LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1976

EDWIN M. KAISER

Department of Chemistry, University of Missouri-Columbia, Columbia,
Missouri 65201 (U.S.A.)

CONTENTS

1. REVIEWS AND BOOKS

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

- ^{13}C NMR of organolithium reagents [1,2].
- Fast reaction studies of carbanions in solution [3].
- Use of lithium organocuprate addition reactions as models for an electron-transfer process [4].
- Recent developments in the use of organolithium reagents in organic synthesis [5].
- Regiospecific preparation and synthetic uses of ketone enolates [6].
- Annulation [7].
- Syntheses of carotenoids [8,9].
- Preparation of alkenes from tosylhydrazones [10].

Lithium, Annual Survey covering the year 1975 see J.Organometal.Chem., 130 (1977) 1-131.

- Recent methods for the synthesis of polyfluoroaromatic compounds [11].
- Preparation and chemistry of unsaturated lactones [12].
- Nucleophilic substitutions at acetylenic carbon [13].
- Allopolarization - effects of substituents on the reactions of ambifunctional anions [14].
- Nucleophilic acylation reagents [15].
- Synthetic utility of 2-oxazolines [16].
- Solutions of alkali metals in ammonia and other solvents [17].
- Metal-ammonia reduction and related reactions of α,β-unsaturated carbonyl compounds [18].
- Boron "ate" complexes in organic synthesis [19,20,21,22].
- Boranes and heteroboranes [23].
- Metalloborane derivatives with ligand-metal single bonds [24].
- Transition metals in organic synthesis [25].
- σ-Alkyl and -aryl complexes of group 4-7 transition metals [26].
- Metal-carbene complexes in organic synthesis [27].
- Metal assisted nucleophilic aromatic substitution in π-arene-metal complexes [28].
- Transition metal dialkylamides and disilylamides [29,30].
- Gold chemistry [31].
- σ-Bonded actinide organometallics [32,33,34].
- Alkali metal derivatives of tin [35].
- Preparation of chiral trioganotin halides using organolithium reagents [36].
- Preparation of new homoleptic alkyls and amides [37,38].
- Inorganic five-membered ring systems consisting of silicon, nitrogen, and other hetero elements [39].

2. STRUCTURE AND BONDING STUDIES

X-ray diffraction has been employed to determine the molecular and crystal structures of dilithiated stilbene complexed with tetramethylethylenediamine (TMEDA) (Fig. 1) and with pentamethyldiethylenetriamine (PMDTA) (Fig. 2) [40]. In each structure, the hydrocarbon portion is planar with the aromatic rings trans to one another. The lithium atoms chelated by the amines are located at equal distances above and below the midpoint of the olefinic bond of the stilbene molecule. The stilbene bis(lithium PMDTA) structure is said to be the first π-delocalized carbanion complex to be isolated and so characterized which contains other than disolvated lithium atoms.

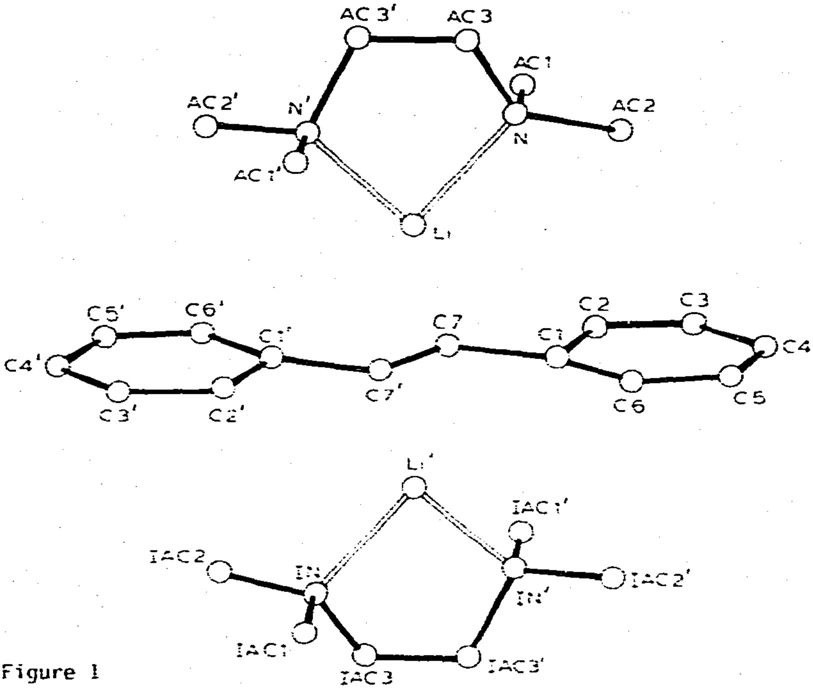


Figure 1

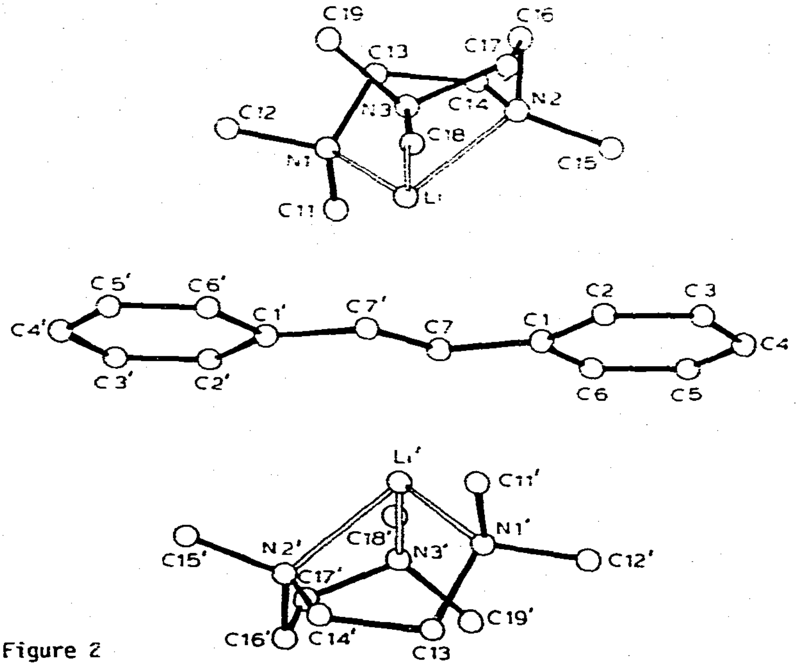
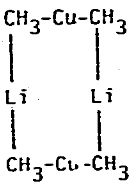


Figure 2

Solution X-ray scattering methods, vapor pressure depression, and 'H NMR have been used to determine that lithium dimethylcuprate exists as a dimer in diethyl ether solution most probably as structure 1 [41]. The copper-copper distance is estimated to 4.4±0.7 Å and the methyl groups are either equivalent or undergo very rapid exchange even at -60°. Based on kinetic studies on the reaction of 1 with methyl iodide, the authors conclude that the dimeric structure of 1 is important and accounts for its unusual reactivity in Corey-Posner reactions. In another paper, 'H NMR has been employed at -136° to show the presence in dimethyl ether of LiCu(CH$_3$)$_2$, LiCu$_2$(CH$_3$)$_3$ (2), and Li$_2$Cu(CH$_3$)$_3$ (3) [42].



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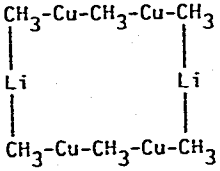

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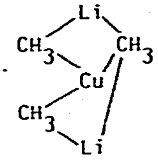
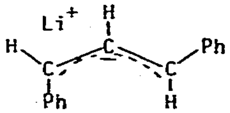


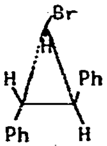
3

A large number of other publications also described the use of 'H NMR to study organolithium reagents. First, line shape analysis in 300 MHz 'H NMR spectra of R- and racemic 2-methylbutyllithium hexamers in pentane has revealed fine structure as a result of chemical shifts among diastereomeric aggregates [43]. The spectra of the racemic reagent indicated 1) an inversion at carbon bonded to lithium which occurs within a hexamer aggregate and 2) an interaggregational exchange of organolithiums between magnetically inequivalent sites. In constrast, the R-lithium reagent showed a line shape change ascribed only to the inversion process. The heats and entropies of activation for the two processes are listed.

The unstable lithio-Z,E-1,3-diphenylallyl anion (4-Z,E) has been obtained by metalation of cis-1,3-diphenylpropene and by reduction of 5 by lithium metal as evidenced by NMR spectroscopy on its perdeuteratedphenyl derivative. The rate of isomerization of 4-Z,E to the more stable 4-E,E was followed by NMR and the following values are recorded: ΔH^{*} = 17.3±1.8 kcal/mol, ΔS^{*} = 2.0±8 e.u., $t_{1/2}$(-30°) = 2.9 min. The later value explains why previous workers failed to observe 4-Z,E in similar studies.



4-Z,E



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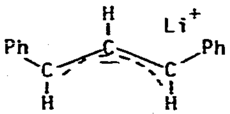
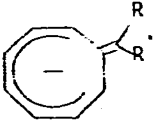


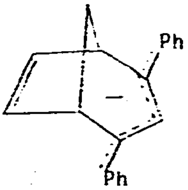
4-E,E

Several 9-aryl derivatives of methylenecyclooctatrienyl anions (6) were studied by both ^{1}H NMR and UV to test the effect of such aryl groups on the magnitude of ring currents [45]. Since the chemical shifts of the eight-membered ring protons gave linear plots with the σ_p values of the phenyl substituents and since the trend of λ_{max} values relative to σ_p is opposite to that observed with para-substituted styrenes, the authors conclude that a ring current effect is being observed which is a function of the HOMO-LUMO energy gap. These results support the current theory that paratropism results from low-lying excited states accessible through allowed magnetic dipole transitions.



6

A comparison of the ^{1}H NMR spectrum of 7 with that of 8 reveals a sufficient number of similarities that one might conclude that 7 is a completely delocalized, homoaromatic compound [46]. Since earlier work had demonstrated that 7 is not homoaromatic, a caveat is issued against reaching such conclusions based on NMR alone without also considering stabilities relative to an appropriate reference compound.



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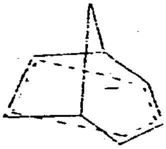
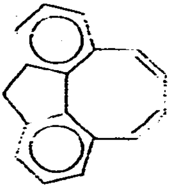


8

Metalation of hydrocarbon 9 by n-butyllithium has given an anion, 10 or 11, whose ^{1}H NMR was compared to that of 12, a peripheral perturbed aromatic [13] annulenyl system [47]. It is concluded that structure 10 best fits the data. This anion is apparently the first example of a perturbed annulenyl anion exhibiting anti-aromatic properties.



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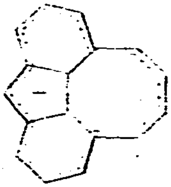

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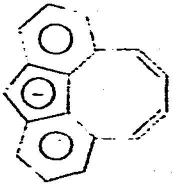

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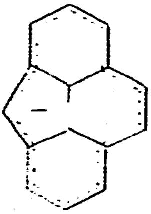

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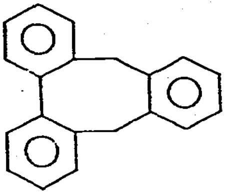
A novel n-butyllithium catalyzed rearrangement of 13 to 14 has been shown by ^{1}H NMR to involve the intermediacy of carbanions 15 and 16 [48]. Similar spectra were obtained for the corresponding intermediates in the conversion of 17 to 18. The latter represents a new and very convenient route for the preparation of the 4,8-dihydrodibenzo[cd,gh]pentalene system.



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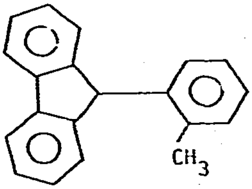

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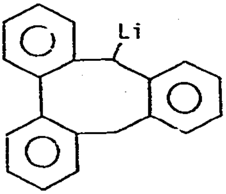

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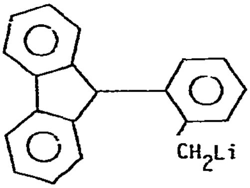

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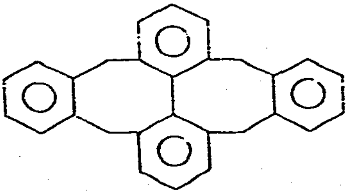

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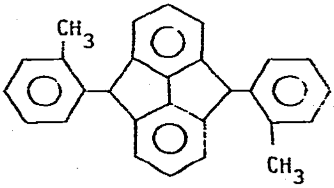
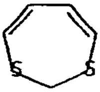


18

Two cyclic sulfur-containing 10-π electron anionic systems have been studied by NMR to determine the extent of aromaticity. In the first case, metalation of 19 gave 20, the ^{1}H NMR of which led the authors to speculate the presence of a planar, 10 π-aromatic delocalized system [49]. Secondly, metalation of a mixture of 21 and 22 afforded 23 whose ^{1}H and ^{13}C NMR suggest that negative charge is delocalized into the thiophene ring of this molecule [50].



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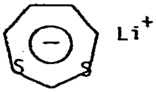

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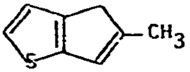

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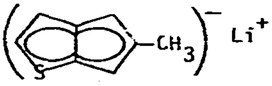
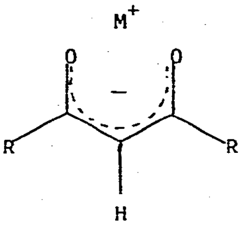


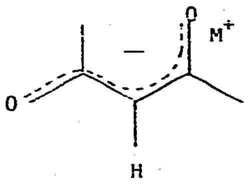
23

Evidence has now been provided by 'H NMR, far infrared, and conductance data for the previously inferred ion-pair structures of alkali dibenzoylmethides (24) and alkali dipivaloylmethides (25) [51]. Each of the techniques provided data as a function of the positive charge density of the cation. For example, the greatest downfield shift in the 'H NMR spectra was produced by the lithium cation while the smallest downfield shift was effected by the cesium cation. In two other papers, 'H NMR has been employed to study the amounts of E,Z- (26) and Z,Z- (27) alkali acetylacetonates in methanol as a function of alkali cation [52,53]. In this solvent, chelation is unimportant except when the cation is lithium and the E,Z-isomer (26) predominates. The integrated intensities of the signals from both conformations have been employed as an "indicator" in the titration of sodioacetylacetone with lithium salts [53].



24, R = Ph

25, R = $\underline{t}$-C_4H_9.



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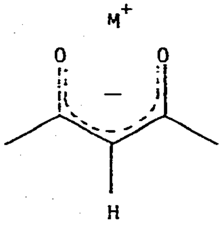
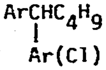


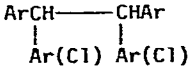
27

Radical intermediates in the reactions of diarylchloromethanes and aryldichloromethanes (aryl = phenyl and pentafluorophenyl) with n-butyllithium were studied by 'H and ^{19}F chemically induced nuclear polarization effects [54]. Such effects were observed on 28 and 29 arising from in-cage recombination of arylmethyl and butyl radicals and recombinations of arylmethyl radicals, respectively.



$\underset{\text{Ar(Cl)}}{\text{ArCHC}_4\text{H}_9}$

28

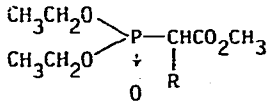


$\underset{\text{Ar(Cl)}}{\text{ArCH}}\text{——}\underset{\text{Ar(Cl)}}{\text{CHAr}}$

29

The first example of diastereotopic groups caused by a tricoordinate negatively charged silicon atom has been observed in the case of diisopropylphenylsilyllithium [55]. Thus, the 'H 270 MHz NMR spectra of this compound revealed the nonequivalence of the diastereotopic methyl groups even up to temperatures of 185°. A barrier to inversion about silicon of >24 kcal/mol is suggested.

Metalation of two phosphonate esters (30, R = H or CH_3) has been shown by ^1H, ^{13}C, and ^{31}P NMR spectroscopy to afford either 31 or 32 depending upon the metalating agent [56]. Thus, while n-butyllithium affords only 31, lithium-t-butoxide and potassium t-butoxide gives both 31 and 32; the latter species predominates with potassium cation.



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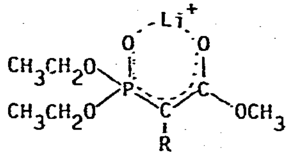

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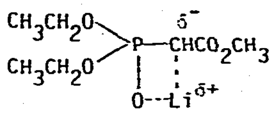


32

Finally, ^1H NMR, infrared, and Raman data have been published for alkoxide 33 and corresponding sulfur and selenium derivatives, and for lithium salt 34 and the related arsenic derivatives [57]. These species were prepared by reaction of silylethers, phosphines, and arsines.

H_3SiOLi

33

$(H_3Si)_2PLi$

34

Several papers were devoted to ^{13}C NMR of organolithiums. Thus, such spectra were obtained from tetraphenylethylene and the dilithio and disodio salts of its dianion [58]. Upfield shifts of 52.66 ppm and 43.42 ppm for the lithium and sodium salts, respectively, compared to the parent compound confirms the hypothesis that the former cation is closer to the dianion than is the latter one. That solutions of the dianion containing both lithium and sodium cations gave lines for both the dilithio and disodio salts as well as only one other midway between the above two lines is suggestive that cations are rapidly exchanged by both inter- and intramolecular reactions. Ultraviolet spectra of the dianions are also reported.

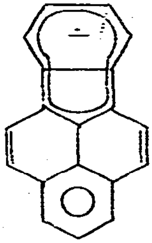
Solvation of alkali diphenylmethanes has been studied by ^{13}C NMR as a function of the metal, solvent, and temperature [59]. The authors discuss the existence of a linear dependence between the contact ion alpha-carbon chemical shift and the cation size, the solvent dependency on these chemical shifts where shielding occurs in the order methyl-THF>THF>DME, and solvation of the ion pairs as the temperature is decreased causing the negative charge to be spread more evenly throughout the π-system. The danger of comparing the chemical shifts of lithium salts to those of other alkali metal salts is emphasized.

The ^{13}C NMR spectra of several metal enolates derived from acetophenone, cyclohexanones, and others have been obtained and the chemical shift of the enolate α-carbon atoms compared with the same carbon atoms of the corresponding enol acetates and trimethylsilyl enol ethers [60]. The difference in chemical shift of the enolates compared to the reference compounds seems to be related to the π-electron density at the α-carbon and is a function of the cation (K^+>Na^+>Li^+), the solvent (DME>THF>ether), and added ligands like HMPA and certain crown ethers.

A ^{13}C NMR study of several α-lithiosulfoxides and sulfones does not support the theory that such carbanions are pyramidal even in a benzylic position [61]. Thus, the $^{1}J(^{13}C\text{-}H)$ coupling constants of the lithiosulfoxides and sulfones were found to be higher than those in the parent sulfur compounds, a result ascribed to a change in the hybridization state. This increase in the coupling constant is in the opposite direction realized with the model compounds methyllithium and methane where the coupling constant is smaller in the organolithium reagent than in the hydrocarbon.

In the area of ESR, the effect of 1,3-carbon-carbon interactions on spin density in radicals derived from benzocyclobutenes, cyclobutene, and trans-2-butene is discussed [62]. The authors conclude that "spin densities simply can not be understood adequately without recognition of these interactions." That cation radical hyperconjugation is not necessarily greater than such anion spin transmissions to β-hydrogens is discussed.

ESR spectra have been reported for phenalene 35 [63], phenylazulene 36 [63], the lithium ketyl of 2,2,6,6-tetramethylcyclohexanone [64], alkali metal ketyls of various thienyl and thiazoyl ketones including the affect of dibenzo-18-crown-6 ether [65], five arylphospine derivatives [66], and alkali metal adducts of phenylacetylene [67]. In the latter case, infrared and optical spectroscopy were also employed to demonstrate the reduced nature of such species.



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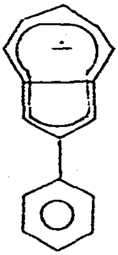


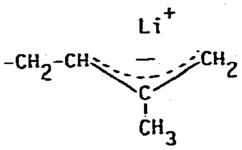
36

Spectroscopic studies using techniques other than NMR and ESR continue to be investigated. Thus, the infrared and Raman spectra of alkali metal derivatives of nitromethane in the C-H stretching region have been investigated [68]. Bands at 3040 and 3170 cm^{-1} are ascribed to the aci-nitro formulation with a sp^2 hybridized carbon atom.

The infrared spectra of several alkali metal derivatives of manganese carbonylates were obtained to indicate the nature of the carbonyl anion environment [69]. The data, in connection with kinetic and conductivity experiments, provided information about the nature of bonding and complexation phenomena in contact and solvent separated ion pairs as well as in free ions of several species. In an unrelated study, resolution of vibronic structure and the directions of the transition moments of lithiotetracyanoquinidomethane have been obtained by the use of absorption spectroscopy at 860-560 nm [70].

Ultraviolet spectroscopy and ESR have been employed to measure the equilibrium constants of the disproportionation of the ion pairs of lithium naphthalenide, anthracenide, tetracenide, perylenide, and pyrenide in ether [71]. The reactions are favored by the interaction of the cations with the resulting dianions causing an increase in the coulombic energy.

The ion pair propagation in the polymerization of isoprene in THF has been studied with the aid of UV spectroscopy to check for the occurrence of side-reactions [72]. Three types of anionic centers are observed at 287 nm, 305 nm, and 335 nm, two of which may be due to 37 and 38.



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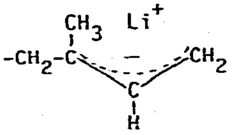

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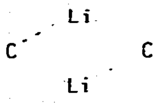
Other papers of interest in this area include a study of ion pairing of arylthiolate anions in THF and DMF determined by optical spectroscopy [73], the ion pairing of fluorenyl alkali metal compounds in the presence of poly-(ethylene oxide) using visible spectra [74], ion pair formation of carbanions of xanthene and thioxanthene studied by absorption and fluorescence spectra [75], and determination of molecular weights of non-volatile substances by field desorption mass spectrometry using lithium cation attachment [76].

In the area of calculations on organolithium reagents, five papers were concerned with methyllithium [77-81]. Depending upon the basis sets employed, the following values have been described: C-Li bond length (Å): 2.021, 1.969, 1.727, 2.025; C-H bond length (Å): 1.089, 1.122, 1.090 (Ha) and 1.068 (Hb), 1.078, 1.0623 to 1.1185 (depending upon angle); ∠HCH: 105.8°, 104.2°; total energy (hartrees): -47.0206, -46.7767, -46.9596, -39.318 to -39.401, -46.419 (if tetrahedral), -46.247 (if planar), -46.4203. Monomeric methyllithium is said to consist mostly of ionic bonding with about 0.8 electrons transferred from the lithium to the methyl [77]. The bond separationenergy of the C-Li bond is suggested to be -5.6 kcal/mol [78] and the inversion barrier ranges from 0.4 to 20.31 depending upon bond angles [79]. Methyllithium tetramer is described as having bond lengths as follows (Å): Li-Li:2.369-2.68; Li-C: 2.25-2.31; C-H: 0.95-1.095 [81]. The total energy of this species has been calculated to be -185.4886 to -185.8611 hartrees [81]. Clusters containing ten atoms of lithium are also described [81].

