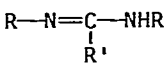
CCCXLIV



CCCXLV

A new preparation of vinyl ketones from vinyllithium and carboxylic acids has been found to be successful provided DME is used as the solvent [295]. 2-Lithio-1,6-dimethoxybenzene undergoes acylation with esters to give sterically hindered ketones in high yields [296]. Two-fold addition of the above carbanion affords even more sterically hindered carbinols. The stereochemical course of the reaction between several organolithiums and β-asymmetric aminoketones has been investigated; no single model of asymmetric induction seems to be suitable for the prediction of the results obtained [297].

Reaction of organolithiums with several non-routine electrophiles has been reported. Thus, carbodiimides give iminoamines like CCCXLVI [298], iminocarbonates give a variety of products [299], and lithiodithianes with salts like CCCXLVII give aminodithianes which, upon hydrolysis, afford aminoaldehydes [300]



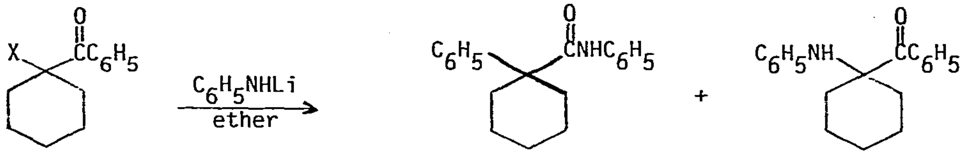
$$R{-}N{=}\underset{\substack{|\\R'}}{C}{-}NHR$$

CCCXLVI

$$RCH{=}\overset{+}{N}R'_2\ \ \overset{-}{Cl}$$

CCCXLVII

Finally, a quasi-Favorskii rearrangement of α-haloketones has been realized under homogeneous conditions as illustrated [301]. Previously, such conditions were thought to result only in the direct replacement of the α-halogen by the nucleophile.



VII. Copper-Lithium Reagents and Their Reactions

Oxidative coupling via organocopper compounds [302] and the organic chemistry of copper-containing compounds [303] have been reviewed.

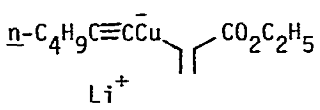
A direct and convenient preparation of sulfur containing cuprates, ArSCuRLi, has been described [304]. Ate complexes containing lithium, copper, and mercury like CCCXLVIII have been prepared and some of their chemistry described [305]. The advantage of using such compounds stems from the fact that the alkyl group originally bound to the mercury in the organomercurial retains its configurational stability but is more reactive than that in the organomercurial.

$$\mathrm{RHgBr} + \mathrm{ICuP}(\underline{n}\text{-}\mathrm{C_4H_9})_3 \xrightarrow[-78°]{\mathrm{THF}} \xrightarrow[\substack{\mathrm{THF}\\ -78°}]{3\underline{t}\text{-}\mathrm{C_4H_9Li}} \mathrm{RCuLiHg}(\underline{t}\text{-}\mathrm{C_4H_9})_3$$

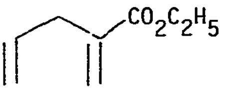
CCCXLVIII

Mixed ate complexes, R_1R_2CuLi, have been reacted with n-amyl bromide, methyl vinyl ketone, and nitrobenzene to determine the relative reactivities of the R groups [306]. Those groups that form stable, unreactive copper (I) compounds (1-pentynyl, t-butyl, and phenyl) show the smallest reactivity. The mixed ate complex, LiCuH($\underline{n}$-C_4H_9), and related ones have been shown to be reducing agents since they usually transfer a hydride to various alkyl halides, α, β-unsaturated ketones, and aldehydes [307].

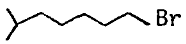
A novel ethyl acrylate synthon, CCCXLIX, has been prepared and shown to react with allylic and propargylic halides to give unsaturated esters like CCCL [308]. Reactions of α, Ω-dibromoalkanes with Grignard reagents catalyzed by Li_2CuCl_4 result in halopolycarbon homologation of the Grignard reagent in moderate to excellent yields; for example, i-propylmagnesium bromide with 1,5-dibromopentane gives CCCLI [309]. Similar reactions of Grignard reagents with tosylates catalyzed by Li_2CuCl_4 give mixed Wurtz-type products in fair to excellent yield [310].



CCCXLIX

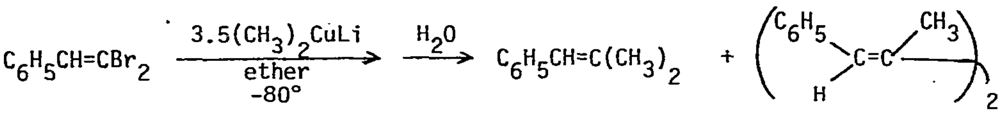


CCCL



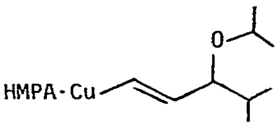
CCCLI

Vinylic gem-dibromides or iodides react with lithium cuprates with displacement of the halogen by either alkyl or copper or both [311]. An example is included. 1,2-Divinylbromides and 1,2-dibromobenzenes with such reagents

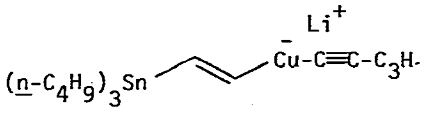


afford acetylenes and aralkanes, respectively. α, α-Dichloroesters similarly undergo either metalation or displacement depending upon temperature [312].

