LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1980 *

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[*] Previous survey see J. Organometal. Chem., 203 (1980) 1 - 148.

1. REVIEWS AND BOOKS

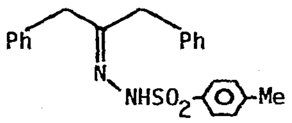
Reviews, books, and chapters in books devoted either wholly or in part to organolithium chemistry included the following:

- Stereocontrol in the synthesis of acylic systems: applications to natural product synthesis [1].
- Stereo- and regiochemistry of nucleophilic and organometallic displacement reactions of allylic compounds [2].
- Carbanion rearrangements [3].
- Molecular rearrangements of organosilicon compounds [4].
- Rearrangements involving tetraorganyl borates [5].
- An entire issue of the Journal of Physical Chemistry devoted to the fifth international conference on excess electrons and metal-ammonia solutions [6].
- Synthetic methods using α-heterosubstituted organometallics [7].
- α-Allenic ketones [8].
- Methodology for the construction of quaternary carbon centers [9].
- Organolithium catalysis of olefin and diene polymerization [10].
- An introduction to synthesis using organocopper reagents [11].
- Steric control in prostaglandin synthesis involving bicyclic and tricyclic intermediates [12].
- Metal atoms as reactive intermediates [13].
- Metal-salt-catalyzed carbenoids [14].
- Chemistry of optically active sulfur compounds [15].
- Synthesis, structures, and physical and chemical properties of metal and metalloid amides [16].
- A personal account of the early days of simple and complex metal hydrides of the main group metals [17].
- Selectivity in organometallic reactions through anchimeric coordination [18].
- Nucleophilic addition to transition metal complexes [19].
- New phosphaneborane chemistry [20].
- 1,5-Electrocyclizations [21].

2. PREPARATION OF ORGANOLITHIUM DERIVATIVES

A. Metalation at sp^3 carbon

Before beginning the discussion on metalations, it is appropriate to mention three papers concerned with the preparation of LDA and the accurate determination of organolithium reagents. First, LDA can now be prepared in molar quantities without the use of the expensive butyllithium or related reagents by reducing styrene with lithium in the presence of diisopropylamine [22]. The LDA so prepared has been used to synthesize six silyl enol ethers regioselectively (65-89%). The two new indicators useful in determining concentrations of organolithiums are 1 [23] and 2 [24] which form orange and red dianions, respectively.



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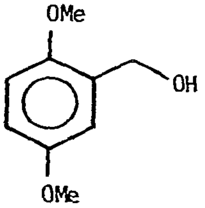

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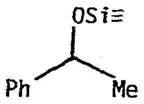
While hexameric, uncoordinated 3 has been found to be stable for months in hydrocarbons such as benzene, toluene, and the xylenes, it metalated more acidic compounds such as fluorene and phenylacetylene [25]. In contrast, coordinated 4 combined with benzene and toluene to afford phenyltrimethylsilane and benzyltrimethylsilane, respectively along with lithium hydride. Reagent 4 also metalated fluorene and phenylacetylene. Both compounds added in an oxophilic fashion to acetophenone to yield 5 in unspecified yield.

$(LiSiMe_3)_6$

3

$(LiSiMe_3)_2 \cdot (TMEDA)_3$

4



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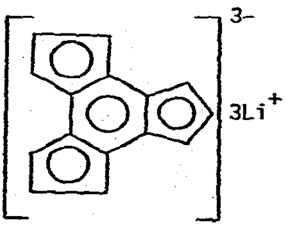
Trindene trianion 6 has been obtained from 7 and 8 with three equivalents of n-butyllithium in THF [26]. Condensation of 6 with ferrous chloride gave only traces of a sandwich compound containing three iron atoms. In contrast, the dilithio derivative corresponding to 6 formed sandwich compounds containing two iron atoms.



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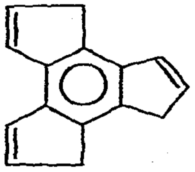

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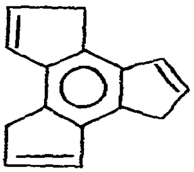

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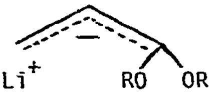
Dialkoxyallyllithiums 9 (R = Me, Et), prepared by metalation of the parent allylic acetals by s-butyllithium, have been found to serve as synthons of 10 since condensation with silicon- and tin chlorides followed by hydrolysis affords β-silyl- and β-stannylpropionic acid esters 11 [27].



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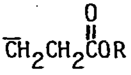

$\overset{-}{C}H_2CH_2\overset{O}{\overset{\|}{C}}OR$

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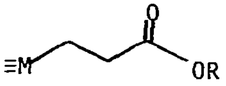

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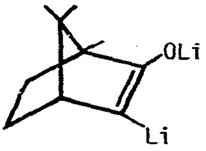
α-keto dianions illustrated by 12 have been prepared by metalation of α-bromoketones or addition of methyllithium to bromo enol acetates followed by metal-halogen exchange by t-butyllithium [28]. Dianion 12 has been trapped by D_2O in DOAc and by chlorotrimethylsilane to afford 13 and 14, respectively. Several other examples are listed.



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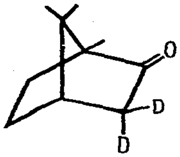

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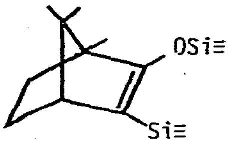

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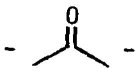
α,α'-Dianions of ketones unstabilized by phenyl or other electron withdrawing groups have been prepared by treatment of the parent organic acid with potassium hydride followed by n-butyllithium [29]. Three such multiple anions so prepared are shown. The reagents undergo mono-alkylation and -acylation at a much higher rate than do the corresponding monoanions.



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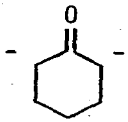

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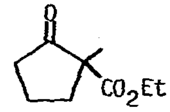
17

The previously described concept of selective reduction of difunctional molecules via enolate protection has been found to be successful provided the initially formed enolate enjoys stability [30]. For example, treatment of 18 with LDA followed by $LiAlH_4$ and quenching gave 19 (76%). In contrast, 20 failed to afford the desired reduction products in synthetically useful yields. The paper lists six other compounds which were successfully reduced and three others which failed.



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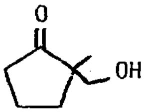

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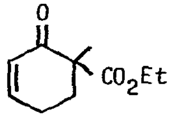
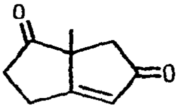


20

Selective enolate formation of 21, the bicyclo [3.3.0] analogue of the Wieland-Miescher ketone, has been realized using LDA to generate kinetic enolate 22 which, in turn, was silylated to afford 23 [31]. The authors are performing regio- and stereoselective transformations toward natural products using the above methodology.



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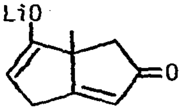

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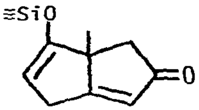
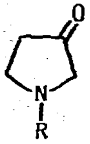


23

The direction of the enolization of 11 tertiary α-amino ketones has been studied with excess LDA at -78° (kinetic base), a deficiency of lithium hexamethyldisilazide (thermodynamic base), and triethylamine/DMF (thermodynamic acid) [32]. Except in the case of 3-pyrrolidinones 24 where enolization occurs away from nitrogen, the amount of enolization towards nitrogen increases as the electron withdrawing ability of the substituent on nitrogen increases as in 25, 26, and 27. Enolate formation of N-alkyl substituted amino ketones with LDA at low temperature gave distributions similar to the all-carbon systems.



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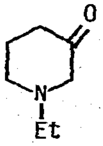

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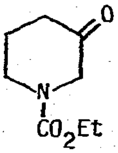

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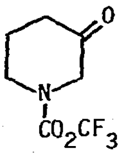
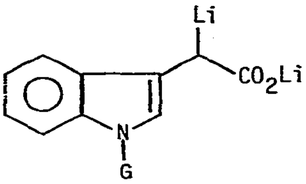


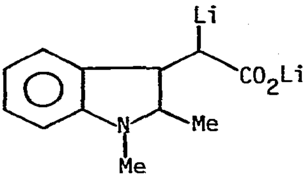
27

Multiple lithium derivatives such as 28 and 29 have been prepared by simple treatment of the parent compounds with n-butyllithium in THF at -78° [33]. Condensations of such compounds with a variety of electrophiles are reported. Another paper reported the similar preparation and condensations of thiophene derivatives 30-33 [34].



(G = Li, Me)

28



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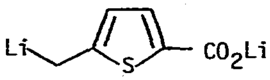

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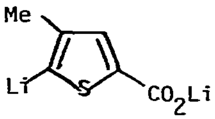

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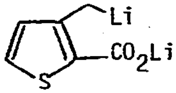

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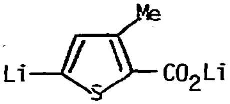
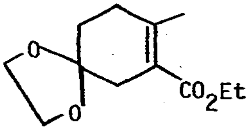


33

Esters 34 and 35 have been deprotonated at the methyl groups by lithium isopropylcyclohexylamide as evidenced by methylation to give 36 and 37, resprectively [35]. Similar chemistry was realized on ester 38 though the dioxolane ring was opened in some cases to give products such as 39. This work is being applied to the synthesis of anthracyclines.



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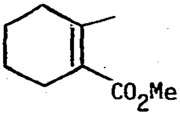

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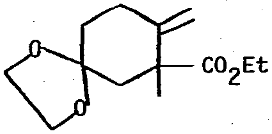

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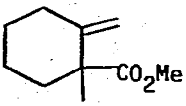

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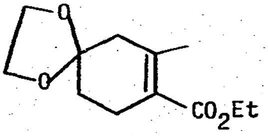

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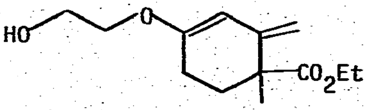
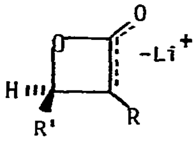


39

3-Lithio-2-oxetanones 40 (R usually = Ph, R' usually = t-Bu and i-Pr), prepared from the parent β-lactones and LDA in THF at -78°, have been combined with alkyl halides (R"X) to afford mostly 41 [36]. An ester (R" = CO_2Me) and ketone (R" = COPh) have similarly been obtained from 40 with methyl chloroacetate and benzoyl chloride, respectively. Interestingly, while the use of phenyl isothiocyanate on 40 followed by methyl fluorosulfate at -78° gave 42 (R = Ph, R′ = iPr), warming the reaction mixture for ten minutes prior to the addition of the latter reagent yielded 43 apparently via 44 [37]. The formation of 45, the hydrolysis product, represents only the third known example of 2-thietanimines.



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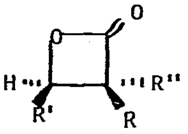

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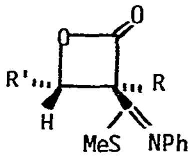

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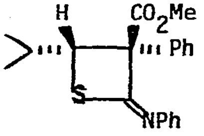

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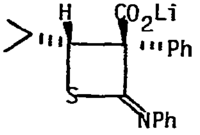

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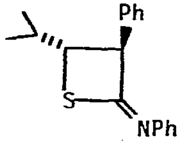

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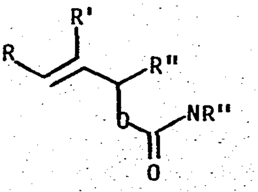
The protection of hydroxy groups as carbamates with concomitant enhancement of the acidity of carbon-hydrogen bonds has been studied in allyl systems 46 [38]. For example, treatment of 46 (R = R' = R" = F, R"' = Et) with three equivalents of dimethyl carbonate and two equivalents of LDA followed by benzyl bromide gave 48 via 47. It should be noted that the γ-product shown predominated over the α-isomer in a ratio of 95:5. Such products may be used in the preparation of 4-oxoalkanoates and 3-buten-4-olides.



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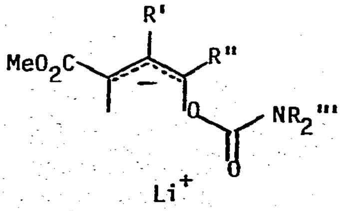

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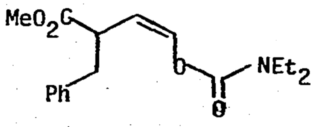
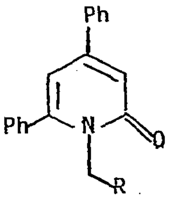


48

Several papers described additional examples of the preparation and reactions of dipole stabilized organolithium derivatives. Thus, pyridones 49 (R = H, Me) with LDA have been found to afford 50 via 51 as evidenced by condensation with a variety of electrophiles [39]. Self-condensation products 52 arose from two equivalents of 49, LDA, and one equivalent of electrophiles. Another type of product observed, 53, was realized from 49, ethyllithium, and the electrophiles.



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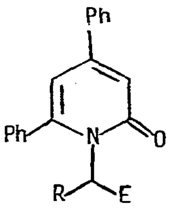

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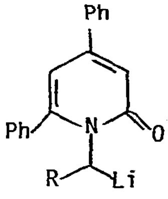

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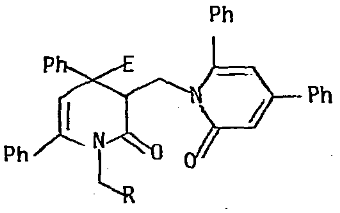

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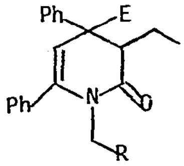
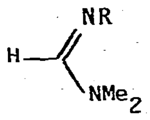


53

Amidines 54 (R = C-C_6H_{11}, n-Bu, t-Bu) have been converted by t-butyllithium to 55, then combined with alkyl halides, aldehydes, and ketones to yield 56 [40]. It should be noted that the formyl proton is not removed. Formamidine derivatives of piperidine, diethylamine, and 1,2,3,4-tetrahydroisoquinoline have also been metalated and alkylated.



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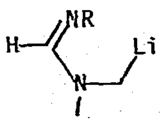

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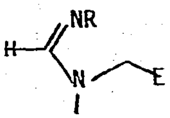
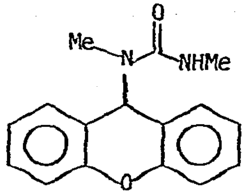


56

Urea 57 has been converted by two equivalents of LDA at -40° to dilithio derivative 58 as evidenced by methylation to give 59, and by deuteration [41]. Interestingly, both the N-monolithio derivatives of 57 and 59 rearrange at 25° to 60 (R = H and Me, respectively).



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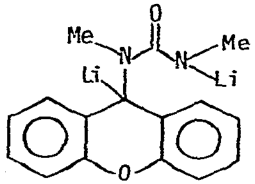

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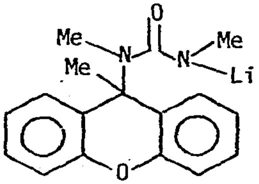

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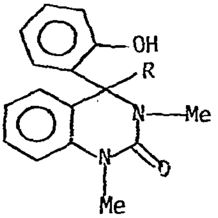
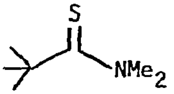


60

N,N-Dimethylthioamide 61 has been metalated by s-butyllithium both in the absence and presence of HMPA or TMEDA to afford 62 [42]. Subsequent condensations of 62 were realized with a variety of electrophiles to give 63 which can be hydrolyzed to pivalamides, cleaved to secondary amines, and reduced to neopentylamines.



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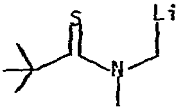

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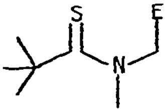
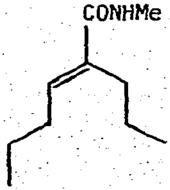


63

Turning to carbanions stabilized by carboxamides, α,β-unsaturated secondary amides have been found to undergo metalation at the β'-position and to combine with electrophiles at this same position [43]. The process is illustrated by the transformation of 64 to 65 followed by the addition of acetone and heat to afford lactone 66 (52%). A second paper described similar chemistry on N-t-butylmethacrylamide effected by n-butyllithium · TMEDA [44].



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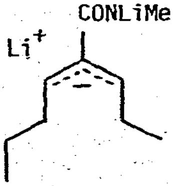

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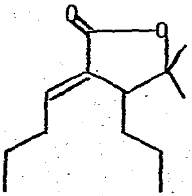
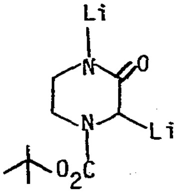


66

Other lithiocarboxamides prepared and subsequently condensed with electrophiles were 67 [45], 68 [46], and 69 [47].



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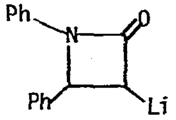

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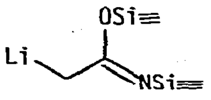
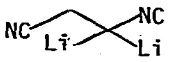


69

1,1-Dilithio derivatives 70 [48] and 71 [49] have been obtained by metalation of the parent isocyanides with two equivalents of n-butyllithium in THF at low temperatures. While 70 combines with ketones to give oxazines 72, 71 reacts with α,β-unsaturated esters to yield oxazoles such as 73. The latter condensations at the carbonyl group are to be contrasted with similar reactions of the corresponding monolithio derivatives of 71 at the β-carbon of such α,β-unsaturated esters to afford pyrroles. The preparation of 1-lithio-1,3-propylene diisocyanide and 1-lithio-1,4-butylene diisocyanide [48] and other condensations of 71 [49] are discussed.



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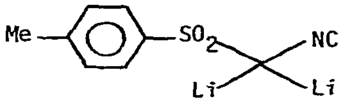

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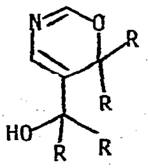

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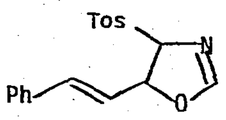
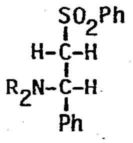


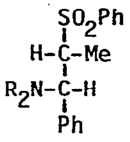
73

Diastereoselective deprotonation of either of the diastereotropic protons of β-aminoalkyl sulfones 74 can be achieved depending upon the type of amino group [50]. Thus, treatment of 74 with n-butyllithium and methyl iodide afforded 75 and 76 in a ratio of 84:16 and 94:6 when R = Me, Me and morpholine, respectively. In contrast, the reaction sequence gave 75 and 76 in a ratio of 13:87 when R = H,H and afforded only 76 when R = Me,H. The results are ascribed to gauche interactions versus chelation effects.



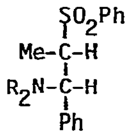
$$\begin{array}{c}SO_2Ph\\ |\\ H\text{-}C\text{-}H\\ |\\ R_2N\text{-}C\text{-}H\\ |\\ Ph\end{array}$$

74



$$\begin{array}{c}SO_2Ph\\ |\\ H\text{-}C\text{-}Me\\ |\\ R_2N\text{-}C\text{-}H\\ |\\ Ph\end{array}$$

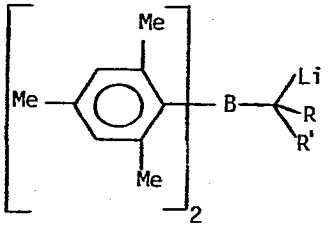
75



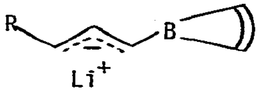
$$\begin{array}{c}SO_2Ph\\ |\\ Me\text{-}C\text{-}H\\ |\\ R_2N\text{-}C\text{-}H\\ |\\ Ph\end{array}$$

76

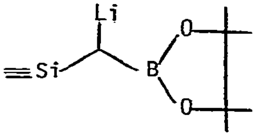
Additional examples of carbanions adjacent to boron continue to be described. Among those reported in 1980 by metalation of the parent compounds were 77 (R,R' = H,Me,Ph) using lithium dicyclohexylamide [51], and 78 (R = n-Bu, Me) [52] and 79 [53] using LiTMP. Reagents 78 were combined with trimethylsilyl- and tin compounds as part of the erythro-selective synthesis of β-alkyl alcohol derivatives.



77

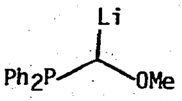


78



79

A convenient method for the transformation of ketones (R_2CO) to homologated aldehydes (R_2CHCHO) has been effected by treatment of the ketones with the new lithium reagent 80 [54]. Compound 80 is prepared by metalation of $Ph_2PCH_2OCH_3$ with s-butyllithium. The method is illustrated by the conversion of 81 to 82 (91%).



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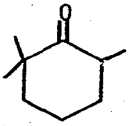
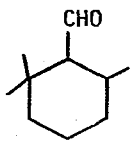
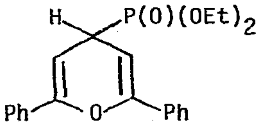


81

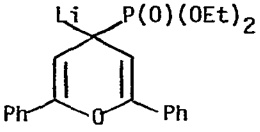


82

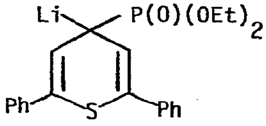
Phosphonate 83 has been deprotonated by n-butyllithium in THF at -78° to afford 84, a reagent which, upon condensation with ketones, affords a convenient route to unsymmetrical $\Delta^{4,4'}$-tetraphenyl-4-(thiopyranyl)-4H-pyran and related compounds [55]. The related anion 85 can be equilibrated to the isomeric 86 [56]. Unsymmetrically substituted bipyrans have also been prepared using 87, itself synthesized from 88 and n-butyllithium [57].



83



84



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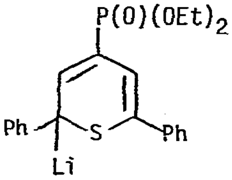
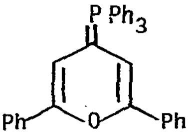


86



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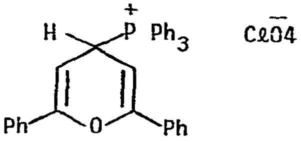
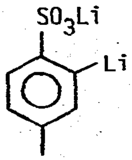


88

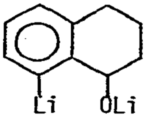
B. Metalation at sp^2 carbon

Electrophilic substituents may now be introduced ortho to sulfonic acid moieties by o-lithiation of lithium arenesulfonates followed by condensation with electrophiles [58]. For example, treatment of 89, prepared from lithium p-toluenesulfonate and n-butyllithium (10 min), with iodine followed by removal of the SO_3H group gave m-iodotoluene (65%). Several other examples are listed.

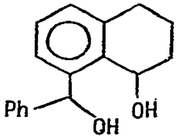


89

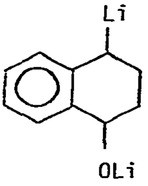
A full paper appeared in 1980 which discussed double deprotonations of benzylic alcohols by n-butyllithium · TMEDA in pentane to afford o-lithioalkoxides which were then condensed with alkyl halides and other electrophiles to afford certain derivatives[59]. The methodology is illustrated by the preparation of 90 and its conversion by benzaldehyde to 91 (69%). Interestingly, upon standing for 48 hr. at 25°, 90 rearranges to 92. A very large number of additional examples are included in the paper.



90

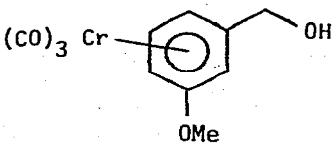


91

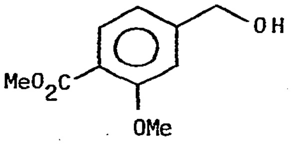


92

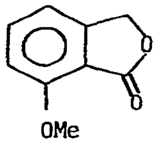
The regiolithiation of benzyl alcohols is changed when such compounds are complexed with chromium tricarbonyl [60]. Thus, metalation of 93 with n-butyllithium · TMEDA followed by carbonation, removal of the metal, and esterification afforded 94 and 95 in a ratio of 77:23. Similar chemistry on m-methoxybenzyl alcohol itself yielded 94 and 95 in a ratio of 10:90. Several other examples are presented including such regioselective lithiations of methoxybenzamides. Two full papers discussed the metalation and condensations of (benzene) tricarbonylchromium [61] and a variety of its derivatives [62].



93

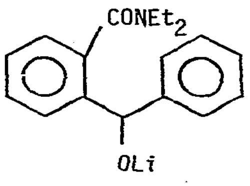


94



95

One-pot tandem directed metalations of benzamides and benzyl alcohols have been employed to synthesize polycyclic aromatic hydrocarbons including ellipticine alkaloids [63]. For example, lithiation of N,N-diethylbenzamide and condensation with benzaldehyde gave 96 which, upon further lithiation by n-butyllithium afforded 97. The latter compound cyclized to 98 which was converted to anthraquinone (43%) upon standing at room temperature for 12 hr.



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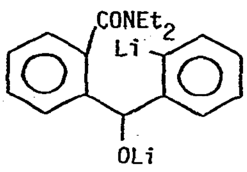

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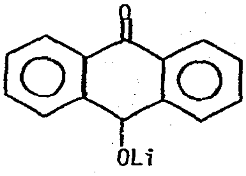
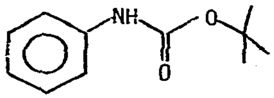


98

The t-butoxycarbonyl group has been touted as a conveniently removed moiety in the ortho functionalization of aniline derivatives as illustrated in the conversion of 99 to 100, and then to 101 [64]. The blocking group is removed by HCl in 50% aqueous THF.



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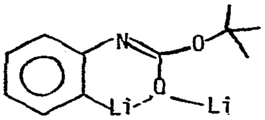

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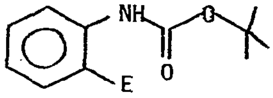
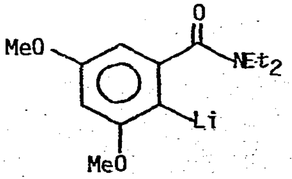
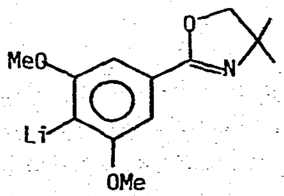


101

That N,N-diethylcarboxamido has stronger activating ability than the oxazoline moiety has been confirmed by the preparation of 102 and mostly 103 from the respective parent compounds and n-butyllithium in THF at -78° [65]. Interesting solvent and base effects were noted in the metalations of the parent oxazoline since 103 was favored with n-butyllithium in THF at low temperature while 104 was the predominant derivative with this base in ether and DME. Moreover, in THF, t-butyllithium and s-butyllithium promoted the formation of 103 and 104, respectively.



102



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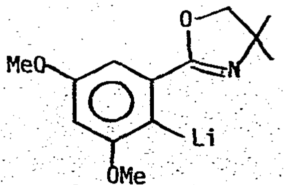
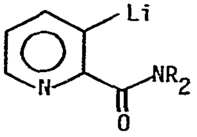


104

Lithium derivatives 105-107 (R = i-Pr) have been prepared by metalation of the parent pyridines by LDA then combined with electrophiles [66]. The corresponding N,N-diethyl derivatives also underwent o-lithiation but the resulting organolithium reagents immediately self-condensed to afford ketoamides illustrated by 108.



