LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1977*

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*Lithium, Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 143 (1977) pages 1 - 97.

1. REVIEWS AND BOOKS

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

- Application of infrared and Raman spectroscopy to the study of structure and bonding of organometallics [1].
- Solvent effects on species formed by cation-electron and electron-electron interactions [2].
- The use of ESR spectroscopy to study solvation of radical anions and cations [3].
- Ion-solvent and ion-ion interactions of alkali metal tetraalkylaluminates in nonaqueous solvents studied by IR, UV, and NMR spectroscopy [4].
- Mechanisms of the reactions of organometallics with organohalides including discussions of classic nucleophilic substitution routes versus single electron transfer processes [5].
- Hard and soft acids and bases in organic chemistry [6].
- Intramolecular coordination in organolithiums derived from metalations, metal-halogen exchanges, and addition reactions [7].
- Preparation and reactions of di- and polyalkali metal derivatives (multiple anions) of heterofunctionally substituted organic molecules [8].
- Polyalkali metal derivatives of polyketones and ketoesters in the synthesis of polyketide-type aromatic natural products [9].
- Condensations of lithioenaminones [10].
- Alkali metal enolates: Structural evidence from X-ray, spectroscopic, and physicochemical methods; reactivities as a function of solvent, cation, and co-reagents [11].
- Alkene synthesis from lithioorganosilicon compounds [12].
- Preparation and reactions of O-silylated enolates [13].
- Umpolung of the reactivity of carbonyl compounds using S,S-acetals and other sulfur-containing reagents [14].
- Theoretical and practical aspects of carbanions derived from sulfones [15].
- Recent progress of synthetic methods employing lithioorganosulfur compounds [16].
- Recent or improved procedures for the use of α-metalated isocyanides in organic synthesis [17].
- Rearrangement of lithium dialkyl-9-borabicyclo[3.3.1]nonane ate complexes [18].
- Synthesis of polycyclic carbon-phosphorus heterocycles [19].
- Preparation and properties of arylgold complexes [20].

2. STRUCTURAL STUDIES

Single crystal X-ray crystallography has been used to determine the structure of 1,2-dilithioacenaphthene (1) complexed with two TMEDA molecules [21]. The report represents the first stereochemical investigation of a main group metal coordinated to a carbocyclic (4n + 2)π anion derived from a 4nπ precursor with the same nuclear framework. In the structure (Figure 1), the acenaphthene fragment is nearly planar with the two TMEDA moieties coordinated to both sides of the five membered ring of the hydrocarbon. The length of the C_3-C_4 and the C_1-C_2 bonds are said to be 1.30Å and 1.42Å, respectively.

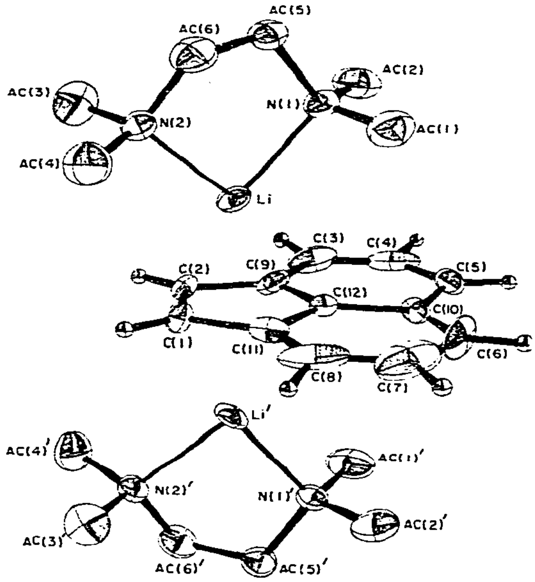
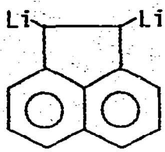


Figure 1

A similar investigation on lithium indenofluorenide 2 at -160° gave the structure shown in Figure 2 [22]. The isolation of 2 is unique because crystallization of the highly delocalized carbanion as a dimer was achieved without crystallization-promoting or stabilizing ligands. The structure itself in which the nearly planar anions are mutually parallel at a distance of 3.9Å represents the first example of lithium being in linear coordination with two hexahapto-bonded six-membered ring ligands in the form of a bis(arene) metal sandwich type of compound. The lithium atoms are not oriented on the carbon center of highest charge density, but rather are concentrically situated between two six-membered rings at a distance of 1.93Å from each.



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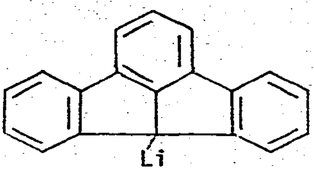

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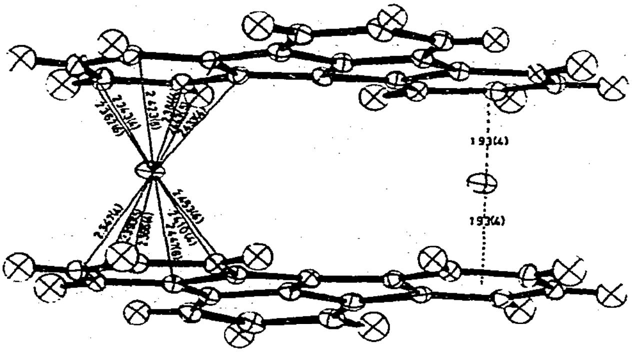


Figure 2

3. APPLICATION OF MOLECULAR ORBITAL THEORY

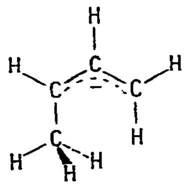
Methyllithium has been examined using STO-3G optimized geometry to afford the following: total energy, -46.42159 hartrees; lithium-carbon bond length, 2.009Å; carbon-hydrogen bond length, 1.083Å; H-C-H angle, 106.2°; overlap population, σ 0.58, π 0.05; total electron population on lithium, σ 2.78, π 0.06; total electron transfer to lithium, -0.16 [23]. The results are compared to those obtained in earlier studies. A systematic set of 32 other neutral molecules and complexes containing lithium or beryllium bonded to other first short period atoms (lithium to fluorine) are also similarly examined. The methyl group of methyllithium is said to be not far from tetrahedral but is more pyramidal than that of any other A-CH_3 system for first row A.

The inversion barriers of pyramidal carbanions have been calculated with the CNDO/2 method and been found to parallel ab initio results using an STO-3G basis set [24]. The following trend with E_{inv} in kcal/mol is listed: $\overline{C}H_2CH_3$ (6.7) < $\overline{C}H_2CHO$ (14.7) < $\overline{C}H_3$ (19.2) < $\overline{C}H_2OH$ (20.3) < $\overline{C}H_2F$ (32.6) < $\overline{C}H(OH)F$ (36.8) < $\overline{C}HF_2$ (53.3). The data, interpreted in terms of the interaction between the lone pair on carbon and the σ^*_{CH} orbital, follow qualitative concepts on electronegativity and overlap, and on force constants.

The model systems CH_3Li-NR_3, formed between methyllithium and aliphatic amines, have been studied using the CNDO/2 method [25]. The molecular parameters for the hydrogen-bonded system, H_3CH---NH_3, were ascertained for comparison. The molecular properties calculated included the interaction energy, the equilibrium distance, the amount of charge transferred, and the enhancement of dipole moment. Significant correlation between such properties and the ionization potentials of the amines was found. The lithium bond of CH_3Li-NH_3 complex was found to be considerably stronger than the hydrogen bond of the H_3CH-NH_3 complex.

Calculations using a STO-3G-basis set were carried out on ethyllithium and 2-lithiobutane to obtain information about the hydride-donating properties, the syn-anti elimination modes, and the Hofmann-Saytzeff orientation of such compounds [26].

In the area of allyllithiums, four levels of theory have been used to study the cis and trans isomers of the crotyl anion, cation, and free radical [27]. It is suggested that the cis-crotyl anion 3 is more stable than the trans isomer by 1.4-1.5 kcal/mol, the preference being ascribed to the possibility of cyclic conjugation in the former species. These results are contrasted with the preferred trans-carbon skeletons of the crotyl cations and radicals. The authors also suggest that the methyl group staggered with the partial double bond as in 3 is more stable than an eclipsed methyl group as illustrated in 4.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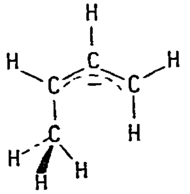
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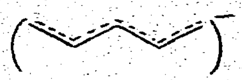
CNDO II calculations have been performed on the three different conformations (5-7) of the free pentadienyl anion and on five different structures of pentadienyllithium (8-12) [28]. The calculated energy of each species is listed. The calculations indicate that the central atom in each structure should be more reactive than the two terminal carbon atoms. There is more than one potential bonding site for the lithium in 9-12.

5

(-40.5734)

6

(-40.5734)



7

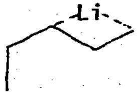
(-40.5731)

8

(-41.3623)

9

(-41.2850)



10

(-41.2278)

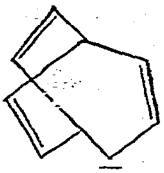
11

(-41.2273)

12

(-41.2063)

The stabilities and the electronic structures of $(CH)_9^-$ systems 13 and 14 along with the corresponding cations were studied using INDO calculations [29]. It is suggested that the C_6-C_7 and C_8-C_9 π systems of 13 are bent towards the C_2-C_3-C_4 π-system and the resulting conjugative interaction of the C_2-C_7(C_2-C_8) and C_4-C_6(C_4-C_9) bonds stabilizes the molecule. The electronic energy of 13 and 14 are listed as -8101.3 eV and -7896.8 eV, respectively. That the stability of 14 is close to that of 15 indicates that the rearrangement of 15 to 13 may proceed via 14. It is believed that the sum of the total overlap populations could be a quantitative measure of aromaticity for three dimensional unsaturated $(CH)_n$ systems.



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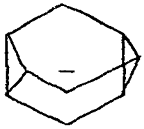

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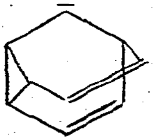

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The acidities of several substituted methanes have been determined both in the gas phase and in aqueous solution using the CNDO/2 method [30]. The energy differences between an anion and its conjugate acid in atomic units are listed as follows: methane, 1.0347; ethane, 0.9912; acetonitrile, 0.9403; acetone, 0.8928; acetaldehyde, 0.8870; nitromethane, 0.8719; acetylacetone, 0.8750; and chloroform, 0.9241. The results generally parallel those in "aqueous solution" and previously reported pKa values.

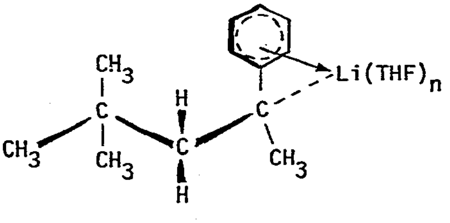
Other papers of interest in this area include the electronic structure of methylene radical anion and its dimer [31], benzene-lithium cation complex formation [32], molecular complexes of lithium with ammonia, water, hydrogen sulfide, and hydrofluoric acid [33], nonparametric resonance energies of arbitrary conjugated systems [34], and the Huckel rule and effective discontinuity of cyclic conjugation [35].

4. SPECTROSCOPIC DETERMINATIONS

A. NMR Spectroscopy

The effect of adding electron donors such as dimethyl ether, diethyl ether, triethylamine, and diethylsulfide to hexameric n-butyllithium in isooctane has been studied by ^1H NMR [36]. In each case, such donors caused an upfield shift of the α-CH_2 signal but downfield shifts of the α-methyl signals of the donors. The authors indicate that in the case of dimethyl ether, a complex with a 1:1 composition is obtained. In contrast, fewer than four equivalents of the other donors add to the n-butyllithium tetramer. Data about the stability of such complexes are discussed.

1,3,3-Trimethyl-1-phenyllithium, a model compound for the active chain end in the polymerization of α-methylstyrene with butyllithium, has been studied by ^1H and ^{13}C NMR spectroscopy [37]. It is suggested that the α-carbon atom of this compound is substantially sp^2-hybridized and that the lithium atom is located in the space over the phenyl-α-carbon bond. The lithium atom is believed to be interacting with the π-electrons as shown in 16.



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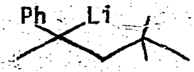
Organometallics 17-19 enriched with α-^{13}C have been studied by ^{13}C NMR spectroscopy to determine the hybridizations of the α-carbon atoms [38]. While the ^{13}C-^{13}C coupling constants of 17 and 19 suggest the presence of sp^2-hybridized α-carbons, those of 18 indicate sp^3-hybridization despite slow rotation on the NMR time scale about the C_1-C_2 bond at -60°.



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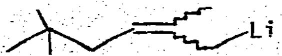

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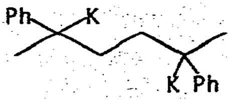

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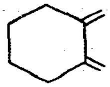
^{13}C NMR spectra of indenyl- and cyclopentadienyllithium in several ethers and in DMSO-d_6 have also been obtained [39]. As the polarity of the solvents is increased, the chemical shifts change downfield for the C_1-C_3 carbons and upfield for the C_4-C_7 carbons. It is suggested that the above changes in indenyl lithium arise from a displacement of negative charge from the five- to the six-membered ring due to a change in the ion-pair equilibrium toward solvent separated ions. In contrast to earlier speculation, the authors believe the lithium cation is positioned above the five-membered ring.

In order to determine if 1,2-adducts can be realized in the initial steps of alkyllithium-initiated polymerization of 1,3-butadienes, diene 20 was treate with t-butyllithium-d_9 and the 100-MHz ^1H NMR spectrum obtained [40]. The spectral data were consistent only with 1,4-adduct 21; olefinic protons expected in a 1,2-adduct were absent. Incidentally, transoid diene 22 and t-butyllithium fail to react over a period of 120 hr. under identical conditions lending credence to the hypothesis that such additions occur via a cis-addition mechanism.



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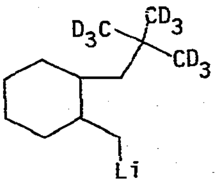

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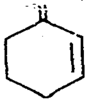

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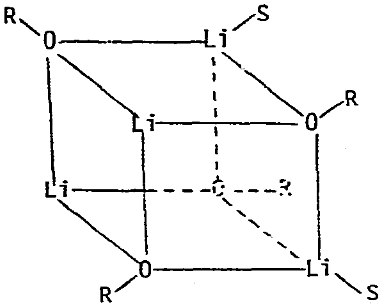
Isoprene has been polymerized by t-butyllithium in benzene-d_6 in an NMR spin tube followed by the addition of dioxane to afford three dioxane-lithium cation complexes of the oligopolyisoprenyllithium system [41]. At 250 MHz, signals are reported for vinyl protons assigned not only to cis- and trans-1,4-adducts, but also to a 3,4-adduct.

Another in a series of papers on the NMR spectra of picolyl-type carbanions appeared in 1977 [42]. This one describes the ^{13}C and ^1H NMR spectra of lithio salts of amino-, hydroxy-, and thiopicolines in several polar solvents and discloses that a linear relationship exists between the ^{13}C chemical shifts and the calculated π-electron densities. That upfield shifts of the ring protons of picolyllithium and its derivatives at both lower temperatures and in HMPA (compared to THF) are observed is ascribed to greater solvent separation of the ion pairs.

An extensive study of lithioisobutyrophenone aggregates in ethers using ^{1}H, ^{13}C, and ^{7}Li magnetic resonance spectroscopy has led to the suggestion that the two species observed are like tetramer 23 and dimer 24 [43]. The complex obtained between the enolate and lithium chloride is shown to have the formula $Li_4Cl(C_{10}H_{11}O)_3$.



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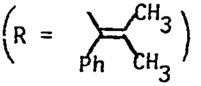

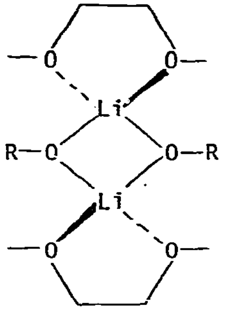

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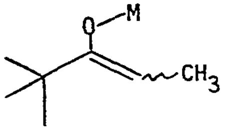
Enolates derived from 2,2-dimethyl-3-pentanone have also been studied by ^{13}C NMR and by IR spectroscopy [44]. Both structures 25 and 26 can be observed depending upon the metal and the solvent.



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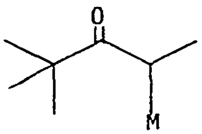

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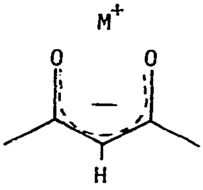
A full paper discusses the stereochemical consequences of ionic bonding in alkali metal acetylacetonates as studied by ^{1}H NMR spectroscopy [45]. Thus, only a dimer of 27 is present at low lithium concentrations while 27 is accompanied by 28 when the cation is sodium or potassium. Titrations of sodioacetylacetone with lithium perchlorate and 18-crown-6 are discussed. The free energy of activation at the coalescence point for topomerization of the anion was determined to be 13.7 kcal/mol by complete line shape analysis.



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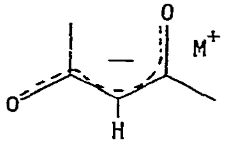

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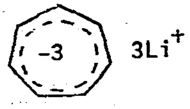
^{1}H and ^{13}C NMR spectra of various 2-lithio-1,3-dithianes both substituted and unsubstituted in the 4- and 6- positions revealed the presence of two distinct types of species, one in THF and the other in HMPA [46]. While the species in the THF appears to involve substantial association between carbanion and cation, that in HMPA is a looser ion pair. The authors suggest that lithium-sulfur coordination and concomitant ion pairing are not required for the high stereo selectivities exhibited by such carbanions toward electrophiles.

^{1}H NMR spectra have been recorded for the following compounds prepared by metalation of appropriate precursors: 29 [47], 30 [48], 31 [49], 32 [50], 33 [50], 34 [51], and 35 [52]. Some comments about these anions seem appropriate. Thus, the previously unauthenticated 29 has been obtained by metalation of either



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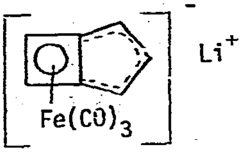

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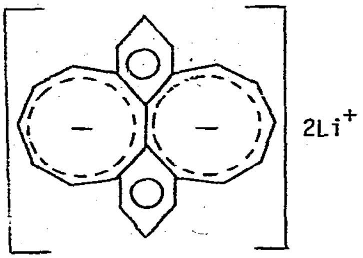

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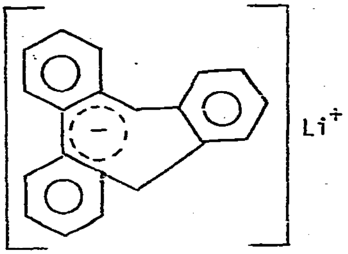

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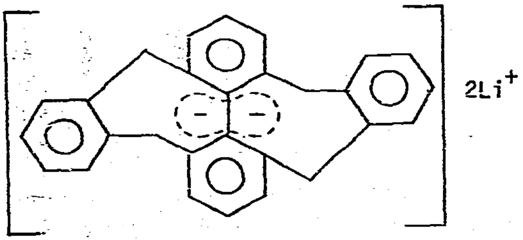

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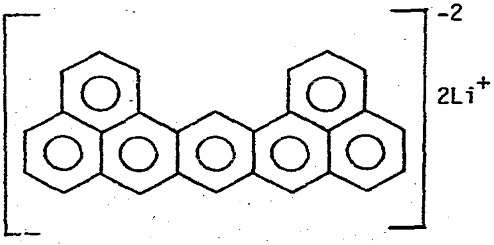

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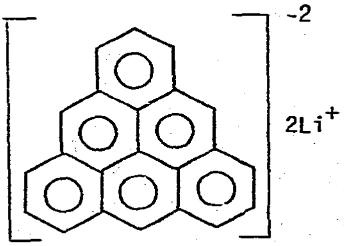


35

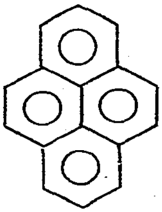
1,3,6-heptatriene or 1,6-heptadiene [47]. In contrast, metalation of 1,4-heptadiene gave trilithioheptatriene. Though the anion of uncomplexed 30 had only been obtained previously in dilute solution, the use of the transition metal complex allows the formation of the stable, spectroscopically observable species [48]. The potassium salt of 30 and of the corresponding trimethylphosphite substituted complex were also prepared. Dianion 31 represents the first derivative of the hitherto unknown nonalenide anion system [49]. Anions 32 and 33 are examples of benzannelated homopentadienyl and homopentalenyl systems, respectively [50]. In accordance with MO theory, 34 and a related dication have been prepared from a non-Kekulé even alternate dibenzo[de,jk]pentacenyl system by butyllithium and sulfuric acid-d_2, respectively [51]. Finally, 35 illustrates the first example of a triangulenyl dianion [52].