Similarly, total energies of methylenedilithium have been calculated to be (hartrees) -53.744 [78], -53.131 (cis,tetrahedral) [80], -53.074 to -53.030

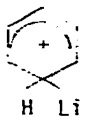
(trans, planar) [80], and -53.7165 to -53.7851 [82]. Lithioacetylene is likewise described by the following: C-Li bond length: 1.931 Å; C-C bond length: 1.208 Å; C-H bond length: 1.056 Å [77]. Another paper discusses the electronic charge distribution in this compound [83] while a third paper predicts, using calculations, that monomeric dilithioacetylene has a double bridged ground state structure of 39 rather than 40 [84]. A wide variety of other organolithiums are discussed including ethyllithium and vinyllithium [77], ethyllithium and $LiCH_2X$ where X = BeH, NH_2, OH, F, and BH_2 [78], 1-3-dilithiopropane, difluorodilithiomethane, tri- and tetralithiomethane, 41 and its 1-1-dilithio salt, 1-fluoro-1-lithiocyclopropane, 42, and others described below [80].



39

Li-C≡C-Li

40



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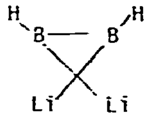
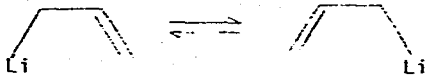


42

Using STO/3G atomic orbitals, computations were performed on both the covalent (43) and ion pair (44) structures of allyllithium [85]. It is concluded that 44 is more stable than 43 by 8 kcal/mol. In an attempt to determine the affect of solvent on this species, computations were also performed on allyllithium coordinated to two water molecules.



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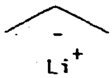
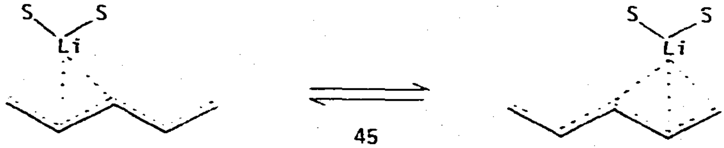


44

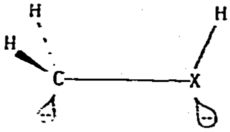
A calculated structure of pentadienyllithium bis(dimethyl ether) has been proposed which contains a bridged lithium interacting by both π- and σ- bonds [86]. Since C_1 and C_5 have previously been shown to be equivalent on the NMR time scale, this structure is said to be equilibrating as shown (45) where S = solvent dimethyl ether. The affect of methyl groups on such anions is discussed. In another paper dealing with cyclopentadienyllithium, it has been suggested that the lithium atom is most stable above the middle of the ring [87].



45

Other ring systems similarly studied have included lithiocyclopropane [80,88], 1-1-dilithiocyclopropane [80], cyclopropane radical anion [89], cyclopropenyl anions [90], 3,3-dilithiocyclopropene [80], the electrocyclic reaction between the radical anions of cyclobutene and butadiene [91], and other aromatic and antiaromatic 4-, 5-, 6-, 7-, 8-, and 9-membered ring anions and dianions [88].

Two papers discussed certain aspects of α-oxy- and α-thiocarbanions [92, 93]. Both agree that carbanions alpha to sulfur are stabilized by overlap of the orbital containing the lone electron pair of the carbanion and a σ^* antibonding orbital on the sulfur atom rather than by $(d \rightarrow p)_\pi$ bonding. Such stabilization is conformationally dependent where conformer 46 (w or e) is more stable than conformer 47 (y or a). Similar n_C-σ^*_{OH} overlap integrals are proposed for α-oxycarbanions. It is suggested that in such carbanion precursors, the C-H bond antiperiplanar to the lone pair of electrons on the α-heteroatom is much less acidic than that in its gauche rotamer.



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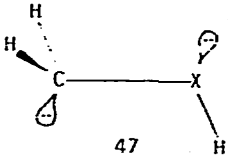
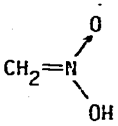


47

An ab initio study has been performed on nitromethane, its aci-nitro tautomer [48], and its conjugate base 49 [94]. The anion is best described as planar but has an extremely shallow potential curve to pyramidal inversion. The total energies (hartrees) for the species using an extended basis set are parent: -243.2630; 48: -243.2532; 49: -242.6873.



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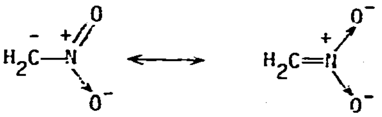
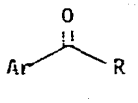


49

Other papers discussing molecular orbital calculations have been concerned with the $S_{RN}1$ mechanism of aromatic substitution [95], the structure of tricyanomethide [96], and the structure of the lithium adduct of methylenephosphorane [97].

3. KINETICS AND MECHANISM

Several types of ketones have been condensed with lithium dimethylcuprate to test if the nature of the products could determine if electron transfer processes had occurred to afford radical anion intermediates [98,99]. Thus, aryl alkyl ketones 50 with this cuprate gave methyl carbinols arising from 1,2-additions. Though ketyls may have been present, no products arising from 51 were detected. Similar reaction of the cuprate with cyclopropyl ketones 52 gave some of the desired ring-opened products like 53; however, such products were ascribed to direct attack by the copper reagent on the cyclopropyl ring rather than to an electron transfer process. On the other hand, such electron transfer was observed in the conversion of acetoxy- and bromoketones 54 to ketone 55 and of β-cyclopropyl enone 56 to β,γ-unsaturated ketone 57. In another paper, it is disclosed that the reaction of certain diaryl ketones with lithium dimethylcuprate affords ketyls [100].



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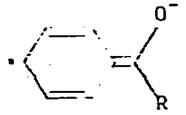

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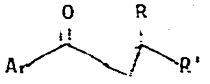

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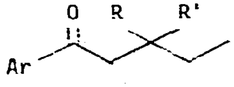

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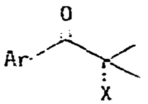

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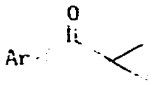

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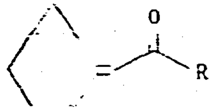

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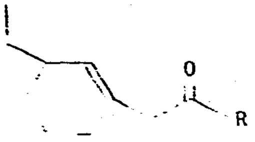


57

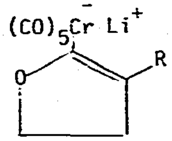
The electron transfer efficiency of 9-methoxyfluorenide in methanol has been studied as a function of the nature and concentration of the counterions [101]. It was found that the second-order rate constants for ionization and for irreversible nitrobenzene-oxygen trapping efficiency are in the order $(CH_3)_4N^+\bar{O}H > KOCH_3 > NaOCH_3 > LiOCH_3$.

Benzhydryl and benzyl fluorides have been dimerized to ethane derivatives by lithium naphthalene apparently by a classical displacement mechanism [102]. These results are contrasted to similar coupling reactions of corresponding chlorides which occur via an electron transfer mechanism through a geminate radical pair intermediate. Similar mechanisms are suggested to explain the rate differences in the reactions of diphenylmethyllithium with benzylic fluorides and chlorides.

A paper describing gas phase carbanions generated in a pulsed electron high-pressure mass spectrometer is of interest since it discloses relative and absolute gas phase acidities of several carbon and nitrogen acids [103]. Such acidities are compared to solution acidities, and the importance of solvation energies is discussed. Another paper describes the measurement of proton-transfer rates of a variety of delocalized anions with related neutral species as determined by pulsed ion cyclotron resonance spectroscopy [104].

The relative reactivities of 58 and 59 towards alkyl halides have been studied in an effort to determine why desired monoalkylations of species like

58 afford mixtures of mono- and dialkylated products [105]. The authors conclude that such carbene anions suffer dialkylation because of the greater reactivity of the more substituted anion.



58, R = H
59, R = CH_3

The equilibrium anionic polymerization of n-valeraldehyde effected by lithium benzophenone has been investigated [106]. Enthalpy and entropy values of -5.3 ± 0.3 kcal/mole and -25.7 ± 1.4 cal/mol-deg, respectively, have been disclosed.

Equilibrium solution acidities of a number of phosphinylacetic acid esters in diglyme and in DMSO have been disclosed [107]. In an unrelated paper, it has now been established that kinetic differentiating effects of C-H acids are observed not only with different anions but also with different alkali cations [108].

The kinetics of the disproportionation of alkali tetracenide radical anions to the parent compound and its dianion have been determined as a function of the alkali cation and solvent using flash photolysis [109]. The study illustrates that factors other than steric ones may be responsible for certain dianion salts being more stable than their corresponding radical anions.

Rate constants for the protonation of 1,3-diphenylallyllithium and sodium by fluorene have been determined spectrophotometrically in a variety of ethereal solvents [110]. It was found that the loose ion pair of the lithium species is protonated about 100 times faster than the tight ion pair, and that the sodium tight ion pair is protonated four-five orders of magnitude faster than the corresponding lithium tight ion pair. In another study, fluorenyllithium has been alkylated under conditions favoring free carbanions and solvent separated ion pairs [111]. The kinetics revealed the former system reacted two-three times more rapidly than the latter one.

The ratio of O- to C-alkylation of alkali derivatives of ethyl acetoacetate has been found to be a function of the cation, the solvent, and the alkylating agent and is ascribed to the tightness of ion pairs [112]. Thus, more O-alkylation is realized with the potassium than with the lithium salt and in HMPA than DMF. The ionicities of the solvents are deemed more important than their dielectric constants.

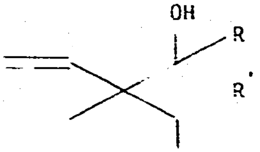
Other kinetic studies have been performed on the systems bromobenzene, benzaldehyde, and lithium [113], n-butyllithium and 4-methylmercaptoacetophenone [114], and styrene and lithium diethylamide [115].

In the area of stereochemistry, the Z/E equilibrium compositions of several 2-alkenyl organometallics 60 (R = CH_3, CH_3CH_2, i-C_3H_7, t-C_4H_9) have been studied as a function of cation, R, and solvent [116]. It was found that the Z/E ratio increased in the order Li<Na<K<Cs and hexane < THF. Moreover, the endo (cis) preference between R and the alkalimethyl carbon seemed not very dependent on the electronic capacity or the size of R. Reasons are suggested for the above observations.

$$RCH = CHCH_2M$$

60

3-Methyl-2-pentenyllithium has been condensed with a variety of benzaldehydes, acetophenone, acetone, and hexafluoroacetone to study the relative amounts of branched (61) and linear alcohols (62) as a function of electronic factors [117]. The ratio of 61/62 decreases in reactions of benzaldehydes with p-electron withdrawing groups. The opposite is realized with p-electron donating groups. Only 61 and only 62 are obtained with acetone and hexafluoroacetone, respectively. The results are interpreted in terms of hard-soft acid-base theory.



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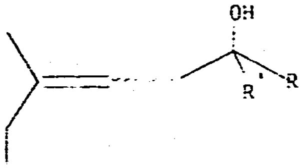
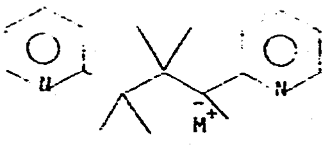


62

The effect of ion pair structures on the methylation stereochemistry of 63 has been studied in THF by varying the cation systematically from lithium to the higher alkali metals [118]. Thus, while the lithium salt 63 reacted stereospecifically with methyl iodide to afford meso-64 (> 99%), the rubidium salt 63 gave nearly a 50-50 mixture of meso-64 and racemic-64. The results are rationalized in terms of a cation side approach of methyl iodide to diastereomer 65.



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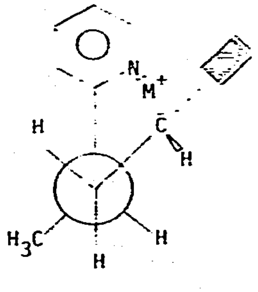
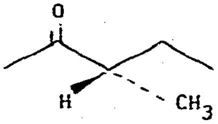


65

Metalation of (+)-(S)-3-methyl-2-pentanone (66) by LDIPA has been shown to afford (S)-enolate 67 with less than 10% racemization [119]. Reagent 67 has been reacted with alkylhalides, acid chlorides, aldehydes, and ketones to give optically active products.



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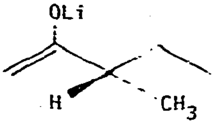


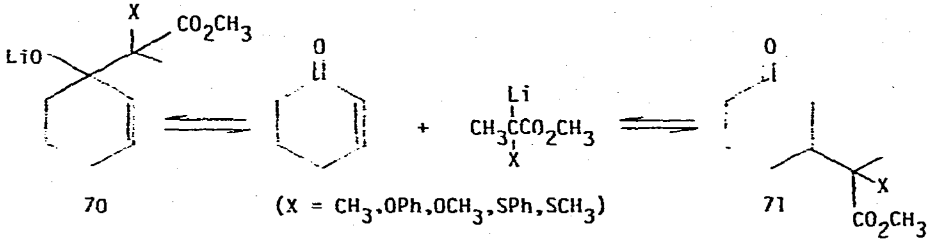
67

In the continuation of an earlier study concerned with the stereochemistry of addition reactions to carbonyls in terms of orbital factors, the relative amounts of 68 and 69 from 4-t-butylcyclohexanone with MCH_2Y were found to vary with the metallic cation [120]. Thus, less 69 was obtained with $LiCH_2Y$ than with $BrZnCH_2Y$ where $Y = CO_2C_2H_5$, $CONR_2$, CN, and CO_2M.

68

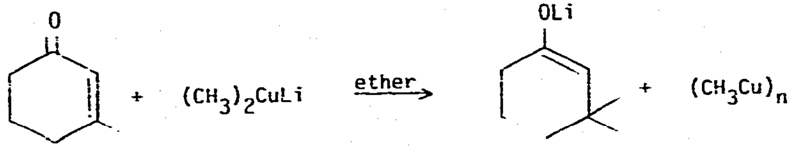
69

Several lithium ester enolates have been condensed with 2-cyclohexenone to afford the 1,2-adducts 70 at -78° by a kinetically controlled process [121]. Interestingly, when the reaction mixtures are allowed to warm to 25° before quenching, the thermodynamically controlled 1,4-adducts 71 are obtained. In one case, a similar condensation with a lithioacetonide was found to be irreversible affording only a 1,2-adduct.



70 $(X = CH_3, OPh, OCH_3, SPh, SCH_3)$ 71

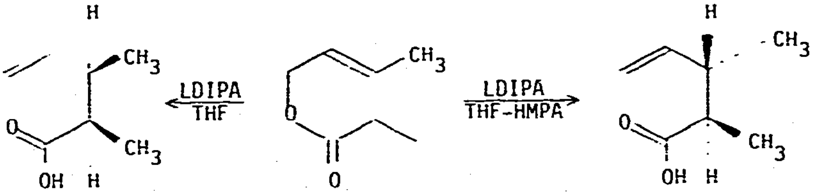
The intermediate organometallic obtained from the conjugate addition of lithium dimethylcuprate to enone 72 has been found to consist of soluble lithium enolate 73 and insoluble $(CH_3Cu)_n$ precipitate as evidenced by ^{13}C NMR spectroscopy [122]. It is suggested that lithium rather than copper enolates are probably intermediates in all such conjugate additions of lithium cuprates even when the organocopper product remains in solution.



72 73

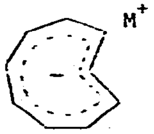
Other sutudies in this area have been concerned with the carbonation of (S)-lithiobenzyl methyl sulfoxide to afford (R)-α-methylsulphinylphenylacetic acid [123], the stereochemistry of the silylation of 9-alkyl-10-lithio-9,10-dihydroanthracenes [124], and the inversion of configuration at the chiral trivalent phosphorus atoms of two phosphinate esters by methyllithium and sodium methoxide [125].

Several papers describing rearrangements of organolithiums appeared in 1976. A continuation of the study of the ester enolate Claisen rearrangement has resulted in the discovery that choice of solvent dictates stereochemical control [126]. For example, lithio-(E)-crotyl propanoate (74) rearranges to erythro acid 75 in THF and to threo acid 76 in THF-HMPA. It is suggested that Z- and E-type enolates are formed in THF and in THF-HMPA, respectively. This reaction has also been employed in the construction of the prostanoid skeleton [127].



75 74 76

The isomerization of alkali cis,cis,cis,trans-[9]annulene anion 77 to the more stable all cis 78 has been found to require a much higher activation energy than topomerization where the $\Delta G^{\ddagger}$ of the isomerization ranged from 29.6-34.8 kcal/mol for lithium and potassium cations, respectively [128]. Isomerization of 77 to 78 has also been effected by protons and by photochemical and thermal processes.



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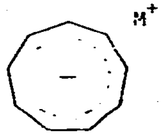
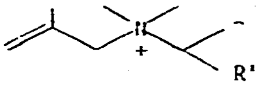


78

A full paper appeared describing the interaction of lithium dialkylcuprates with cholesteryl and 5-norbornen-2-yl tosylates in which the double bond of the ring systems participate in substitution reactions [129]. Similar results were found for the cyclopropane ring of cyclopropylmethylcarbinyl tosylate. As a result, skeletal reorganizations are observed in these reactions which occur with retention of configuration at the nucleofugal sp^3- carbon atom.

Several quaternary salts (79) of methallyamines have been subjected to the Stevens rearrangement by n-butyllithium and other bases [130]. When R and R' were methyl, ethyl, n-propyl, and n-butyl, the reaction proceeded via a mixture of 80 and 81 which rearranged to 82 and 83, respectively. With larger alkyl groups like i-propyl and cyclohexyl, only 82 arising from 80 was observed.



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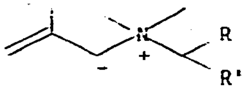

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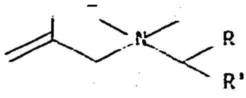

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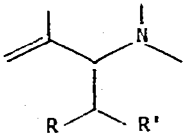

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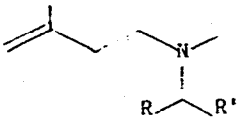
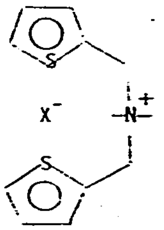


83

Quaternary salts 84 (X = Cl,I) were also treated with a variety of strong bases to afford Stevens rearranged product 85 and Sommelet rearranged product 86 [131]. The amines arose from a common intermediate 87.



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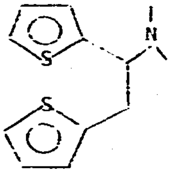

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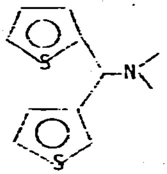

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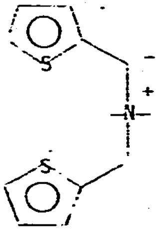
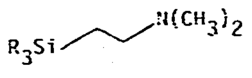


87

Similar rearrangements have been observed in the reactions of silylethylamines 88 and benzyne, generated from o-fluorobromobenzene and n-butyllithium [132]. Among the products observed were 89-91. The cyclization to give 90 was induced by excess n-butyllithium.



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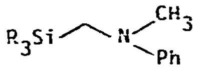

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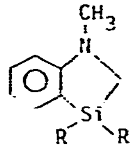

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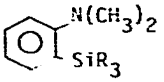
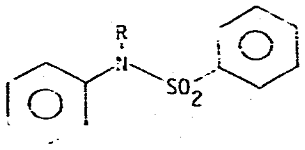
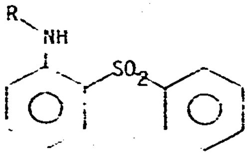


91

Certain N-arylbenzenesulfonamides like 92 have been found to rearrange to sulfones like 93 upon treatment with organolithium reagents [133]. The first step in such reactions is metalation of a ring hydrogen atom ortho to the sulfonyl group.

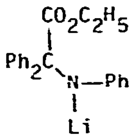


92



93

The previously reported 1,2-anionic rearrangement of 94 to 95 has now been found to be reversible [134]. Thus, 95 may be converted to 94 by the use of lithium counter ion. The relative stabilities of sodio-95 versus lithio-94 are discussed.



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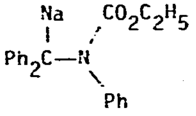
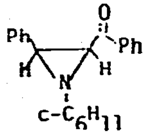


95

Ketazines have been converted to pyrroles or tetrahydropyridazines via their dilithio salts as illustrated in Scheme 1 [135]. Which product is formed is determined by the nature of the R and Ar groups.

A mechanism has now been proposed for the conversion of 96 to 97 involving, among other proposed intermediates, lithioaziridine 98 which has been trapped with methanol-O-d [136].



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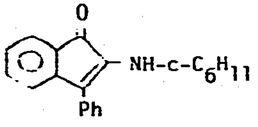

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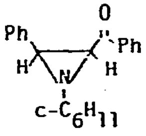
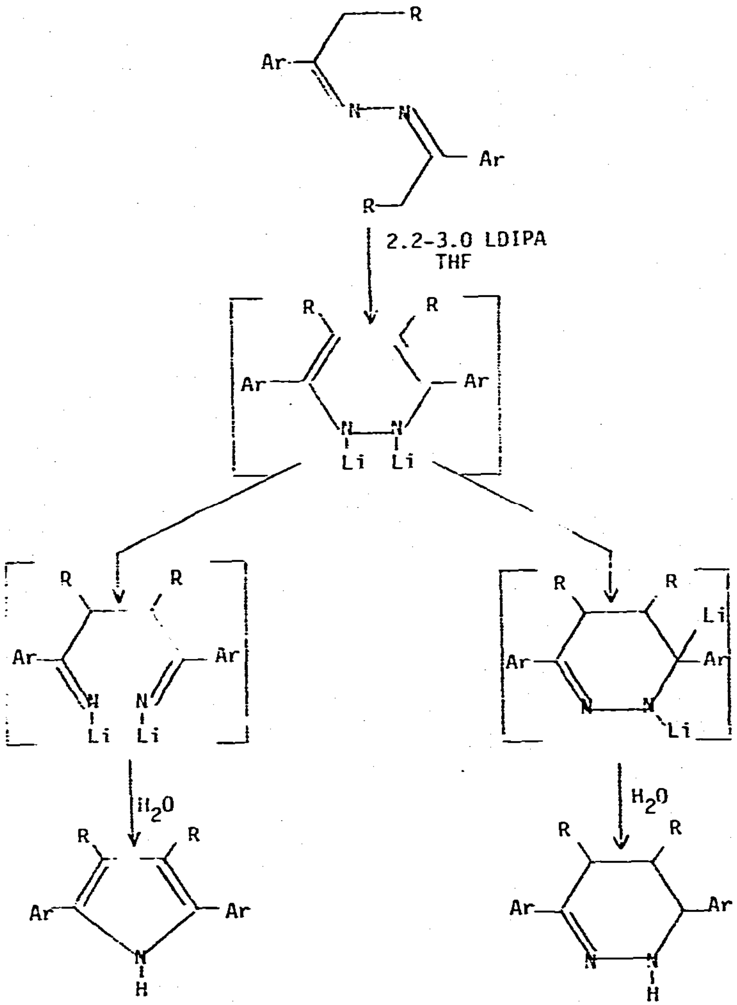


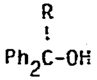
98

Scheme 1



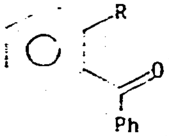
Products 99-101 (R = 5-hexenyl or cyclopentylmethyl) have been obtained from the Wittig rearrangement of benzhydryl 5-hexenyl ether in THF effected by n-butyl- and methyllithium [137]. Those products containing the 5-hexenyl group arise via intramolecular pathways which may involve routes other than secondary recombination of alkyl radical and ketyl. The cyclizations leading to 99-101 which contain the cyclopentylmethyl group are said to occur with 5-

hexenyl radicals which escape reaction with geminate partners but later react with appropriate ketyls.