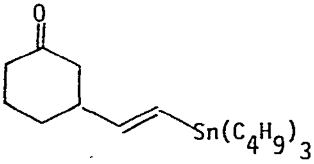
A new solubilized mixed organocuprate reagent, CCCLII, has been found usefl in the synthesis of certain prostaglandins [313]. Introduction of ethynyl group to α, β-unsaturated carbonyl compounds may now be accomplished by the use of cuprate CCCLIII and subsequent conversion of vinylstannanes like CCCLIV to acetylenes like CCCLV by lead tetraacetate [314]. Cuprates derived from halovinyltrimethylsilanes, for example, CCCLVI, have also been prepared and found to undergo conjugate addition to α, β-unsaturated ketones to give vinylsilanes [315].



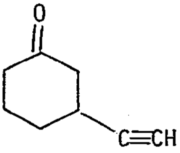
CCCLII



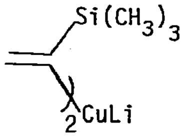
CCCLIII



CCCLIV

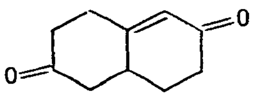


CCCLV

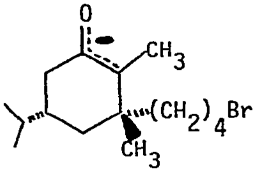


CCCLVI

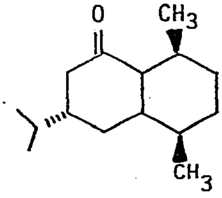
Endione CCCLVII has been found to react with lithium dimethylcuprate at the saturated carbonyl group at low temperature [316]. The regiospecifically generated enolate anion CCCLVIII from addition of this same cuprate to an α, β-unsaturated ketone undergoes ring closure only to <u>cis</u>-decalone CCCLIX [317]. This same paper has described the preparation of the new species, lithium methylvinylcuprate, which transfers a vinyl group to α, β-unsaturated ketones. Other enolates derived from related additions have been trapped by phenylselenium bromide [318].



CCCLVII

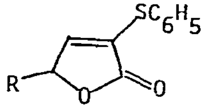


CCCLVIII

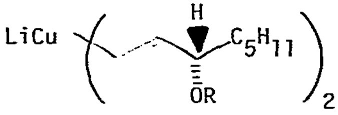


CCCLIX

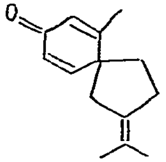
Some other papers describing lithium cuprate chemistry deserve mention. Thus, new additions of lithium cuprates to α,β-acetylenic sulfoxides to give cis-vinyl sulfoxides have been reported [319]. A key step in a new synthetic method for the preparation of β-monosubstituted or β,γ-disubstituted butenolide involves conjugate addition of ate complexes to lactones like CCCLX [320]. Ate complex CCCLXI has been added to cyclopentenone as part of a short and converging synthesis of prostaglandins [321]. Dienone CCCLXII has been treated with lithium dimethylcuprate as part of a total synthesis of β-vetivone [322].



CCCLX



CCCLXI

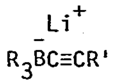


CCCLXII

A general ketone synthesis using thioesters and copper ate complexes with efficient utilization of the latter has been described [323]. Pyridine has been found to undergo addition of various lithium cuprates in the presence of an electrophile like methyl chloroformate to afford 4-substituted-1,4-dihydr pyridine derivatives [324]. Interaction of lithium divinylcuprate with a substituted epoxycyclopentane has been successfully employed to achieve correct regiospecificity in a total synthesis of prostaglandins [325]. Finally, evidence has been presented that the precursors to allylic alcohols in the reactions of α-chloroepoxides with lithium dialkylcuprates are probably carbenoids followed by a lithiated epoxide [326].

The remaining papers in this section deal with lithium ate complexes of metals other than copper. Several lithium trialkylacetylenicboron complexes like CCCLXIII have been prepared from trialkylboranes and lithium acetylides.

Reaction of these complexes with iodine, then potassium hydroxide, [327,328], or with methanesulfinyl chloride [329] gives acetylenes like CCCLXIV. Similar reaction with propionic acid then basic peroxide affords olefins like CCCLXV [330]. Reaction of CCCLXIII with 1,2-epoxybutane gives intermediate CCCLXVI which can be converted to hydroxyketones, homoallylic alcohols, or tetrasubstituted olefins depending on co-reagents [331]. Interaction of chloroacetylide CCCLXVII with trialkylboranes gives allenes like CCCLXVIII [332].