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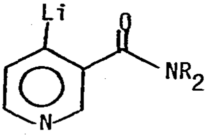

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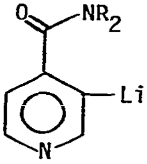

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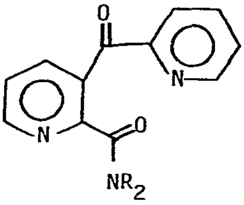
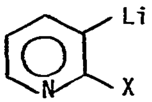


108

Halopyridines have also been regioselectively lithiated using LDA at -78° in THF to give 109-111 [67]. While the greatest effort was directed towards the chloro derivatives, the stability of 110 seemed to be in decreasing order X = F>>Cl>Br>>I. Condensations with certain electrophiles are described.



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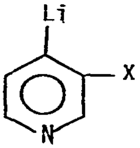
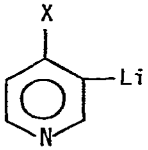
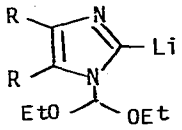


110



111

Other organolithium derivatives of heterocycles similarly prepared and condensed with electrophiles were 112 [68], 113 [69], 114 and 115 [70], 116 [71], 117 [72], and 118 and 119 [73]. Lithiation of 120 by n-butyllithium gave 121 which isomerized to 122 in the presence of HMPA [74]. Also prepared from the parent compounds by metalation were 123 and 124 [75], and 125 [76].



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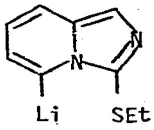

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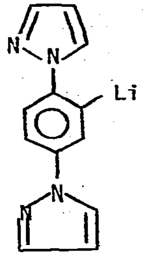

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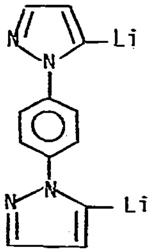

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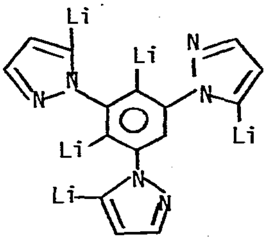

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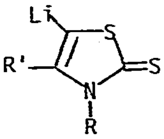

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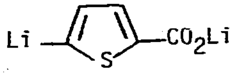

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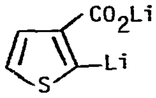

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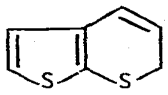

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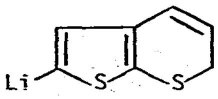

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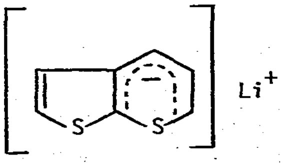

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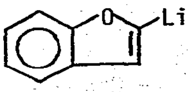

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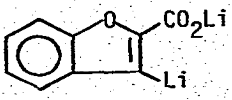

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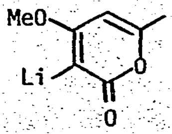
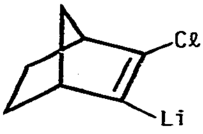


125

Lithium derivative 126 has now been generated in the absence of excess metalating agent by treatment of 127 with t-butyllithium in THF-pentane at -45° [77]. No detectable decomposition of 126 was noted even at 25° unless extra t-butyl- , n-butyl-, or methyllithium were added. Condensations of 126 with electrophiles are reported.



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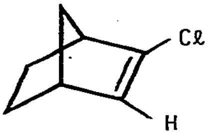
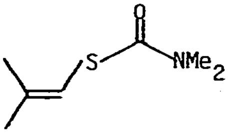


127

Vinyl metalation of 128 by LDA or t-butyllithium to yield 129 has been described [78]. The reagent combines with ketones to ultimately afford enethiolates illustrated by 130.



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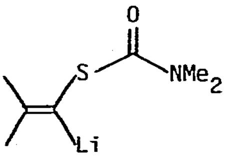

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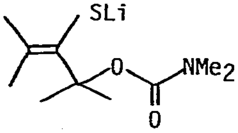
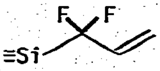


130

C. Miscellaneous Methods

gem-Difluoroallyllithium has now been prepared more conveniently by treatment of mixtures (5:2 to 20:1) of $CF_2BrCH = CH_2$ and $CF_2 = CHCH_2Br$ with n-butyllithium in THF-ether-pentane at -95° [79]. Such reactions in the presence of chlorosilanes led to the formation of 131 (R = Me, Et, Pr). The newer method is especially useful in condensations of the organolithium with aldehydes to afford 132 (R or R' = H, aliphatic, aromatic) (41-95%) free from the isomeric 133.



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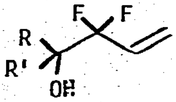

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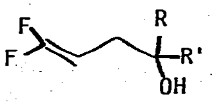
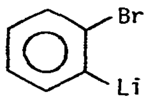


133

o-Bromophenyllithium (134) has been prepared in >95% yield by reaction of o-dibromobenzene with n-butyllithium in ether-THF at -110° [80]. Not surprisingly, this reagent is very temperature sensitive and decomposes to a large number of products at temperatures up to -90°. Despite this, 134 has been combined with a variety of electrophiles to give 135. Lithium-bromine exchange was also utilized in the conversion of 136 to perfluorofluorenone [81].



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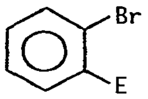

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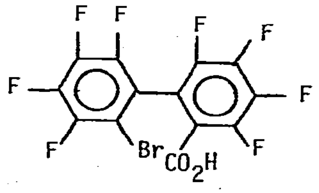
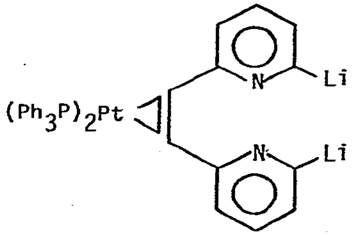


136

Lithium-halogen exchange has also been utilized in the preparation of 2,6-dilithiopyridine from 2,6-diiodo- and 2,6-dibromopyridine [82], 137 from the corresponding dibromo derivative [83], 8-lithioquinoline from 8-bromoquinoline [84], 138 from the dibromo derivative [85], and 139 (R = H or alkyl) from the related chloro- and bromosilanes [86].



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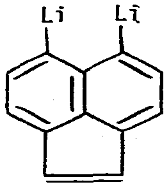

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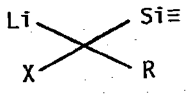
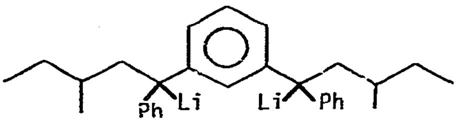


139

Dilithium derivative 140 has been obtained from the addition of two equivalents of s-butyllithium to 141 in toluene at 25° [87]. Reagent 140 is suitable as a soluble bifunctional initiator for certain polymerizations.



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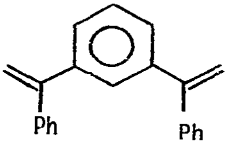
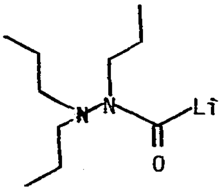


141

Tripropylcarbazoyllithium (142) has been prepared by carbonylation of 143 in THF-hexane at -75° [88]. While 142 combines with electrophiles at low temperature, it undergoes rearrangement at higher temperatures to afford 144.



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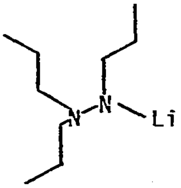

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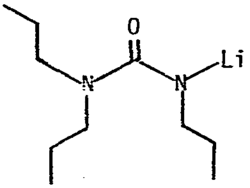
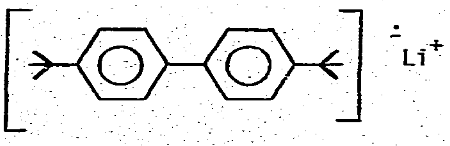


144

Alkyllithium reagents have been prepared by reaction of alkyl halides with certain lithium radical anions, especially 145 [89]. For example, the full paper describes the conversion of 7-chloronorcarane to 7-lithionorcarane (95%) by 145. Other radical anions studied which were inferior to 145 included lithium naphthalenide and lithium di-t-butylnaphthalenide. The combination of lithium 1-(dimethylamino)naphthalenide or lithium naphthalenide with α-(phenylthio)ethers has been found to constitute a general preparative method for α-lithioethers as illustrated by the formation of 146 from 147 [90].



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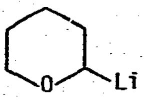

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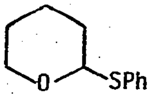
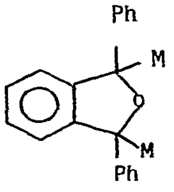


147

2,2,3,3-Tetramethylcyclopropyllithium has been synthesized in ethyl ether from the corresponding cyclopropyl bromide and lithium wire or lithium dispersion containing 2% of sodium [91]. The reagent, less stable than the non-methylated derivative, has been combined with certain silicon and tin chlorides.

Dianions 148 (M=Li,Na,K) [92] and 149 [93] have been prepared by reduction of parent systems 150 (THF) and 151 (ammonia), respectively. Condensations of both reagents with electrophiles are described.



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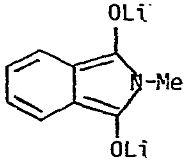

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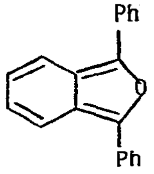

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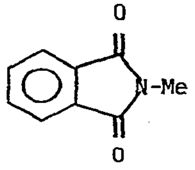
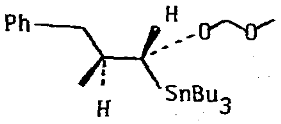


151

Tin-lithium exchange has been employed to prepare α-alkoxyorganolithium reagents which have been found to be configurationally stable [94]. For example, 152 and n-butyllithium give 153. Such a metal-metal exchange process has also been used to synthesize 1,4-dilithio derivative 154 from 155 [95], and 156 from 157 [96]).



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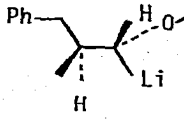

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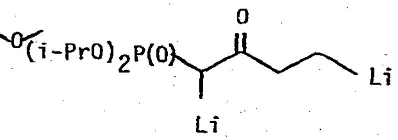

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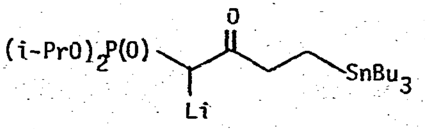

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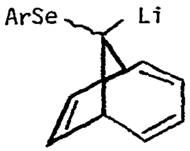
156

157

Other carbanions prepared included 158 from 159 and n-butyllithium [97], and 160 from the parent polymer and enolates such as lithiodiethyl malonate [98].



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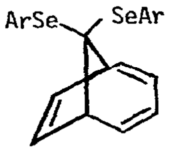

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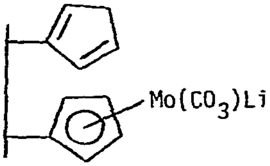


160

3. STRUCTURAL STUDIES

A review article concerned with alkali metal-transition metal π-complexes contains a large number of previously described crystal structures of organolithiums [99]. Those pictured include the following:

$[Li(THF)_4]^+[(C_2H_4)_2Ni(PR_2)Ni(C_2H_4)_2]^-$ $(R=C_6H_{11})$

$[(LiC_6H_5)_2(THF)_4]NiC_{14}H_{10}$

$[(LiC_6H_5)_3Ni]_2N_2$

$\{C_6H_5[NaEt_2O]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OEt)_4Et_2O\}_2$

$[Li(TMEDA)]_2Ni(CDT)$

$Li_2Ni[Me_2NCH_2CH_2CH_2CH_2NMe_2]_3$

$[Li(TMEDA)]_2Ni(norbornene)_2$

$[Li(TMEDA)](\pi\text{-}C_5H_5)Fe(C_2H_4)_2$

$[Li(TMEDA)]_2Fe(C_2H_4)_4$

Structures first described in 1980 included that of the dimer of dilithiobenzophenone complexed with THF and TMEDA (Figure 1) [100]. In this compound, both lithium atoms (Li1,Li1') interact with one lone pair of the carbonyl oxygen via three-center bonding while the other lone pair is directed towards one of the Li2 lithium atoms.

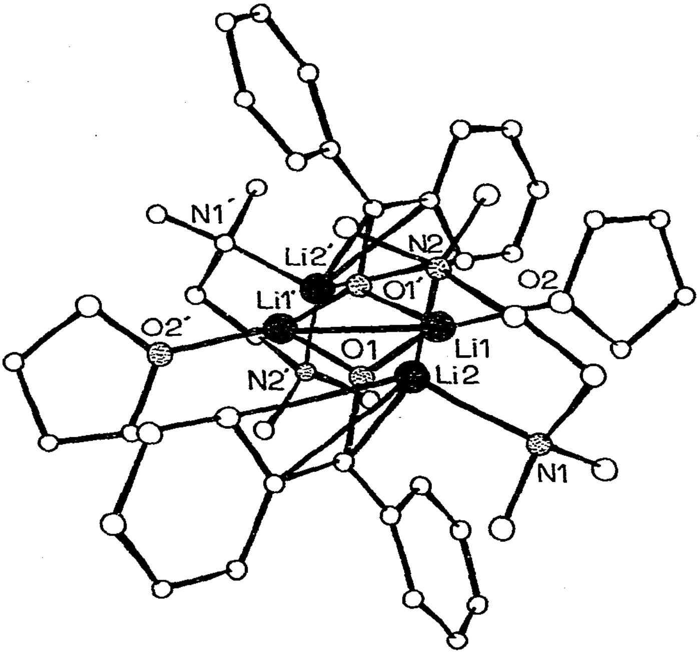


Figure 1. Dilithiobenzophenone dimer from B. Bogdanovic, C. Kruger, and B. Wermeckes; Angew. Chem., 92 (1980) 844; Angew. Chem. Int. Ed. Engl., 19 (1980) 817.

The crystal structure of the dimer of 2-lithio-2-methyl-1,3-dithiane complexed with TMEDA is shown in Figure 2 [101]. The lithium atoms occupy equatorial positions in which interaction between the negative carbon center of one ring is equal to that with a sulfur atom of the other ring. The authors speculate that this type of structure may be preserved in THF where the oxygen atom of the solvent may assume the role of the nitrogen atoms of the TMEDA. Figure 3 shows the structure of $Li_3Co_3(CO)_{10} \cdot i\text{-}Pr_2O$ which consists of the ions Li^+ and $[Co_3(CO)_{10}]^-$ [102]. The cations are surrounded in an approximate tetrahedron by one ether oxygen atom and three carbonyl oxygen atoms of three different cluster units.

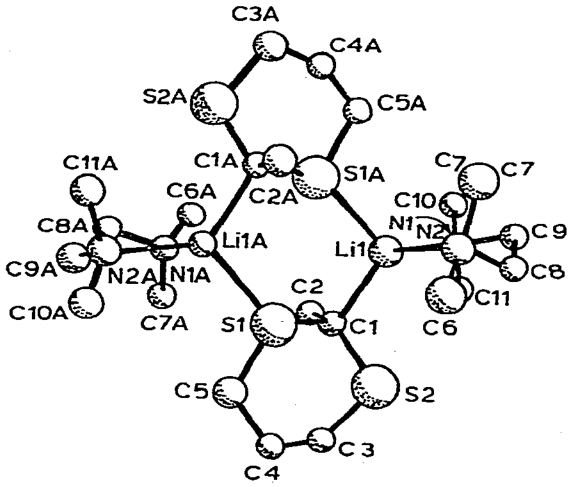


Figure 2. 2-Lithio-2-methyl-1,3-dithiane·TMEDA dimer from R. Amstutz, D. Seebach, P. Seiler, B. Schweizer, and J. D. Dunitz; Angew. Chem., 92 (1980) 59; Angew. Chem. Int. Ed. Engl, 19 (1980) 53.

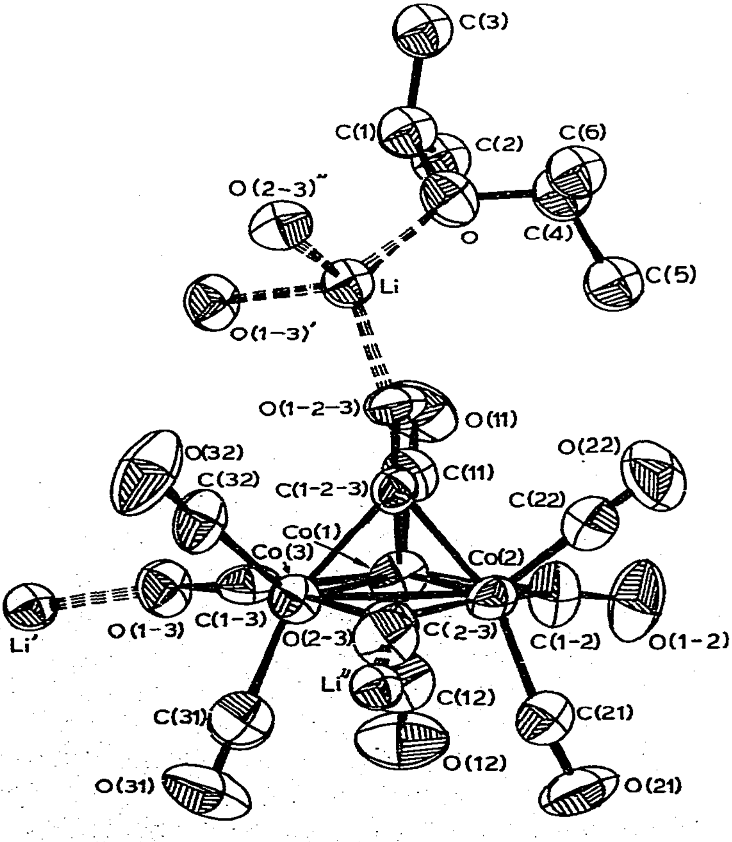


Figure 3. LiCo$_3$(CO)$_{10}$·i-Pr$_2$O from H.-N. Adams, G. Fachinetti, and J. Strahle; Angew. Chem., 92 (1980) 441; Angew. Chem. Ed. Engl, 19 (1980) 404.

The crystal structure of hexameric trimethylsilyllithium is shown in Figure 4 [103]. The core of lithium atoms surrounded by trimethylsilyl groups is described as a six-membered ring in a highly folded chain conformation or as a distorted octahedron. The bonding is suggested to consist of four-centered electron-deficient Si-Li bonds.

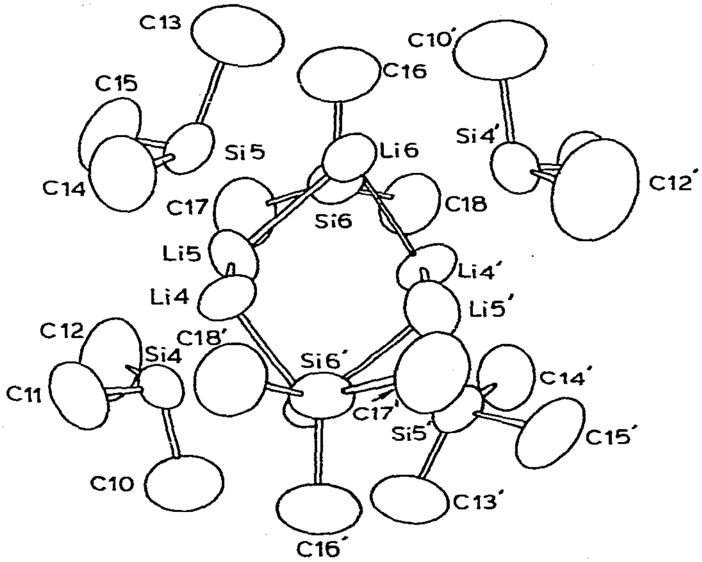


Figure 4. $(LiSiMe_3)_6$ from W. H. Ilsley, T.F. Schaaf, M.D. Glick, and J.P. Oliver; J. Am.Chem. Soc., 102 (1980) 3769.

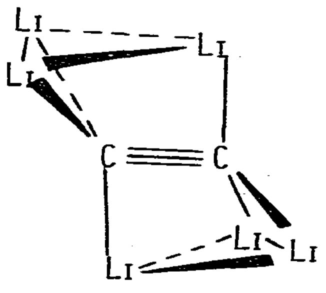
Crystal structures were also described for $[Li(OC_6H_2Me\text{-}4\text{-}t\text{-}Bu_2\text{-}2,6)(OEt)_2]_2$ [104] and lithium bis(dithioxalato)nickelate (II) [105].

4. APPLICATION OF MOLECULAR ORBITAL THEORY

The number of papers discussing molecular orbital calculations on organolithium reagents continued to increase in 1980. The "most complete and elaborate theoretical treatment of the methyllithium molecule performed to date" has been accomplished using the near Hartree-Fock basis set plus configuration interaction calculations [106]. The problem was studied with the aid of electron density and density difference maps. The authors conclude that the most reasonable estimate for the charge separation along the C-Li bond is 0.55-0.60 electron, a half-covalent value consistent with ionic mechanisms which does not prohibit occasional radical behavior. INDO molecular orbital calculations using finite perturbation theory have been employed to study the effect of aggregation on the ^7Li-^{13}C coupling constant in methyllithium [107]. That a value of over 200 Hz is suggested for the monomeric compound supports the alleged predominantly covalent character of the carbon-lithium bond. A third paper described the use of the computationally efficient partial retention of diatomic differential overlap (PRDDO) method to obtain optimized geometries and wave functions for $(CH_3Li)_n$ where n=1-6, and for $(C_2H_5Li)_n$ where n=1,2 [108]. Calculation of binding energies revealed the existence of stable planar arrangements of lithium and carbon atoms for the dimer through the hexamer. The calculations also indicated that a condensed tetramer and condensed hexamer are stable. Multicentered bonding involving closed three-center Li-C-Li and closed four-centered Li_3C bonds are found in such clusters. Using the Gaussian 76 program, the planar H_2CLi^- species has been found to be stabilized relative to H_3C^- [109]. The planar structure, the short C-Li bond (1.85Å), and the stabilization of the compound are ascribed to p-orbital involvement of the lithium atom. This hypothesis is supported by calculations showing that H_2CNa^-, where the sodium p-orbitals are much higher in energy than those of lithium, is highly destabilized relative to H_3C^-.

The Gaussian 76 program has also been employed to determine three favorable minima on the singlet potential energy surface for C_2Li_6 [110]. The three isomers, represented by structures 161, 162, and 163, are characterized by triple, double, and single carbon-carbon bonds, respectively.

Stabilization of the carbanions $XCH_2CH_2^-$ ($X=F,CF_3$) produced by deprotonation of the parent ethane derivatives has been shown using ab initio calculations at the 4-31 level to differ in the three conformations 164, 165, and 166 [111]. The deprotonation energies (E/kJ mol^{-1}) are listed below for each. That conformationally independent and conformationally dependent mechanisms are operating



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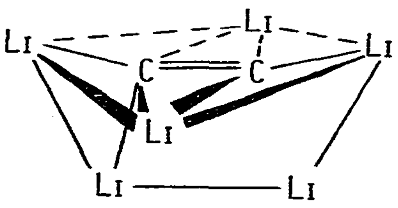

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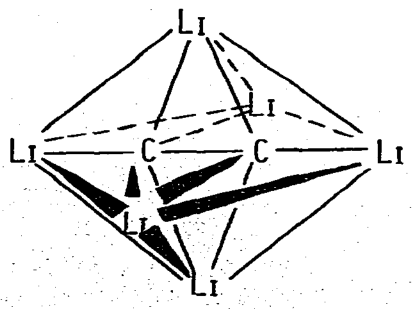

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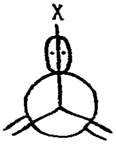
are ascribed to induction and negative hyperconjugation, respectively.



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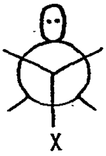

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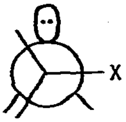
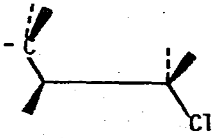


166

F	1859.3	1852.8	1886.6
CF_3	1838.8	1845.5	1867.2

Similar studies using the 3G and 4-31G basis sets have revealed the importance of long range stereoelectronic effects and the W-arrangement in β-haloanions [112]. For example, protonation energies reveal that 167 and 168 are more stable than 169 and 170, respectively. As a result, the parent β-haloalcohols are more acidic by several pK units in the trans than in the cis or gauche conformation. Likewise, hydrogen atoms beta to carbon-halogen bonds in planar W-arrangements are more acidic than those in other conformations. The results, ascribed to two-electron interactions between an anion lone pair orbital and the empty σ^*_{c-x} orbital, are extended to a variety of halobicyclic materials.

167



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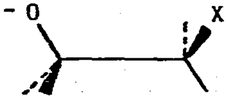

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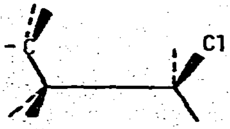

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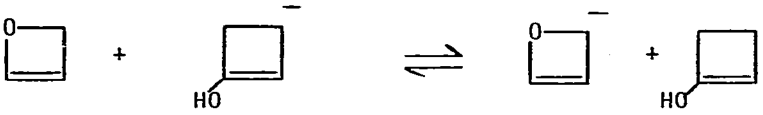
Using the isodesmic reaction shown below in order to relate the stability of the six-pi electron oxetenyl anion 171 with model system 172, calculations have revealed a cyclic resonance stabilization of about 20 kcal/mol for 171 [113]. In contrast, the four-pi electron cation corresponding to 171 was found to be destabilized by about 50 kcal/mol.

The self-consistent electron pairs (SCEP) method has been employed to reveal that the allenic anion H_2CCCH^- is bent, resembling allene [114]. The presence of triple bond character is apparently responsible for the relatively low barrier to inverison of 7 kcal.



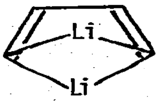
172 171

A "mixed" basis set using STO-3G calculations on all atoms except the negatively charged carbon along with 4-31 calculations on the latter atom has been utilized to predict the pKa value of 33 for benzocyclopropene [115]. This method also provided derived pKa values for other active hydrogen compounds as follows: cyclopentadiene, 15; toluene, 41; cyclopropene, 60; and ethane, 63.5. The results are compared to those obtained in the base cleavage of certain trimethylsilyl derivatives.

The Mobius 3-cyclobutenyl anion has been studied in conjunction with the 3-cyclobutenyl cation using MINDO/3 to evaluate homoaromaticity [116]. In planar optimized structures, the homodelocalization energy of the cation is about 4 kcal greater than that of the anion. σ-Nonclassical effects are stabilizing in the cation but destabilizing in the anion.

A large number of substituted pentadienyl anions has been studied by MNDO to reveal the order of stabilities of the geometric forms to be W>S>U by about 1.0 and 3.7 kcal/mol, respectively [117]. Stabilization of the anions by substitution of methyl for hydrogen in the 1- and 3-positions is ascribed to polarization rather than induction or negative hyperconjugation. Charge densities (3->1->2-) are discussed.

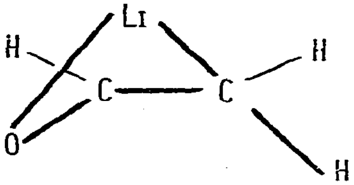
A variety of structures have been considered for $R_4C_4Li_2$ by employing one Huckel and one Mobius molecular orbitals [118]. The authors propose that the most favorable structure is that represented by 173.