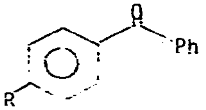


$Ph_2C(R)-OH$

99

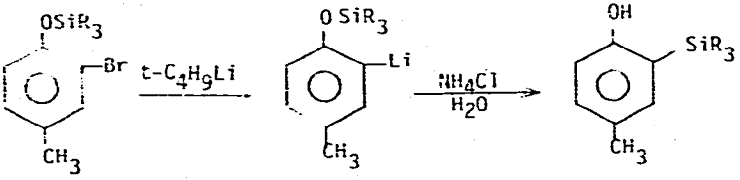


100



101

Two papers discussed anionic O to C rearrangements in lithio-O-trialkylsiloxybenzenes, pyridines, and other heterocyclics [138,139]. The process, illustrated by the conversion of 102 to 103, occurs by an intramolecular route in some cases, but by an intermolecular route in others. In contrast, lithio-N-trialkylsilylarylamines fail to undergo such rearrangements.



102

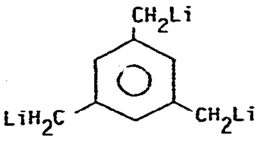
103

Other papers discussing rearrangements have been concerned with the conversion of 5,5-diphenyl-4-thiacyclohexene to (E)-2,2-diphenyl-1-methylthiovinylcyclopropane [140], the use of the Wittig rearrangement of a dithiacyclophane as a portion of the synthesis of the first cyclophane within a cyclophane [141], and cine substitution in the reactions of tributylstannyllithium with aromatic fluorides and chlorides [142].

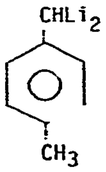
4. METALATIONS

A. At sp^3 Carbon

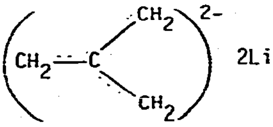
Several polymethylbenzenes have been metalated by n-butyllithium/TMEDA in hexane to afford mono-, di-, and trilithio derivatives as evidenced by silylation [143]. For example, mesitylene gave mostly 104 while p-xylene yielded exclusively 105. The energies of these and related species have been calculated and are included in the paper.



104



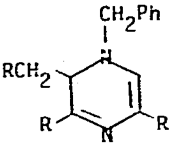
105



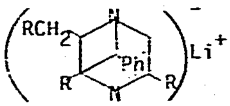
106

Four methallybenzenes and isobutene have been similarly metalated by the above reagent to afford corresponding dilithio derivatives which were methylated by methyl bromide [144]. That dilithio species were present was confirmed by NMR spectroscopy. The methylated derivatives arising from cross conjugated dienes were obtained in preference to those arising from linear ones. The authors discuss at great length the question of the aromaticity of the trimethylenemethane dianion (106) obtained by dimetalation of isobutene.

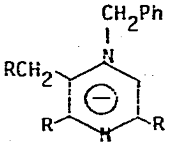
Metalation of 1,2-dihydropyrazines 107 (R = Ph or p-ClC$_6$H$_5$) with n-butyllithium occurs at a benzylic carbon to give bicyclic 108 rather than 109, a system containing formally delocalized 8π-electrons [145]. Hydrolysis of 108 then yields 110.



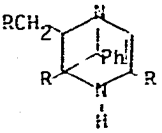
107



108

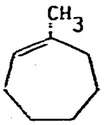


109

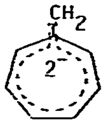


110

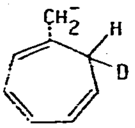
A combination of metalation-metal hydride elimination reactions by n-butyllithium-potassium t-pentoxide has been employed to convert 1-methylcyclohept-1-ene(111) to dianion 112, a very stable species which does not behave as a simple cycloheptatriene [146]. Deuteration of 112 affords the known methylenecycloheptatrienyl anion 113.



111

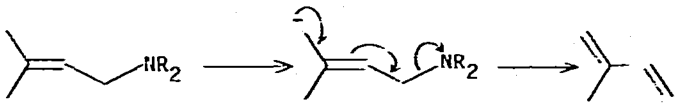


112



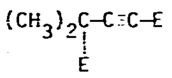
113

Metalation of squalene by s-butyllithium/TMEDA has been found to occur only on a methyl group [147]. In another paper, metalation of a methyl group of prenylamine 114 by n-butyllithium results in an interesting isomerization and elimination to give isoprene [148]. Other related examples are listed.

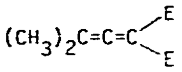


114

Polymetalation of acetylenes continued to be studied in 1976. Thus, reaction of 1- and 2-butyne and 3-methylbutyne with alkyllithiums has been shown to yield CH$_3$C$_3$Li$_3$ and (CH$_3$)$_2$C$_3$Li$_2$, respectively [149]. Such species have been condensed with a variety of electrophiles to usually afford polysubstituted acetylenes and allenes like 115 and 116, the ratio of which depends upon the size of the electrophile. An IR study suggests the above lithium containing species are best described as propargylides. A second paper in this series discussed sequential derivatization of these organometallics by diethyl sulfate and chlorotrimethylsilane [150]. For example, C_3Li_4 gives mostly 117 along with some 118 and 119. The results are ascribed to propargylic sites and diethyl sulfate being soft and acetylide sites and chlorotrimethylsilane being hard. A third paper describes the preparation and reactions of $CH_3C_5Li_3$, derivatization of which gives mostly allenynes and some cumulenes and diacetylenes [115].


$(CH_3)_2\underset{E}{C}-C\equiv C-E$

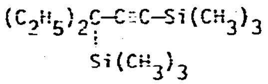
115



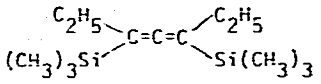
116

$(C_2H_5)_3C-C\equiv C-Si(CH_3)_3$

117

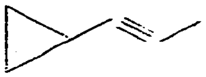

$(C_2H_5)_2\underset{Si(CH_3)_3}{C}-C\equiv C-Si(CH_3)_3$

118

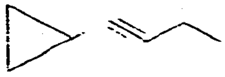


119

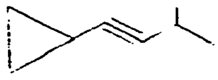
Cyclopropylacetylenes 120-122 have been metalated by n-butyllithium to yield propargylic lithium reagents which have been condensed with a variety of electrophiles [152]. While 120 and 122 were metalated only at the methyl and α-ring carbon, respectively, 121 gave a mixture of α- and α'-monolithium reagents.



120

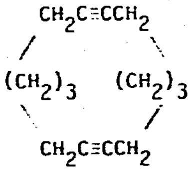


121

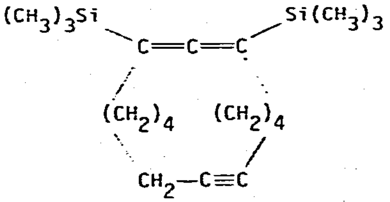


122

Regioselective dimetalations have been effected on 1,8-cyclotetradecadiyne (123) by n-butyllithium to afford 124 after quenching with chlorotrimethylsilane [153]. The authors suggest that both metalations occur at the same carbon atom.



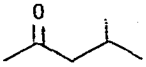
123



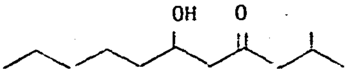
124

Seven 1-arylpropynes containing various ring substituents have been mono-, di-, and trilithiated on the methyl group as evidenced by silylation [154]. Pseudo-first order rate constants for the monometalations were calculated.

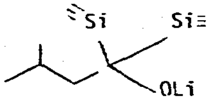
Several methyl ketones have been regiospecifically condensed on their methyl carbon atoms with aldehydes as illustrated by the conversion of 125 to 126 [155]. The success of the method is ascribed to effecting the metalations by bulky bases like 127 in the presence of the aldehyde co-reagent. Similar bases have been employed to prepare β-hydroxyesters from esters [156].



125

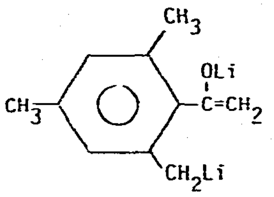


126

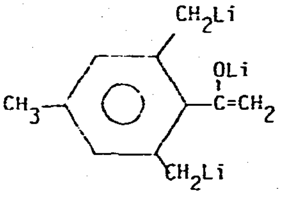


127

Several ring mono- and trimethylacetophenone lithium enolates have been further metalated by n-butyllithium/TMEDA in hexane to give species like 128 and 129 [157]. It was established that o-methyl-hydrogens and o-hydrogens are ionized in preference to p-methyl-hydrogens, probably because of chelation effects. An additional α-hydrogen may also be abstracted leading to the formation of an acetylene via elimination of lithium oxide.

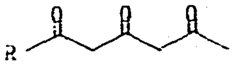


128

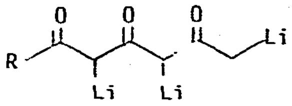


129

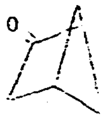
A full paper has appeared describing the conversion of triketones like 130 to their trilithio salts 131 by LDIPA in THF [158]. Previous attempts to prepare such trianions using alkali metal amides failed because these reagents are too weakly basic.



130



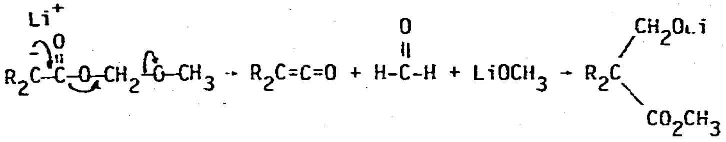
131



132

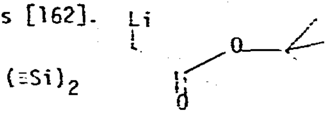
A similar base, lithium cyclohexyisopropylamide, was found necessary to effect ionization of 132 [159].

Lithium enolates from methoxymethyl esters like 133, though stable at -78°, fragment as indicated at 25° and recombine to afford hydracrylic esters like 134 [160]. Glycidic esters may be prepared similarly by metalation of α-bromomethoxymethyl esters.

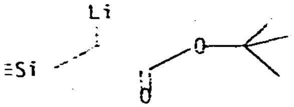


133 134

Lithio-t-butyl bis(trimethylsilyl)acetate (135) has been obtained by metalation of the parent silylester by LDIPA and condensed with a variety of aldehydes to give α-silylated vinyl esters [161]. The latter esters have been shown to be Michael acceptors. Lithio-t-butyl trimethylsilylacetate (136), prepared similarly, reacts with aldehydes and ketones to yield α,β-unsaturated esters [162].

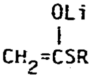


135

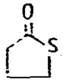


136

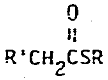
Lithium thio ester enolates like 137 and γ-thiolbutyrolactone (138) have been found capable of undergoing alkylation to afford thiol esters like 139 [163]. The enolates are generated by metalation of the parent thio ester by LDIPA at -78°. Lithiolactone 138 has also been condensed with formaldehyde as part of the preparation of α-methylene-γ-thiobutyrolactone [164].


$CH_2{=}\overset{OLi}{\overset{|}{C}}SR$

137

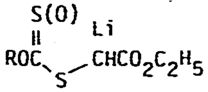


138

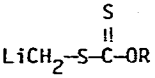

$R'CH_2\overset{O}{\overset{\|}{C}}SR$

139

Certain thio esters continue to be metalated alpha to sulfur by LDIPA. For example, the resulting organolithiums 140 and 141 have been condensed with aldehydes and ketones to afford α,β-unsaturated esters [165] and chiral thiiranes [166], respectively.

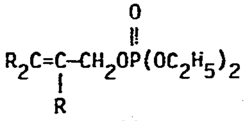

$RO\overset{S(O)}{\overset{\|}{C}}{-}S{-}\overset{Li}{C}HCO_2C_2H_5$

140

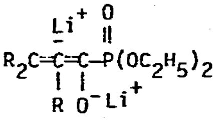

$LiCH_2{-}S{-}\overset{S}{\overset{\|}{C}}{-}OR$

141

A variety of phosphate esters and phosphoramides like 142 have been dimetalated by n-butyllithium to give intermediates like 143 [167]. Condensations of 143 with aldehydes yields lactones.

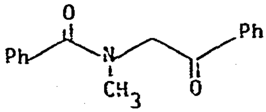

$R_2C{=}\underset{R}{\underset{|}{C}}{-}CH_2O\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$

142


$R_2C{=}\underset{R}{\underset{|}{\overset{Li^+}{\overset{-}{C}}}}{=}\underset{O^-Li^+}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$

143

Interaction of N,N-dimethylbenzamide with LiTMP to afford 144 proceeds via the dipole stabilized 145 [168]. The latter organolithium reagent may arise from metalation of the methyl group syn to the carbonyl oxygen. Though other examples of similar carbanions are described, a related reaction on N,N-diethylbenzamide results only in ring metalation ortho to the carboxamide functional group. In a different paper, the metalation of N,N-dimethylthiopivalamide by s-butyllithium to afford 146 is discussed [169]. That 146 is apparently more stable than 145 is evidenced by its sufficient life-time to be condensed with alkyl halides, aldehydes, ketones, and DMF. Such condensations represent nucleophilic aminoalkylation.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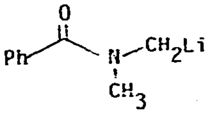
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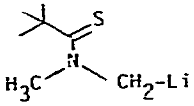
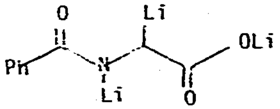

146

Hippuric acid has been converted to its trilithio salt 147 by LDIPA/TMEDA and then alkylated to give 148 [170]. Dilithio salts 149 and 150 have been similarly prepared and condensed with alkyl halides [170,171].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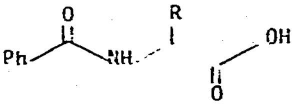
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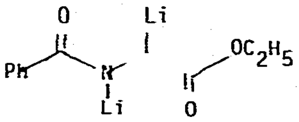
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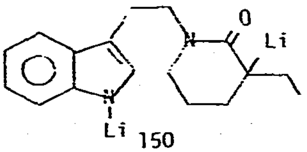
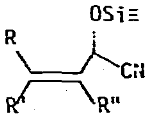

150

Metalation of 151 with LDIPA has yielded 152 [172]. Subsequent reaction of 152 with a large number of alkylating agents gave α,β-unsaturated ketones in excellent yields. Similar metalation of acrolein cyanohydrin has been employed as part of the synthesis of species like 153 [173].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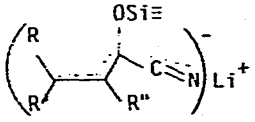
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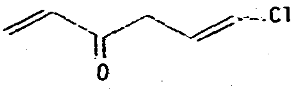
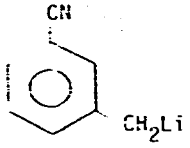
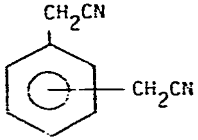

153

m-Tolunitrile has been metalated for the first time using LDIPA to afford 154 [174]. Condensations with ketones and alkyl halides are described. In a different study, the three isomeric bis(cyanomethyl)benzenes 155 have been reacted with various amounts of methyllithium and methyl iodide to give products arising from multimethylation [175].

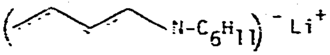


154



155

Several papers disclosed additional examples of the metalation of imines with bases such as LDIPA, lithium/diethylamine in benzene/HMPA, and lithium diethylamide. Such metalated amines like 156 and 157 have been alkylated by alkyl halides [176], α-bromoacetals and ketals [177], dihaloalkanes [178], dihaloalkenes [179], epoxides [180], and chlorotrimethylsilane [181]. A bis-imine has also been metalated by methyllithium to give 158 which has been C- or N-alkylated as a function of the cation and solvent [182].



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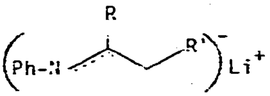

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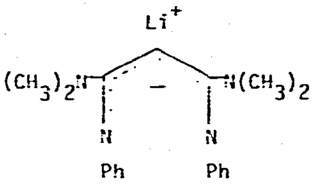
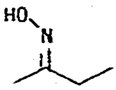


158

In the area of oximes, the position of α-metalation has been shown to be governed by the configuration of the oxime as evidenced by subsequent alkylation and condensations with aldehydes and ketones [183] and by deuteration [184]. Thus 159 and 160 afford 161 and 162, respectively. In the case of oximes from cyclic ketones like cyclohexanone and their O-methyl ethers, alkylation by methy iodide occurred to give the axially substituted product [185,186]. Such dilithio oximes have also been condensed with aroyl chlorides to give 4-acylisoxazoles [187] and with aldehydes and ketones to yield 2-isoxazolines [188]. Several lithiated oximes also underwent addition of organolithiums to afford, after work up, hydroxylamines like 163 [189].



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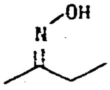

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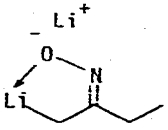

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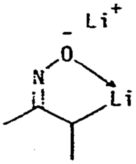

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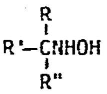
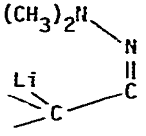


163

A large number of N,N-dimethylhydrazones of enolizable aldehydes and ketones have been regiospecifically metalated by LDIPA to give species like 164 [190,191,192] and 165 [193]. Reagents 164 and 165 have been reacted with a variety of electrophiles to afford alkylated derivatives [190,193], α,β-unsaturated aldehydes [191], β-hydroxycarbonyl, γ-hydroxycarbonyl, 1,4- and 1,5-dicarbonyl compounds, other polyfunctional compounds [192], and α-thiomethyl compounds [194]. The use of chiral 165 in alkylation reactions gave, after hydrolysis, chiral ketones [193].



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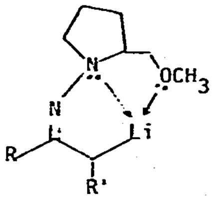
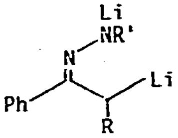


165

Several other phenylhydrazones, N-benzoylhydrazones, and N-p-tosylhydrazones have similarly been converted to dilithio species like 166 [195,196] while certain hydrazones have been metalated to give trilithio reagents like 167 [197]. All of these reagents have been condensed with electrophiles.



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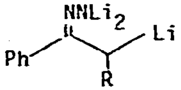
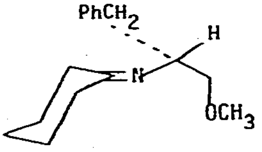


167

Metalation of chiral 168 affords chiral lithioenamine 169 which has been alkylated by several alkyl halides and dimethyl sulfate to give, after hydrolysis, optically active ketones [198]. In a different paper, metalation of pyrrolidine enamines from certain indanones and a cyclopentenone were effected by n-butyllithium [199]. The results obtained from subsequent methylation reactions are presented.



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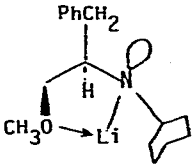
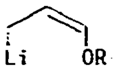


169

Allyloxy carbanions like 170 continued to be prepared by metalation of allyl ethers by s-butyllithium [200,201,202]. Condensation of 170 (R = $Si(CH_3)_3$) with aldehydes and cyclic ketones gave mostly α-type products like 171 [200]. Internal cyclization reactions of 170 have been observed when R contains epoxy or chloro substituents [201]. In the case of the related pentadienyl lithium 172, condensations with a variety of electrophiles usually afforded mostly γ-substituted products like 173 [202].



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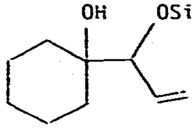

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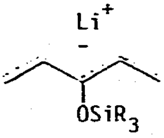

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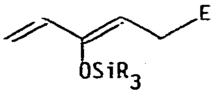
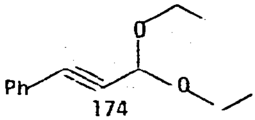
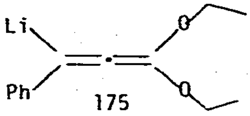


173

Metalation of propargylic acetal 174 by n-butyllithium/TMEDA gives a carbanion which reacts with alkylating agents as if it were exclusively 175 [203]. Hydrolysis of the resulting ketone acetals yields α,β-unsaturated esters.

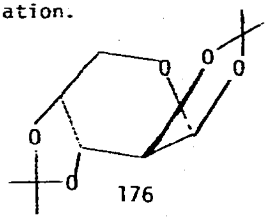


174



175

Certain O-isopropylidene derivatives of D-arabinose and D-fructose have been reacted with n-butyllithium to cause the elimination of acetone [204]. The process, illustrated by the conversion of 176 to 177, apparently involves ring metalation.



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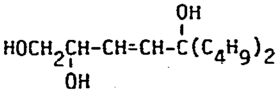
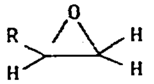


$HOCH_2\underset{OH}{CH}-CH=CH-\overset{OH}{C}(C_4H_9)_2$

177

Lithiation of 178 and phenylated derivatives where R is a silyl, phosphinyl, phenylsulfonyl, ethoxycarbonyl, and cyano stereospecifically affords 1,2-epoxyalkyllithium reagents 179 [205,206]. Such reagents have been condensed with a variety of electrophiles.



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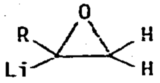
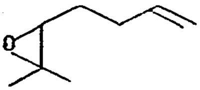


179

Choice of solvent has been found to be very important in the interaction of lithium diethylamide with γ,δ-unsaturated epoxides [207]. For example, 180 gives 181 and 182 in ether and HMPA, respectively.