$\overset{\text{Li}^+}{R_3\bar{B}C{\equiv}CR'}$

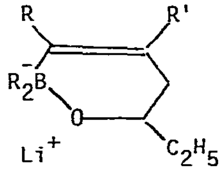
CCCLXIII

$RC{\equiv}CR'$

CCCLXIV

$RCH{=}CHR'$

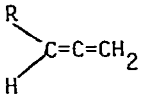
CCCLXV



CCCLXVI

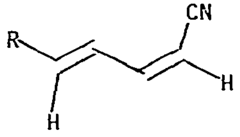
$LiC{\equiv}CCH_2Cl$

CCCLXVII



CCCLXVIII

Interaction of 2-bromo-6-lithiopyridine with trialkylboranes affords a new, unprecedented cleavage of the pyridine ring to give a simple, stereospecific preparation in high yields of 2(Z), 4(E)-alkadienenitriles (CCCLXIX) [333]. Treatment of 9-mesityl-9-boraanthracene (XV , R=H) with organolithiums affords XVII (R=H) which undergoes reaction with various electrophiles at the C_{10}-atom to give XV (R=E) [334].



CCCLXIX

Convenient routes to mixed organoboranes not available by hydroboration have been realized by interaction of chloro- or methoxydialkylboranes with organolithiums [335]. Reaction of boranes with dichloromethyl methyl ether in the presence of bulky bases like the lithium alkoxide of triethyl carbinol affords α-chloroborinic esters which are useful in the preparation of internal olefins [336]. Some of the chemistry of lithium triborylmethide (CCCLXX), obtained from the reaction of methyllithium with methanetetraboronic acid (CCCLXXI), has been described [337,338,339]. The preparation of unsymmetrical ketones can be achieved by interaction of chlorodialkylboranes with organolithium adducts of t-butylisonitrile [340].

$$\left((CH_3O)_2B\right)_3CLi$$

CCCLXX

$$\left((CH_3O)_2B\right)_4C$$

CCCLXXI

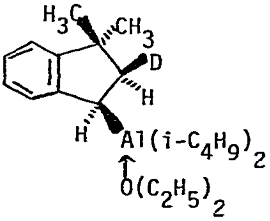
While gem-dialuminum species CCCLXXII has failed to give olefins with ketones, prior treatment with n-butyllithium apparently has given CCCLXXIII which acts as a methylenation agent towards aldehydes and ketones [341]. As part of a study of the stereochemical course of cleavage reactions, interaction of aluminum compound CCCLXXIV with methyllithium affords an intermediate ate complex that undergoes reversible dissociation to a carbanion that undergoes inversion [342].

$$CH_2(AlBr_2)_2$$

CCCLXXII

$$LiCH_2AlBr_2$$

CCCLXXIII



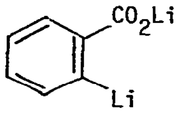
CCCLXXIV

The mechanism and stereochemistry of ate complex addition to ketones has been studied [343]. For example, addition of lithium tetraalkylaluminates to 4-*t*-butylcyclohexanone occurs predominately by axial attack to give equitorial alcohol. In contrast, related ate complexes of boron, magnesium, and zinc occur mostly by equitorial attack to afford axial alcohol. Other examples are cited. A similar study of conjugate additions of lithium tetramethylaluminate has been published [344].

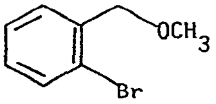
Finally, the reaction of certain ate complexes of selenium with ketones to give alcohols has been described [345]. Also, various alkoxide complexes of berylium have been reported [346].

VIII. Lithium-Halogen Exchange Reactions

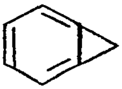
Lithiation of the isomeric bromobenzoic acids to give dilithio salts like CCCLXXV have been re-examined as a function of temperature [347]. Though such species are stable at -100°, they self-condense at -20° to give benzoylbenzoic acids. At -75°, these dilithio salts react with esters to afford substituted benzoylbenzoic acids [348]. The isomeric methyl bromobenzoates likewise undergo selective metal-halogen exchange rather than addition to the ester with *n*-butyllithium at -95°. As above, these species undergo self-condensation at -75° to give benzoylbenzoic esters. Bromoether CCCLXXVI also undergoes metal-halogen exchange at -40° to apparently give the lithiated ether which, upon heating for one hour, cyclizes to benzocyclopropene CCCLXXVII [349]. 1,2-Dilithioferrocene has been prepared by treatment of iodoferrocylmercury with excess *n*-butyllithium [350].



CCCLXXV

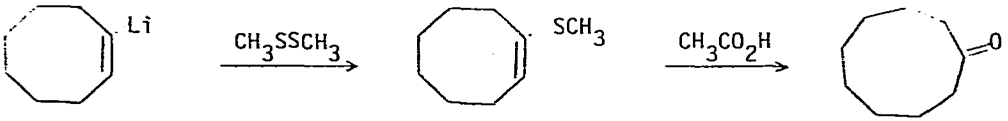


CCCLXXVI

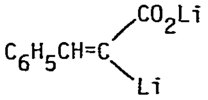


CCCLXXVII

A variety of vinyl bromides have been converted to vinyllithiums by means of t-butyllithium in THF [351]. Such species have been reacted with electrophi like dimethyldisulfide to afford a simple alternative route to ring enlarged ketones as illustrated.

