LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1978*

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TABLE OF CONTENTS

*Lithium; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 158(1978)p.1-92.

1. REVIEWS AND BOOKS

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

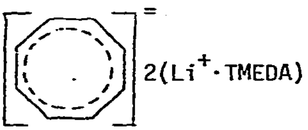
- Reactivity of carbanions and their ion-pairs in substitutions, additions, electron transfers, and proton transfers [1].
- Summary of gas phase acidity measurements involving 60 acids HA [2].
- Skeletal rearrangements of organoalkali metal compounds [3].
- Aromatic substitution by the S_{RN1} mechanism [4].
- A survey of spectral and structural data and an analysis of reactions believed to involve generation of homoaromatic ions [5].
- The role of one-electron transfer in substitution reactions [6].
- Radical, anion, and radical-anion reactions with organic halides [7].
- Propargylic metalation [8].
- Dehydrogenation of polycyclic hydroaromatic compounds by alkyllithium-TMEDA complexes [9].
- Dipole-stablized carbanions adjacent to nitrogen, oxygen, and sulfur [10].
- Formation of multiple bonds in nucleophilic eliminative ring fissions [11].
- Synthesis of conjugated enallenic hydrocarbons [12].
- Synthesis of α-enallenic and α-cumulenic ethers [13].
- Metal β-diketonates and their derivatives [14].
- Carbanions stabilized by sulfur [15].
- Recent developments in synthetic organic sulfur chemistry since 1970 [16].
- Synthetic methods employing organosulfur reagents [17].
- α-Sulfenylated carbonyl compounds in organic synthesis [18].
- Modern organoselenium chemistry [19].
- Synthetic utility of silicon in organic synthesis [20].
- Introduction of fluorine into organic molecules [21].
- Formation of asymmetric carbon-carbon bonds using chiral lithiooxazolines [22].
- Unsaturated carbenes [23].
- New applications of malononitrile in organic chemistry [24,25].
- Multiple metal-to-metal bonds [26,27].
- Preparation of unusual metal alkyls [28].
- Selectivity and specificity in the chemical reactions of carbene and carbyne metal complexes [29].
- Preparation of Group V heterobenzenes [30].

2. PREPARATION OF CARBANIONS

A. Metalation at sp^3 Carbon

Crystalline dilithio salt 1 has been obtained from diene 2 or triene 3 and n-butyllithium-TMEDA [31]. The conversion of 2 to 1 apparently proceeds via 4 which undergoes elimination of lithium hydride and TMEDA to afford 3.

In contrast, similar reaction of diene 5 and triene 6 with the same metalating agent failed to give 1. Oxidation of 1 with cadmium(II) chloride or oxygen conveniently affords cyclooctatetraene in nearly quantitative yield.



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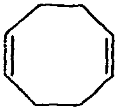

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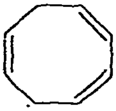

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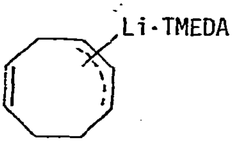

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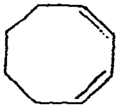

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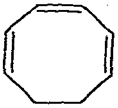

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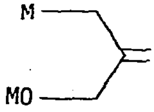
The dialkali derivative 7 has been obtained from methallyl alcohol and potassium t-butoxide-n-butyllithium [32]. Subsequent condensations with ketones and aldehydes gives diols 8 which have been oxidized to α-methylene-γ-lactones 9.



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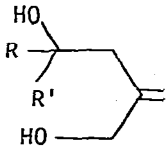

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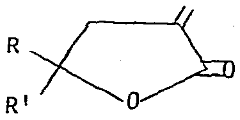

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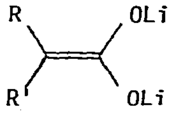
α-Hydroxy- and α-alkoxycarboxylic acids have been converted to polylithio derivatives 10-13 by lithium diisopropylamide (LDIPA), then alkylated or condensed with carbonyl-containing electrophiles to afford products 14-17, respectively [33-36].

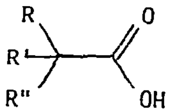


10: R=Ph,Me,H; R'=OLi

11: R=OPh; R'=H

12: R=OCH$_2$PH; R'=H

13: R = R'=H



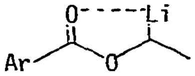
14: R=Ph,Me,H; R'=OH

15: R=OPh; R'=H

16: R=OCH$_2$Ph; R'=H

17: R = R'=H

Additional research on dipole-stabilized carbanions was described in 1978. Thus, ethyl 2,4,6-triisopropylbenzoate has been converted to 18 by s-butyllithium·TMEDA, then condensed with a variety of electrophiles to yield 19 [31-64%) [37]. Since subsequent reduction of 19 with lithium aluminum hydride gives 20, 18 serves as α-lithioalkyl alcohol synthon 21. A thorough full paper discussed the preparation and reactions of a variety of dipole-stabilized carbanions derived from thioesters 22 [38]. In most cases, the R of 22 was aromatic. Metalation of 22 by LiTMP gave systems analogous to 18 which either self-condensed with unmetalated thioester (R not sterically hindered) to afford dibenzoylmethanes or were sufficiently stable (R sterically hindered) to be combined with a variety of electrophiles to yield products similar to 19. One particularly interesting experiment provided evidence that carbanions can indeed be stabilized by dipoles. Thus, the equilibrium between methyl 2,4,6-triisopropylthiobenzoate and thiomethylmethyllithium·TMEDA was found to lie on the side of 23 by at least an order of magnitude.



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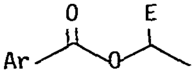

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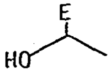

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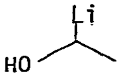

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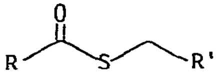

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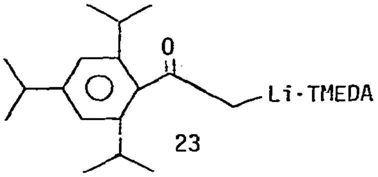

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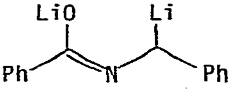
Dipole-stabilized lithioamides were also further studied in 1978. For example, dilithio salts 24 and 25 were obtained from N-benzylbenzamide [39] and N-allylbenzamides [40] with LDIPA, then combined with electrophiles to afford 26 and 27, respectively. It should be noted that the condensations on 25 gave only the γ-alkylated products. Interestingly, upon warming from -78° to -10°, lithioamides 25 were found to isomerize stereospecifically to enamides 28 [40]. In related research, the preparation of synthons such as 29 has been realized in the reactions of monolithio dipole-stabilized amides 30 [41] and 31 [42] with electrophiles followed by hydrolysis or reduction. Also discussed are the preparation and condensations of several other related carbanions such as 32 [41].



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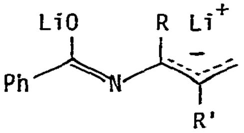

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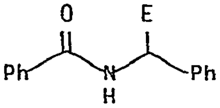

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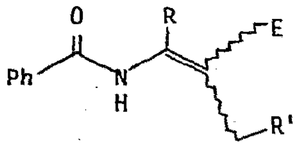
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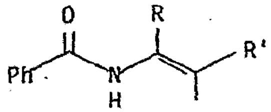
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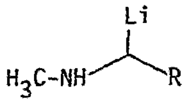
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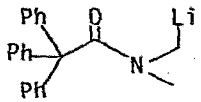
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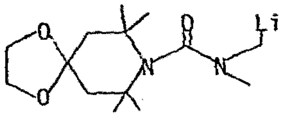
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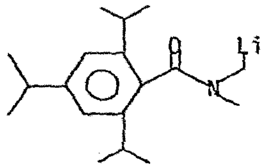
32

Not surprisingly, a large number of new carbanions stabilized by carbonyl groups were described in 1978. Thus, aminoester 33 has been converted to enolate 34 by LDIPA, then alkylated to afford Mannich bases 35 [43]. Enolate 34 is considered to be a synthon of acylate 36. Enolate 37, prepared from 38 and LDIPA-HMPA, has been shown to serve as a synthon of α-acetylene-α-amino acids [44].


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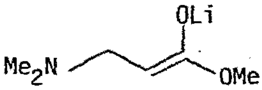
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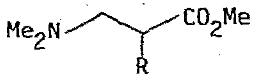
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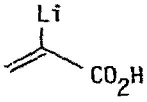
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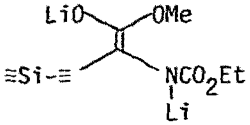
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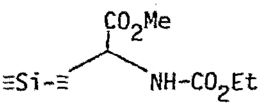
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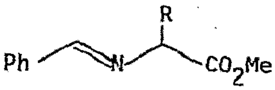
Racemic mixtures of iminoesters 39 have been converted to optically active 39 by deprotonation using LDIPA followed by protonation with optically active tartaric acids [45]. *Iminoester 40 has been metalated by lithium hexa*methyldisilazide to afford 41 [46]. Subsequent exclusive α-alkylation and hydrolysis gives α-vinyl amino acids.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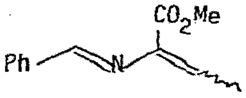
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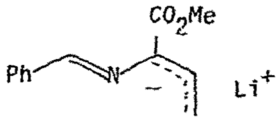
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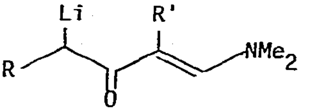
Vinylogous amide carbanions 42 have been obtained by metalation of the parent amides using LiTMP [47]. Condensations of 42 with aldehydes and ketones followed by treatment with methanolic hydrochloric acid affords 2,3-dihydro-4-pyrones (43) (37-67%). Similar α-metalation of optically active amide 44 with LDIPA followed by alkylation with ethyl iodide has been shown to yield 45 and 46 in a ratio of 76/24 [48]. The use of magnesium cation gave 45 and 46 in a ratio of 95/5. Subsequent conversions of 45 to chiral acids and ketones are described. Lactams such as 47 [49] and a variety of thioamides, for example 48 [50], have also been α-lithiated by LDIPA and n-butyllithium, respectively. The resulting carbanions have been sulfenylated and condensed with iodine to afford 49 and 50, respectively. The latter compounds arise via dithiacope rearrangements.



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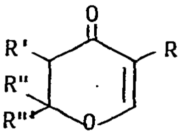

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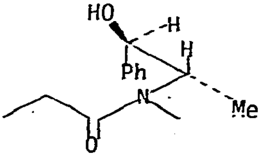

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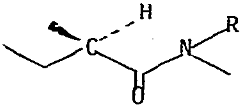

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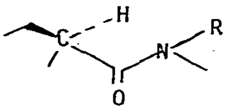

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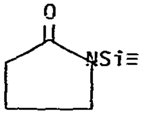

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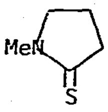

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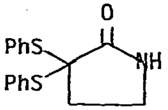

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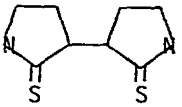

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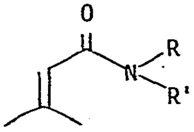
Amides 51 have been converted to α-lithio salts (R = R' = alkyl) by LDIPA or n-butyllithium [51]. The resulting carbanions have been combined with a variety of alkyl halides to give mostly 52 along with small amounts of 53. Interestingly, addition of copper(II) iodide to the lithio salts prior to the addition of the alkyl halide resulted in dramatic increases of 53 at the expense of 52.



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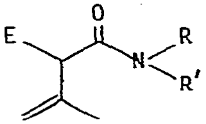

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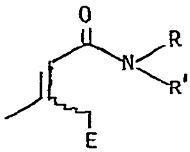

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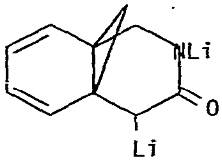
In other papers dealing with amides, dilithio salt 54 was prepared by metalation of the parent compound by LDIPA as part of the synthesis of 55 [52]. A variety of N-sodio and N-lithio salts of benzamide systems such as 56 have been found to undergo cyclizations to yield oxazepinones, oxazinones, pyrrolidones, and other compounds as a function of the metallic cation, the base, and the starting benzamide [53]. Finally, new 1,3-dicarbanion 57 has been obtained by dimetalation of the parent acetoamide with sodium hydride followed by n-butyllithium [54]. Treatment of 57 with a variety of electrophiles gave 58 (54-92%).



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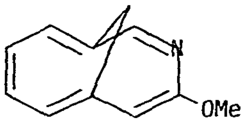

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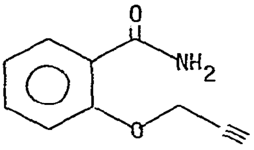

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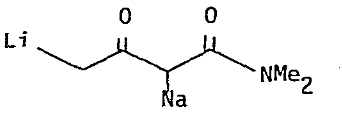

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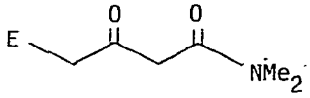

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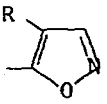
Related to 57, new dianions 60 of acetoacetonitrile have been obtained by dimetalation of 5-methylisoxazoles 59 using LDIPA [55]. Condensations of 60 with a variety of electrophiles afford 61. In another paper, interest in metalating aminonitriles has been revived as illustrated by the conversion of 62 to 63 [56]. Since subsequent alkylation and hydrolysis gives aldehydes, 62 serves as a latent acyl carbanion precursor. Two-fold alkylations of 62 followed by hydrolysis yields ketones.



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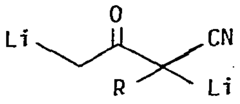

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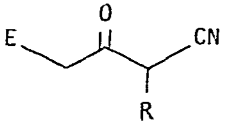

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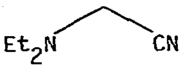

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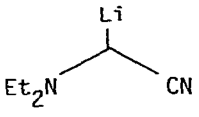
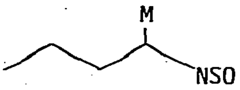


63

α-Carbon alkylation of amines has been effected by means of the new α-alkali derivatives 64 of N-sulfinylamines such as 65, prepared by metalation of the latter with n-butyllithium, triphenylmethyllithium, or potassium t-butoxide [57]. Treatment of 64 with allyl halides and Michael acceptors followed by hydrolysis conveniently affords amines such as 66.



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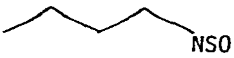

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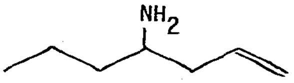
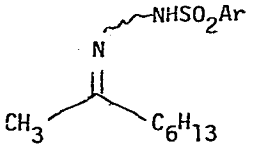


66

Two full papers appeared in 1978 which described the details of the conversions of arylsulfonylhydrazones to vinyllithium reagents [58-59]. Thus, for example, 67 has been treated with two equivalents of n-butyllithium to give 68 which, in turn, has been combined with a variety of electrophiles [58]. Similar reaction of tosylhydrazones containing only tertiary α-hydrogens with LDIPA likewise afford vinyllithiums which have been hydrolyzed to yield trisubstituted alkenes [59]. The procedure is illustrated by the preparation of 2,6-dimethyl-3-heptene from 69 (74%). The high degree of regiospecificity in such reactions is controlled by the stereochemistry of the imino bond [59,60]. Precursors of the vinyllithium reagents such as 70 have been trapped with aldehydes and ketones at lower temperatures, then converted to alkoxyvinyllithium reagents such as 71; hydrolysis gives homoallylic alcohols [60]. Reagents such as 71 have also been carboxylated with carbon dioxide to afford α-methylene-γ-lactones [61]. In other work, α-phenylsulfenyltosylhydrazones of cyclic alkanones have been 1,2-transposed to ketones using alkyllithium reagents [62]. For example, 72 yields 2-tetralone.



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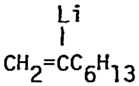
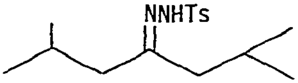


$CH_2{=}\overset{\overset{\text{Li}}{|}}{C}C_6H_{13}$

68



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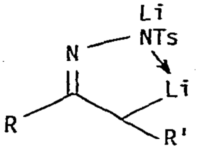

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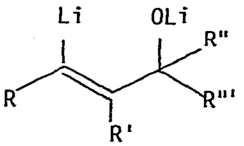

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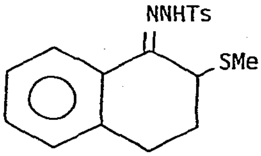
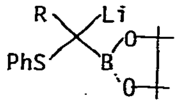


72

Several other papers describing new carbanions prepared by metalation at sp^3 carbon deserve mention in this section. Thus, lithiothioboronic esters 73 have been synthesized using LDIPA, then combined with alkyl halides and carbonyl-containing compounds to afford 74 [63]. Lithiostannacyclohexadienes 75 have been obtained similarly, then condensed with halosilanes, -germanes, and -stannanes to give products such as 76 [64]. Anions 77 have been regioselectively generated using LDIPA at -78°, then reacted with aldehydes to regiospecifically yield aldols [65]. Interestingly, the opposite regiochemistry was realized using boron trifluoride etherate instead of LDIPA. Other anions similarly prepared and reacted included 78 [66], 79 [67], and 80 [68].



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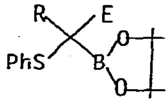

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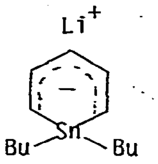

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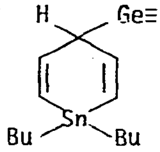

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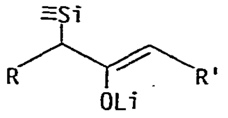

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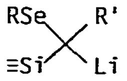

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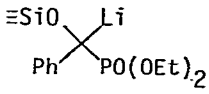

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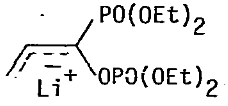
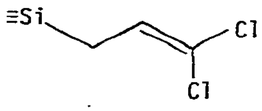


80

B. Metalation at sp^2 Carbon

Dichloroallylsilane 81 has been found to undergo vinyl metalation by n-butyllithium to afford 82 [69]. The latter compound undergoes β-elimination of lithium chloride followed by metal-halogen exchange to give acetylene 83 which was trapped with chlorotrimethylsilane. Lithio derivative 83 was also metalated at the allylic carbon atom to yield a dilithio species.



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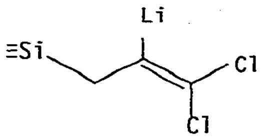
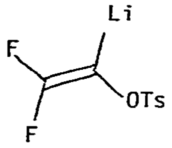


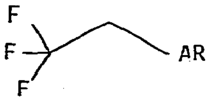
82

83

Difluorotosyloxyvinyllithium 84 has been prepared by treatment of 2,2,2-trifluoroethyl tosylate with two equivalents of LDIPA, then combined with aldehydes and ketones to afford α-keto acids [70]. Similar treatment of 2,2,2-trifluoroethyl ethers and thioethers 85 (A = O,S) with excess butyl- or phenyllithiums (R'Li) has been shown to conveniently give acetylenic ethers and thioethers 86 [71].



84



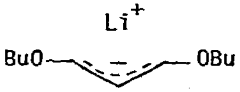
85

$R'-\equiv-AR$

86

Only vinyl metalation of 1,3-dibutoxypropene by t-butyllithium/HMPA to yield 87 has been realized even though the formation of the allylic anion 88 was possible [72]. In another paper, it was disclosed that similar vinyl metalation of 1,3-dienyl ethers and sulfides to afford 89 (A = O,S) was effected by n-butyllithium-potassium t-butoxide [73]. Both 87 and 89 were condensed with electrophiles to give expected products.

87



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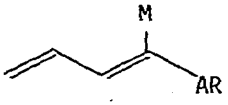
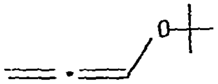


89

Terminal metalation has been realized on allene 90 using lithium dicyclohexylamide to afford 91 which, in turn, has been converted to α,β-unsaturated aldehydes by alkylation and hydrolysis [74]. Similar terminal metalation was also obtained in the reactions of α-alkylmethoxyallenes [74]. For example, treatment of 92 with n-butyllithium, then ethyl iodide yielded 93 which was hydrolyzed to 3-nonen-5-one. The previously described α-lithiomethoxyallene has been combined with α,β-unsaturated ketones to afford allenes such as 94 which have been conveniently converted to dihydrofuran-3(2H)-ones such as 95 [75].