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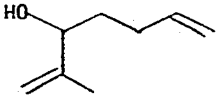
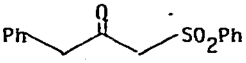


181

182

β-Ketosulfone 183 has been converted to its corresponding dilithio salt by LDIPA, then alkylated by 1,3-dibromopropane [208]. Subsequent cyclizations via either C- or O-alkylation are described. Dilithio salts 184 and 185 have similarly been prepared from the corresponding sulfinyl- and sulfonylpropionic acids, then condensed with cyclopentanone to afford γ-lactones [209].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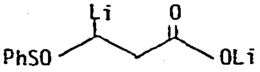
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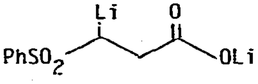
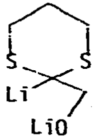

185

Other sulfur-containing organolithium reagents prepared by metalation of the parent compounds have been 186 used in the synthesis of pillarose [210], 187 used to prepare monothioglycols [211], and acyl anion equivalent 188 where Z = PhS or Ph_2PO used in the synthesis of certain ketones [212].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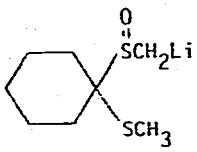
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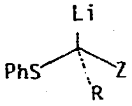
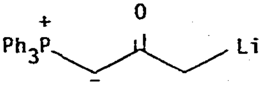

188

A full paper describing the preparation and reactions of ylide anion 189 has appeared [213]. Species 189, prepared by metalation of ylide 190 with n-butyllithium, was condensed with a variety of electrophiles in synthetically useful reactions.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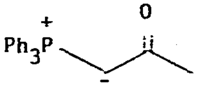
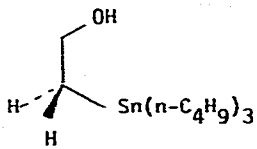

190

Hydroxytin reagent 191 has possibly been converted to dianion 192 by n-butyllithium as evidenced by reactions with alkyl halides and carbonyl-containing compounds to afford 193 [214]. A full paper appeared which discussed the conversion of α-vinylbenzyl alcohol to a dilithio salt [215].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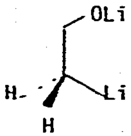
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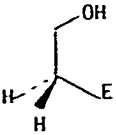
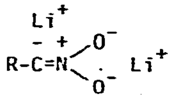
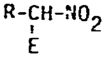

193

A variety of nitroalkanes have been doubly metalated by n-butyllithium to afford species like 194 [216]. Such reagents were condensed at carbon with electrophiles to give 195.

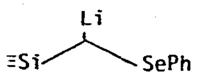


194



$R\text{-}\underset{E}{CH}\text{-}NO_2$

195

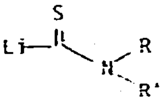


196

Finally, organolithium reagent 196, prepared by metalation of the parent compound by LDIPA, has been alkylated then oxidized to aldehydes [217]. Compound 196 is thus synthetically equivalent to a formyl carbanion.

B. AT sp^2 CARBON AND AT NITROGEN

Three papers described metalation of the sp^2-hydrogen atom of formamide derivatives to give unmasked acyl carbanions. Thus, treatment of a large number of formamides (R and R' = alkyl, aryl) with LDIPA at -100° afforded 197 which was condensed with a variety of electrophiles to yield species like 198 [218]. Organolithiums 199 (R = CH_2OCH_3 and CH_3) [219] and 200 [220] were similarly obtained and reacted with aldehydes and ketones.



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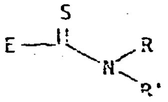

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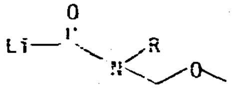

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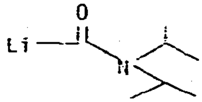
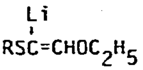


200

Compounds like 201 (R = Ph, n-C_5H_{11}) which contain both alkyl (or aryl) thio and alkoxy groups have been studied to determine the site of vinylic metalation by t-butyllithium [221]. That such reactions occurred regiospecifically alpha to sulfur to give 202 was demonstrated by condensations with electrophiles to afford 203. In another study involving a comparison of the rates of metalation of ene-sulfides versus ene-ethers, the former compounds were metalated faster than the latter ones [222]. Vinyl rather than allyl metalation predominated with such ene-sulfides.

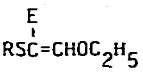
$RSCH{=}CHOC_2H_5$

201



$RS\overset{Li}{C}{=}CHOC_2H_5$

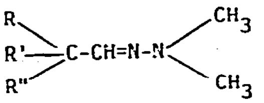
202



$RS\overset{E}{C}{=}CHOC_2H_5$

203

In contrast to References 190-194, interaction of branched N,N-dimethylhydrazones like 204 with lithium in diethylamine/benzene/HMPA affords nitriles presumably via vinyllithium reagent 205 [223]. The product nitriles from such eliminations with α-hydrogens underwent in situ metalation as evidenced by condensations with alkyl halides, aldehydes, ketones, and epoxides [224].



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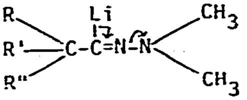
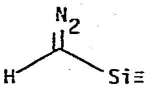


205

Diazo compound 206 has been metalated by n-butyllithium at -100° to give 207 [225]. This lithiated species has been reacted with benzaldehyde and ketones to afford 208 (65-80%) which has then been converted to epoxides and aldehydes.



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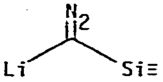

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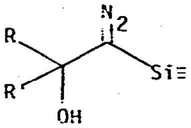
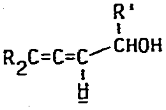


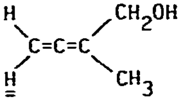
208

The underlined allenic hydrogen atoms in compounds 209-212 have been metalated by n-butyllithium and subsequently replaced by alkyl groups [226,227].



$R_2C{=}C{=}\underset{\underline{H}}{C}-\overset{R'}{C}HOH$

209



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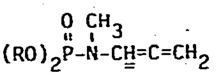
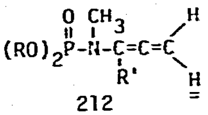


$(RO)_2\overset{O}{P}-\overset{CH_3}{N}-C\underline{H}{=}C{=}CH_2$

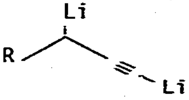
211



$(RO)_2\overset{O}{P}-\overset{CH_3}{N}-\underset{R'}{C}{=}C{=}\overset{H}{\underset{\underline{H}}{C}}$

212

Terminal acetylenes with propargylic hydrogen atoms have been dimetalated with n-butyllithium to give 213 which reacts regiospecifically with alkyl halides to afford 214 [228]. Such alkylations are followed by reactions with other electrophiles at the terminal carbanion to yield 215. Other acetylenic carbon-lithium systems have been condensed with cuprous chloride and acetic acid-O-d to give octamethylcyclododeca-1,3,7,9-tetrayne [229] and monodeuterioacetylene [230], respectively.



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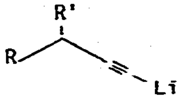
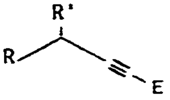


214

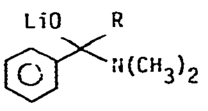


215

Turning to aromatic compounds, a large number of p-substituted anisoles were metalated by n-butyllithium to ascertain a ranking of ortho-directing substituents [231]. The following order has been established: $-SO_2N(CH_3)_2$, $-SO_2NHCH_3$, $-CONHCH_3$, $-CH_2N(CH_3)_2 > -OCH_3 > -CH_2CH_2N(CH_3)_2$, $-NME_2$, $-CF_3$, F.

Similar results were established for several o- and m-substituted anisoles. The effect of TMEDA in such directed metalations was studied.

A regiospecific route to o-substituted aryl ketones has been effected by adding organolithium reagents across the carbonyl group of N,N-dimethylbenzamides, o-metalating with n-butyllithium, condensing with various electrophiles, and hydrolyzing [232]. The method is illustrated by 216, 217, and 218. Thiobenzamides have also been o-metalated and condensed with electrophiles to afford 219 [233].



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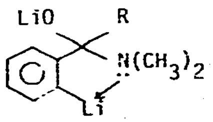

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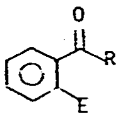

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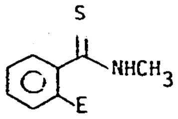
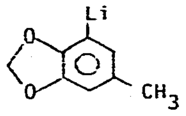


219

Metalation of several parent methylenedioxy compounds by n-butyllithium has been shown to give 220 [234], 221 [234], and 222 [235], respectively. Organolithium reagent 223, prepared from metal halogen exchange of the corresponding bromo compound at -78°, isomerized to 222 at ambient temperature [235]. All of these lithiated species were condensed with electrophiles.



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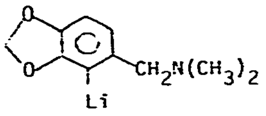

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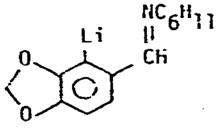

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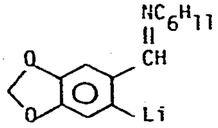
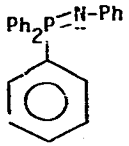


223

The site of regiospecific directed metalations of thiophenes substituted with dimethylaminomethyl, methoxymethyl, and carboxamides was shown to be a function of the ring position of the substituents [236]. Thus, 2- and 3-substituted thiophenes were lithiated in the 5- and 2-positions, respectively; 2,5-disubstituted systems were metalated only at the 3-position. Such intermediates were condensed with electrophiles.

Other directed metalations have been effected on imides like 224 to give 225 [237], methoxymethylferrocene [238], and ferrocene 226 to give 227 [239].



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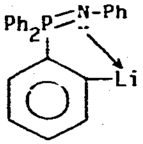

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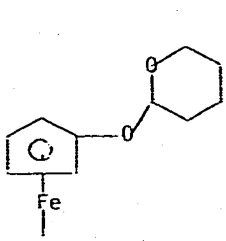

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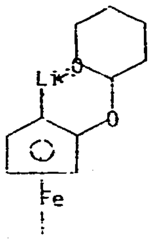


227

In other work dealing with metalation of aromatics, benzyne has been produced by reaction of phenyl benzenesulfonate with LiTMP [240] and lithiation of 1-methyl-5-methoxyindole with n-butyllithium has been found to be nonselective giving three different organolithium intermediates [241]. Also, cross-linked polystyrene has been ring lithiated with n-butyllithium-TMEDA [242-244] and chromium species 228 has been converted to 229 (G = Si≡, CO_2Li, others) by metalation with t-butyllithium followed by condensations with electrophiles [245].

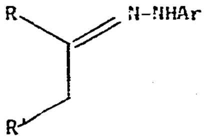
$(Ph)Cr(C_6F_5H)$

228

$(Ph)Cr(C_6F_5G)$

229

Metalation of arylsulfonylhydrazones like 230 by organolithium reagents to give vinyllithium reagents like 231 continues to be studied. Condensations of 231 to afford 232 have been realized with dimethylformamide [246], carbon dioxide, aldehydes, ketones, and alkyl halides [247], and chlorotrimethylsilane [248].



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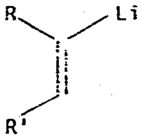

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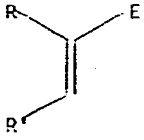
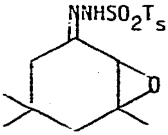


232

α-Epoxytosylhydrazones like 233 have been treated with n-butyllithium and phenylcopper to give 234, apparently via ring-opened intermediate 235 [249]. Other examples are cited.



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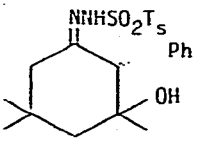

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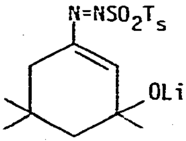
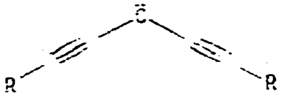


235

Other related tosylhydrazone chemistry has been concerned with the stereochemistry of this functional group and its relation to the regiospecificity of olefin formation [250], the use of this reaction in the preparation of 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene from α-pinene [251], pyrolyses to possibly afford diethynylcarbene 236 [252] and to study stereoelectronic control of migration [253] and as part of a test for bridge-bending [254], and in a study involving the conversion of 237 to 238 [255].



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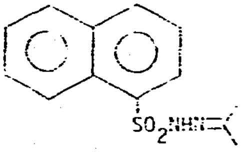

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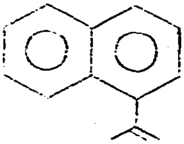
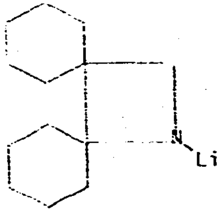


238

Two other nitrogen-containing species, 239 [256] and 240 [257], have also been prepared by metalation. Reagent 239 is a hydride donor and reduces nonenolizable ketones to alkoxides while dianion 240 decomposes at 170-200° to give carbodiimides.



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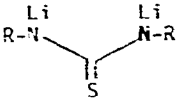
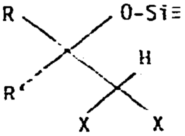


240

5. LITHIUM CARBENOIDS AND OTHER HALOGEN-SUBSTITUTED ORGANOLITHIUMS

Lithium dichloro- and dibromomethide have been added to ketones and the resulting alkoxides silylated to give 241 [258]. Subsequent treatment with n-butyllithium (X = Cl) or LDIPA (X = Br) provides a convenient route to 1,1-dihaloalkenes like 242. Carbenoids like 243 and 244 have also been condensed with ketones and aldehydes to afford 242 (X = Br) [259] and vinyl sulfides 245 [260], respectively. Lithium dibromomethide has been employed as part of the synthesis of an unusual $(CH)_{12}$ hydrocarbon [261].



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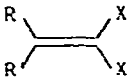

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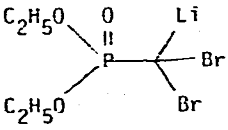

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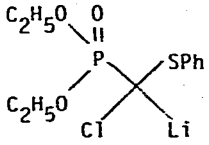

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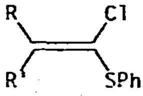
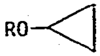


245

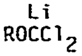
A variety of cyclopropanol derivatives 246 have been prepared via carbenoids [262-264]. Thus, treatment of 247 where R = alkyls [262], esters and amides [263], and 2-chloroethyl [264] with LiTMP gave 248 which were condensed with large numbers of alkenes and acetylenes to afford 246.



246

$ROCHCL_2$

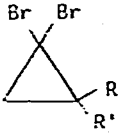
247



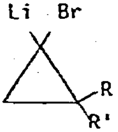
$ROC(Li)Cl_2$

248

In the area of cyclopropyl carbenoids, 249 (R = vinyl or diethoxymethyl, R' = H) has been converted to 250 by t-butyllithium, then alkylated or hydrolyzed to give 251 [265]. The preparation of copper reagents from 251 is discussed. In a related study, 249 (R = methyl, R' = $COCH_3$) was converted to 252 by methyllithium via nucleophilic addition to the carbonyl and halogen-metal exchange [266]. Other examples of this stereospecific synthesis of α-bromocyclopropyl alcohols are cited.



249



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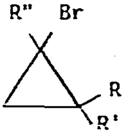

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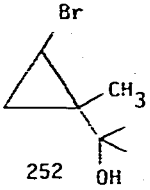
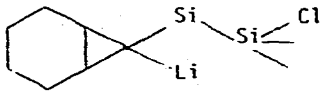


252

Carbenoids containing endo-lithium-exo-halogen have similarly been prepared from 8,8-dibromo- and 8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane [267, 268], 9,9-dibromo-cis-bicyclo[6.1.0]nonanes [269] and nonenes [270], and geminal dibromocyclopropanes annelated to six-, seven-, and eight-membered rings [271]. Some of the above species were condensed with electrophiles while others were thermolized or converted to allenes.

Organolithium 253 has been generated from the corresponding bromolithium reagent and a dichlorodisilane followed by metal-halogen exchange with n-butyllithium [272]. Cyclization of 253 led to 1,2-disilacyclopropane 254. Other cyclizations have been realized on bis(silyl) system 255 with dimethyldihalo derivatives of silicon, germanium, and tin to afford 256 [273].



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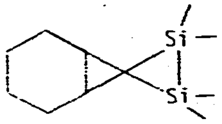
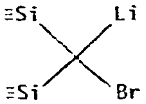


254



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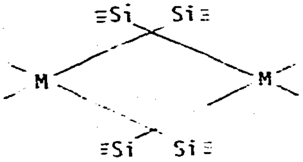
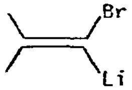


256
(M = Si,Ge,Sn)



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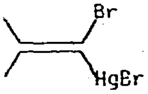


258

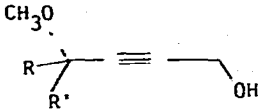
Finally, lithium dichloromethide has been condensed with trimethylborate to give dichloromethaneboronic acid [274], and vinyl system 257 has been converted to 258 by mercuric bromide [275]. Mercury reagent 258 has been shown to be useful in transferring isopropylidene carbene to olefins.

6. ADDITION AND SUBSTITUTION REACTIONS

A simpler method than double titration has been suggested for the standardization of alkyllithium solutions [276]. The procedure involves addition through a syringe of butyl- or methyllithium to a weighed amount of diphenylacetic acid in THF until the yellow end point due to dilithiodiphenylacetate is reached.

In the area of aliphatic and aromatic organolithiums, an efficient dilithium initiator soluble in benzene or heptane has been achieved by adding two equivalents of n-butyllithium to one equivalent of m-divinylbenzene [277]. The initiator has been employed in the polymerization of styrene and isoprene.

Alkoxypropargylic alcohols 259 have been found to react with n-butyllithium to give allenic alcohols 269 [278]. Similar additions of butyl- and benzyllithium to 261 and subsequent hydrolyses to allyl alcohols are discussed.



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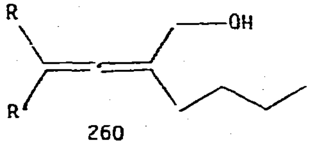

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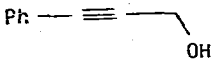
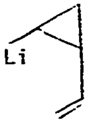


261

Both cis- and trans-lithiocyclopropanes 262 have been added to alkoxycycloalkenones such as 263 to give vinylcyclopropanes such as 264 [279]. Functionalized cycloheptanes are then obtained by heating 264.



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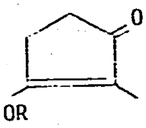

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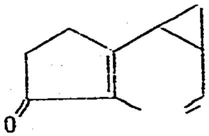
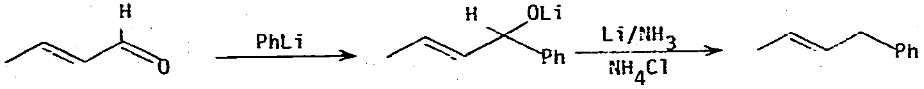


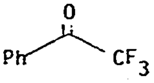
264

Tandem phenylation by phenyllithium-reduction by lithium/ammonia has been further investigated as a method of converting α,β-unsaturated aldehydes and ketones to β,γ-unsaturated aromatic hydrocarbons [280]. The process is illustrated by the sequence 265 → 266 → 267.



265 266 267

Phenyllithium and related reagents have been added to perfluoroanhydrides to afford ketones like 268 and esters like 269 [281]. They have also been added to α,β-butenolides to give allylic alcohols like 270 [282], reacted with certain sulfonate esters at sulfur to yield sulfones [283], combined with carboxylic acids to afford ketones and carbinols [284], and added to an aminoketone as part of the synthesis ofdibenz[b,f,l]azapentalenes [285].



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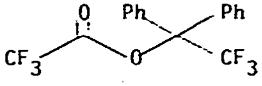

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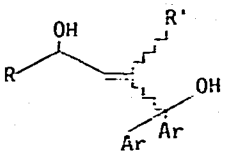
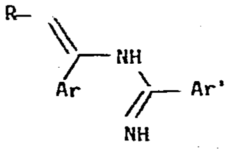


270

Enamidines 271 have been obtained by addition of butyl- and methyllithium across the nitrile triple bond of arylnitriles [286]. Such reactions proceed via the intermediacy of 272 and 273. In a different paper, ketones were synthesized from pyridyllithiums and non-enolizable nitriles [287].



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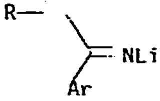

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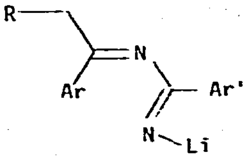
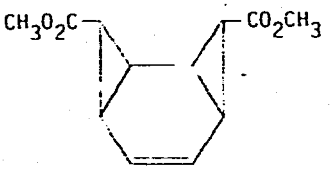


273

In contrast to earlier results, condensation of cyclooctatetraenedilithium with carbon dioxide and diazomethane has been shown to give tricyclic 274 and non-cyclic tetraene 275 [288].



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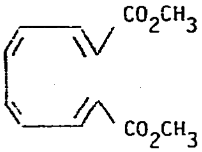
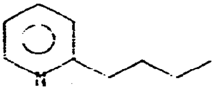


275

Interaction of pyridine with metal-free n-butyllithium in pentane has been reported to give 2-n-butylpyridine (276) but no 4-n-butylpyridine (277) [289]. In contrast, reaction between n-butyl chloride and lithium metal in pyridine gave mostly 277 and less than 1% of 276. The results are compared with those obtained with magnesium species. Derivative 277 might arise from 278.



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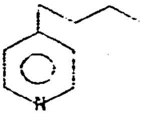

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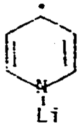
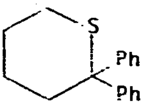


278

Cyclic thioethers like 279 and related ones have been found to undergo attack at sulfur by t-butyllithium to afford ring opened products like 280 [290]. The driving force for such reactions is ascribed to the stability of benzhydrylic carbanions like 281. Attack at sulfur by organolithiums has also been realized on thiete 282 and its 1,1-dioxide to give 283 and its related dioxide derivative, respectively [291], and at the alkylthio sulfur of phosphinodithioate esters like 284 to yield phosphine sulfides [292].



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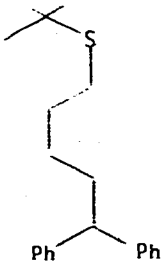

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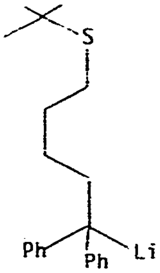

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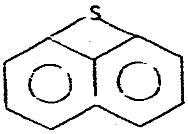

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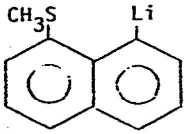

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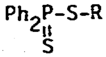
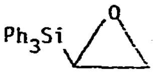


$Ph_2\underset{\underset{S}{\|}}{P}\text{-S-R}$

284

Epoxyethylsilanes like 285 have been treated with phenyllithium to give tetraphenylsilane and styrene [293]. Using deuterated analogues of 285, it was determined that the phenyllithium attacked the carbon alpha to silicon in a non-stereospecific manner. Similar chemistry on both cis- and trans-286 gave mostly trans-stilbene. The results are compared with those obtained using diisobutylaluminum and various amines.