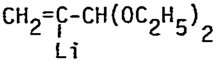


α-Lithiated lithiocinnamates (CCCLXXVIII) [352] and α-lithiated acetals like CCCLXXIX [353] have been prepared from the corresponding bromo compounds and n-butyllithium at low temperatures. Condensation of the latter with aldehydes represents another example of directed aldolizations.



$\mathrm{C_6H_5CH{=}C}\begin{array}{l}\diagup\mathrm{CO_2Li}\\ \diagdown\mathrm{Li}\end{array}$

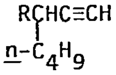
CCCLXXVIII



$\mathrm{CH_2{=}\underset{Li}{\underset{|}{C}}{-}CH(OC_2H_5)_2}$

CCCLXXIX

A new preparation of 3-butylalk-1-ynes (CCCLXXX) from 1-bromoacetylenes like CCCLXXXI and n-butyllithium has been described [354]. The reaction presumably occurs via dilithio salt CCCLXXXII.

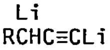


$\mathrm{R\underset{\underline{n}\text{-}C_4H_9}{\underset{|}{C}}HC{\equiv}CH}$

CCCLXXX

$\mathrm{RCH_2C{\equiv}CBr}$

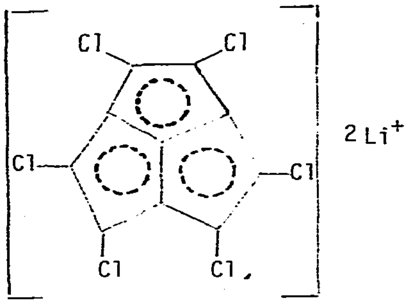
CCCLXXXI



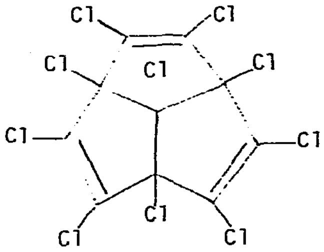
$\mathrm{R\overset{Li}{C}HC{\equiv}CLi}$

CCCLXXXII

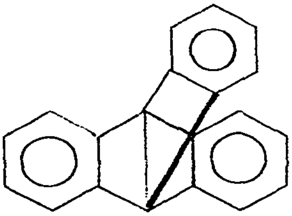
The preparation of the first known derivative of the acepentylendiide system, CCCLXXXIII, has been prepared by reaction of n-butyllithium with CCCLXXXIV [355]. 9,10-Dihalotriptycenes have been reacted with a variety of basic reagents in an attempt to form bridged triptycene CCCLXXXV [356]. However, though single metal-halogen exchange was realized as evidenced by reaction with electrophiles, the bridge could not be closed to give the desired product.



CCCLXXXIII

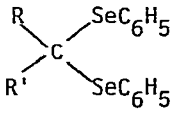


CCCLXXXIV

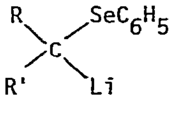


CCCLXXXV

Finally, two papers have described the conversion of gem-diselenides like CCCLXXXVI to lithioselenides like CCCLXXXVII by means of n-butyllithium [345,357]. The latter compounds are masked vinyllithium reagents.



CCCLXXXVI

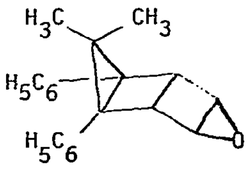


CCCLXXXVII

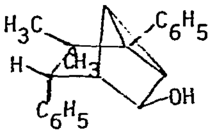
IX. Reductions and Radical Anions

Reactions of the radical anions and dianions of aromatic hydrocarbons [358], and the base-catalyzed carbon-carbon addition reactions of hydrocarbons [359] have been reviewed.

Reductive cleavages of cyclopropyl rings by lithium in ammonia have been described which provide a convenient route to otherwise difficultly accessible strained tricyclic alcohols [360]. The process is illustrated by the conversion of CCCLXXXVIII to CCCLXXXIX in a yield of 90%. Similar reductions of vinylcyclopropane, though slow at -33°, afford mostly Z-2-pentene at 25° [361]. Also, reduction of benzocyclopropane (CCCLXXVII) by lithium/ammonia/ethanol gives mostly 2,5-dihydrotoluene [349].