Other NMR studies have been concerned with the stoichiometry of lithium salts of several aldehyde dimethylhydrazones [53], the composition of lithium methylcuprates in ether solvents [54], the structure of indolyl-metal ion pairs in the ground state and the first excited state [55], and the ^{19}F NMR spectra of carbanions derived from polyfluorodiarylacetonitriles [56], perfluoro-9-phenylfluorene [57], and heptafluoronaphthyl-containing carbanions [58].

B. ESR, UV, and IR Spectroscopy

In the area of ESR spectroscopy, aromatic hydrocarbons, heteroaromatics, aldehydes, ketones, α-diketones, β-diketone enolates, quinones, sulfones, sulfoxides, nitro-, nitroso-, and azobenzenes, cyanides, and phosphine oxides have been converted to radical anions by reaction with n-butyllithium and Grignard reagents in the presence of transition metal systems such as nickel(II)acetylacetonate [59]. Well-resolved ESR spectra are obtained from the above compounds where the role of the transition metal is believed to mediate the transfer of one electron to the substrate and stabilize the radical anions.

The nature of ion pairing in systems derived from pyrene (36) [60] and perylene (37) [61] with alkali metals in various ethers have been studied by ESR spectroscopy. With both radical anions, loose ion pairs or free ions were observed with lithium, sodium, and potassium in DME and THF. Thermodynamic data for the dissociation of ion pairs into free ions are described for several metal-solvent combinations.



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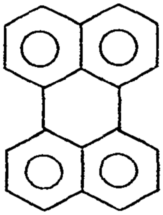
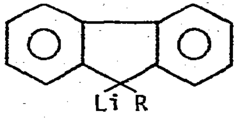


37

Also studied by ESR spectroscopy was the chelation of alkali metal cations by radical anions derived from 1,2,4,5-tetramesitoylbenzene [62], and the effect of complexation of radical anion pairs from dicarbonyl derivatives of dibenzo-18-crown-6 [63].

Turning to UV spectroscopy, spectra of several 9-substituted fluorenide ions have been recorded [64,65]. Thus, while the lithium salts (38) of fluorene, 9-methylfluorene, and 9-phenylfluorene are solvent separated ion pairs in DME, that of 9-methyoxycarbonylfluorene is an intimate one [64]. Lithio-9-cyanofluorene in DME also exists as an intimate ion pair. The reactivity of all of the above species with alkyl halides was determined.



38, R = $H, CH_3, C_6H_5, CO_2CH_3$, CN

UV spectroscopy was also employed to determine the thermodynamic acidities of a series of nitriles, esters, and ketones using 9-phenylfluorene as the standard acid [66]. In DME, the pKa values varied with replacement of lithium cation by cesium cation indicating the presence of intimate ion pairs involving intramolecular coordination. In contrast, with one exception, the acidity of the compounds in DMSO was virtually independent of the cation, presumably because ion pairs of such species are not formed in this solvent.

IR spectra of a variety of mono- and dialkali metal derivatives of three bis(cyanomethyl)arenes [67] and of 32 reduced α,β-diarylacrylonitriles [68] have been recorded. In the former cases, the monoanions exist as "free" carbanions in DMSO and in HMPA while in the latter ones, the initially obtained radical anions dimerize to dicarbanions.

C. Ion Cyclotron Resonance Spectroscopy

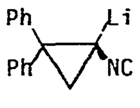
In an effort to elucidate the reasons why alkenyl organometallics prefer to adopt cis skeletal geometries, and the role of the metallic cations in such systems, the relative acidities of cis- and trans-2-butene have been measured using ICR spectroscopy [69]. The authors conclude that the preference for cis geometries of 1-methylallyl organometallics arises from differences in interaction energies among the allyl skeleton, the metal, and the solvent. Such preference is said to be not ascribable to the free anions.

ICR spectroscopy has also been employed to measure the acidities of aldehydes and ketones [70], the acid-base properties of a variety of substituted benzenes [71], the gas-phase acidities of alkanethiols [72], and the gas phase electron affinities of enolate radicals [73] and of allyl and cyanomethyl radicals [74]. This technique has also been used to determine the free energies of the proton transfer equilibria of CD_3NH^-, CD_3O^-, and CD_3S^- with their conjugate acids as part of a study investigating anionic hyperconjugation [75]. The authors conclude that a methyl group may donate or accept electronic charge depending upon the substituent to which it is attached.

Two other papers should be mentioned here since they deal with related topics. Thus, the extent of exchange of 32 carbanions with deuterium oxide in the gas phase has been determined using a flowing afterglow system [76]. Finally, an electrochemical technique has been employed to ascertain the basicities of benzyl, allyl, and propargyl anions [77].

5. STEREOCHEMICAL ASPECTS

The configurational stability of chiral isocyanocyclopropyl anion 39 has been studied [78]. In contrast to isomeric anion 40, 39 was found to be configurationally stable at -72°C even in the presence of adducts such as TMEDA, HMPA, and crown ethers or when the cation was changed from lithium to other alkali metals. Thus, 39 is capable of maintaining its configuration as a contact, solvent separated, or free ion pair. It is concluded that the isocyanide moiety stabilizes carbanions via an electron withdrawing inductive effect rather than by resonance. The results are compared with the open-chain analogue 41. Not only is 41 more difficult to metalate than 39 but the resulting anion 42 was racemized under all conditions employed.



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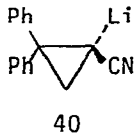

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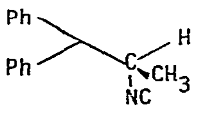

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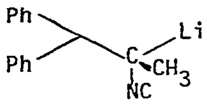
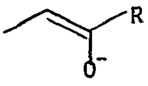


42

Complete kinetic stereoselection has been observed in the condensations of preformed lithium enolates with aldehydes [79]. Thus, provided R is bulky, Z-enolates (43) and E-enolates (44) with the electrophiles afford erythro (45) and threo (46) aldols, respectively. Opposite results can be realized by using the benzyltimethylammonium cation rather than lithium ion. Suggested transition states for the reactions are shown.



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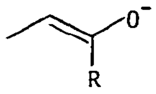

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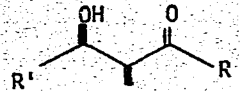

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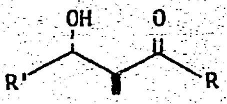
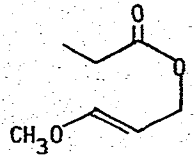


46

Aldol-type products have also been generated stereoselectively by an extension of the ester enolate Claisen rearrangement [80]. For example, lithiation and subsequent silylation of 47 in THF and in 23% HMPA-THF followed by heating gave 48 and 49 in ratios of 18/82 and 80/20, respectively. Other examples are shown.



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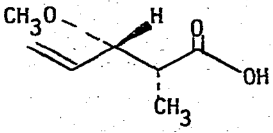

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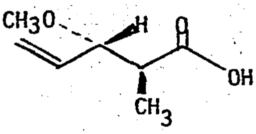
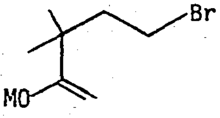


49

In accord with the hypothesis that 5-Endo-Trigonal alkylations are disfavored while 6-Endo-Trigonal alkylations are favored, enolate 50 (M = Li or K) has been found to cyclize to 51, not 52 [81]. In contrast, 53 cyclizes to 54, not 55. Another paper has discussed C-alkylations of ketones in terms of orbital control [82].



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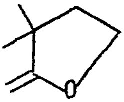

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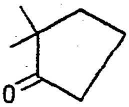

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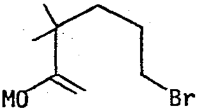

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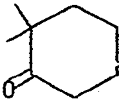

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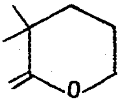
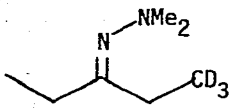


55

Metalation of ketone dimethylhydrazones has now been shown to occur by initial anti deprotonation to give anti anions which rearrange to the syn isomers [83]. The process is illustrated by the conversion of 56 to 57, then to 58. The clear kinetic preference for anti metalation is ascribed to the steric bulk of the dimethylamino group which blocks syn deprotonation. Attractive through-space non-bonded interaction is suggested to stabilize the syn but not the anti carbanions.



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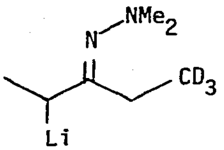

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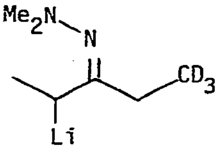
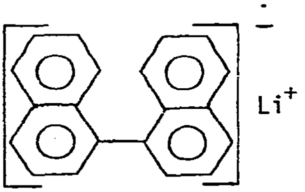


58

Direct experimental evidence has now been obtained to support the hypothesis that reactions of lithium anthracene with alkyl halides can proceed by both an SN_2 process as well as by single electron transfer [84]. That an SN_2 reaction also occurs was suggested by the fact that alkylation with optically active 2-octyl haides and mesylate occurs with a leaving group partial inversion of configuration. In an unrelated study, lithium 1,1'-binaphthyl (59) has been shown to undergo aminoalkylation by reagent 60 regio- and stereoselectively at the 4-position [85]. The reaction seems to occur via a flattened alkali metal radical anion.

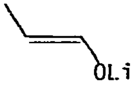


59

Me_2NCMe_2CN

60

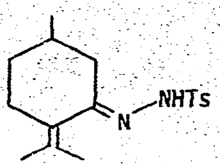
Stereochemical evidence has been described which indicates that vinylic radicals are intermediates in the conversion of vinyllithiums to lithium enolates by dioxygen [86]. Thus, for example, treatment of (E)-1-lithio-1-propene with O_2 at -78° gave enolates 61 and 62 as evidenced by acetylation. In contrast, reaction of the above carbanion with lithium t-butyl peroxide gave only (E)-enolate 61. Such retention of configuration precludes vinyl radical intermediates in the latter reaction. Similar results were obtained with other vinyl-lithium reagents.



61

62

The conversion of tosylhydrazones to olefins by organolithium reagents has been studied as a function of the stereochemistry of the hydrazone, the base, and the solvent [87]. Thus, while 63 and 64 both afforded only 65 with methyllithium in benzene, 63 gave 65 and 64 yielded mostly 66 with n-butyllithium in TMEDA. The mechanism of these transformations involving abstraction of α'- versus γ-hydrogen atoms is discussed.



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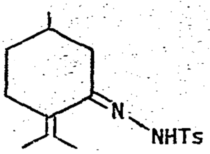

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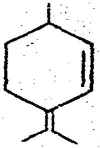

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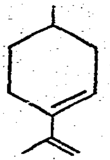
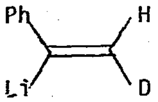


66

6. KINETICS

The kinetics of the equilibrium between 67 and 68 and related compounds have been measured using ^1H NMR spectroscopy [88]. The equilibrium was found to be 0.5 order in organometallic. This suggests that a key step in the reaction is deaggregation into two sub-units, probably a dimer into a monomer. Using lineshape analysis, it is further suggested that the monomer binds additional solvent molecules to give 69 so that a transition state such as 70 can energetically be reached. The above interpretation supports Curtin's earlier lateral shift mechanism which can not operate in a tighter less solvated ion pair.



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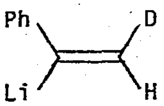

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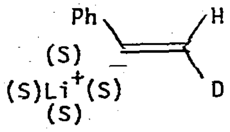
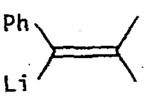


69

70

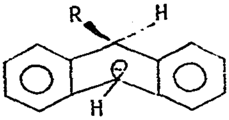
A second paper disclosed that vinyllithium reagents such as 71 do not invert but instead rearrange irreversibly to afford an allyl anion such as 72 [89]. This unprecedented rearrangement is also 0.5 order in 71 again suggesting a key deaggregation step. The rearrangement is intermolecular and a reactivity scale of vinyllithium reagents in transmetalations with β,β-dimethylstyrene has been discussed [90].



71

72

In an effort to reconcile previous inconsistent results in alkylations of 73, kinetic studies have been performed not only on 73 but also on diphenylmethyllithium [91]. The reactions are first order in both the anions and in the alkyl halides. It was noted that as the size of R was increased, the rate of the reactions decreased and the amount of cis product increased. While the rates are equal for 73 (R = H) and diphenylmethyllithium with primary alkyl halides, there is a larger decrease in the rate of reaction of the latter carbanion compared to 73 (R = H). Moreover, 73 and secondary alkyl halides afford mainly trans products. Schemes are discussed to rationalize the results.



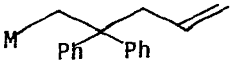
73

Alkylations of several ketone enolates by alkyl iodides, alkyl bromides, and allyl chloride in DMSO exhibit second order kinetics [92]. For alkyl chlorides though, a very rapid rate was observed over the first 20-30% of the reaction followed by a slower one which was first order in enolate but independent of the concentration of the halide. It is suggested that the enolates complex with lithium halide to afford a less active species.

The rates of monometalation of the propargylic positions of alkylphenylacetylenes [93] and of the reduction of benzophenone-1-^{14}C by lithium benzhydrate [94] have also been measured.

7. REARRANGEMENTS

Another in an excellent series of papers on the rearrangement of carbanions containing only carbon and hydrogen appeared in 1977 [95]. The current study involved carbanions 74 which rearranged by allyl migration to 75 (M = Li) in THF at 0° and by phenyl migration to 76 (M = K, Cs) in THF at -75°. When 74 was labeled with ^{14}C at the C-3 position, 75 was obtained with ^{14}C at the terminal C-5 position (inversion) at lower temperatures and in the presence of potassium t-butoxide and 18-crown-6. In contrast, ^{14}C was scrambled between the C-3 and C-5 positions of 75 when labeled 74 was rearranged at higher temperature. It is suggested that 75 is obtained via loose ion pairs either by a [2,3]-sigmatropic rearrangement (inversion of ^{14}C) or by dissociation-recombination (scrambling of ^{14}C). On the other hand, 76 probably arises via a tight ion pair through a [1,2]-sigmatropic process.



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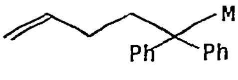

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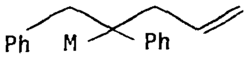
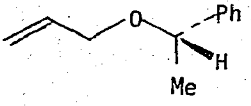


76

Chiral allylether 77 has been subjected to the [1,2]- and [1,4]-Wittig rearrangement by n-butyllithium and the resulting alkoxide intermediates reduced to their corresponding alcohols 78-80 [96]. That the extent of racemization is similar (30±5%) for the [1,2]-products 78 and 79 and for the [1,4]-product 80 suggests that both rearrangements are occurring via a non-concerted radical mechanism involving 81 and 82. The results are compared with an earlier described Stevens rearrangement of an analogous chiral ammonium salt. In another paper, that CIDNP is not observed in the products of the Wittig rearrangement of ethers is postulated to be due to the formation of large aggregates in solution which have short relaxation times [97]. Certain by-products in this study, though, did exhibit such polarization. For example, polarized methane was observed in the rearrangement of 3-methoxy-1-butene.



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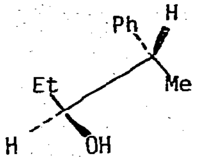

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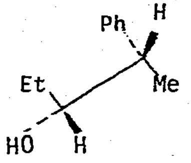

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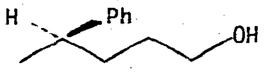

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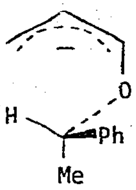

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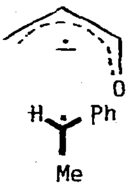
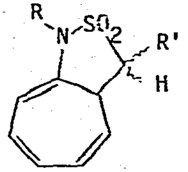


82

Both cis- and trans-γ-sultames 83 (R = H, Me, Et, Ph) are converted by n-butyllithium to carbanions 84 which rearrange to sulfonamides 85 at 25° [98]. It is postulated that the anions undergo thermally allowed disrotatory ring closure to a norcaradiene intermediate. The cis isomers of 83 are isomerized to an equilbrium mixture of 85-90% trans 83 without rearrangement provided the temperature is maintained at -78°.



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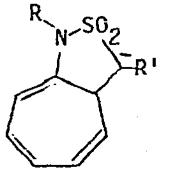

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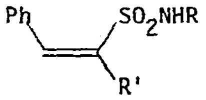
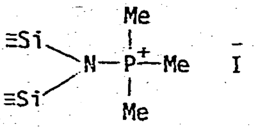


85

The conversion of 86 to 87 by n-butyllithium represents the first example of a facile migration of a silyl substituent from nitrogen to carbon [99].



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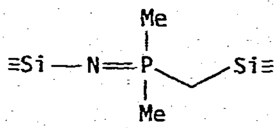
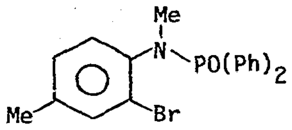


87

Finally, [1,3]-rearrangement of 88-90 to 91-93, respectively have been effected by n-butyllithium in THF at low temperatures [100].



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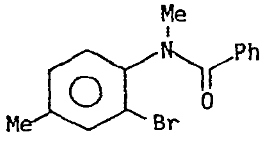

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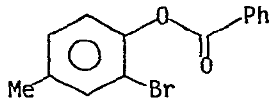

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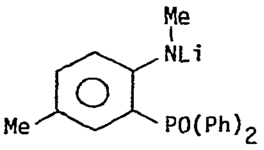

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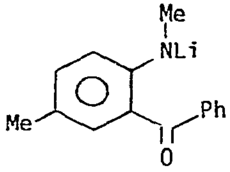

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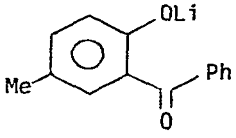


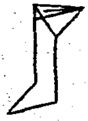
93

8. OTHER PHYSICAL-ORGANIC CHEMISTRY

Two papers discussed enthalpies of organolithiums. First, the enthalpies of interaction of n-butyl-, ethyl-, isopropyl-, t-butyl-, and trimethylsilyllithiums with several ethers, tetrahydrothiophene, triethylamine, and triethylphosphine were measured by high dilution calorimetry [101]. The order of basicities was found to be independent of the organolithium. With the exception of t-butyllithium, larger enthalpies were observed for tetrameric than for hexameric species. More sensitivity to the steric requirements of THF and 2-methyl and 2,5-dimethyl derivatives was observed with hexameric n-butyllithium than with tetrameric trimethylsilyl or isopropyllithium.

In the second paper, the enthalpies of protonation in ether (and the values in kcal/mol observed) of the isomeric allyl- (-50.9±1.3), trans-1-propenyl (-52.0±0.5), and 2-propenyllithiums (-66.7±2.5) as well as those of phenyl- (-59.0±0.8) and ethyllithium (-64.6±1.3) have been measured [102]. The data are discussed in terms of the aggregation of such compounds. The authors conclude: "Clearly, meaningful enthalpic comparison of isomers should be limited to cases in which associations are similar."

Two papers described chemistry of organolithiums involving elimination-addition mechanisms. Thus, evidence has been presented to suggest the presence of short-lived bicyclo[1.1.0]but-1(3)-ene 94 in the reaction of 95 with several organolithium reagents to afford 96 in high yields [103]. Other mechanistic pathways leading to 96 are considered but rejected. In the other paper, additional evidence for the earlier suggested formation of butalene has been provided by the conversion of 97 to 98 and the corresponding m-derivative by lithium diethylamide in diethylamine-d_1 [104]. The current reaction is thought to proceed via butalene derivative 99.



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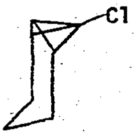

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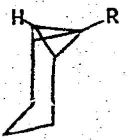

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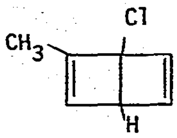

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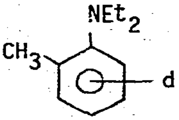

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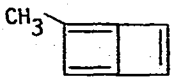
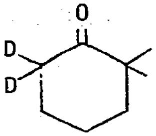


99

Potentiometry has been employed to determine the temperature dependence of the difference between the first and second redox potentials of perylene radical anions [105]. The data lead to ΔG° and thus ΔH° and ΔS° of the disproportiona tion of these species to hydrocarbon and dianion. A rather dramatic metallic cation effect is observed particularly with sodium ion.