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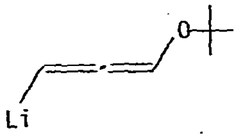

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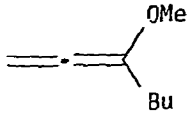

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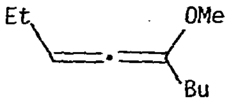

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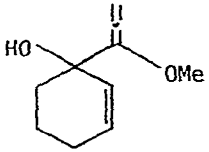

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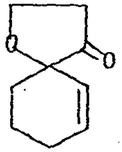
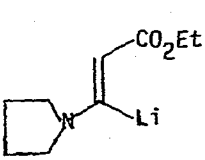


95

Vinyllithium reagent 96 has been obtained by kinetically controlled metalation of the parent aminoester using t-butyllithium at -100° [76]. Subsequent condensations with aldehydes or ketones and α,β-unsaturated ketones have been shown to give 2-buten-4-olides 97 and cyclopentenones 98, respectively. Reagent 96 may be considered to be equivalent to cyclopropenone.



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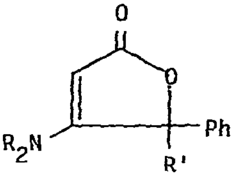

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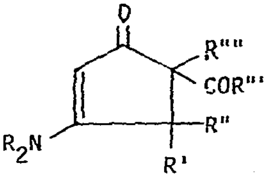
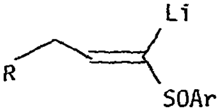


98

Two papers reported that α,β-unsaturated sulfoxides 99 undergo vinyl rather than allyl metalation to afford 100 [77,78]. In contrast to most vinyl carbanions, 100 was obtained in the E-configuration regardless of whether the starting sulfoxides possessed the Z- or E-configuration. A variety of condensations of 100 with electrophiles is reported. Interestingly, simple stirring of 100 at 100° followed by the addition of solid ammonium chloride caused facile elimination of the phenylsulfinyl moiety to give allenes in good yields [78]. Another paper describes similar metalation of selenoalkenes by KDIPA-lithium t-butoxide to afford vinylmetal reagents 101 [79].

99



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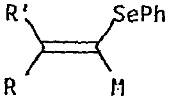
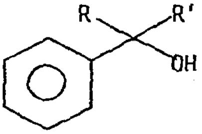


101

In the area of aromatic compounds, benzyl alcohols 102 (R = H, R' = H, Me, Et, Bu; R = R' = Me) have been converted to dilithio species 103 by two equivalents of n-butyllithium, then condensed with alkyl halides, aldehydes, and ketones to give 104 [80].



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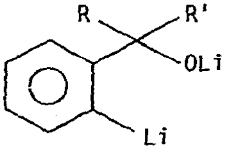

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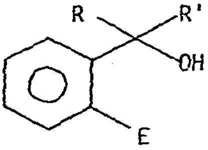
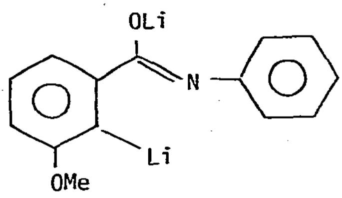


104

Several papers [81-84] described o-metalations of benzamide derivatives to yield lithium reagents such as 105, and their subsequent use in the preparation of anthrones [81], anthraquinones [81,83], contiguously tri- and tetrasubstituted alkoxybenzenes [82], and phthalideisoquinoline alkaloids [84]. Directed metalation on pyridine at its 3-position has been accomplished using the oxazoline moiety [85]. Thus, treatment of 106 with methyllithium has been found to afford 107 which was trapped with a variety of electrophiles.



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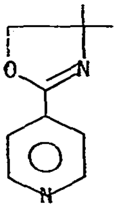

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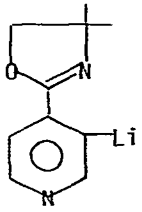
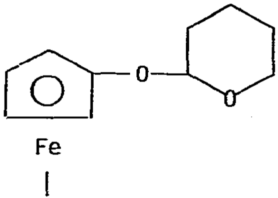
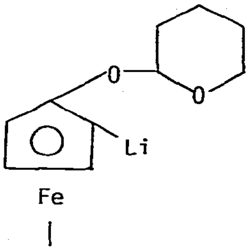


107

Finally, in this section, ferrocene derivative 108 has been metalated by n-butyllithium to give 109 which was then combined with carbon dioxide and other reagents [86].



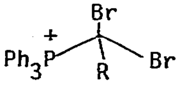
108



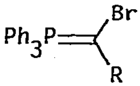
109

C. Lithium-Halogen Exchange

Phosphonium salts 110 have been converted by n-butyllithium to ylides 111 which have been condensed with aldehydes to afford α-bromoalkenes [87].

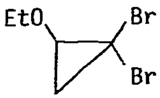


110



111

Cyclopropyl derivative 112 has been converted by n-butyllithium to 113 which has been trapped by a variety of electrophiles to ultimately give, after hydrolysis, 2-substituted propenals [88,89]. Of particular interest are 114 and 115 which are useful for the synthesis of homoterpenoid and terpenoid structures, respectively [89]. The groups R in the latter structures are derived from aldehyde co-reagents used in the condensations with 113.



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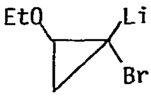

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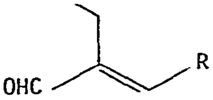

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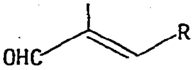
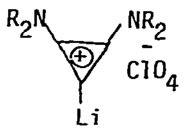


115

Cyclopropenium ion 116 has been prepared from 117 and n-butyllithium [90].

Treatment of 116 with chlorocyclopropenium ions afforded species such as 118.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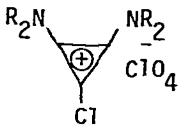
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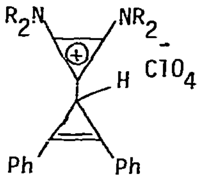
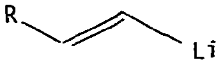

118

In a typically thorough paper, the vinyllithium reagents 119-124 have been prepared from the corresponding vinyl bromides and t-butyllithium [91]. Condensations of each of the reagents with a variety of electrophiles is disclosed.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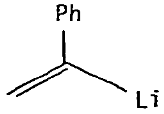
120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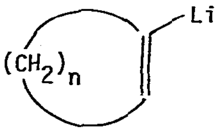
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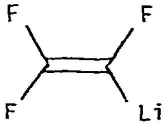
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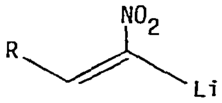
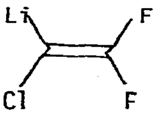

124

Other vinyllithium reagents prepared similarly were 125 from the vinyl chloride [92], 126 from the vinyl bromide (though the E-vinyl bromide gave only metalation) [93], dilithio reagents 127 from bromoacids [94], 128 and related compounds from bromoketals [95,96], 129 from the bromo bisketal [97], and 130 (three isomers) from the three isomeric bromocycloheptatrienes [98]. Reagents 127 and 128 have been employed in the synthesis of α,β-butenolides [94] and α,β-unsaturated ketones [95,96], respectively. Vinyllithium 129 is an umpolung of quinone [97]. Reagents 130 have been used to prepare transition metal complexes of cycloheptatrienylidene [98].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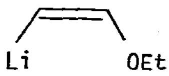
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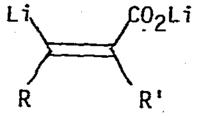
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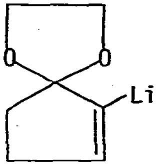

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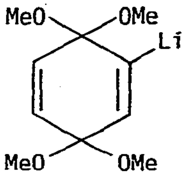

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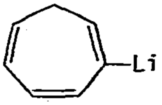
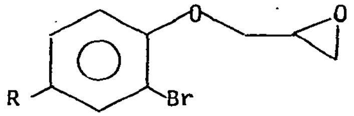


130

Finally, two papers dealing with lithium-halogen exchange of aryl halides deserve mention. Thus, treatment of epoxyhalides 131 with n-butyllithium at -100° affords 132 which undergo cyclization to 133 [99]. Two bromouracils have been converted to their lithio derivatives at low temperature, then combined with tri-n-butyl borate to give boryl derivatives [100]. The process is illustrated by the conversion of 134 to 135.



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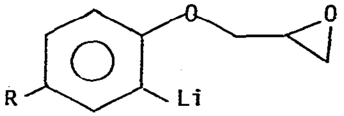

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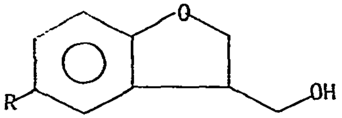

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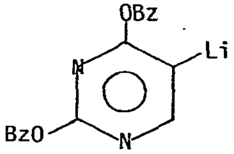

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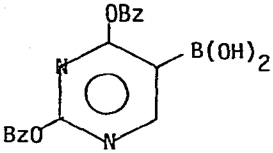
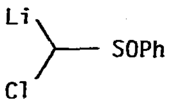


135

D. Miscellaneous Methods

Chloromethyl phenyl sulfoxide has been converted to lithio derivative 136 which has been alkylated, remetalated to give 137, then silated to afford thiol esters 138 via the silicon Pummerer rearrangement [101].



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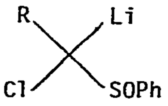

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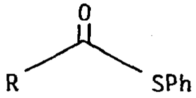
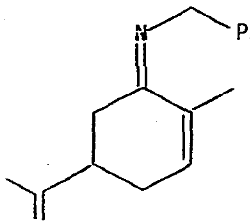


138

Two papers described the regiospecific generation of lithioenamines by addition of organolithium reagents to α,β-unsaturated imines [102,103]. The process is illustrated by the isomerization of imine 139 to 140 by catalytic amounts of potassium t-butoxide, addition of t-butyllithium to yield 141, and alkylation and hydrolysis to afford 142.



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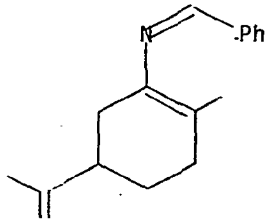

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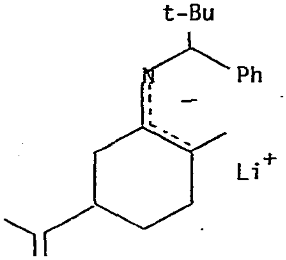

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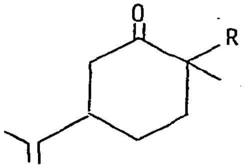
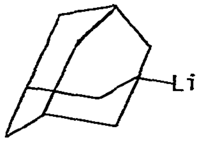


142

1-Adamantyllithium (143) has been prepared in a yield greater than 80% by treatment of 1-chloroadamantane with freshly cleaned 2% sodium-lithium alloy [104]. The technique has also been employed to synthesize 2-adamantyl-, 1-twistyl-, 1-diadamantyl-, and 1-triptycyllithium reagents [105]. In another paper, it was disclosed that while 143 does not react with hexamethylacetone at -20°, 1-bromoadamantane, the ketone, and lithium powder do afford the alcohol 144 at this temperature [106]. The authors conclude that this Barbier reaction does not occur by formation of an organometallic compound.



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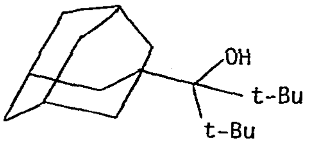
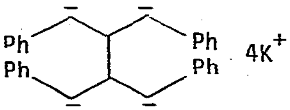


144

1,3-Diphenylallyllithium (145) has been reduced by potassium metal to tetraanion 146 which apparently arose from radical dianion 147 [107]. Species 147 was also converted to trianion 148. A similar trianion was obtained by reduction of 1,2,3-triphenylallyllithium using lithium, sodium, potassium, cesium, and alkali naphthalenide.

145



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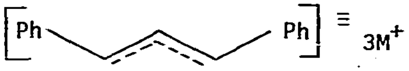
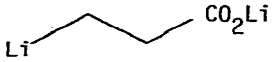


148

γ-Lactones may now be conveniently prepared by interaction of dilithio salt 149 and carbonyl compounds followed by cyclization with a trace of p-toluenesulfonic acid [108]. Reagent 149 is synthesized from lithium 3-bromopropanote (150) and lithium naphthalenide.



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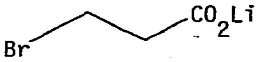
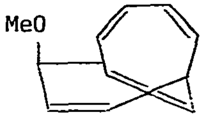


150

Other reductions reported have included the preparation of a C_{11} carbanion from 151 and lithium metal [109], the conversion of a large number of alkyl phenyl sulfides to alkyllithium reagents by lithium naphthalenide or lithium dispersion as illustrated by 152 and 153 [110], and the synthesis of cyclopropyl anions 154 from the corresponding 1,1-dithioketals and lithium naphthalenide [111]. It should be mentioned that sulfides such as 152 are prepared from terminal alkenes and thiophenol. Thus, the preparations of reagents such as 153 by this method are equivalent to hydrolithiation of α-olefins [110].



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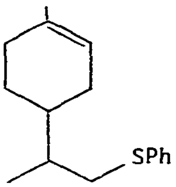

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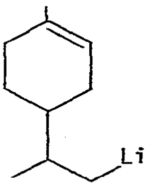

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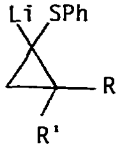


154

3. STRUCTURAL STUDIES

The structures of several organolithium reagents complexed with diamines were reported in 1978. Thus, reaction of methyllithium and tetramethylethylenediamine (TMEDA) was found to give $(MeLi)_4(TMEDA)_2$ linked through Li-TMEDA-Li bridges [112]. The Li-Li and Li-C bond distances were found to be 256-257 pm and 223-227 pm, respectively. The structure is shown in figure 1.

Similarly, phenyllithium and TMEDA were found to form a dimer in which two lithium atoms are linked by two phenyl groups [113]. Each lithium atom obtains fourfold coordination by bonding with respective ligands. The C-Li

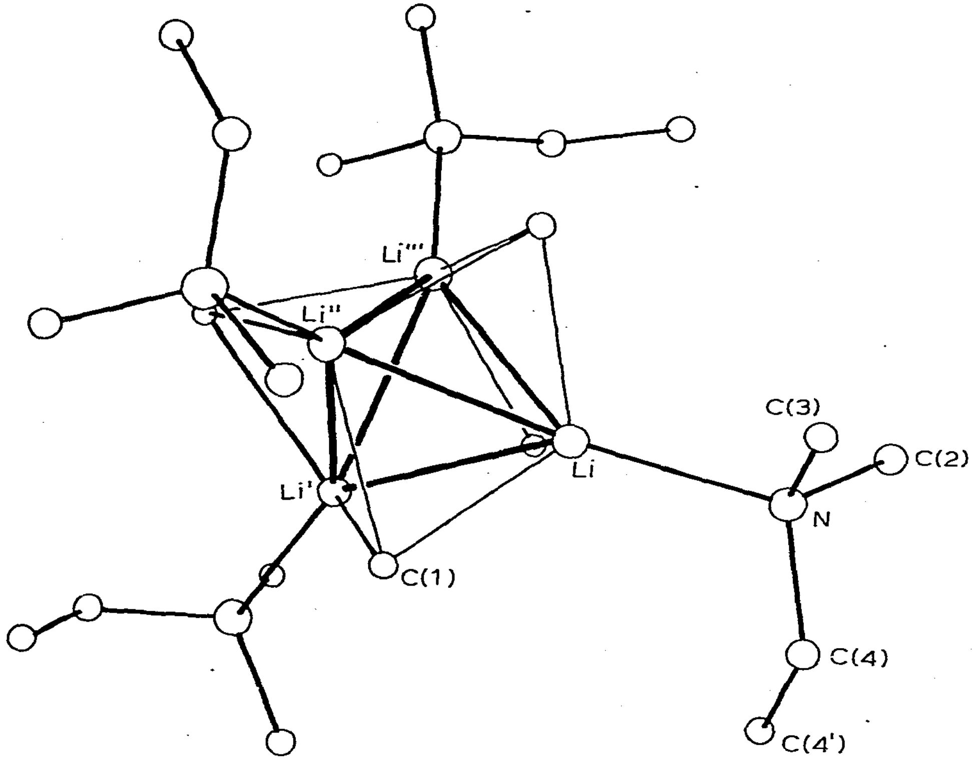


Figure 1

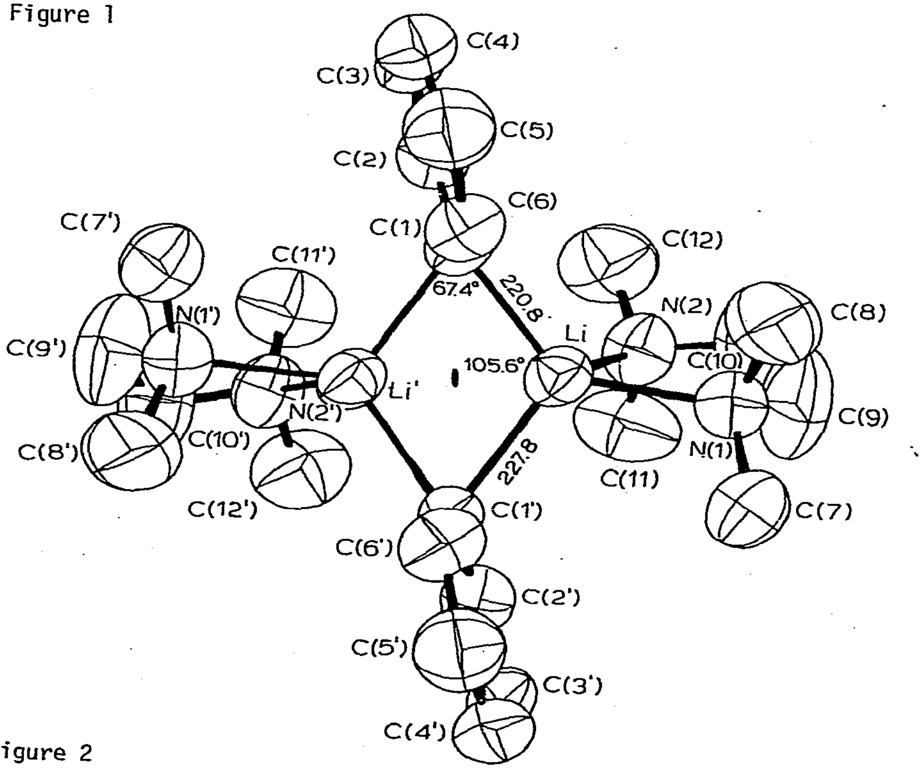


Figure 2

bond distances lie between 220.8-227.8 pm (Figure 2).

Next, the structure of crystalline, dimeric 1,1'-dilithioferrocene complexed with pentamethyldiethyltriamine is shown in Figure 3 [114]. While one of the lithium atoms is coordinated with all three of the triamine nitrogen atoms, the other one bridges between respective carbon atoms of a cyclopentadienyl ring of separate ferrocenes to form the dimer. Bond lengths, bond angles, and other data are reported.

Finally, a portion of the structure of the compound formed from phenyllithium, diphenylmagnesium, and TMEDA is shown in Figure 4 [115]. The compound is

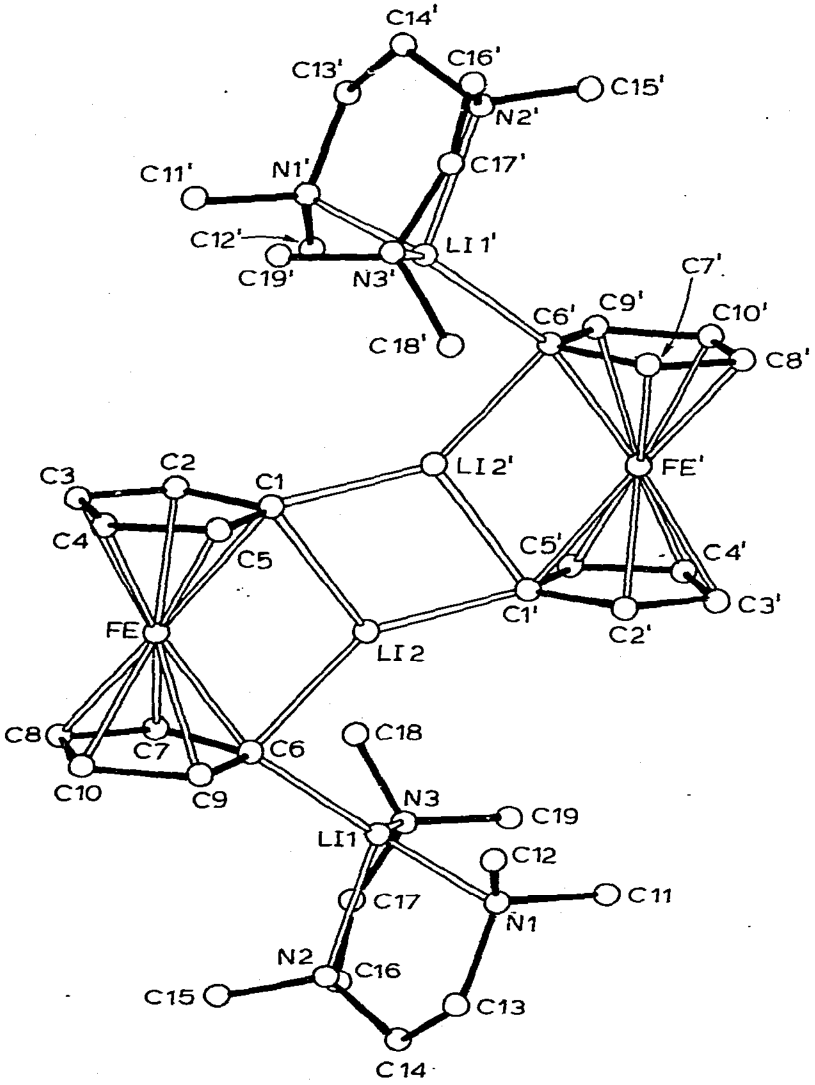


Figure 3

described as a dimeric doubly negative triphenylmagnesate species in which both Li·TMEDA moieties are linked to the magnesium species with each lithium atom between two terminal phenyl groups.