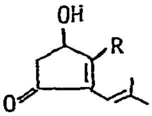


CCCLXXXVIII

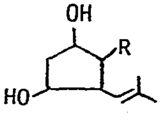


CCCLXXXIX

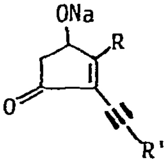
In connection with prostaglandin syntheses, several unsaturated cyclopentene derivatives have been reduced by lithium/ammonia/alcohol. Thus CCCXC and the corresponding diketone give cis- and trans-CCCXCI [362], CCCXCII affords cis-CCCXCI [363], and CCCXCIII gives trans-CCCXCI [364]. The stereochemistry above refers to the alkyl side-chains only.



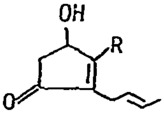
CCCXC



CCCXCI

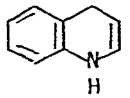


CCCXCII

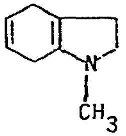


CCCXCIII

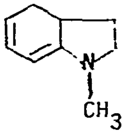
Lithium/ammonia reduction of quinoline has now been shown to afford 1,4-dihydroquinoline (CCCXCIV), not the previously reported 1,2-dihydro isomer [365]. The Birch reduction of N-methylindole has been shown to give dihydro product CCCXCV in high yield [366]. The conjugated diene CCCXCVI can be obtained by distillation of CCCXCV from an acidic ion-exchange resin.



CCCXCIV

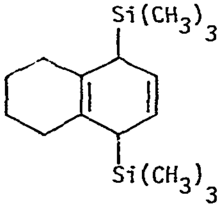


CCCXCV

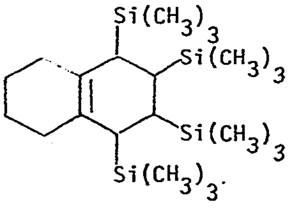


CCCXCVI

Lithium reductions of biphenyl and certain of its derivatives have been examined in ammonia in the absence or presence of a proton source other than ammonia and the extent of reduction compared [367]. Similar reduction of biphenyl has also been effected in HMPA [368]. Tetralin has been reduced by lithium in THF in the presence of chlorotrimethylsilane to afford di- and tetrasilylated derivatives CCCXCVII and CCCXCVIII [369]. 2-Methoxytetralin has been reduced by lithium/HMPA/ethanol as a model for related planned reductions of certain steroid derivatives [370].

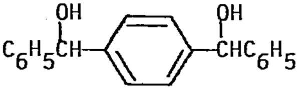


CCCXCVII

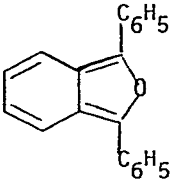


CCCXCVIII

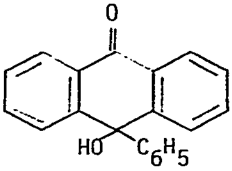
A systematic study of the alkali metal reductions of the isomeric dibenzoyl benzenes under aprotic conditions has been described [371]. The para isomer affords only diol CCCXCIX-ketoalcohol is absent. The ortho isomer interestingly gives CD with lithium/ammonia and CDI with potassium/ammonia. Related reductions of the meta isomer are sluggish. Explanations are given to justify the observed products.



CCCXCIX

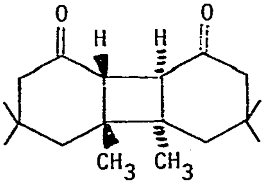


CD

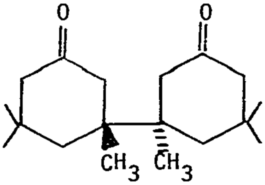


CDI

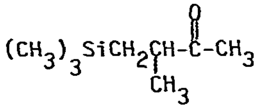
Several other carbonyl-containing compounds have also been reduced by lithium. Thus, 1,4-diketone CDII is converted to a diol in ammonia/t-butyl alcohol which, upon oxidation by chromium trioxide, is converted to diketone CDIII [372]. The first example of direct C-silylation of α, β-unsaturated ketones has been effected by lithium in THF in the presence of chlorotrimethylsilane [373]. Thus, methyl α-methylvinyl ketone has been converted to CDIV in fair yield. α, β-unsaturated esters have been shown to undergo similar transformations [374]. Lithium/ammonia has been demonstrated to constitute a non-epimerizing method for the conversion of benzoate CDV to methylene derivative CDVI [375]. Finally, the scope of the cleavage of benzyl esters by lithium/ammonia/alcohol has been determined [376].



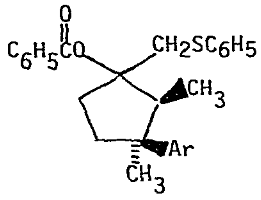
CDII



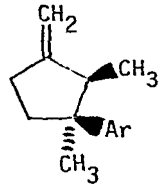
CDIII


$$(CH_3)_3SiCH_2\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CH_3$$

CDIV



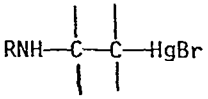
CDV



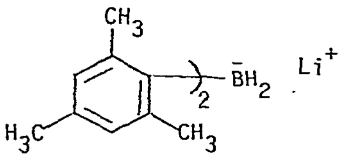
CDVI

Known cleavages of allyl alcohols and ethers by lithium/ammonia or amines have been applied to the syntheses of vitamin D_3 [377] and desmosterol [378]. Similar reductions of tetrahydrocannabinols [379] and of certain epoxides [380] have been reported.