Other papers that deserve mention include the disproportionation of saturated alkali metal ketyls derived from 100 to afford enolates and alcoholates [106], single electron transfer in the alkylations of dialkali anil 101 [107], and free radical intermediates in certain alkylations of lithium trimethyltin and $CpFe(CO)_2Na$ [108].



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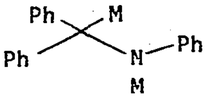
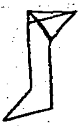


101

9. PREPARATION OF CARBANIONS

A. Metalation at sp^3 Carbon

Tricycloheptane 102 has been metalated by n-butyllithium in ether to afford 103 (G = Li) [109]. This species, in turn, has been condensed with a variety of electrophiles to give 103 in which G is SMe, SeMe, $ArSO_2$, NC, Cl, and others.



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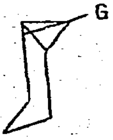
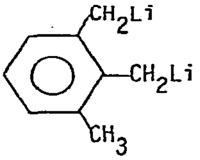


103

The selectivity of the polymetalation of tri- and tetramethylbenzenes has been studied [110]. For example, in addition to monolithiated products, 1,2,3-trimethylbenzene with n-butyllithium·TMEDA and n-butyllithium·potassium t-butoxide gave 104 and 105, respectively, as evidenced by silylation with chlorotrimethylsilane. Similar results were realized with 1,2,4-trimethyl-, 1,2,3,5-tetramethyl-, and 1,2,4,5-tetramethylbenzenes. Interestingly, while metalation of p-xylene with butyllithium·TMEDA was earlier reported to afford gem-dilithio species 106, the use of the mixed reagent n-butyllithium·potassium t-butoxide is now reported to yield 107.



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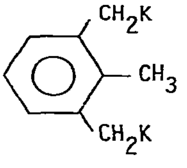

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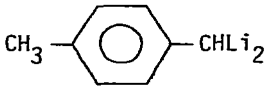

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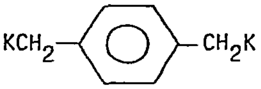
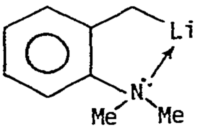


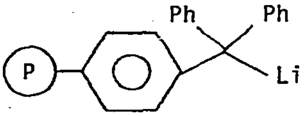
107

A new chelated C,N-benzyllithium reagent 108 has been synthesized from N,N-dimethyl-o-toluidine and n-butyllithium [111]. Compound 108 has been condensed with a variety of transition metal halides.



108

Polymeric triphenylmethyllithium (109) has been prepared from polymeric triphenylmethane and methyl- or n-butyllithium [112]. The reagent has been successfully employed in "wolf and lamb" reactions; for example, 109, 110, and acetophenone give dibenzoylmethane in a yield of 96%.



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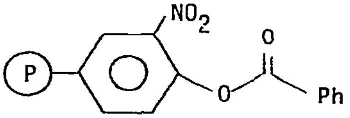
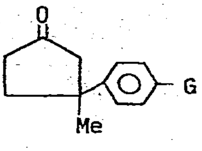


110

Benzylic-type carbanions were also studied in the stereospecific lithiation of certain ferrocenophanes [113], and in the preparation of stibatriptycene and the related arsenic-containing compound [114].

Remote β-aryl groups have been found capable of directing the regiochemistry of enolate formation of substituted cyclopentanones [115]. For example, 111

(G = OMe), LDIPA, and chlorotrimethylsilane afford 112 and 113 in a ratio of 7.4/1.0. In contrast, the same reaction with G = NO_2 gives 112 and 113 in a ratio of 0.9/1.0. The results are ascribed to complex formation between the π-electrons of the aryl rings and the lithium cations as depicted in 114. Related to the above, β-aryl groups on enolates direct subsequent alkylations cis to themselves with essentially no epimerization to the more stable trans isomer [116]. For example, 2-cyclopentenone, lithium diphenylcuprate, and allyl bromide yield 115 (67%) and 116 (5%). Other π-electron moieties such as β-allyl and β-vinyl groups do not direct α-alkylations cis to themselves.



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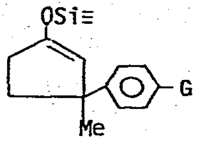

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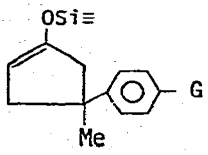

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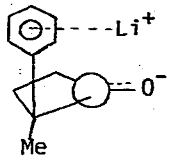

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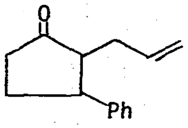

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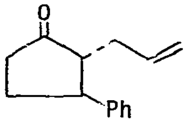
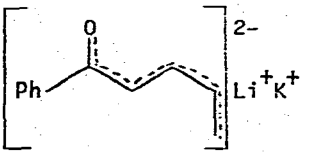
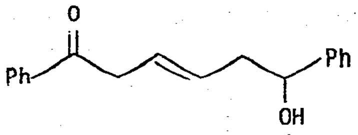


116

Allylacetophenone has been doubly metalated by potassium hydride followed by s-butyllithium to afford 117, an umpolung reagent which reacts with electrophiles at the terminal carbon [117]. For example, 117 and benzaldehyde give 118.

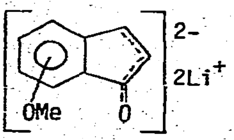


117



118

6-Methoxy-1-indanone has likewise been converted to dianion 119 by LDIPA [118]. This homoenolate undergoes alkylation in the 3-position to afford 120.



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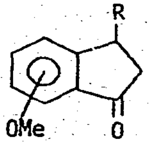
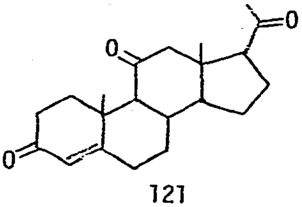


120

Selective enolate formation of polycarbonyl-containing compounds provides protection against reduction by lithium aluminum hydride [119]. Carbonyls not so enolized are selectively reduced as illustrated by the conversion of 121-122.



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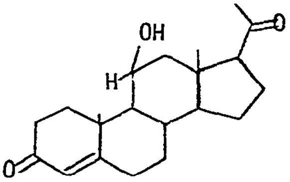
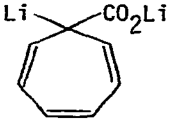
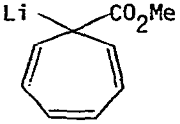


122

Several 7-lithio derivatives (123-125) of cycloheptatriene-7-carboxylic acid systems have been prepared by metalation of the parent active hydrogen compounds, then condensed with various electrophiles [120].



123



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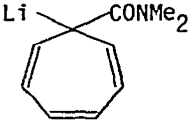
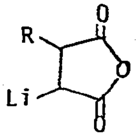
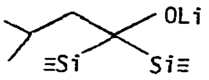


125

The lithium enolate 126 derived from succinic anhydride and pentoxide 127 has been successfully condensed with aldehydes [121]. Hydrolysis and treatment with diazomethane gives lactones such as 128 by ring-opening of the anhydride and recyclization of the hydroxydiacid.



126



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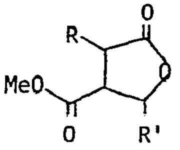
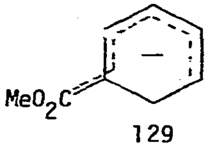


128

Enolates 129 have been obtained from dihydroaromatic esters such as 130 using LDIPA on the active hydrogen compound at -78° [122]. Attempted metalation on the corresponding carboxylic acid afforded only benzoic acid. Condensations of 129 to afford 131 are discussed.



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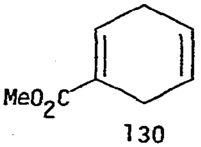

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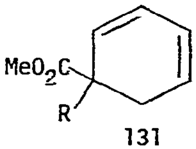
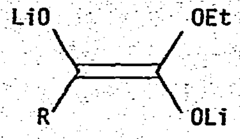


131

α-Hydroxyesters and α-mercaptoesters have been converted to dianions 132 and 133, respectively, by LDIPA at -78° [123,124]. While 132 reacts with alkyl halides and ketones at carbon only, 133 reacts with the former reagents at both carbon and sulfur. Reagent 133 also condenses with ketones to give α,β-unsaturated esters.



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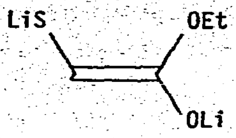
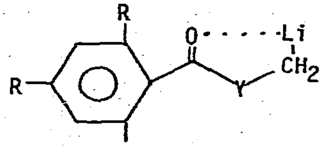


133

Additional examples of dipole-stabilized carbanions appeared in 1977. Thus, metalation of parent compounds with s-butyllithium·TMEDA or n-butyllithium gave 134 (Y = O, NMe, S) which were combined with a variety of electrophiles to afford 135 in fair to excellent yields [125,126]. The latter condensations are to be contrasted with earlier reports of such carbanions without large R groups which underwent self-condensation. Dipole stabilized N-lithiomethyl succinimides have also been described [127].



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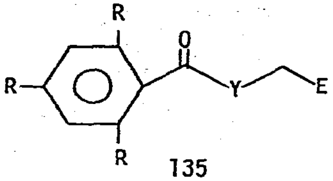
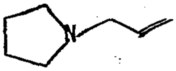


135

Allyl dialkylamine 136 has been converted to 137 by s-butyllithium at -10°; 137 is a new homoenolate [128]. Though this species reacts with alkyl halides exclusively at the γ-position to give 138, it combines with aldehydes and ketones at both the α- and γ-carbon atoms to yield a mixture of alcohols. α-Attack in the latter condensations is strongly favored when the cation is changed from lithium to zinc.



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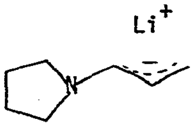

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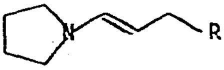
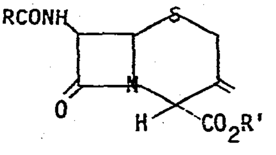


138

The conversion of cephalosporin 139 to 140 by lithium methoxide and t-butyl hypochlorite has been ascribed to activation of the usually inert 3-exo-methylene by conversion to an allylic anion [129].



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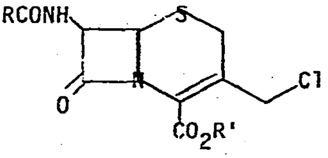
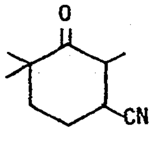
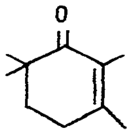


140

Dilithio salts of β-ketonitriles have been synthesized from the parent compounds and LDIPA, then monoalkylated alpha to the cyano moiety [130]. Elimination of cyanide completes the synthonic process of β-alkylation of α,β-unsaturated ketones. The process is illustrated by methylation of 141 to afford 142 (75%).

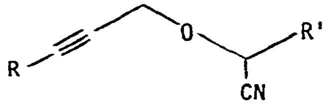


141



142

Methylation of cyanoethers such as 143 by two equivalents of LDIPA at -78° has been shown to give pure α-allenic ketones 144 via [2.3]-sigmatropic rearrangements [131]. Similar rearrangements of the related allylic systems give γ-ketoaldehydes, γ-diketones, or β,γ-unsaturated ketones [132, 133].



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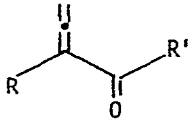
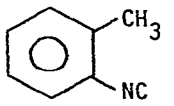


144

An efficient synthesis of indole has been realized by metalation of 145 with LDIPA to afford 146 which cyclized spontaneously at 25° [134]. Alternatively, 145 has been condensed with electrophiles to give 147 at -78°. Subsequent metalation and cyclization represents a convenient synthesis of 3-alkylindoles.



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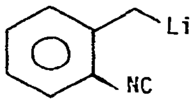
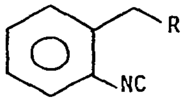
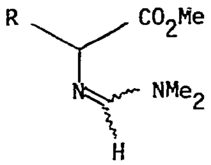


146



147

Two iminoester derivatives, 148 [135] and 149 [136], have been metalated by LDIPA. Subsequent alkylation and hydrolysis conveniently affords alkylated amino acids. Also studied were metalations of imines 150 [137] and 151 [138].



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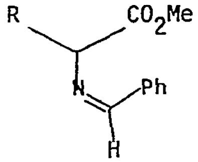

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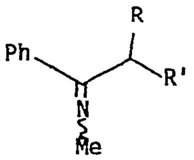

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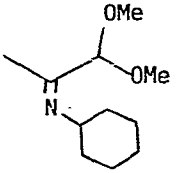
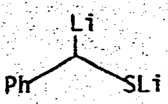
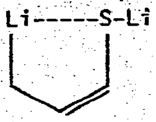


151

A full paper appeared in 1977 which describes the dimetalation of benzyl- and allylmercaptan by n-butyllithium·TMEDA to give 152 and 153, respectively [139]. Subsequent condensations with electrophiles are realized on both carbon and on sulfur. For example, 152, dimethyldisulfide, and benzyl bromide yield 154. Similar results are realized with 153, though it preferentially reacts at the γ- rather than at the α-position.



152



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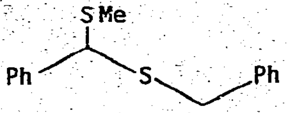
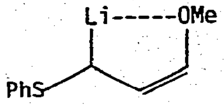


154

Lithiation of 3-methoxy-1-phenylthio-1-propene by LDIPA has afforded 155, a β-formylvinyl anion equivalent [140]. Alkylations with a variety of alkyl halide have given mixtures of 156 and 157 in which the former product predominates.



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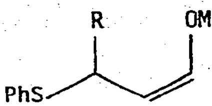

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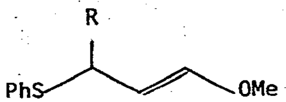
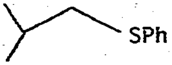


157

Higher homologs of methyl phenyl sulfide have now been successfully metalate by t-butyllithium in THF·HMPA at -78° [141]. For example, 158 has been converted to 159 which was condensed with 11 different electrophiles. Other carbanions similarly generated alpha to a sulfur have included 160 [142], 161 [143], 162 [144], and 163 [145].



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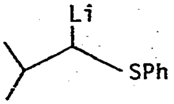

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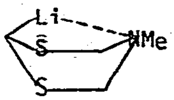

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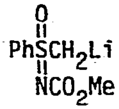

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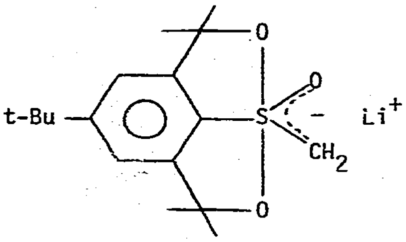

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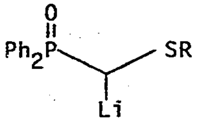
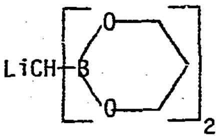
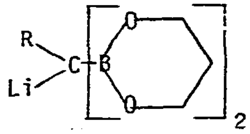


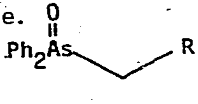
163

gem-Diboronic esters have been metalated by LiTMP to afford 164 and 165 [146]. Alkylations of 164 afford aldehydes; for example, 164 and n-butyl iodide give pentanal (86%). In contrast, 165 and esters $R'CO_2CH_3$ yield ketones $R'COCH_2R$


164


165

Arsine oxides 166 have been converted to lithium derivatives by LDIPA, then condensed with electrophiles to afford 167 [147]. The latter compounds can be transformed to 168 by LAH and halogens, and to 169 by LAH, bromine, and a nucleophile.



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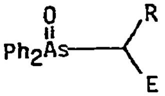

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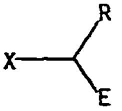

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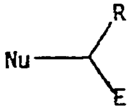
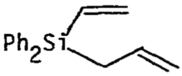


169

Allylvinylsilane 170 has been found to undergo metalation to give 171 and addition to afford 172 by methyllithium·TMEDA and n-butyllithium·TMEDA, respectively [148]. Both 171 and 172 were condensed with several chlorosilanes.



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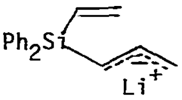
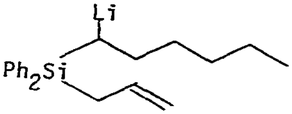
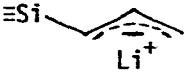


171

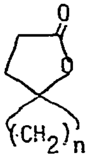


172

In contrast to the above, interaction of allyltrimethylsilane with n-butyllithium in THF at -78° gave metalated intermediate 173, a new β-acylcarbanion equivalent [149]. Subsequent condensations with cyclic ketones afforded spirolactones illustrated by 174.

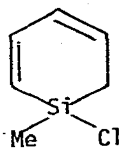


173



174

Treatment of 175 with lithiohexamethyldisilazane in the presence of perfluoro-2-butyne to give 176 is believed to have proceeded via silabenzene 177 [150]. Attempts to trap intermediate 178 using a large excess of chloromethylsilane have been unsuccessful.



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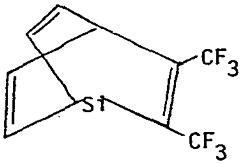
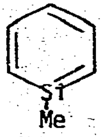
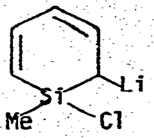


176



177

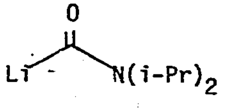


178

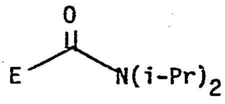
B. Metalation at sp^2 Carbon

Reactive positions toward lithiation of aromatic compounds have been identified by using $^{13}C-^1H$ coupling constants as selectivity parameters [151]. Correct predictions are made when differences of coupling constants > 5 Hz. If hetero-substituents are absent, correct predictions are also made for differences of 2 - 5 Hz. For example, $J^{13}C-^1H/Hz$ for the 3-, 4- and 5-carbon atoms of 2-methylfuran are 174, 173, and 199, respectively. In agreement with the above, this compound is metalated by n-butyllithium at the 5-carbon atom.

Optimum conditions have been established for the formation of 179 by metalation of N,N-diisopropylformamide by using t-butyllithium in ether/THF/pentane at -95° [152]. Subsequent condensations with electrophiles to afford 180 are described.

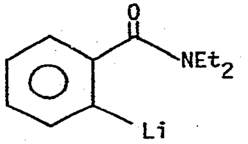


179

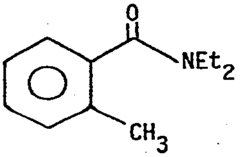


180

o-Metalation of N,N-diethylbenzamide by s-butyllithium·TMEDA has been accomplished at -78° [153]. The resulting organometallic (181) and related ones possessing m- and p-substituents have been combined with electrophiles in fair to excellent yield. For example, methyl iodide gives 182 (75%).

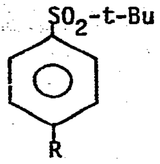


181



182

Sulfones 183 (R = H or Me) have apparently been o-metalated by organolithiums to afford dilithio derivatives 184 which, under the conditions of the reaction, eliminate alkylsulfinate ion to yield benzynes 185 [154]. That benzynes 185 are intermediates in the above lithiations was confirmed by the preparation of 184 from the 2,6-dibromosulfones and n-butyllithium at low temperature followed by carbonation. A temperature increase in the latter transformations before carbonation likewise gave benzynes 185.



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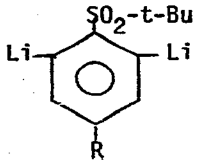

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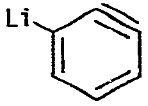
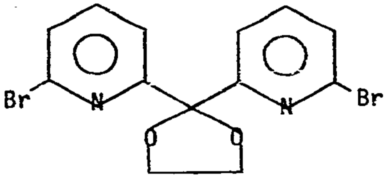
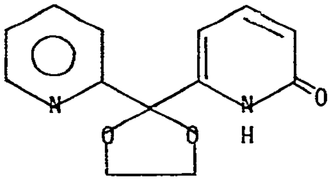


185

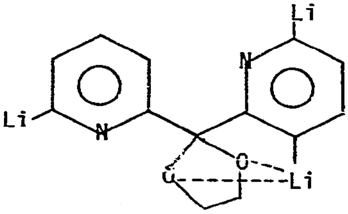
Reaction of 186 with n-butyllithium at -40° to ultimately afford pyridone 187 has been shown to proceed via selective metalation of the 3-position of the pyridine ring [155]. Deuteration experiments support the intermediacy of 188.