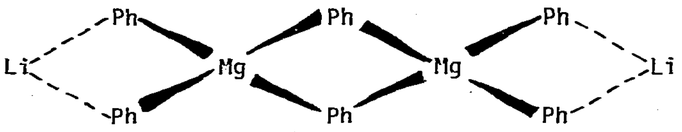


Figure 4

Other structures described in 1978 included lithiohexamethyldisilazane dimer (Figure 5) [116], dilithiocyanamide [117,118], and a lithium-platinum-hydrogen ternary hydride with the limiting phase composition of $LiPtH_{0.66}$ [119].

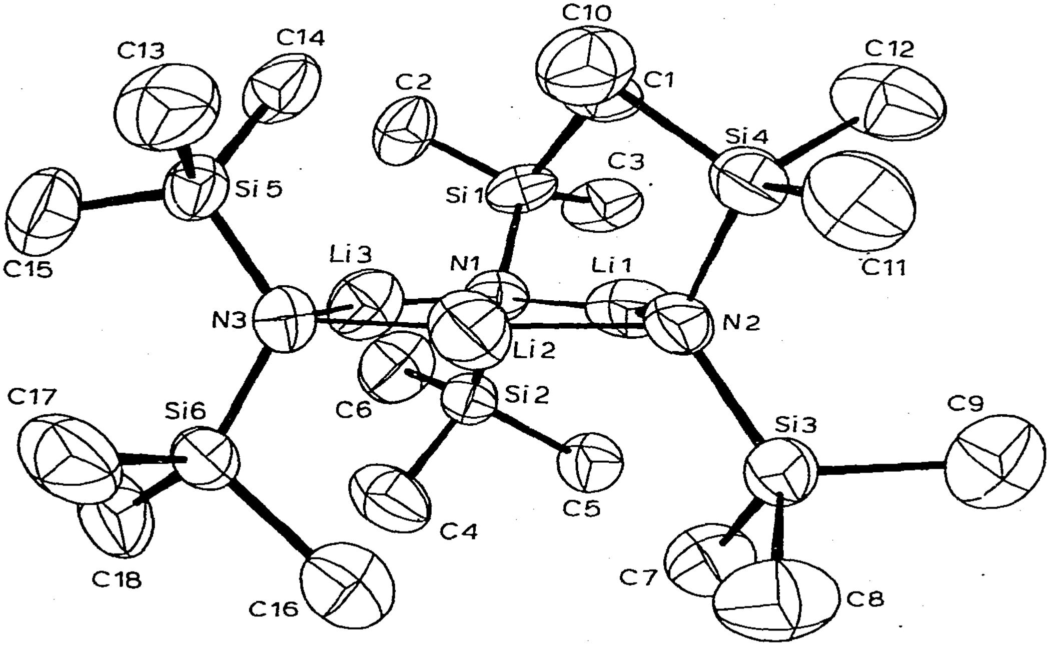


Figure 5

4. APPLICATION OF MOLECULAR ORBITAL THEORY

Using the 4-31G basis set, theoretical heats for proton transfer reactions between methoxide/water, methylacetylide/acetylene, and acetate/formic acid have been compared with the experimental heats to demonstrate that the methyl substituent increases the acidity of water but decreases the acidities of acetylene and formic acid [120]. The authors conclude that "stabilization of an anion is likely to occur when the acid function has high-lying occupied orbitals which can interact effectively with the methyl-group orbitals; destabilization is likely to occur when the acid function has low-lying orbitals of appropriate symmetry." Another paper discusses the stability of alkyl anions and concludes that 1) alkyl radicals have very small electron affinities and that, as a result, alkyl anions do not exist as stable compounds, and 2) that the negative charge in carbanions is not stabilized by methyl substituents [121].

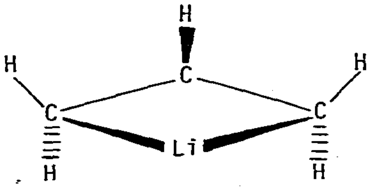
The effects of aggregation on the inversion barriers of primary alkyllithiums have been studied by ab initio MO theory using the Gaussian 70 series of programs [122]. As a result of the calculations, the inversions are said to involve RCH_2Li_2 fragments in which a planar RCH_2 moiety is stabilized by two lithium atoms.

Split valence basis RHF/4-31G single point calculations have indicated that the most stable geometry for dimeric dilithiomethane is that represented by 155 which consists of a "head to head" structure with the four lithium atoms bridging two perpendicular methylene moieties [123]. A variety of other "head to head" as well as "head to tail" structures were considered. In agreement with earlier predictions, a near degeneracy of the singlet and triplet electronic states of dilithiomethane has been calculated as follows (kcal): planar singlet, 8.3; planar triplet, 3.9; tetrahedral singlet, 0.0; tetrahedral triplet, 2.1 [124]. Interestingly, while the singlets show large dipole moments of polarity C^-Li^+, the moments of the triplets are smaller and show the opposite polarity (C^+Li^-).

155

Two papers have described additional studies on allyl anions using STO-3G and 4-31G basis sets [125,126] and 6-31G calculations [126]. Both studies conclude that the C_1-C_2 and C_2-C_3 bond lengths are equal (1.378-1390Å)[125] and 1.401Å [126]). The C_1-C_2-C_3 bond angles are listed as being 132.5° [125] and 123° [126]. Structure 156 was found to be most stable at all levels [126]. While one paper reports that "both pyramidal and planar structures are of essentially equal energy with no apparent inversion barrier" [125], the other suggests that the allyl portion of allyllithium "is significantly distorted from a planar arrangement in order to enhance bonding between the allyl anion HOMO (on C_1, C_3) and the lithium p-orbital with axis parallel to C_1-C_3" [126].

While ab initio results have shown that, in general, allylic anions are more stable than vinylic ones [125], another MO study has revealed that sub-



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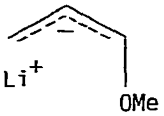
stitution of alkoxy moieties for vinyl hydrogen atoms can modify this trend [127]. For example, though the energy difference between allyl and propenyl anions was calculated to be 24.8 kcal/mole, the difference between 157 and 158 was found to be only 2.1 kcal/mole. Destabilization of both types of anions and enhancement of the acidity of vinyl carbon-hydrogen bonds by such oxygen constituents is discussed. Another paper discussed the formation of the $C_2H_3^-$ vinyl anion itself in terms of its formation from hydride ion and acetylene [128]. It was thus disclosed that the stability of $C_2H_3^-$ relative to H^- and C_2H_2 is 26 kcal/mole. The rearrangement barriers of the vinyl anion are high in energy, the lowest being 40 kcal/mole.



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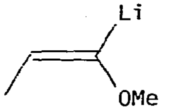

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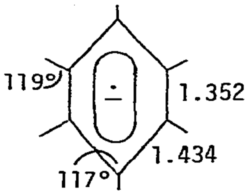
Ab initio calculations using the STO-3G and 4-31G basis sets have been performed on benzene radical anion [129]. The studies show that the best calculated structures are 159 and 160 (D_{2h} symmetry) whose interconversion requires little energy. That similar results are obtained with fluorobenzene radical anion suggests that 159 and 160 might serve as useful models for the radical anions of other subsituted benzenes.



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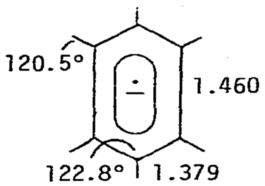

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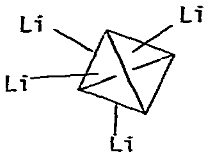
Other papers in this area which may be of interest discussed calculated energies for proton abstraction from substituted benzenes [130], heptotropic shifts across the face of cyclopentadienide [131], the structure of nitromethyl anion [132], complex formation between formaldehyde and lithium [133], formation and dissociation of Li_2H [134], the binding of thiols to alkali and alkaline earth metals [135], studies on LiCNO, LiNCO, and LiOCN [136], and solvation of lithium and sodium cations in ammonia [137].

5. SPECTROSCOPIC DETERMINATIONS

A. NMR Spectroscopy

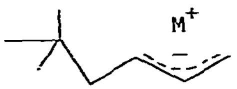
^{6}Li relaxation data and nuclear Overhauser enhancement factors have been determined for methyl-, butyl-, and phenyllithium [138]. The data are complemented by ^{7}Li and ^{13}C relaxation times. The ^{6}Li T1 values have been found to be in the order of tens of seconds and their relaxation are two-three orders of magnitude less efficient than ^{7}Li.

The ^{13}C-NMR peak of dilithioacetylene at $\delta = 75.0$ gradually disappears and is replaced by one at $\delta = 57.2$ upon irradiation in liquid ammonia at -45° [139]. The new peak is ascribed to C_4Li_4, which, on the basis of MO calculations, is suggested to possess face-centered tetrahedrane structure 161. The empirical formula C_4Li_4 is supported by field desorption mass spectrometry.



161

The ^{13}C-NMR spectra of metal derivatives 162 and 163 (M = Li, Na, K, Rb, Cs, Hg, and $SiMe_3$) have been recorded in THF and, in some cases (M = Li), in C_6D_6, ether, and dimethoxyethane [140]. The authors conclude that the alkali metal derivatives can best be described as being essentially delocalized ionic species while the mercury and silicon derivatives are more covalent. Only small temperature effects were observed down to -80°.



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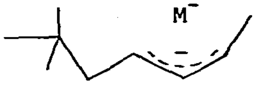
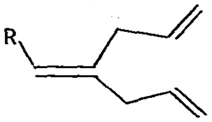


163

Both NMR and UV have been employed to study the propagation of isoprene initiated by oligo isoprenyllithium complexed by TMEDA [141]. In benzene, triplets at 458 and 484 Hz (from TMS) are shifted appreciably upfield upon the addition of catalytic amounts of TMEDA. The shifts correspond to changes to a 3,4-structure in the high polymer accompanied by trans-cis isomerization. In cyclohexane solvent, shifts in the UV spectra as a function of the concentration of TMEDA were ascribed to dissociation of polyisoprenyllithium aggregates.

Metalation of 164 (R = Ph, H) by n-butyllithium in THF at 25° gave ten-electron cross-conjugated dianions 165 whose ^{1}H-NMR spectra are described [142]. Based on calculated barriers to rotation, the authors conclude that 165 most likely exists in the WW conformation. Interestingly, the second metalations of 164 were found to be faster than the first ones.



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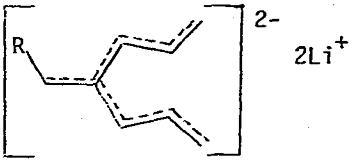

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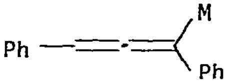
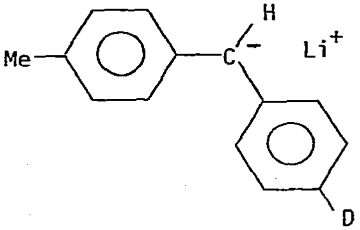
^{1}H- and ^{13}C-NMR spectroscopy accompanied by CNDO II MO calculations on allenyl anion 166 have led to the suggestion that the species is planar with the charge concentrated on the more substituted (CHPh) end of the molecule [143].



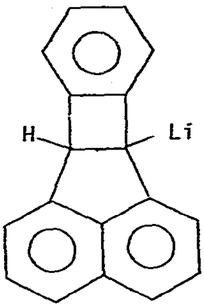
166

The ^{1}H and ^{13}C[^{1}H]-DNMR (270 MHz) spectra of lithiodiphenylmethane derivative 167 have revealed that the rings in this compound rotate at different rates [144]. The spectra are consistent with reduced π-bonding of the methylated ring to the benzylic carbon and a reduced barrier to rotation of this ring compared to the other one.

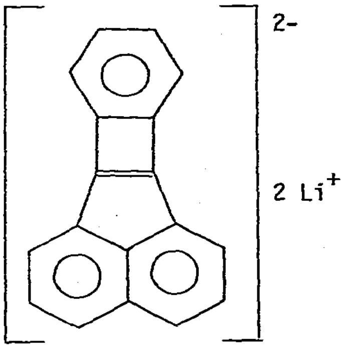


167

Mono- and dilithio salts 168a and 168b have been obtained by metalation of the parent hydrocarbon using n-butyllithium in 2-methyltetrahydrofuran and pentane·TMEDA, respectively [145]. The latter compound was obtained as a dark purple crystalline material of formula $2Li^+\cdot 168b\cdot 2TMEDA$. The ^{1}H-NMR spectrum of 168a suggests that exclusive delocalization of the charge occurs into the naphthalene moiety. That the ^{1}H-NMR spectrum of 168b shows significant differences from those of the dianions of acenaphthylene and fluoranthene is ascribed to the necessity of invoking canonical forms of 168b which contain cyclobutadiene rings.

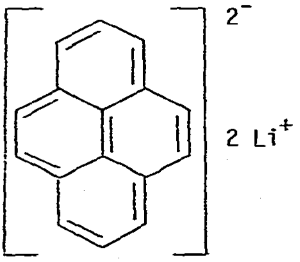


168a



168b

The ^{1}H-NMR spectra of 169-171, prepared by careful reduction of the parent hydrocarbons, as well as the ^{1}H-NMR spectra of the parent hydrocarbons and the ESR spectra of the corresponding radical anions have been studied to estimate the importance of perimeter structures in polycycles [146]. The authors conclude that "due to the nodal properties of the highest MO, a perimeter-type conjugation is to be preferred in the ions of polycyclic π-systems although this situation seems unlikely for electrostatic reasons and although Huckel's rule predicts an electronic destablization."



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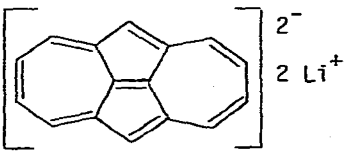

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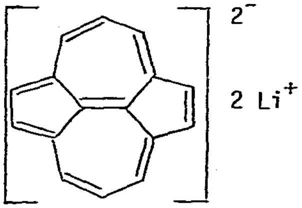
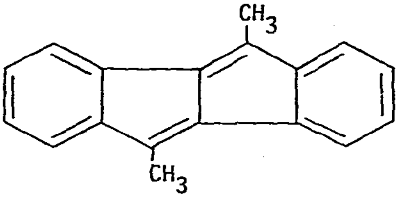


171

Pentalene derivatives 172 and 173 have been reduced by lithium and metalated by n-butyllithium, respectively, to afford 18π aromatic systems 174 [147]. Based on the chemical shifts of their ^{1}H-NMR spectra, 174 may be considered as perturbed peripheral [16]annulene dianions. Conversion of 172 to a 14π aromatic system by SbF_5/SO_2ClF is also reported. The above examples represent the first examples of a fused 4nπ polycyclic system containing a pentalene nucleus to show aromatic character as both a dianion and a dication.



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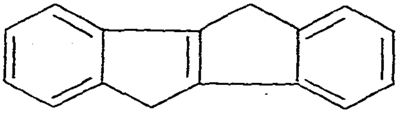

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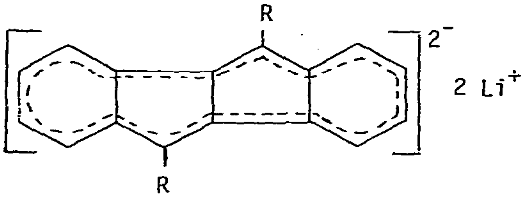
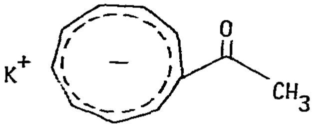


174

9-Acetyl-cis,cis,cis,cis-cyclonona-1,3,5,7-tetraene has been converted to aromatic [9]annulene anion 175 and olefinic nonafulvene 176 by potassium bis(trimethylsilyl)amide and lithium bis(trimethylsilyl)amide, respectively, as evidenced by their ^{1}H-NMR spectra [148].



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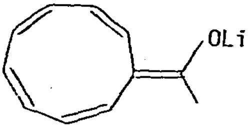
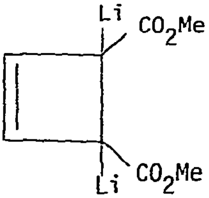


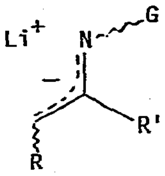
176

Turning to carbanions derived from molecules other than hydrocarbons, dilithio species 177 has been generated by metalation of the parent compound using LDIPA [149]. The ^{1}H-NMR and ^{13}C-NMR spectra as well as deuteration experiments to afford the 1,2-dideuterio derivatives have led the authors to conclude that the dianion "does not benefit from aromatic delocalization."



177

Other compounds whose ^{13}C-NMR spectra have been obtained included a variety of imines and hydrazones 178 (G = Me or tertiary nitrogen, R and R' = aliphatic) [150], and amine derivatives 179 and 180 [151].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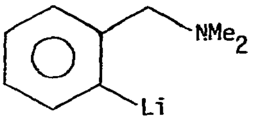
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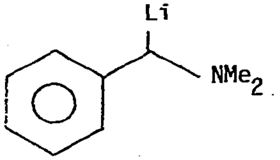
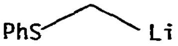

180

Several papers discussed the structure and subsequent stereochemistry in reactions of a variety of carbanions alpha to sulfur after studying their NMR spectra. Thus, in the series 181-184, ^{13}C-NMR revealed that the metalated carbon is nearly pyramidal in 181 and nearly planar in 182 regardless of whether the cation is lithium or potassium [152]. In contrast, the structures of 183 and 184 are intermediate in hybridization which is a function of both the cation and the solvent. Reagent 182 is shown to exist in THF at low temperature as aggregates which are disrupted by HMPA or external lithium salts. Carbanions 185 and 186 have similarly been found to be planar [153]. ^{13}C-NMR and condensations with a variety of electrophiles in the presence or absence of added lithium salts have led several authors to conclude that the stereochemistry of such reactions is a function of lithium chelation [154-156].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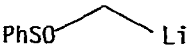
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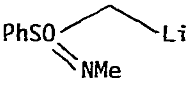
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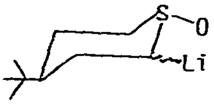
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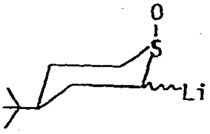
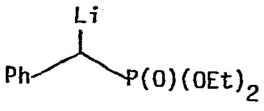

186

Other studies in this area have been concerned with the ^{1}H- and ^{13}C-NMR spectra of phenyllithium adducts of certain pyrimidines, pyridines, and pyrazine [157], the ^{1}H, ^{13}C, ^{31}P- and ^{7}Li-NMR spectra of 187 and 188 [158], the ^{31}P-NMR spectrum of 189 to provide direct observation of a tetracoordinated phosphorane species [159], the ^{1}H- and ^{7}Li-NMR spectra of 190 and 191 which lead to the conclusion that the lower limit to inversion at trivalent silicon and germanium can be set at about 24 kcal/mol [160], and the ^{1}H- and ^{13}C-NMR spectra of 192 (M = Ge, Sn, Pb) to demonstrate that such compounds possess a skew sandwich structure [161].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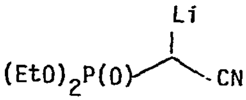
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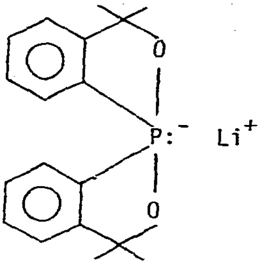
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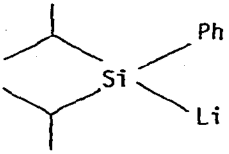
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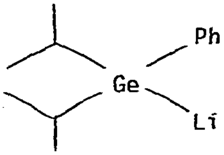

191

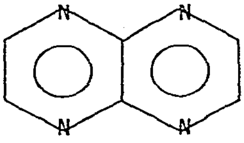
$M(C_5H_4CH_3)_2$

192

B. Other Spectroscopy

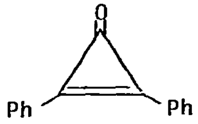
A unique doublet splitting of the EPR spectrum of lithium benzonitrile, prepared from the parent nitrile and n-butyllithium in the presence of HMPA, has been ascribed to a portion of the unpaired spin density being transferred from the radical anion to the HMPA [162]. Such splitting was not observed in the absence of HMPA.