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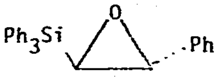
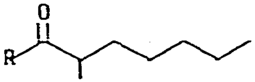


286

Addition of methyllithium to β-ketosilane 287 afforded an intermediate β-alkoxysilane which upon treatment with potassium t-butoxide or glacial acetic acid gave olefins 288 and 289, respectively [294]. The olefins arose from syn- and anti-elimination of hydroxy and trimethylsilyl, respectively.



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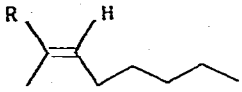

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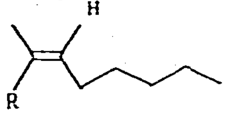
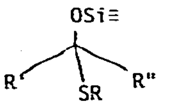


289

The course of reaction of O-trimethylsilyl hemithioacetals and ketals (290) with organolithiums (R'''Li) is a function of solvent [295]. Thus, 291 is obtained in THF or ether while 292 is formed in HMPA or TMEDA.



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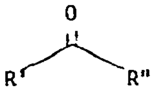

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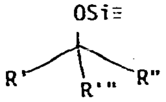
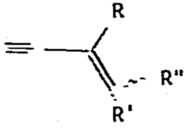


292

A variety of allyl- and saturated lithium reagents have been added to conjugated enynes 293 where R' = alkyl [296] and amino or hydroxyl groups [297]. The 1,2-addition products obtained such as 294 are in contrast to 3,4- and mixtures of 1,2- and 1,4-addition products realized with corresponding organozinc and magnesium reagents, respectively.



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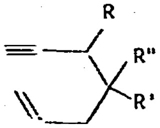
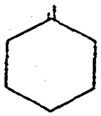


294

Condensation of dilithiobutadiene and other di- and triene dianions with α,ω-dihaloalkanes have been found to give cyclic products from initial alkylation at the most negatively charged carbon atom followed by secondary alkylation to afford the smallest ring possible [298]. For example, 295 is obtained from 296 and 1,3-dibromopropane. In other papers, pentadienyllithium 297 has been employed in the synthesis of monoterpenes [299], and cyclopentadienyllithium has been added to benzyne to give phenylcyclopentadiene rather than cycloaddition products [300].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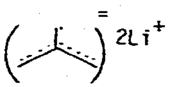

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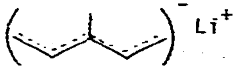
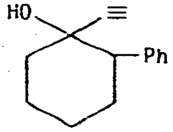


297

A variety of annulenes continue to be synthesized using lithium acetylides. Among those formed were 1,8-bisdehydro[14]annulenes [301], 6,8,15,17-tetrakisdehydro[18]annulenes [302-305], a 6,17,23-trisdehydro[22]biannulene [306], and a 2,4,13,15-tetrakisdehydro[22]annulene [307].

Carbonyl addition to 2-phenylcyclohexanone was found to be non-stereospecific with lithium acetylide giving a 1:1 mixture of the cis-trans alcohols 298 [308]. In contrast, similar additions of 299 and 300 were more stereospecific; for example, the latter reagent afforded the cis-alcohol with a threo-erythro ratio of 5:1.



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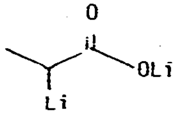

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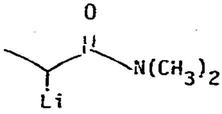
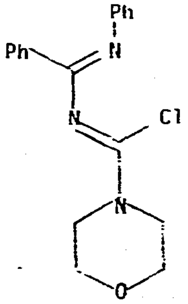
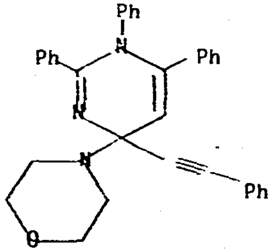


300

Lithium acetylides have also been condensed with chlorobenzamides like 301 to give pyrimidine derivatives like 302 [309], and with Group V trihalides to yield 303 (M = P, As, and Sb) [310]. Such organolithiums have also been employed in the synthesis of certain prostaglandins [311,312].



301

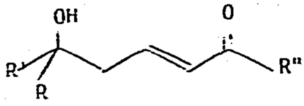


302

$M[C\equiv CCF_3]_3$

303

Turning to organolithiums stabilized by carbonyls and other electron withdrawing groups, vinylogous aldols like 304 have been synthesized using kinetic enolates derived from 305 and ketones [313]. Such reactions constitute the conversion of 306 to 304. Methyl ethyl and methyl propyl ketones have also been converted to their kinetic enolates by lithium diethylamide in HMPA/benzene/ether and then condensed with aldehydes and ketones to give β-hydroxyketones [314].



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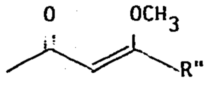

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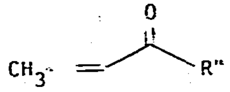
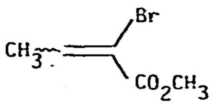


306

The enolates of several cyclohex-2-enones have been condensed with bi-annelating reagent 307 to afford tricyclo compounds 308 [315]. The lithium enolate of cycloocta-2,4,6-trienone (309) has been treated with alkyl halides to yield 310 via C-alkylation [316]. In contrast, reaction of 309 with acyl chlorides gave only O-acyl derivatives.



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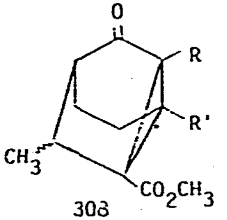

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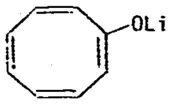

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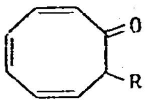
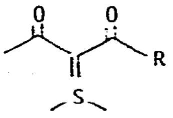


310

Sulfonium ylides 311 (R = CH_3, OC_2H_5) have been converted to 312 by n-butyllithium or LDIPA, then alkylated and acylated to yield 313 [317]. A variety of lithium enolates of aldehydes, ketones, esters, and carboxylic acids have been thiolated by certain disulfides, sulfur, and sulfenyl chlorides to afford 314 [318].



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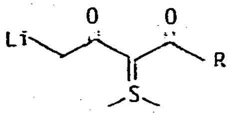

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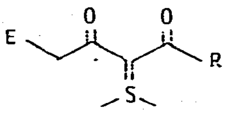
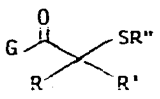


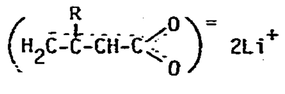
313



314

Ketone enolates have also been alkylated by methylene halides catalyzed by cuprous chloride [319], condensed with citraconic anhydride to give two butenolides [320], and used in the total synthesis of sativenediols [321].

The chemistry of dilithio salts of α,β-unsaturated acids continues to be studied. Thus, alkylation of salts illustrated by 315 afford more α- (316) than γ-products 317 [322,323]. In contrast, the use of lithium cuprates in such reactions gives only γ-products 317. Among the acids studied were 2-butynoic and 3-methylcrotonic acid [322], and 3-methyl-2-hexenoic, crotonic, senecioic, tiglic, and angelic acids [323].



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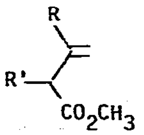

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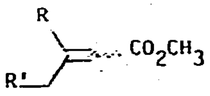
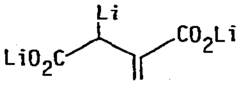


317

Trilithioitaconic acid (318) has been condensed with aldehydes and ketones to afford α-methylenelactones like 319 [324]. Dilithiopropiolic acid (320) has similarly been reacted with certain chiral epoxides to give optically active δ-n-hexadecalactone [325].



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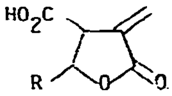

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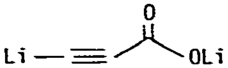
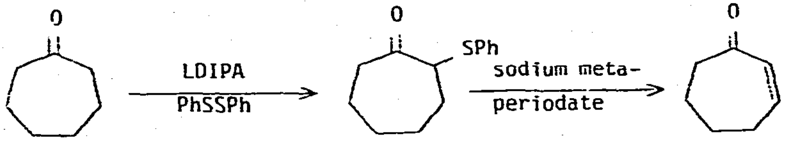


320

Related salts of acids have been oxygenated with molecular oxygen [326, 327], coupled with formaldehyde [328], and condensed with carbon disulfide [329]. Monoalkali carboxylate anions have been directly alkylated to yield esters [330].

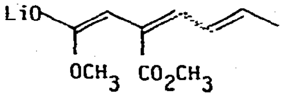
A full paper appeared describing sulfenylations and dehydrosulfenylations of esters and ketones [331]. The process is illustrated by the conversion of cycloheptanone (321) to enone 322.



321

322

Lithium enolates of alkylidene succinates (323) have been condensed with bromomalonate esters like 324 to give products like 325 [332]. The reactions occur by displacement of 323 on bromine to afford malonate anions which recombine by conjugate addition-elimination.



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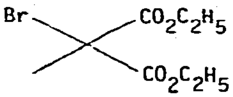

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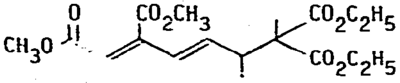
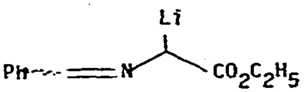


325

Benzylidene derivatives of glycine esters have been lithiated by LDIPA to yield 326 which can be alkylated to give 327 [333]. Simple hydrolysis of 327 to 328 thus finishes the overall conversion of "glycine" to higher α-amino acids. Potassium t-butoxide may be employed instead of LDIPA.



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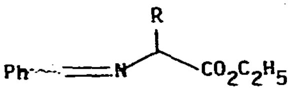

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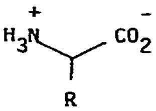
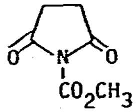


328

Several α-lithioesters and nitriles have been added to N-protected succinimides like 329 to yield polyfunctional products like 330 [334]. In other papers, ethyl lithiofarnesoate has been found to undergo α-hydroxylation with oxygen and α-thiomethylation with methyl methanethiosulfonate [335], and ethyl lithiodiazoacetate has been added to 331 to afford 332 [336].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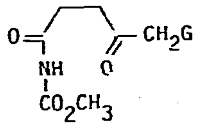
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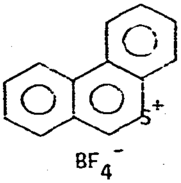
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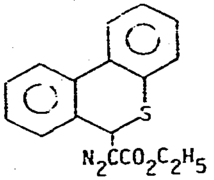
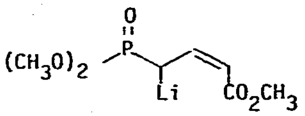

332

Organolithiums derived from phosphorus esters and amides have been employed as follows. Reagent 333 has been condensed with 310 (R = H) as part of the synthesis of a 1,5-methano[10]annulene system [337] and reagent 334 has been added to ketones as part of a new spiroannelation leading to quaternary carbon-containing cyclohexanones [338]. Diethyl-1-alkyl-2-oxoalkanephosphonates have been prepared by alkylation of 335 followed by acylation of a subsequently prepared α-copper reagent [339]. Finally, condensations of 336 with acetophenone have been found to be stereoselective and give different diastereoisomers of 337 depending upon the solvent and the presence or absence of lithium bromide [340].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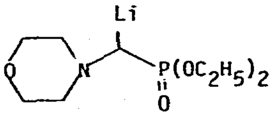
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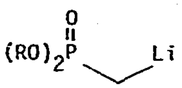
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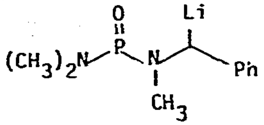
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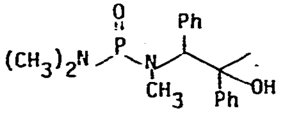
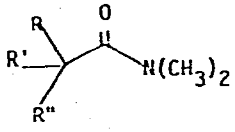

337

N,N-Disubstituted amides and N-substituted lactams have been α-lithiated by lithium dialkylamides in HMPA, then alkylated to afford species like 338 and 339, respectively [341]. Lithiolactams have also been sulfenylated and selenenylated to give products like 340 [342].



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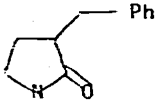

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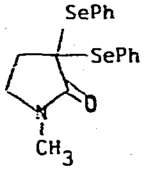
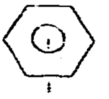


340

Reaction of lithioacetonitrile and related compounds with 341 has been proposed to yield intermediate 342 [343]. Some chemistry of 342 is discussed.



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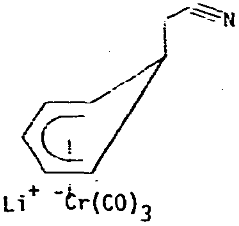
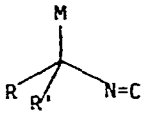


342

Other lithionitriles have been hydroxylated [344,345], alkylated [346,347], silylated [348], and employed in the synthesis of S-cuparenone [349].

α-Metalated isocyanides like 343 (M = Li,K) have been condensed with aldehydes and ketones to give intermediates 344 [350]. The latter compounds cyclize to 345, methanolysis of which yields 2-oxazolines. Both 344 and 345 have been trapped with electrophiles. In contrast, 345 is converted to 346 when M = K, R = hydrogen, and R' = pyridyl, ultimately affording formamides [351]. Species like 343 have also been condensed with epoxides to yield 3-amino alcohols [352] and with carbon disulfide to give 347 which, upon methylation, affords 348 [353].



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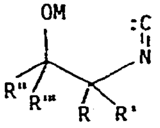

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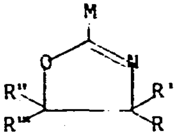

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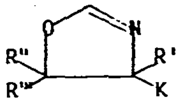

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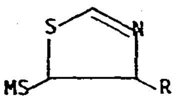

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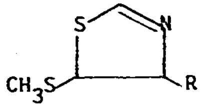
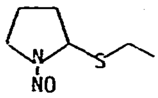


348

Under the topic of miscellaneous nitrogen compounds, synthetic details of the displacement of nitro groups of p-substituted nitrobenzenes by reagents like lithio-2-nitropropane in HMPA have been published [354]. α-Thioethyl-N-nitrosopyrrolidine (349) and 2,5-dialkyl-N-nitrosopyrrolidines have been synthesized from the lithio-N-nitroso compound and ethyl methoxycarbonyl disulfide [355] and alkyl halides [356], respectively. Finally, the wide variety of products arising from dilithio salt 350 and certain acid chlorides, chloroacid chlorides, and chloroesters has been described [357].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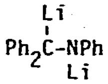
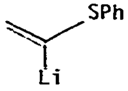

$\mathrm{Ph_2}\overset{\mathrm{Li}}{\mathrm{C}}\mathrm{-N}\underset{\mathrm{Li}}{\mathrm{Ph}}$

350

Turning to sulfur-stabilized organolithiums, phenyl vinyl sulfides have been conveniently metalated by LDIPA in THF-HMPA to give species like 351 which condense with aldehydes and ketones to afford 352 [358]. The latter compounds are useful in the synthesis of 1,4-diketones and cyclopentenones. Another paper describes the use of 353 for cyclopentanone formation in which the limitations of an earlier method such as low yields are overcome [359]. Phenylthiomethyllithium (354) [360], and bis(phenylthio) reagent 355 [361,362] have been used to prepare a precursor of vernolepin and α-phenylthioketones, respectively.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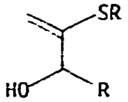
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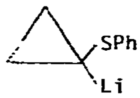
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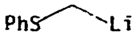
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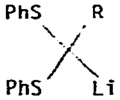
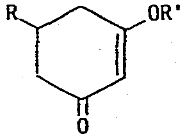

355

2-Lithio-1,3-dithianes have been conveniently alkylated with arenesulfonates of primary alcohols [363], added to 356 to give 357 [364], condensed with tropylium fluoroborate to afford 358 [365], and employed in the synthesis of fraudulent branched-chain sugars from certain ribofuranosides [366].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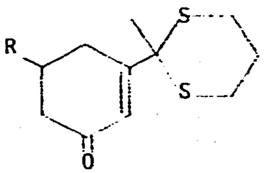
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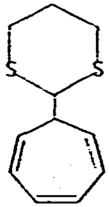
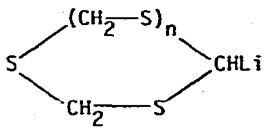
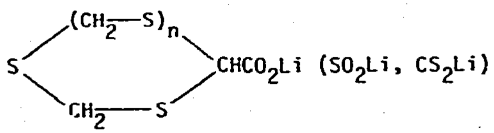
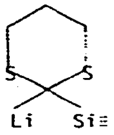

358

Monolithiated s-trithiane, tetrathiocane, and pentathiecane (359, n = 1, 2, and 3) have been condensed with carbon dioxide, sulfur dioxide, and carbon disulfide to give 360 [367].


359 (n = 1,2,3)


360 (n = 1,2,3)

Lithiodithiane 361 adds in a 1,2-fashion to 2-methoxyacrolein to afford 362, a compound which subsequently enters into Michael condensations and Diels-alder reactions [368]. Dithiane 361 also has been added to other aldehydes and ketones to give ketene thioacetals like 363 [369]. The latter compounds are conveniently converted into α-haloesters with NCS or NBS.



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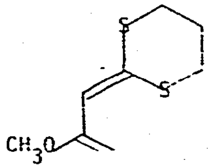

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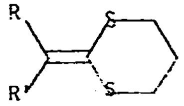
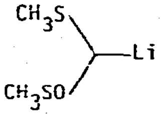


363

Interaction of 364 and 365 has been shown to afford (R)- and (S)-4-hydroxy-2-cyclopentenones [370]. Finally, tris(methylthio)methyllithium (366) has been employed in the synthesis of dl-protolichesterinic acid [371].



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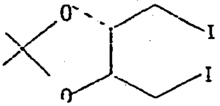

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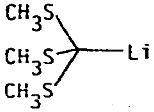
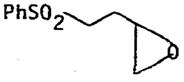


366

Lithiation of epoxysulfones like 367 leads to cyclopropyl derivatives like 368 [372,373]. Interestingly, metalation of 367 with methylmagnesium iodide instead of n-butyllithium or LDIPA affords cyclobutyl products like 369 [373]. Epoxynitriles behave similarly [373].



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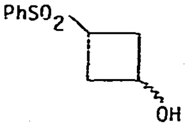
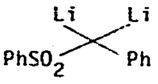
368



369

Additional chemistry of 1,1-dilithio systems 370 and 371 has been reported [374]. A variety of monolithiosulfones have been alkylated [375-378] and condensed with carbon disulfide [379] and with epoxides [380].

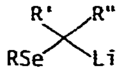


370

$Li_2CHSON(CH_3)_2$

371

α-Selenoalkyllithiums like 372 have been converted to α-selenoaldehydes 373 (G = H) by DMF, α-selenoketones 373 (G = R) by acid chlorides, α-selenoesters 373 (G = OCH_3) by methyl chloroformate, and to α-selenoacids 373 (G = OH) by carbon dioxide [381]. Similar treatment of 372 with α,β-unsaturated ketones ultimately affords α,β-unsaturated epoxides [382].



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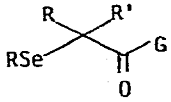
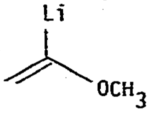


373

Methoxyvinyllithium (374) continues to be employed in synthesis as evidenced by its reaction with ketones and esters to give dihydroxyacetones [383] and 3-hydroxy-2,4-pentanediones [384], respectively. The related ethoxyvinyllithium (375) has been condensed with halosilanes to afford, after hydrolysis, the first stable acylsilanes like 376 [385].



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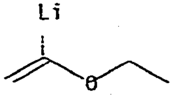

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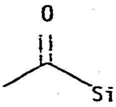
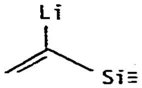


376

Lithiovinylsilane 377 has been condensed with aldehydes to give alcohols like 378 [386]. The latter compounds were converted to the corresponding chlorides and the stereochemistry of the reaction was studied. Lithiosilylesters 379 and amides 380, prepared by metalation, have been alkylated to give C- or S-alkylated products depending upon the electrophile employed [387].



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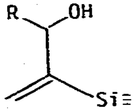

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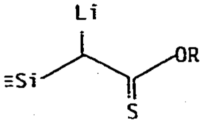

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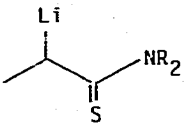
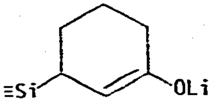


380

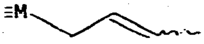
Dimethylphenylsilyllithium has been condensed with several epoxides to stereospecifically afford olefins [388]. The related trimethylsilyllithium has been added to cyclohexenones to yield 381 [389]. Subsequent chemistry of 381 is described. Lithium reagents 382 (M = Si,Ge,Sn, and Pb) have been coupled with crotyl chlorides to give 383 in which retention of the double bond configuration is observed [390].



381

R_3MLi

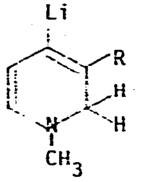
382



383

7. HETEROCYCLES

Several papers discussed certain aspects of dihydropyridines. Thus, a large number of N-substituted 1,2-, 1,4-, and 1,6-dihydropyridine and dihydronicotinic acid derivatives have been treated with LDIPA and potassium t-butoxide to determine the extent and position of metalation [391]. Although the pyridine derivatives gave little or no metalation, the dihydronicotinic acid compounds afforded vinyl organolithiums like 384-386 (R = carboxamides and CN) as evidenced by deuteration experiments.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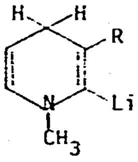
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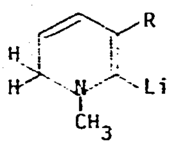
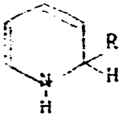

386

In contrast, N-unsubstituted 1,2-dihydropyridines like 387 have been N-lithiated and the ambident organometallics condensed with electrophiles to give 5-substituted pyridines like 388 [392]. Incidentally, a new synthesis of N-alkyl-1,2-dihydropyridines involves the conversion of 389 to 390 by methyllithium and heating the corresponding N-alkyl derivatives [393].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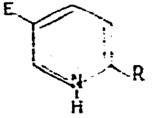
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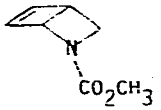
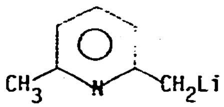

389


390

A full paper described a series of 1,5-diketones which have been synthesized by alkylation of 2-lithiomethyl-6-methylpyridine (391) followed by Birch reduction [394]. The direction of base-catalyzed aldol cyclization of such diketones is discussed. In another paper, 2,2-bipyridyl was treated with alkyl- and aryllithiums to afford either 392 or 393 as a function of the stoichiometry and temperature [395].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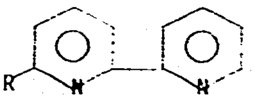
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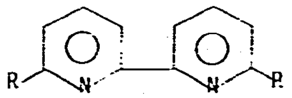
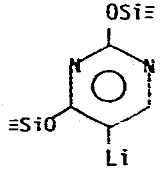

393

5-Lithiouracil derivative 394 has been found to rearrange apparently via an intramolecular process to 395 [396]. Although dilithioisocytosine 396 underwent a similar rearrangement, dilithiocytosine 397 was stable presumably because of the high electron density on nitrogen.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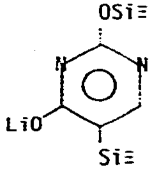
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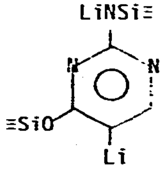
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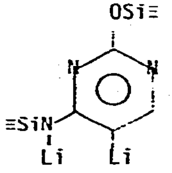
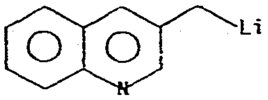

397

3-Methylquinoline has been metalated for the first time using LDIPA in THF-HMPA to afford 398 which was condensed with aldehydes, ketones, and alkyl halides to give 399 [397]. Similar treatment of cycloalkenoisoquinolines 400 yielded mostly metalation products 401 and little or no addition products 402 when n = 5,6 [398]. In contrast, large amounts of 402 were realized when n = 7,8.