173

Substituent interactions of a series of benzyl and anilide anions substituted in the meta- and para positions with CH_3, NH_2, OH, OMe, F, NO_2, CN, CHO, and CF_3 have been investigated using the minimal STO-3G basis set [119]. Among others, the authors conclude that the effect of substituents on the acidities of the parent compounds is more important in the anions than in the acids themselves. They warn that "the substituted phenoxides are satisfactory models for the corresponding benzyl anions in the gas phase but not in solution, owing to specific solvation effects."

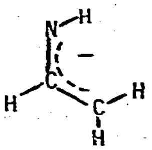
Configuration interaction calculations using a Dunning-Huzinaga basis set on acetaldehyde enolate have been used to find a low-energy Rydberg-like excited anion lying 1.82 eV above the anion ground state [120]. This excited anion is probably responsible for the resonances previously observed in electron photodetachment experiments. Another paper described the use of the Dunning and Hay contraction along with polarization (d) functions to study the lithium enolate of acetaldehyde [121]. The lowest energy structure was found to be 174, a chiral enolate with geometry similar to allyllithiums.



174

Fully optimized geometries and relative energies of syn- and anti-acetaldehyde imine, their anions, vinylamine, and related systems have been obtained using 4-31G calculations [122]. To illustrate the results, the CCN angles in syn-175 and anti-176 were found to be 133° and 128°, respectively. That the syn-conformations in this and related anions are more stable than the anti-conformations is ascribed to electrostatic repulsion between the electrons at C-3 and the lone-pair electrons at N-1. The C-3 atom of 175 was found to possess significant negative charge ($q\pi$=-0.54, $q\sigma$=-0.01).

Three local minima in singlet STO-3G potential surfaces of lithioacetonitrile were found to correspond to 177, 178, and 179 [123]. The CCN system in 177, the most stable compound, is significantly bent (24.4°). Another paper



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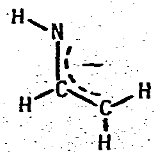

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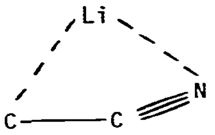
disclosed CNDO/2 calculations to determine the stable geometry and electronic structure of certain conformations of 180 (n=1-3) [124]. The work confirmed that intramolecular complexation exists between the lithium ion and cyanide groups located down the chain.



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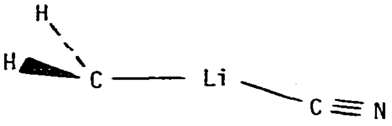

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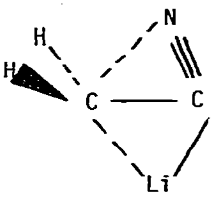

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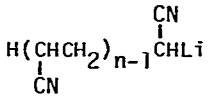
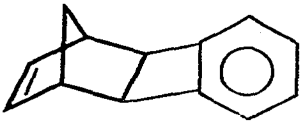


$H(\underset{CN}{CH}CH_2)_{n-1}\overset{CN}{CHLi}$

180

A review of experimental data coupled with 4-31G calculations on certain sulfonium salts has led to the conclusion that "the proton that lies most nearly perpendicular to the axis of the sulfur lone pair will undergo abstraction by base at the greatest rate" [125]. Lone-pair repulsions are minimized in such processes.

Several papers discussed the application of molecular orbital theory to the Birch reduction. Three of the papers were concerned with the structures and stabilities of the radical anions of substituted benzenes [126], the structures and stabilities of substituted cyclohexadienyl radicals [127], and the structures and stabilities of cyclohexadienyl anions [128]. Among other conclusions, it is revealed that kinetic protonation of the substituted benzene radical anions occurs ortho or meta to π-donor substituents and ipso or para to π-acceptor groups. In contrast, thermodynamic protonation in such systems occurs ortho to methyl and strong π-donors such as OH, OMe, and NH_2, and para to other groups. In the case of the monoanions of cyclohexadienes, kinetic protonation occurs preferentially at the carbon atom para to the first protonation site regardless of substituent or its position on the ring. The enhanced rates of the reduction of the double bond in 181 by lithium in ammonia/t-butyl alcohol has been ascribed to the presence of sizable through-three-bond interactions as verified by Huckel calculations [129]. Similar through four- and six-bond interactions have also been demonstrated in other systems [130]. That 182, 183, and 184 are reduced about 10^5 times more readily than norbornene has been explained in terms of through-space interactions operating between the two lowest unoccupied molecular orbitals in these compounds [131].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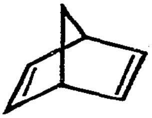
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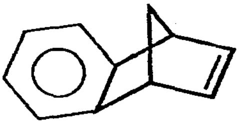
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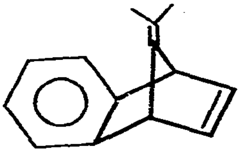

184

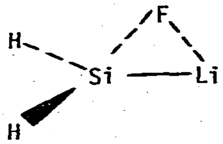
In a study describing ab initio calculations on $CSiH^-$, $CSiH_2$, and $CSiH_3^+$, deprotonation of $CSiH_2$ showed an energy surface with a minimum corresponding to 185 and a maximum corresponding to 186 [132]. Another paper discussed the use of the Gaussian 76 series to study the silylenoid SiH_2LiF [133]. Four minima, 187-190, were found on the potential energy surface with 187 and 188 being the most stable ones.

$H\text{-}C\equiv Si^-$

185

$H\text{-}Si\equiv C^-$

186



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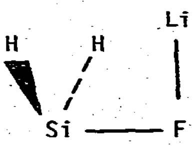

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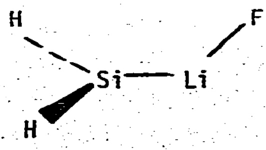

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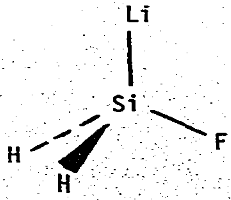

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Finally, configuration interaction calculations have been employed to reveal that PLi_3 shows a minimum at a bond angle of about 102° with a barrier of approximately 2.2 kcal/mol [134].

5. SPECTROSCOPIC DETERMINATIONS

A. NMR Spectroscopy

The low temperature ^{13}C-NMR spectra of 16 ^{13}C- and ^6Li-labeled chloro-, bromo-, and iodolithium carbenoids have been described [135]. The types of compounds studied are shown below. All of these carbenoids except 194 displayed $^1J(^7Li,^{13}C)$ coupling of about 45 Hz. Usually, the exchange of hydrogen or halogen by lithium was found to cause deshielding of the ^{13}C-signal by up to 289 and 434 ppm, respectively and a decrease of $^1J(^1H,^{13}C)$ and $^1J(^{13}C,^{13}C)$ couplings of up to 104 and 30 Hz, respectively.

X_2CHLi

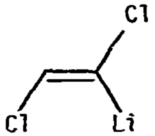
191

X_3CLi

192

$MeCBR_2Li$

193



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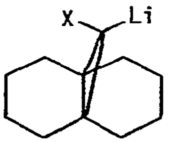

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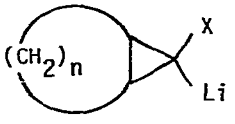
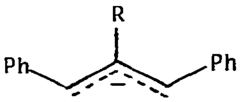


196

Peaks due to different propyllithium aggregates have been observed in high field ^{13}C NMR of $CH_3CH_2{}^{13}CH_2{}^6Li$ [136]. The distribution of the aggregates with aggregation numbers of 6,8, and 9 varies with temperature and all undergo fast intraaggregate carbon-lithium bond exchange from the collision of two aggregates. Coupling (^{13}C-^6Li) and chemical shifts due to interaggregate carbon-lithium bond exchanges are reported. Various equilibrium constants and thermodynamic data connecting the aggregates are given.

The conformations and barriers to rotation of 1,3-diphenylallyllithiums 197-199 have been studied by ^1H-NMR spectroscopy [137]. The only compound to exist predominantly in the exo, exo-conformation (197) was the parent one (R=H). The endo, exo-conformer (198) predominated when R=Me and CN while the endo, endo-material was preferred when R=Et, Ph, iPr, and t-Bu. Steric interaction is diminished in 199 by a rotation of the phenyl rings out of the plane of the allyl carbon system and by an increase of the sp^2 angles. The barriers to rotation range from 19.1 kcal/mol (R=H) to 12.5 kcal/mol (R=i-Pr). The anions are said to be solvent separated ion pairs. Three other papers discussed the application of Saunders' isotopic perturbation method to allyllithium by determining the ^{13}C-NMR spectra of this compound deuterated at C_1 [138-140]. The authors ruled out equilibrating unsymmetrical structures for the material and favored one such as 200. While one paper suggested that the C_1-Li and C_3-Li bond lengths are similar but not identical [139], another proposed a symmetrical bridged structure [140].



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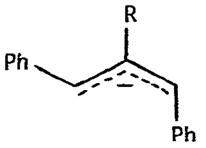
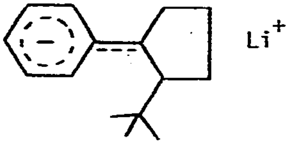


198

199

200

Both 'H and ^{13}C-NMR spectra have been reported for a variety of organolithiums obtained by the addition of t-butyllithium to 1-phenylcyloalkenes [141] and certain α-methylstyrenes [142, 143]. For example, both the 'H- and ^{13}C-NMR results for 201 support the conclusion that the compound exists as a solvent separated ion pair. Such interaction of t-butyllithium with 1-phenylcyclobutene, -cyclohexene, and -cycloheptene gave polymerization, allylic deprotonation, and aromatic ring metalation, respectively. Loose ion pairs containing conjugated anions where the ring shifts were found to be independent of ligand and counterion were found in adducts 202 (X=H, Me_3Si(Ge, Sn), MeS, PhS, c-Pr, Ph, MeO, Pr) [142]. The substituent X displayed a critical effect on the barriers to rotation where the latter largely reflected changes in ground-state energies of the anions. Compound 202 itself (X=H) has been generated in cyclopentane in the absence as well as in the presence of ethers and tertiary amines [143]. The NMR spectra for each of the resulting stable solutions were identical in the presence of the ethers and amines but different from that in cyclopentane alone, a result consistent with the presence of loose and tight ion-pairs, respectively.



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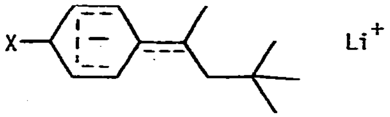
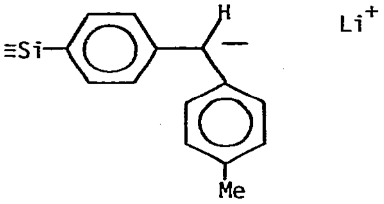


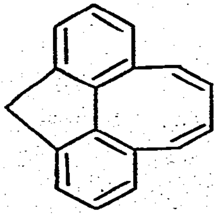
202

Two other papers also described NMR spectroscopy of benzylic systems. First, 7-phenylnorbornyllithium has been shown by low-temperature ^{13}C-NMR spectroscopy to be a pyrimidal system where $\Delta G^{\ddagger}_{205} = 9.4 \pm 0.2$ kcal/mol and $\Delta H^{\ddagger} = 6.7 \pm 2$ kcal/mol [144]. In contrast, the spectra for the related potassium and cesium derivatives were consistent with planar carbanions. The other paper used both 'H and ^{13}C NMR spectroscopy to demonstrate stabilization of the diphenylmethyl anion 203 by a para trimethylsilyl group where the 4-methylphenyl moiety rotates 200 times greater than the 4-trimethylphenyl group at 255°K [145]. The results were confirmed by MO calculations.



203

Peripheral delocalization in the monolithium derivative of 204 [146], the parent cyclophanetetraene 205 and its dilithium derivative [147], and 206 and its dilithium derivative [148] has been suggested based on NMR studies. Also reported were the 'H-NMR spectrum of the tetraanion of 205 and the 'H- and ^{13}C-NMR spectra of the tetraanion of 206.



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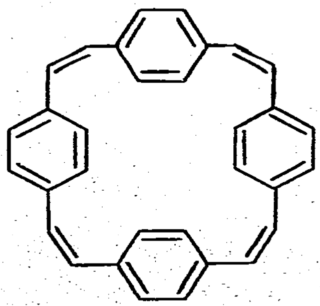

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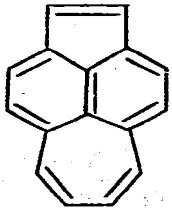
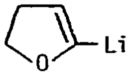


206

Vinyllithium derivatives 207-209, prepared by metalation of the parent compounds, have been examined by ^{13}C-NMR spectroscopy [149]. While all of the carbon resonances are shifted relative to the parent ethers, the largest shifts (downfield) are noted on the carbons bonded to the lithium atoms (56-61 ppm).



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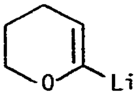

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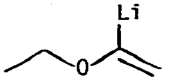
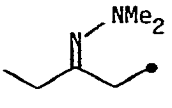


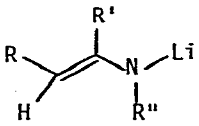
209

The deprotonation of (Z)-[1-^{13}C]-3-pentanone dimethylhydrazone (210) was studied by ^{13}C-NMR spectroscopy to reveal low regioselectivity and the absence of isomerization of the Z-to the E-isomer [150]. The authors state that "generalizations regarding the regioselectivity of kinetic deprotonation of all C=N carbonyl derivatives can not be made." Another paper discussed the 'H-NMR spectra of a large number of 1-azaallyl anions 211 prepared by metalation of the parent compounds [151].



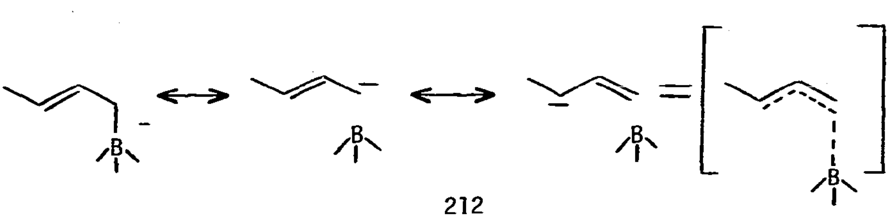
(● = ^{13}C)

210



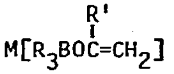
211

The presence of σ-π conjugation thereby enhancing the negative charge on the gamma carbon of allylic boron ate complexes illustrated by 212 has been demonstrated using ^{13}C-NMR studies [152]. Thus, the gamma and beta carbon atoms in such compounds are shielded and deshielded, respectively. Other NMR studies on ate complexes described coupling constants between ^{11}B-^{13}C, ^{13}C-'H, and ^{11}B-'H for $LiBMe_4$ [153], and 'H, ^{7}Li, ^{13}C, and ^{27}Al NMR spectra for lithium t-butoxyaluminates [154]. The latter investigation revealed that the equilibrium shown in equation 1 had a Keg = 2.2×10^{-2}. 'H- and ^{11}B-NMR have been used to show that while lithium ketone enolates do not detectably interact with triorganoboranes, the corresponding potassium enolates do react to afford enoxyborates 213 [155].



212

$$3\ Li(t\text{-}BuO)_2AlH_2 \rightleftharpoons 2\ Li(t\text{-}BuO)_3AlH + LiAlH_4 \qquad (1)$$



$M[R_3BO\overset{R'}{\overset{|}{C}}{=}CH_2]$

213

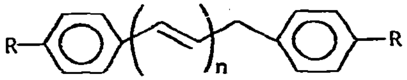
NMR spectra have also been reported for $[R_2NCH_2CH_2CH_2Li]_n$ [156], the tetralithium derivative of 9,9'-bianthryl [157], trimethylsilyl carbonates $M(O_2COSiMe_3)$ [158], a series of phenylsilylanions including Ph_3SiLi, $Ph_2MeSiLi$, $PhMe_2SiLi$, and Me_3SiK [159], and alkali derivatives of diethyl (carbomethoxymethyl) phosphonate [160].

B. Other spectroscopy

Earlier photoisomerizations of substituted allyl ions have been extended to a study of 1,3-diphenylallyllithium at temperatures below -40° [161]. In this case, the relaxation of the photochemically generated Z,E-conformation to the E,E-isomer is very slow. When irradiation with white light is prolonged, a photostationary state shifts towards the E,E-conformation as the temperature is lowered. It is suggested that at very low temperatures, the excitation energies can only be lost from the E,E* species by fluorescence perhaps accompanied by non-radiative processes. Similar but temperature insensitive isomerizations of the 2-aza-1,3-diphenylallyl anion are reported. Fluorescence spectroscopy for the lithium and potassium salts of 1,3-diphenylpropene and 1,5-diphenylpentadiene have been reported though such fluorescence did not allow unambiguous assignment of either the type of ion pair or the anion geometry [162]. In contrast to the above, solutions of 1,3-diphenylallyl carbanions in liquid ammonia were found to be photoinsensitive and the shifts in the visible absorption spectra were ascribed to a thermally induced change in the E,E/E,Z equilibrium [163]. Other papers discussed the nature of the ion pairs of alkali derivatives of 214 [164] and 215 [165]. In the latter case, the thermodynamic parameters for the change tight to loose ion pair are reported.

Loose ion pairs of 9-alkyl-10-lithio-9,10-dihydroanthracene (216) have been found to absorb at about 450 nm [166]. The corresponding contact ion pairs absorb at about 400 nm when R = H,Me,Et and 415 nm when R = t-Bu. The results of NMR studies on these systems is also described.

214



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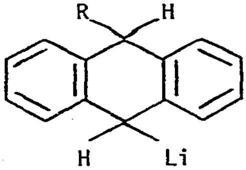


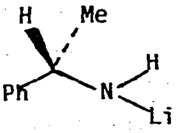
216

The effect of temperature on the structures of the fluorescent ion pairs of alkali metal derivatives of indole and 7-methylindole have been studied by absorption and fluorescence shifts [167]. The emitting lithium, sodium, and potassium salts have a σ-type structure at -180°. The stable ion pair structures in the S_1 state are a σ-complex for lithioindole and π-complexes for the sodium and potassium salts.

Although lithium metal is not involved, ICR results have been mentioned in these chapters because of their potential interest to organolithium chemists. Papers in 1980 concerned with this area discussed homoconjugation versus charge dipole interaction effects in the stabilization of carbanions in the gas phase [168], ipso-substitution reactions of certain alkyl phenyl ethers [169], the formation of vinyl anions versus conjugate addition in reactions of methoxide with acrylonitrile [170], the importance of solvation on the gas-phase proton transfer reaction between cyclopentadienyl anion and alcohols [171], and the gas phase acidities of fluorinated acetones [172].

6. STEREOCHEMICAL ASPECTS

Enantioselective deprotonation has been realized for the first time in the rearrangement of cyclohexene oxide to cyclohexenol effected by chiral lithium amide bases [173]. The induction of asymmetry ranged from 3% to 31% ee with 217 and 218, respectively.



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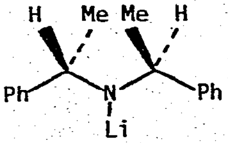
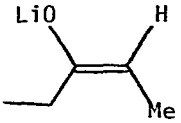


218

Deprotonation of 3-pentanone to stereoselectively afford E- and Z-enolates 219 and 220 has been shown to operate under thermodynamic versus kinetic control [174]. Thus, treatment of this ketone with 1.1 equivalents of LiTMP gave 219 and 220 in a ratio of 87:13. Addition of 0.2 equivalents of the ketone to the above mixture caused a rapid isomerization to an equilibrium mixture of 219 and 220 in a ratio of 16:84. That the isomerization could even be effected by benzophenone, a ketone devoid of α-hydrogrens, led the authors to speculate that the mechanism involves a reversible aldol condensation rather than proton transfer between un-ionized ketone and the enolates. Though kinetic enolate 219 was not isomerized by the presence of HMPA or TMEDA, the isomerization by the extra ketone was faster in the presence of these additives. The adducts also caused a modest shift in the position of the enolate equilibrium of 219 and 220 ranging from a ratio of 6:94 (4.0 equiv of HMPA) to 16:84 (1.0 equiv of TMEDA). The respective amounts of the enolates were determined by silylation with chlorotrimethylsilane.



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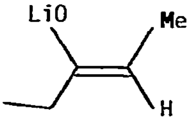
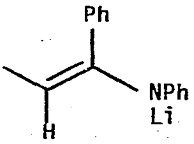


220

Kinetic versus thermodynamic control was also observed in the deprotonations of certain anils by LDA [175]. For example, the 75:25 mixture of 221 and 222 from 223 and LDA was converted by excess 223 to one which contained these anions in a ratio of 5:95. Stereospecific N-protonation of 221 and 222 by methanol to yield sec-enamines is described. Similar results are reported for other anils.



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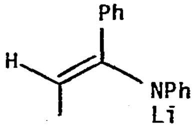

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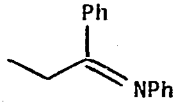
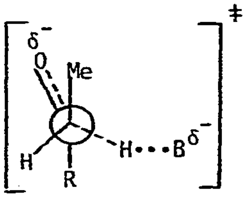


223

Several papers discussed additional studies on acyclic stereoselection. A large number of ethyl ketones and propionic acid derivatives have been converted to their lithium enolates and combined with benzaldehyde under kinetic conditions to reveal a correlation between the structure of the enolate and the stereostructure of the resulting aldol [176]. The choice of amide base used to effect deprotonation of the active hydrogen compounds was found to be important since, for example, LiTMP usually gave more trans-enolate than LDA while lithium hexamethyldisilazane afforded more cis-enolate. The results are discussed in terms of transition states 224 and 225 where the former is more stable than the latter when R = Me by 800 cal/mol. The stereoselectivity in the subsequent aldol condensation, (e.g., most cis-enolates react stereospecifically) is ascribed to transition state 226. Isomerization of the initially formed aldol adducts to corresponding threo isomers is compared to that of zinc enolates. While silyl ether 227 has been found to react with benzaldehyde to yield only erythro 228 [176], lithium enolates derived from 229 (R = Me,t-Bu) combine with aldehydes to give only threo-2-alkyl-3-hydroxycarboxylic acids [177].

Similar studies on the addition of lithium enolates of esters and ketones to aldehydes 230-232 revealed that the predominant product is predicted by 233 where the alkoxide is assumed to be the "large" group [178]. Another paper described related chemistry of reagents such as 234 [179]. For example, this enolate and 235 afforded 236 and 237 in a ratio of 15:1. Additional papers discussed zirconium enolates as new erythro-selective aldol condensation reagents [180] and enantioselective aldol condensations using boron enolates [181].



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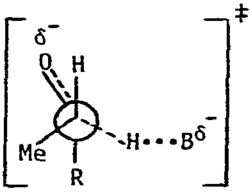

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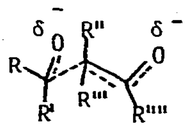

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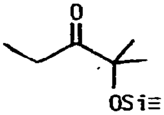

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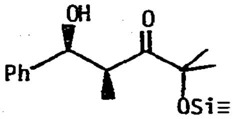

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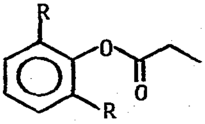

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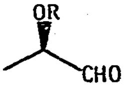
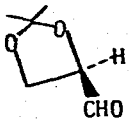


(R = t-BuMe$_2$Si,
PhCH$_2$,
PhCH$_2$OCH$_2$

230



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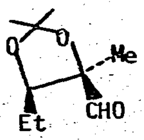
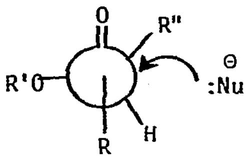


232

Greater than 90% erythro-selective branching of malic esters has been realized upon alkylation of dilithio derivatives 238 (R = Me,Et), obtained by treatment of 239 with two equivalents of LDA [182]. Erythro products 240 and 241 were also obtained by Michael condensation of enantiomerically enriched 242



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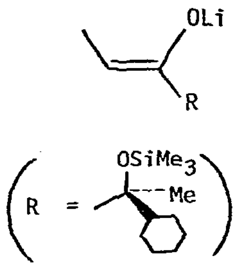

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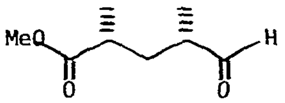

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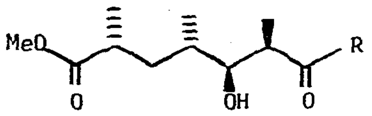

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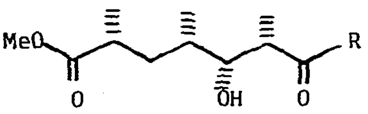
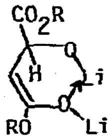


237

and 243 with nitroethylene, respectively [183]. Such stereocontrol was, however, not observed in such reactions with more highly substituted nitroalkenes.



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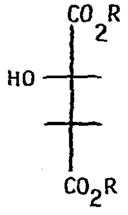

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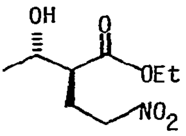

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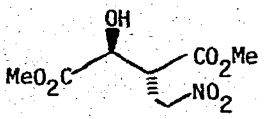

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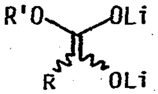
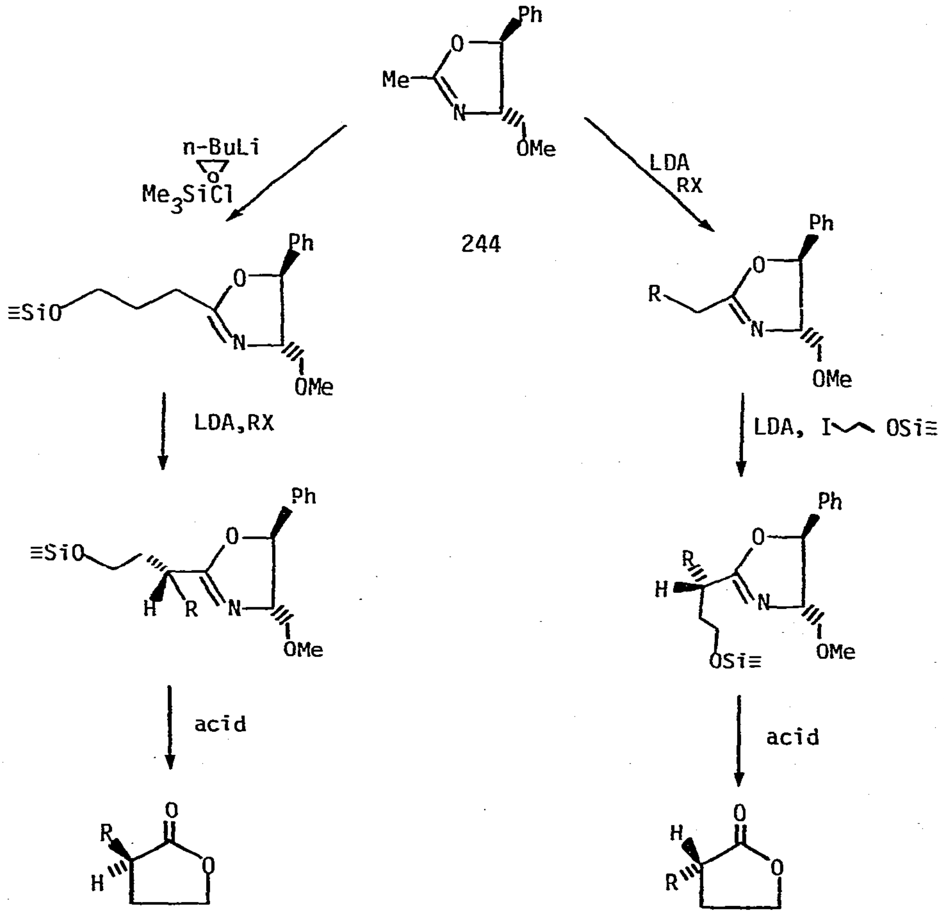


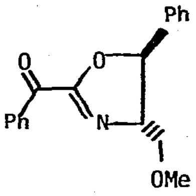
242 (R = Me, R' = Et)

243 (R = CO$_2$Me, R' = Me)

A full paper described the use of chiral oxazolines to synthesize chiral 2-substituted butyro- and valerolactones [184]. The process is illustrated by successive alkylations of 244 followed by hydrolysis. It should be noted either enantiomer of the lactones could be obtained by merely reversing the order of introduction of the alkyl groups. The lactones prepared had an ee of 60-86%.