The ESR spectra of the lithium, sodium, and potassium radical anions of 193 have been studied in more detail than in a previous investigation [163]. It is suggested that "the cation should be located on the molecular plane either along the axis coincident with the C_9-C_{10} bond or in the proximity of the nitrogen lone pairs."


193

A reinvestigation of the ESR spectra of di-t-butylketyl-alkali metal ion pairs, prepared by reduction of di-t-butyl ketone and all of the alkali metals, has led to the conclusion that the spectra previously ascribed to a biradical species is really due to ionic aggregates comprised of a ketyl radical, two alkali cations, and possibly a diamagnetic anion [164].

Several ketones and esters have been reduced by lithium in HMPA and the resulting products studied by ESR spectroscopy [165]. For example, 194 gives 195. o-Phenylene carbonate and bicyclo[4.2.1]nona-2,4,7-trien-9-one undergo similar decarbonylation while phthaloyl peroxide suffers decarboxylation to afford the radical anion of biphenylene. The preparation of several semidiones are also described [165,166].



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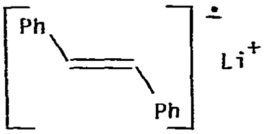
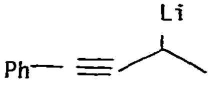


195

Using matrix isolation ESR techniques, it has been found that lithium atoms react with water and ammonia to form one to one molecular complexes whose stability is ascribed to the sharing of the oxygen and nitrogen unshared pairs of electrons with the metal [167]. The lithium-water reaction also gives a one to two complex of metal to Lewis base.

UV spectroscopy has been employed to determine the kinetics of the metalation of 1-phenyl-1-butyne by n-butyllithium to afford 196 and 197 [168]. Similar studies have been performed on 1-phenyl-1-propyne.



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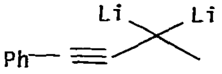
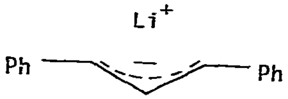


197

UV spectroscopy continued to be used to study ion pairing of carbanions. Those investigated included the excited states of fluorenyl (Fl) and fluoradenyl (Fd) salts [169], 9-propylfluorenyllithium and α,ω-bis(9-fluorenyllithium)polymethylenes [170], and several arylmethane carbanions [171,172]. In the case of the excited states of Fl and Fd salts, the proportion of separated ion pairs was found to be higher in the first excited state than in the ground state. Similar to the ground states, the amount of separated ion pairs in such first excited states increased from THP to THF to DME.

Illumination of a THF solution of 198 at low temperature with white light gave material whose absorption spectrum has been ascribed to the abnormal cis, trans conformer [173]. Upon standing in the dark, this conformer was reconverted to the more normal trans, trans one, a process found to be faster for tight than for loose ion pairs. Similar results were realized with 1,3-diphenylbutenyl carbanions.



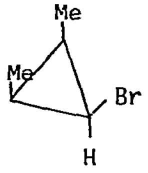
198

IR spectroscopy has been employed to determine that -ΔH for the interconversion of 3 $(i\text{-PrLi})_4 \rightleftharpoons 2(i\text{-PrLi})_6$ is 4.9±1.2 kcal/mol where the equilibrium constant at -47° is 3.4ℓ/mol [174]. IR data are listed for $i\text{-Pr}^7\text{Li}$, $i\text{-Pr}^6\text{Li}$, $s\text{-Bu}^7\text{Li}$, $s\text{-Bu}^6\text{Li}$, i-PrLi·THF, and $i\text{-PrLi}\cdot\text{NMe}_3$. Full papers also appeared describing IR studies on lithioacetonitrile [175] and lithium, sodium, and potassium derivatives of several aliphatic ketones [176].

Finally, it seems appropriate to list several papers which have described gas-phase studies. These included the determination that CH_3^- is pyramidal in this phase with an electron affinity of 1.8±0.7 kcal/mol [177], the gas-phase acidities of a number of sulfones, ketones, and other active hydrogen compounds [178], photodetachment of pentadienyl and heptatrienyl anions [179], gas-phase binding energies of lithium cation to Lewis bases [180], thermochemical properties of cluster ions involving lithium and sodium cations solvated by ammonia [181], and nucleophilic reactions of a variety of anions with PF_3 and OPF_3 [182].

6. STEREOCHEMICAL ASPECTS

In contrast to earlier results with sodium naphthalenide and optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane, the interaction of lithium naphthalenide with either 199 or 200 gave, after carboxylation and methylation, identical mixtures of 201 and 202 (R = CO_2Me) (9:92 ratio) [183]. Similar identical mixtures were obtained from cis- and trans-1-bromo-2-phenylcyclopropanes. The authors conclude that intermediate radicals 203 and 204 undergo inversion to reach thermodynamic equilibrium faster than electron transfer from lithium naphthalenide to afford configurationally stable carbanions 201 and 202 (R = Li).



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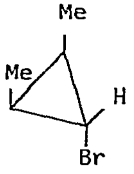

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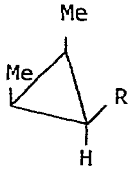

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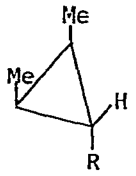

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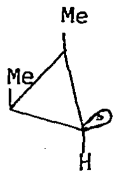

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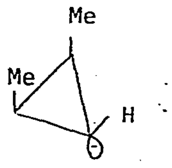
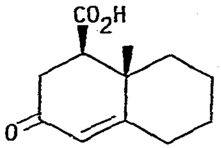


204

The stereochemistry of the reduction of octalone derivative 205 to afford either 206 or 207 has been restudied because of a question concerning structural assignments [184,185]. Thus, while treatment of 205 with lithium in anhydrous ammonia gives only 206, similar treatment of 205 in "wet" ammonia yields mostly 207. The latter result is ascribed to protonation of a carbanion from the β face by water held in the solvent shell of the β-oriented lithium carboxylate. Interestingly, the use of methanol or ethanol in this reaction affords only the normal trans product.



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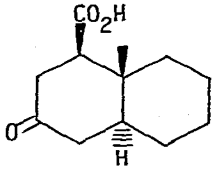

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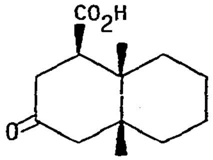
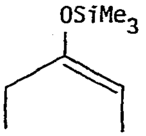


207

Both Z- and E-enolate anions may be conveniently prepared from a given active hydrogen compound [186]. For example, 3-pentanone has been converted to 208 and 209 by LiTMP/Me_3SiCl and ethyl trimethylsilylacetate/tetrabutylammonium fluoride, respectively. Other examples of the use of the latter reagent system are included.



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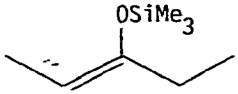
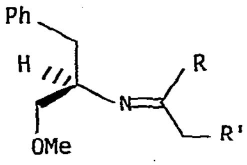


209

The assymetric alkylation of ketones has now been extended to acyclic ones by conversion of 210 (R and R' = aliphatic or phenyl) to 211 by LDIPA followed by addition of methyl or ethyl iodides [187]. Simple hydrolysis of 211 affords 212 (48-90%). That heating the lithioenamine to 66° prior to the alkylation results in large increases in the per cent of enantiomeric excess especially with smaller R and R' groups has been ascribed to equilibration of the kinetically formed mixture of 213 and 214 towards the more thermodynamically stable 213. Another paper describes the use of imine 215 in the similar preparation of α-alkylated cyclic ketones [188]. Thus, such ketones may now be prepared using t-butyl ester or methoxymethyl substituents on the imines to be metalated.

Lithiation and alkylation of the N-isopropylimines of several cycloalkanones (C_5-C_{12}) such as 216 have been followed by ^{13}C-NMR spectroscopy to determine the syn-anti stereoselectivity in such alkylations [189]. Each reaction was found to be totally stereoselective, yielding syn product only, though the ^{13}C-NMR spectra revealed that the products underwent subsequent isomerization to the more thermodynamically stable anti configurations. In fact, at



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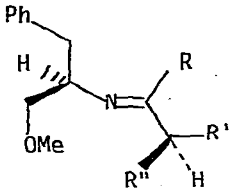

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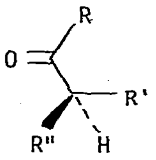

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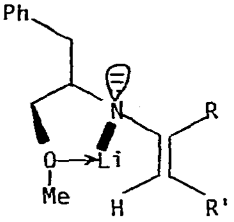

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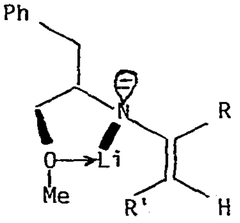

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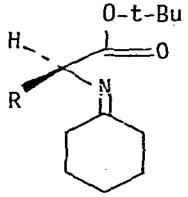

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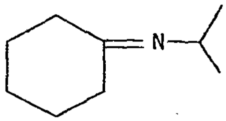
equilibration, the reaction mixtures had isomerized from $\geq$ 99% to 17-31% of the syn isomer. The reason for such high stabilities of syn-lithioimines is not readily apparent though the authors do discuss several possible causes. Another paper describes the regioselective conversion of several imines derived from aliphatic ketones and cyclohexylamines to hydroxyketones by lithium dialkylamides and oxygen [190].



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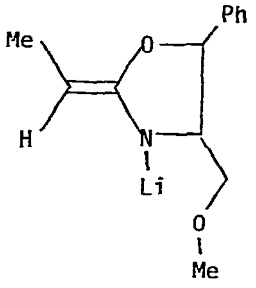
Two independent studies of the ^{13}C-NMR spectra of lithiooxazolines 217, 218, and others have led to the conclusion that such species do not equilibrate [191,192]. Since both lithium species disappear at the same rate upon alkylation, asymmetic syntheses using such carbanions proceed by stereoselective metalation of the parent oxazolines "followed by a stereoselective electrophilic attack on one diastereotopic face of these chiral nucleophiles by an alkyl halide."

The stereochemistry in the formation and reactions of lithiated oximes continued to be studied in 1978. Thus, using oxime 219, lithiation with n-butyllithium and alkylation with methyl iodide to afford 220 lent support to syn-lithiation and syn-alkylation of such compounds [193]. It should be noted that



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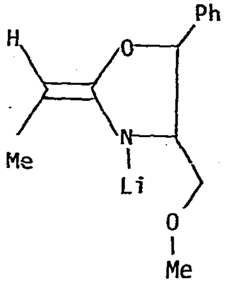

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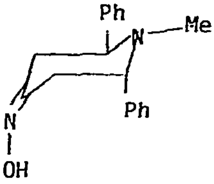
the alkylation is also conformationally specific giving rise only to axially substituted oxime. In another paper, several oximes were converted to their O-THP derivatives which, in turn, were lithiated, then quenched or combined with acetone [194]. For example, a 68:32 mixture of 221-222 was lithiated with LDIPA at -78°, then treated with methanol to give a 80:20 mixture of the starting materials. Repetition of the above reaction at -50° yielded only 221 (95%). The authors conclude that equilibration between 223 and 224 is rapid and favors 223. They also suggest that formation of 223 is both kinetically and thermodynamically favored. The above regiospecificity realized with dilithiooximes has been applied to the synthesis of isoxazoles [195].



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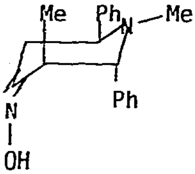

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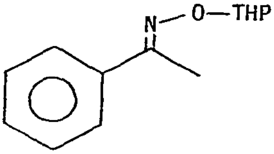

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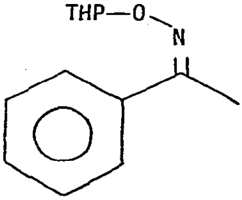

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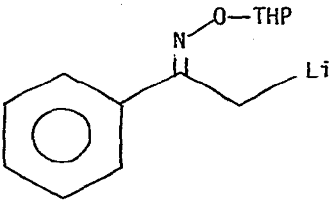

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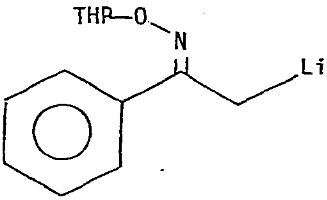

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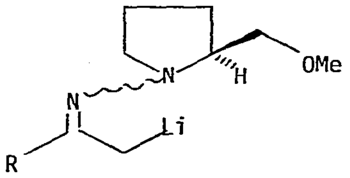
Two full papers described the synthetic usefulness of the lithiation and subsequent condensations with electrophiles of dimethylhydrazones [196,197]. Among the highlights described, alkylations occur regiospecifically at the least substituted α-carbon atom, cyclohexanone derivatives undergo selective axial alkylation, and the compounds may be used to conveniently synthesize α-alkylaldehydes and ketones, β- and γ-hydroxyketones, 1,4- and 1,5-dicarbonyl reagents, dihydro-α-pyrones, and others. Such hydrazones have also been used to effect regiospecific and enantioselective aldol reactions as illustrated by the conversion of 225 to 226 using R'COR"/Me$_3$SiCl followed by oxidative hydrolysis to give 227 [198], and to prepare 1,3-diketones using acid chlorides followed by hydrolysis with acidic methanol [199].



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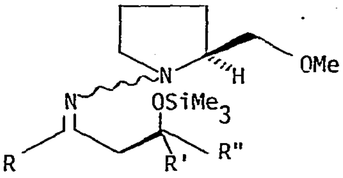

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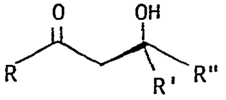

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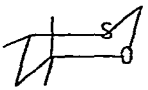
Two sequential asymmetic inductions have been reported on certain 1,3-oxathianes [200]. For example, metalation of 228 (44% enantiomeric excess-ee) with n-butyllithium followed by addition of benzaldehyde gave equitorially substituted diastereomeric alcohols which, after treatment with DMSO/trifluoroacetic anhydride, afforded ketone 229 (44% ee). Subsequent addition of methylmagnesium iodide yielded mostly 230 (>95%). Other examples are cited.



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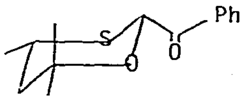

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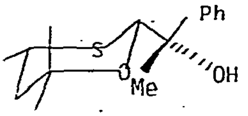

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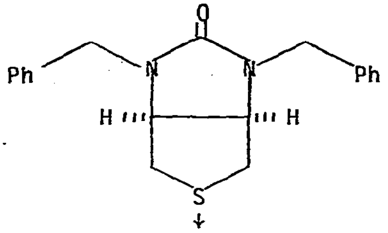
Other examples of stereoselective alkylation of sulfoxides have been applied to the synthesis of biotin [201]. Thus, treatment of 231 with methyllithium in THF/HMPA or diglyme/HMPA followed by the addition of t-butyl 5-iodopentanoate afforded 232 where the side-chain is trans to the S-O bond.

Three other papers in this area include a study of the stereochemistry of protonation of 9-t-butyl-10-lithio-9,10-dihydroanthracene [202], stereoselectivity in the addition of delocalized carbanions to cyclohexanones [203], and the effect of the size on alkyl groups R on asymmetric induction in additions to 233 [204].



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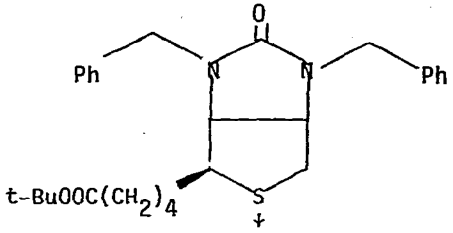

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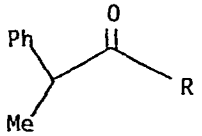

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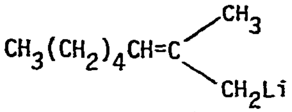
7. KINETICS

The kinetic acidities of certain cycloalkenes towards lithium cyclohexylamide-N-d have been determined in cyclohexylamine-N,N-d_2 [205]. Relative rates at 50° are listed as follows: cycloheptene, 1; cyclopentene, 0.063; cyclohexene, 0.193; cyclooctene, 0.206; benzene, 0.505; toluene, 119. The results of LCAO-MO calculations on theoretical models are interpreted in terms of the dihedral angle of C=C-H, the ease of rehybridization of the carbon to undergo ionization, and the allylic C-C-C angle.

Fresh solutions of n-butyllithium in ethyl ether and in THF were prepared in a flow system and the rate of decay of the UV absorption bands measured to determine the kinetics of the monomer-tetramer equilibrium [206]. The equilibrium constants for these dissociations are of the order 10^{-4} mol^3 ℓ^{-3} in THF and 10^{-16}mol^3 ℓ^{-3} in ether. Dissociation into monomer is substantial below 10^{-2} M in THF but is insignificant at 10^{-4} M in ether.

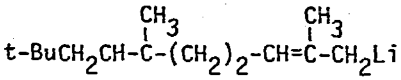
The previously described study of the dimerization of the sodium salt of diphenylethylene radical anion has now been expanded to the corresponding lithium, potassium, and cesium salts [207]. The dimerization constant of the radical anion is largest for the cesium ion pairs and lowest for the lithium system, although the aggregates are all tight, i.e., not solvent separated, regardless of the cation.

Polyisoprene, prepared by s-butyllithium initiation in cyclohexane, was found to possess larger amounts of trans-1,4 linkages as the initiator concentration was increased and as the monomer concentration was decreased [208]. To verify the hypothesis that the amount of trans content increases as a result of isomerization of cis-active centers, the rates of isomerization of model compounds 234 and 235 have been determined.



$CH_3(CH_2)_4CH{=}C(CH_3)CH_2Li$

234

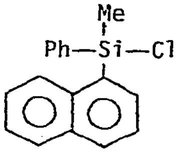


$t\text{-}BuCH_2CH\text{-}\overset{CH_3}{C}\text{-}(CH_2)_2\text{-}CH{=}\overset{CH_3}{C}\text{-}CH_2Li$

235

Other kinetic studies of polymer systems included the effect of mixed dimerization of monomeric polymers in styrene terminated by 1,1-diphenylethylene units [209] and in the styrene-butadiene and styrene-p-methylstyrene systems [210], a study of the initiation reaction of the polymerization of p-t-butylstyrene by butyllithium [211], and the kinetics of the polymerization of methacrylonitrile initiated by n-butyllithium [212] and by 1,1-diphenyl-n-hexyllithium and s-butyllithium [213].

Both kinetics and stereochemistry have been studied in the reactions of 236, 237, and other silanes with alkyllithiums to further study the mechanisms of nucleophilic displacement on silicon [214]. That the rates of such substitutions on 236 with n-butyllithium are increased in the presence of lithium complexating agents indicates that electrophilic assistance has been removed and that the mechanism is controlled by the electronic character of the nucleophile. That such complexating agents promote retention of configuration supports the above contention that such reactions do not proceed via the SN_i-S_i process. Another paper described the stereochemical results obtained in the substitutions of certain bromo- and thiophenylsilanes with several nucleophiles [215]. As a result, the following trend has been provided for inversion to retention of leaving groups attached to silicon in such reactions: Br≈Cl>>SR≈F>>OMe>H.