186

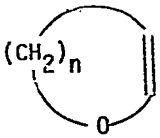


187

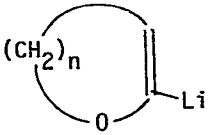


188

In the area of vinyl ethers, cyclic systems 189 (n = 1, 2) have been converted to 190 by alkyllithiums in THF [156, 157]. That 190 was present was confirmed by nmr and by subsequent condensations with electrophiles.

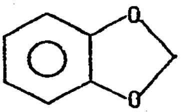


189



190

The site of metalation of 191 - 193 by n-butyllithium has been determined by carbonations [158]. Thus, while 191 and 193 undergo aromatic ring metalation ortho to oxygen, 192 is converted to the α-methylene lithium derivative.



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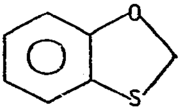
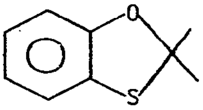


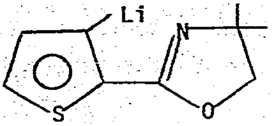
192



193

A full paper appeared describing a wide variety of conditions used to prepare dilithio derivatives of furan, thiophene, N-methylpyrrole and others [159]. Directions are provided to prepare the 2,5-dilithio derivatives of furan and thiophene in nearly quantitative yields.

Other lithiations have been effected on parent heterocycles to give thienyloxazoline 194 [160], tetrathiafulvalene 195 [161], and dithiin 196 [162].



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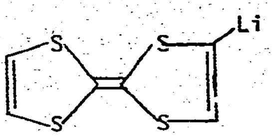

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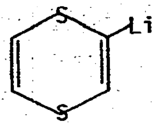
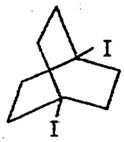


196

C. Lithium-Halogen Exchange

Certain diiobicyclooctanes have been reacted with t-butyllithium to afford [2.2.2]- and [3.2.1]propellanes [163]. For example, 197 gave a mixture of 193 and 199 which were trapped by molecular bromine. Reactions of dihalonorbornanes are also discussed.



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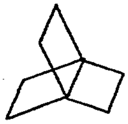

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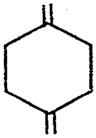
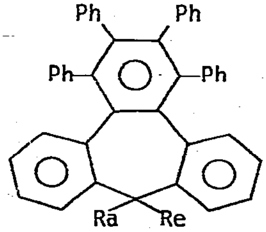


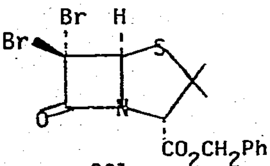
199

Quasi-axial hydrogen and chlorine atoms of 200 have been converted to quasi-axial lithium reagents [164]. Such systems do not equilibrate with the quasi-equatorial isomers except when Re = methyl.



200

Enolates have been prepared from several 6α-halopenicillanates and related compounds using n-butyllithium or methylmagnesium bromide [165]. The process is illustrated by the conversion of 201 to 202. The enolates have been condensed with acetaldehyde to give diastereoisomers.



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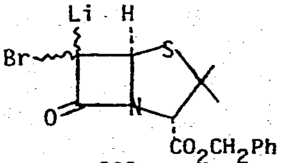
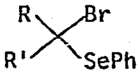


202

Other aliphatic carbon-halogen systems subjected to metal-halogen exchange included 203 (R,R' = H, CH_3, n-C_6H_{12}) to give 204 [166] and 205 (R = a phosphorous ester or tosylate) to afford 206 [167]. The latter material upon heating is postulated to yield a silaethene.



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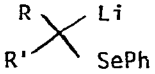

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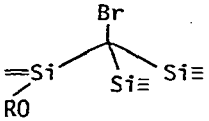

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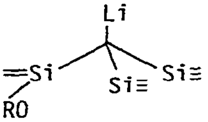
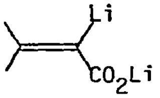


206

2-Bromo-3-methyl-2-butenoic acid and n-butyllithium at -100° gave 207, a species sufficiently stable to condense with electrophiles in fair to good yields [168]. Side-products derived from allyl- rather than vinyllithium reagents are ascribed to the presence of trianion 208. β-Lithioenamines 209 [169] and silylvinyllithium 210 [170] have been similarly prepared from their corresponding vinylbromides.



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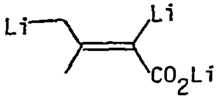

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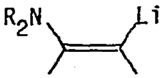

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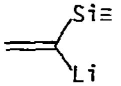
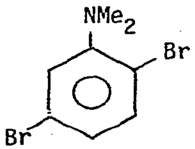
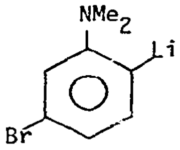


210

Selective lithium-bromine exchange of 2,5-dibromobenzenes and 2,5-dibromopyridine appear to be directed by coordination of the lithium with ring substituents where the products are those determined by thermodynamic control [171]. The process is illustrated by the conversion of 211 to 212.

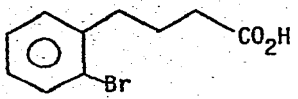


211



212

An anionic equivalent of the Friedel-Crafts cycloacylation has been described [172]. Among the several examples listed, 213 with organolithium reagents affords 214 (73%). In contrast, 215 gives rearranged product 216 apparently via 217 and 218. Such a rearrangement should be compared to related ones described earlier [100].



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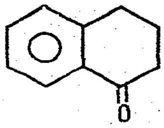

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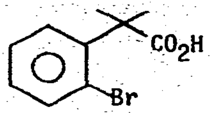

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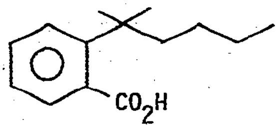

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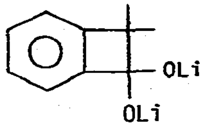
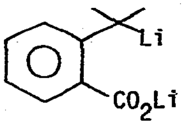
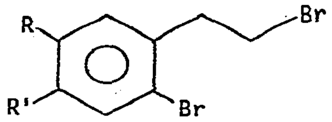


217

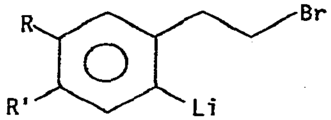


218

Other cyclizations have been realized by selectively converting the arylbromide of dibromo compounds 219 to 220 [173, 174]. The latter reagents have been condensed with benzonitrile and the intermediate N-lithio salts cyclized to 3,4-dihydro-1-phenylisoquinolines [173]. In contrast, allowing solutions of 220 to warm in the absence of co-reagents causes cyclizations to benzocyclobutenes [174].



219



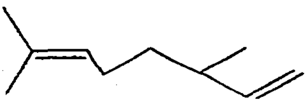
220

Other studies in this area have been concerned with lithium-bromine exchange of 2,7-dibromonaphthalene [175] and ring-opening reactions of 3-thienyllithiums derived from 3-iodothiophenes and phenyllithium [176].

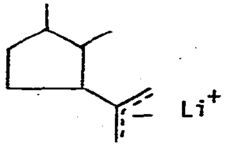
10. ADDITION AND SUBSTITUTION REACTIONS

A. Alkyl-, Aryl-, Allyl-, and Vinyllithiums

Cyclization of diene 221by n-butyllithium to afford 222 represents a novel polar equivalent of the ene reaction [177]. Subsequent protonation gives the corresponding isoprenylcyclopentane.

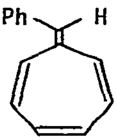


221



222

n-Butyllithium has been found to add to heptafulvene 223 by both a 1,8- and a 1,6-addition mode to give 224 and 225, respectively [178]. The related 8,8-diphenyl system undergoes a similar 1,6-addition accompanied by a less important 1,2-addition on the 7-membered ring. In contrast, both fulvenes are protonated at the exocyclic methylene carbon.



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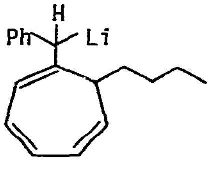

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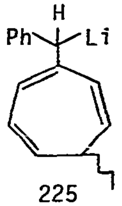
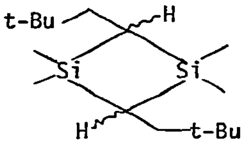


225

The condensation of t-butyllithium with dimethylvinylsilane has afforded Z- and E-1,3-disilacylclobutanes 226 in high yield rather than the expected t-butyldimethylvinylsilane [179]. Since efforts to trap intermediate 227 failed, it is suggested that the reaction may involve 228 leading to a silaethylene, dimerization of which should give 226.



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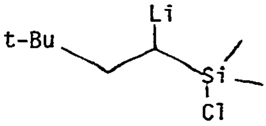
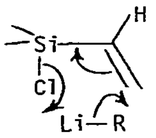
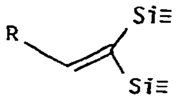


227

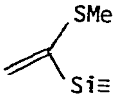


228

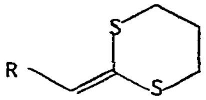
A full paper appeared which described the addition of a variety of alkyllithiums to olefins 229-232 [180]. Subsequent condensations with electrophiles are discussed.



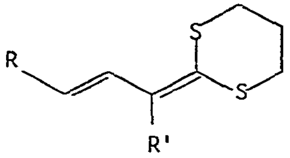
229
(R=H,Ph)



230

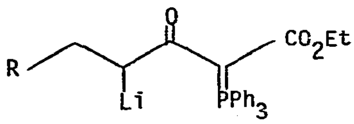


231
(R=H,Ph)

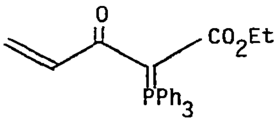


232

Conjugate addition products such as 233 have been realized in reactions of alkyllithiums with α,β-unsaturated systems such as 234 [181]. The phosphorane derivative effectively precludes 1,2-addtion because of its charge density. Subsequent alkylation of 233 followed by conversion of the acyl phosphorane to esters conveniently gives highly substituted carboxylic acid derivatives.

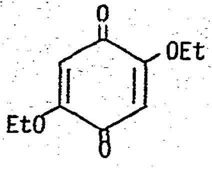


233

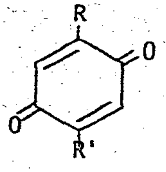


234

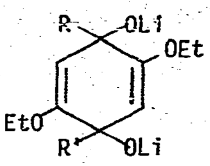
2,5-Diethoxy- and 2,5-dichloro-1,4-benzoquinones have been alkylated, alkynylated and arylated at the 2-5 positions by organolithiums [182]. The reactions which occur by 1,2-addition to the carbonyl groups are illustrated by the transformation of 235 to 236 via 237. The conversion of 237 to 236 is effected by sulfuric acid in glyme.



235

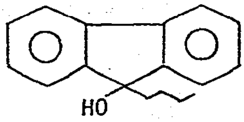


236

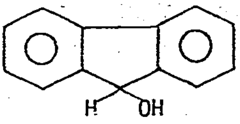


237

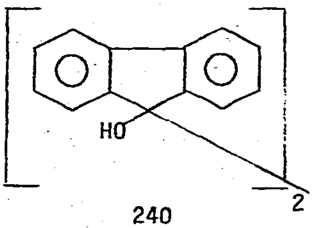
Iron-sulfur cluster $[Fe_4S_4(SPh)_4]^{-2}[n\text{-}Bu_4N]_2^+$ has been shown to function as an electron-transfer agent in reactions of fluorenone with n-butyllithium [183]. Thus, while only alcohol 238 is obtained in the absence of the cluster, reduced products 239 and 240 are realized in its presence.



238



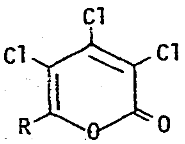
239



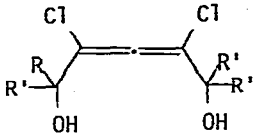
240

One other paper involving addition of alkyllithiums to ketones deserves mention. A simple, effective method for alkylative 1,3-carbonyl transposition has been realized by adding organolithiums in a 1,2-fashion to α,β-unsaturated ketones followed by oxidation with pyridinium chlorochromate [184].

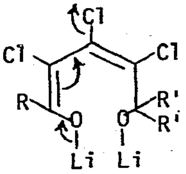
Pyrones 241 undergo ring-cleavage reactions with organolithiums (R = R' = aliphatic or aromatic) to afford 242 [185]. 1,2-Addition products 243 are presumably intermediates in these transformations.



241

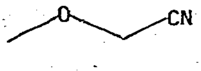


242

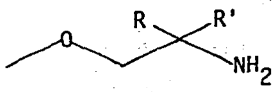


243

Cyanoethers such as 244 have been condensed with Grignard reagents (RMgX) followed by organolithiums (R'Li) to give mixtures of ketones R'COR and amines 245 [186]. Ketones appear to be favored with more bulky Grignard reactions such as isopropylmagnesium bromide.

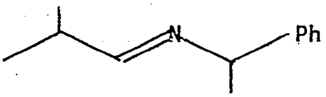


244

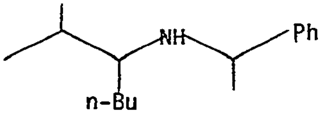


245

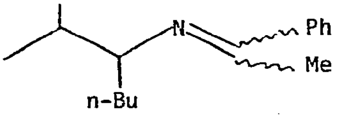
n-Butyllithium has been reacted with several imines to yield mixtures of products, some of which must arise from loss of lithium hydride from N-lithio intermediates [187]. For example, 246 affords 247 (59%), 248 (14%), and 249 (10%).



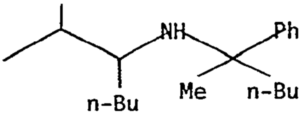
246



247

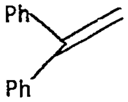


248

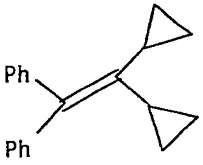


249

Hydride abstractions from other organolithium reagents have also been effected by triphenylmethyl tetrafluoroborate and certain trialkylboranes [188, 189]. For example, 1,1-diphenyl-1-hexyllithium and the above salt afford 1,1-diphenyl-1-hexene (65%) [188]. Another example is provided by the two-fold sequential treatment of 250 with cyclopropyllithium-triphenylborane to give 251 (61%) [189].

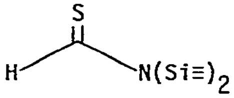


250

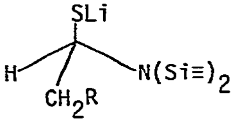


251

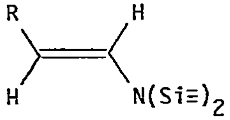
Thioformamides 252 have been condensed with RCH_2Li to yield 253 which arise by carbophilic addition [190]. Subsequent silylation of 253 with chlorotrimethylsilane affords silylated enamines 254.



252



253



254

n-Butyl, s-butyl-, and ethyllithium have been reacted with trifyl source 255 to give triflones 256 [191]. In contrast, methyl-, t-butyllithium, and others failed to undergo such condensations.

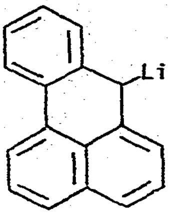
$PhN(SO_2CF_3)_2$

255

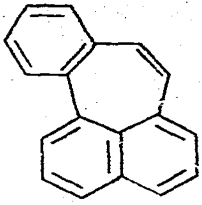
RSO_2CF_3

256

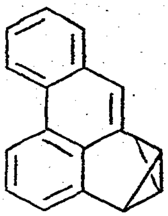
Organolithium reagent 257 has been reacted with chlorocarbene to afford 258 and 259 [192]. The reaction is interesting because more than one site of the anion is attacked by the carbene.



257

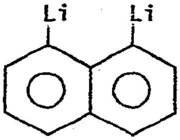


258



259

1,8-Dilithionaphthalene (260) has been condensed with sulfur, selenium, and/or tellurium to give 261 [193, 194]. The M and M' in 261 are the same or different chalogens.



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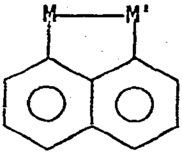

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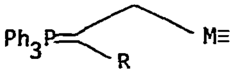
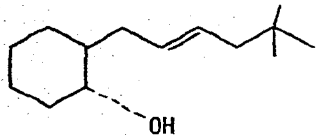
Other papers involving the use of aryllithiums included thiophile addition of phenyllithium to thioketone-S-oxides to afford α,β-unsaturated sulfoxides [195], the stability of dilithium salts derived from organolithiums and carboxylic acids [196], and the decomposition and byproducts from reactions involving pentafluorophenyllithium [197].

Ylides 262 (R = H:M = Si, Sn; R = CH_3, M = Si) have been synthesized from the corresponding phosphonium iodides and organolithium reagents such as LDIPA, then condensed with aldehydes and ketones to give allylic silanes and stannanes [198]. The latter compounds have been converted by methyllithium to allyllithium reagents, the chemistry of which is illustrated by numerous examples all in excellent yields.



262

In a stereochemical study, neopentylallyllithium has been condensed with cis- and trans-2,3-epoxybutane and with cyclohexene oxide in pentane and in THF [199]. For example, the latter epoxide gave 263-265 where the amount of 263 was greater in THF than in pentane. It should be noted that both "normal" and "rearranged" products arise via trans additions of the organolithiums to the epoxide.



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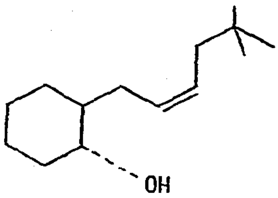

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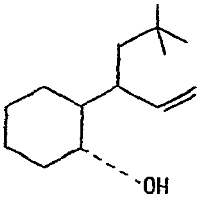
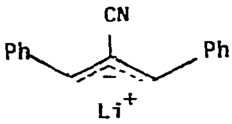


265

The stereochemistry of the products derived from the [3+2]cycloaddition of 266 with trans-silbene has now been determined [200]. Of the ten possible diastereomeric 2,3,4,5-tetraphenylcyclopentane-1-carbonitriles, only 267 and 268 are observed. The authors discuss the mechanism of the transformation in terms of concerted versus stepwise pathways.



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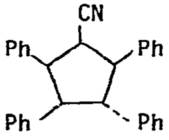

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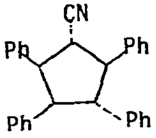
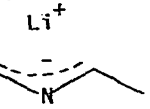


268

Eight more papers appeared in 1977 which discussed the preparation and reactions of azallyllithium reagents. The most widely studied compound of this class of reagents has been trans,trans-1,3-diphenyl-2-azaallyllithium (269), prepared by metalation of 270 or by ring opening of 271. Compound 269 has been condensed with acenaphthalene [201], phenylisocyanate and related heterocumulenes [202], 1,3-dienes [203], vinylsulfides and related selenides, phosphines, arsines, and silanes [204], and acetylenes [205] to afford cycloadducts. Similar chemistry has been reported for 272 [206], 273 where G = $SiPh_3$ and $P(O)Ph_2$ [207], and 274 [208].



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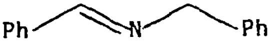

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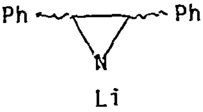

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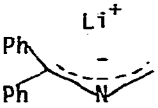

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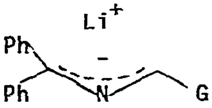

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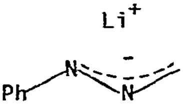
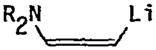


274

Also studied in 1977 were addition reactions of allyllithium reagents with conjugated enynes and diynes [209, 210], and condensations of 275 and 276 with aldehydes and ketones to give α,β-unsaturated aldehydes [211, 212].

275

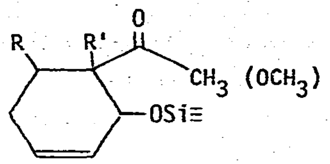


276

B. Carbanions Stabilized by Carbonyls

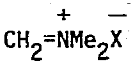
Dienolate anion 277, generated from the corresponding enol silyl ethers and n-butyllithium, has been found to react at its γ-carbon atom with α,β-unsaturated ketones and esters to afford cyclic products 278 [213]. This new annelation reaction is successful provided the cyclic alkoxides are trapped with chlorotrimethylsilane.