Chiral α-substituted α-hydroxyacids with an ee of 30-87% have been obtained by addition of organolithiums and Grignard reagents to chiral ketooxazolines followed by hydrolysis [185]. For example, 245 and p-tolyllithium gave S-246 with an ee of 76%. Two other papers reported on 1,3-asymmetric induction in the reduction of isoxazolines to give α-amino alcohols [186, 187]. The work is illustrated by the conversion of 247 to 248 and 249 in a ratio of 85:15.



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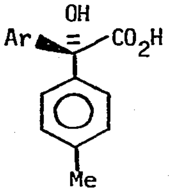

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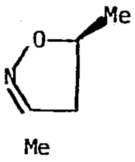

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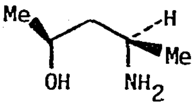

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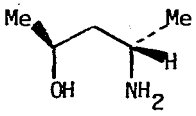
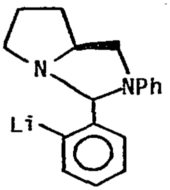


249

Chiral aryllithium 250 containing the aminal function has been found to add to a variety of aldehydes with high enantioface selectivity [188]. Thus, interaction of 250 with propanal followed by hydrolysis yielded lactol 251 (51%) with an ee of 88%. Other examples are listed.



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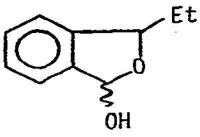
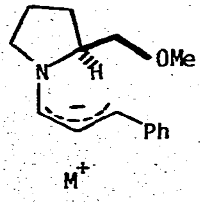


251

Metalated chiral allylamine 252, acting as a chiral homoenolate equivalent, has been alkylated to afford, after hydrolysis, β-substituted aldehydes 253 with ee up to 67% [189]. In 253, R = Me, Et, i-Pr, n-Bu, and allyl.



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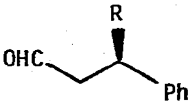
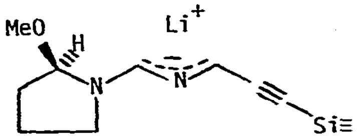


253

The previously described lithium pyrrolidine 254 has now been alkylated to give propargyl amines illustrated by 255 [190].



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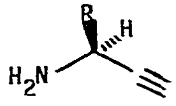
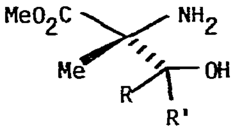


255

α-Methylserines 256 have now been synthesized by condensations of lithiated lactims 257 with aldehydes and ketones to initially form 258 [191]. The process is completed by simple hydrolysis.



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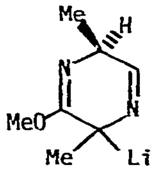

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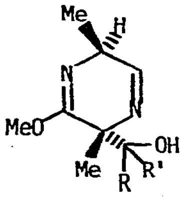
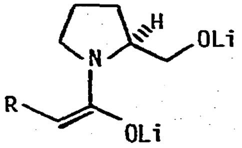


258

Two papers were concerned with alkylation of chiral amide enolates derived from prolinol [192, 193]. Thus, methylation of the dilithio salt 259 (R = n-C_8H_{17}) has afforded S-260 with an ee of 56%. In contrast, condensation of 259 (R = Me) with 1-iodooctane gave R-260 (66% ee). Interestingly, methylation of lithioether 261 (R = n-C_8H_{17}) yielded R-262 (82% ee). O-Silyl derivatives afforded stereochemical results similar to those realized with 261. The enolates are presumed to exist in the Z-geometry at least when R = Me [193].



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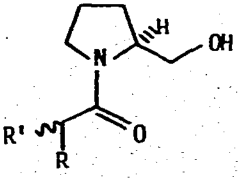

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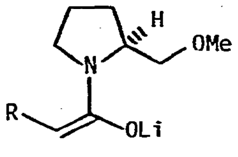

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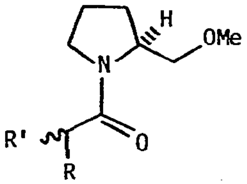

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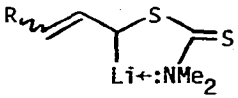
Lithio-2-alkenyl dithiocarbamates have been found to combine predominantly at the α-position with benzaldehyde in a stereospecific fashion [194]. Thus, Z-263 and E-263 with this aldehyde gave mostly 264 (erythro) and 265 (threo), respectively. That 266 (M = Li, Mg) condensed with several aldehydes to afford erythro adducts 267 in almost every case led the authors to suggest that 266 exists in the Z-configuration [195].



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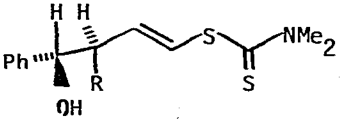

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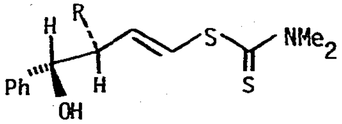

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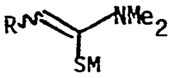

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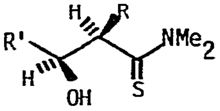
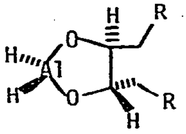


267

Several papers described additional examples of asymmetric manipulations using chiral lithium ate complexes. Among the reagents described were 268 (R = NMe_2, pyrrolidino, piperidino, $NMeC_8H_{17}$, NMePh, NMe-$(CH_2CH_2O)_3$-Me, OMe, and others) to reduce ketones [196], lithium aluminum hydride complexed with 4-(dimethylamino)-3-methyl-1,2-diphenyl-2-butanol (Darvon alcohol) to reduce α,β-acetylenic ketones and acetophenone [197], and lithium aluminum hydride partially decomposed by (-)-N-methylephedrine and N-ethylaniline to reduce α,β-unsaturated ketones [198]. Another paper disclosed asymmetric alkylations of methyl phenylglyoxalate by lithium tetrabutylaluminate modified by (-)-N-methylephedrine and by Darvon alcohol [199]. The reagent complexed with the latter alcohol gave 269 with an optical yield of 43%.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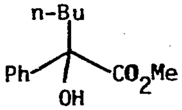
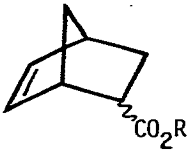

269

The stereochemistry of the alkylation of a variety of acid and ester derivatives of norbornene, norbornane and cyclohexane have been reported [200]. Thus, alkylation of exo- and endo-270 (R = H and Me) and their saturated analogs via their lithium enolates predominantly yields exo-derivatives 271. In contrast, while methylation of dilithiocyclohexanecarboxylates affords more axial alkylation (a/e = 0.4-2.7), similar reaction of cyclohexane lithium ester enolates give more equitorial alkylation (e/a = 4-9).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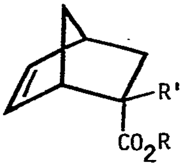
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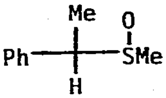
Methylation of solid lithiobenzyl methyl sulfoxide has been found to be stereospecific [201]. Thus, while treatment of this solid with liquid methyl iodide yielded 272-273/274-275 in a ratio of 5:1, use of methyl iodide vapor and nitrogen afforded one single diastereoisomer identical with 272 and 273. The authors conclude that one diastereoisomer is present in the solid state whose reactivity is highly stereoselective with a non-chelating reagent. Another paper described deuterations of this same lithiosulfoxide in the presence and absence of triethylaluminum to yield inversion and retention products, respectively [202].

Other studies in this area were concerned with stereoselectivity in the alkylation of sulfonium salts [203], the stereochemistry of certain arylmethanephosphonate carbanions with Schiff bases as a function of solvent and counterion [204], and deracemization of α-aminoacids by enantioselective protonation [205].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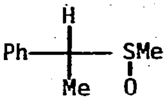
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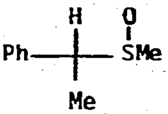
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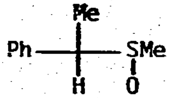
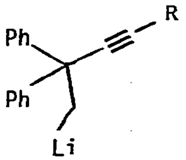

275

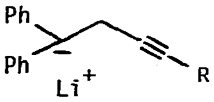
7. OTHER PHYSICAL ORGANIC CHEMISTRY

A very extensive paper disclosed that acetylenic groups can undergo sigmatropic [1,2] shifts in certain organolithiums [206]. Thus, warming THF solutions of 276 and 277, prepared from the corresponding chlorides and lithium, from -75° to 0° gave 278 and 279, respectively as evidenced by carbonations. Interestingly, the cesium derivative of 277 underwent [1,2] migration of phenyl to afford 280 which was metalated further by 277. Cyclic transition states or intermediates 281 and 282 are proposed for the respective rearrangements. That each of the above reactions proceeds within contact or tight ion pairs is supported by CNDO/2 calculations.



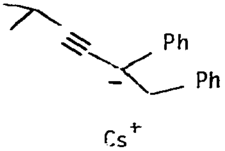
276, R = Me

277, R = t-Bu



278, R = Me

279, R = t-Bu



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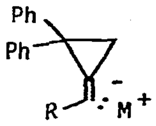

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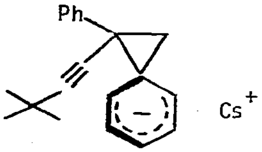
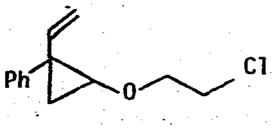


282

1,3-Dienes may now be conveniently converted to functionalized cyclopentenes by a route which involves the rearrangement of the lithium salts of 2-vinylcyclopropanols [207]. For example, cleavage of ethers 283 and 284, obtained from 2-phenyl-1,3-butadiene and :$CHOCH_2CH_2Cl$, with n-butyllithium afforded 285 (90%). An alternative route utilized gem-dibromocyclopropanes.



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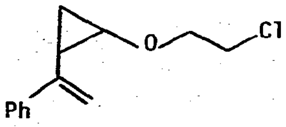

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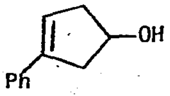
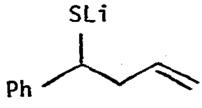
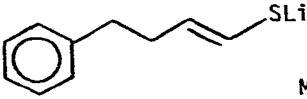
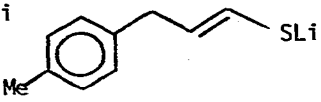


285

Additional work appeared in 1980 which was concerned with rearrangements of lithium derivatives of allyl benzyl thioether [208]. A large number of rearrangement products illustrated by 286 and 287 are reported which originate from benzylic and allylic carbanions, respectively. Of special interest is the para rearranged product 288.







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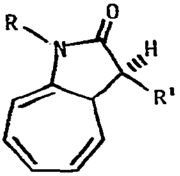
288

Amides 289 (R = Me, t-Bu, Ph; R' = Ar, Me, t-Bu) have been shown to rearrange to cinnamic acid derivatives 290 (68-87%) [209]. The reactions presumably proceed via 291 and norcaradiene 292.



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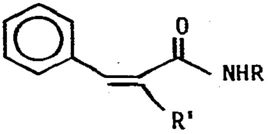

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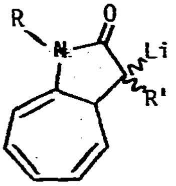

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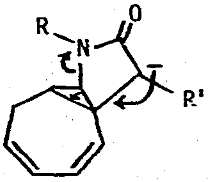
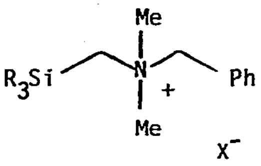


292

The effect of silicon on Sommelet-Hauser and Stevens rearrangement products in the reactions of 293 with n-butyllithium and sodium amide have been studied [210]. Among the products obtained were 294 and 295 via the Sommelet-Hauser route and 296 by the Stevens rearrangement; several non-silylated derivatives were realized also. While 296 was not obtained with sodium amide regardless of the organic groups on silicon, the use of n-butyllithium gave more of 294 and 295 when this group was Ph_3Si. Incidentally, an extension of earlier work on the interaction of azetidinium halides with strong bases appeared in 1980 [211]. In the current study, the use of n-butyllithium on, for example, 297, gave 298 and four other amines. The results of deuterium labeling are reported.



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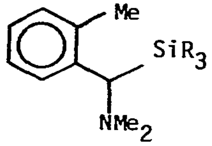

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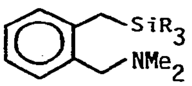

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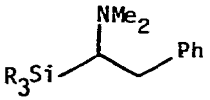

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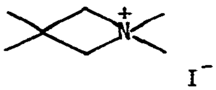

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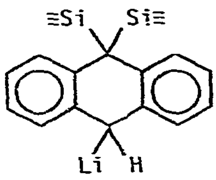
298

A 1,4-rearrangement of a trimethylsilyl group of 299 to afford 300 is believed to involve an intramolecular pathway [212]. Several ω-lithioalkyltrimethylsilanes, though stable in ethyl ether, underwent rearrangements upon addition of THF [213]. For example, 301 and 303 gave 302 and 304, respectively; 303 was formed by an intramolecular 1,5-proton shift. 5-Lithiopentyltrimethylsilane underwent both a 1,7-proton shift and ring closure.

Propargyl alcohols 305 with n-butyllithium give alkoxides 306 which rearrange to allenes 307 [214]. Lithio derivatives 307 have been trapped by alkyl halides to afford 308 (82-94%). The latter compounds are conveniently converted to α,β-unsaturated ketones by acid. Another paper described the interesting conversion of 309 to 310 by HMPA [215]. The reaction is under investigation.



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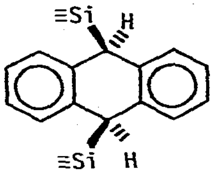

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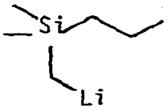

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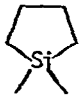

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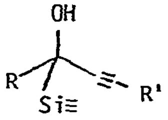

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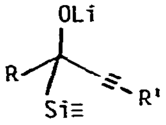

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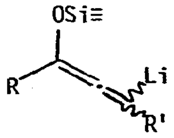

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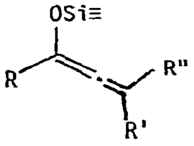

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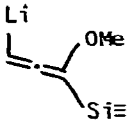

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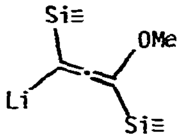

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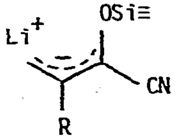

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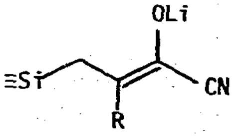

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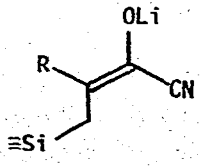

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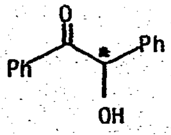
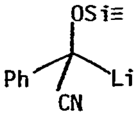


314

Though stable and capable of being silylated at -78°, 311 (R = H, Me) rearrange at 25° to Z-312 accompanied by E-313 [216]. The rearrangements are slowed by the presence of triethylsilyl compared to trimethylsilyl groups. Another paper described the preparation of specifically labeled 314 from 315 and 1-^{13}C-benzaldehyde via 316 and 317 followed by loss of LiCN and hydrolysis [217].



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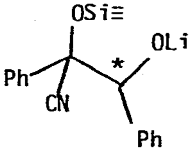

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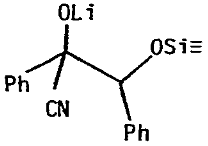
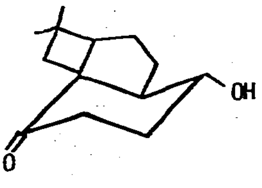


317

Rearrangement of silicon from carbon to oxygen has also been found important in the preparation of silyl enol ethers from silylallylic alcohols [218] and in certain 1,2-asymmetric inductions of methyllithium-vinylsulfonylsilanes to give hydroxysulfones [219].

Turning to other areas, it has been found using 318 that the rates of hydride transfer between two carbonyl groups can be affected in opposed ways by choice of the cation and base employed [220]. Thus, using isopropoxide, the rate of intermolecular hydride transfer from the base to give 319 increased with increasing Lewis acidity of the cation ($Al^{3+} > Li^{+} > Ba^{2+} > Na^{+} > K^{+}$). In contrast, the rate of the intramolecular transfer to give 320 increased in the reverse cationic order of increasing metal-oxygen basic character ($Ba^{2+} > K^{+} > Na^{+} > Li^{+} > Al^{3+}$). Moreover, the rate of the latter process increased with increasing basicity of different alkoxides (e.g., t-AmOK>EtOK). The results are ascribed to whether a cyclic transition state is possible or is stereochemically prohibited.



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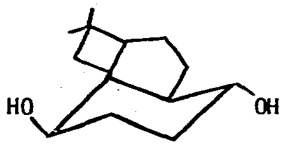

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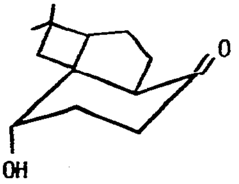
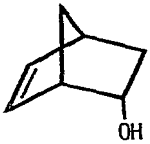


320

Dibenzyl disulfide has been found to undergo metalation 7.5 times faster than dibenzyl sulfide using LDA [221]. The results are consistent with MO theory which focuses on the interaction between the carbon lone pair and an adjacent σ^* orbital. In another study, it has been found that allyl sulfides are kinetically more acidic than allyl selenides towards amide bases [222]. The same study revealed that vinyl sulfides are less acidic than vinyl selenides.

The relative rates of the addition of n-butyllithium to several bicyclic alcohols was studied in an effort to determine the effect of the hydroxyl group [223]. For example, that the rates of 321>322>323 suggest that OH assists in the addition to 321 but retards in the reaction on 323. The implications of the above are discussed.



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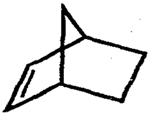

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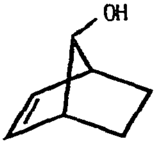
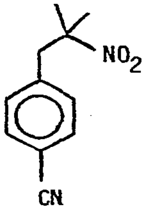


323

The amount of ion-pairing between anions of organic acids and metal cations may now be quantitatively estimated in conjunction with acidity measurements [224]. The method involves spectrophotometric determination of the perturbation by a metal iodide of the equilibrium between an indicator anion which does not ion pair, an anion which does ion pair, and their conjugate acids. Specific results are discussed for the anions of several β-dicarbonyl compounds, nitromethane, and phenylacetic acid.

Electron-transfer chain reactions at saturated carbon can be achieved in the absence of nitro groups on the compound undergoing substitution [225]. For example, 324 is obtained from 325 and lithio-2-nitropropane. Nitro groups may also be absent in the nucleophile as illustrated by the converison of 326 to 327 by PhSNa.



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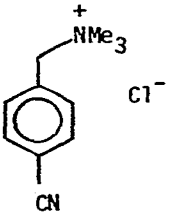

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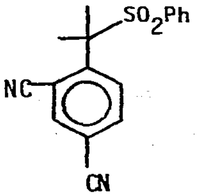

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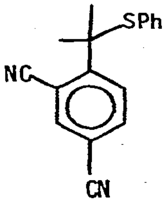
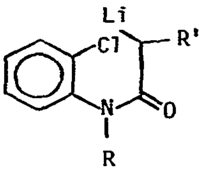


327

The relative reactivities of a series of anions in competitive $S_{RN}1$ reactions have been determined in order to ascertain the importance of ion-pairing effects [226]. For example, $k(EtO_2C)_2C(Me)Li/kMe2C = NO_2Li$ towards 2-chloro-2-nitropropane ranged from 0.22 in HMPA to >70 in THF, a result ascribed to an increase in ion pairing and a decrease in reactivity of the nitronate anion from HMPA to THF. Other anions are also listed.

Additional examples of ring-closures effected via the photo-$S_{RN}1$ reaction were reported in 1980. Thus, six-, seven-, eight-, and ten-membered rings have been synthesized from intramolecular coupling of ketone enolates, though β-hydrogen transfer constituted a side reaction in solvents such as HMPA, DMF, or THF [227]. Such hydrogen transfer could be avoided by substituting the carbons alpha and beta to the carbonyl with carbon substitutents rather than hydrogen. A second paper reported similar cyclizations of lithio- and dilithio-N-acyl-o-chloroanilines [228]. For example, 328 gave 329. None of the above cyclizations involved benzyne intermediates.



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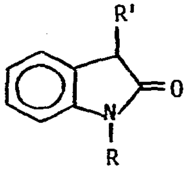
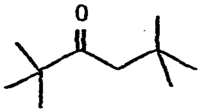


329

Single electron transfer processes were believed responsible for the formation of 330 in the reaction of 331 with LiTMP [229]. In fact, α-proton abstraction from 331 to give the enolate was not observed as evidenced by labeling experiments. Additional evidence has been obtained to support single electron transfer in the alkylation of 332 [230]. Thus, the use of cyclopropylmethyl bromide and iodide yielded rearranged products indicative of a radical process.

Irradiation of 1:1 mixtures of 333 or fluorene with their lithium salts at the surface of a doped single-crystal n-type TiO_2 electrode has afforded dimers 334 and bifluorenyl, respectively [231]. Similar irradiations in THF in the absence of such an electrode gave only tetraphenylcyclopentadiene and fluorene upon quenching with acid.



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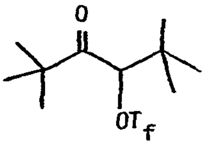

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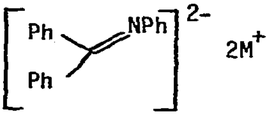

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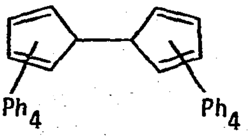
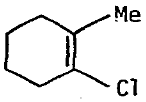


334

A full paper discussing the interaction of 1-chloro-2-alkylcycloalkenes with organolithiums to afford fused-ring cyclopropanes was published in 1980 [232]. For example, six-, seven-, and eight-membered cyclic chloroolefins give bicyclo[4.1.0]heptanes, -[5.1.0]octanes, and -[6.1.0]nonanes, respectively. To illustrate the process, 335 and phenyllithium yield 336 (90%). The mechanism has been shown to involve ionization of an allylic hydrogen, α-elimination of LiCl to afford an allylic carbene, intramolecular addition of the latter to the double bond, and addition to the resulting cyclopropene by the organolithium.



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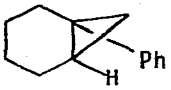


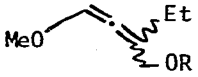
336

Elimination of alkoxides from bis-propargylic ethers such as 337 by treatment with alkali amides in liquid ammonia to afford 1,3-enynes has been shown to proceed via short-lived carbanions [233]. Thus, treatment of 337 with lithium amide apparently gave 338 as evidenced by alkylation with ethyl bromide to afford 339 and other alkylated derivatives.

337

$(\mathrm{MeO{-}CH{-}C{=}CCH_2OMe})^{-}\mathrm{Li}^{+}$

338



339

The effect of cryptand[2.1.1] on reactions of n-butyllithium and other organolithiums with various organic materials has been studied [234]. In general, the cryptand enhanced the basicity and diminished the nucleophilicity of the reagents. For example, such complexed reagents and alkyl halides gave only products of elimination.

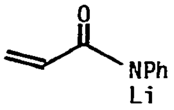
Other papers in this area were concerned with the heats of formation of the [16]annulene dianion [235], the heats of interaction of tetrahydrofurans with poly(isoprenyl)- and poly(styryl)lithiums [236], the enthalpies of solvated anthracene anion radical ion pairs with water [237], the determination of the basicities of benzyl, allyl, and t-butylpropargyl anions by cyclic voltammetry [238], the construction of the phase diagram of the lithium-methylamine system (239], and the synthesis of α,β-unsaturated aldehydes via prototropic rearrangement of N-(prop-2-ynyl)amines by n-butyllithium to 1-aminopropa-1,2-dienes followed by hydrolysis [240].

8. ADDITION AND SUBSTITUTION REACTIONS

A. Alkyl-, Aryl-, Alkynyl-, Allyl-, Vinyl-, and Allenyllithiums

Alkyllithium and -magnesium derivatives may be converted to alkenes by ethylene and nickel chloride as illustrated by the conversion of decyllithium to decene (70%) [241]. The reaction involves β-hydride transfer from the organometallic to the ethylene.

Three papers discussed additional examples of 1,4-additions of organolithiums to α,β-unsaturated amides [242-244]. Such reactions are observed on both secondary and tertiary amides. In the former case, addition occurs on lithiated species such as 340 to afford 341 [242]. The intermediate enolates have been trapped with electrophiles to give products such as 342 [243]. The methodology has been applied to the synthesis of 1-aryltetralin lignans galcatin and isogalcatin [244].



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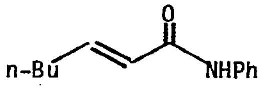

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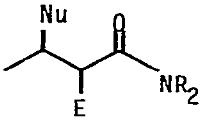
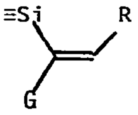


342

Substituted hetero-olefins have now been found to undergo addition of lithium alkyl reagents [245]. For example, 343 (R = i-Pr,Ph; G = SO_2Ph) and methyllithium give 344. Other examples are described where G = $SiMe_3$ but not PhSe. n-Butyllithium has also been added to 345 to give 346 [246]. Interestingly, addition of methyllithium to allene sulfoxide 347 occurs at sulfur to yield 348 [247].



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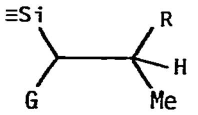

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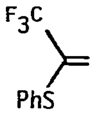

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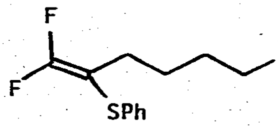

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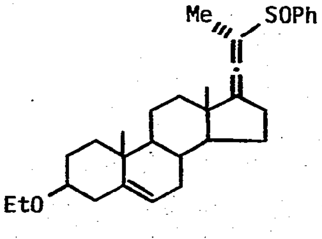

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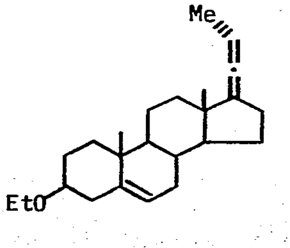
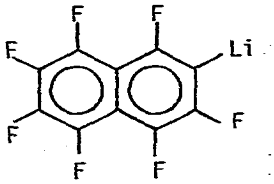


348

Lithionaphthalene 349 has been found to undergo substitution by n-butyllithium to afford 350, a species which has been trapped by several electrophiles [248].