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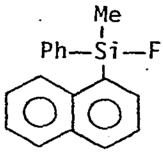

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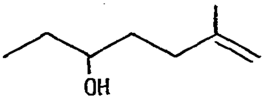
Finally, another paper in a series appeared which discussed the kinetics of the reactions of n-butyllithium with a variety of unsymmetrical alkyl t-butyl peroxides [216].

8. REARRANGEMENTS

Several papers described [2,3]-sigmatropic rearrangements of organometallics. Thus, such reactions on allyl stannyl ethers have been found to afford Z-trisubstituted olefin apparently via a transition state which prefers pseudoaxial substitution

[217]. The sequence is illustrated by the conversion of 238 to 239 by potassium hydride/iodomethyltrimethyltin; 239 is then converted to 240 by n-butyllithium.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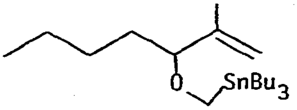
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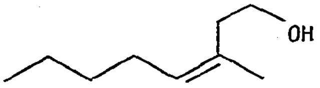
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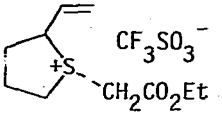
Three full papers discussed ring expansions by such rearrangements. For example, salt 241 is converted to 242 by a variety of bases including LDIPA, potassium carbonate, 1,5-diazabicyclo[5.4.0]undec-5-ene, and potassium t-butoxide in acetonitrile [218]. The last base gives the highest yields. Other examples included the conversion of 243 to 244 by LDIPA [219], and the use of unstabilized sulfonium ylides in these ring expansions [220]. The preparation of certain N-containing heterocycles are also listed [218,219].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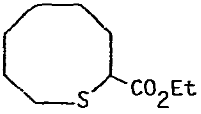
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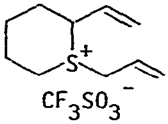
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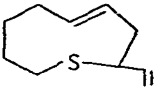
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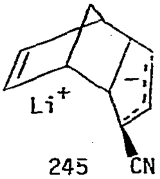
Going in the opposite direction, anions 245 and 246, prepared from the parent compounds and LiTMP, have been found to undergo (4+2)-cycloreversions to lithium cyanocyclopentadienide and cyclopentadiene [221]. Other examples are listed including ones which revert to benzene and the same cyclopentadienide anion.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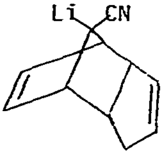
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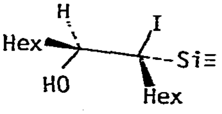
Alcohol 247 and its diastereoisomer have been converted to silylketone 248 (90%) via a hydrogen migration by means of n-butyllithium [222]. In contrast, while 247 similarly afforded 248 (92%) using methylmagnesium iodide/magnesium iodide, the diastereoisomer of 247 gave a mixture of 248 (29%) and enolate 249 (43%) with these reagents.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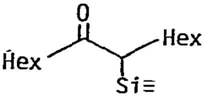
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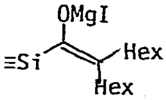
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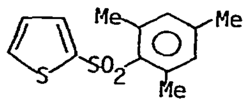
Some mesityl α-thienyl sulfones have been found to undergo the Truce-Smiles rearrangement with strong bases to afford sulfinic acids which have a beta orientation on the thiophene rings [223]. The process, illustrated by the conversion of 250 to 251, apparently proceeds via elimination of sulfinate from 252.



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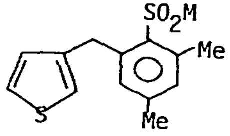

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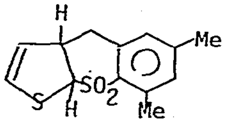
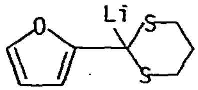


252

While lithiodithiane 253, prepared in THF at -78° from the parent compound and n-butyllithium, was sufficiently stable at this temperature to combine with typical electrophiles, at -20°, 253 underwent rearrangement to 254 [224]. The latter compound was combined with crotonaldehyde to give 255.



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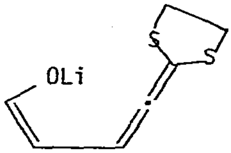

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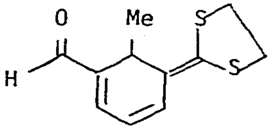
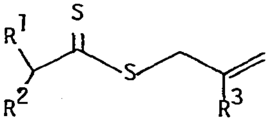


255

Treatment of alkanedithioates 256 (R^1,R^2,R^3 = H or Me) with lithium amide at -60° gave anions 257 which rearranged to 258 at 50° [225]. Subsequent hydrolysis afforded γ,δ-unsaturated dithioacids.



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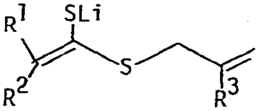

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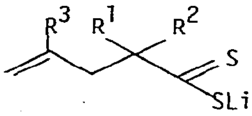

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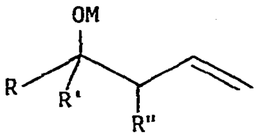
A full paper appeared in 1978 which described the rearrangement of the dilithio salts of alkyl aryl ketazines to pyrroles, tetrahydropyridazines, or pyrazoles as a function of temperature, solvent, and the ketazine [226].

A large number of papers appeared in 1978 which discussed reversible additions of organometallics to carbonyl-containing compounds. Since many of these reactions involve two intermediates which are isomeric to one another, it seems appropriate to consider these papers at this point. Thus, the rate of reversal of a large number of hindered alkoxides 259 (R and R' = Et, i-Pr, t-Bu, Ph, c-C_6H_{11}, R" = Me, i-Pr, Ph, M = Li, MgBr) was studied as a function of the steric bulk of the organometallic [227]. Such reactions were shown to afford rearranged alkoxides 260 and, when α-hydrogens were present, the enolates of 261. The data indicate that lithium alkoxides reverse about ten times more rapidly than the magnesium salts and that the rates decrease in the order t-Bu > i-Pr ≈ c-C_6H_{11} > Ph > Et.



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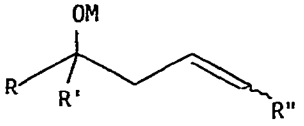

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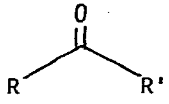
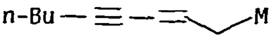


261

A similar study has been performed on γ-acetylenic-α-allyl systems 262 (M = Li ZnBr, and MgCl) [228]. With all three organometallics, less of alcohols 263 and more of alcohols 264 were obtained as the steric bulk of the alkyl groups of the co-reagent ketone, RCOR', increased. Halozinc alkoxides derived from 263 isomerized to those corresponding to 264, especially with bulky R and R' groups. The authors indicate that reversions in these systems are slower than those realized with α,γ-diethylenic organometallics.



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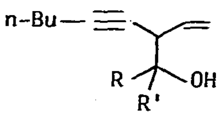

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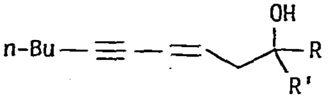
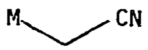


264

The influence of cations in nucleophilic additions of anions to carbonyl compounds has been discussed in terms of carbonyl complexation versus ionic association with the nucleophile [229]. Among the many conclusions reached in this paper, the authors indicate that complexation control favors 1,2-attack of α,β-unsaturated carbonyl compounds. In contrast, association control or the use of complexation agents such as HMPA which themselves bind strongly with the cation favors 1,4-attack on such electrophiles. Numerous examples are provided. STO-3G calculations were performed on acrolein and on acrolein complexed at oxygen with lithium and sodium cations. Not only are the energy levels of the LUMO lower in the complexes, but the atomic coefficients in the LUMO of C_1 and C_3 are inverted. These results suggest that regioselective attacks by nucleophiles at the carbonyl carbon atoms occur as much under charge control as under frontier orbital control.

While nitrile 265 combines irreversibly with certain α,β-unsaturated ketones to afford 1,2-adducts 266 ($R''' = H$), nitrile 267 reversibly affords 266 under kinetic control, ultimately leading to cyanoketones 268 ($R''' = Ph$) by 1,4-addition [230].



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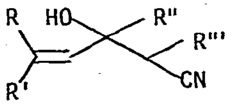

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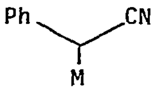

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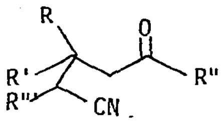
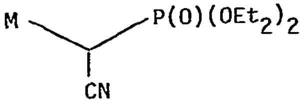


268

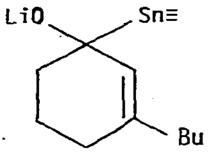
Other papers in this area described the following on α,β-unsaturated ketones and related compounds:

- Influence of lithium cation on the reactions of 269 with α,β-unsaturated ketones under kinetic control [231].



269

- Kinetically controlled 1,2- and thermodynamically controlled 1,4-additions of trimethylstannyllithium (but not trimethylsilyllithium) to 3-butyl-2-cyclohexenone to afford 270 and 271, respectively [232].



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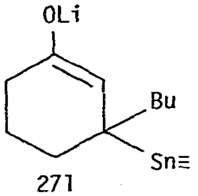
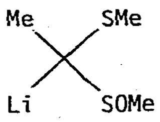


271

- 1,2- and 1,4-additions of t-butyllithium to 2-cyclohexenone in ether or THF/-20% HMPA, respectively [232].

- Kinetically controlled 1,4- and thermodynamically controlled 1,2-additions of carbanions such as 272 to give 273 and 274, respectively [233].



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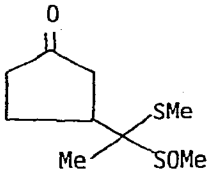

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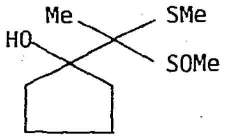

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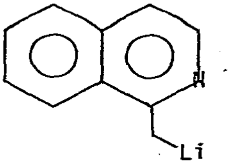
- Kinetically controlled 1,2- and thermodynamically controlled 1,4-additions of lithiomethylnitrogenous heterocycles such as 275 and 276 to yield alcohols and ketones, respectively [234].



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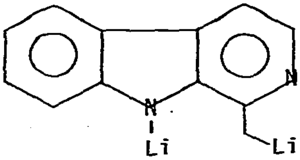
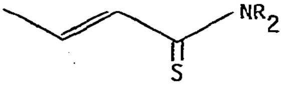


276

- Selective 1,4-additions of a variety of organolithium and magnesium derivatives to α,β-unsaturated thioamides such as 277 [235].



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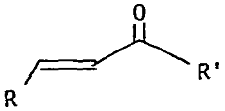
- Continuous transition from 1,2- to 1,4-additions in the reactions of dilithiocarboxylic acids with α,β-unsaturated ketones 278 as a function of R and R' all under kinetic control [236].



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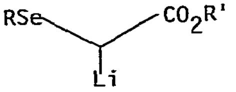
- Kinetically controlled 1,2- and thermodynamically controlled 1,4-additions of selenoesters 279 to 2-cyclohexenone [237].



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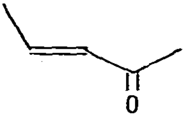
- Retardation or inhibition of the 1,4-addition of certain lithium organocuprates to 280, 281, and 282 in THF, DME, and DMF [238].



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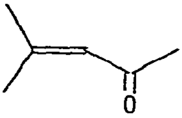

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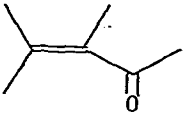
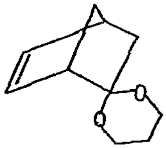


282

Other papers deserving mention discussed the addition of alkyllithium reagents derived from alkenyldioxanes such as 283 to afford 284 [239], high regioselectivity in Michael additions of preformed enolates to ethyl acrylate and methyl β-chloroacrylate [240], and the isomerization of dilithio salts of cis-1,2-diols such as 285 to mixtures of the cis-trans diols by heat [241]. The latter reactions were shown to occur by oxidation-reduction rather than by reverse pinacol coupling.



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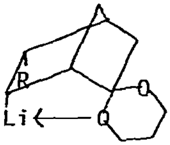

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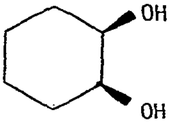
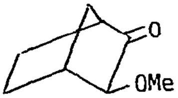


285

9. OTHER PHYSICAL-ORGANIC CHEMISTRY

Two papers described reductions of ketones by LDIPA. Thus, a large number of α-halo and α-methoxyketones with enolizable hydrogen atoms have been converted to lithium alkoxides by this base, then trapped with chlorotrimethylsilane or acetic anhydride [242]. The reduction is illustrated by the conversion of 286 to 287. The oxidation product, 288, was isolated. Similar treatment of benzophenone with LDIPA to afford benzhydrol and tetraphenylethylene oxide has been ascribed to an electron-transfer process [243]. The latter compound has been observed previously in the reactions of certain organolithium reagents, benzophenone, and HMPA. Another paper described the use of (S)-(+)-1-lithio-2-methylpiperidine in such reductions to yield (R)-alcohols [244].



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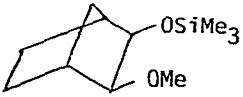

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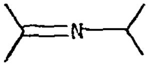
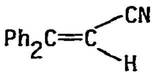


288

The nature of the anionic intermediates in alkali metal reductions of aromatic hydrocarbons has been discussed further [245]. Thus, anthracene and naphthalene with lithium or sodium in ammonia give dianions which are quickly protonated by the solvent to yield monoanions. In the case of anthracene, at least, the quenching procedure (direct vs. inverse neutralization or alkylation) is said to be the most significant factor in the reaction.

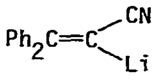
That methanolysis of phenyl acetate shows a rate increase in the presence of certain sodium salts but a rate decrease in the presence of lithium cations has been ascribed to association control, that is, association of the cation with the nucleophile [246]. The relative importance of this effect in contrast to complexation of the cation with the carbonyl oxygen is discussed. The latter complexation predominates with aliphatic esters.

Acrylonitrile 289 has been found to react with n-butyllithium to afford anion 290 as well as addition-elimination products 291 and 292 which arise from loss of cyanide and hydride ions, respectively [247]. Anion 290 has been combined with a variety of electrophiles [248].



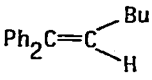
$Ph_2C{=}C(CN)H$

289



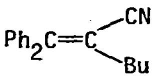
$Ph_2C{=}C(CN)Li$

290



$Ph_2C{=}C(Bu)H$

291



$Ph_2C{=}C(CN)Bu$

292

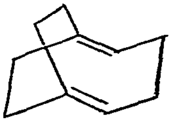
Three papers discussed the influence of HMPA on certain reactions of epoxides effected by lithium amides [249-251]. Thus, the use of this solvent has been found to suppress α-elimination in simple epoxides [249,251] and to promote γ-elimination on γ,δ-unsaturated epoxides [250].

Other papers in this section provide evidence that polarization of carbon-sulfur σ-bonds is important in accounting for the regiochemistry of carbon-hydrogen acidification by sulfur [252], discuss the reactivity and ion pairing of alkali β-ketoenolates using a variety of techniques [253], show the effect of alkyl substituents on the stereochemistry between enolates and aldehydes and ketones [254], and list various thermodynamic data for the effect of counterions and solvents on the disproportionation of radical anions of perylene and tetracene [255] and for the equilibrium anionic polymerization of 4,7-dioxaoctanal and n-octanal [256].

10. ADDITION AND SUBSTITUTION REACTIONS

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

Bridgehead diene 293 has been prepared by reaction of t-butyllithium with diiodo derivative 294 [257]. The reaction appears to proceed via a displacement on one of the iodines by the organolithium reagent.



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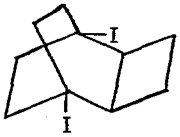
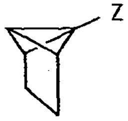


294

Hydrocarbon 295 (Z = H) has been metalated by n-butyllithium, then converted to 295 (Z = Cl) by p-toluenesulfonyl chloride [258]. Subsequent butylation and phenylation by butyllithium and phenyllithium, repectively, to afford 295 (Z = Bu, Ph) are said to proceed via the intermediacy of alkene 296. A similar alkene, 297, has been trapped by anthracene [259] and combined with a variety of lithium mercaptans and amides [260].



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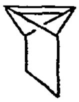

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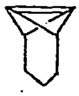
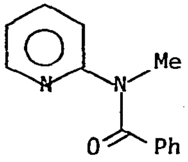


297

Although more widely studied with Grignard than with organolithium reagents, sequential two-fold addition of butyllithium to 298 has been found to give alcohol 299 (98%) [261]. Reaction of 298 or the corresponding propionamide with Grignard reagents yields ketones (75-98%). In another paper, a variety of organolithium reagents (RLi) have been reported to add to N-vinyllactam 300 to afford cyclic imines 301 (19-79%) [262]. Imines such as 302 have themselves been shown to give secondary amines with RLi by addition of the latter reagents to both metalated and non-metalated azomethines [263].



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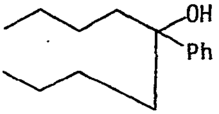

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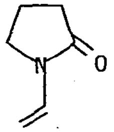

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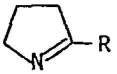

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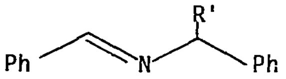
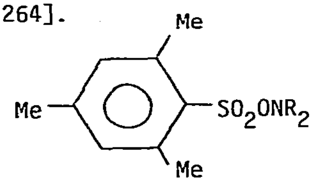


302

N,N-Dimethyl- and N,N-diethylamines have been synthesized from a large number (twelve) of organolithium reagents and hydroxylamine derivatives 303 and 304 [264].



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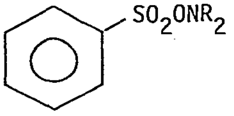
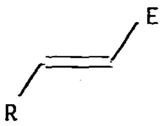


304

E-Disubstituted alkenes 305 may be prepared (50-81%) by addition of RLi to phenyl vinyl selenide, trapping with an electrophile, and oxidative elimination [265]. Reagents 306 and 307 are intermediates in the process. The electrophiles included aldehydes, ketones, alkyl halides, N_2O, nitriles, and others.



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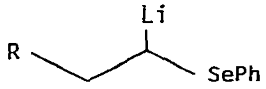

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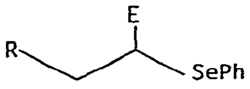
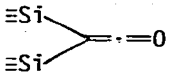


307

Trimethylsilylketene has been metalated by several alkyllithiums and LDIPA to yield 308 as evidenced by trapping with trimethylsilyl chloride to afford 309 (15-30%) [266]. Efforts to trap 308 with other electrophiles have, to date, been unsuccessful.

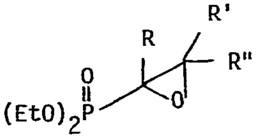
$\equiv$Si—$\equiv$—OLi

308



309

Interaction of n-butyllithium with epoxyphosphonates 310 has been found to give allyl alcohols 311 (mostly E) presumably via addition of the RLi to the phosphorus followed by a butyl migration, then an elimination [267].



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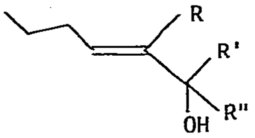
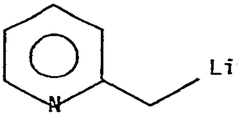


311

Saturated organolithium reagents have also been employed to synthesize gem-dinitroalkanes by addition to α,β-unsaturated nitro compounds followed by trapping with tetranitromethane [268], to prepare dilithio anionic polymer initiators based on double 1,1-diphenylethylene compounds [269], to study the anionic polymerization of perdeuterated methyl methacrylate effected by n-butyllithium [270], and to study the stereochemistry in the addition of methyllithium to methyl substituted cyclopentanones [271].

α-(2-Pyridyl) ketones may now be conveniently prepared in substantially higher yields than previously reported by acylating picolyl- and lutidyllithiums with N,N-dimethylcarboxamides [272]. The process is illustrated by the conversion of 312 to 313 using N,N-dimethylacetamide (79%).



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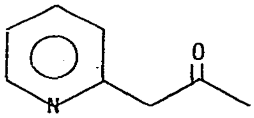
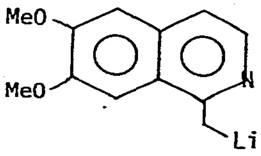


313

A new carbanion, 314, prepared by metalation of the parent heterocycle by n-butyllithium, has been combined with a variety of electrophiles to afford expected products [273]. Additional examples of condensations of the related dihydro derivative 315 have been reported [274]. In an unrelated paper, silyl derivative 316 has been metalated by n-butyllithium, then combined with certain electrophiles [275]. While the use of D_2O gave only 9-trimethylsilyl-9-deuterio-9,10-dihydronaphthalene, alkylation revealed that the 10-lithio derivative is formed first followed by a 1,4-hydrogen rearrangement to yield the 9-lithio species.