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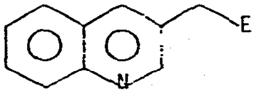

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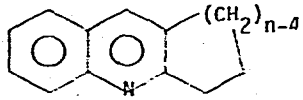

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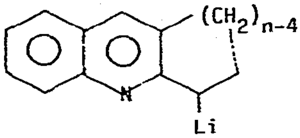

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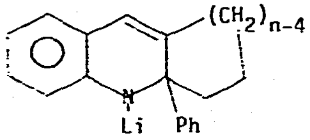
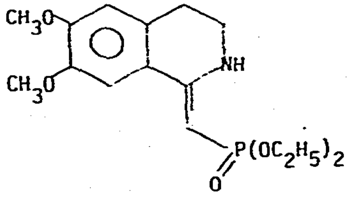


402

Tetrahydroisoquinoline 403 has been metalated by n-butyllithium, then alkylated to give 404 [399]. Metalation of either 403 or 404 by sodium hydride followed by condensation with aldehydes and ketones afforded 405.



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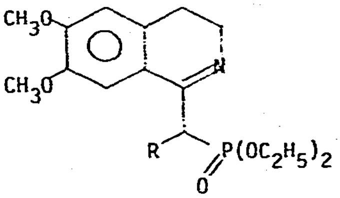

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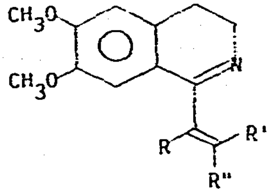
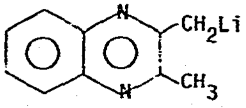


405

Either monolithio (406) or dilithio (407) salts of 2,3-dimethylquinoxaline may be prepared by treatment of the parent dimethylated heterocycle with one or two equivalents of LDIPA in THF/HMPA [400]. Subsequent condensations with electrophiles afford a variety of 2,3-substituted quinoxalines.



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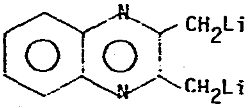
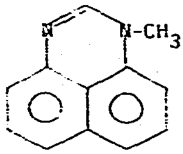


407

Perimidines like 408 react with alkyl and aryllithium reagents to give mostly products like 409 which arise by addition of RLi across the C=N linkage [401]. In one case, ring lithiation occurred to afford 410 in low yield.



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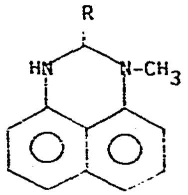

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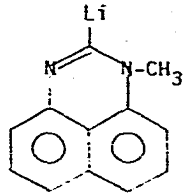
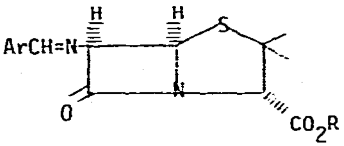


410

An unsuccessful attempt to convert 411 to 412 via 413 by means of strong bases like phenyllithium has been reported [402]. Instead of obtaining the desired 412, mostly 411 was recovered despite quenching by D_2O-CD_3CO_2D.



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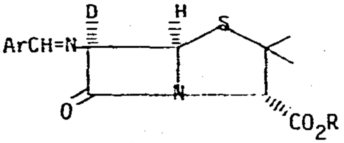

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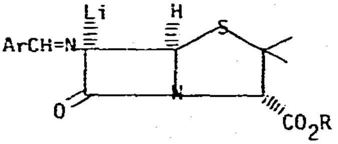
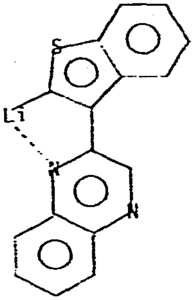


413

Additional examples of heterocyclotetraaromatics have been described [403]. Thus, 414, prepared by metalation, cyclizes to 415 with or without copper(II) salts though the yield is higher in their presence. The related non-benzo system was also cyclized by copper(II) fluoride.



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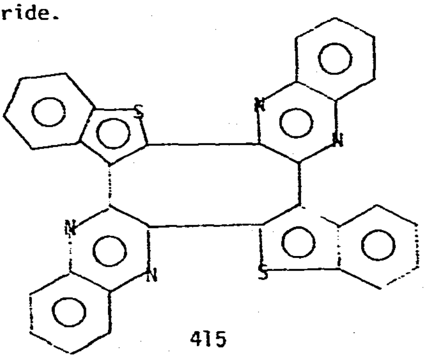
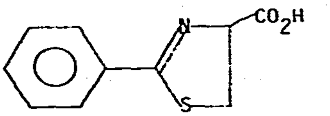


415

4,5-Dihydro-1,3-thiazoli-4-carboxylic acid (416) has been dimetalated by n-butyllithium, but not LDIPA, to give 417 [404]. Subsequent condensations with various electrophiles to give α-substituted products are described.



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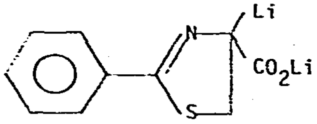
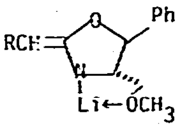


417

Lithiated oxazolines continued to be extensively investigated in 1976. Thus, a full paper described the alkylation of chiral system 418 to give 419, hydrolysis of which affords S-α-alkylalkanoic acids 420 in enantiomeric purity of 45-85% [405]. Interestingly, sequential two-fold metalation and two-fold alkylation of 418 (R = H) gives either (R)- or (S)- acids depending upon the order of introduction of alkyl groups. For example, methylation-butylation yields (S)-(+)-420 while butylation-methylation affords (R)-(-)-420. Such stereoselectivity is ascribed to an underside entry of the alkylating agent to 418 via initial halide-lithium cation complexation.



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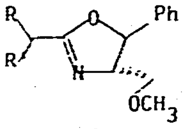
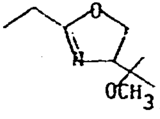


419

420

Lithiooxazoline 418 (R = H) has been found to be capable of chiral recognition towards racemic alkyl halides [406]. Thus, racemic secondary alkyl bromides and iodides are kinetically resolved by 418 to give unreacted alkyl halides enriched in the R enantiomer and oxazolines 419 which, upon hydrolysis, afford 3-alkylalkanoic acids (420) likewise enriched in the R enantiomer. The procedure allows the establishment of absolute configurations of secondary alkyl halides and 420 using only 418.

Chiral oxazolines 421 and 422 have been derived from L-serine to determine if they might also serve as suitable precursors to optically acid acids [407,408]. Butylation of 421 followed by hydrolysis gave (S)-(+)-2-methylhexanoic acid (420) though the authors predicted the acid should have possessed the R configuration [407]. Conversion of 422 to 423 followed by conjugate addition of n-butyllithium and hydrolysis gave (S)-(+)-424 [408]. The latter technique of conjugate addition-hydrolysis has also been employed on methoxy-containing systems like 425 to yield methoxyacids like 426 and their lactones [409].



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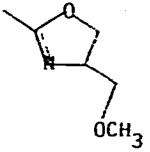

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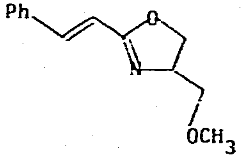

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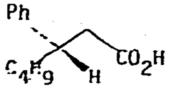

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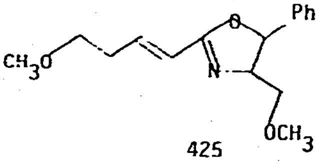

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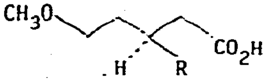
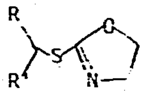


426

Related oxazoline chemistry included the conversion of 427 to thiiranes 428 via 429 [410] and the autoxidation of 430 by molecular oxygen to the corresponding 2-benzoyl derivative [411]. 2-Isoxazolines have also been metalated by LDIPA to afford 431 and 432; the former compounds fragment to α,β-unsaturated oximes [412].



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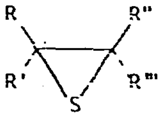

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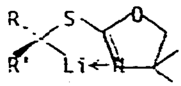

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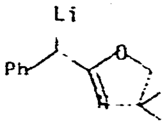

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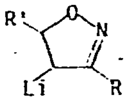

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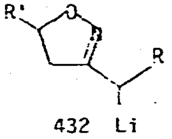
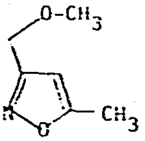


432

Metalation of isoxazoles 433 and 434 by n-butyllithium yielded both ring- (436) and methyl group (435) lithiation [413]. In contrast, the use of LDIPA on these systems gave only 435.



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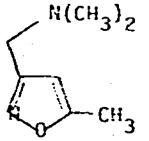

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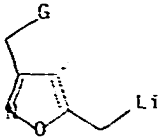

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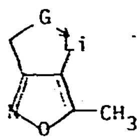
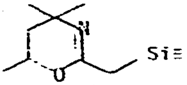


436

Oxazine derivatives 437 and 438 have been found to react with unsymmetrical ketones and aldehydes, respectively, to afford olefins stereospecifically [414]. Thus, 437 gave 439 while 438 afforded 440.



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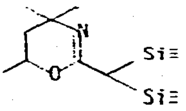

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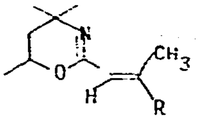

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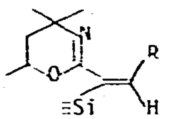
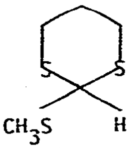


440

Thiomethyldithiane 441 has been lithiated, then alkylated or condensed with aldehydes and ketones to give esters or α-hydroxyesters, respectively [415]. 1,3-Dithiane-1-oxides have also been metalated and condensed with electrophiles [416]. Thus, 442 with LDIPA afforded a 2-lithio derivative arising from preferential abstraction of the C-2 equitorial proton. Reaction of this lithio salt with certain electrophiles occurred cis to the sulfoxide oxygen by a factor of 3-4:1. Other stereochemical results are discussed for the condensations of 443 (R = CH_3 and Ph) with electrophiles.



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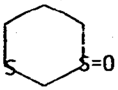

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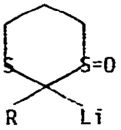
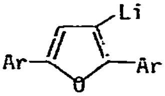


443

A large number of papers appeared in 1976 describing additional ring-openings of lithium derivatives of furans, thiophenes, selenophenes, and tellurophenes. Thus, 2,5-diaryl-3-lithiofurans 444 have been found to open even at -65° to allenes 445 and ketoacetylenes 446 [417]. Similar chemistry of certain 2,5-dialkyl-3-lithio-thiophenes and selenophenes occurs to afford substituted vinylacetylenes like 447 (M = S and Se) [418-421]. In contrast, 3-lithiothiophenes containing 2-chloro and 2-dimethylaminomethyl groups are stable and do not open [420,421]. Such ring openings have been employed in the conversion of 448 to 449 [422].



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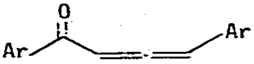

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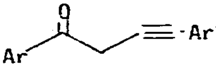

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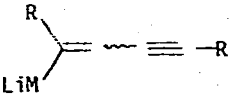

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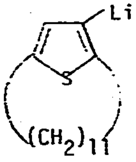

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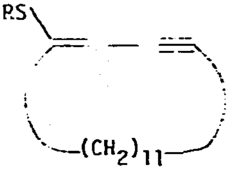
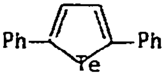


449

Several other examples of such ring-openings without the intervention of 3-halo compounds have also been described. Thus, treatment of 450 by a variety of strong bases in polar solvents gives 447 (R = SCH_3) via metalation at the three position of the heterocycle [423]. Products arising from substitution on the sulfur of the side-chain and abstraction of a thiomethyl proton are discussed. Metalation of 451 by n-butyllithium/TMEDA has been found to afford dilithiobutadiene 452 as evidenced by condensation with electrophiles [424]. Condensed selenophenes 453, 454, and 455 also open with methyllithium to give products in which the selenium— but not the sulfur— containing rings are cleaved [425].

450



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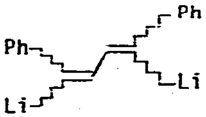

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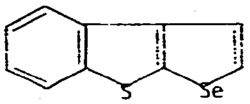

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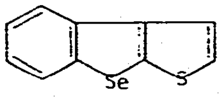

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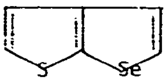
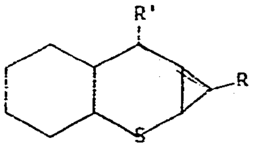


455

Other papers concerned with organolithiums and heterocycles have described the rearrangement of tricyclic systems like 456 to 457 [426], the halogen-metal exchange reactions of a variety of dihalothiophenes [427], the preparation of 2-chloro- and 2-bromotellurophenes from 2-lithiotellurophene [428], and the preparation and subsequent silylation of 458 and related compounds [429].



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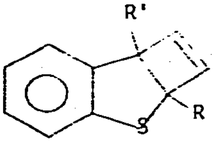

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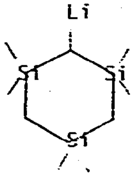
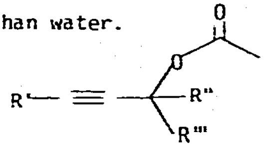


458

8. COPPER-LITHIUM REAGENTS AND OTHER "ATE" COMPLEXES

Propargylic acetates 459 have been converted by R_2CuLi to either 460 or 461 merely by running the reactions at -10° and -50°, respectively [430]. Similar reactions on propargylic acetals 462 gave allyl acetals like 463 [431]. Intermediate ate complexes like 464 have been trapped by electrophiles other than water.



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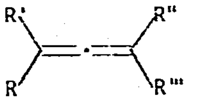

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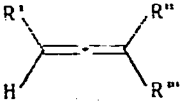

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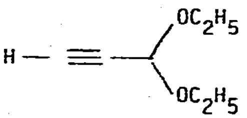

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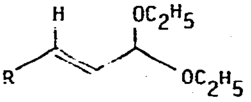

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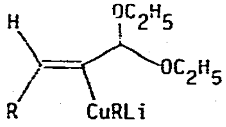
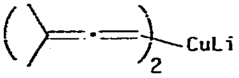


464

Methyl propiolate has served as a co-reagent to allenic cuprates like 465 to afford 466 [432], and to cyclopropyl cuprates like 467 to yield 468 [433]. Similar products were obtained using the latter cuprates and an acetylenic ketone [433]. Related additions of other cuprates on acetylene itself followed by condensation with electrophiles like iodine to give vinyl iodides [434], and on allenic ketones like 469 to afford mostly 470 [435] have also been reported. Similar 1,2-additions to an allenic phosphine oxide have been described [436].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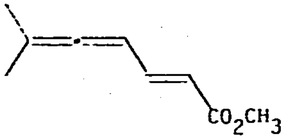
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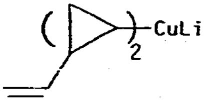
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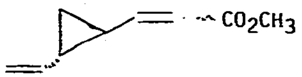
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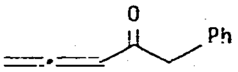
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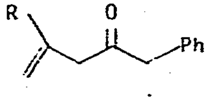
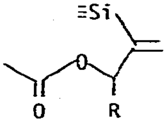

470

Various cuprates have also been condensed with certain allyl acetates [437-439] and with allyl halides [440] to give olefins. The reactions are illustrated by the conversion of 471 to 472 [437].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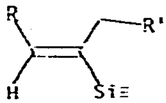
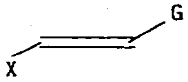

472

Several papers discussed the interaction of cuprates (R_2CuLi) with β-halo-α,β-unsaturated compounds 473 to afford substitution 474 and addition products 475. Thus, 475 was realized when X = Cl, G = COR, and R = methyl [441], but 474 was obtained when X = Cl, G = COR, and R = cyclopropyl [442]. Similarly, only 474 was realized when X = Br, G = COR, R = cyclopropyl [443], X = I, G = COR, R = 2-vinylcyclopropyl [444], and X = Br, G = CO_2H or CO_2CH_3, R = methyl and n-butyl [445].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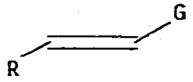
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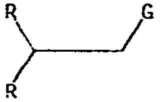
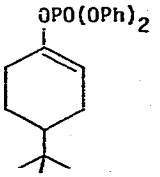

475

Dialkylcuprates have also been used to convert enol diphenylphosphate esters like 476 to olefins like 477 [446], and ketones like 478 to ones like 479 [447].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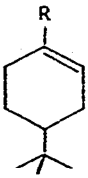
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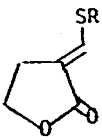
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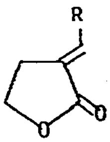
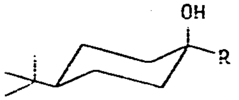

479

Additional examples of the condensation of dilithium trialkylcuprates 480 with cyclohexanones further demonstrate the superiority of these reagents over alkyllithiums [448]. For example, dilithium tri-n-butylcuprate and n-butyllithium add to t-butylcyclohexanone to afford 481 in 97% and 86%, respectively. Reagents 480 also have been added in a 1,4-fashion to α,β-unsaturated carbonyl compounds. In other papers dealing with conjugate additions, the rate of reaction of lithium diphenylcuprate with 1-mesityl-3-methyl-2-butenone has been found to increase in the presence of triphenylphosphine; the cuprate is, however, decomposed by added tetracyanoethylene [449]. Lithium dimethylcuprate has been condensed with pyranosides like 482 to afford 483 [450], and with oxo-enones like 484 to give 485 via regiospecific intramolecular aldol condensations [451].

R_3CuLi_2

480



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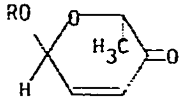

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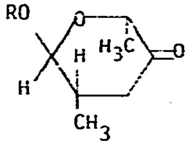

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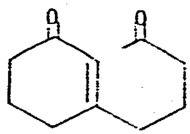

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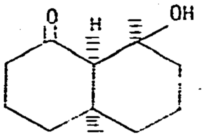
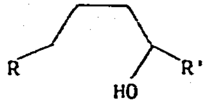


485

Lithium cuprates have been found to cleave THF and 2-methyltetrahydrofuran to alcohols 486 (R' = H or CH_3) [452], and to convert sulfinate esters to sulfoxides [453]. Lithium dimethylcuprate has been stereospecifically and regioselectively added to iron salts 487 to yield 488 [454].



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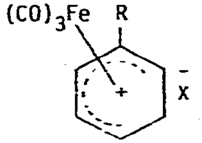

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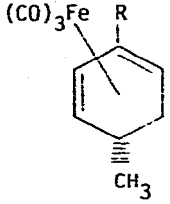
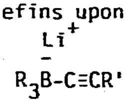


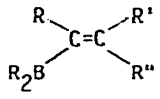
488

Lithium cuprates were employed as part of the synthesis of a variety of natural products in 1976 including methyl jasmonate and related compounds [455], spirovetivanes [456], prostaglandins [457-459], a naturally occurring macrolide from Cephalosporium recifei [460], certain α-methylene-γ-butyrolactones [461], dl-sesquicarene and dl-sirenin [462], a sex pheromone of the German cockroach [463], and the acyclic side chain of several natural products [464].

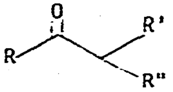
Turning to lithium organoborates, alkynyltrialkylborates 489 have been alkylated on the β-carbon by methyl sulfate, triethyloxonium fluoroborate, and other active alkyl halides to afford 490 which, after oxidation, gives ketones like 491 [465]. Reagents 489 have also been alkylated by α-haloketones, esters, and nitriles, and by a propargylic bromide to ultimately yield 1,4-diketones, γ-ketoesters, γ-ketonitriles, and γ-ketoalkynes [466]. The use of methanesulfonic acid instead of alkyl halides leads to ketones 492 after oxidation [467]. Details are provided about the conversion of 490 to Z or E-olefins upon hydrolysis by carboxylic acids.


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

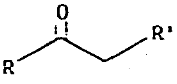
489



490

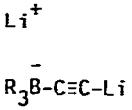


491

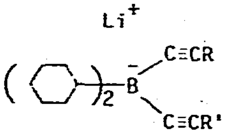


492

Boron reagents 489 (R' = H) have been converted to dilithio salts 493 which undergo alkylation at the acetylenic carbon to give 489 (R' = alkyls, allyls, trimethylsilyl) [468]. Subsequent iodination then affords unsymmetrical acetylenes. Similar rearrangements of 494 [469] and of 495 [470] have been employed to synthesize unsymmetrical conjugated diynes. Intermediates 494 and 495 were prepared by condensation of appropriate lithium acetylides with the corresponding alkynyldialkylboranes. Iodination of other borate reagents has been studied to determine suitability of such reactions for the synthesis of prostaglandins [471,472].


$Li^+ \; R_3\overset{-}{B}\text{-}C{\equiv}C\text{-}Li$

493



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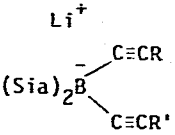
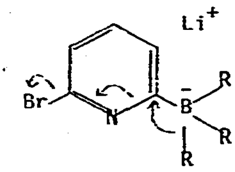


495

Reagent 489 has been condensed with tri-n-butyltin chloride to give 490 (R" = $Sn(n\text{-}C_4H_9)_3$)which, upon treatment with formic acid, affords Z-olefins [473]. The use of other electrophiles like trimethylaluminum chloride and phenylsulfenyl chloride apparently yielded 490 and an isomer since hydrolysis gave mixtures of Z- and E-olefins.

2-Bromo-6-lithiopyridine has been added to trialkylboranes to presumably afford intermediates like 496 which decompose to vinylboranes 497 [474]. Acetic acid treatment of 497 to give 498 illustrates the utility of the method for the preparation of pentadienenitriles.