277



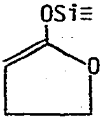
278

Mannich reactions have now been effected on preformed carbanions by the use of methylene ammonium trifluoroacetate 279 [214] and the corresponding iodide [215, 216]. The process is illustrated by the conversion of 280 to 281 (63%). Enolates derived from ketones, aldehydes, and acids behave similarly.



$CH_2=\overset{+}{N}Me_2\overset{-}{X}$

279



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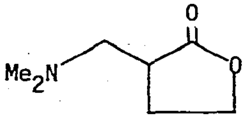
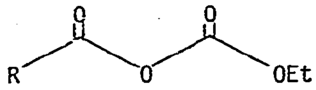


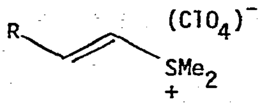
281

Improvements in the yields of β-diketones derived from enolates and acylating agents have been realized by using mixed anhydrides 282 [217] or acid chlorides [218]. The former method has also been applied to the preparation of β-ketoesters from ester enolates. The enolates in the latter method are best generated from the ketones and mesityllithium at low temperature.



282

Other ketone enolates have been employed in the sythesis of ω-bromoketones [219] and of bicyclo[2.2.2]octenes and bicyclo[3.2.2]nonanes [220], condensed with 283 to give acylcyclopropanes 284 or oxiranes 285 depending upon the structure of the enolate [221], and dimerized to 1,4-diketones by copper(II) chloride [222] or copper(II) trifluoromethanesulfonate [223].



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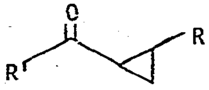

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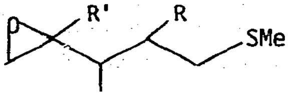
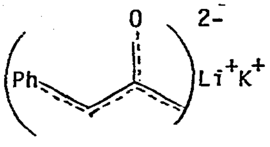


285

The regiospecificity of alkylations of dialkali salt 286, derived from *benzyl methyl ketone, potassium hydride, and n-butyllithium*, has been found to be a function of the alkyl halide [224]. Thus, while primary alkyl and allyl halides gave mixtures of 287 and 288, secondary alkyl bromides afforded exclusively 288. Formation of 288 is novel since alkylation of earlier dianions derived from diketones yielded products corresponding to 287.



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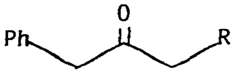

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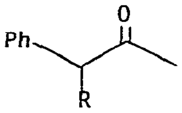
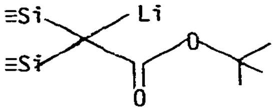


288

A convenient synthesis of δ-alkoxy-β-ketoesters from lithiosodio-β-ketoesters and α-chloroethers has been described [225]. Such compounds are useful in certain annelation reactions.

The first isolation of a ketene from decomposition of an ester enolate was realized when a THF solution of 289 was allowed to warm from -78° to 25° to afford 290 (60%) [226].



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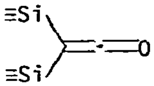
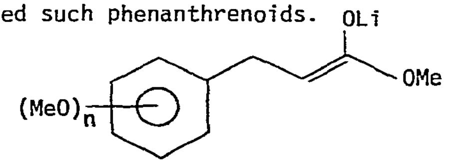


290

A variety of methoxylated ester enolates 291 and their corresponding phenylsulfones have been condensed with quinones 292 and 293 to give products such as 284 [227]. Subsequent acid-catalyzed cyclizations to polycyclic materials represent an alternative to the oxidative phenolic coupling reactions normally employed to prepared such phenanthrenoids.



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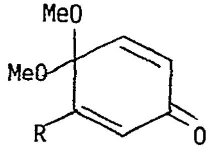

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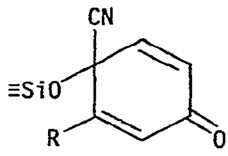

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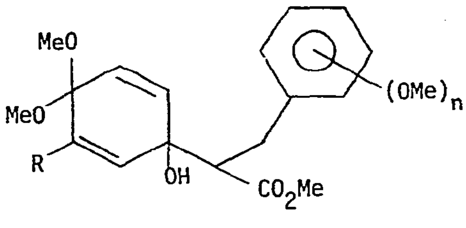
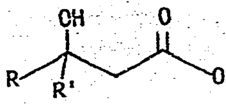


294

β-hydroxyesters 295 (R, R' = alkyl, aryl, or hydrogen) have been converted to dilithium salts 296 by LDIPA. Such salts have been cyclized by iodine at -78° to yield epoxyesters 297 [228]. Products 297 are stereochemically pure where the largest R group is trans to the ester moiety.



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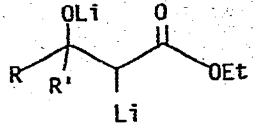

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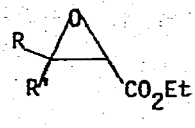
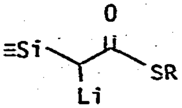


297

Thiol esters 298 have been lithiated, then condensed with aldehydes and ketones to afford α,β-unsaturated thiol esters 299 (49-77%) [229]. Another highly delocalized enolate, lithium ethyl diazoacetate, has been added to thiochroman-4-ones to give thiepin β-oxoesters [230]. For example, 300 yields 301. Such reactions fail with ethyl diazoacetate itself.



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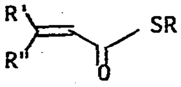

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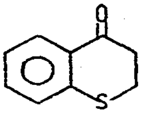

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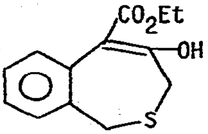
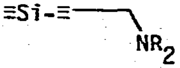


301

Other papers of interest include the preparation and condensations of lithium methyl dimethoxyacetate [231], sulfenylation and halogenation of multiple anions derived from substituted glutarimides [232], the synthesis of highly substituted ketones by acylations of dilithiocarboxylates [233], the conversion of arylacetic acids to dilithio salts by n-butyllithium rather than LDIPA and subsequent oxygenations [234], specific directive effects in the cleavage of vicinal hydroxyepoxides by dilithiocarboxylates [235], and the preparation of triarylstannylacetic acids from the latter dianions and iodotriarylstannanes [236].

C. Amines, Imines, Ethers, and Related Compounds

Propargylamines 302 have been metalated by n-butyllithium, then condensed with aldehydes and ketones in the presence of zinc iodide to afford previously undescribed aminohydroxyacetylenes 303 [237]. The related propargylicimine 304 and vinylamine 305 have been metalated then alkylated and combined with ketones as part of the synthesis of β,γ-unsaturated acids [238] and 2-butenolides [239], respectively.



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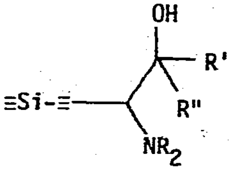

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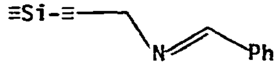

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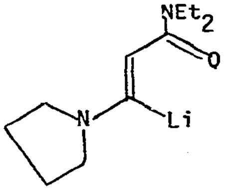
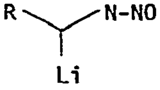


305

Several full papers appeared in 1977 which discussed additional aspects of the chemistry of lithionitrosamines [240-243]. Thus, full details are disclosed for the preparation of five 2-lithio-N-nitrosamines 306 and subsequent condensations with alkyl, allyl and benzyl halides, and with aldehydes and ketones [240]. The regio- and stereochemistry of such transformations on cyclic systems has been studied [241]. For example, lithiation-deuteration of 3-methyl-N-nitrosopiperidine affords 307 (45%) and 308 (45%) accompanied by 5% each of the corresponding trans isomers. Other condensations reported include 306 (R = t-Bu, i-Pr, Me) with arylnitriles to give 1,2,3-triazoles 309 [242], and allyl systems 310 with alkyl halides to yield 311 [243]. Related combinations of 310 with aldehydes and ketones occur at both the α- and γ-positions though the latter is favored under thermodynamic conditions.



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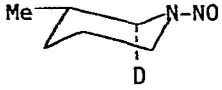

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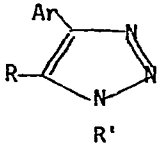

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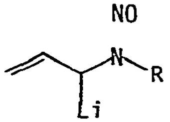

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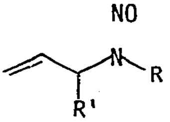
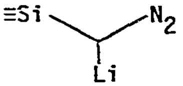


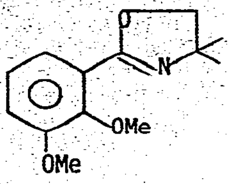
311

Organolithium 312 has been condensed with aromatic carbonyl compounds to afford alkynes [244]. The simple procedure is illustrated by the conversion of 312 to diphenylacetylene by benzophenone.



312

The o-methoxy groups of aryloxazolines 313 have been conveniently replaced by amine moieties using certain lithium amides [245]. For example, 313 and lithium N-methylanilide give 314 which is cyclized by acid to acridone 315 (50%). Another paper discussed the effect of the 5-substituent on asymmetric induction in reactions of chiral oxazolines [246].



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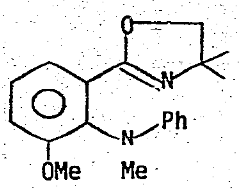

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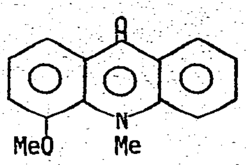
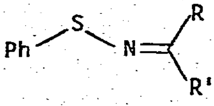


315

Secondary and tertiary carbinamines may now be easily synthesized from sulfenamides 316 and organolithium reagents [247]. The reactions proceed via intermediates 317.



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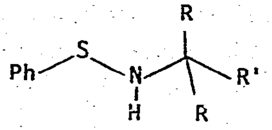
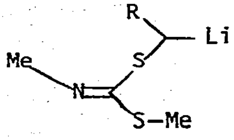


317

Metalated imines continued to find use in organic synthesis. Thus, 318 has been condensed with aldehydes and ketones as part of a preparation of thiiranes [248] while 319 has been employed to synthesize 1,5-diketones [249]. The latter have been cyclized by n-butyllithium to give 320 rather than the more thermodynamically stable 321.



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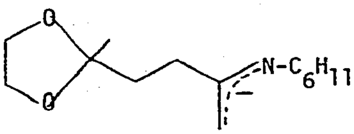

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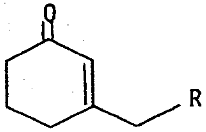

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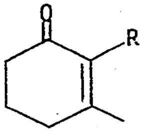
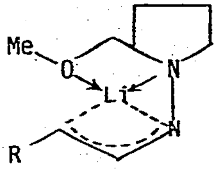


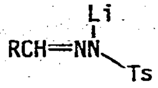
321

Alkylation of lithiohydrazones 322 has been employed to prepare the first example of α-chiral aldehydes [250].

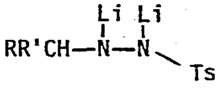


322

Tosylhydrazones of aldehydes RCHO have been converted to RCH_2R' by two equivalents of n-, s-, and t-butyllithium (R'Li) apparently via 323, 324, and 325 [251].


$RCH{=}N\overset{Li}{N}{-}Ts$

323

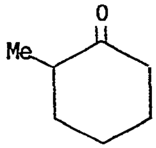

$RR'CH{-}\overset{Li}{N}{-}\overset{Li}{N}{-}Ts$

324

$RR'CHN{=}NLi$

325

Vinylsilanes, -germanes, and -stannanes have been prepared directly from tosylhydrazones, four equivalents of n-butyllithium, and R_3MX [252]. The process is illustrated by the conversion of 326 to 327 (61%) where 328 is an intermediate.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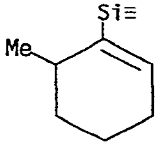
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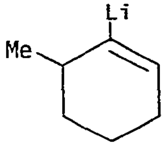
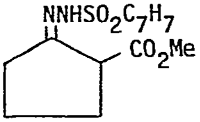

328

In a similar but unrelated procedure, β-carboalkoxytosylhydrazones such as 329 have been treated with three equivalents of LDIPA and the reactions, then hydrolyzed or alkylated to afford β,γ-unsaturated esters 330 or 331, respectively [253]. Many other examples are listed.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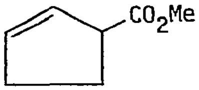
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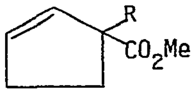
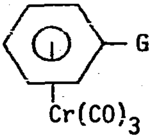

331

Lithiated tosylhydrazones have also been employed to prepare certain tetracyclooctanes [254], ethynylbicyclooctenes and -nonenes [255], and phenyltrimethylsilylcarbene [256], and in the study of hydrogen migration in 2-carbena-6,6-dimethylnorbornane [257].

Two papers described additional lithium chemistry of arene-chromium complexes. First, 332 (G = Me, OMe) has been condensed with lithionitriles, lithioesters, and lithiodithiane to give mostly meta derivatives 333 in excellent yields [258]. Secondly, nitriles such as 334 (n = 3,4; R = H, Me) have been cyclized to 335 by LiTMP or LDIPA followed by oxidative quenching with iodine [259].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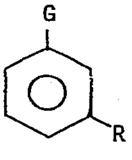
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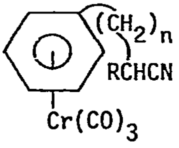
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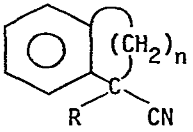
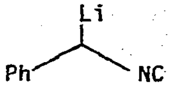

335

Lithiated isocyanides such as 336 have been alkylated to afford higher isocyanides which can be hydrolyzed to amines [260]. The sequence constitutes a synthonic conversion of a primary amine to one with a longer chain. Other papers in this area have described the preparation of 337 from 338 and subsequent reactions with a variety of electrophiles [261], the addition of ethyl lithioisocyanoacetate to 339 to give 340 [262], and the condensation of α-metalated isocyanides with Schiff bases to yield 2-unsubstituted-2-imidazolines [263 The latter process is illustrated by the conversion of 336 and 341 to 342.



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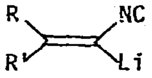

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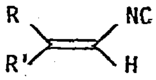

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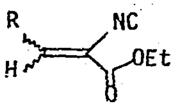

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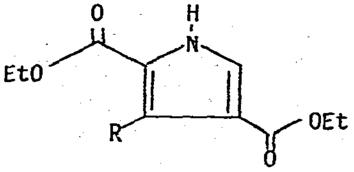

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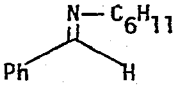
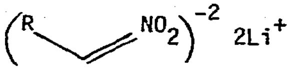


341

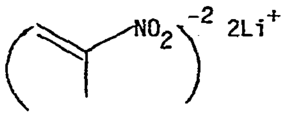
342

Additional examples of the preparation and reactions of dianions derived from nitroalkanes have been described [264]. Included in this paper are alkylations of α,α-dilithio salt 343 and of α,β-doubly deprotonated systems 344-346.



343

(R=H, alkyl, Ph)



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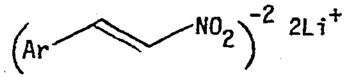

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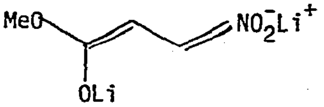
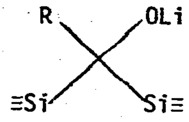


346

Other papers in this section include the C-alkylation, O-acylation, and O-silylation of the lithium enolate of acetaldehyde derived from THF and organolithiums [265], the conversion of alkoxides 347 to acylsilanes 348 by benzophenone [266], and the alkylations of 1,3-oxathienyllithium (349) [267].



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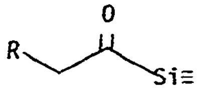

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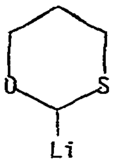
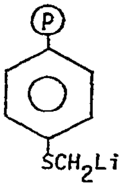


349

D. Carbanions Stabilized by Sulfur

Alkyl iodides have been homologated by polymeric phenylthiomethyllithium (350) [268]. For example, 350 and 1-iodooctane afford 351 which is converted to 1-iodononane by sodium iodide-methyl iodide.



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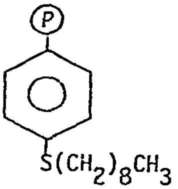
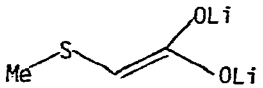


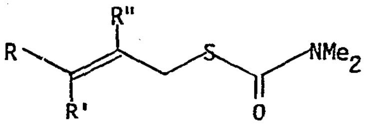
351

Full papers appeared in 1977 which described lithiations of cyclopropyl phenyl sulfides and subsequent condensations with aldehydes and ketones [269], and sulfenylations of dilithio salts of carboxylic acids as well as additional chemistry of 352 [270].



352

As part of the conversion of aldehydes and ketones to α,β-unsaturated aldehydes, allylic thiolcarbamates 353 have been sulfenylated by LDIPA and dimethyl disulfide to give 354 [271]. Treatment of the latter materials with aqueous mercuric chloride completes the process.



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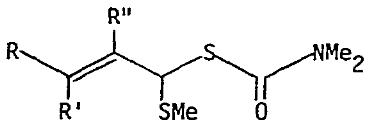
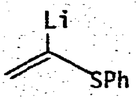


354

Vinyllithium reagent 355 has been condensed with chlorotrimethylsilane to yield 356 [272]. Similar results are reported for 355 and certain disulfides, as well as selenium and tin electrophiles. In another paper, the related 357 has been deuterated, alkylated, sulfenylated, and combined with benzaldehyde to afford 358 (68-100%) [273].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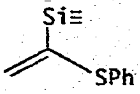
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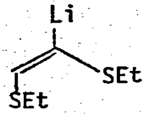
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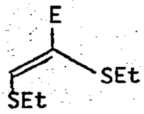
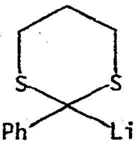

358

The reaction of dithiane 359 with 4-t-butylcyclohexanone has been studied as a function of solvent and time [274]. Thus, adduct 360 is formed under thermodynamic control from these reagents in THF. The kinetically controlled 361, seen early in the reaction mixture, is absent after four hours. In contrast, alkoxide 360 is unstable in HMPA and reverts to 359 and ketone to ultimately give the enolate of the latter compound.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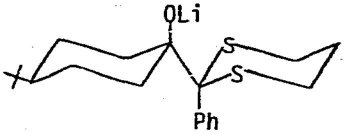
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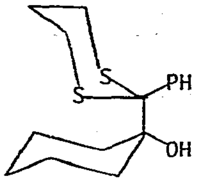
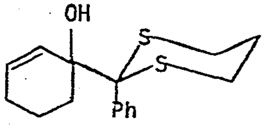
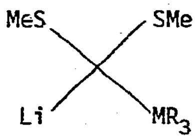

361

Dithiane 359 and others have been reacted with a variety of α,β-unsaturated ketones to afford 1,2-adducts such as 362 and 1,4-adducts illustrated by 363 at low and high temperatures, respectively [275]. Even higher yields of 362, the kinetically controlled product, are realized when the THF solvent in these reactions is diluted with hexane.


362


363

Substituted bis(methylthio)methanes 364 (M = Si, Sn, R = alkyl, phenyl) have been found to add to cycloalkanones in a 1,4-fashion in THF-hexane at -40° to give 365 (n = 2,3,4) [276]. Enolates 365 have been alkylated in situ to yield 2,3-disubstituted cycloalkanones. Reagents 364 and related ones have also been successfully combined with aldehydes and ketones to afford olefins containing sulfur, selenium, silicon, and tin in vinyl positions [277].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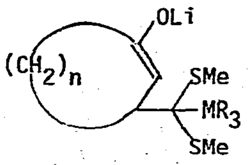
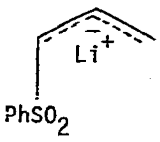

365

Lithium reagent 366, obtained by metalation of allyl phenyl sulfone with n-butyllithium, undergoes alkylation regioselectively at the α-position to give β,γ-unsaturated sulfones 367 [278].



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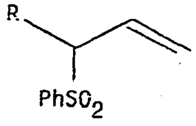
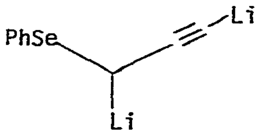


367

Dilithiopropargyl selenide 368 has been alkylated by alkyl halides (RX), then condensed with other electrophiles to yield 369 [279]. Subsequent oxidation affords α,β-unsaturated products 370.