Turning to aryllithium reagents, a new synthesis of 3,4-dihydroisoquinones has been realized using the selective metal-halogen exchange of o-bromo-2-



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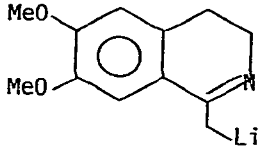

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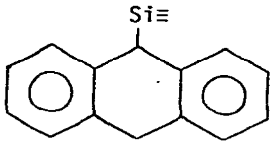

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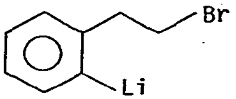
phenylethyl bromide by t-butyllithium to afford 317 [276]. Condensation of the latter with nitriles gave 318 which underwent cyclization to the heterocycles. In another paper, it was disclosed that dibromide 319 is converted to 320 by phenyllithium [277].



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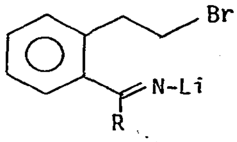

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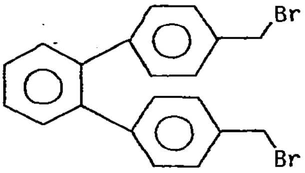

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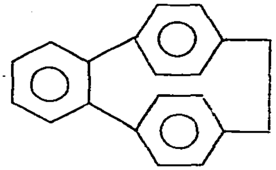

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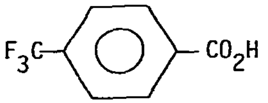
A careful, systematic study on the carbonation of o-, m-, and p-trifluoromethylphenyllithiums has been reported [278]. Not surprisingly, the products obtained included carboxylic acids, ketones, and alcohols. For example, the pouring of the p-lithio derivative over crushed CO_2 gave 321 (64%) while the bubbling of gaseous CO_2 into the carbanion yielded 322 (89%).



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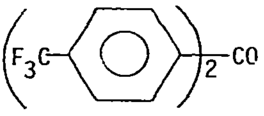
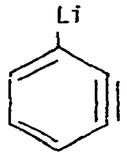


322

As predicted, the regiochemistry in additions of a variety of organolithium reagents to purported 3-lithioarynes such as 323 leads only to adducts such as 324 as evidenced by carbonation to afford m-phthalic acid derivatives [279]. The formation of 323 from 2,6-dibromoarylsulfones had been reported previously.

Several papers discussed additional aspects of the organolithium chemistry of oxazolines. A full paper discussed the scope and limitations of the nucleophilic displacement of methoxy groups ortho to oxazolines by a large number of



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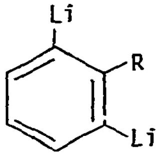
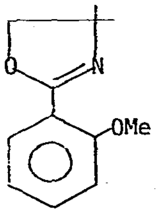


324

organolithium and magnesium derivatives [280]. The process is illustrated by the conversion of 325 to 326 (22%) by n-butyllithium in THF at -45°; hydrolysis of the heterocyclic side-chain conveniently gives acids such as 327. Most yields were higher than that cited in the above example. The initial nucleophilic substitutions work well except for delocalized carbanions. Another paper described the related displacement of fluorine from 328 [281]. For example, treatment of 328 with n-butyllithium at -45° yields 326 (92%). It would appear that use of 328 in such condensations will thus be more synthetically useful than 325.



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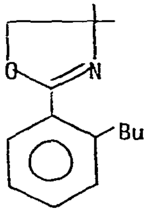

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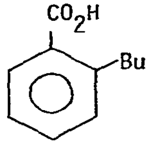

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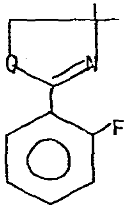
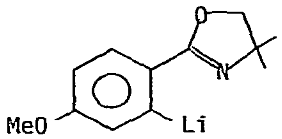


328

The previously described o-lithio derivative 329, prepared by metalation of the parent oxazoline, has been employed in the synthesis of certain methoxy-7,12-dimethylbenz[a]anthracenes [282]. Although similar o-metalation of pyridine derivative 106 (page 12) has been effected by methyllithium in THF at -78°, other alkyllithiums and LDIPA add to the pyridine ring of this compound to afford, at this time, unspecified products [85]. In contrast, interaction of alkyllithiums and phenyllithium in ether with the 3-substituted pyridine derivative 330 gives addition products 331 [283]. Subsequent hydrolysis of 331 yields 1,4-dihydropyridine derivatives.



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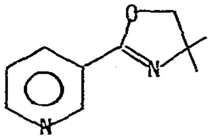

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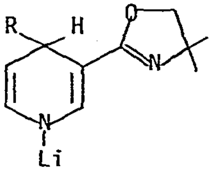

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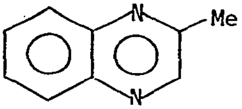
Phenyllithium, butyllithium, and others have been similarly added to pyridine itself to afford 2,5-dihydro derivatives [284], to 5,6-disubstituted pyrimidines to give, after oxidation, 4,5,6-trisubstituted pyrimidines [285], to quinoxaline 332 to yield 2,3- and 2,2,3-substituted reduced heterocycles [286], and to heterocycle 333 to afford 334 [287]. Both 332 and 333 also underwent some metalation at the methyl group and at the 4-position, respectively.



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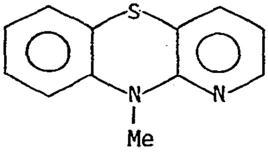

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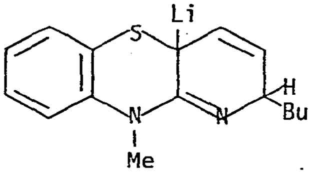
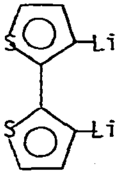


334

Several additional heterocyclotetraaromatics have been prepared using lithio derivatives of the heterocycles [288]. For example, dilithiobithiophene 335 has been converted to 336 by $FeCl_3$ (24%). The tetrabenzo derivative and the furan analogue of 335 as well as others are described. In an unrelated paper, condensations of 2-t-butoxy-5-lithiofuran with aldehydes and ketones followed by acid-catalyzed dehydration have been described as providing a general route to γ-alkylidene butenolides 337 [289].



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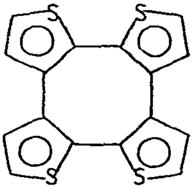

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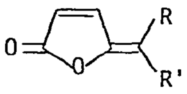

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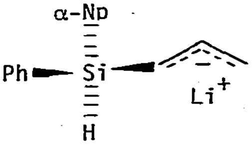
Allyllithium reagents such as 338 have been combined with chlorosilanes as part of the attempt to prepare asymmetric disilacyclopentanes [290]. Allyllithium, allylmagnesium bromide, and others have been combined with 339 as part of a study of the chemistry of the first bifunctional enantiomeric silicon compounds such as 340 [291]. Incidentally, a third paper concerned with organosilicon chemistry discussed the relationship between the stereochemistry of nucleophilic substitution at silicon by alkyllithiums, Grignard reagents, and alanes and the electronic character of the nucleophile [292]. It was concluded that reagents which add in a 1,2-fashion to α,β-unsaturated carbonyl compounds react at silicon with retention of configuration while those which add conjugatively to such systems react at silicon with inversion.



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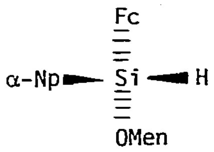

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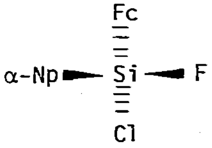
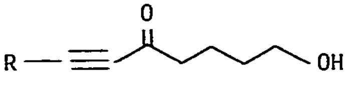


340

α,β-Acetylenic ketones have been prepared by condensation of lithium acetylides with lactones [293]. The process is illustrated by the reaction of 1-lithio-1-hexyne with δ-valerolactone to afford 341 (80%) (see reference 317 also). Lithium acetylides have also been combined with branched alkyl halides to give branched chain acetylenes [294], and with sulfur dichloride or thionyl chloride to yield sulfides such as 342 [295]. Lithium derivative 343 has been reacted with 344 to afford 345 [296].



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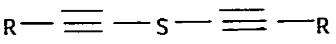

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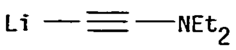

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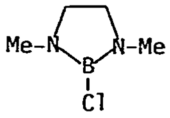

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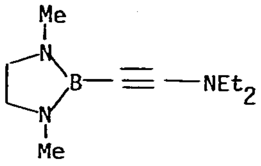
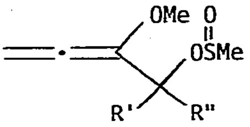


345

Other papers in this area described the preparation of certain branched-chain sugars using methoxyvinyllithium [297], α-addition and o-metalation of phenylisocyanide [298], isocyanide-metal exchange in the reaction of lithiodithiane with triphenylmethyl isocyanide [299], elimination of the methanesulfinic ester group from 346 by RCuBr·MgX·LiBr to give 347 [300], and the synthesis of long chain terminally bifunctionalized alkane and alkene derivatives by reaction of 348 with α,ω-dihalides catalyzed by Li_2CuCl_4 [301].



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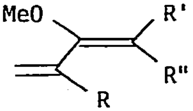

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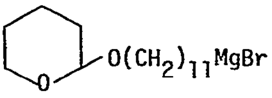
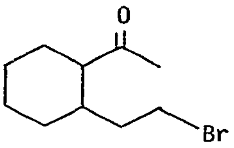


348

B. Carbanions Stabilized by Carbonyls

Three papers discussed intramolecular cyclization of metal enolates derived from haloketones [302-304]. The process is illustrated by the conversion of 349 to terminal enolate 350 using LDIPA in ether-hexane; addition of HMPA to the latter affords 351 (79-80%) [302]. Several other examples are cited [302] including the preparation of perhydroazulene 352 from 353 [303] and the stereospecific synthesis of a cis-decalone from a cyclohexanone derivative [304]. Interestingly, the potassium isomer of 353 cyclizes to 354 (86-94%) [303].



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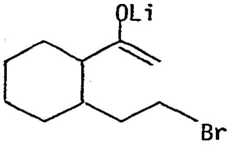

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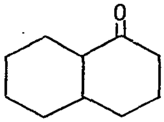

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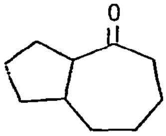

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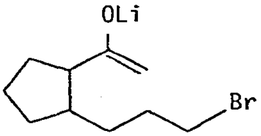

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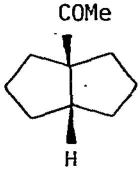
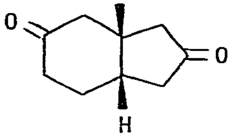


354

Angularly substituted cis-hydrindanes such as 355, of interest in the construction of natural products, may be prepared by alkylation of kinetic enolate 356 by 357 followed by addition of methyllithium and hydrolysis to afford 358 [305]. The process, which should be general, is completed by cyclization with potassium carbonate, hydrolysis, and decarboxylation.



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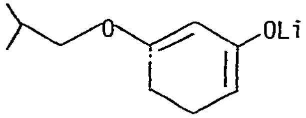

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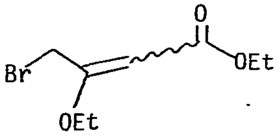

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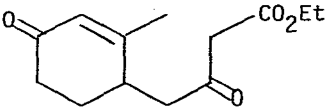
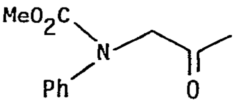


358

A variety of α-aminoketones have been enolyzed under both thermodynamic and kinetic control to determine the effect of such α-nitrogen atoms on the direction of enolization [306]. Methods are outlined for most cases where enolization can be effected toward nitrogen. For example, 359 yields 360 and 361 in a ratio of 4.5/1.



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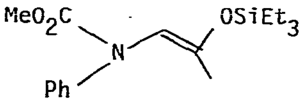

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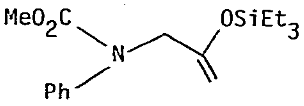
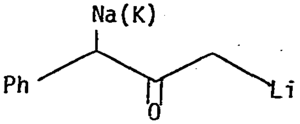


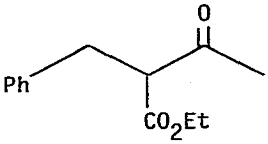
361

Another paper appeared which discussed the regioalkylation of dialkaliphenylacetone (362) [307]. It is reported that methylation occurs at either the α- or the α'-carbon as a function of the metal cation and that methylation at the terminal position does not predominate in any case examined.



362

A variety of β-ketoesters have been lithiated, combined with paraformaldehyde, then deacylated simply by heating to give α-methylenation products [308]. The sequence is illustrated by the conversion of 363 to 364 (96%).



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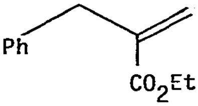
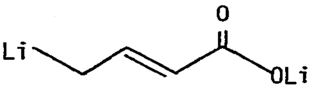


364

A full paper appeared in 1978 which described the oxidation of a large number of ester and ketone enolates by MoO_5·pyridine·HMPA to afford their α-hydroxy derivatives (34-85%) [309]. A related paper discussed the synthesis of 17α-hydroxymethyl 20-keto steroids by treatment of lithium enolates with dimethyl carbonate followed by saponification [310].

Dilithiocrotonate (365) has been found to add to cyclohexanone to give α-product 366 and γ-adduct 367 at short and long reaction times, respectively [311]. This dianion has also been found to add to α,β-unsaturated ketones in a 1,2- or 1,4-fashion by kinetic and thermodynamic control, respectively. These results should be compared with those reported in references 227-238. Similar results are reported for dilithiodimethylacrylate.



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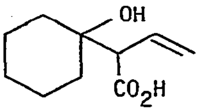

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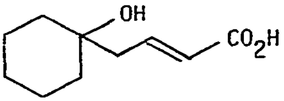
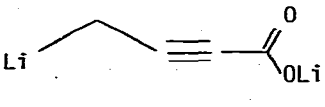


367

Additional chemistry of 368 [312] and 369 [313] was described in 1978. In the first case, 368 was combined with several aldehydes to afford natually occurring 5,6-dihydro-2H-pyran-2-ones [312]. Dianion 369 was likewise combined with aldehydes and ketones [313].



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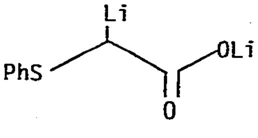

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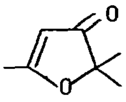
Regioselectivity in the reactions of lithium dienolates derived from esters continued to be studied in 1978. Thus, although most prior work had shown that such systems undergo nearly exclusive α- rather than γ-alkylation, the latter was observed in condensations of lithio derivatives of furanones and α,β-unsaturated ketones such as 370 and 371, respectively [314]. The authors suggest that, to date, such γ-alkylation has been observed in all cases when the dienolate contains an exocyclic double bond, as in 372 and 373 for example. Another paper described related condensations of 374 [315]. Thus, while this dianion and alkyl halides gave products arising from α-attack only, the use of bromine, benzenesulfenyl chloride, and benzeneselenyl bromide afforded products of γ-attack such as 375.



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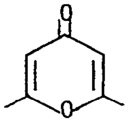

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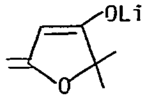

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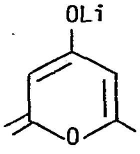

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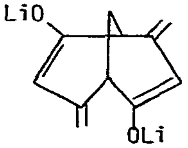

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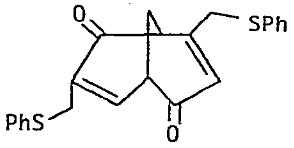
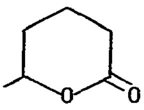


375

Other papers dealing with enolates derived from esters discussed the methylation of the lithium salt of the enantiomers of 376 as part of the synthesis of the carpenter bee pheromone [316], the preparation of cyclic hemiketals such as 377 from lithioesters and δ-valerolactone (see reference 293] [317], ring-opening reactions of α-oxy epoxides with t-butyl dilithioacetate in such reactions [318], acylation of ester enolates with α,α,α-trisubstituted acid chlorides to afford branched β-ketoesters [319], the synthesis of α-halo esters from such enolates and carbon tetrahalides [320], the conversion of 378 to 379 (G = CH_2X, CHX_2, CX_3, CXX_2') by means of polyhalomethane derivatives [321], acylation reactions of the previously described 380 [322], and regio- and stereospecific preparation of α,β-unsaturated esters, acids, and lactones by condensation of 381 and α-lithio-α-selenolactones with aldehydes [323].



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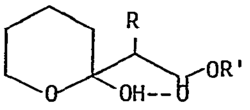

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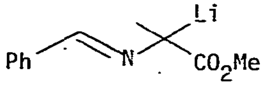

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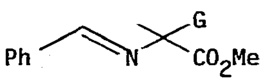

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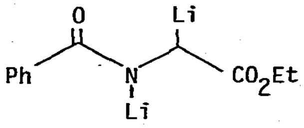

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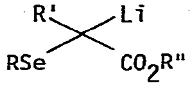
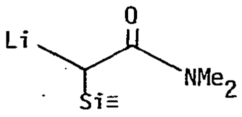


381

The lithium enolates of a variety of amides have been silylated with chlorotrialkylsilanes to afford both C- and O-silylated derivatives [324]. While C-silylation predominates with lithio-N,N-dimethylacetamide, more O-silylation is realized with more highly substituted amides. The O-silyl derivatives were found to isomerize to the C-silyl compounds upon heating. Silylenolate 382 has been combined with aldehydes, ketones, and epoxides to give unsaturated amides [325], with amides such as 383 to yield β-enamino amides such as 384 [326], and with p-quinoline ketals such as 385 to afford p-quinone methide ketals 386, a new class of molecules [327].



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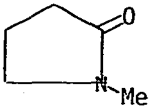

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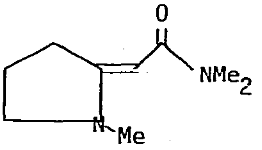

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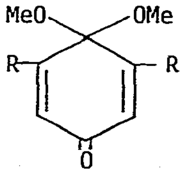

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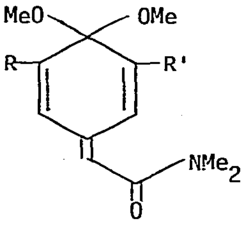


386

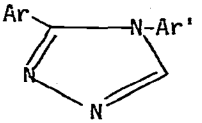
C. Amines, Imines, Ethers, and Related Compounds

Controlled potential electrolytic oxidation has been effected on certain lithium amides to afford hydrazines or azoalkanes [328]. For example, electrolysis of lithium di-n-butylamide at an anode potential of +50 mV gave tetrabutylhydrazine (38%). Similar treatment of lithium cyclohexylamide yielded azocyclohexane (23%).

Lithiodiazomethane (387) has been combined with a variety of imidoyl chlorides to afford triazoles 388 [329]. Such reactions are said to proceed via initial attack of the nitrogen of 387 upon the chlorides.

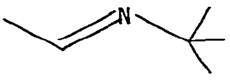
$LiCHN_2$

387



388

α,β-Unsaturated aldehydes have been conveniently prepared by conversion of 389 to 390 by LDIPA/$(EtO)_2POCl$ followed by addition of aldehydes or ketones [330]. For example, the use of benzaldehyde in the sequence gives cinnamaldehyde (70%). Another paper described the interaction of enamino ketones such as 391 and organolithium reagents RLi to afford α,β-unsaturated ketones such as 392 [331]. Lithiated imines have also been employed to synthesize 2-aminotetrahydrofurans and δ-hydroxyketoaldehydes [332], and γ-dicarbonyl compounds [333].



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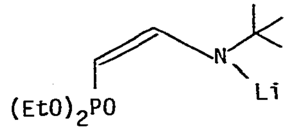

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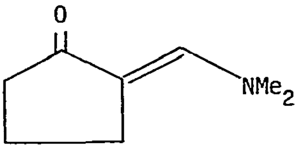

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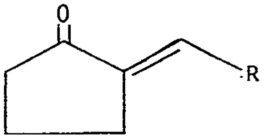
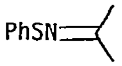


392

In contrast to an earlier report which described the addition of alkyllithium reagents across the imine bond of 393, the use of LDIPA with imines including 393 promotes α-ionization to afford derivatives such as 394 [334]. Subsequent condensations with electrophiles give N-alkylidenearenesulfenamides such as 395.