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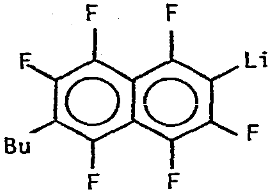
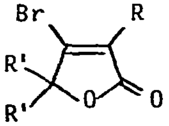


350

Inverse addition of methyl- or phenyllithium to butenolides 351 (R = Me,H; R' = alkyl) has been found to give 352 via 1,2-addition [249]. Acid-catalyzed hydrolysis of 352 without purification yielded 3(2H)-furanones 353 (47-76%).



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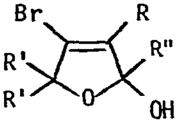

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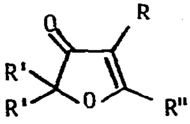
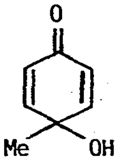


353

In a general reaction, organolithiums have been added to p-benzoquinones in ethyl ether to afford dienones illustrated by 354 [250]. Diols such as 355 (R = Me or H) have also been obtained from 354 and methyllithium in THF. Two-fold additions of methyllithium to a variety of o- and p-quinones followed by reaction with HI have been shown to give methylated derivatives of polycyclic aromatic hydrocarbons illustrated by 356 [251].



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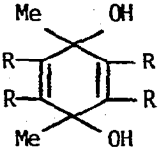

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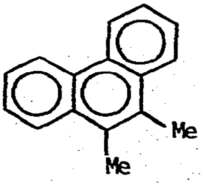
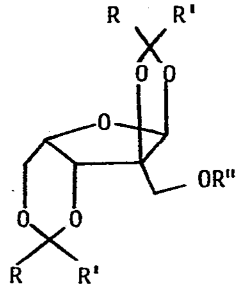


356

Ultrasound irradiation has been shown to be beneficial in the Barbier reaction [252]. For example, n-propyl bromide, benzaldehyde, and lithium in wet technical grade THF, when irradiated, gave 1-phenylbutanol (100%).

Interaction of n-butyllithium with sorbose derivative 357 (R = R' = Me, R" = H) yielded enulofuranose 358 [253]. In contrast, enitol 359 was obtained from 357 (R = Ph, R' = H, R" = H) while rearranged product 360 was realized from 357 (R = R' = Me, R" = CH_2Ph).



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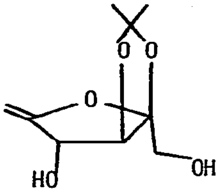

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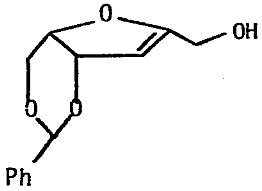

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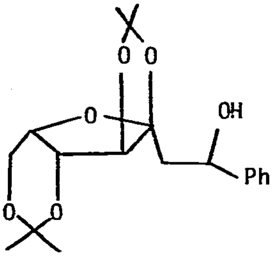
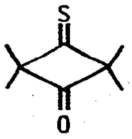


360

While addition of methyllithium to ketothione, 361 followed by water or methyl iodide gave 362 (E = H or Me, respectively), the electrophile chlorotrimethylsilane afforded 363 [254]. The latter product is taken as evidence that the initial addition of methyllithium proceeds via the intermediacy of bishomoenolate anion 364.



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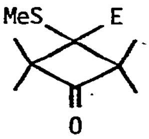

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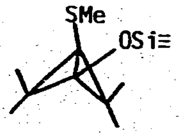

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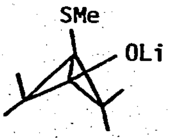
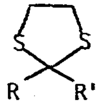


364

1,3-Dithiolanes 365 have been found to undergo fragmentation with n-butyllithium via 366 to afford thiocarbonyl intermediates 367 [255]. The latter compounds react further with the n-butyllithium via C- and S-addition and by hydride transfer. For example, ketones may be converted to mercaptans as illustrated by the preparation of 368 from the dithiolane of 4-t-butylcyclohexanone. Carbonyl transpositions are also reported. Another paper reported the preparation of vinyl alkanedithioates 369 via the related cleavage of 370 effected by LDA [256].



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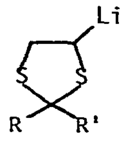

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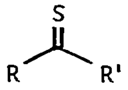

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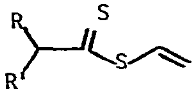

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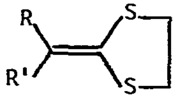
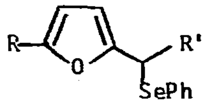


370

Additional examples of ring-opening reactions of α-lithiofurans were realized in the combination of selenides 371 with n-butyllithium to ultimately yield 372 [257]. Alkyllithiums have been added to vinyl azides 373 to give, after hydrolysis, ketones 374 [258]. Alkyllithiums have also been reacted with 375 to afford 376 [259], and with 1,1-difluorocyclopropanes to yield cyclopropenes or mono-substituted acetylenes [260].



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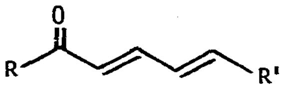

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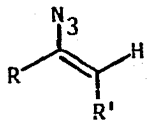

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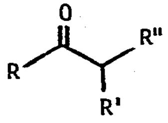

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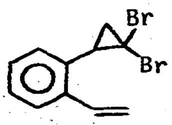

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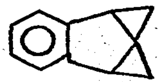
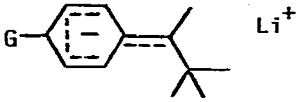


376

Turning to benzylic systems, reaction of 377 (G = Ph, $SiMe_3$), prepared by addition of t-butyllithium to the parent α-methylstyrenes, with molecular oxygen gave hydrocarbons 378-380 instead of the expected alcohols [261]. The results are ascribed to steric hindrance about the benzyl carbon.



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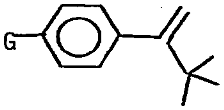

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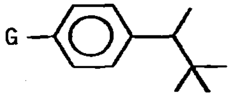

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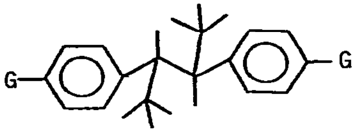
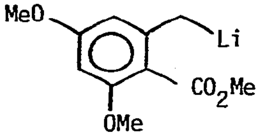


380

Lithium orsellinate (381) has been sulfenylated and selenated to give 382 (Y = S,Se) [262], sulfenylated to afford 383, then 384 [262], and combined with pyrylium salt 385 to yield isocoumarin 386 along with certain pyrones [263].



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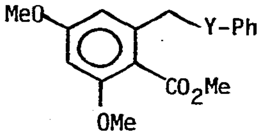

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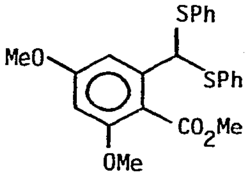

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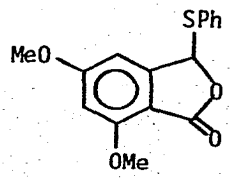

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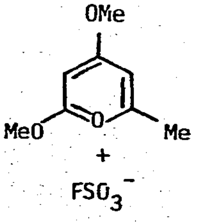

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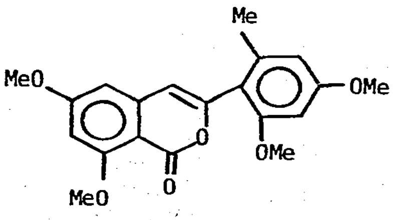
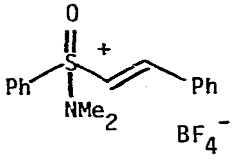


386

A wide variety of carbanions have been combined with vinylsulfoximine derivatives to afford cyclopropyl derivatives [264]. For example, lithioindene and 387 give 388 (59%). Under the influence of bases, such vinylsulfoximine reagents combine with primary amines to yield aziridines, with enamines to afford cyclopropyl derivatives of iminium salts or pyrrolidinium salts, with anions of active methylene compounds to give dihydrofurans and/or cyclopropanes, and with alkali nitroalkanes to yield cyclic nitronic esters and/or nitrocyclopropanes. Another paper described the preparation of 389 (R = X = Cl, R' = Ph; R = R' = $SiMe_3$, X = Br) from 9-lithiofluorene and appropriate halosilanes [265].



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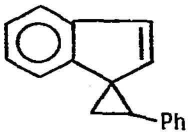

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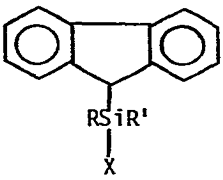
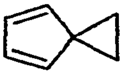


389

A wide variety of benzylic-type and other organolithium reagents have been combined with spirohydrocarbon 390 [266]. For example, 390 and 391 give 392. The site of metalation of 2,4,6-trimethylpyridine continued to be studied by varying the cation and the solvent [267]. The selective formation of the 2- or 4-methyl metalated derivatives is said not to be a function of the basicity of



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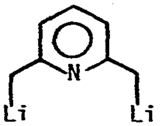

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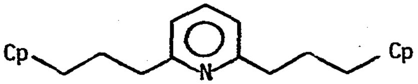
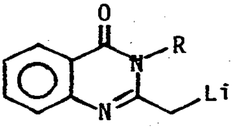


392

Methaqualone has been lithiated by LDA and the resulting 393 (R = o-tolyl) combined with a variety of electrophiles at the 2-methyl group [268]. Similar chemistry was effected on related derivatives (R = Me, Ph). Other papers described condensations of pyrazine derivatives such as 394 [269, 270].



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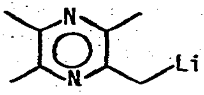
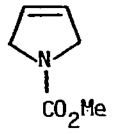


394

Two-fold lithiation and alkylation of pyrroline 395 has been found to afford, after hydrolysis, dialkylated derivatives in which the alkyl groups are trans to one another [271]. A typical product obtained was 396 (38%), a poison of a South African ant. The methodology has been applied to the preparation of certain dehydroindolizidine alkaloids.

Pentadienyllithium has been combined with chlorotrimethylsilane to afford 397 [272, 273]. The latter reagent has been condensed with certain carbonyl compounds *in the presence of* $TiCl_4$ *to give 398 (R" = H) [272]. It has also been*



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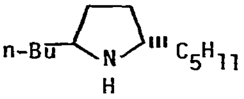
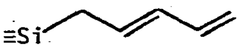


396

lithiated by LDA to afford 399, then combined with aromatic aldehydes and ketones to yield 398 (R" = $SiMe_3$) [273]. The use of cyclohexanone and benzyl bromide on 399 gave mostly or exclusively 400 [273]. 3-Isopropylpentadienyllithium has been employed in the synthesis of cadalanes [274]. Several isomers of 2,4-decadien-1-ol have been respectively obtained by metalation of (Z)- and (E)-1,4-decadiene followed by dimethoxyborylation and oxidation [275].



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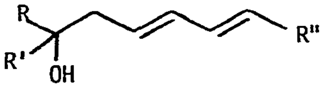

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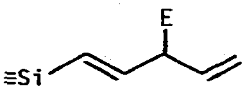
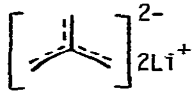


400

Dilithio derivatives 401 and 402 have been found to react with nitriles devoid of α-hydrogens to give pyridines and bicyclics such as 403 and 404, respectively [276]. The products shown are those derived from benzonitrile.



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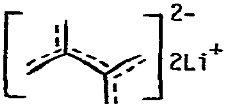

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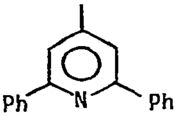

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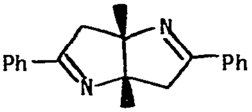
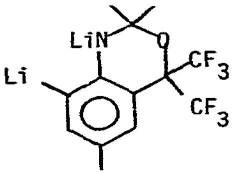


404

Turning to aryllithium reagents, 405, prepared by metal-halogen exchange using two equivalents of n-butyllithium, has been combined with hexafluoroacetone to afford 406 [277]. The latter product is an intermediate in the preparation of 407, the first organobrominane.

The 3-ethoxycarbonylpropionyl group may be conveniently introduced onto aromatic moieties by reaction of aryllithiums with 408 [278]. The process is illustrated by the conversion of phenyllithium to 409 (67%).



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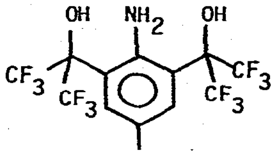

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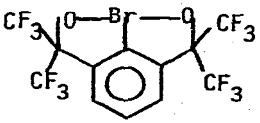

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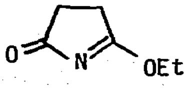

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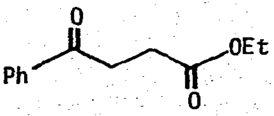
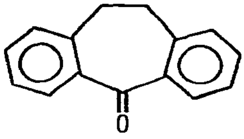


409

Intramolecular condensations of several aryllithiums have led to various types of products. Thus, sequential treatment of o-bromobenzyl bromide with n-butyllithium, carbon dioxide, then additional n-butyllithium gives dibenzosuberone (410) via 411 [279]. Reaction of styrene oxides such as 412 with n-butyllithium/ magnesium bromide has been shown to afford benzocyclobutanols such as 413 [280]. Lithioallyloxybenzanilide 414 has been found to cyclize to yield 415 [281].



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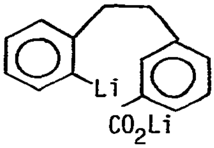

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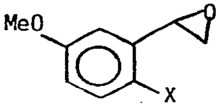

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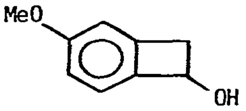

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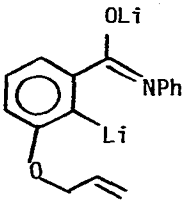

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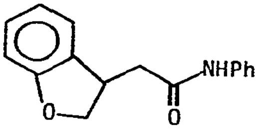
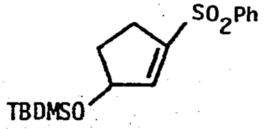


415

The relatively low yields in the conjugate additions of o- and o,o'-substituted aryllithiums to α,β-unsaturated sulfones such as 416 has been ascribed to vinyl metalation to afford 417 [282]. This undesirable side-reaction has been overcome by the use of t-butyl- rather than phenylsulfones.



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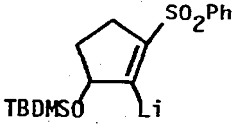
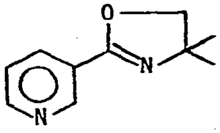


417

Aryllithiums and other related materials have been added to heterocycles such as 418, 419, and 420 to give adducts such as 421 [283], 422 [284], and 423 [285], respectively. The adducts were condensed with electrophiles.



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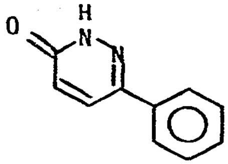

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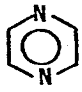

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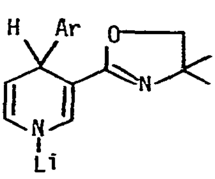

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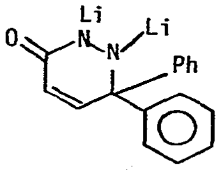

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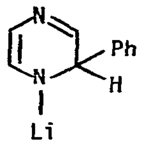
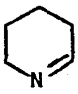


423

Other papers discussing aryllithiums included 2-arylation of piperidine and pyrrolidine as illustrated by the conversion of 424 with 3-lithiopyridine to dl-anabasine (425) [286], condensation of 426 with benzonitrile to yield 427, the first example of a new 10-π electron system, the use of lithio derivatives of 428 in the synthesis of benzylisoquinoline alkaloids [288], bisannelation of arenes with bisaryne equivalents such as 429 [289], the position-specific synthesis of iodotamoxifen via 430 [290], and amination of cyclopentadienyllithium using Me_2NOSO_2Me [291].

Several papers discussed additional condensations of 1,3-dilithioacetylenes such as 431 with electrophiles to afford propargyl derivatives 432 and/or 433. Thus, while 431 and epoxides, benzyl halides, and chlorotrimethylsilane give only



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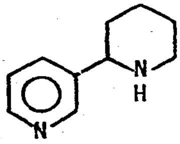

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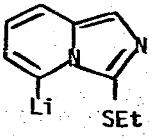

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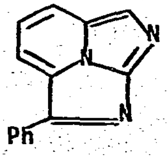

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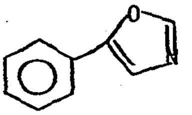

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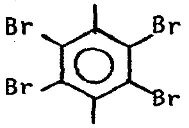

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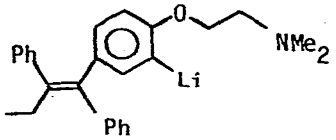
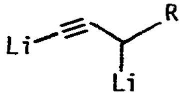


430

432 [292], formaldehyde and cyclic ketones yield 433 [293]. In contrast, 431 and carbon dioxide affords 434 [293]. 1,3-Diols are obtained from such organolithiums and diborane followed by oxidation [294]. For example, 435 eventually gives 436.

A full paper appeared in 1980 which described the facile synthesis of 2,5-disubstituted 1,4-benzoquinones by 1,2-additions of alkynyllithium (and others) to 437 and 438 followed by hydrolysis [295]. The process is illustrated by the conversion of 438 to 439 (63%).



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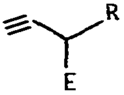

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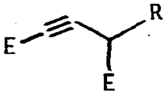

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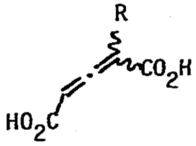

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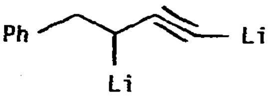

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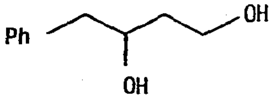

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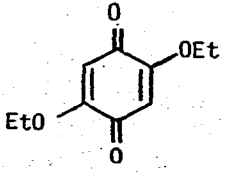

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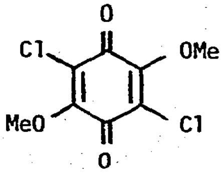

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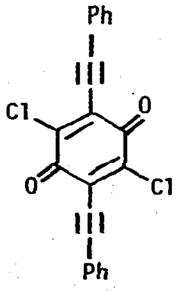
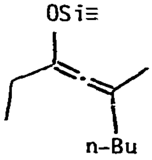


439

Allenolsilyl ethers such as 440 may be conveniently prepared by reaction of alkynyllithiums with alkyl trimethylsilyl ketones and alkyl halides [296]. The specific reagents to synthesize 440 were 1-lithiohexyne, ethyl trimethylsilyl ketone, and methyl iodide. The use of vinyllithiums in the procedure affords enol silyl ethers such as 441.



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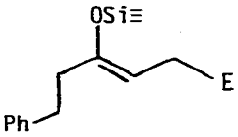
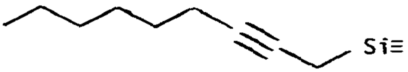


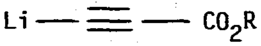
441

Propargylsilanes illustrated by 442 have been synthesized from alkynyllithiums and trimethylsilylmethyl halides [297], sulfonates [297], and triflates [298]. Trimethylsilylmethyl chloride is said to be the reagent of choice for obtaining larger amounts of the products. Such propargylsilanes have also been obtained by condensation of certain sodioacetylides and trimethylsilylmethyl iodide [299].



442

Lithium salts 443 (R = Me, Et), prepared by metalation of the parent compounds by n-butyllithium at low temperature, have been combined with aldehydes and ketones to afford 444 [300]. Reaction of 445 with 2-cyclododecene to give 446 has been used as part of the preparation of dl-muscopyridine [301]. Reagents such as 445 have also been combined with epichlorohydrin to yield 447 (A = OH, OMe, NMe_2 [302].



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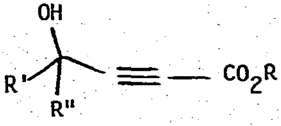

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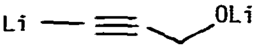

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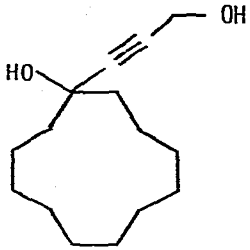

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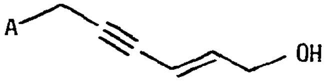
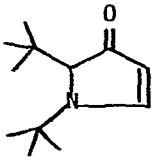


447

Alkynyllithiums have also been added to α-lactams to give pyrrolinones illustrated by 448 [303], to imide 449 to yield 450 [304], to phenyl cyanate to afford cyanoacetylenes such as 451 [305], and to 2-chloroazulenes to give derivatives such as 452 [306]. Finally, diacetylene reagent 453, prepared from 454 and methyllithium, has been alkylated to yield 455 [307].



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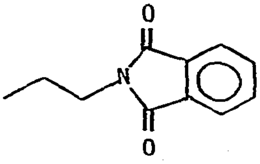

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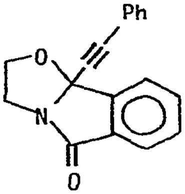

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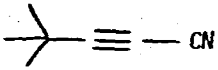

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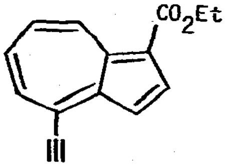

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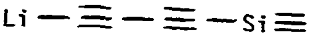

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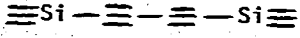

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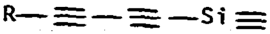
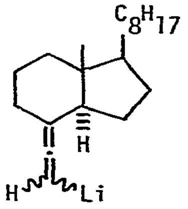


455

Finally, allenyllithium 456 has been combined with 457 as part of the preparation of vitamin D type vinylallenols [308].



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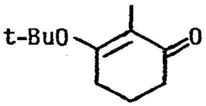
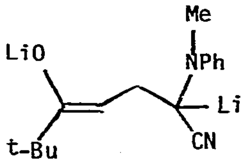


457

B. Carbanions Stabilized by Carbonyls

Site-specific monoalkylations of acyclic enol boranes have been effected by use of lithium dimethylaminoethoxide as an additive [309]. For example, methylation of 458 by methyl iodide in the presence of this alkoxide affords 3-methyl-2-heptanone (88%) unaccompanied by terminal or polymethylation products. Alkylations of 459 to ultimately give 1,4-diketones [310] and of 460 to yield 461 and 462 [311] were also reported. Dianion 459 was obtained by metalation of Michael-adduct 463 while enolate 460 was synthesized by deprotonation of the parent hydroazulene.

458



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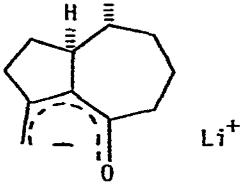

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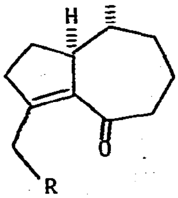

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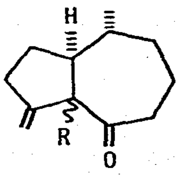

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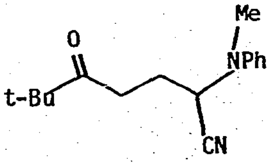
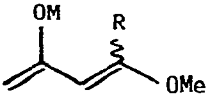


463

C-Acylation of enolates 464 (R = H,Me,OMe) by a variety of acid chlorides followed by acid-catalyzed cyclizations has led to γ-pyrones 465 (R = aliphatic or aromatic) [312, 313]. Related condensations of dilithio-o-hydroxyacetophenones ultimately afford flavones [314].



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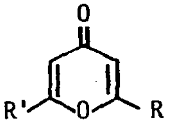
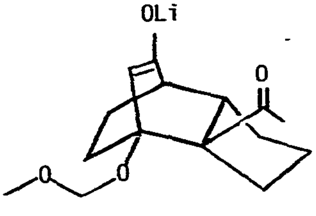


465

Tricyclo[5.2.2.$0^{2,6}$] undecane derivatives such as 466 may now be conveniently obtained by condensation of enolates illustrated by 467 with 1-acetylcyclopentene [315]. Such derivatives are useful in the synthesis of the antibiotic pleuromutilin. Another paper described alpha vinylations of ketones via treatment of their enolates with 468 followed by methanesulfonyl chloride and triethylamine [316]. For example, the method has been employed to convert 469 to 470 (88%).



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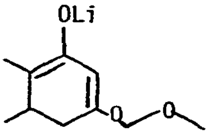

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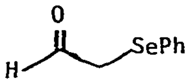

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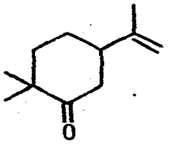

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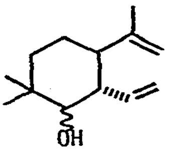
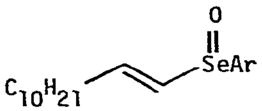


470

Selenium reagents 471 have been combined with enolates to ultimately effect the transfer of ethylene units as illustrated by the conversion of 472 to 473 (63%) [317]. In contrast, the use of 474 and certain organometallics leads to oxetanes [318]. Incidentally, ketone and ester enolates may be directly selenated in lower cost reactions by use of selenium metal followed by alkylation [319]. The method has been employed to synthesize several derivatives including 475 (80%). The more classic selenation of enolates has been used to prepare spirodienones 476 [320].



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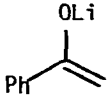

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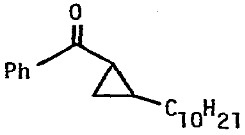

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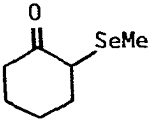

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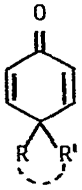
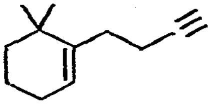


476

Enolates of methyl ketones, prepared in the presence of excess LDA, have been condensed with diethyl chlorophosphate to prepare terminal acetylenes useful in the synthesis of (E)-trisubstituted olefins of terpenoid origin [321]. For example, β-ionone gives 477 (85%). Such ketone enolates have also been combined with alkenyltriphenylphosphonium bromides to afford tricyclo[3.2.1.$0^{2,7}$]octan-6-ones such as 478 [322], sulfine 479 to give disulfides illustrated by 480 [323], and pyridinium salts 481 to yield 482 [324].



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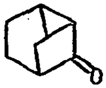
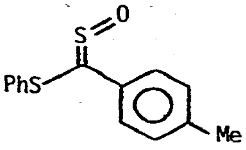


478



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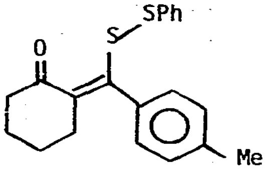

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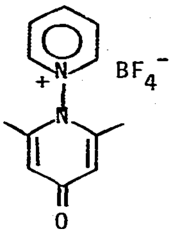

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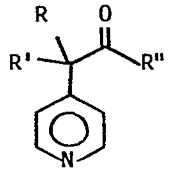
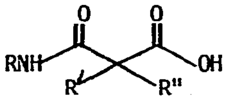


482

The threo/erythro ratios of hydroxyacids have been studied in the condensations of the dianions of carboxylic acids and aldehydes [325]. Under kinetically controlled conditions, the amount of threo product increased with increasing bulkiness of the substituents on either the acid or the aldehyde and decreased with the charge/radius ratio of the counter ions of the acid. Even higher threo-selectivity was observed under thermodynamically controlled conditions. Another paper discussed the steric limits to the alkylation of aliphatic acids and nitriles to afford trialkylated derivatives [326].