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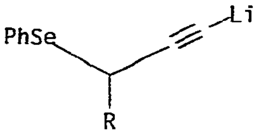

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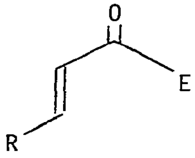
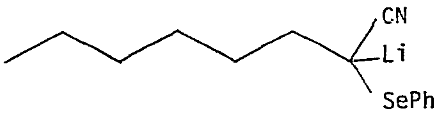


370

Other papers in this area included directed coupling of carbonyl compounds by α-lithioselenides and mercaptans [280], silylation of α-lithioselenides [281], and an alkylation and Michael addition of selenocyanide 371 [282].



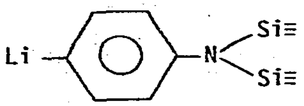
371

E. Polymerization

Hammett plots have been obtained for the reactions of the alkali salts of living polystyrene with 1,1-diphenylethenes disubstituted with methoxy, methyl, and t-butyl groups [283]. The data suggest that in the absence of stronger coordinating molecules such as ethers or tertiary amines, the positive counterion complexes with the monomer, especially with lithium cations. The nucleophilicity of the polystyryllithium system in benzene is nearly identical to that in cyclohexane.

The rates of the polymerization of isoprene initiated by various alkyllithiums have been studied in an effort to determine which step of the reaction is responsible for the occurrence of the overall negative reaction rate [284]. The authors conclude that such rates may be ascribed to the initiation step and are a function of the concentrations of the initiator and the solvent.

Syrene, methyl methacrylate, butadiene, and isoprene have been polymerized by LiC_{12} [285]. Isoprene has also been polymerized by certain binary insertion compounds of potassium and graphite. Yields, solvent effects, and microstructure are discussed. Other initiators described included 372 for the polymerization of 1,3-butadiene and isoprene [286], and 373 for the polymerization of isoprene [287].



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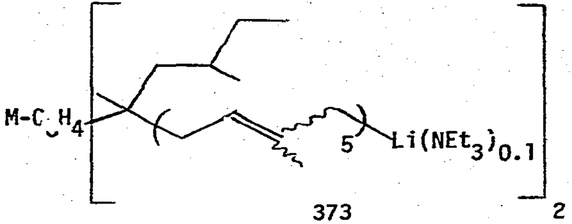
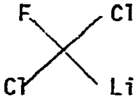


373

Other papers in this area discussed the effect of the polarity of solvent [288] and of alkali alkoxides [289] on the microstructure of poly(methyl methacrylate) prepared by anionic polymerization, nucleophilic substitution by a variety of lithium carbanions onto poly(methyl methacrylate) [290], the copolymerization of 2-methoxyethyl methacrylate with methyl methacrylate [291], and polymerizations and copolymerizations of vinylferrocene in the presence of lithium and n-butyllithium [292].

H. Carbenoids

Interaction of fluorotrichloromethane and fluorotribromomethane with n-butyllithium in the presence of olefins at -116° has afforded cyclopropanes [293]. The results are ascribed to the intermediacy of transient carbenoids 374 and 375. Attempts to prepare fluorocyclopropanes from fluorodiiodo-, fluorodibromo-, difluoro-, and difluorobromomethanes failed. Another paper described the synthesis of 376 (R = H, alkyl) from the corresponding dichloroalkanes and n-butyllithium·TMEDA in almost quantitative yields [294]. Subsequent condensations with carbon dioxide, acid anhydrides, aldehydes, and alkyl halides are discussed.



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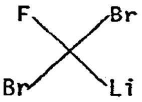

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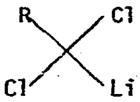
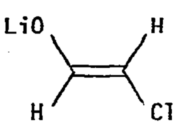


376

Several more papers appeared in 1977 which described additional aspects of β-oxidocarbenoids. Thus, 2,2-dichloroethanol has been converted by n-butyllithium to the novel chloroenolate 377 as evidenced by trapping experiments with tosyl chloride and benzoyl chloride [295]. The reaction proceeds via carbenoid 378. Similar rearrangements on carbenoids related to 378, prepared from dichloromethyllithium and aldehydes and ketones [296], have also been realized to afford α-chloroketones [297]. Additional examples of the conversion of cyclic ketones to their next higher homologues by dibromomethyllithium have been presented [297].



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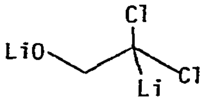
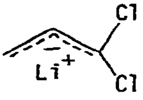


378

Condensations of gem-dichloroalkyllithium (379) with a variety of electrophiles to afford 380 and/or 381 have been discussed in two full papers [298, 299]. Thus, 379 with simple non-halogen containing dialkyl ketones such as acetone gives alcohols 380 (E = $\begin{smallmatrix}R\\R\end{smallmatrix}\!\!>\!C\!<^{OH}$). In contrast, the use of hexafluoroacetone, benzophenone, and benzaldehyde in such reactions yields alcohols 381. Acetophenones substituted in the meta and para positions afford mixtures of 380 and 381. For example, 380 is predominant with p-methoxyacetophenone while 381 is favored with the p-cyano derivative. The results are ascribed to differences in electronic rather than steric effects in the electrophiles. Although thermodynamic and kinetic factors were ruled out in the above reactions, condensations of 379 with chlorotrimethylgermane were found to give 380 and 381 (E = $GeMe_3$) by kinetic and thermodynamic control, respectively [299]. That 379 with chlorotrimethylsilane and methyl iodide afforded 380 while trimethyltin bromide and mercury(II) chloride yielded 381 are explained similarly.



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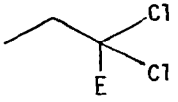

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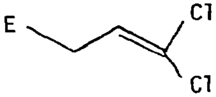
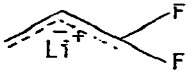


381

gem-Difluoroallyllithium (382) has been prepared from 3,3-difluoroallyltrimethyltin and n-butyllithium at -95° [300]. Though 382 has only limited stability at this temperature, it has been condensed with several chlorosilanes to give 383. Such reactions which occur under kinetic control were successful only when 382 was generated in the presence of the electrophiles. A similar condensation of 382 with 3-pentanone to afford an alcohol related to 380 was effected, but only under the rather special conditions of successive alternate additions of n-butyllithium and the ketone.



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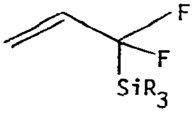
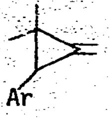


383

Reaction of 3,3-dimethylallene with benzyl chloride and LiTMP has been shown to give 384 and 385 presumably via a phenyl carbenoid [301]. The major emphasis of this paper, though, deals with the formation of 386 and its subsequent transformations by electron transfer and nucleophilic processes. Reagent 386 is conveniently prepared from the parent allene and LiTMP.



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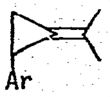

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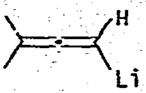
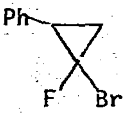


386

The reaction of cyclopropane 387 and n-butyllithium at temperatures below -105° affords carbenoid 388 as evidenced by carboxylation and esterification [302]. Carbenoids 389 and 390 have been prepared similarly. At higher temperatures, 388 decomposes to phenylallene (65%) and 3-phenyl-1-propyne (25%).



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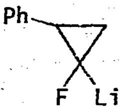

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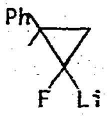
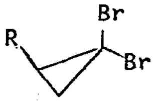


389

390

Certain gem-dibromocyclopropanes have been converted to carbenoids by excess n-butyllithium, then to n-butyllithiocyclopanes via subsequent nucleophilic substitution reactions [303]. The process is illustrated by the conversion of 391 (R = Ph, Ch$_2$OCH$_2$Ph) to mostly 394 via kinetically favored 392 though some thermodynamically favored 393 is also present, especially after longer reaction periods. Stereoselective condensations of 394 with electrophiles are described. For example, addition of benzoyl chloride gives only 395; the isomeric 396 was absent.



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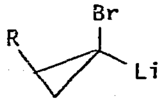

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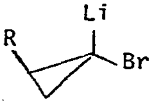

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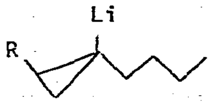

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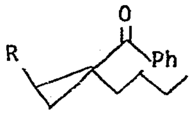

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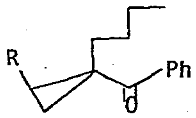
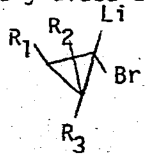


396

Thermodynamically favored 397 (R = H, alkyl, aryl) have been obtained from gem-dibromocyclopropanes and one equivalent of n-butyllithium at -95° [304]. Subsequent alkylations yielded derivatives such as 398.



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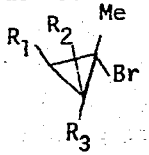
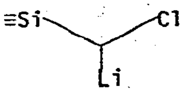


398

α,β-Epoxysilanes may now be conveniently prepared by condensations of carbenoid 399 with ketones [305, 306]. For example, 399 and benzophenone afford 400 (≥ 95%). Bis(trimethylsilyl) carbenoid 401 has also been condensed with aldehydes and ketones [307]. Thus, while 401 and benzophenone gave oxirane 402, other ketones studied had hydrogen atoms alpha to the carbonyl carbon which were ionized to yield enolates and 403. On the other hand, 401 and aldehydes afforded α-bromovinylsilanes 404 non-stereospecifically.



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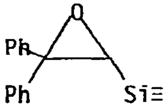

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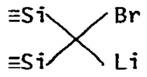

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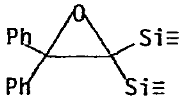

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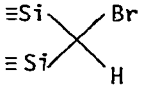

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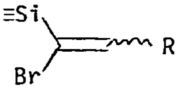
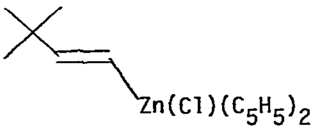


404

Other papers in this area discussed the chemistry of α-lithiooxiranes [308, 309], α-lithio-1,1-dichloroalkane- and 1-chloroalkanephosphonates [310], and α-lithio-α-diphenylphosphinocarbonyl compounds [311].

12. LITHIUM ATE COMPLEXES

Lithium vinyl cuprates may be conveniently prepared stereospecifically from zirconium reagent 405, lithium iodide, and Cu(OSO$_2$CF$_3$) [312]. Best results are obtained by forming the ate complex in the presence of co-reagents such as methyl vinyl ketone. The vinyl copper reagent itself has been synthesized from 405 and copper(I) chloride.



405

The reactivity of the new cuprate reagents 406-408 towards alkyl, cycloalkyl, and aryl halides has been compared with that of lithium dimethylcuprate and methyllithium [313]. In most cases, 406 in THF is clearly superior to the other reagents in such reactions. For example, 1-chlorodecane in THF with 406 and lithium dimethylcuprate give undecane in yields of 100% and 22%, respectively. Another paper discusses the preparation, properties, and some reactions of seven different complex copper hydrides 409 [314]. Reagent Li$_4$CuH$_5$ was found to reduce n-decyl iodide, bromide, chloride, and tosylate to undecane quantitatively.

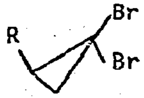
$LiCu_2Me_3$ 406

Li_2CuMe_3 407

$Li_2Cu_3Me_5$ 408

$Li_nCu_mH_{(n+m)}$ 409

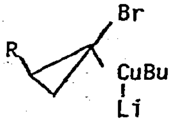
gem-Dibromocyclopropanes 410 (R = Ph, n-C_6H_{13}, CH_2OCH_2Ph) have been condensed with several lithium cuprates to afford products which are a function of both the cuprate employed and the temperature [315]. Thus, 410 with lithium di-n-butylcuprate at -40° to -78° followed by methyl iodide gives mostly 411 accompanied by small amounts of isomeric 412. A similar reaction using the t-butyl rather than the n-butyl copper system yields only the product corresponding to 411. Such reactions are thought to proceed via copper halogen exchange to afford 413 followed by rearrangement to 414. In contrast, 410 (R = Ph) with lithium divinylcuprate at -78° and at -48° gives 415 accompanied by 416 and 417, respectively. Finally, 410 (R = Ph) and lithium dimethylcuprate at -78° and at -38° yields products corresponding to 417 and 415-416, respectively. The latter reactions are said to proceed via copper III species 418.



410

411

412



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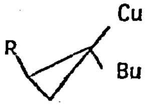

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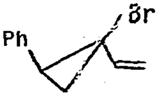

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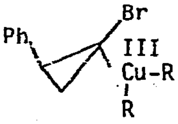
417

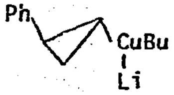


418

Monobromocyclopropane 419 and others have also been treated with lithium di-n-butylcuprate followed by alkyl halides to afford 420 [316]. The reactions are thought to involve 421 as an intermediate and should be compared with the conversions of 410 to 413 and 414 above.

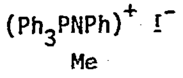
419

420

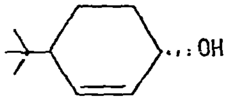


421

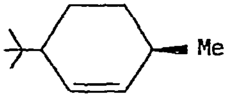
The hydroxyl groups of seven allyl alcohols, α-phenylethyl alcohol, and cyclopropylcarbinol have been substituted by alkyl groups via conversion to lithium alkoxycuprates followed by condensation with phosphonium salt 422 [317]. The procedure, illustrated by conversion of 423 to 424, simply involves treatment of a lithium alkoxide with copper(I) iodide, addition of an alkyl- or aryllithium, and addition of 422. Salts such as 425 are presumably intermediates in these transformations.


$(\mathrm{Ph_3P\underset{Me}{N}Ph})^+\ \mathrm{I}^-$

422



423



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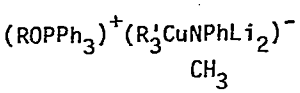
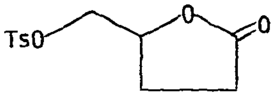
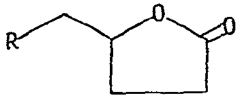

$(\mathrm{ROPPh_3})^+(\mathrm{R'_3Cu\underset{CH_3}{N}PhLi_2})^-$

425

Lactone tosylate 426 has been found to undergo tosylate displacement rather than ring opening by lithium dialkyl- and dialkenylcuprates to give optically active 427 (R = alkyl, alkenyl) [318].

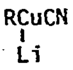


426

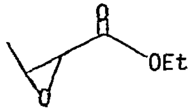


427

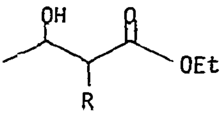
Several epoxides have been cleaved to alcohols by stoichiometric amounts of mixed lithium cuprates 428 (R = Me, n-Bu) [319]. The reactions occur at the least sterically hindered site or at the more electrophilic carbon atom of the epoxides. The process is illustrated by the conversion of 429 to 430. Another paper discussed similar ring cleavages of acetoxy oxiranes by lithium dialkylcuprates to afford ketones [320].


$\mathrm{R\underset{Li}{Cu}CN}$

428

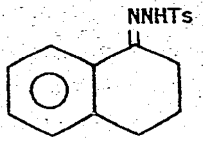


429



430

Several tosylhydrazones have been converted to α-mono- and α,α'-dimethyl or -phenyl derivatives by conversion to α-bromo compounds with tri-N-methylanilinium perbromide followed by admixture with lithium dimethyl- or diphenylcuprate [321]. For example, 431 conveniently gives 432 (65-69%).



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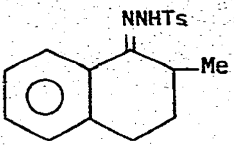
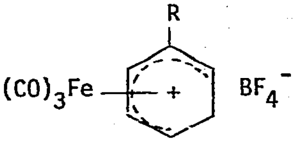


432

Alkylation of salts 434 (R = H, Me, MeO) has been achieved by mixed cuprates 433 (G = S, O) to yield 435 often accompanied by small quantities of 436 [322].

(R'CuGR")Li

433



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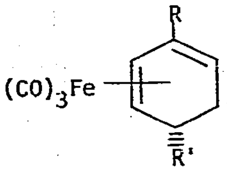

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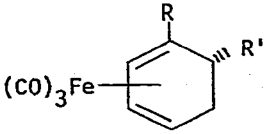
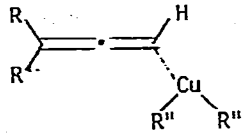
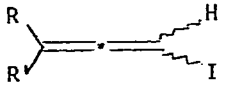


436

Organocopper systems 437, prepared from propargyl acetates and lithium dialkylcuprates, are converted by molecular iodine to iodoallenes 438 [323]. Reagents 437 have also been treated with chloromethyl methyl ether and with acid anhydrides to afford acetylenic ethers and ketones, respectively.

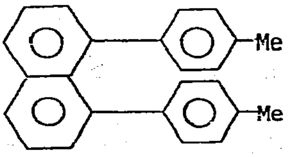


437

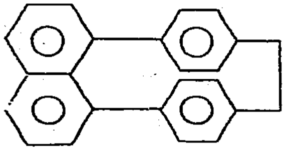


438

Lithium di-p-tolylcuprate has been condensed with 1,8-diiodonaphthalene to give 439 [324]. Subsequent brominations with NBS and cyclization with phenyllithium yields phane 440 (65%). Another paper reports that lithium di-p-tolylcuprate and -aurate are stable tetranuclear species with p-$Ar_4M_2Li_2 \cdot 2Et_2O$ stoichiometry [325].

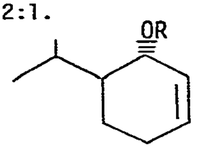


439



440

Mesitoyl esters 441 and 442 both have been found to afford cis-p-menth-2-ene (443) upon treatment with one equivalent of lithium dimethylcuprate in ether at 0° [326]. In contrast, similar treatment of mesitoyl esters 444 and 445 with this reagent both give trans-p-menth-2-ene and 446 in identical ratios of 2:1.



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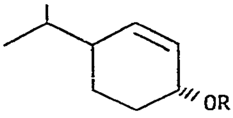

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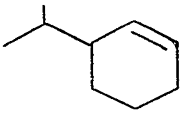

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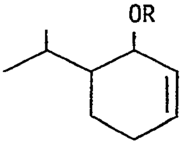

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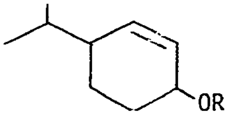

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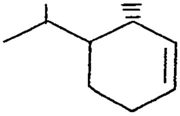
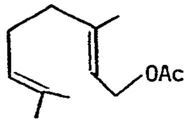


446

Allylic acetates 447-449 have been condensed with mixed cuprates (MeCuG)Li where G = methyl, cyano, and thiophenyl [327]. The alkenes obtained from such reactions are a function of the group G. For example, 447 yields only 450 and only 451 when G = methyl and cyano, respectively. Similarly, 448 affords only 452 and only 450 when G = methyl and cyano, respectively. The results are interpreted in terms of the formation of π-allylic copper complexes.



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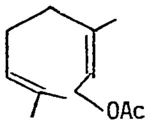

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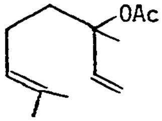

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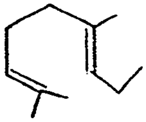
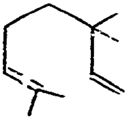


450



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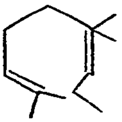
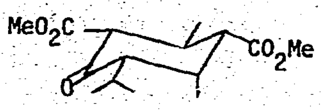


452

The first example of the use of lithium cuprates to oligomerize an α,β-unsaturated ester has been reported [328]. Thus, lithium dimethylcuprate and methyl crotonate give 453 (49%). A mechanistic rationale is proposed to account for the formation of the product. Related additions to (-)menthyl 3-(2-furanyl)acrylate [329], methyl 3-(2-furanyl)acrylate [330], methyl cinnamate [331], cyclopropylacrylic esters [332], and allenylic esters and ketones 454 to afford 455 [333] have been described.



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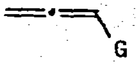

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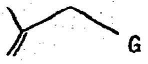
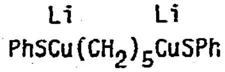
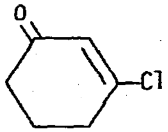


455

A new single-step spiroannelation procedure has been described which utilizes biscuprates [334]. The method is illustrated by the reaction of 456 with 457 to give 458 (40%).