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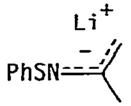

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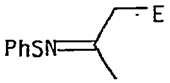
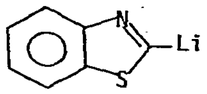


395

Three papers described a plethora of synthetic uses of lithiated benzothiazoles [335-337]. Thus, 396 has been combined with aldehydes and ketones to afford carbinols which have been dehydrated to vinyl derivatives such as 397 [335]. The latter can be conveniently converted to α,β-unsaturated systems 398 or 399. A large number of organolithium reagents have been added to 397 in a 1,4-fashion to give 400 which has itself been alkylated or hydrolyzed, ultimately to 401 [336]. Both 397 and the corresponding saturated system have been metalated by LDIPA, then alkylated and hydrolyzed [336]. Such a sequence on 397 yields 402. A variety of annulations using these systems are described [337]. An unrelated paper described ring metalations of 403 by LDIPA to give 404 (G = Li) followed by alkylation to afford 404 (G = alkyl) [338].



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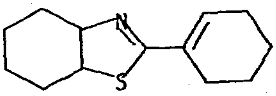

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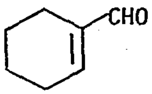

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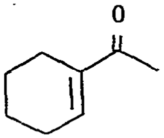

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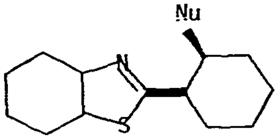

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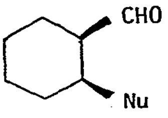

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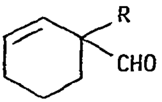

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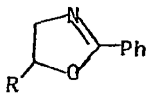

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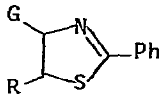
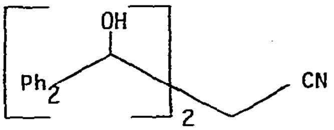


404

Turning to nitriles, lithioacetonitrile and lithiomethoxyacetonitrile have been found to combine with several aryl ketones to give dialdol products such as 405 [339]. The condensations were run at higher temperatures than reported previously. Another paper describes that while treatment of strictly aliphatic nitriles such as acetonitrile with lithium/chlorotrimethylsilane affords cyanosilanes (for example, 406), similar reaction on α-phenylnitriles results in decyanation to give products such as 407 [340]. Lithioisobutyronitrile has been combined with N-methylindoletricarbonyl chromium (0) to yield 408 and 409 [341].



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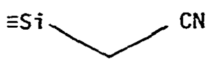

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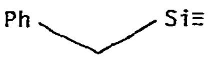

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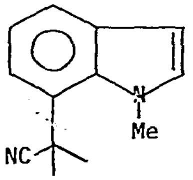

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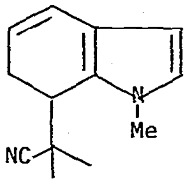
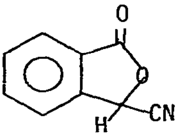


409

Cyanophthalide 410 has been α-lithiated, then combined with α,β-unsaturated ketones in a 1,4-fashion to afford hydroquinones 411 [342]. The reaction apparently proceeds via an interesting cyclization of the intermediate enolate 412 with the phthalide carbonyl carbon. Another paper described the condensation of a lithiocyanohydrin with an isoprenic sulfoxide as part of a synthesis of tagetones [343].



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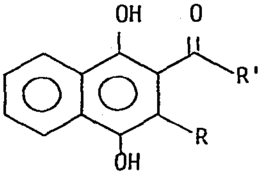

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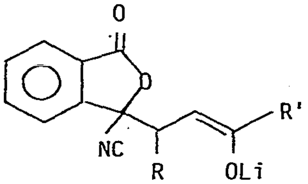
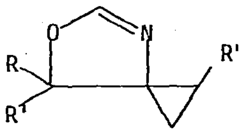


412

Other papers in this area included the preparation of spirocyclopropanes 413 from 1-lithiocyclopropyl isocyanides and carbonyl compounds [344], condensations of dilithioazines 414 with ketones [345], conversion of α-arylated tertiary nitro compounds such as 415 into β-aryl nitroparaffins by displacement of the nitro group with α-lithionitroalkanes [346], double deprotonation with n-butyllithium in THF/HMPA of 416 and 417 to afford 418 and 419, respectively [347], the preparation of silyl nitronates 420 from nitroalkanes, LDIPA, and chlorosilanes [348], selective methylations of pyrone 421 [349], and the preparation of tertiary alkyl N-phenylcarbamates from lithium alkoxides and phenyl isocyanate [350].



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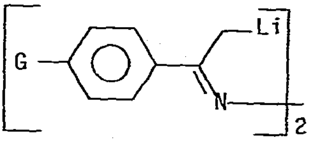

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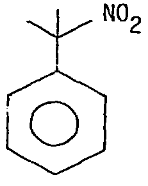

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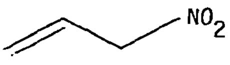

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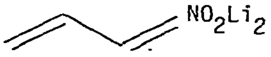

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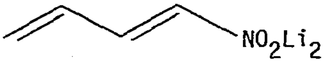

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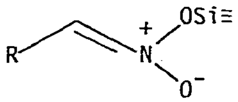

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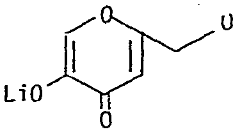
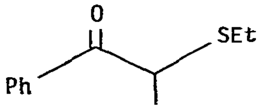


421

D. Carbanions Stabilized by Sulfur and Other Heavier Atoms

α-Thiolketones such as 422 have been prepared regiospecifically by combining vinyllithium reagent 423 with aldehydes followed by isomerization with p-toluenesulfonic acid [351]. Intermediate 423 is conveniently prepared by metalation of the parent vinylsulfide using n- or s-butyllithium.



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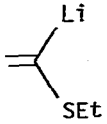
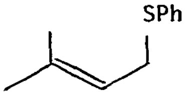


423

Allyl sulfides such as 424 have been lithiated with LDIPA, then silyated with chlorodisilanes to afford products such as 425 [352]. The latter are converted by $Me_3O^+B^-F_4$ to gem-disilanes illustrated by 426.



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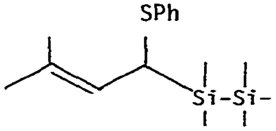

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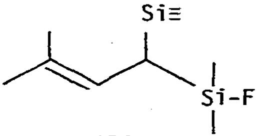
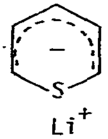


426

Other α-lithiothio ethers, prepared similarly, included 427 which was alkylated by t-butyl bromide and bromocyclohexane to give mostly 428 [353], 429 which underwent intramolecular cyclization as part of the synthesis of 6-Z-hedycaryols [354], and 430 which was combined with aldehydes to yield racemic β-hydroxy sulfides [355].



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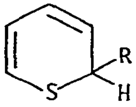

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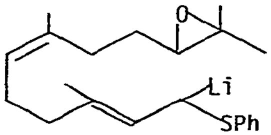

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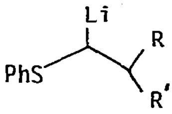
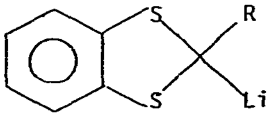


430

Similarly, lithiobenzodithioles 431 have been combined with a variety of electrophiles to ultimately afford 432 [356]. Another paper discussed alkylations of certain lithiodithianes as a route to tertiary acyloins [357].



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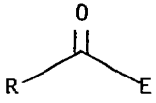
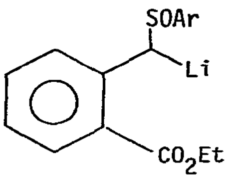


432

Two papers appeared which described syntheses of naphthalene derivatives starting from 433 [358] and 434 [359] with α,β-unsaturated esters and ketones. Aromaticity was obtained in these systems by loss of ArSOH and p-toluenesulfonic acid, respectively.



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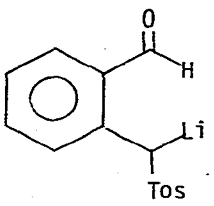
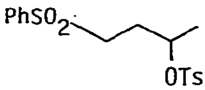


434

Tosyloxysulfones such as 435, prepared from α,β-unsaturated carbonyl compounds, have been cyclized to cyclopropanes such as 436 by LDIPA [360]. Such products themselves were further metalated, then combined with electrophiles. α-Epoxy sulfones 437 have been converted to α-alkyl or α-aryl-α,β-unsaturated cyclopentenones such as 438 by treatment with two equivalents of methyl-, butyl-, or phenyllithium to afford 439 via eliminative ring opening followed by conjugate addition of the organolithium [361]. The process is completed by hydrolysis or alkylation with methyl iodide, oxidation, and elimination of the sulfone moiety. The organolithium addition to intermediate 440 occurred cis to the oxygen when M = Li or Mg and trans to this atom when M = Si≡ [362]. Another paper discussed the conjugate additions of allylsulfonyl carbanions to α,β-unsaturated ketones and esters [363]. Products derived from α- and γ-attack by the carbanion are reported.



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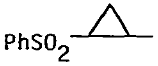

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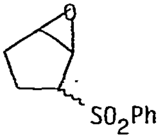

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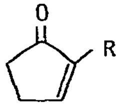

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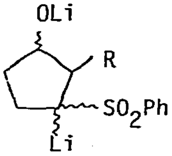

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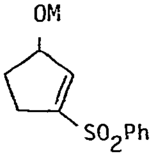
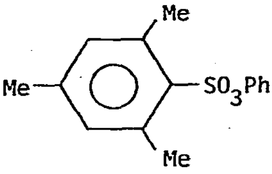


440

Treatment of sulfonates such as 441 and related sulfonanilides with n-butyllithium at -72° has been shown to give 442 [364]. Several mechanisms are postulated for these transformations. Dithio ester 443 has been α-lithiated by LDIPA and combined with isobutyraldehyde as part of the preparation of compounds such as 444 [365]. In another paper, it was disclosed that salt 445 combines with organolithiums, prepared in situ from RX or PhX, to yield 446 [366]. The reaction apparently proceeds via $PhSO^+CH_2$.

Lithium carbanions stabilized by selenium, silicon, and phosphorus continued to be studied in 1978. Thus, anions such as 447 have been reacted with epoxides



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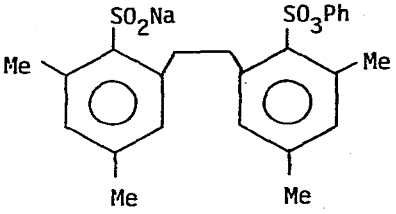

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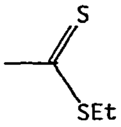

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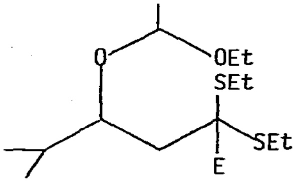

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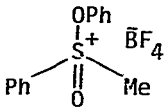

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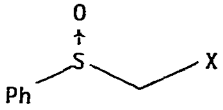
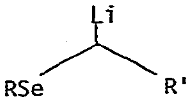


446

to afford γ-hydroxyselenides [367] and with formaldehyde as part of the preparation of allyl alcohols [368]. Carbanion 448 has been prepared from 449 and n-butyllithium, then combined with aldehydes and ketones to give β-hydroxyselenides [369].



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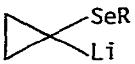

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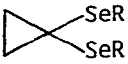
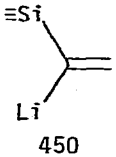


449

Additional examples of the synthesis of carbon-carbon unsaturated systems using α-lithiosilanes have been described. Thus, terminal allenes [370] and tetrasubstituted alkenes [371] have been prepared from systems such as 450 and aldehydes or ketones. 1,3-Dienes have been synthesized similarly from 451 [372]. Carbenoid 452 has likewise been employed to make α-chloro-α,β-unsaturated esters [373].



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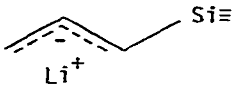

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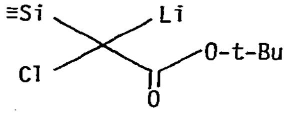
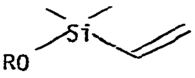


452

An α-lithiosilane is postulated as an intermediate in the reaction of t-butyllithium and others with silanes 453 to afford 454 in hexane at -78° and mostly 455 in THF at this same temperature [374].



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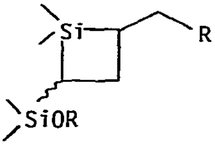

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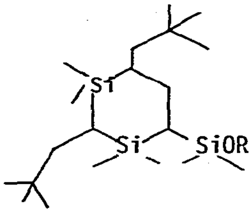
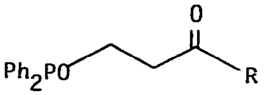


455

In the area of phosphorus-stabilized organolithium reagents, five methods are presented for the formation of 456, the anion of which is equivalent to homoenolate 457 [375]. Phosphane oxide 458 has been lithiated by s-butyllithium, then combined with carbon tetrachloride to give 459 [376]. The latter compound has been cyclized to 460 by lithium diethylamide. Finally, enol ethers have been synthesized from lithium derivatives 461 and ketones [377].



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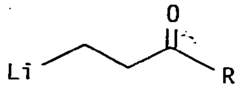

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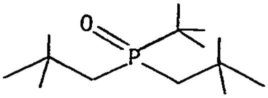

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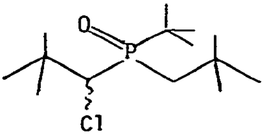

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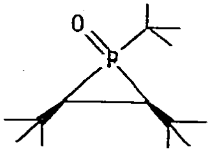

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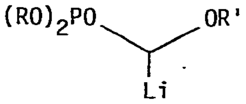


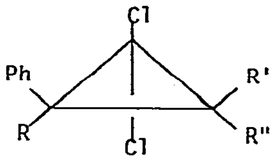
461

E. Polymerization

Since the time this manuscript was begun, all of the papers concerned with polymerization were placed in other sections except for one dealing with the thermal degradation of the alkali salts of poly(methacrylic acid) [378]. This latter study revealed that the principal products of such thermolyses are monomer, the corresponding isobutyrate alkali carbonate and oxide, carbon dioxide, and liquid volatiles which consisted of aldehydes and ketones.

11. CARBENOIDS

1,1-Dichlorocyclopropanes 462 have been converted to acids 463 by lithium-chlorine exchange followed by carboxylation [379]. Although involving carbenes rather than carbenoids, another paper describes evidence for the intermediacy of 464 in reactions of 465 with methyllithium [380].



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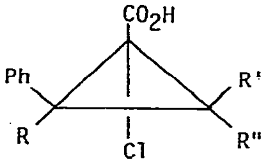

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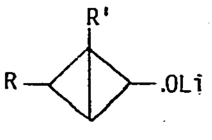

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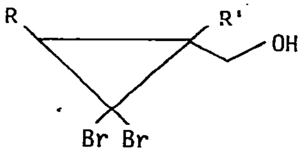
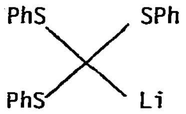


465

Tris(phenylthio)methyllithium (466) has been shown to decompose to carbene 467 [381]. The two species combine to afford 468. A similar pathway has been postulated in the conversion of tetrakis systems such as 469 to rings illustrated by 470 [382].



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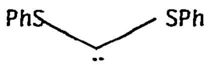

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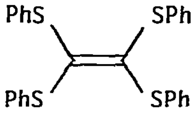

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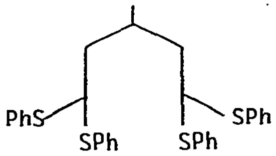

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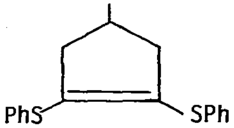
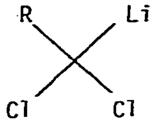


470

A full paper described the scope, mechanism, and utility of the lithium halide induced decomposition of methyl chlorodifluoroacetate in HMPA to afford the chlorodifluoromethide ion or the chlorodifluoromethyllithium-HMPA complex [383]. 1,1-Dichloroalkyllithium reagents 471 have been combined with arsenic(III) chloride to give 472 which, in turn, have been condensed with Co(CO)$_8$ to yield cluster compounds 473 [384]. The latter compounds appear to be derivatives of the unknown arsaacetylenes 474 through chemistry to demonstrate this has not yet been achieved. An unrelated full paper disclosed the details of the conversion of 475 to a variety of compounds via 476 effected by organolithium reagents [385]. Another paper described the reaction of lithiobenz[de]anthracene with methylene chloride-n-butyllithium to afford ring-expanded and tricyclic compounds [386].



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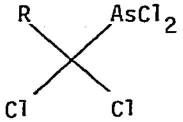


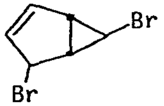
472

$(RCAs)Co_2(CO)_6$

473

RC≡As

474



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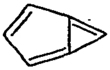
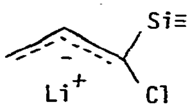
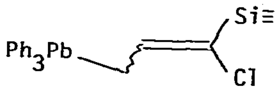


476

Carbenoid 477, prepared from 478 and n-butyllithium, has been combined with several electrophiles to ascertain the regiochemistry of this system [387]. For example, while 477 and 1,1,1-trifluoroacetone gave 479, the anion and acetophenone afforded mostly 480. The results are explained by a combination of steric and electronic effects.



477



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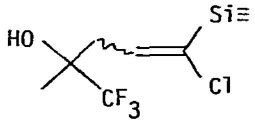

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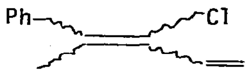
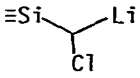


480

Silylcarbenoids such as 481, prepared from 482 and s-butyllithium (-78°), have been employed in the synthesis of 3R-(-)-linalool and β-dihydroionone [388]. The use of LiTMP on 482 at higher temperatures apparently afforded silylcarbene 483 since silylcyclopropanes are obtained in the presence of alkenes [389]. The related stannylcarbene 484 has been prepared similarly. Interaction of dibromosilane 485 with lithium and trialkylboranes (R_3B) followed by oxidation with hydrogen peroxide has been found to yield α-hydroxysilanes 486 [390].



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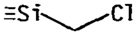

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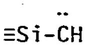
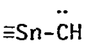


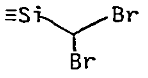
$\equiv Si-\ddot{C}H$

483



$\equiv Sn-\ddot{C}H$

484



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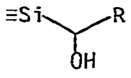
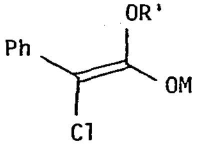


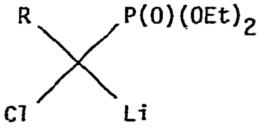
486

The stereochemistry of the additions of enolates 487 to benzaldehyde to afford halohydrins has been studied as a function of the cation [391]. Thus, while the use of lithium cation resulted in the formation of predominantly the erythro products, sodium and potassium cations gave the threo isomers.

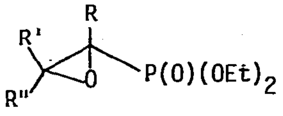


487

Several papers discussed additional aspects of the chemistry of carbenoids derived from phosphonates. Thus, condensation of 488 (R = Me, H) with aldehydes and ketones has been shown to give epoxides such as 489 [392, 393]. The use of an extra equivalent of base in such reactions of 488 with aldehydes yields ketophosphonates illustrated by 490 [394].



488



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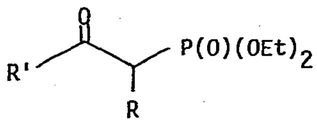
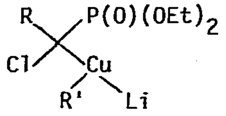


490

The electrophilicity of carbenoids such as 488 has been enhanced by conversion to cuprates such as 491 which transfer an alkyl group from copper to carbon to afford reagents such as 492 [395]. The process may be effected using catalytic amounts of copper(I) salts [396,397].



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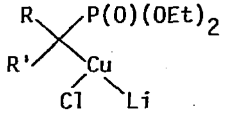
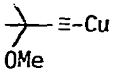


492

Finally, reagents similar to 488 have been acylated by acid chlorides and chlorocarbonates to give α-chloro-α,β-unsaturated ketones [398] and -esters [399], respectively.

12. LITHIUM ATE COMPLEXES

Soluble, but cheap 493 has been found to be synthetically useful for the generation of mixed cuprates 494 [400]. Several examples of the use of such reagents are disclosed.