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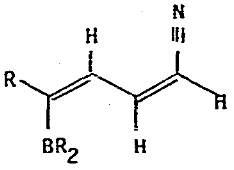

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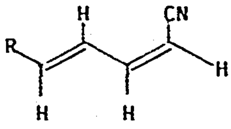
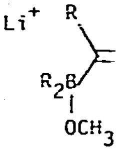


498

Trialkylboranes have also been condensed with α-methoxyvinyllithium to afford 499 which, upon treatment with hydrochloric acid, gives 500 [475]. Oxidation of 500 then yields dialkylmethylmethanols 501.



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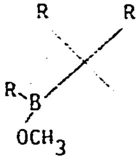
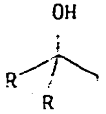
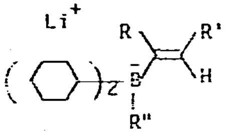


500



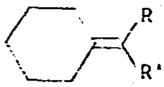
501

The course of hydrolysis of borate 502 depends upon the pH [476]. Thus, treatment of 502 with aqueous sodium hydroxide and aqueous hydrochloric acid affords 503 and 504, respectively. Other examples are described.



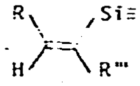
502

503



504

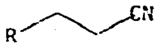
The boron of several lithium borate complexes has been replaced by copper using cuprous iodide to give synthetically useful intermediates. Thus, such replacement on 502 (R = Si≡, R" = CH_3) followed by the addition of alkyl halides (R‴ X) affords vinylsilanes 505 [477]. Similar replacement on 506 followed by addition of acrylonitrile and benzyl halides yields 507 [478] and 1,2-diarylethanes [479], respectively.



505

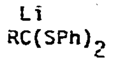
$(R_3BCH_3)^-Li^+$

506



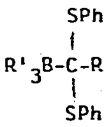
507

Trialkylboranes have been condensed with 508 to give 509 [480]. Subsequent treatment with mercuric chloride and basic hydrogen peroxide affords secondary alcohols 510.



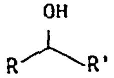
$\overset{\text{Li}}{\text{RC}}(\text{SPh})_2$

508



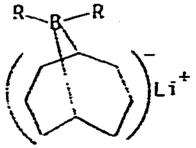
$R'_3B-\underset{\text{SPh}}{\overset{\text{SPh}}{C}}-R$

509



510

Nonane ate complex 511 has now been found capable of reducing ketones [481] and epoxides [482] to alcohols. In the former case, for example, 4-methylcyclohexanone is converted to cis- and trans-4-methylcyclohexanol by 511 in the presence of methanol and lithium methoxide, respectively [481]. Reagent 511 also reduces aldehydes selectively in the presence of ketones, discriminates between isomeric ketones like 2- and 4-heptanones [481], and reduces aromatic and aliphatic epoxides at the most and least hindered positions, respectively [482]. The organoborane remaining after such reductions has been shown to be 512 [483]. It has been conveniently formed by reaction of 511 with acetyl chloride and used in the synthesis of cis-bicyclo[3.3.0]-oct-1-yl systems like 513.



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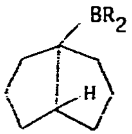

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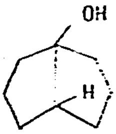
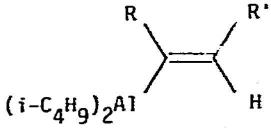


513

Reports appeared in 1976 describing stereoselective reductions of cyclic ketones with lithium trisiamylborohydride [484], and reductions of alkyl tosylates with triethylborohydride [485]. The latter reactions are useful in the deoxygenation of alcohols.

Aluminum ate complexes continued to be investigated. Thus, treatment of 514 (R = Si≡) with methyllithium followed by alkyl halides (R"X) gave vinylsilanes 515 [486,487]. Other alkylations were also effected on compounds 514 where R = phenyl, butyl, and hydrogen to stereospecifically afford substituted ethylenes [487,488]. The use of epoxides instead of alkyl halides in such reactions leads to allyl alcohols 516 [489].



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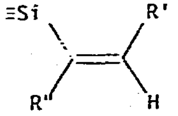

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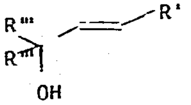


516

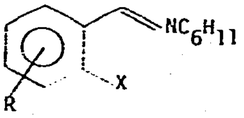
$LiAl(Si\equiv)_4$

517

Finally, alanate 517 has been prepared from chlorotrimethylsilane, aluminum, and lithium in the presence of mercury [490].

9. LITHIUM-HALOGEN EXCHANGE REACTIONS

A variety of o-haloarylimines 518 have been converted to their o-lithio derivatives by n-butyllithium, then coupled to 519 by various copper reagents [491]. Hydrolysis of 519 gave dialdehydes 520.



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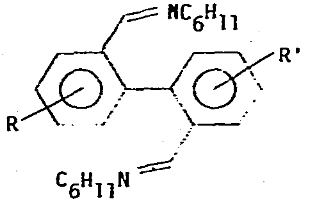

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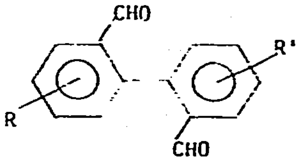
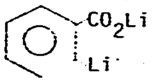


520

Low temperature halogen-metal exchanges on isomeric bromobenzoic acids and derivatives continued to be described in 1976. Thus, o-bromobenzoic acid was converted to its dilithio salt 521 and condensed with ketones to afford spiro systems like 522 [492]. Lithio derivatives 523 [493], 524 [494], and 525 [495] were similarly prepared and condensed with a variety of electrophiles.



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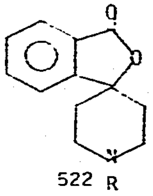

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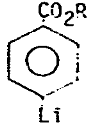

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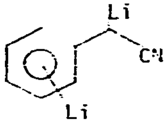

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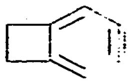
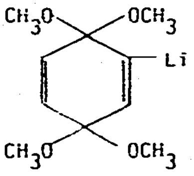


526

Cyclobutabenzyne 526 has been formed from the corresponding dibromo- and bromoiodoaromatics by treatment with n-butyllithium [496]. Benzyne 526 was trapped with furan or allowed to dimerize. Benzyne intermediates were also present in the reactions of 1,2-dibromobenzene with lithium diphenylphosphide and lithium diphenylarsenide [497], and were employed in condensations with certain silylmethyldialkylamines to afford o-silylarylamines [498].

"Umpolung" reagents for quinones like 527 have been prepared by treatment of the corresponding bromo compounds with n-butyllithium [499]. Simple condensation with electrophiles gave derivatives 528.



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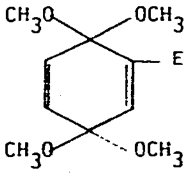
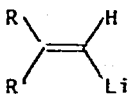


528

Alkenyllithium reagents like 529 have been prepared stereospecifically by reaction of alkyllithiums at low temperature with vinyl iodides [500] and vinyl bromides [501]. Polyhalovinyllithiums like 530 [502,503] and 531 [503] have been prepared similarly by lithium-chlorine exchange. In contrast, treatment of 532 (R = aryl) with organolithiums affords lithium arylacetylides [502].



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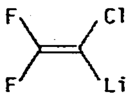

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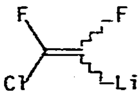

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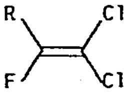
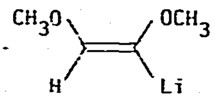


532

Other unsaturated lithium reagents prepared by metal-halogen exchange have included 533 which condenses with carbonyl containing compounds to ultimately give α-methoxy-α,β-unsaturated aldehydes [504], cyclooctatetraenyllithium (534) which is useful in the synthesis of bicyclo-octatetraenyl [505], and various lithium acetylides 534 made from 1-haloacetylenes and n-butyllithium [506].



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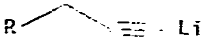
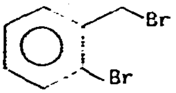


535

In the area of saturated halogen compounds, o-bromobenzyl bromide 536 is converted to benzyllithium 537 by n-butyllithium; 536 couples with starting dibromide to give a bibenzyl derivative [507]. o-Iodobenzyl bromide behaves similarly. On the other hand, o-bromobenzyl chloride 538 is converted to aryllithium 539 which has been condensed with a variety of electrophiles. γ-(o-Bromophenyl)ethyl bromide and γ-(o-bromophenyl)ethyl chloride also afford aryllithium derivatives.



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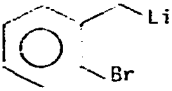

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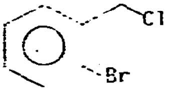

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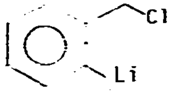
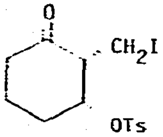


539

Treatment of cis- and trans-iodotosylates 540 with n-butyllithium has given the corresponding lithium reagents which cyclize to 541 stereospecifically [508]. Similar results were obtained on the corresponding 4-enes. In an unrelated paper, certain rotanes like 542 have been prepared by reaction of dibromo precursors like 543 with phenyllithium [509].



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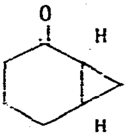

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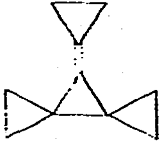

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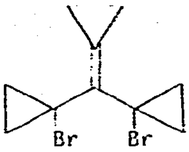
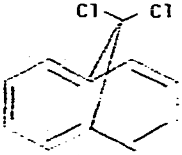


543

Finally, dichloro derivatives 544 [510] and 545 [511] have been converted to carbenes by methyllithium.



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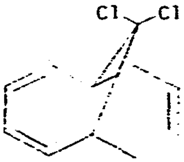
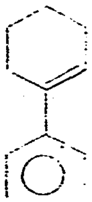


545

10. REDUCTIONS AND RADICAL ANIONS

A review article dealing with reduction of heterocyclic compounds by metal-ammonia solutions and related reagents arrived too late for inclusion in Section 1 [512].

The reduction of biphenyl to its tetrahydro derivatives 546-548 in ammonia has been studied as a function of the metal [513]. The combined yields of 546-548 were 18% with lithium, 12.5% with sodium, and 39% with magnesium. Possible mechanisms are discussed.



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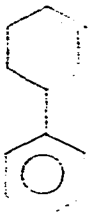

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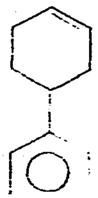
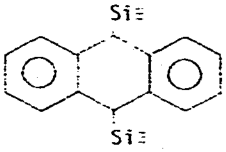


548

Reduction of anthracene by lithium in ether/benzene and sodium in THF has given cis- and trans-549, respectively [514]. Dehydrogenation of 549 was effected by n-butyllithium/TMEDA to afford the corresponding disilylated antracene. Reduction of benzene derivatives in the presence of silylating reagents also yielded silylhydroaromatics [515]. For example, benzene, lithium, and 1,3-dichlorotetramethyldisiloxane in THF affords 550 and 551.



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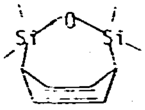

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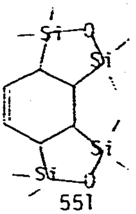
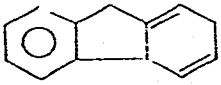


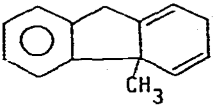
551

Reduction of fluorene by lithium in ammonia for short periods gave mostly dihydro derivatives 552 and 553 [516]. The small amount of tetrahydro products increased with increasing time. Reductive methylation of fluorene with lithium/ammonia/methyl bromide afforded 554 and 9-methyl- and 9,9-dimethyl derivatives. The latter compounds arose from metalation of the 9-hydrogen atoms of the parent compound.



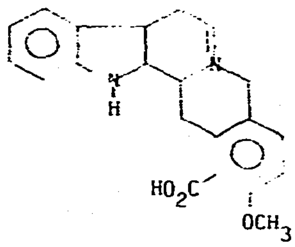
552

553



554

The aromatic E ring of yohimbane 555 has been converted to a cyclohexanone (556) by lithium/ammonia/i-propyl alcohol followed by aqueous acid [517]. Similar reductions of o-methoxybenzoic acid in the presence of alkyl halides (RX) constitute a simple synthesis of 2-alkylcyclohexenones 557 [518].



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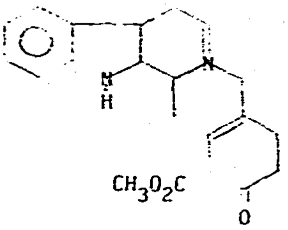

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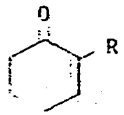
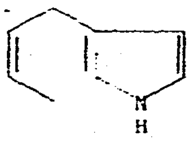


557

Improved procedures for the conversion of indole and carbazole to 558 and 559, respectively, involving the use of lithium/ammonia/methanol have been published [519].



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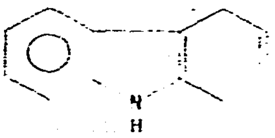
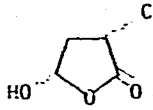


559

Lithium/ammonia has been used to remove the phenolic hydroxyl group masked as a phosphite ester from Δ^8-tetrahydrocannabinol [520]. Lithium/ammonia has also been employed to reduce 3-furoic acid to 560 and 561 via β-elimination, ring opening, and ring reclosure [521]. Thiophenes like 562 have been treated with lithium/ammonia/alcohols to afford, after hydrolysis, aminoketones like 563 [522]. The overall sequence represents the transformation of a thiophene to a butyryl group.



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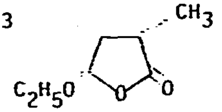
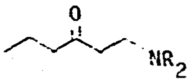


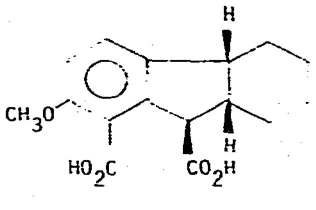
561

562

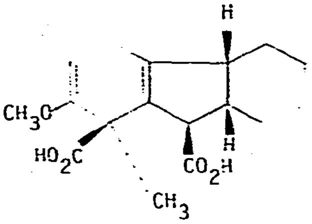


563

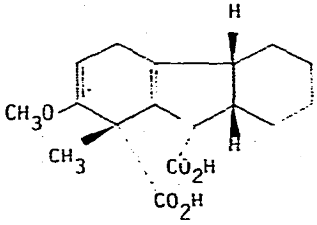
Reductive methylation of 564 and its epimer by lithium in THF followed by methyl iodide gave 565 and 566, respectively [523]. Clearly, the stereochemistry of the 9-carboxyl group controlled that of methylation at C-8 since the methyl group was introduced from the side of the molecule opposite the carboxyl group.



564

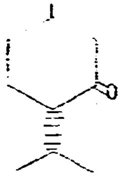


565

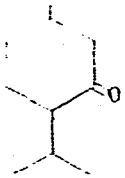


566

Menthone (567)-isomenthone (568) mixtures have been reduced stereoselectively to menthol (569) and neomenthol (570) only by lithium/ammonia [524]. Other reducing systems studied, including sodium and potassium in various media and hydrogen in the presence of ruthenium, rhodium, and platinum, were not stereospecific.



567



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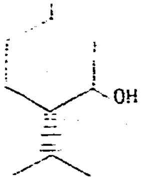
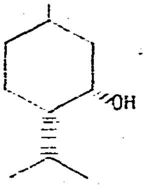


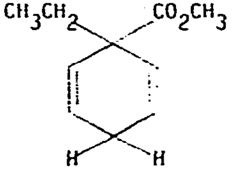
569



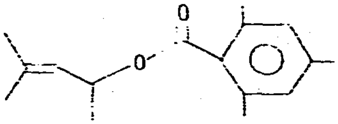
570

An α,β-unsaturated ketone, an epoxide, and a tetrahydrofuran have been reduced by lithium/ammonia or lithium/ethylenediamine as part of the synthesis of 10-epieudesmane sesquiterpenes like intermedeol [525].

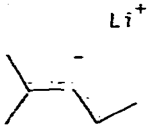
Methyl benzoate has been reductively ethylated by lithium/ammonia/ethyl bromide to afford, among other products, ethyl benzyl ether from O-alkylation, propiophenone from C-alkylation, and 571 from ring reduction [526]. Allyl ester 572 has been converted to allyllithium reagent 573 by lithium in THF in the presence of ketones to give γ-alcohols [527].



571

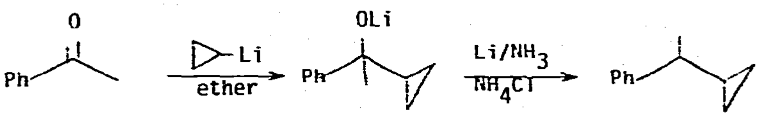


572



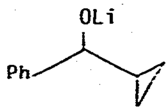
573

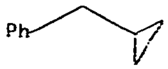
Tandem alkylation-reduction has now been applied to the synthesis of α-cyclopropyl aromatic hydrocarbons [528]. The process is illustrated by the sequence 574 to 576.



574 575 576

Related to the above, cyclopropyl phenyl ketone has been reduced to 577 by lithium/ammonia [529]. Subsequent reduction of 577 by lithium/ammonia in the presence of ammonium chloride and sodium benzoate affords 578 and 579, respectively.


577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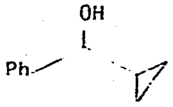
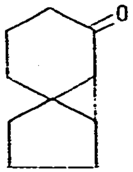

579

In contrast, cyclopropyl rings in compounds like 580 [530,531] and 581 [532] are cleaved by lithium/ammonia to give products like 582 and 583, respectively. The latter reduction also yielded several other products in which the cyclopropyl ring has been opened.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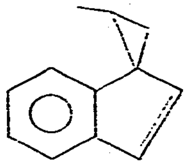
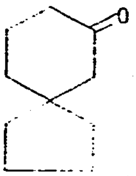
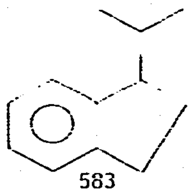
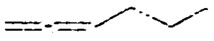

581

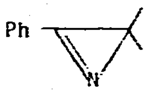

582

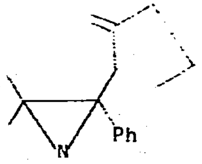

583

The conversion of several organic halides to organolithiums deserves mention. Thus, allenyl chloride (and bromide) 584 was converted to the lithium reagent, then condensed with 585 to give 586 via a cyclization reaction [533].

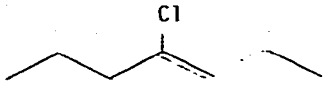

584

X

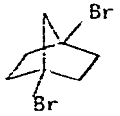

585


586

Reaction of E- and Z-4-chloro-3-heptenes (587) with lithium in THF to afford the vinyllithium reagents and heptenes was not stereospecific since mixtures of the cis and trans hydrocarbons were obtained [534]. Such reductions are presumed to have proceeded via vinylic radicals. In contrast, reaction of 587 with n-butyllithium gave the respective vinyllithiums with retention of configuration.


587

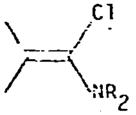
Lithium/ammonia reduction of 588 gave mostly norbornane and a dimer instead of the desired propellane 589 [535]. Similar results were obtained by an electrochemical process.



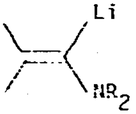
588

589

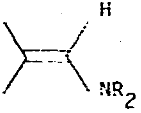
α-Chloroenamines 590 have been converted to 591 by lithium, sodium, and magnesium in solvents like THF and hexane [536]. The major products after reaction with deuterium oxide were enamine 592 and dimer 593. Deuterated enamine 594 was observed with sodium and magnesium only.



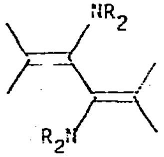
590



591

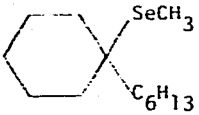


592, H = H
594, H = D

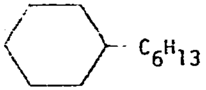


593

Various N-nitrosamines have been cleaved to the corresponding secondary amines in very low yields by lithium and magnesium in ether [537]. Carbon-selenium bonds have been cleaved to give hydrocarbons in good yields by lithium/-ethylamine as illustrated by the conversion of 595 to 596 [538].

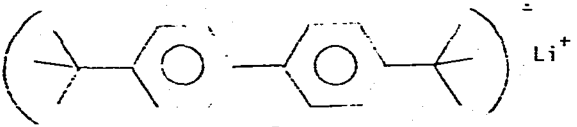


595



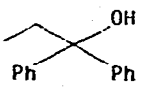
596

Various alkyl chlorides have been quantitatively converted to alkyllithiums by radical anion 597 without contamination of adducts derived from 597 and the alkyllithiums [539]. The success of the method is ascribed to the use of lithium instead of sodium and to the steric bulk of 597.

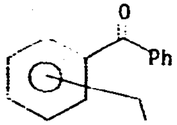


597

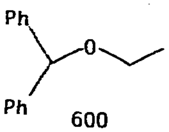
Reactions of benzophenone ketyls with alkyl halides have been studied as a function of the alkali cation and the solvent [540]. For example, the lithium ketyl and ethyl iodide afford 598 and 599 (ortho and para) but no 600 or 601. In contrast, potassium and cesium ketyls give rise to all of these products. The C-alkylations are said to occur via initial electron-transfer steps rather than by nucleophilic displacement.



598



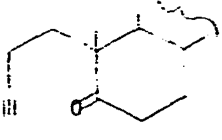
599
(ortho and para)



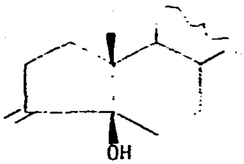
600

601

Overreduction has now been avoided in the cyclization of steroidal acetylenic ketones like 602 to 603 by using alkali naphthalenes instead of alkali metals in liquid ammonia [541]. Lithium naphthalene has also been employed in a new synthesis of (±)-sempervirol [542] and in the reduction of nitrobenzene to azo- and azoxybenzenes [543].



602



603

11. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

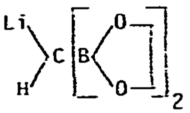
Several 1-cyanocarboranes have been prepared by condensing C-lithium o- and m-carboranes with phenylcyanate [544]. New stable iridium(I) complexes like 604 have been synthesized by reacting 605 with certain lithium carboranes [545]. An anion of phenanthroline-containing 606 has been made by treatment of 606 with n-butyllithium in THF [546].

$(Ph_3P)_2Ir(CO)(\sigma\text{-carb})$ 604

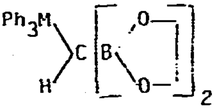
$(Ph_3P)_2Ir(CO)Cl$ 605

$(B_{10}H_{12})Pd(phenan)$ 606

Two full papers appeared in 1976 describing the preparation and reactions of lithium bis(boryl)methide 607 [547,548]. Carbanion 607 has been condensed with derivatives of germanium, tin, and lead to give 608 [547]. Reactions of 607 with carbonyl compounds [547] and benzyl bromide [548], and of lithium derivatives of 608 are discussed.



607



608

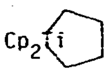
Other boron-containing molecules prepared using lithium were 609 from dimethoxyboron chloride, lithium, and silicon tetrachloride [549] and 610 from 611 and bis(methyl-o-carboranyl)chlorophosphine [550].