$\overset{\text{Li}}{\text{PhSCu}}(\text{CH}_2)_5\overset{\text{Li}}{\text{CuSPh}}$

456



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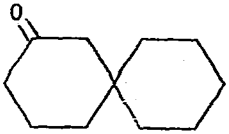
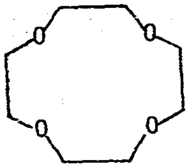
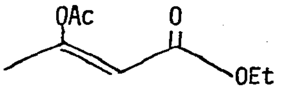


458

The effect of crown ether 459 on reactions of organocuprates with certain organic substrates has been studied [335]. For example, lithium diethylcuprate and 460 yield 461 and 462 in the absence and presence of 459, respectively. In contrast, the reaction of lithium dimethylcuprate with 4-methyl-2-cyclohexenone is completely inhibited by this ether.



459



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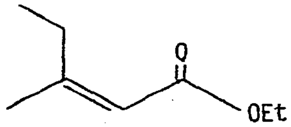

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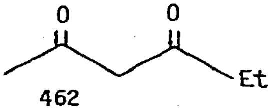
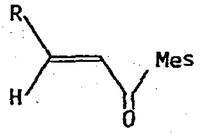


462

A variety of organocuprates have been added to mesityl systems 463 followed by acetylation to determine the ratio of Z/E 464 [336]. Based on the results obtained, the authors conclude that the relative stabilities of the α-copper systems shown is 465 ∿ 466 (R = Me, n-Pr, Ph) > 467 (R' = n-Pr, Ph) > 468.



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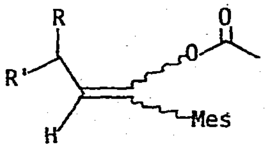

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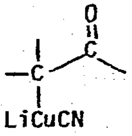
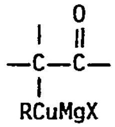
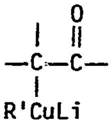


465



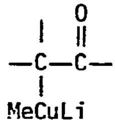
$$-\overset{|}{\underset{\text{RCuMgX}}{C}}-\overset{O}{\overset{\|}{C}}-$$

466



$$-\overset{|}{\underset{\text{R'CuLi}}{C}}-\overset{O}{\overset{\|}{C}}-$$

467



$$-\overset{|}{\underset{\text{MeCuLi}}{C}}-\overset{O}{\overset{\|}{C}}-$$

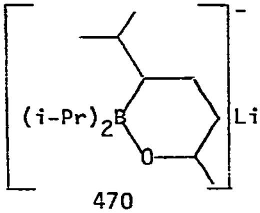
468

Other papers concerned with lithium organocuprates have included a discussion of such reagents derived from 2-lithio-3,3-diethoxypropene [337], reductions of conjugated carbonyl compounds with copper hydride [338], the similarity of the stereochemical results in additions of $MeLi\text{-}LiCuMe_2$, $MeLi\text{-}LiClO_4$, and MeLi-LiBr in additions to 4-t-butylcyclohexanone [339], and the preparation of lithium vinylcuprates from cuprates and certain 1-alkynes [340].

Turning to the area of boron ate complexes, lithium trialkylvinylborates 469 (R = Et, n-Bu, etc.) have been condensed with oxiranes to afford 1,4-alkanediols [341]. For example, 469 (R = i-Pr) and propylene oxide give 6-methyl-2,5-heptanediol (100%) after oxidation, apparently via 470. Reagents 469 also have been combined with aldehydes to yield 1,3-alkanediols [342]. This reaction is illustrated by the conversion of 469 (R = Et) and benzaldehyde to 471, oxidation of which affords 1-phenyl-1,3-pentanediol (78%).

$(R_3\bar{B}\text{-}CH{=}CH_2)Li^+$

469



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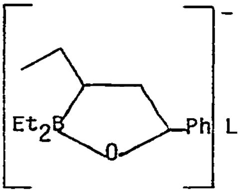
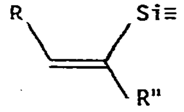
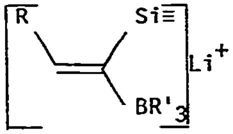


471

A general synthesis of 1,2-dialkylvinylsilanes 472 has been described [343]. The method involves hydroboration of 1-trimethylsilyl-1-alkynes followed by treatment with methyllithium to give ate complex 473. Conversion to the corresponding vinyllithium, then to the related vinylcopper reagents is accomplished by methyllithium and copper(I) iodide, respectively. The process is completed by the addition of triethylphosphite and alkyl halides (R"X). Incidentally, another paper discusses acylation of copper-boron ate complexes 474 prepared similarly from lithium-boron ate systems and copper(I) halides [344].



472

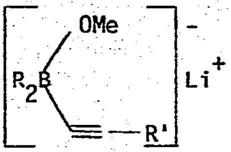


473

$(R_3BMe)Cu$

474

Alkynylborinates 475 have been obtained by reaction of methyl dialkylborinates with alkynyllithiums [345]. Subsequent condensation of 475 with boron trifluoride gives alkynyldialkylboranes.



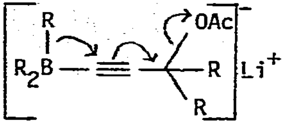
475

Lithium alkynylborates themselves have been shown to undergo Michael additions to Michael acceptors accompanied by alkyl migration to yield olefins [346]. The process is illustrated by the reaction of 476 with 1-nitropropene to afford 477.

$[(n\text{-}C_6H_{13}BC{\equiv}CH]^- Li^+$ 476

$n\text{-}C_6H_{13}CH{=}CHCH(Me)CH_2NO_2$ 477

Acetoxyboron ate complexes 478, prepared from trialkylboranes and lithioethynylalkanol acetates, undergo rearrangement to give allenylic boranes 479 [347]. Treatment of the latter boranes with acetic acid or water affords allenes or acetylenes, respectively. Tosyloxy ate complexes 480, prepared similarly, also undergo rearrangement to yield boranes 481 [348]. Prompt oxidation at -78° of 481 or prior warming of this borane followed by oxidation gives cyclopropyl ketones 482 or homopropargyl alcohols 483, respectively.



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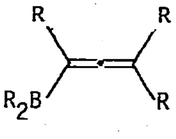

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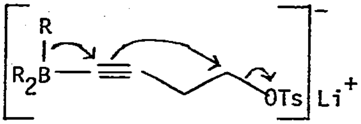
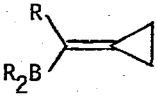


480



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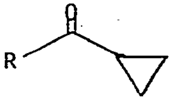
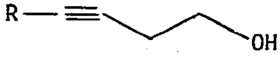


482

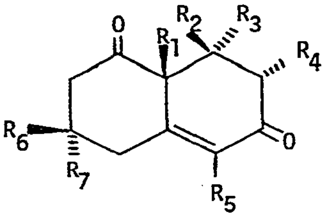


483

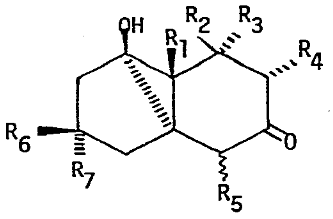
Other papers in this area were concerned with the synthesis of 2-alkynoates and 1-alkynyl aryl ketones from appropriate boron ate complexes and iodine [349], nucleophilic hydroboration of substituted styrenes with lithium triethylborohydride [350], asymmetric reductions of ketones with lithium β-isopinocampheyl-9-borabicyclo[3.3.1]nonyl hydride [351], stereoselective reductions of 4-t-butylcyclohexanone by lithium trialkylaluminates [352], a stereoselective synthesis of symmetrically substituted trans-enynes from conjugated diynes by lithium diisobutylmethylaluminum hydride [353], and conjugate additions of R_3ZnLi systems to α,β-unsaturated ketones [354].

13. REDUCTIONS AND RADICAL ANIONS

The scope of the conversion of bicyclic enediones 484 to fused-ring cyclopropanol derivatives 485 by lithium in ammonia has now been determined [355]. In these compounds, R, is methyl or allyl while the others are methyl or hydrogen. It is suggested that the neighboring ketone facilitates reduction of the enone to a radical anion.

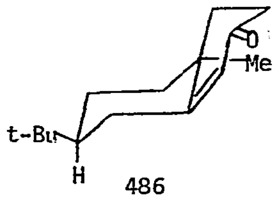


484

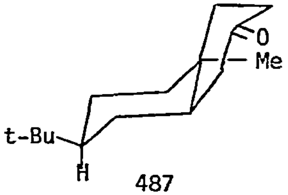


485

Octalone derivative 486, held in the configuration shown by the t-butyl group, has been reduced by lithium in ammonia to afford cis-decalone 487 rather than the normally obtained trans derivative [356].

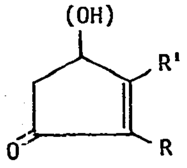


486

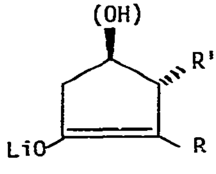


487

The stereochemistry of the reduction of certain 2,3-dialkylcyclopentenones 488 (R = i-Pr, t-Bu) by lithium in ammonia to give 489 has been studied as a function of the alkyl groups [357]. The authors conclude that their results "support the view that the transition state involved during protonation of the intermediate enolate anion resembles the reactants in geometry and that the resulting stereochemistry is determined only by a combination of steric interference, torsional strain, and electrostatic effects in the transition state."

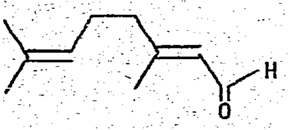


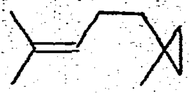
488



489

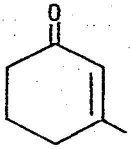
Several α,β-unsaturated aldehydes and esters have been converted to cyclopropane derivatives via lithium/ammonia reduction of intermediate thioether-mesylates [358]. The process is illustrated by the conversion of 490 to 491 via 492.

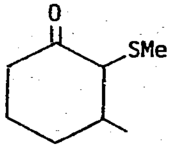

490


491

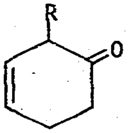

492

Enolates prepared by lithium/ammonia/t-butyl alcohol reduction of α,β-unsaturated ketones have been sulfenylated by dimethyl disulfide [359]. For example, 493 yields 494 (48%).


493


494

Birch reductions of aromatic systems continued to be investigated. Thus, methoxy- and dimethylaminobenzoic acids were reduced both in the presence and in the absence of methanol [360]. Alkylation of certain of the dianion intermediates to afford species such as 495 is reported. Several silylphenoxides have been similarly reduced to dihydro derivatives as part of the α'-functionalization of β,γ-unsaturated cyclohexenones [361]. The process is illustrated by the reduction of 496 to 497.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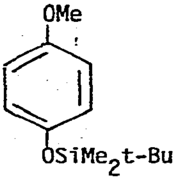
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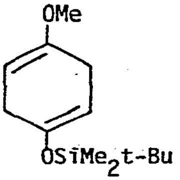
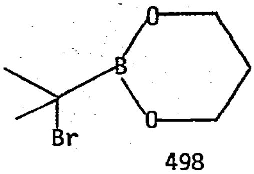

497

Other papers concerned with reductions discussed reductive-elimination of cyclic phosphate derivatives to give alkenes [362], reductive dimerization of acetophenone by lithium in the presence of (S,S)-(+)-1,4-bis(dimethylamino-2,3-dimethoxybutane to yield chiral pinacol [363], reductive cleavage of the propargyl oxygen bond of acetylenic epoxides to afford homopropargyl alcohols [364 and tandem phenylation-reduction of esters and lactones to yield aromatic hydrocarbons or alcohols [365].

14. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

Working across the periodic table from left to right, α-bromodioxaborinanes such as 498 have been found to undergo attack by organolithium reagents at the α-carbon atom rather than at boron to conveniently afford products illustrated by 499 [366].



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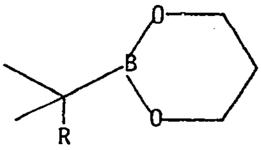
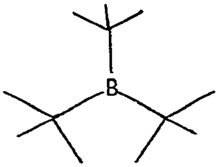


499

Alkyl- and aryl halides have been condensed with diborane in the presence of lithium metal in THF to give, after oxidation, alcohols and phenols, respectively [367]. The yields of such products are higher using the above technique than are those obtained by employing preformed organolithium reagents.

The preparation of tri-t-butylborane 500 has been achieved by condensing t-butyllithium with trimethylborate or the corresponding thioester [368]. Borane 500 undergoes addition with nucleophiles; for example, 500 and methyllithium yield ate complex 501.



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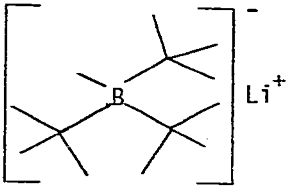
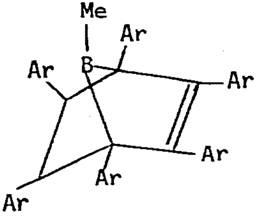


501

A nondegenerate, anionic [1,2] carbon-boron shift has been realized upon treatment of 502 or the corresponding 7-chloro system with methyllithium to afford 503 [369]. Borate 504 is apparently an intermediate in such transformations. Degenerate, net twofold [1,3]suprafacial sigmatropic rearrangements of 7-monosubstituted systems 502 themselves are discussed.



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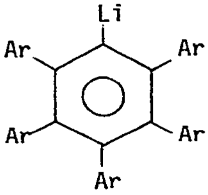

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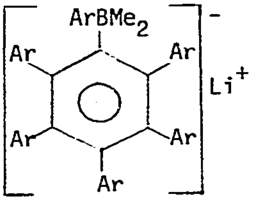
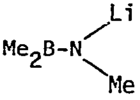


504

Boron-nitrogen system 505 has been condensed with various organolithium reagents in several solvents to give 506 and 507 [370]. Thus, 505 and methyllithium yields mostly 506 in ethyl ether or triethylamine and mostly 507 in THF or TMEDA. Compound 507 decomposes to methane and 506 while 506 combines with 505 to afford 508 and lithium tetramethylborate. Pure 506 has been obtained from 505 and t-butyllithium in pentane.

$Me_2B\text{-}NHMe$

505

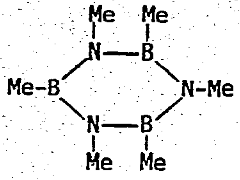


$Me_2B\text{-}N(Li)Me$

506

$[Me_3B\text{-}NHMe]^- Li^+$

507



508

Choice of solvent has been shown to be critical in the reactions of alkali metal hydrides with trialkylboranes. Thus, while sodium hydride combines with trimethylborane to give sodium trimethylborohydride in the absence of solvents, the related reaction with lithium hydride only proceeds in ethereal solvents [371]. Further addition of trimethylborane to lithium trimethylborohydride occurs in highly solvating ethers such as THF, glyme, and diglyme to afford 1:2 adduct 509 [372]. Product 509, though, is not obtained in ethyl or n-butyl ethers.

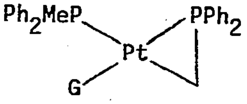
$$[Me_3B\text{---}H\text{---}BMe_3]^- Li^+$$

509

A full paper appeared in 1977 which discussed the preparation of the first actinide metallocarborane, 510, from uranium(IV) chloride and $C_2B_9H_{11}$ dianions [373]. The crystal structure of 510 is described. In an unrelated paper, reaction of 1-Li-2-Ph-1,2-$B_{10}C_2H_{10}$ with cis-$(Ph_2MeP)_2PtCl_2$ in ether has been shown to yield 511 (G = 2-Ph-1,2-$B_{10}C_2H_{10}$) which contains the three-membered ring system shown [374].

$[U(C_2B_9H_{11})_2Cl_2]^{2-}2M^+$

510



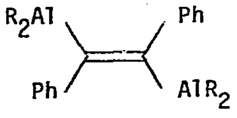
511

Phenyllithium and lithium aluminum hydride have been combined in ether to give 512-514 when the ratios of the reactants were 1:1, 2:1, and 3:1, respectively [375]. Lithium hydride is a by-product in these reactions which apparently reacts with lithium aluminum hydride to afford 512 when less than an excess of phenyllithium is present in the reaction mixtures.

Li_3AlH_6	$LiAlPh_2H_2$	$LiAlPh_3H$
512	513	514

Other papers concerned with Group III elements have discussed the convenient preparation of solvated 515 from tolan, dialkylaluminum chloride, and lithium metal [376], the synthesis of heterocycle 516 from 1,4-dilithio-1,2,3,4-

tetraphenyl-1,3-butadiene and dichlorophenylaluminum [377], the isolation of several thallium(III) ate complexes such as 517 prepared by thallium halides, perfluorophenyllithium, and tetralkylammonium bromides [378], and the synthesis of 518 from thallium(III) chloride and lithium hexamethyldisilazane [379].



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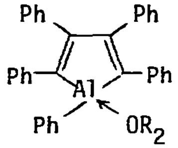


516

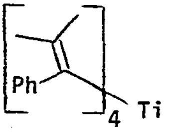
$(R_4N)[Tl(C_6F_5)_4]$

517

$Tl[N(Si\equiv)_2]_3$

518

The first stable homoleptic alkenyls of Ti, Zr, Hf, and Cr, illustrated by 519, have been prepared from vinyllithium 520 and appropriate transition metal halides [380]. Similar condensations have been employed to synthesize tetramesityltitanium [381], cyclic silicon-containing heterocycles 521 [382] and 522 [383] from dilithium reagents, and titanium and vanadium systems 523 (R = $CHPh_2$,$(CH(Si\equiv)_2)$ [384]. Reductions of Ti(IV) and V(IV) to Ti(III) and V(III) in the preparation of 523 have also been noted in condensations of 524 with ethyllithium [385].



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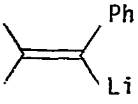

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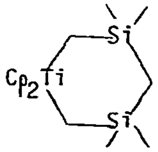

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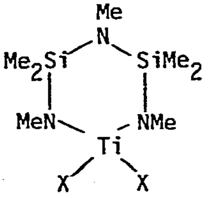
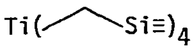


522

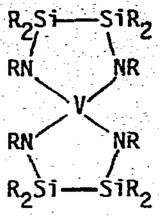
$(C_5H_5)_2MR$

523



524

In the vanadium triad, spirocycles 525 and 526 have been obtained by reaction of dilithio salts such as 527 with vanadium(IV) chloride [386]. Full details have now been published describing the preparation of 528 from the aryllithium and vanadium(III) chloride [387]. The presence of a triple bond between the vanadium atoms in 528 has been demonstrated by x-ray crystallography. Paramagnetic alkyls Cp_2NbMe_2 and $(MeCp)_2TaMe_2$ have been prepared from the corresponding halides and methyllithium [388]. Finally, unstable niobium reagent 529 has been converted to $(C_5H_5)_2NbCl$ by hydrochloric acid [389].



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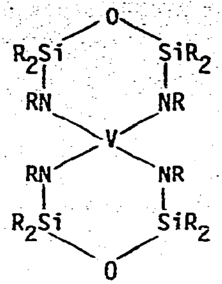

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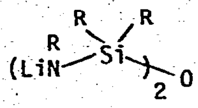

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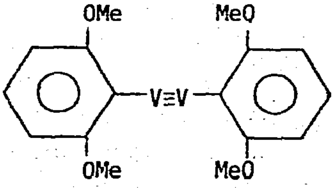


528

$Li[(C_5H_5)_2Nb(C_4H_9)Cl]$

529

Dichromium and dimolybdenum compounds corresponding to 528 have been obtained by condensation of the aryllithium with $Cr_2(OAc)_4$ and an unstated molybdenum precursor, respectively [390]. The Cr-Cr and Mo-Mo bond lengths in these compounds are shorter than previously described ones. A full paper discusses reactions of methyllithium with tungsten(IV) and tungsten(V) chlorides to afford 530 and 531 [391]. A crystal structure determination on 531 has been employed to affirm the presence of a quadruple bond between the tungsten atoms [392]. Similar reaction of 532 with methyllithium and lithiomethyltrimethylsilane has afforded 533 and 534, respectively [393]. The bromine in 533 arises from the presence of lithium bromide in the methyllithium. The ^1H and ^{13}C NMR and the UV spectra of several chromium, molybdenum, and rhenium containing compounds similar to 530 have been reported [394]. A full paper appeared which discussed the preparation and spectral properties of 535 [395]. The results of x-ray diffraction studies are disclosed.