Malonamic acids 483 and their 3-thio derivatives have been obtained by treatment of dilithium salts of carboxylic acids with aliphatic or aromatic isocyanates and thiocyanates, respectively [327]. Lactone 484 has been prepared from 485 and 486 as part of the synthesis of lepiochlorin, a chlorinated antibiotic [328]. Alkylations of the dilithium derivatives of 487 (R = Et or $-(CH_2)_3-$) have also been reported [329]. Another study utilized lithium α-halocarboxylates and α-halocarboxylic esters as the alkyl halides in such reactions [330].



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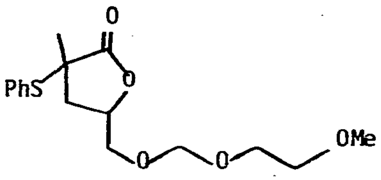

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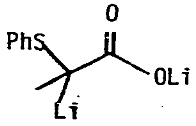

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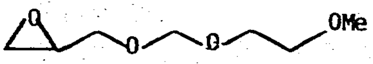

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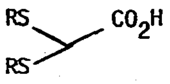
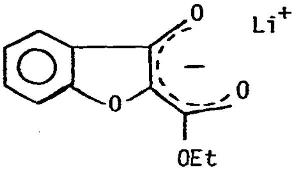


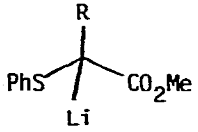
487

Alkylations of lithium enolate 488 have shown a marked tendency towards reaction at oxygen especially when compared to the corresponding sodium derivative [331]. Such O-nucleophilicity is enhanced with alkyl sulfonates or sulfate but diminished with alkyl halides and triflate. Solvent effects were found to have minimal effects on the selectivity.



488

The direction of the equilibrium in condensations of 489 with aldehydes has been found to be a function of the metallic cation, hydroxyesters 490 being favored in the presence of zinc cations while starting materials predominate with lithium cations [332]. The major product in most cases had the erythro conformation.



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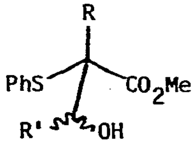

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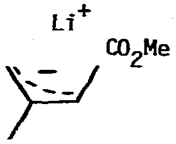

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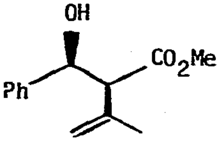
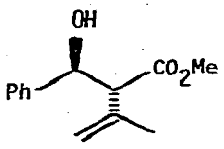


492

Enolates derived from crotonate esters substituted in the 3-position with alkyl, alkoxy, or dialkylamino groups combine with aldehydes to afford stereoisomeric hydroxyesters or α-pyrones at -70° and 15°, respectively [333]. For example, 491 and benzaldehyde gives 492 and 493 (60:40) at the lower temperature and 494 at the higher one.



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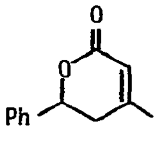
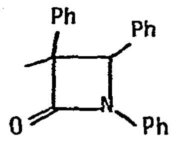


494

β-Lactams have been conveniently obtained from ester enolates and substituted aryl imines as illustrated by the formation of 495 (90%) from 496 and 497 [334]. Optically active β-lactams with up to 60% ee were realized with chiral enolates.



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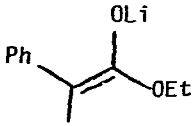

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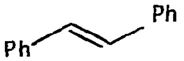
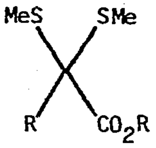


497

Lithium ester enolates have also been combined with highly substituted acid chlorides as part of a general synthetic route to bi-secondary ketones [335], with 498 to afford 499 [336], with chlorotrimethylsilane followed by CF$_3$OF to give α-fluoroesters such as 500 [337], and with π-allylpalladium chloride complexes in the presence of triethylamine and HMPA to yield alkylated cyclopropanes illustrated by 501 [338]. Dilithio derivatives 502 (n = 3,4) have been dialkylated by α,Ω-dihalides and -ditosylates to afford bicyclics 503 (m = 3-5) [339]. Another paper reported the use of the enolate Claisen rearrangement as part of the synthesis of (-)- and (+)-nonatic acids [340].

$MeSO_2SMe$

498



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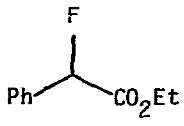

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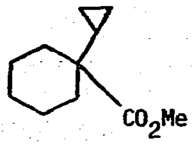

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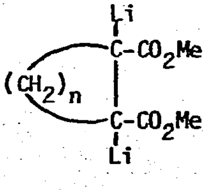

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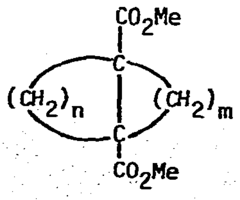
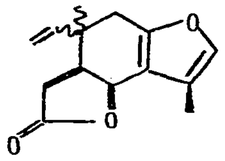


503

Several lactones have been converted to their lithium enolates and combined with electrophiles as part of the synthesis of natural products. Among them were the enolates of 504 and Eschenmoser's salt to afford isolinderalactone [341], methylation of 505 as part of the preparation of a segment of calcimycin [342], and alkylation of 506 as part of the synthesis of ($\pm$)-trichodiene [343].



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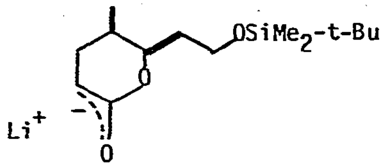

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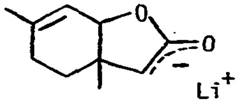
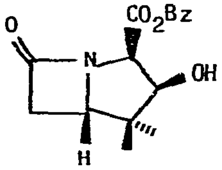


506

Carbapenam 507 has been synthesized from 508 and LiN(TMS)$_2$ followed by quenching with p-toluenesulfonic acid [344]. Reagent 508 itself was prepared from 509, benzyl bromoacetate, and LiN(TMS)$_2$ followed by oxidation. Another paper discussed the condensation of 510 with acetaldehyde as part of the preparation of racemic 6-α-hydroxyethylpenemcarboxylic acids [345].



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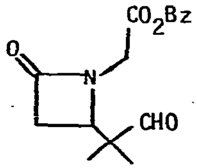

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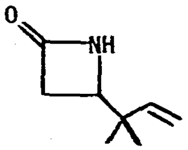

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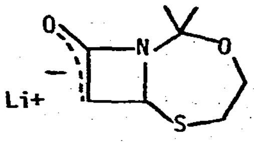
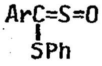


510

A wide variety of organometallic reagents including N,N-diethyl α-lithio-n-butyramide have been added to sulfines 511-513 (Ar = p-MeC$_6$H$_4$) to afford 514-516, respectively [346].

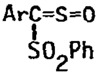
$Ar_2C{=}S{=}O$

511



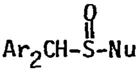
$ArC(SPh){=}S{=}O$

512



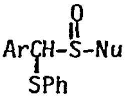
$ArC(SO_2Ph){=}S{=}O$

513



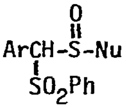
$Ar_2CH{-}S(=O){-}Nu$

514



$ArCH(SPh){-}S(=O){-}Nu$

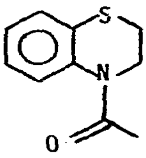
515



$ArCH(SO_2Ph){-}S(=O){-}Nu$

516

Finally, phenothiazine 517 has been found to undergo an interesting Claisen-type of condensation upon treatment with n-butyllithium to give 518 [347].



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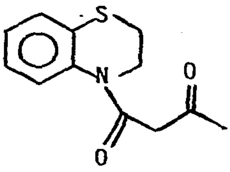
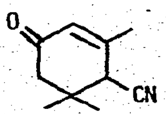


518

C. Nitriles, Amines, Imines, Ethers, and Related Compounds

4-Cyanoisophorone (519) may now be conveniently synthesized by cyclodimerization of 520 to 521 with lithium diethylamide followed by acid catalyzed hydrolysis [348].



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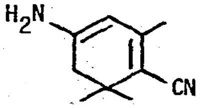
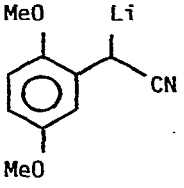
520



521

Linear polyclic quinone systems have been obtained by 1,4-addition of lithionitriles to α,β-unsaturated esters followed by cyclization and oxidative decyanation [349, 350]. The method is illustrated by the condensation of 522 with 523 to afford 524, cyclization of the parent acid of the latter to 525, and conversion to 526.



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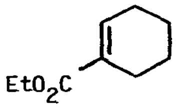

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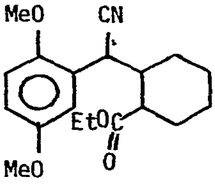

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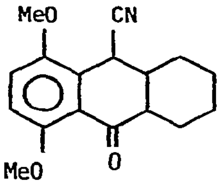

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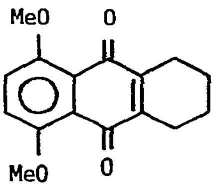
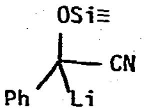


526

O-Trimethylsilyl derivatives of cyanohydrins continued to be metalated and subsequently combined with electrophiles. For example, 527 has been found to combine with 528 in ether and THF to afford mostly 529 and 530, respectively [351]. Product 530 arises from loss of LiCN from 1,2-adduct 531. 1,2-Adducts are formed exclusively in THF and DME in the presence of HMPA or 12-crown-4.

α,β-Unsaturated reagents 532 have been found to undergo alkylation at the 1-position [352, 353]. For example, 532 and 533 (R = MEM) give 534 as part of the synthesis of an acetogenin [352]. The alkylated derivatives can be hydrolyzed to α,β-unsaturated ketones as illustrated by the β-phenylation of 535 to yield 536, then 537 [353].



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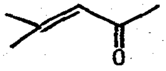

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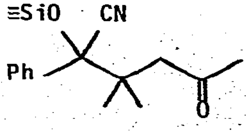

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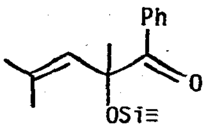

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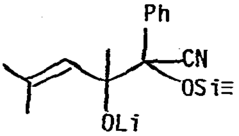

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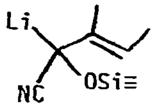

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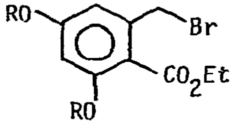

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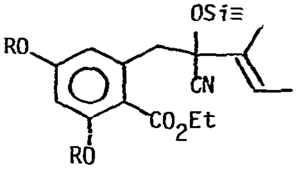

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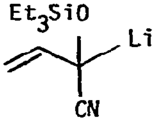

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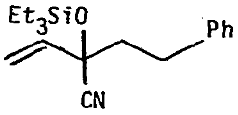

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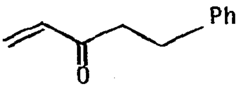
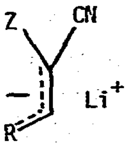


537

Nitrile derivatives 538 (Z = ethoxyethyl [354], dimethylamino and piperidino [355]) have been found to add to ketones via alpha and gamma attack at -78° and 0° to afford 539 and 540, respectively. Both modes of reaction are potentially useful in three carbon annelations. The latter compounds give spirolactones.



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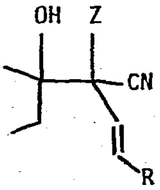

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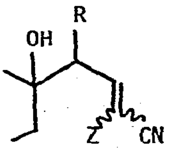
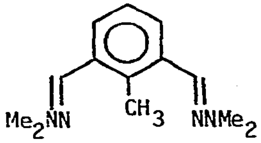


540

The previously described metalation of a methyl group ortho to a nitrile has been extended to 2,6-dicyanotoluene [356]. Interestingly, the latter compound appears to be an intermediate in the metalation of 541 with LDA. In other papers, lithiophenylacetonitrile has been added to sulfine 542 to yield 543 [357], and additional examples of condensation of α-lithionitriles with aromatics complexed with chromium have been described [358].



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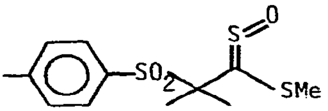

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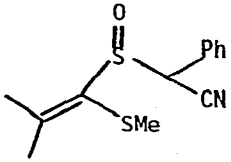
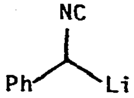


543

Another in an excellent series of papers describing the chemistry of metalated isocyanides was concerned with their reactions with certain 1,3-dipoles [359]. The currently described chemistry is illustrated by the condensation of 544 with nitrones, benzonitrile oxide, and phenylazide to afford 545, 546, and 547, respectively.



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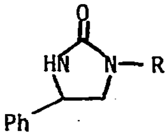

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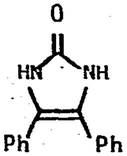

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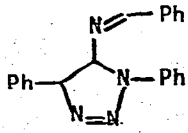
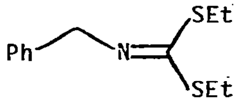


547

Three papers described additional aspects of the chemistry of metalated nitrogen derivatives of carbonic acid [360-362]. Thus, 548 has been converted to 549, a synthon of 550, by n-butyllithium in THF-HMPA-hexane or by potassium t-butoxide in THF, then alkylated to give 551 [360]. Reagents such as 552 have been metalated by LDA to yield 553 which have been condensed with aldehydes and ketones to afford 554 via 555 [361]. Quaternization of 554 with methyl iodide leads to thiiranes 556 [362].



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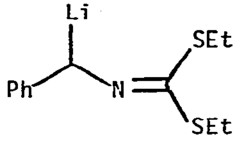

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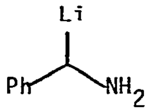

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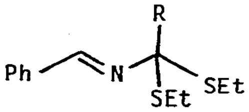

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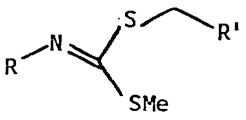

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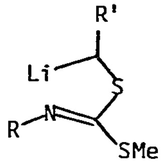

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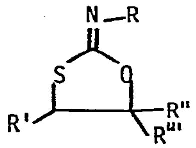

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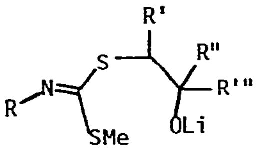

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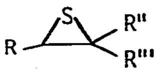
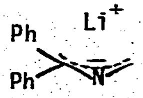


556

The first examples of $[6 + 3^-]$ cycloadditions have been realized in the reactions of certain azaallyl systems and cylcoheptatriene [363]. For example, 557 and this triene gives 558. Cycloadditions of such reagents with arylallenes yields pyrrolidines such as 559 [364]. Δ'-pyrrolines illustrated by 560 are similarly obtained from 561 and α,β-unsaturated esters [365].



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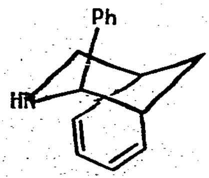

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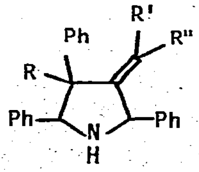

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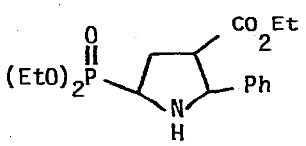

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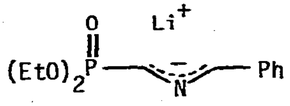
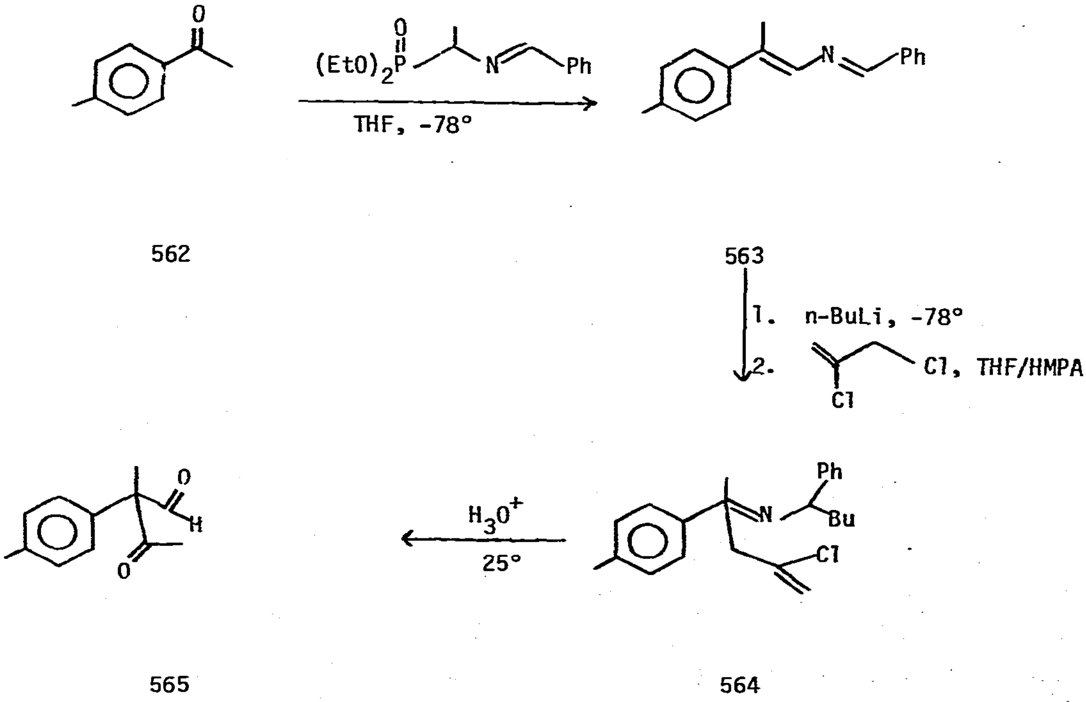


561

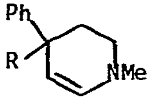
Geminal disubstitution at the carbonyl carbon atom of aldehydes and ketones can be effected often in a single flask by condensation of metalloenamines with electrophiles followed by hydrolysis [366]. The method is illustrated by the following sequence:



Metalated enamines such as 566 have been alkylated to afford 567 as part of the synthesis of morphine-based analgesics [367]. Other related papers discussed regioselective additions of lithioimines and hydrazones to α,β-unsaturated ketones [368], silylation of lithioimines with trimethylsilyl triflate to give N-silylenamines 568 [369], the ring opening of isoxazolines 569 by LDA to yield α-enoximes 570 [370], the use of 571 in Horner-Wittig reactions [371], oxygenation by oxygen of lithionitrosamines to afford hydroperoxy derivatives illustrated by 572 [372], the use of lithionitrosamine derivatives in the synthesis of $(\pm)$-

macrostomine [373], the trapping of lithiohexamethylphosphoramide with aldehydes and ketones to give 573 [374], sulfenylation of 574 (375), the conversion of oxaziridine 575 to 576 and 577 by lithium amide bases [376], and the preparation of 578 from the N-lithioimine and sulfur [377]. Another paper described the preparation of vinylsilanes from ketones using the lithium derivatives of their benzene- or p-toluenesulfonylhydrazones and chlorotrimethylsilane [378]. Such vinylsilanes are useful in 1,2-carbonyl transpositions [379].

566



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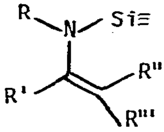

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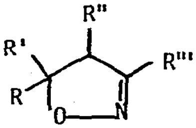

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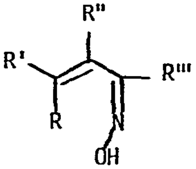

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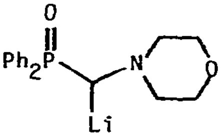

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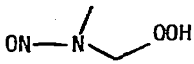

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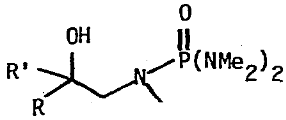

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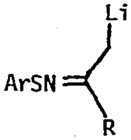

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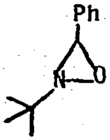

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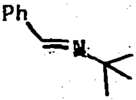

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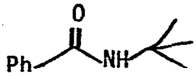

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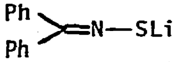
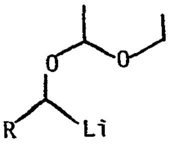


578

Specifically-substituted cyclopentanones may be obtained from organolithiums 579, derived from both aliphatic and aromatic aldehydes, and 580 [380]. The method is illustrated by the formation of 581 from 579 (R = m-methoxyphenyl), followed by treatment with triethyl orthoacetate to afford 582.



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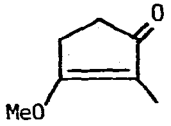

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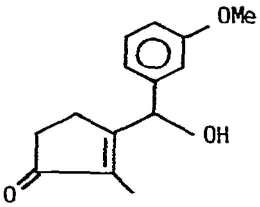

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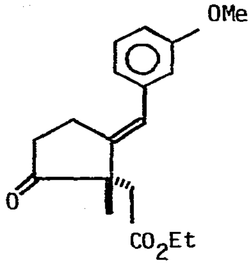
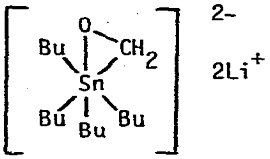


582

Dianion derivative 583 has been found to be a synthon of $LiOCH_2Li$ since its condensation with 584 gives 585 (15.4%) accompanied by 586 (8.5%) [381]. Other examples are cited. Another paper discussed the acylation of dilithiobenzophenone and related species to yield 587, 588, and other products [382].



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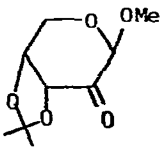

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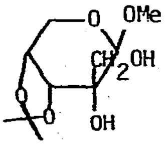
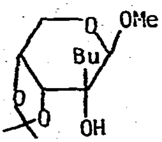


585



586

$Ar_2C(COR)OCOR$

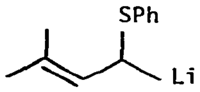
587

$Ar_2C{=}CR(OCOR)$

588

D. Carbanions Stabilized by Sulfur and Other Heavier Atoms

Lithiated allyl sulfide 589 has been found to condense with 590 mostly at the α-position to afford 591 which, upon warming, gives cyclopropyl derivative 592 [383]. In contrast, 593 combine with aldehydes and ketones mostly at the γ-position to yield 594 [384]. Reagents 593 add to cyclopentenone in a 1,4-fashion predominantly at the α-position in HMPA to afford 595 [385]. In THF, the latter reactions give mixtures of 1,2-adducts arising from both α- and γ-attack.



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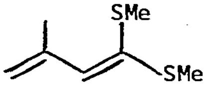

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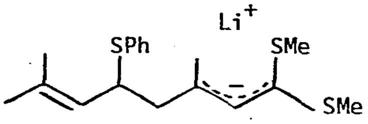

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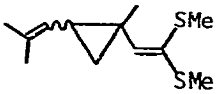

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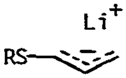

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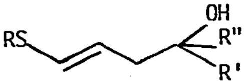

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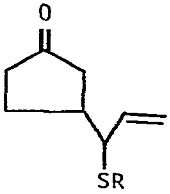

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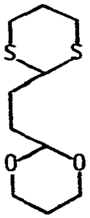

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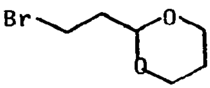

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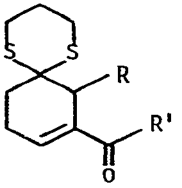
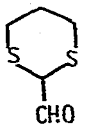


598

Dithiane reagent 596, obtained by alkylation of lithiodithiane with 597, has been used to effect the annelation of α,β-unsaturated ketones to 598 [386]. Several specific examples are listed. 2-Formyl-1,3-dithiane (599) has been formed from lithiodithiane and DMF, then alkylated in situ with several allyl halides to afford 600 [387]. Lithiobis(phenylthio)acetals 601 have now been successfully alkylated in hexane provided the reactions are run in the presence of TMEDA [388].



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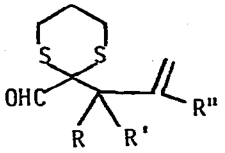

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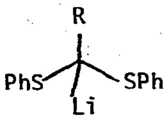

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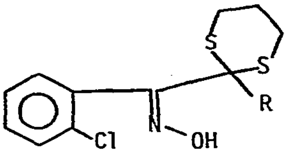
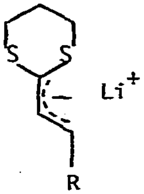


602

Lithiodithiane has been combined with nitrile oxides to yield 602, reagents which have been converted to α-diketones by trifluoroacetic acid and formalin [389].

γ-Lactones may be conveniently synthesized by condensation of ketene thioacetal anions and carbonyl compounds followed by cyclization with mercury (II) chloride [390]. For example, 603 (R = H) and benzaldehyde afford 604 which cyclizes to 605. Another paper disclosed that alkylations of 603 gave only α-products when R = Me but yielded both α- and γ-products when R = Ph[391]. The α:γ ratio increases with increasing hardness of the leaving group and the carbocation derived from the alkyl halide.



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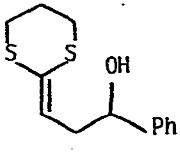

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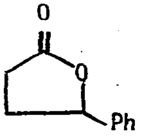
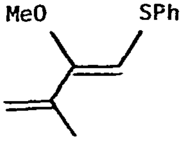


605

Related papers have been concerned with the 1,2-addition of 601 (R = H) to methacrolein as part of the preparation of 606 [392], reactions of 2-methyl-2-lithio-1,3-dithiane and 607 with enol ethers of β-diketones as part of the synthesis of daunomycinone [393], additional studies on 1,2- versus 1,4-additions on α,β-unsaturated systems [394, 395], and ring expansions of cyclic ketones using 608 [396]. The latter process is illustrated by the conversion of cyclopentanone to 609 (60%).



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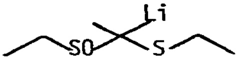
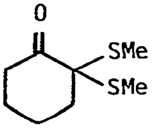


607

$(MeS)_3CLi$

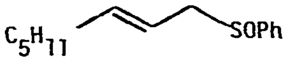
608



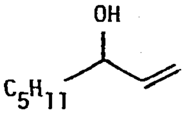
609

Aldehydes and ketones have been converted to one-carbon homologous allyl alcohols by lithiomethyl phenyl sulfoxide via the intermediacy of vinyl sulfoxides [397]. For example, n-heptanal and the lithiosulfoxide give 610, then 611, and finally 612.

610

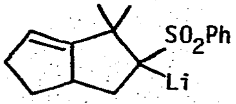


611



612

α-Lithiosulfones have been oxidized by MoOPH as a route to ketones as illustrated by the conversion of 613 to 614 [398]. Other papers in this area were concerned with the preparation and alkylation of lithioalkoxyalkyl phenyl sulfones [399], reaction between 1,1-dilithioalkyl phenyl sulfones and ω-bromoesters [400], and the use of α-lithiosulfones in the total synthesis of the chartreusin aglycon [401].