An interesting amine synthesis has been described which involves aminomercuration of olefins to give species like CDVII [381]. Reduction of the latter by lithium in THF completes the process. A new crystalline reducing agent, CDVIII, suitable for stereoselective reduction of ketones, has been described [382].


$$RNH-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-HgBr$$

CDVII



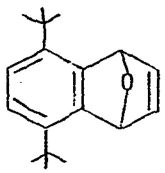
CDVIII

Turning to radical-anions, α-nitrosulfones have been found to react with lithionitroalkanes, lithioesters, and other nucleophiles with displacement of the sulfone group [383]. The reaction which proceeds in high yields is illustrated.

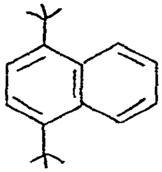
Aliphatic and aromatic trimethylammonium iodides like CDIX have been found to undergo cleavage with the lithium radical-anion of naphthalene to afford trimethylamine and R-R and/or RH [384]. This same radical-anion effects a one-step aromatization of benzyne-furan Diels-Alder adducts like CDX to give naphthalenes like CDXI [385]. Finally, this radical-anion has been employed to convert certain α-amino acids to their dilithio salts which undergo reaction with electrophiles at the α-carbon [386].

$R\overset{+}{N}(CH_3)_3\ I^-$

CDIX



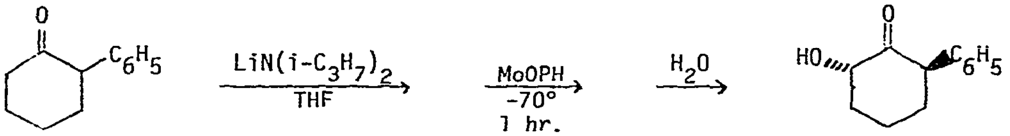
CDX



CDXI

X. Reactions with Inorganic and Organometallic Compounds

A novel conversion of ketone enolates to acyloins and of ester enolates to α-hydroxyesters has been effected by a complex of molybdenum peroxide·pyridine·HMPA (MoOPH) [387]. The process is illustrated by the conversion of CDXII to CDXIII.

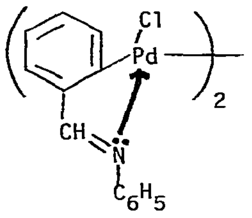


CDXII

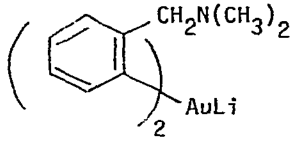
CDXIII

Treatment of palladium complex CDXIV with organolithiums and triphenylphosphine constitutes a convenient method of preparing o-alkylbenzaldehydes in high yields; for example, methyllithium and CDXIV give o-tolualdehyde in a yield of 95% [388]. A gold-containing compound, CDXV, somewhat similar to

CDXIV, has been prepared by treatment of o-lithiobenzyldimethylamine with gold (I) bromide·triphenylphosphine or with alkylgold·triphenylphosphine complexes [389]. CDXV is thermally stable, exists as a discrete dimer in benzene, and is useful in the preparation of uncomplexed (RAu)n species.

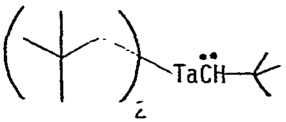


CDXIV

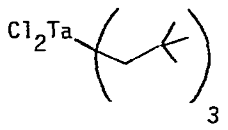


CDXV

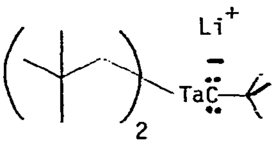
Several papers have described additional chemistry of transition metal-carbene complexes. The preparation of CDXVI from CDXVII and neopentyllithium illustrates that nonstabilized carbenoid ligands containing α-hydrogen are stable [390]. Treatment of CDXVI with n-butyllithium·TMEDA apparently affords carbene anion CDXVIII as evidenced by deuteration.



CDXVI

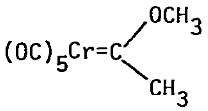


CDXVII



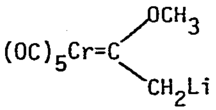
CDXVIII

Treatment of chromium species CDXIX, one of the most acidic neutral carbon acids known, with n-butyllithium at -78° gives CDXX which has been reacted with electrophiles like epoxides, α-bromoesters, and bis(triphenylphosphine)iminium chloride; the latter electrophile affords a stable salt of CDXX which can be weighed in air [391,392]. An attempt to prepare a vinylphenylcarbene complex from CDXXI and vinyllithium gave 1-phenyl-1-methoxy-2-propene in a yield of 43% [393].