$Si[B(OCH_3)_2]_4$ 609

$(CH_3\text{-o-}CB_{10}H_{10}C)_3P$ 610

$CH_3\text{-o-}CB_{10}H_{10}CLi$ 611

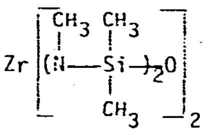
In the area of transition metals, n-butyllithium has been employed to intercalate lithium into layered MX_2 compounds where M = Ti, Zr, Hf, V, Nb, and Ta, X = S, Se, and Te [551]. A limiting composition of $LiMX_2$ was obtained in all cases except VSe_2 which gave Li_2VSe_2. A full paper appeared describing the details of the preparation of titanium(IV) metallocycloes like 612 from dilithioalkanes and titanium dichlorides [552]. The characterization and reactions of the metallocycles is discussed. Other compounds in this family prepared from alkyllithiums included tetrakis(pentafluorophenyl)zirconium [553], dicyclopentadienylzirconium and hafnium dicarbonyls [554], bis(fluorenyl)dimethylzirconium (613) [555], and zirconium(IV) amides like 614 [556].



612

$(C_{13}H_9)_2Zr(CH_3)_2$

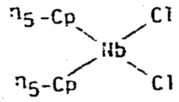
613



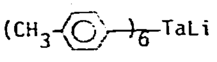
$$\mathrm{Zr}\left[(\overset{CH_3}{N}-\underset{CH_3}{\overset{CH_3}{Si}}\!-)_2O\right]_2$$

614

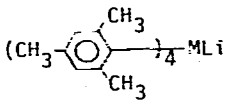
Cyclopentadienylniobium compounds like 615 have been prepared from substituted lithium cyclopentadienes and niobium(V)chloride [557,558]. Other compounds similarly prepared include pentamethylniobium [559], pentamethyltantalum [559], hexacoordinated tantalum complex 616 [560], and tetamesityl compounds 617 (M = V, Cr) [561,562].



615

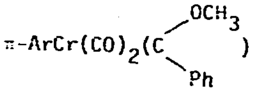


616



617

Carbene complex 618 has been synthesized from π-aryltricarbonylchromium reagents, phenyllithium, then trimethyloxonium fluoroborate [563]. Carbyne complex 619 has been prepared from the corresponding tungsten-bromine reagent and lithium cyclopentadiene [564]. Compound 620 was prepared from chromium hexacarbonyl, lithium dithiane, and triethyloxonium fluoroborate [565]. Chromium and tungsten complexes 621 have been condensed with organolithiums to give species like 622 [566] and 623 [567].

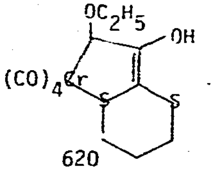


$$\pi\text{-}\mathrm{ArCr(CO)_2}\left(C\begin{smallmatrix}OCH_3\\ Ph\end{smallmatrix}\right)$$

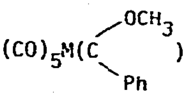
618

π-$C_5H_5(CO)_2W{\equiv}CR$

619

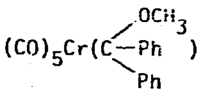


620



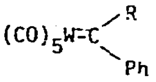
$$\mathrm{(CO)_5M}\left(C\begin{smallmatrix}OCH_3\\ Ph\end{smallmatrix}\right)$$

621



$$\mathrm{(CO)_5Cr}\left(C\begin{smallmatrix}OCH_3\\ Ph\\ Ph\end{smallmatrix}\right)$$

622



$$\mathrm{(CO)_5W{=}C}\begin{smallmatrix}R\\ Ph\end{smallmatrix}$$

623

Several more papers appeared discussing the preparation, structure, and properties of molybdenum and tungsten compounds comtaining metal-metal multiple bonds. Thus, full papers describe the reactions of lithium dialkylamides with molybdenum(III) chloride to give 624 [568] and with tungsten(IV) chloride to afford 625 [569] and 626 [570]. Other examples are cited. In addition, reaction of 626 with methyllithium yields 627 [571]. A related condensation of anti-626 with lithiomethyltrimethylsilane has been shown to occur with retention of configuration at tungsten via a bimolecular four-center mechanism [572].

$Mo_2(NMe_2)_6$

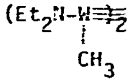
624

$W_2(NMe_2)_6$

625

$W_2Cl_2(NEt_2)_4$

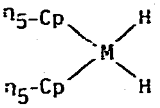
626



$(Et_2N-\underset{CH_3}{W}\equiv)_2$

627

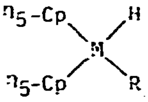
Dihydrides 628 (M = Mo, W) react with n-butyllithium to give tetramer 629; the latter reacts as a nucleophile at the transition metal with alkyl halides, acid chlorides, esters, and benzaldehyde to afford metal-carbon systems like 630 [573].



628

$((C_5H_5)_2MHLi)_4$

629

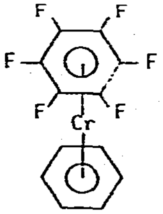


630

Other chemistry in this family included the preparation of tungstate ion 631 from hexamethyltungsten and methyllithium [574], the replacement of one or more fluorines of 632 by organolithiums [575], the stereospecific addition of phenyllithium across the azo linkage of 633 [576], and α-arylation of ethers and tertiary amines by 634 [577].

$W(CH_3)_8Li_2$

631



632

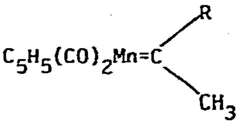
$[C_5H_5Mo(CO)_2NN]PF_6$

633

$PhWCl_6Li$

634

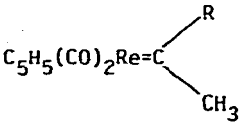
Manganese compounds 635 (R = CH_3, Ph), prepared by reaction of methyllithium with 636, represent carbene complexes where a dialkyl- or arylalkylcarbene is stabilized as a ligand to a metal atom [578]. An analogous rhenium complex (637) has been obtained similarly [579].



635

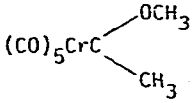
$C_5H_5(CO)_2Mn\equiv CR$

636



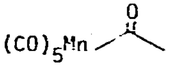
637

MO calculations have been performed on 638 and 639 to determine factors which control the site of nucleophilic attack on such species [580]. It is concluded that these reactions are frontier rather than charge controlled and that attack at coordinated CO is much more likely for the acyl species (639) than for the carbene complex (638). Experimentally, methyllithium has been condensed with 640 and 641 at CO to give 642 [581] and 643 [582], respectively. Protonation of 643 afforded the enol tautomer of a metalloacetylacetone molecule [582].

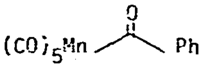


$(CO)_5CrC(OCH_3)(CH_3)$

638



639



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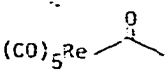

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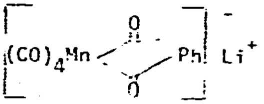
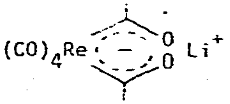
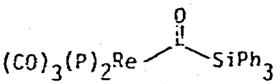


642



643

The first acylsilane derivative of a transition metal, 644, has been synthesized from 645 and triphenylsilyllithium [583].



644

$(CO)_4Re(P_2)$.

645

Other rhenium and manganese compounds prepared in 1976 include octamethyldirhenate(III) (646) from methyllithium and rhenium pentachloride or 647 [584], octamethylrhenate(VI) (648) from methyllithium and hexamethylrhenium [585], and allenylidene compound 649 from t-butyllithium and acetylene complex 650 [586].

$Li_2Re_2(CH_3)_8$

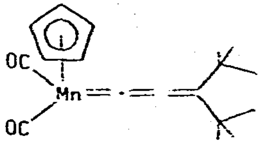
646

$Re_2(OCPh)_4Cl_2$

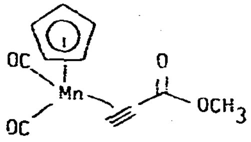
647

$Li_2Re(CH_3)_8$

648



649



650

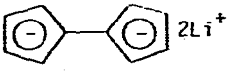
Lithium cycloheptatrienyltricarbonyl ferrate (651) has been reacted with various metal carbonyl halides to give heterodimetallic complexes 652 (M = Mn, Re, X = 3 and M = Rh, X = 2) [587]. Dilithiofulvalene (653) has been converted to bis(fulvalene)diiron (654) by iron(II) chloride [588]. Polymethylferrocenes [589] and 1,1',2,2',4,4'-hexakistrimethylferrocene [590] have been prepared by treatment of appropriate lithium cyclopentadienes with iron(II) bromide and chloride, respectively.

$(C_7H_7)Fe(CO)_3Li$

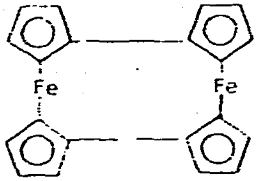
651

$(C_7H_7)Fe(CO)_3M(CO)_x$

652



653



654

Two related bis(cyclooctadiene)cobaltlithium compounds 655 and 656 have been prepared from 1,5-cyclooctadiene(cyclooctenyl)cobalt and phenyllithium [591] and from cobaltocene and lithium in the presence of cyclooctadiene [592], respectively. Iridium complexes like 657 have been synthesized from the corresponding iridium chloride and aryllithiums [593]. Two papers described nucleophilic reactions of lithium-cobalt-phthalocyanines as model reactions for a new protecting group for peptide syntheses [594,595].

$(C_8H_{12})_2CoLi(LiPh)\cdot 2(C_2H_5)_2O$

655

$(C_8H_{12})_2CoLi(THF)_x$

656

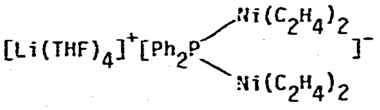
$(CO)Ir(Ar)(PPh_3)_2$

657

Novel nickel (0) complexes with σ-M°-C bonding, illustrated by 658, have been prepared from bis(cyclooctadienyl)nickel, organolithiums (RLi), TMEDA, and ethylene [596]. Similarly, reaction of this same nickel reagent, lithium dialkylphosphine, and ethylene affords compounds like 659 [597].

$[Li(2TMEDA)]^+[PhNi(C_2H_4)_2]^-$

658



$[Li(THF)_4]^+[Ph_2P(Ni(C_2H_4)_2)_2]^-$

659

"Side-on" dinitrogen-nickel complex 660 has been prepared by reaction of all-trans-1,5,9-cyclododecatrienenickel with phenyllithium/phenylsodium and nitrogen in ether [598]. Ethylenebis(phenyllithium)nickel and the related phenylsodium compound have been synthesized by reaction of the same trienenickel reagent, phenyllithium, phenylsodium, and ethylene [599].

$[Ph(NaOC_2H_5)_2]_2[Ph_2Ni]_2N_2NaLi_6(OC_2H_5)_4$

660

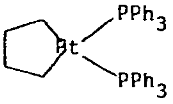
Other compounds in this family recently described include platinum carbonyl dianions like 661 by reduction of platinum chloride systems or preformed platinum carbonyl systems by lithium [600], platinum complexes like 662 from the corresponding chlorides and perfluorophenyllithium [601], benzylnickel chloride from a complexed nickel(II) chloride and lithium tribenzyltin [602], and metallocycles like 663 from the platinum chloride and 1,4-dilithiobutane [603].

$Pt_3(CO)_6Li_2$

661

$(C_6F_5)_2Pt(PR_3)$

662



663

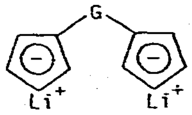
A variety of thorium derivatives 664 (R = alkyl and alkenyl) have been prepared by reaction of the thorium chloride derivative with organolithiums and Grignard reagents [604]. Ring-bridged uranium halides 665 have similarly been made by condensation of 666 (G = CH_2, Si≡, n-propyl) with uranium(IV) chloride [605].

$(\eta_5\text{-}C_5H_5)_3ThR$

664

$[G(C_5H_4)_2]_2U_2Cl_5Li(THF)_2$

665



666

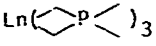
Terbium and holmium compounds 667 (R = t-C_4H_9) have been synthesized from the reaction of 668 and lithium di-t-butylphosphide [606]. Ylide 669 has been prepared by the interaction of 670 with n-butyllithium [607].

$(C_5H_5)_2M\text{-}PR_2$

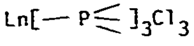
667

$(C_5H_5)_2MCl$

668



669



670

The first organogold(I) complex containing a S-donor, 671, has been prepared by reaction of perfluorophenyllithium and 672 [608].

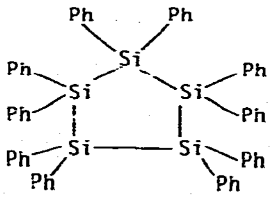
$(C_6F_5)AuSC_4H_8$

671

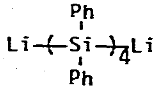
$ClAuSC_4H_8$

672

Turning to Group IV of the Periodic Table, it has been found that perarylcyclopentasilane 673 may be prepared by treatment of either 674 or 675 with potassium tetrachloroplatinate [609]. The latter reagent is said to act as a lithium sink. This same paper describes cleavage reactions of perarylcyclotetrasilane with lithium metal.

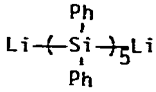


673



$Li{-}(SiPh_2)_4{-}Li$

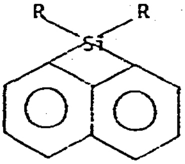
674



$Li{-}(SiPh_2)_5{-}Li$

675

Other preparations of cyclic silicon-containing compounds are illustrated by 676 from 1,8-dilithionaphthalene and dialkyldichlorosilanes [610], 677 from ylide 678 and disilane 679 [611], and 680 from 681 and dichlorodimethylsilane [612].



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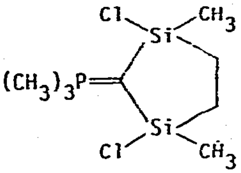

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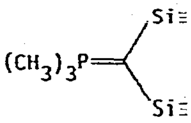

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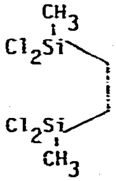

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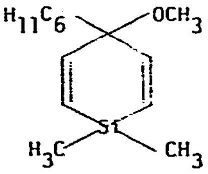
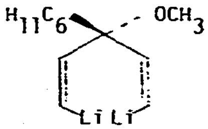
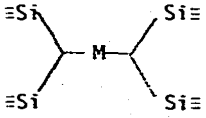


680

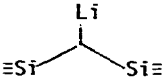


681

Divalent species 682 (M = Ge, Sn, Pb) have been prepared from 683 and 684, or, when M = Sn or Pb, from 683 and MCl_2 [613,614].



682



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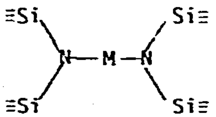
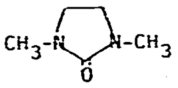


684

Imidazolidinone derivative 685 has been tested for its suitability as an aprotic solvent for organometallic reactions by reacting chlorotrimethylsilane with ketones and lithium metal to give disilyated derivatives like 686 [615]. It is concluded that 685 lies between THF and HMPA in promoting such reactions.



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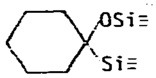
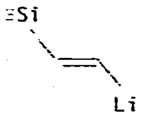


686

Other chemistry in this group included the addition of organolithiums and Grignard reagents across the nitrile linkage of α-germyl nitriles like 687 [616], the preparation of 688 from the corresponding tin reagent by trans-metalation [617], the synthesis of triphenylsilyllithium from 689 and methyllithium [618], and the conversion of lithium cyclopentadiene to cyclopentadienylgermanium trichloride using germanium(IV) chloride [619].

$(C_2H_5)_3GeCH_2CN$

687

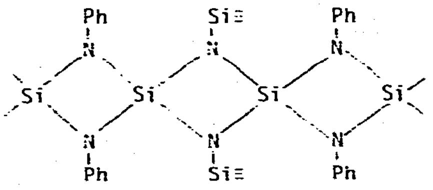


688

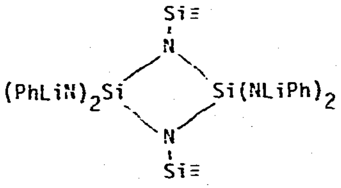
$(CO)_4CoSiPh_3$

689

An interesting dispirotetrasilazane 690 has been obtained from tetralithio derivative 691 and dichlorodimethylsilane [620]. The synthesis of 691 was effected using $\equiv SiNSiCl_3$ and n-butyllithium followed by addition of aniline, then more n-butyllithium.

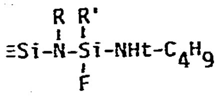


690



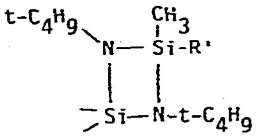
691

Treatment of silicon-nitrogen systems 692a-c with n-butyllithium also gave cyclic systems. Thus, 692a ($R = t\text{-}C_4H_9$, $R' = Ph$) and 692b ($R = R' = t\text{-}C_4H_9$) afforded 693a-b apparently via methanide migration to a silicenium ylide [621, 622]. In contrast, 692c ($R = i\text{-}C_3H_7$, $R' = Ph$) with the smaller i-propyl group yielded 694 presumably via a silicenium ion [622]. Reaction of silyl system 695 with n-butyllithium gave 696 via the latter route [623]. On the other hand, similar metalation of 697 gave only N-lithiation, the first such organometallic to be prepared [624].

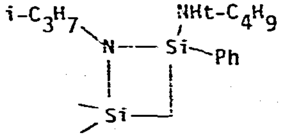


$\equiv Si-N(R)-Si(R')(F)-NHt-C_4H_9$

692a (R=t-C_4H_9, R'=Ph)
692b (R=R'=t-C_4H_9)
692c (R=i-C_3H_7, R'=Ph)



693a (R'=Ph)
693b (R'=t-C_4H_9)



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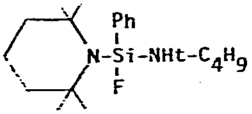

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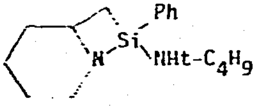

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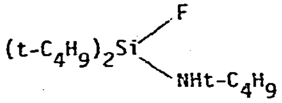
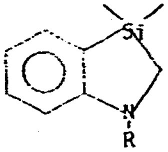
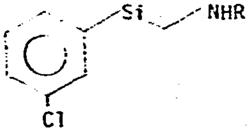


697

Azosilolines like 698 have been synthesized from benzyne precursors 699 and phenyllithium [625].



698



699

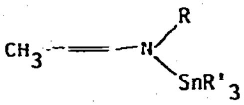
Silylated aldimines (700) may now be simply prepared by treatment of new boron ate complexes 701 [626,627] with chlorotrimethylsilane [628]. The imino-enamino-tin metalotropic system, for example, 702-703, can be obtained in better yields than previoulsy described by treating iminolithium reagents with chlorotributyltin [629]. Similarly, metalloimines 704 have been obtained from 705 and metal halides [630].

$\equiv Si-N=CHR$

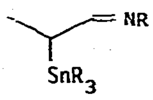
700

$M^+(C_2H_5)_3\bar{B}-N=CHR$

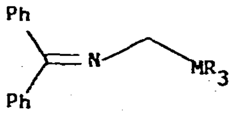
701



702



703



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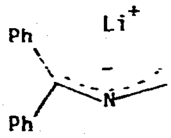
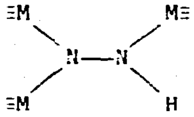
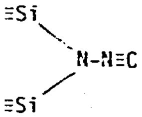


705

Nitrogen-nitrogen and nitrogen-oxygen systems have also been combined with lithium and Group IV systems. Thus, reaction of 706 (M = Si), carbon tetrachloride, and butyllithium affords aminoisocyanide 707 [631]. Similar reaction of 706 (M = Ge) with an organolithium, then hexachloroethane gives germyldiimine 708 [632]. Several tris(organosilyl)hydroxylamines like 709 have been synthesized from 710, n-butyllithium, and chlorosilanes [633]. Finally, bis(trimethylsilyl)hydroxylamines (711) have been prepared from phenylhydroxylamine, n-butyllithium, and chlorotrimethlsilane [634].



706



707

$\equiv Ge\text{-}N{=}N\text{-}Ge\equiv$

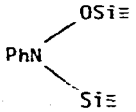
708

$(\equiv Si)_2NOSi\equiv$

709

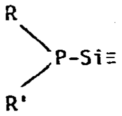
$\equiv SiNHOSi\equiv$

710



711

Organosilylphosphines like 712 have been prepared by reduction of phosphines with lithium followed by addition of chlorotrimethylsilane [635]. Silylphosphinelithium compound 713 has been synthesized from 714 and organolithiums like n-butyllithium [636].



712

$(\equiv Si)_2P\text{-}Li$

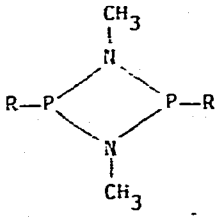
713

$(\equiv Si)_3P$

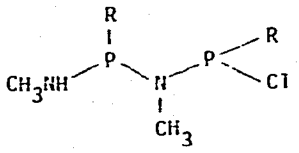
714

Calculations have been performed on the activation of nitrogen in $\pi\text{-}Li_nN_2$ complexes [637]. The authors conclude that stabilization of the electronic states in which the N-N bond is highly loosened can occur and that certain of these states can be described as occurring from one- or two-electron reduction of nitrogen.

Diazadiphosphetidines like 715 have been prepared by treatment of 716 with phenyllithium [638]. Phosphineimines like 717 have been synthesized from tetraphenylphosphonium chloride and lithium alkylamides [639]. The use of lithium dialkylamides, though, affords homolytic decomposition of phosphorus compounds or the formation of N,N-dialkylanilines, depending on the size of the alkyl group.



715



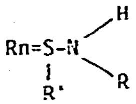
716

Ph$_3$P=NR

717

Lithium diphenylphosphide and arsenide have been condensed with 1,2-dichloroethenes to give stereospecifically mono- or diphosphino- and arsinoethylenes, depending upon the central atom and the stoichiometry [640]. Mixed phosphinoarsinoethylenes are also described. Other Group V and VI compounds prepared using lithium chemistry have include 718 from lithium cyclopentadienes and chlorodialkylphosphines [641], sulfur compounds 719 from sulfurdiimines 720 and organolithiums and Grignard reagents [642], lithiosulphimide 721 from the parent compound and n-butyllithium [643], methylalkoxy(alkylthio)silanes like 722 from methylalkoxychlorosilanes and lithium mercaptides [644], and α-silylcarbanions from 723 and n-butyllithium [645]. Finally, sulfur-tin derivatives of a glucopyranose have been prepared by reaction of 724 with a pyranose bromide [646].

718



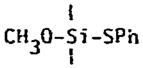
719

RN=S=NR

720

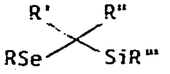
$(CF_3)_2S=NLi$

721



$CH_3O-Si-SPh$

722



723

R_3SnSLi

724

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