$Li_4W_2Me_8 \cdot 4Et_2O$

530

$Li_4W_2Me_{8-x}Cl_x \cdot 4Et_2O$

531

$W_2Cl_2(NEt_2)_4$

532

$W_2Br_2(NEt_2)_4$

533

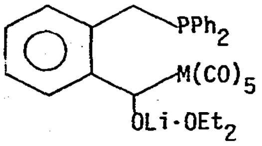
$W_2(CH_2SiMe_3)_2(NEt_2)_4$

534

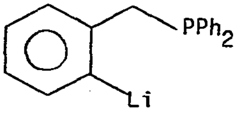
$W(NMe_2)_6$

535

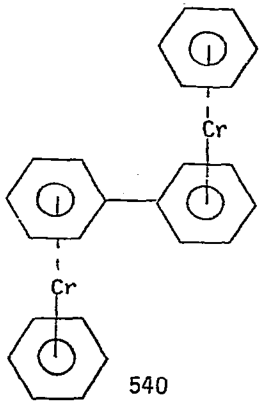
Other compounds in this group prepared using organolithium reagents included solvated $LiCrMes_3$ and Li_2CrMes_4 from mesityllithium and solvated $CrMes_2$ [396], $(C_5H_5)_2W(CH_2CR{=}CH_2)_2$ from $(C_5H_5)_2WHLi$ and allyl chlorides [397], $RR'CNOM(CO)_2C_5H_5$ (M=Mo and W) from RR'C = NOLi and $C_5H_5M(CO)_3Cl$ [398], reagents 536 (M = Cr, Mo, and W) from 537 and $M(CO)_6$ [399], and 538 [400] and 539 [401] by metalation of the corresponding parent phosphines with n-butyl- or methyllithium. Reagents 538 and 539 have been condensed with chloro derivatives of silicon, titanium, antimony, and others. Finally, sandwich compound 540 has been synthesized from lithio-bis-benzenechromium and o-bromoanisole [402].



536



537



540

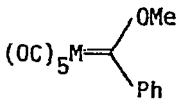
cis-$Mo(CO)_4(Me_2PLi)_2$

538

cis-$Mo(CO)_4(PhPHLi)_2$

539

A large number of papers again appeared which described carbene complexes of chromium and tungsten. Thus, full papers described the addition of aryllithium reagents to 541 to afford 542; treatment of 542 with silicagel/pentane [403] or with hydrochloric acid at -78° [404] gave diarylcarbene complexes 543.



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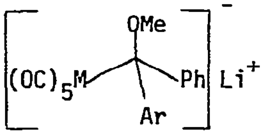
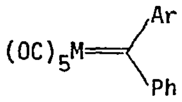
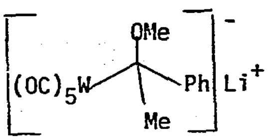


542



543

Addition of methyllithium to 541 has given 544 which has been characterized by IR and NMR [405] and been trapped by bis(triphenylphosphine)iminium chloride [406]. Attempts to generate methylphenylcarbene complex 545 with hydrochloric acid gave styrene and diphenylmethylcyclopropanes [405]. The instability of 545 is ascribed to the high reactivity of the methyl hydrogens which undergo β-eliminations.



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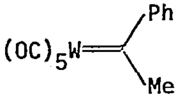
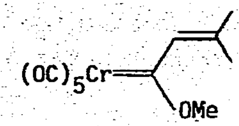
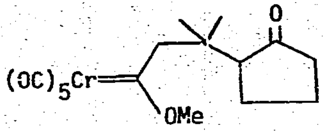
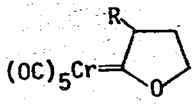


545

Full details have been disclosed about conjugate additions of ketone enolates to vinylcarbene complexes [407]. For example, lithiocyclopentanone and chromium complex 546 affords 547 (79%). In contrast, carbene anions themselves are capable of entering into conjugate additions as illustrated by the conversion of 548 (R = H) to 548 (R = $CH_2CH_2COCH_3$) by n-butyllithium and methyl vinyl ketone [408]. Other examples are cited.


546


547


548

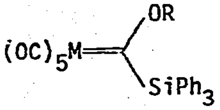
Carbene derivatives containing Group IV atoms bonded to the transition metal, the alpha carbon, or the β-oxygen have been described. Thus, 549 (M = Mo, W; M' = Ge, Sn) have been obtained from 550, organolithium reagents RLi, and alkyl halides R'X [409]. The use of triphenylsilyllithium on hexacarbonyl derivatives of chromium, molybdenum, and tungsten followed by alkylating agents has afforded silylcarbene complexes 551 [410]. Metal carbene complexes 552 have been proposed as intermediates in the reactions of tungsten(II) chloride with lithiomethyltrimethylsilane and =germane to give trimethylchlorosilane (germane), ethylene, and propylene [411]. In contrast, 553 has been O-silylated to yield 554 (M = Cr, W; R = Me, Ar) [412].

$C_5H_5M(CO)_2(M'Ph_3)C(OR')R$

549

$C_5H_5M(CO)_3M'Ph_3$

550

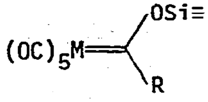

551

$Cl_4W{=}CH_2$

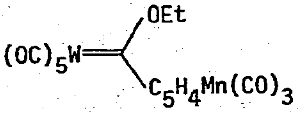
552

$[(OC)_5MC(O)R]^-Li^+$

553

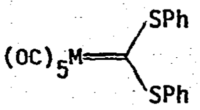

554

Other papers discussed the preparation of 555 from tungsten hexacarbonyl and 556 [413], the synthesis of 557 (M = Cr, W) from the solvated metal pentacarbonyls and tris-phenylthiomethyllithium [414], and the conversion of carbyne complex 558 to benzyl phenyl ketone by phenyllithium [415].


555

$LiC_5H_4Mn(CO)_3$

556



557

$Br(OC)_4WCPh$

558

Dirhenium decacarbonyl and 559 each have been condensed with aryllithium reagents followed by $Me_3O^+BF_4^-$ to afford new μ-methylidene complexes 560 [416].

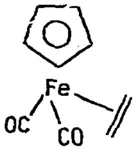
$Re_2(CO)_9C(OMe)Ar$

559

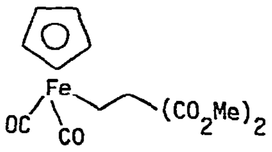
$Re_2(CO)_8[C(OMe)Ar]_2$

560

Olefins which are generally not good candidates as coreagents with nucleophiles have been activated towards nucleophilic addition by dicarbonylcyclopentadienyliron moieties [417]. This new method of forming carbon-carbon bonds is illustrated by the conversion of 561 to 562 by lithium dimethylmalonate (98%).

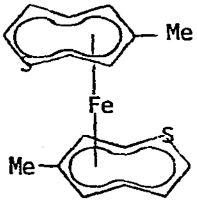


561

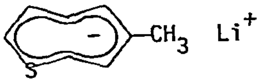


562

Heteroferrocene 563 and an isomer have been synthesized from 564 and iron(II) chloride [418].



563



564

In contrast to alkyllithiums, phenyllithium condenses with 565 and related compounds at -78° to give 566 with retention of configuration at silicon [419]. The reactions presumably proceed via 567. The earlier described reactions of 565 with alkyllithiums gave silyl metallic reagents.

$Ph_3SiCo(CO)_4$

565

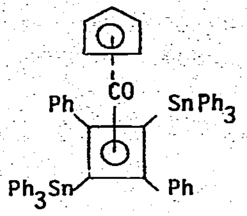
$Ph_3SiCOPh$

566

$[Ph_3SiCo(CO)_3COPh]^- Li^+$

567

Cobalt containing sandwich compound 568 has been converted to lithium reagent 569, silylation of which affords 570 [420]. Though the tin moiety of 570 has also been replaced with lithium, attempts to prepare a dilithio derivative from 568 have been unsuccessful.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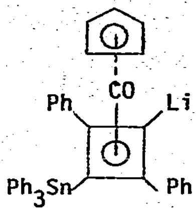
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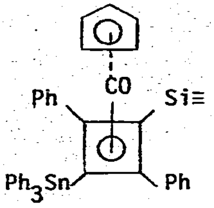

570

The cobalt valence shell of d^9 in 571 has been increased to d^{10} in 572 by reduction of the former reagent with alkali metals in ether [421]. Such cobalt anions are reducing agents, bases, and nucleophiles.

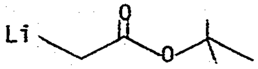
$(Me_3P)_4Co$

571

$[(Me_3P)_4Co]^- M^+$

572

Lithium ester enolates may now be conveniently arylated and vinylated by aryl and vinyl halides in the presence of nickel(II) bromide [422]. The procedure is illustrated by the reaction of 573 and 574 to afford 575 (94%).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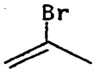
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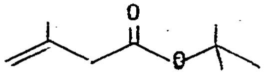

575

The synthesis of the first peralkylplatinum complexes 576 and 577 have been effected by condensation of methyllithium with appropriate methylplatinum precursors [423]. Alkylations as well as the vibrational and NMR spectra of 576 and 577 are discussed.

$Li_2[PtMe_6]$

576

$Li_2[PtMe_4]$

577

Cyclooctadienyldimethylpalladium has now been obtained in high yield from the corresponding dichlorocyclooctadienylpalladium and lithium dimethylcuprate [424]. Other systems prepared by similar displacement of halides have included mixed copper cluster compounds 578 using lithium acetylides [425], silylcopper reagent 579 from lithiomethyltrimethylsilane [426], and mixed Cu-Ag, Ag-Au, and Cu-Au complexes 580 using 581 [427]. Another paper discussed the stability of 582 and 583 as determined by hydrolysis, thermolysis, and oxidation [428].

$Ar_4Cu_6(C\equiv CR)_2$ $[Cu(CH_2SiMe_3)]_4$ $R_4M_4M'_2X_2$

578 579 580

$R_4Au_2Li_2$ Me_2AuLi Me_4AuLi

581 582 583

The reaction of 584 with alane has afforded 585 rather than the expected 586 [429]. Similar results were obtained with 587 to give 588.

$LiZnMe_2H$ $LiZnMe_2AlH_4$ $LiZnH_3$

584 585 586

$LiZn_2Me_4H$ $LiZn_2Me_4AlH_4$

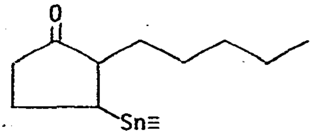
587 588

Organouranium compounds with six or eight uranium to carbon σ-bonds were first reported in 1977 [430]. Thus, organolithium reagents with uranium tetrachloride and uranium pentaethoxide have yielded 589 and 590, respectively. Similar condensations of uranium tetrachloride with appropriate organometallic reagents have been employed to prepare bis(indenyl)(dialkyl)uraniums 591 (R = Me, t-Bu) [431] and monomeric amidouranium complex 592 [432].

$Li_2UR_6\cdot 8Et_2O$ $Li_3UR_8\cdot 3$ dioxane $(C_9H_7)_2UR_2$ $U(Ph_2N)_4$

589 590 591 592

Turning to Group IV, trimethylstannyllithium has been found to be a key synthetic reagent for new dialkylative enone transpositions [433]. The process is illustrated by the reaction of 2-cyclopentenone, the stannyllithium, and 1-iodopentane to give 593; subsequent addition of methyllithium, chromium trioxide, and sodium hydroxide affords dihydrojasmone 594.



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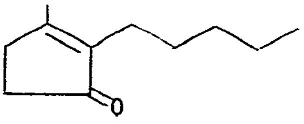
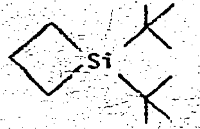


594

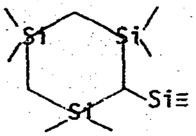
1,1-Di-t-butyl-1-silacyclobutane (595) has been prepared from t-butyllithium and the corresponding gem-dichloroheterocycle [434]. Silacyclohexane derivative 596 has been obtained from dilithio reagent 597 and dichlorodimethylsilane [435].


595


596


597

Trisilacyclohexane 598 has been metalated by n-butyllithium under kinetic control to give 599 which has been trapped by silylation to yield 600 [436]. Intermediate 599 gradually rearranges to the more thermodynamically stable 601 which has also been silylated to afford 602. Similar results have been obtained with 603.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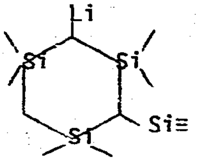
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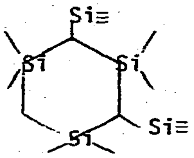
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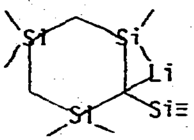
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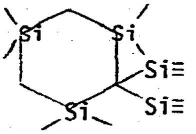
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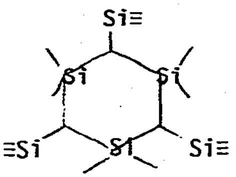
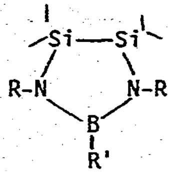

603

A large number of papers discussed the preparation and reactions of compounds derived from members of several groups of the periodic table. Thus, cyclobordisildiazanes 604 (R = alkyl, R' = alkyl, aryl, nitrogen, Cl) have been prepared from dilithio salts 605 and dichlorodisilanes and from dilithio salts 606 and dichloroboranes [437].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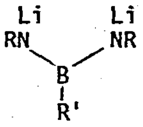
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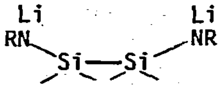

606

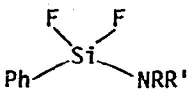
The first silylphosphinoboranes have been synthesized from metalated disilylphosphines and substituted boron halides [438]. For example, 607 and 608 give 609.

$(\equiv Si)_2PLi$ 607

$(Me_2N)_2BCl$ 608

$(\equiv Si)_2P\text{-}B(NMe_2)_2$ 609

N-Lithioamines and halosilanes have been combined to afford alkylaminofluorosilanes such as 610 [439]. Halosilylamines themselves have been cyclized by organolithium reagents to four-membered [440], five-membered [441], and eight-membered rings [442] illustrated by 611, 612, and 613, respectively. Lithium salts 614 and 615 have been condensed with appropriate halosilanes and -germanes to give the expected ring-substituted silanes and germanes [443].



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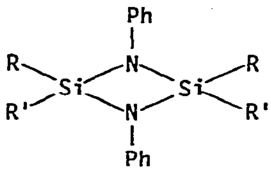

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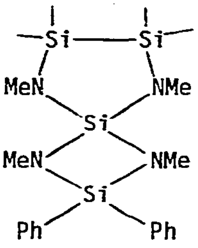

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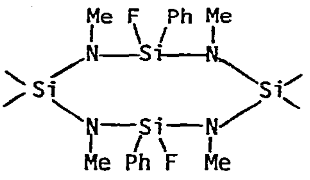

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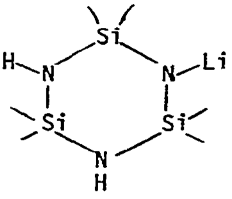

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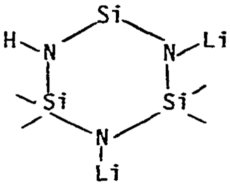
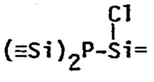


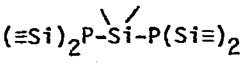
615

Reagent 607 has been condensed with dichlorodimethylsilane to yield 616 or 617 depending upon the amount of 607 used [444]. Similar reactions of 607 with chlorophosphines afford products such as 618. Related condensations have been employed to obtain (silylcyclopentadienyl)phosphines such as 619 [445] and chelating ligands 620 where X and X' = N, P, and As [446].



$(\equiv Si)_2P\text{-}\overset{Cl}{Si}{=}$

616

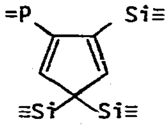


$(\equiv Si)_2P\text{-}Si\text{-}P(Si\equiv)_2$

617

$(\equiv Si)_2P\text{-}PPh_2$

618

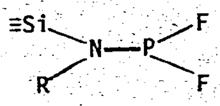


619

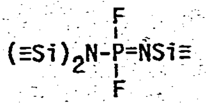
$Me_2XGeMe_2CH_2X'Me_2$

620

N-Lithiosilylamines have been combined with halophosphines to afford N-silylaminophosphines such as 621 [447], phosphinimines illustrated by 622 [448], and bis(trimethylsilyl)aminophosphines such as 623 [449].



621



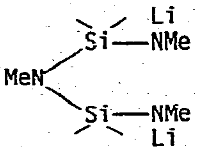
$(\equiv Si)_2N\text{-}PF_2\text{=}NSi\equiv$

622

$(\equiv Si)_2NPMe_2$

623

Five new ring systems containing silicon, germanium, and nitrogen have been obtained by methods similar to those described earlier [450]. For example, dilithio salt 624 and germanium tetrachloride give 625. In an unrelated paper, bis(germyl)phosphine 626 and 1,2-dibromoethane afford tetrakis(germyl)diphosphine 627 perhaps via a bromophosphine intermediate [451].



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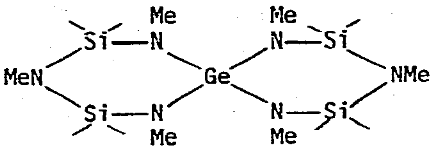
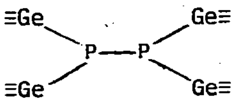


625

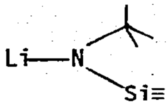
$(\equiv Ge)_2PLi$

626

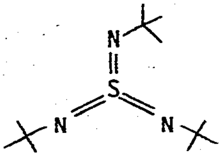


627

Silylamide 628 has been combined with NSF_3 to give a variety of products including 629 [452]. The reaction proceeds via 630.



628



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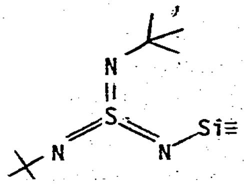
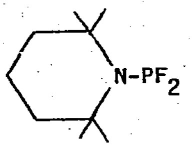
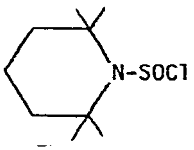


630

Lithium tetramethylpiperidide has been condensed with phosphorus trihalides, phosphorous oxyfluoride, thionyl chloride, and thionyl bromide to yield adducts such as 631 and 632 [453].

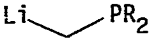


631



632

Dialkylmethylphosphines have been metalated by t-butyllithium to afford 633 (R = Me, t-Bu) [454]. Such organometallics have been condensed with methyl iodide, chlorodialkylphosphines, and other electrophiles to give 634. Metalated diphosphine 635 has been employed in the synthesis of macrocyclic ligand systems such as 636 [455]. Interaction of phosphonium salt 637 with methyllithium at -60° has been shown to give 638 (48%) [456].



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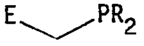

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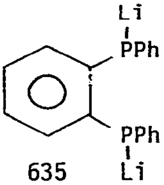

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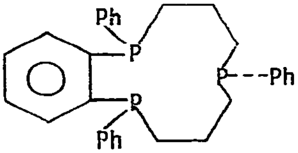

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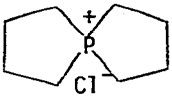

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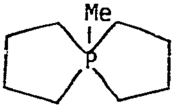
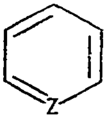


638

In contrast to pyridine, phosphabenzene and the correpsonding arsenic and antimony analogs (639, Z = P, As, Sb) undergo reaction with methyllithium at the heteroatom to yield 640 [457]. Hydrolysis of 640 affords dihydro derivatives of 639.



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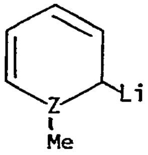


640

Methyl(diphenyl)arsane oxide (641) has been metalated for the first time by employing LDIPA in THF [458]. The resulting 642 has been combined with alkyl halides, aldehydes, and ketones.

$Ph_2As(O)CH_3$

641

$Ph_2As(O)CH_2Li$

642

Finally, two research groups have independently reported that lithium alkynethiolates 643 (R = alkyl, aryl, R'$_3$M) combine with chlorosilanes to afford 644 [459, 460]. Subsequent conversions of 644 to thioketenes and to

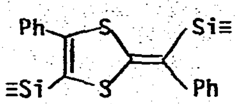
1,3-dithioles such as 645 are described.

$RC{\equiv}CSLi$

643

$RC{\equiv}CSSiR'_3$

644



645

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