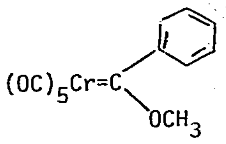
$(OC)_5Cr{=}C(OCH_3)CH_3$

CDXIX



$(OC)_5Cr{=}C(OCH_3)CH_2Li$

CDXX

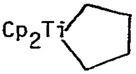


CDXXI

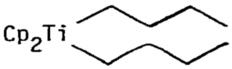
More examples of group IV elements σ-bonded to transition metals continue to be described. Thus, treatment of molybdenum (II) acetate with methyllithium in ether affords CDXXII in a yield of 81%; vinyllithium is similar [394]. The products are thermally stable at 25°. Reaction of titanocene dichloride with 1,4-dilithiobutane gives the new metallocycle, CDXXIII, which is stable below -30° [395]. The stability and chemistry of CDXXIII is contrasted with that of open-chain CDXXIV.

$Li_4Mo_2(CH_3)_8$

CDXXII



CDXXIII



CDXXIV

σ-Alkyl and σ-aryl titanium derivatives like CDXXV have been prepared by interaction of methyl- and perfluorophenyllithium with chlorotriisopropoxytitanium at -35° [396]. Similar treatment of monoalkyl- or aryltitanocene chloride with organolithiums has afforded mixed complexes like CDXXVI. The sulfur containing titanium compound CDXXVII has been prepared from titanocene dichloride and lithiomethylthiophenol [397].

$RTi(O\text{-}\underline{i}\text{-}C_3H_7)_3$

CDXXV

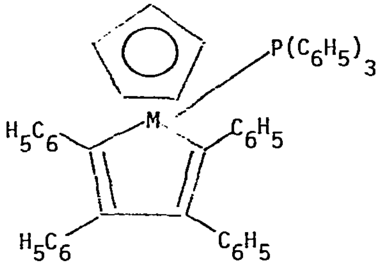
$Cp_2Ti(R)C_6H_5$

CDXXVI

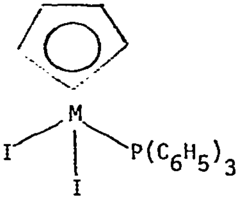
$Cp_2Ti(CH_2SC_6H_5)_2$

CDXXVII

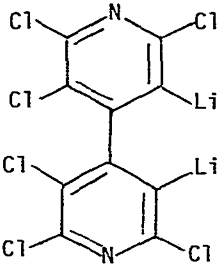
Mixed σ,π-type compounds of rhodium and iridium (CDXXVIII) have been obtained from 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene and CDXXIX (M=Rh, Ir); a similar reaction on CDXXIX (M=Co) gave a sandwich compound [398]. In contrast, interaction of dilithio salt CDXXX with titanocene dichloride resulted in displacement of only one chlorine atom and a cyclic compound was not obtained [399].



CDXXVIII

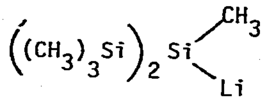


CDXXIX

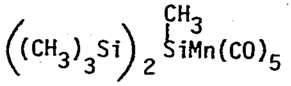


CDXXX

The preparation of transition metal compounds containing polysilyl ligands has been described [400]. For example, CDXXXI and bromomanganese pentacarbonyl give CDXXXII. Silicon-, germanium-, and tin-iron and manganese bonds have been retained in reactions of perfluorophenyllithium with compounds like CDXXXIII to give compounds like CDXXXIV [401].



CDXXXI



$\left((CH_3)_3Si\right)_2\overset{CH_3}{\overset{|}{Si}}Mn(CO)_5$

CDXXXII

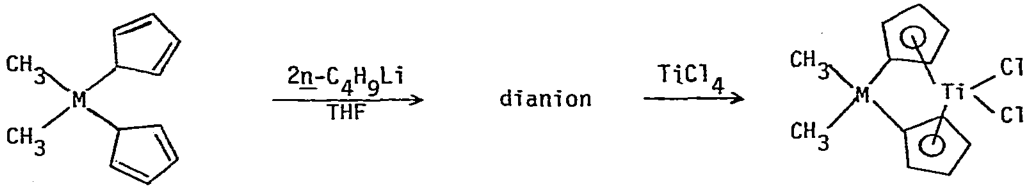
$Fe(CO)_2CpGeCl_3$

CDXXXIII

$(C_6F_5)_3GeFe(CO)_2Cp$

CDXXXIV

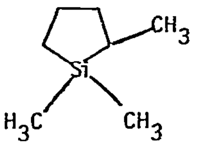
The first monomeric metallocenophanes with a heteroatom comprising the bridge have been described by the process shown where M = silicon and germanium [402].



Cleavage of silylmercury compound CDXXXV with lithium gives, after hydrolysis, silacyclopentane CDXXXVI [403]. The reaction is the first example of an intramolecular addition of Si-Li to an olefin and constitutes a new route to cyclic organosilanes. A related cyclization from mercurial CDXXXVII affords methylcyclopentane [404].