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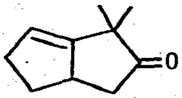
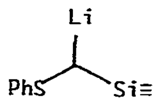


614

Carbanion 615 has been condensed with carboxamides to afford 616 [402] and with alkylating agents followed by m-chloroperbenzoic acid to give aldehydes [403, 404]. The latter process is illustrated by alkylation of 615 with bromomethylcyclohexane and the oxidizing agent to yield 617 which rearranges to 618. Hydrolysis of the latter affords 619. Acylbenzenes can be obtained by alkylation of 620 and subsequent oxidation and hydrolysis [405].



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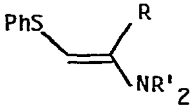

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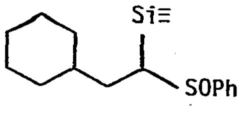

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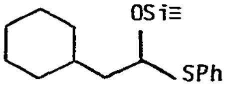

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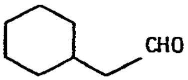
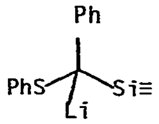
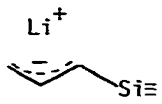


619



620

Carbanions alpha to silicon itself continued to be studied in 1980. Thus, the (trimethylsilyl)allyl anion (621) has been combined at the γ-position with aldehydes and ketones to afford products such as 622 as part of the synthesis of γ-lactones [406]. Condensation of 623 with imines has been found to stereospecifically afford (E)-alkenylpyridines 624 [407]. Reagent 625 has been alkylated as part of the preparation of o-xylylenes [408]. Diazomethane derivatives 626 (M = M' = Si; M = Si, M' = Ge; M = M' = Ge) have been obtained from the corresponding lithium reagents 627 and tosyl azide [409]. Silaethylenes arising from addition of t-butyllithium to vinyldimethylchlorosilane have been cycloadded to certain alkenes in hydrocarbon solvents but not in THF [410].



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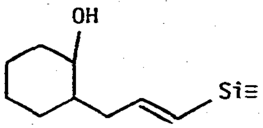

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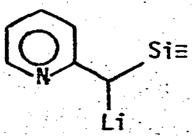

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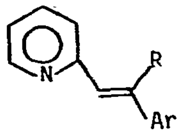

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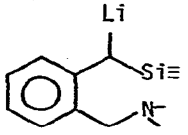

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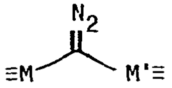

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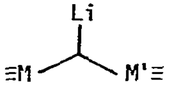
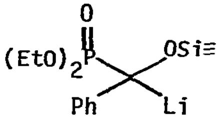


627

Phosphonate system 628, a new acyl anion equivalent, has been condensed with aldehydes and ketones to afford α-hydroxyketones [411, 412]. A key step in the process is a 1,4-oxygen-oxygen silicon migration shown in 629.



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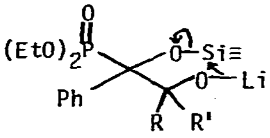


629

Finally, a large number of mixed-metal derivatives such as 630 (M = Si,Ge) have been prepared from 631, itself synthesized from 632 and phenyllithium [413].

$(Ph_3Pb)_2CHMMe_3$

630

$(Ph_3Pb)_2CHLi$

631

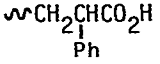
$(Ph_3Pb)_3CH$

632

E. Polymerization

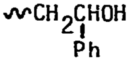
The oligomerization stereochemistry of vinyl monomers derived from vinylpyridines continued to be studied [414]. Thus, while addition of 2-vinylpyridine to lithium and sodium salts of 2-ethylpyridine gave >95% isotatic oligomers, dimerization of 4-vinylpyridine and addition of 4-vinylpyridine to α-lithio-2-ethylpyridine were not stereospecific. In each case, the reactions were quenched with methyl iodide. The stereospecificity is ascribed to coordination of lithium and sodium (but not potassium) cations with the nitrogen unshared pair of electrons of the penultimate 2-pyridine unit in an achiral ion pair.

Polystyryllithium, prepared by anionic polymerization, has been carbonated with solid and gaseous carbon dioxide to afford 633 (>90%) [415]. Similar results were achieved with polystyrylmagnesium bromide. The organolithium reagent was also combined with oxygen to give 634, 635, and coupling products illustrated by 636. The polystyryllithium may be analyzed by the amount of 1-decene liberated in its reaction with 1,2-dibromodecene [416]. Polystyrene has been ring-lithiated by s-butyllithium·TMEDA then treated with oxygen to yield ring-hydroxylated derivatives [417].



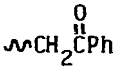
$\sim CH_2\underset{Ph}{\underset{|}{C}}HCO_2H$

633



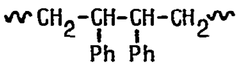
$\sim CH_2\underset{Ph}{\underset{|}{C}}HOH$

634



$\sim CH_2\overset{O}{\overset{\|}{C}}Ph$

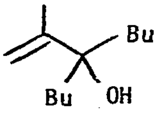
635



$\sim CH_2-\underset{Ph}{\underset{|}{CH}}-\underset{Ph}{\underset{|}{CH}}-CH_2\sim$

636

Methyl methacrylate has been polymerized by n-butyllithium in toluene at -78° to afford 637 and 638 (n=1,2,3, and 4) [418]. Another paper discussed three possible mechanisms for the termination of the anionic polymerization of this ester [419]. The mechanisms include an intermolecular reaction with the monomer ester function, an intramolecular cyclization of the anion, and reaction with the polymer ester moiety.



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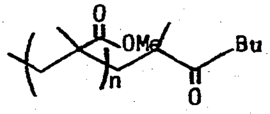
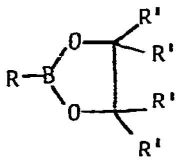


638

Other papers concerned with polymerization not covered elsewhere in this article discussed the structural regularity and crystallization of polyisoprenyllithium and lithium poly(styrene-b-isoprene-b-styrene) [420], the kinetics of the addition of 1,1-diphenylethene to lithium polyhexa-1,4-dienyl in benzene [421], the determination of the degree of association of polyisoprenyllithium in heptane [422], the multimodal molecular weight distribution of polydienyllithium compounds caused by thermolytic side reactions [423], and reaction of poly(difluorophosphazene) with phenyllithium [424].

F. Carbenoids

Boronic esters 639 (R = alkyl, R' = H or Me) have been homologated by trimethylsilylchloromethyllithium to afford 640 which rearranges to 641 [425]. Similar results have been achieved with dichloromethyllithium [426]. Of particular interest is boronic ester 642 which leads to chiral alcohols [427]. For example, (+)-642, dichloromethyllithium, and methylmagnesium bromide give 643 which, upon oxidation, yields (S)-1-phenylethanol (100%). A second homologation on 643 followed by oxidation affords 3-phenyl-2-butanol (90% erythro, 10% threo).



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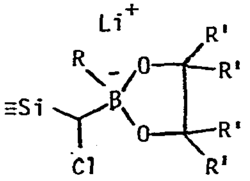

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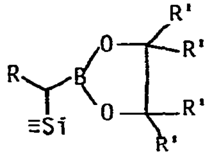

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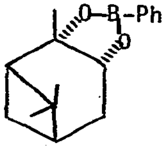

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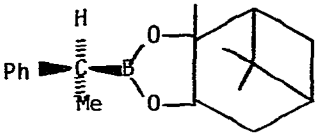
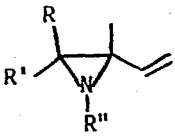


643

1,1-Dichloro- and 1,1-dibromoalkyllithiums have been added to esters to give 1,1-dihaloketones [428]. The latter carbenoids, prepared by metalation of dibromoalkanes with LDA [429] and by metal-halogen exchange on 1,1,1-tribromoalkanes [430], have been combined with various electrophiles. Aziridines 644 have been obtained from gem-dichloro(methyl)allyllithium and aldimines and ketimines [431].

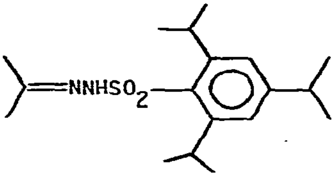


644

Other papers appropriate for this section were concerned with the reduction of gem-dibromocyclopropyl oximes by organolithium derivatives [432], regiosepcificity of cyclopropylidene C-H insertion reactions within [m.n.1]-propellane frameworks [433], twofold cyclopropylidene C-H insertion as a route to hexacylic bis(bicyclo[1.1.0]butanes) [434], and dimerization of bridgehead olefins formed from tricyclic cyclopropylidenes [435].

9. LITHIUM ATE COMPLEXES

Lithium and magnesium salts of secondary and tertiary aldehyde tosylhydrazones combine with copper reagents to afford new hindered cuprates which can be alkylated to give branched hydrocarbons [436]. For example, isopropylcyclohexane is obtained from the tosylhydrazone of cyclohexane carboxaldehyde, methyllithium, Me_2CuLi or Me_5CuLi_4, and methyl iodide. Vinyl cuprates have been obtained from hydrazones such as 645, t-butyllithium and PhSCu [437]. Such cuprates have been added in a 1,4-fashion to enones.



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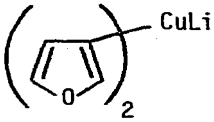

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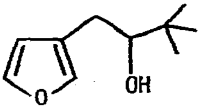


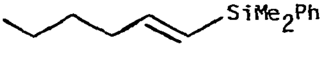
647

A new cuprate, 646, has been found capable of combining with certain epoxides to afford furan-alcohols illustrated by 647 [438]. The nucleophilicity of 646 is dramatically enhanced by the use of two extra equivalents of 3-lithiofuran in the preparation of the cuprate.

Vinylsilanes have been conveniently obtained from the addition of 648 to acetylenes followed by hydrolysis [439]. Thus, this reagent with 1-hexyne gives 649 (94%). The intermediate vinylcopper derivatives were also trapped with a variety of electrophiles. Vinylstannanes 650 and 651 have been prepared by addition of 652 to 653 at -100° to 78° and at -78° to -43°, respectively [440]. Other examples are cited including, in some cases, their conversion to (E)- and (Z)-4-lithio-1,3-pentadienes. Several other papers described similar preparations of Z-alkenylcuprates and their condensations with electrophiles as part of the synthesis of certain sex pheromones [441, 442] and in the preparation of α,β-butenolides [443,444].

$PhMe_2SiCu{\cdot}LiCN$

648



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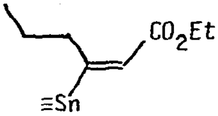

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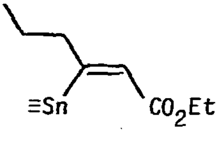
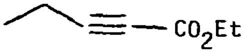


651

$(PhSCuSnMe_3)Li$

652



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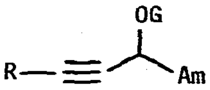

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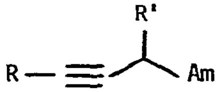

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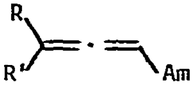


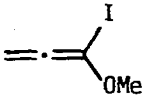
656

A variety of variables in the reaction of propargylic derivatives 654 (G = Ac, Tos, CO_2Me) with organocuprates were studied to determine the best conditions to obtain acetylenes 655 or allenes 656 [445]. The nature of the cuprate was most critical since di- or trialkylorganocuprates gave 655 while $MeCu{\cdot}LiBr{\cdot}MgBrI$ favored the formation of 656. Leaving groups, solvent, temperature, and substitution on 654 were also studied. Allenes have been prepared from propargyl alcohols and cuprates using the previously described 657 [446]. On the other hand, 1-alkynyl ethers 658 have been synthesized from 659 and cuprates [447].

$n\text{-}Bu_3\overset{+}{P}N(Me)Ph\ \ I^-$

657

658



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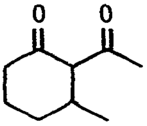

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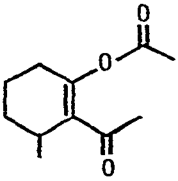

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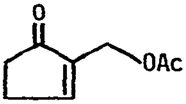
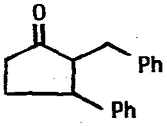


662

Turning to the area of α,β-ethylenic systems, acylation with acetyl chloride of enolates derived from cyclohexenone (and others) has been found to afford C-mono- (660) and C,O-diacyl (661) derivatives rather than the previously described O-acyl products [448]. Bis-β,β'-conjugate addition has been realized on enones which possess functional groups such as acetoxy, phenylthio, chloro, and trimethylsilyloxy on the β'-carbon atom [449]. For example, 662 and lithium diphenylcuprate give 663 (trans:cis>20:1). Advantage has been taken of the useful chemistry of the phenylselenium moiety by adding cuprates to systems such as 664 to yield 665, then converting them to exo- or endocyclic enones [450].



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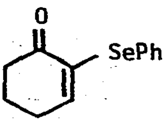

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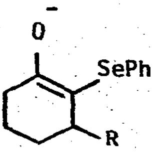

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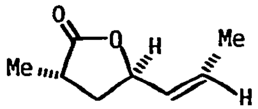

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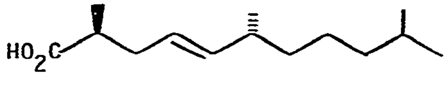

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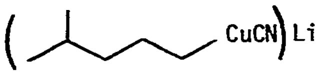
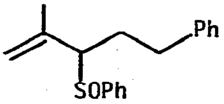


668

LiGRCu

669

Chirality transfer has been realized in condensations of vinyl lactones with alkylcyanocuprates[451]. The method is illustrated by the conversion of 666 to 667 by 668. Optically active adducts have also been obtained from mixed heterocuprates 669 (G = chiral alkoxy and thioalkoxy) and α,β-unsaturated ketones [452] and from chiral cuprates and α,β-unsaturated esters of chiral alcohols [453].



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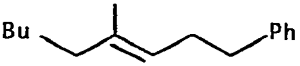

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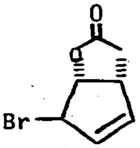

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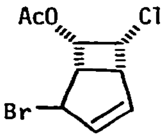
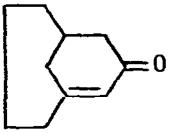


673

Trisubstituted olefins may be prepared by γ-substitution of allylic sulfoxides and sulfones with lithium dialkylcuprates [454]. For example, 670 and lithium di-n-butylcuprate give mostly 671 (75%) (E:Z = 93:7). An unrelated full paper discussed SN' reactions on a variety of cyclopentenyl bromides by lithium dibutylcuprate [455]. While lactones such as 672 reacted predominantly in an anti-fashion, those such as 673 reacted via the syn-mode.

Other papers concerned with cuprates and enones described the addition of lithium dimethylcuprate to ketones such as 674 as part of a study on strained double bonds [456], two syntheses of Brefeldin A [457, 458], the preparation of 16-halomethyl derivatives of 15-deoxy-16-hydroxyprostaglandin E2 [459], the stereoselective syntheses of (±)-gymnomitrol and (±)-gymnomitrene [460], and 1,4-additions to α,β-unsaturated aldehydes [461]. Vinylnitrosamines such as 675 have been condensed with lithium di-n-butylcuprate to afford 676 [462]. Similarly, cuprates have been added to vinylphosphonic esters illustrated by 677 to give 678 [463], and to epoxides 679 to yield 680 [464].



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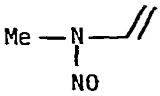
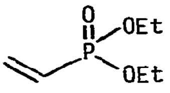


675

676

Lithium methylcuprate complexed with chiral alcohols and amines has been combined with cyclohexene oxide to afford chiral 2-methyl-1-cyclohexanol in low optical purities [465]. A similar ring opening has been realized in the conversion of thebaine to 7β-methyldihydrothebaine-φ with lithium dimethylcuprate [466].

Chiral β-alkoxyaldehydes have been condensed with cuprates in chelation-controlled nucleophilic additions to give alkoxyalcohols with diastereomeric purities of about 15-30:1 [467]. The system is illustrated by the conversion of 681 to 682 (90%) (threo:erythro = >20:1). Another related paper described similar condensations of Grignard reagents with α-alkoxyketones [468].



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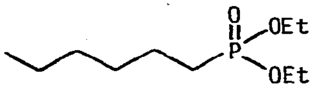

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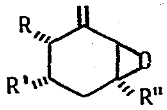

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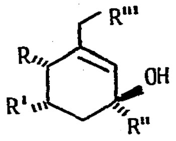

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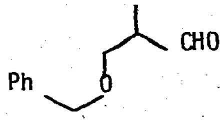

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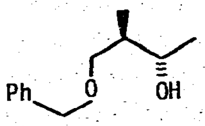
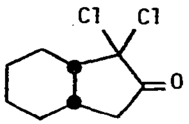


682

Two papers described three-carbon homologations of organometallics using β-propiolactones [469, 470]. While Grignard reagents and catalytic amounts of copper (I) bromide are used in some cases [469], lithium and bromomagnesium cuprates are employed in others [470]. The method is illustrated by the conversion of β-propiolactone to heptanoic acid (90%) by lithium dibutylcuprate.

α,α-Dichlorocyclopentanes have been transformed by lithium dimethylcuprate to a variety of alkylated and non-alkylated ketones and enones via α-chloro enolates [471]. For example, 683, lithium dimethylcuprate, and methyl iodide afford 684. Cuprates such as 685 derived from quinone derivatives have been alkylated to give products illustrated by 686 [472]. Olefins may be conveniently obtained by the regio- and stereoselective coupling of cuprates with enol trifluoromethansulfonates as in the conversion of 687 to 688 with lithium diphenylcuprate [473].



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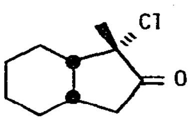

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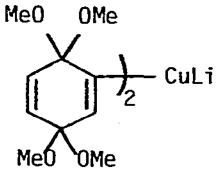

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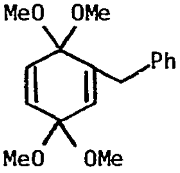

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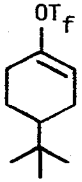

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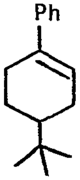
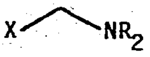


688

Allylic amines have been obtained by interaction of vinylcuprates with aminating agents 689 where X = PhS and n-BuO [474]. Another paper disclosed that amines can be N-alkylated by cuprates and molecular oxygen [475]. Thus, dibenzylamine, lithium dibutylcuprate, and oxygen afford 690 (62%).



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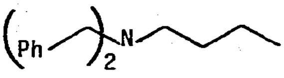
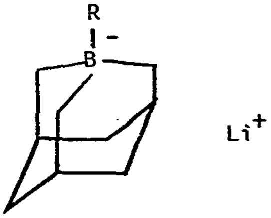


690

Lithium diarylcuprates condense with diborane to give intermediate boron reagents which have been oxidized to phenols and arylboronic acids [476]. Similar results were obtained with organocadmium reagents.

Unexpectedly, acylation of 691 (R = Me, N-Bu, Ph) by acetyl chloride has been found to afford methylidene derivatives 692 [477]. The products are apparently formed by loss of hydride ion from the β-carbon.



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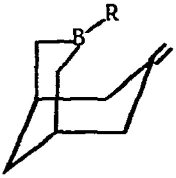
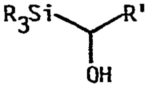


692

α-Hydroxysilanes 693 have been prepared from carbenoids such as 694 and trialkylboranes followed by oxidation [478]. The reactions proceed via ate complexes 695 and rearranged intermediates 696.



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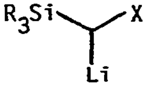
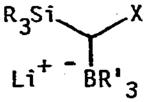


694

Condensations of lithioethers with organoboranes have proven to be synthetically useful. Thus, lithiomethoxyallene and such boron compounds, especially those derived from 9-BBN, give 697 which yield methoxycyclopropanes 698 (73-83%) upon treatment with acetic acid [479]. Similarly, reaction of 699 with trialkylboranes affords 700 which are converted to symmetric 1,1-dialkylethenes 701 by acid [480].



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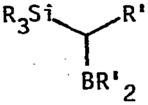

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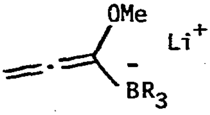

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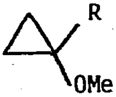

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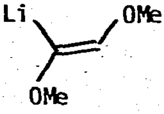

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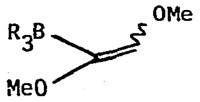

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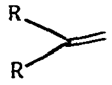
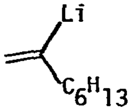


701

1,1-Dialkylethenes have been obtained from vinyllithiums derived from trisylhydrazones and trialkylboranes followed by iodine [481]. For example, 702, tri-n-propylborane, and iodine give 703 (69%). A related preparation of trisubstituted ethenes has been improved by the use of alkyl-9-BBN on vinyllithiums and iodine [482].



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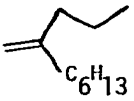
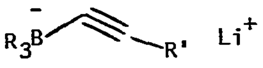


703

Michael condensations of lithium alkynyltrialkylborates effected by titanium (III) chloride have now been reported [483]. Thus, 704 and methyl vinyl ketone afford 705.



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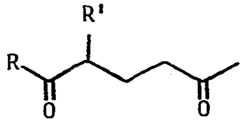
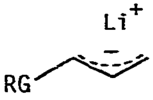


705

Other papers appropriate for this section discussed lithium triethylborohydride as a powerful and selective reducing agent [484] including its reaction with alkyl halides [485], and homologation of carbonyl compounds to aldehydes with lithium bis(ethylenedioxyboryl)methide, a non-ate reagent [486].

Turning to aluminum ate complexes, the regiochemistry in condensations of heterosubstituted allylic carbanions 706 (G = O or S) can be controlled by prior complexation with triethylaluminum [487]. The resulting ate systems 707 combine with both carbonyl compounds and reactive alkyl halides to afford α-derivatives 708.



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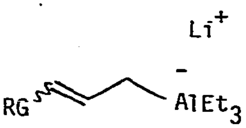

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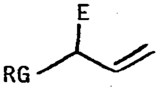
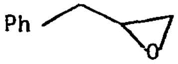


708

The regioselectivity of reductions of 2-cyclohexenone by lithium aluminum hydride have been reversed by the use of [2.1.1] cryptand [488]. Thus, while the reduction occurs mostly at the carbonyl in the absence of the cryptand, the olefin is reduced in its presence.

Epoxides can be alkylated by lithium and sodium tetraalkylaluminates as illustrated by the conversion of 709 to 710 [489]. The reactions are accelerated by transition metal salts, particularly nickel (II) chloride and bromide. Transition metal compound Cp_2TiCl_2 promotes the reduction of terminal alkenes and internal alkynes by lithium aluminum hydride and others via the intermediacy of alkyl- and vinylaluminum reagents, respectively [490].



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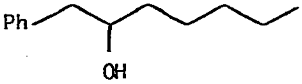


710

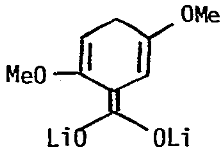
Finally, dialkynylaluminum reagents such as 711 (Me = Li,Na) have been prepared from the monoalkynyl reagents and the lithium or sodium acetylides [491]. Complexes (1:1) of 711 with dioxane possess more covalent bonding to the metal by alkynyl groups than by the alkyl groups in Me_4AlM. The IR and NMR spectra of the compounds are reported.

$$Me_2(MeC{\equiv}C)_2AlM$$

711

10. REDUCTIONS AND RADICAL ANIONS

Anionic intermediates in the lithium-ammonia reductions of certain aromatic systems continue to be trapped by electrophiles. For example, 712 has been alkylated as part of a direct synthesis of dihydrofluoren-2-ones [492]; 713 and others have been condensed with methyl crotonate via a 1,4-route [493], and lithium anthracenide has been dimerized by $BeCl_2$ [494]. In contrast, dilithioanthracene and this halide in THF afford 714 via cleavage of the solvent.



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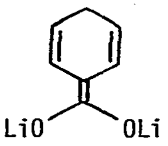

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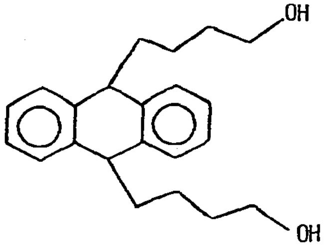
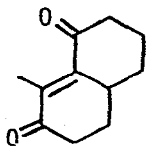


714

Reductive-alkylations of enediones by lithium-ammonia-THF have been found to give predominantly equatorial products [495]. For example, 715 yields mostly 716. The method has been employed to prepare adrenosterone [496]. Another paper revealed that higher yields of ketone are realized in lithium-ethylamine reductions of α,β-unsaturated ketones run at -78° rather than at the boiling point of the amine [497].



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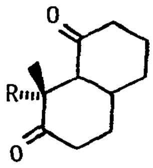
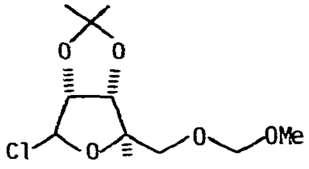


716

Reactions of cyclopropyl halides with alkali naphthalenides were further studied leading the authors to conclude that "inversions of free secondary and tertiary cyclopropyl radicals are always faster than bimolecular SET reactions with MN; net retention is not observed" [498]. Thus, retention of configuration is not due to the competition of electron transfer to and inversion of the cyclopropyl radicals. Radical equilibria and competing electron transfers have been used to explain the amounts of syn- and anti-deuteration in a series of cyclopropyl chlorides with alkali metals, magnesium, lithium naphthalenide, and dilithionaphthalene [499]. Rate-structure profiles have been determined for the reduction of alkyl bromides with lithium 4,4-dimethylbenzophenone and other reducing agents to suggest that the carbon-halogen bond is significantly broken in the transition state [500]. Lithium-ammonia reductions have been employed in the conversion of furanoids and pyranoids to glycals as illustrated in the preparation of 718 from 717 [501].



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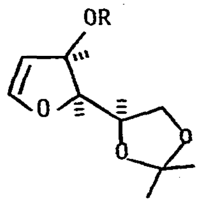
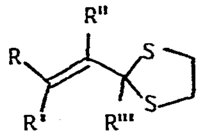
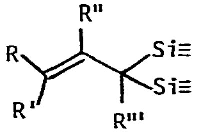


718

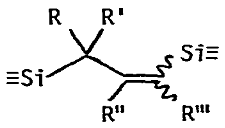
Reductive silylations of 719 with lithium in the presence of chlorotrimethylsilane have given 720 and/or 721 [502]. The conversion of thioketals such as 722 to lithium derivatives 723 has been improved by the use of lithium 1-(dimethylamino)-naphthalenide [503].



719



720



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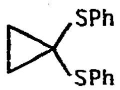

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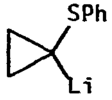
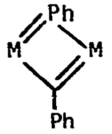


723

Other papers of interest discussed the cleavage of dibenzofuran derivatives with lithium metal [504], stereoselective reduction of cyclic and bicyclic ketones by lithium alkoxymagnesium hydrides [505], evaluation of lithium hydride as a reducing agent and a hydrometalation reagent [506], deoxygenation of epoxides to alkenes by lithium in THF [507], and reduction of α,β-unsaturated compounds by lithium amides containing α-hydrogen atoms [508]. The latter two papers were devoid of certain key references.