$\left(CH_2{=}CH(CH_2)_3Si(CH_3)_2\right)_2Hg$

CDXXXV

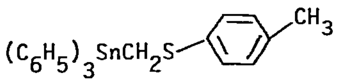


CDXXXVI

$Hg\left((CH_2)_4CH{=}CH_2\right)_2$

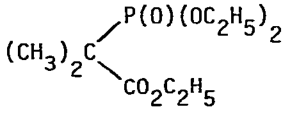
CDXXXVII

A rare example of a compound (CDXXXVIII) containing sulfur alpha to tin has been synthesized by treatment of p-chloromethylthiocresol with lithium triphenylstannane [405]. The corresponding germanium compound was prepared similarly. Mono-, di-, or trialkylgallium compounds may now be synthesized by reaction of gallium trichloride with the appropriate amount of organolithium reagent [406]. For example, tri-*n*-butylgallium has been obtained in a yield of 97%.



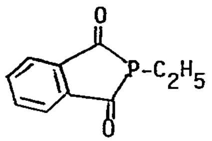
CDXXXVIII

Additional carbon-phosphorus systems have also been described. For example, treatment of lithioethyl isobutyrate with diethyl chlorophosphate gives ester CDXXXIX [407]. Reaction of dilithioethylphosphine with *o*-phthaloyl chloride affords CDXL [408]. Addition of methyllithium to triphenylphosphine sulfide gives CDXLI which has been phosphorylated by various chlorodialkylphosphines to give phosphinomethylphosphine sulfides [409].

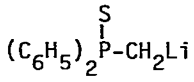


$(CH_3)_2C(P(O)(OC_2H_5)_2)(CO_2C_2H_5)$

CDXXXIX



CDXL

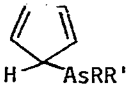


$(C_6H_5)_2P(=S)-CH_2Li$

CDXLI

Reaction of lithium cyclopentadienide with arsenic trihalides or methyl derivatives thereof afford CDXLII; such molecules have fluxional structures [410]. Interaction of lithium diphenylarsine with aromatic ketones and quinones has been shown to give only tetraphenyldiarsine [411]. Organolithiums have been reacted with sulfuryl chloride to give alkanesulfonyl chlorides in fair yields

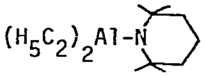
[412]. A new, improved preparation of tris(dialkylamino)boranes (CDXLIII) which involves reaction of lithium dialkylamides with boron trifluoride etherate has been described [413]. A similar reaction between chlorodiethylaluminum with a substituted lithium piperidide affords CDXLIV, a compound that effects regiospecific isomerization of epoxides to allylic alcohols [414].



CDXLII

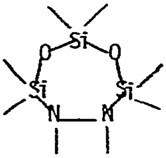
$(R_2N)_3B$

CDXLIII

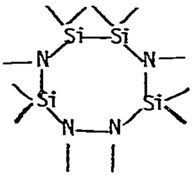


CDXLIV

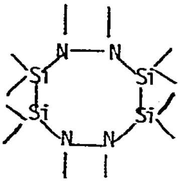
Several new ring systems containing silicon and nitrogen have been prepared from appropriate lithiated diamines or hydrazines and dichlorodisilanes or siloxanes. The systems include CDXLV [415], CDXLVI [415], and CDXLVII [416]; the substituents on each ring are methyl groups.



CDXLV

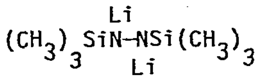


CDXLVl



CDXLVII

Bis(trimethylsilyl)diimine has been converted to 1,2-dianion CDXLVIII in ether but only to the corresponding radical anion in THF [417]. The latter compound is thermally unstable and its mode of decomposition depends upon the metallic cation, the temperature, and the solvent. Reaction of lithium bis(trimethylsilyl)amide with tin (II) chloride gives the novel organosilylamino derivative CDXLIX in which the tin is stabilized as Sn (II) [418].



$(CH_3)_3Si\overset{Li}{N}-\underset{Li}{N}Si(CH_3)_3$

CDXLVIII

$\left((CH_3)_3Si\right)_2N-Sn-N\left(Si(CH_3)_3\right)_2$

CDXLIX

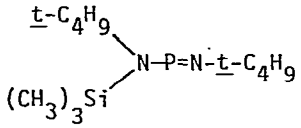
Interaction of lithiohexamethyldisilazane with phosphorus trichloride gives CDL which, upon distillation, affords the metaphosphoric acid derivative CDLI [419]. A related compound, CDLII, has been prepared in a similar reaction sequence [420].

$\left[\left((CH_3)_3Si\right)_2N\right]_2PCl$

CDL

$\left((CH_3)_3Si\right)_2N-P=NSi(CH_3)_3$

CDLI



CDLII

Finally, certain silylated phosphines like CDLIII and CDLIV have been prepared from the reaction of lithiodimethylphosphine, aluminum chloride, and a halosilane [421]. The acid-base chemistry of such species with lithiated phosphines has been discussed [422].

$H_3SiP(CH_3)_2$

CDLIII

$(CH_3)_3SiP(CH_3)_2$

CDLIV

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