Interaction of $NdCl_3$ and YCl_3 with benzyllithium has afforded carbene type products described by 724 or 725 or 726 [509]. Such materials were accompanied by the formation of 1,2-diphenylethane, -ethene, and -ethyne as well as diphenylmethane, Similar results were realized with neophyllithium.



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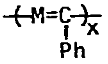


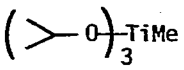
$-\!(M{=}\underset{Ph}{C})_x\!-$

725

PhC≡M

726

Titanium reagent 727, prepared from 728 and methyllithium has been found to be a highly selective nucleophilic methylating reagent [510]. Thus, 727 transfers a methyl group to aldehydes at -70 to -20° and to ketones between 25-80°. It adds to α,β-unsaturated aldehydes and ketones via 1,2-addition but does not react with esters,S-thiolates, nitriles, or epoxides.



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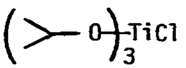


728

Among the new compounds reported in 1980 which contained group IVA and VA metals were 729 (M=Ti,Zr) from the chlorides and 730 [511], 731 from lithiohexamethyldisilazane and $TaCl_5$ [512], 732 from 733 and the dichloride [513], 734 (R = $n\text{-}C_8H_{17}$ and $(CH_2)_4CH = CH_2$) and 735 from 736 and the respective chlorides [514], and 737 and 738 from lithiopentamethylcyclopentadiene and the di- and trichlorides, respectively [515]. Aldol diastereoselection via zirconium enolates such as 739 (R = S-t-Bu, OMe, O-t-Bu, Ph, $N(CH_2)_4$, and $N\text{-}i\text{-}Pr_2$) and aldehydes has been disclosed [516]. Reagents 739 were prepared from the lithium enolates and the zirconium dichloride reagent.

$M[(NCMe_3)_2SiMe_2]_2$

729

$(LiNCMe_3)_2SiMe_2$

730

$Ta[N(SiMe_3)_2]_2Cl_3$

731

$Cp_2TiSiPh_2(SiPh_2)_2SiPh_2$

732

$Li_2Si_4Ph_8$

733

$Cp_2ZrRCH_2PPh_2$

734

$Cp_2Zr(CH_2PPh_2)_2$

735

$LiCH_2PPh_2$

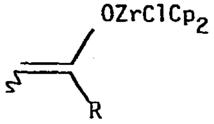
736

$Ta(C_5Me_5)(CHPh)(CH_2Ph)Cl$

737

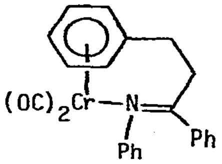
$Ta(C_5Me_5)(CH_2Ph)_2Cl_2$

738



739

Arenechromium species continue to be employed in organic synthesis. For example, 740 and methyllithium give, upon hydrolysis, 741 (ee = 94%) [517]. Styrene derivatives illustrated by 742 have been combined with a variety of carbanions then electrophiles to ultimately afford 743 [518]. The electrophiles included acid, methyl iodide, acid chlorides, and diphenyl disulfide.



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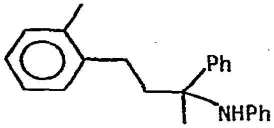
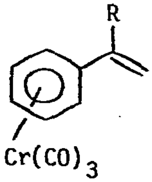
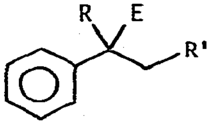


741



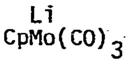
742



743

Certain transition metal anionic reagents such as 744 have been synthesized by reduction of the corresponding dinuclear compounds with alkali metal adducts of napthalene, phenanthrene, anthracene, and benzophenone [519]. Another paper discussed the relative reactivities of twenty-some transition metal nucleophiles including 744 towards methyl iodide and methyl tosylate [520]. With the exception of three reagents, a common SN_2 mechanism is suggested. Compounds such as 745 have been found capable of reducing carbon dioxide to carbon monoxide [521].

The transformation was also effected by the sodium salt of 745 and by related carbonyl derivatives of iron and ruthenium. Cyclic products 746 (M = Mo, n = 4; M = Ni, n = 2) have been obtained from 747 and 1,3-dibromopropane [522]. Lithiation on the phosphorus atoms of 746 was realized with methyllithium.

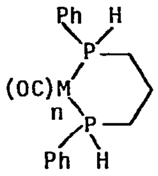


$\overset{\mathrm{Li}}{\mathrm{CpMo(CO)_3}}$

744

$Li_2W(CO)_5$

745



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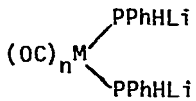
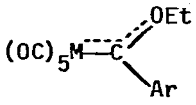


747

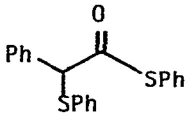
The hexacarbonyls of chromium, molybdenum, and tungsten have been combined with aryllithiums, then Et_3O^+ BF_4^- to afford 748 (Ar = $C_6H_5Cr(CO)_3$) [523], $C_5H_4RuC_5H_5$ [524], and $C_5H_3CH_3FeC_5H_4CH_3$ [524]). Carbyne 749 has been found to undergo two-fold addition of lithium thiophenoxide to give 750 [525].



748

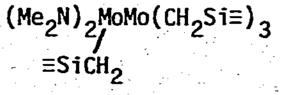
$PhC{\equiv}Cr(CO)_4Br$

749



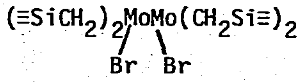
750

1,1-Dimethylamidosilylmolybdenum system 751 has been obtained from 752 and lithium dimethylamide [526, 527]. Interestingly, the use of methyllithium [526] and diethylamine give 1,2-derivatives illustrated by 753. NMR spectra of certain of the compounds are described. Several additional examples of quadruply bonded derivatives of group VIA were prepared using lithiated nitrogenous heterocycles [528, 529] and amides [530-532].



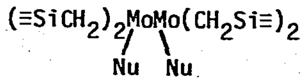
$(Me_2N)_2\underset{\equiv SiCH_2}{Mo}Mo(CH_2Si{\equiv})_3$

751



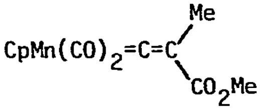
$({\equiv}SiCH_2)_2\underset{Br}{Mo}\underset{Br}{Mo}(CH_2Si{\equiv})_2$

752



$({\equiv}SiCH_2)_2\underset{Nu}{Mo}\underset{Nu}{Mo}(CH_2Si{\equiv})_2$

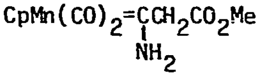
753


$CpMn(CO)_2{=}C{=}C(Me)(CO_2Me)$

754

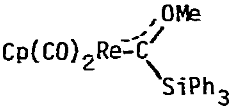
$CpMn(CO)_2HC{\equiv}C{-}CO_2Me$

755

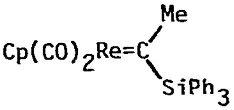

$CpMn(CO)_2{=}C(NH_2)CH_2CO_2Me$

756

Vinylidene complexes such as 754 have been obtained from 755, t-butyllithium, and $MeOSO_2F$ [533]. Other products are reported including carbene complex 756, obtained from 755 and sodium amide. Carbene complex 757 has been prepared from $C_pRe(CO)_3$, $LiSiPh_3$, and the same methylating agent as above [534]. Subsequent treatment of 757 with boron trifluoride and methyllithium gives 758.


$Cp(CO)_2Re{-}C(OMe)(SiPh_3)$

757


$Cp(CO)_2Re{=}C(Me)(SiPh_3)$

758

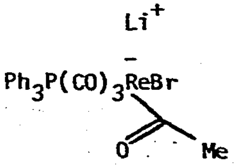
$Ph_3P(CO)_4ReBr$

759

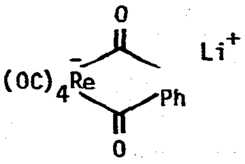
$Ph_3P(CO)_4ReMe$

760

Based on IR and NMR spectroscopy, the substitution on 759 by methyllithium to afford 760 has been postulated to proceed via attack upon coordinated carbon monoxide as in 761 [535]. Mixed acylrhenate 762 has been prepared by reacting the benzoyl- and acetylpenta-carbonyl derivatives with methyl- and phenyllithium, respectively [536]. Detailed studies of the rearrangements of the tetramethylammonia derivative of 762 are reported.



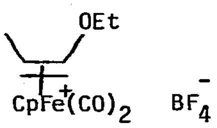
761



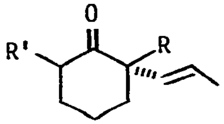
762

Finely divided, pyrophoric iron powder has been obtained by reduction of iron (II) chloride with lithium in glyme, then combined with C_6F_5I to afford $FePh_2$ [537]. The same technique has been applied to the preparation of nickel and cobalt powders.

Several unsaturated systems complexed by iron species have served as carbocation synthons. For example, vinyl cation equivalents 763 have been combined with enolates to ultimately give products such as 764 [538]. Complex 765 has been reacted with a variety of nucleophiles such as lithium diphenylcuprate and iodine to yield 766 [539]. Alkyllithiums have been added to 767 (Y = H,Me,OMe) in methylene chloride to afford mostly 768 [540].



763



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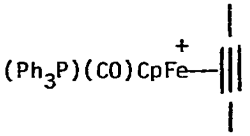

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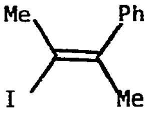
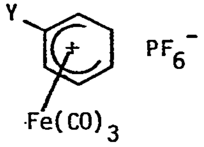


766



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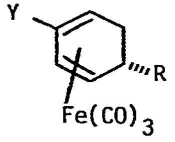
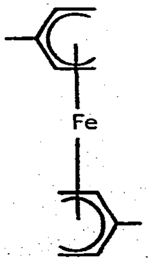
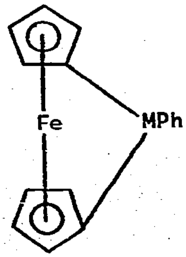


768

"Open ferrocenes" illustrated by 769 have been obtained from pentadienyl-anions and iron (II) chloride [541]. An X-ray study was performed on one such compound and the NMR spectra are described for two others. Ferrocenophanes 770 (M = P,As) have been obtained from 1,1'-dilithioferrocene·TMEDA and the metal dichlorides [542]. Oligonuclear ruthenocenes 771 (N = 2,3,4) have been synthesized from 1,1'-diiodoruthenocene · TMEDA [543].



769



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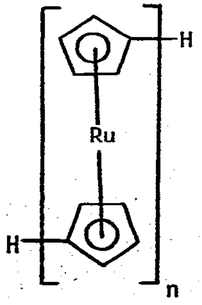
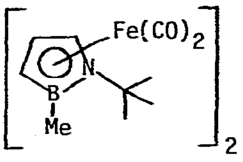


771

Diiron complex 772 has been obtained from iron pentacarbonyl and 773, itself prepared from 774 and dibromomethylborane [544]. Complex 775 and an isomer have been synthesized from organolithium reagents such as 776 and $C_p(CO)_2FeI$ [545]. The first iron complex containing a terminal P-functional phosphido group, 777, has been prepared from the chloro and bromo iron reagents and $LiP(SiMe_3)_2$ [546].



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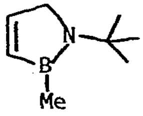

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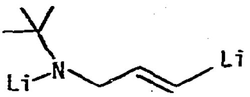

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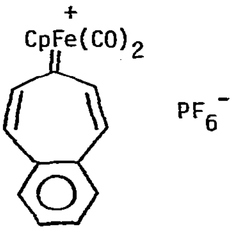

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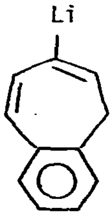
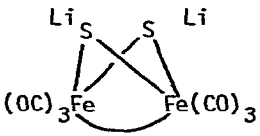


776

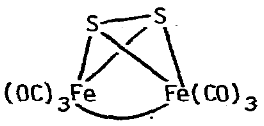
$(OC)_2CpFeP(SiMe_3)_2$

777

The previously described dianion 778 (M = Na,K) has been prepared in quantitative yield by treatment of the parent 779 with two equivalents of lithium triethylborohydride [547]. Condensations of 778 with a variety of electrophiles is described. Another paper discussed the use of cluster 780 as a catalyst in the hydrogenation of cis- and trans-stilbenes [548].



778



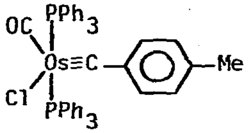
779

$(Fe_4S_4Cl_4)^{2-}2Li^+$

780

Finally, in this sub-group, osmium-carbyne complex 781 has been obtained from 782 with two equivalents of p-tolyllithium [549]. The crystal structure and some chemistry of 781 is presented.

The first reported methylene-bridged binuclear cobalt compound, 783, has been prepared from lithioacetaldehyde, $LiMe_5C_p$, and cobalt (II) chloride [550]. The enolate was prepared in situ from n-butyllithium and THF. Other compounds of interest in this sub-group were thioesters such as 784 from 785 and lithium thiophenoxide [551], dimeric formamidino species 786 (M = Rh,In) [552],



781

$OsCl_2(CCl_2)(CO)(PPh_3)_2$

782

diene-iridium compounds such as 787 from the iridium chlorides and organolithium reagents (R = Me,Ph) [553], and 788 (R = Me,Ph) from 789, ethylene, and RLi[554].

$Co_2(Me_5C_p)(\mu\text{-}CH_2)(\mu\text{-}CO)$

783

$PhSC(O)CCo_3(CO)_9$

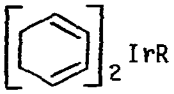
784

$BrCCo_3(CO)_9$

785

$(OC)_2M[CH(NR)_2]_2$

786



787

$RCo(C_2H_4)(PMe_3)_3$

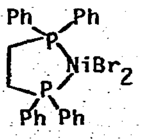
788

$ClCo(PMe_3)_3$

789

Condensation of 790 with 791 has been found to afford 792 which, upon heating, isomerizes to 793 [555]. Another paper described the crystal structure of 794, prepared from lithium benzophenoneimide and di-1,5-cyclooctadienenickel [556].

Ferrocenylcopper has been prepared from lithioferrocene and $[BrCuPPh_3]_4$ [557]. A large number of organogold compounds with built-in ligands have been synthesized from organolithium reagents and aurylphosphorus and -arsenic reagents [558]. For example, 795 and 796 give, after addition of triphenylphosphine, 797. Reagent 796 has also been employed to convert quinolyl- and phenanthridinyllithiums to the corresponding arylgold reagents as illustrated by



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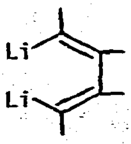

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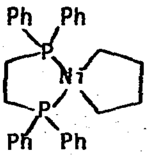

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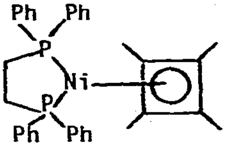
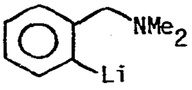


793

$(Ph_2C{=}NH)_2(Ph_2C{=}NLi)_3Ni_2 \cdot OEt_2$

794

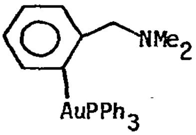
the conversion of 798 (M = Li) to 798 (M = Au) [559]. Alkylsilver reagents stabilized by lithium bromide have been used to effect 1,5-substitution of enynyl sulfinates to afford butatrienes as illustrated by the conversion of 799 to 800 by t-BuAg·3LiBr [560].



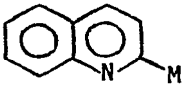
795

$ClAuAsPh_3$

796



797



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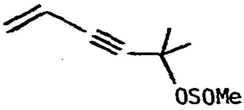
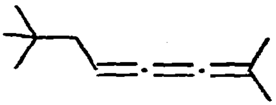
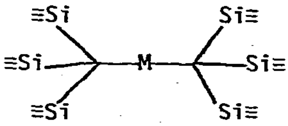


799



800

Zinc and cadmium reagents 801 have been obtained from the related methyllithium reagent and zinc and cadmium chlorides [561]. The new compounds are stable below 300°.



801

Mercury reagent 802 has been obtained from 803 and mercury (II) chloride [562]. Reaction of 803 with MeHgCl affords 804. Another paper reported the crystal structures of 805 and 806 [563].

$[Me_2B\text{-}N(Me)]_2Hg$

802

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

803

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

804

$Li_2Hg(SiMe_2Ph)_4$

805

$Li_2Hg(SiMe_3)_4$

806

Reagent 803 has also been combined with a variety of chloro derivatives of boron, silicon, phosphorus, and arsenic to give products such as 807-810, respectively [564]. Borolidines 811 [565] and oxaborata system 812[566] have been prepared from 813 and 814, and from lithio-N,N-dimethylacetamide and bromodimethylborane, respectively.

$Me_2B\text{-}NMe\text{-}BMe\text{-}NMe_2$

807

$Me_2Si(NMe\text{-}BMe_2)_2$

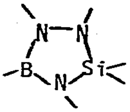
808

$Me_2B\text{-}NMe\text{-}PMe_2$

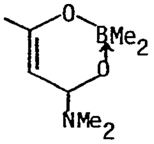
809

$Me_2B\text{-}NMe\text{-}AsMe_2$

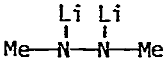
810



811



812



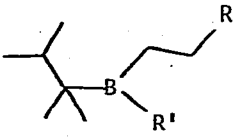
$Me\text{—}\overset{Li}{N}\text{—}\overset{Li}{N}\text{—}Me$

813

$BrB(Me)\text{-}NMe\text{-}SiMe_2Br$

814

Thexyldiorganoboranes 815 have been prepared from thexylchoroborane, alkenes ($H_2C = CHR$), and organolithiums or Grignard reagents (R'M) [567]. The latter reagents included alkyl- and vinyl systems. Another paper described a general procedure for the synthesis of lithium trialkylborohydrides from trialkylboranes and t-butyllithium [568].

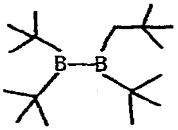


815

The first tetraalkyldiboranes were reported in 1980 [569, 570]. For example, treatment of 816 with three equivalents of t-butyllithium and one equivalent of neopentyllithium affords 817 (69%). Attempts to prepare 818 from $LiSiMe_3$ and trimethylborate were found to give instead ate complex 819 [571]. Several other similar ate complexes are described.

$(MeO)_2B\text{-}B(OMe)_2$

816



817

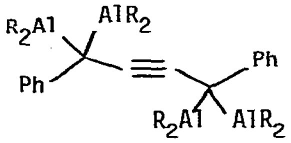
$B(SiMe_3)_3$

818

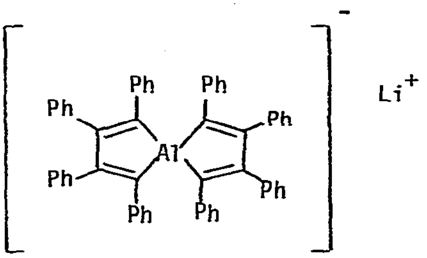
$LiB(SiMe_3)_4$

819

Tetrakis (aluminum) derivatives 820 (R = Me,Et) have been obtained from 1,4-diphenylbutadiyne, dialkylaluminum halides, and lithium [572]. Aluminum chloride and 1,2,3,4-tetraphenyl-1,4-dilithiobutadiene in ether have been found to yield complex 821 [573]. The stoichiometry and solvent are critical in such reactions.



820



821

Silylaluminum 822 [574] and -gallium 823 [575] derivatives have been synthesized from the metals, chlorotrimethylsilane, and lithium. Interaction of this chloride with gallium trichloride, and lithium affords 824 [575]. Products 823 and 824 are the first organosilylgallium compounds reported.

$Al(SiMe_3)_3$

822

$LiGa(SiMe_3)_4$

823

$Ga(SiMe_3)_3$

824

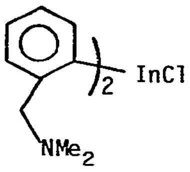
Other compounds in this family prepared from organolithiums and metal halides were 825 and 826 [576], 827 [577], and various mono-, tris-, tetrakis-, and hexakis (pentahalophenyl)thalliate (III) complexes [578, 579].

$Ga[CH(SiMe_3)_2]_3$

825

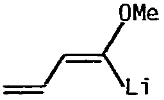
$In[CH(SiMe_3)_2]_3$

826

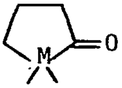


827

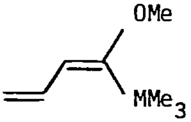
Condensation of vinyllithium 828 with dimethylchlorosilane and -germane followed by chloroplatinic acid and mineral acid gave ring systems 829 (M = Si,Ge) [580]. Metallovinyl ethers such as 830 (M = Si,Ge,Sn) have similarly been obtained from 828 and Me_3MCl [581].



828

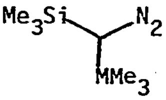


829

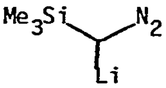


830

Diazoalkanes 831 (M = Si,Ge) have been prepared from 832 and the respective metal chlorides [582]. Two other routes for the preparation of such compounds where M = Si, Ge, Sn, and Pb are described. Previously unreported tricyclic oxasilepins such as 833 have been synthesized from O,O'-dilithiobenzyl phenyl ether and dichlorosilanes [583]. Condensation of dichlorodiethylsilane with lithium has been found to afford mostly $(Et_2Si)_5$ and $(Et_2Si)_7$ accompanied by smaller amounts of $(Et_2Si)_8$ and $(Et_2Si)_6$ [584].



831



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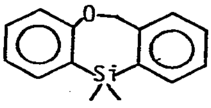
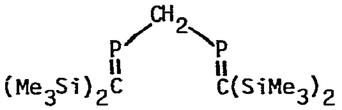


833

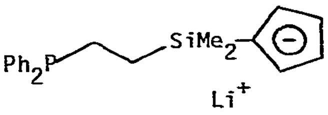
Double ylides illustrated by 834 have been prepared from 835, n-butyllithium and methylene halides [585]. Difunctional ligand 836 has been synthesized by addition of lithiocyclopentadiene to 837 followed by deprotonation with n-butyllithium [586].



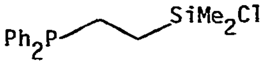
834

$Ph_2PCH(SiMe_3)_2$

835

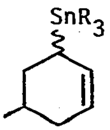


836

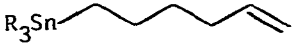


837

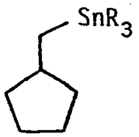
Interaction of R_3SnLi (R = Me,Bu) with cis- and trans-5-methyl-3-chlorocyclohexenes to afford 838 has been shown to proceed with inversion of configuration [587]. The use of radical probes 6-bromo- and 6-iodo-1-hexenes as substrates with R_3SnLi (R = Ph,Me) gave stannyl derivatives 839, but not 840 [588]. The authors suggest that the absence of 840 does not preclude the intermediacy of free radicals. Triphenylstannyllithium has been added to carbon disulfide as evidenced by alkylation with methyl iodide to yield 841 [589].



838

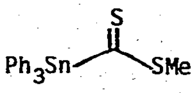


839



840

Compounds containing atoms from both groups IV and V directly bonded to one another continued to be actively studied. For example, systems such as 842 [590] and 843 [591] have been obtained by silylation of the parent N-lithio derivatives. While 1,3-silyl rearrangements are observed in certain of these cases [592, 593], ring contractions are observed in others [594, 595]. Similarly prepared were phosphorylated carbosilanes illustrated by 844 [596] and $MeP(SiMe_2)n$ where n = 4-6 [597].



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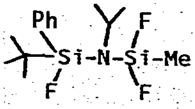

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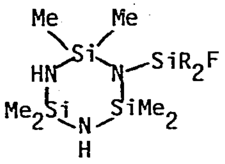

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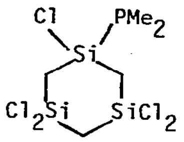
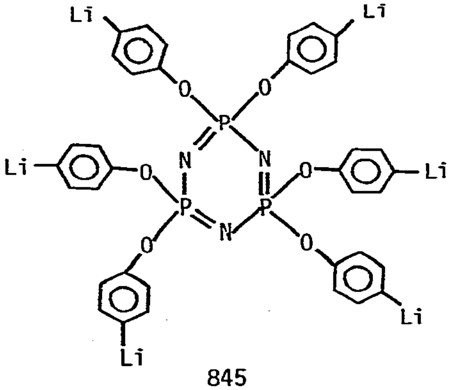


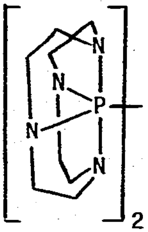
844

Lithiated cyclotriphosphazene 845 has been prepared from the corresponding hexabromo derivative and n-butyllithium, then combined with a variety of electrophiles such as Ph_2PCl, carbon dioxide, n-butyl bromide, and others to give normal products [598].



845

The first compound with a P(V)-P(V) bond, 846, has been obtained by condensation of 847 (G = Li) with 847 (G = F) [599]. The crystal structure of 846 is reported.



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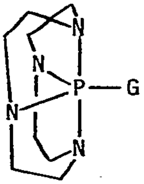
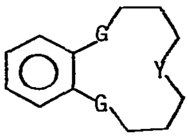


847

Eleven-membered macrocycles illustrated by 848 (G = PPh, AsMe, O, S, NMe) have been obtained from 849 and 850 (Y = PPh, AsPh, S, O, NMe; X = Br, Cl, OMS) [600, 601]. NMR and crystal structure data for many of the compounds are described.



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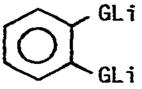

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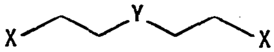
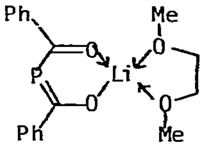


850

Other papers concerned with phosphorus discussed the benzoylation of $LiPH_2$ to afford 851 [602] and the synthesis of additional examples of diphosphaferrocenes illustrated by 852 [603].



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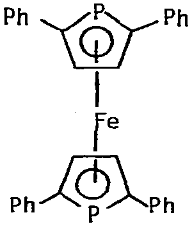
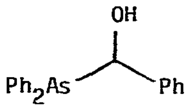


852

α-Hydroxyarsines such as 853 have been obtained from lithiodiphenylarsine and aldehydes [604]. In unrelated studies, arsine 854 has been converted to 855 by methyllithium [605] and α-hydroxybismuthane 856 has been synthesized from 857 and benzophenone [606]. Reagent 857 itself was prepared from 858 and phenyllithium.



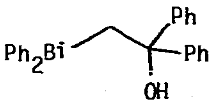
853

$(Me_3Si)_3As$

854

$(Me_3Si)_2AsLi$

855



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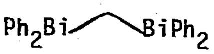

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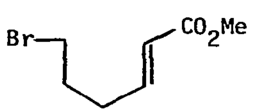

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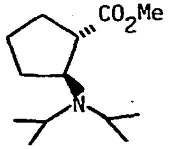

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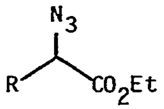

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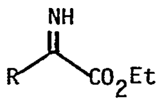

862

Finally, two other papers are of interest. First, MIRC (Michael initiated ring closure) has now been effected by LDA as illustrated by the conversion of 859 to 860 [607]. Secondly, α-azido esters 861 have been converted to α-amino esters 862 by lithium ethoxide [608]. Such products are conveniently converted to α-keto esters by simple hydrolysis.

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