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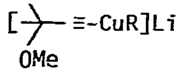
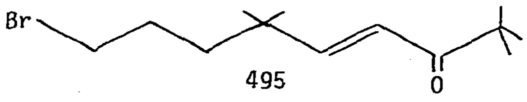


494

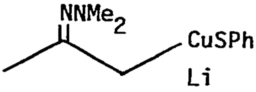
HMPA has been found to dramatically affect the regiochemistry in the reactions of lithium dimethylcuprate with bromoketone 495 [401]. Thus, while these reagents and dimethyl sulfide in ethyl ether result in conjugate addition (83-92%), the presence of HMPA causes displacement of the bromine by methyl (72-97%).



495

Mixed cuprate 496 has been found to be useful in conjugate additions to afford reagents such as 497 which, themselves, are employed in a variety of annulations [402]. Another paper describes the use of chiral cuprate 498 with α,β-unsaturated carbonyl compounds to give adducts with as much as 4.4% asymmetric induction [403].

A full paper appeared in 1978 which described the syn-addition of lithium cuprates and monoalkylcopper(I) reagents to α,β-acetylenic sulfoxides to afford products such as 499 [404]. A second paper described similar additions to benzenesulfonylacetylene to give 500 and 501 with R_2CuLi and $R_2'CuLi$, respectively [405].



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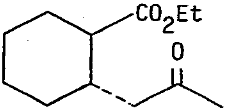

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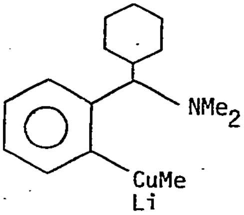

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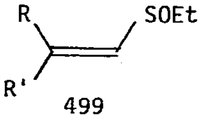
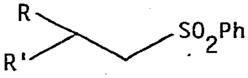


499

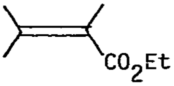
$RCH{=}CHSO_2Ph$

500



501

Incidentally, while certain higher substituted α,β-unsaturated carbonyl compounds such as 502 fail to add lithium di-n-butylcuprate (< 1%), the use of 503 in such condensations has been found to be successful [406].

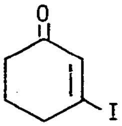


502

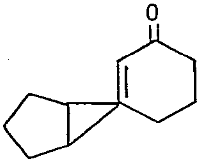
$RCu \cdot BF_3$

503

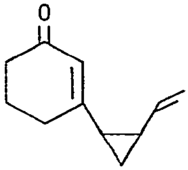
Additional examples of reactions of cuprates and β-iodo systems such as 504 have been utilized in the preparation of cyclopropyl derivatives such as 505 [407] and 506 [408] as well as stannyl reagent 507 [409].



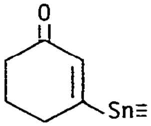
504



505

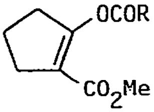


506



507

Other additional-elimination reactions of cuprates have been realized on 508 to give 509 [410] and on 510 to yield 511 [411] but not on furanones such as 512 [412]. That only conjugate addition on the latter systems to afford 513 is realized has been ascribed to the fact that such β-eliminations would entail a retro-5-endo-trigonal reaction, a process disfavored by the Baldwin rules.



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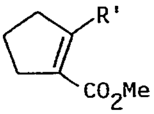


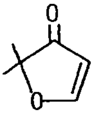
509

$XCH{=}CHSO_2Ph$

510

$RCH{=}CHSO_2Ph$

511



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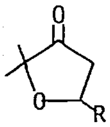
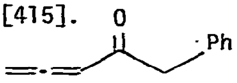
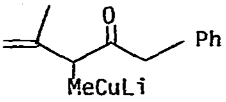


513

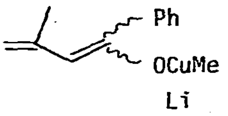
A full paper discussed a more complete investigation of the 1,2-addition of lithium dimethylcuprate to 514 to afford 515 which gradually isomerizes to 516 as evidenced by NMR and IR spectroscopy [413]. Similar 1,2-additions have been realized on certain allenic sulfones and sulfoxides [414] and on allenic phosphine oxides [415].



514

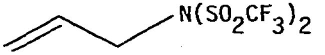


515

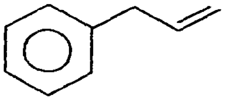


516

Organocuprates have been found to displace sulfonimides to afford alkyl or aryl derivatives as illustrated by the conversion of 517 to 518 using lithium diphenylcuprate (73%) [416].

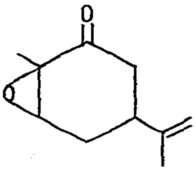


517



518

Epoxyketones such as 519 have been reduced by lithium dimethylcuprate to species such as 520 which have been trapped by methyl iodide but not other alkylating agents to afford products such as 521 [417]. Another paper described regiospecific transformations of diepoxides with cuprate 522 [418]. For example, 523 and this cuprate gave 524.



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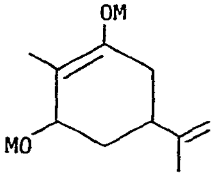

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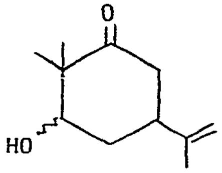
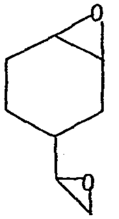


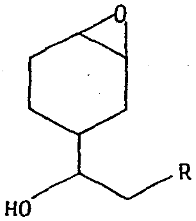
521

$R(CN)CuLi$

522

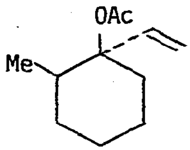


523



524

The chemistry of cuprates and allylic electrophiles continued to be studied in 1978. Thus, while treatment of 525 with lithium dimethylcuprate yielded only 526, reaction of isomeric 527 with this cuprate afforded a mixture of 526 and 528 [419]. Reaction of vinylcuprates with allyl halides has been employed to synthesize 1,4-alkadienes [420]. For example, 529/CuI/Me_2S and 1-chloro-2-butene gave 530. Allylic alkoxides such as 531 have been converted to alkenes such as 532 by 533 [421].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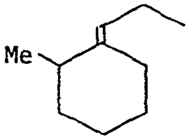
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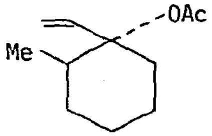
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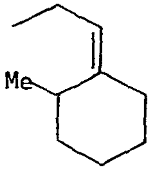
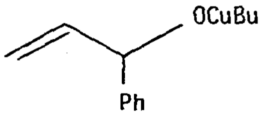

528

$CH_3(CH_2)_5CH{=}CHLi$

529

$CH_3CH{=}CHCH_2CH{=}CH(CH_2)_5CH_3$

530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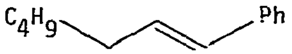
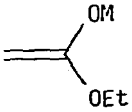

532

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

533

Allenes continued to be prepared from lithium cuprates and propargylic systems. Thus, copper enolates such as 534 (M = Cu) combine with propargyl bromide to afford 535 (39%) [422]. In contrast, the corresponding lithium enolate 534 (M = Li) and this halide gave only direct displacement product 536. Lithium dialkylcuprates and propargyl halides also afford allenes as illustrated in the conversion of 537 to 538 using lithium di-n-butylcuprate [423]. The use of chiral propargyl carbamates in such reactions has been shown to yield chiral allenes [424]. Despite all of the above, treatment of silylpropargyl acetate 539 with R_2CuLi gives direct displacement products in which the acetylene moiety is retained [425].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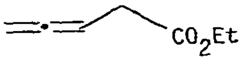
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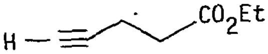
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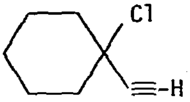
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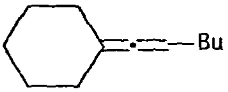
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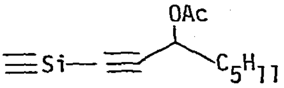
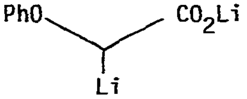
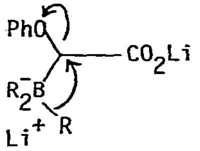

539

Other papers dealing with cuprates have described the acylation of such species derived from phosphonates to afford β-ketophosphonates [426] and the conversion of alkyl halides to alkanes by complex metal hydrides ranging in composition from $LiCuH_2$ to Li_5CuH_6 [427]. Reactions of such species with enones and cyclic ketones to give reduction products are also reported.

Turning to boron ate complexes, dilithiophenoxyacetate (540) has been combined with a variety of trialkylboranes to afford, upon hydrolysis, alkylacetic acids [428]. For example, trioctylborane and 540 give decanoic acid (90%) apparently via 541.

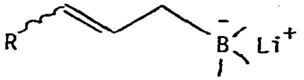


540



541

Allylic boron ate complexes 542 have been found to combine in a head to tail fashion with allyl chlorides and bromides 543 to give coupled products 544 in fair to excellent yields [429]. The related complexes 545 have been added to acrolein to yield homopropargyl alcohols 546 and α-allenic alcohols 547 at low and room temperature, respectively [430].



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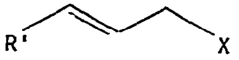

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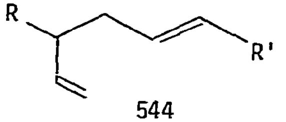

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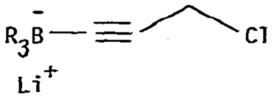

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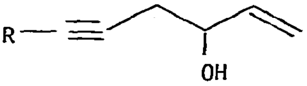

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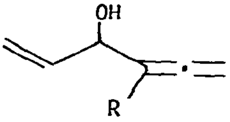
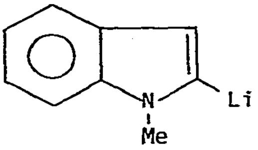


547

Lithioindoles such as 548 and vinyllithium have been combined with trialkylboranes (R_3B), iodine, and H_2O_2 to afford 549 [431] and trisubstituted olefins such as 550 [432], respectively.



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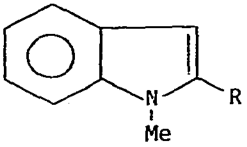

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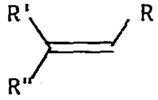
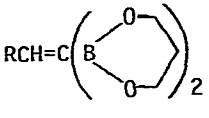


550

Migration of the methyl group from boron to carbon in the conversion of 551 to 552 by two equivalents of methyllithium is said to occur during the oxidation step with H_2O_2 [433]. Several possible intermediates are discussed.



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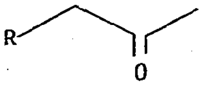
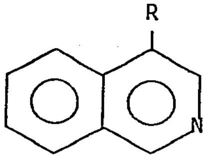


552

Other papers in this area discussed steric effects in the reactions of certain trialkylboranes with lithium and sodium hydrides [434], the synthesis of new germyl aluminates such as 553 by reduction of aryl digermanes by $LiAlH_4$ [435], and the preparation of 4-alkylisoquinolines 554 by combination of isoquinoline, $LiAlH_4$, and alkyl halides [436].

$(Ph_3Ge\text{-}AlH_3)^-Li^+$

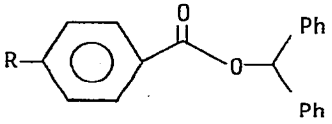
553



554

13. REDUCTIONS AND RADICAL-ANIONS

Several benzhydryl benzoates (555) have been found to undergo deoxygenation with lithium naphthalenide to afford ketones 556 [437]. Acetates of sterically hindered secondary alcohols and of tertiary alcohols are converted by lithium in ethylamine to alkanes rather than to alcohols [438]. The process is illustrated by the conversion of caryolan-1-ol acetate to caryolane (90%).



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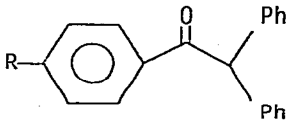
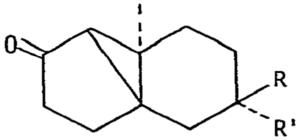


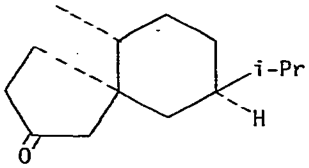
556

Four more tricyclodecan-3-ones have been reduced by lithium in liquid ammonia as illustrated by the conversion of 557 and 558 to 559 and 560, respectively [439]. The results are discussed in terms of equilibration of intermediate carbanions and the rate of protonation of kinetically generated anions.



557 (R=i-Pr, R'=H)

558 (R=H, R'=i-Pr)



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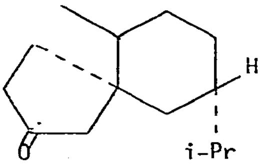
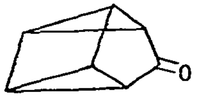


560

Lithium-ammonia reduction of several bridged dicyclopropyl ketones to afford products in which both cyclopropane rings have been cleaved has been ascribed to two electron reductions occurring by pericyclic processes [440]. The process is illustrated by the conversion of 561 to 562, 563, and other products. That carbanions are involved has been demonstrated by deuterolysis [441].



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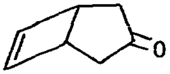

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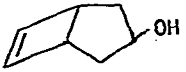
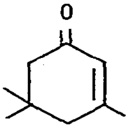


563

A large excess of "lithium bronze" ($Li \cdot 4NH_3$) has been found not to be necessary to effect convenient reduction of α,β-unsaturated ketones to saturated ones [442]. For example, this reagent converts 564 to 565 (97-98%). More normal "lithium blue" reductions have been employed in the conversion of 566 to 567 [443] and in a study of the stereochemistry of the reductions of 568 to 569 [444].



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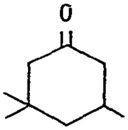

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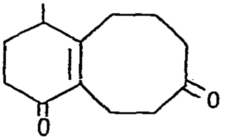

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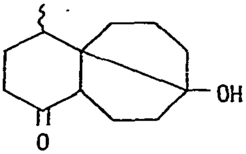

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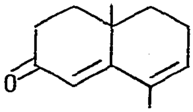

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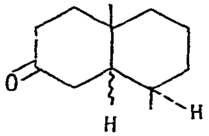
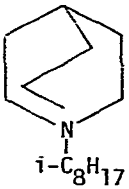


569

Lithium anthracenide has been alkylated by s-octyl fluoride with 42% inversion and 58% racemization, and by 570 to give 571 via ring opening [445]. The results are said to verify that such reactions can proceed by both S_N2 and by electron transfer processes.



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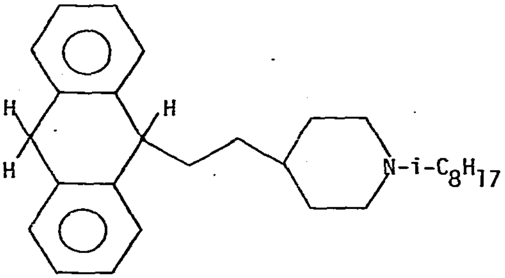
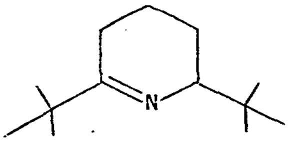


571

Alkali metal reductions of isomeric terphenyls and of biphenyl in HMPA have resulted in some cleavage of the Ar-Ar bonds since up to 25% of dihydrobiphenyls and -benzene were obtained, respectively [446]. New, severely hindered nitrogen bases such as 572 have been obtained by lithium-ammonia reduction of 2,6-di-t-butylpyridine [447]. Additional examples of reductive silylation of monoaromatics have been described as illustrated by the conversion of p-cresol to 573 using chlorodimethylsilane and lithium in THF [448].



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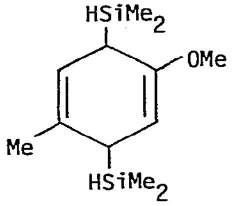
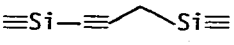


573

Other papers in this section discussed the preparation of 574 by reductive silylation of 575 (R = Me, $SiMe_3$) using chlorotrimethylsilane and lithium in THF [449], the synthesis of middle-ring cyclosilanes $(Me_2Si)_n$ (n = 8,9) from dichlorodimethylsilane and lithium in THF [450], the conversion of chloroalkoxides 576, prepared from Grignard reagents and chloroketones, to trisubstituted alkenes by lithium [451], and the preparation [452] and electrochemical behavior [453] of M^+Au^-.



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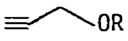

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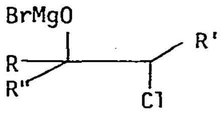


576

14. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

As in the past, this section will be divided into the families of the periodic table proceeding from left to right. First, $LiMgH_3$ has been prepared by the addition of $LiMgPh_3$ to $LiAlH_4$ [454]. Other ate complexes described in this paper included $LiMgH_nR_{3-n}$ (n = 1,2; R = Me,Et,Bu), prepared from RLi and alkylmagnesium hydrides or MgH_2, and $LiMg_2H_5$, synthesized from n-butyllithium and MgH_2 in a 1:2 molar ratio.

Several new organic derivatives of lanthanides were reported in 1978. Thus, dicyclopentadienylerbium and -ytterbium chlorides have been combined with lithiotriphenylstannane to afford 577 (M = Er,Yb) [455]. A similar germanium derivative was likewise obtained from the erbium chloride reagent. Erbium(III) chloride itself was condensed with trimethylsilylmethyllithium to give 578 [456]. Ate complexes 579 (M = Er,Lu) were also obtained from the metal (III) chlorides and six equivalents of methyllithium in the presence of TMEDA [457].

Cp_2MSnPh_3

577

578

$(Me_6M)(Li{\cdot}TMEDA)_3$

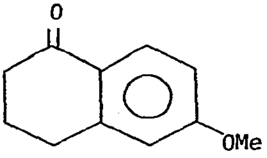
579

New thermally stable bis(cyclopentadienyl) derivatives 580 of thorium and uranium have been prepared from the corresponding new dichlorides and methyllithium [458]. Hydrogenation of 580 yielded the first organoactinide hydrides.

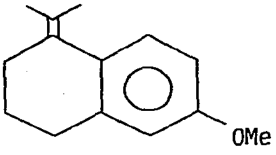
$$(Me_5C_5)_2MMe_2$$

580

A full paper described the titanium-induced reductive coupling of carbonyls to olefins as illustrated by the conversion of benzophenone to tetraphenylethylene (80%) and the mixed coupling of 581 and acetone to 582 (85%) [459]. The titanium metal is conveniently obtained from titanium(III) chloride and lithium metal.

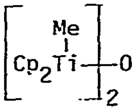


581



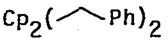
582

Several organotitanium systems were prepared from organolithium reagents including 583 from the dichloride and methyllithium [460], dibenzyl- and diphenyltitanium from 584 and 585 with benzyl- and phenyllithium, respectively [461], titanium, vanadium, chromium, and scandium systems such as 586 from 587 and appropriate halides [462], paramagnetic chelated derivatives such as 588 from 587, diketones, and metal (III) chlorides [463], and fully methylated silylamide derivative 589 and related compounds from halotitanium species [464]. The first chiral zirconocene compound, 590, was prepared from chiral α-phenethylcyclopentadiene, 591, and methyllithium [465].



$[Cp_2Ti(Me)]_2O$

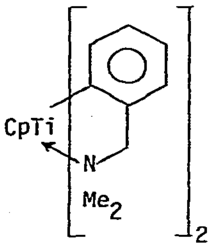
583



584

Cp_2TiPh_2

585



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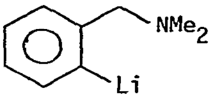

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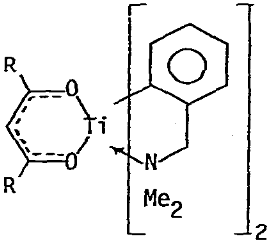

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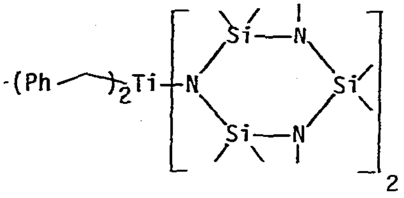

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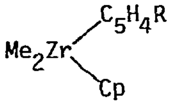
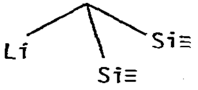


590

$CpZrCl_3$

591

A full paper described the details of the preparation, properties, and structures of tris[bis(trimethylsilyl)methyl] derivatives of titanium(III), zirconium(IV), hafnium(IV), vanadium(III), and chromium(III) [466]. Each of the compounds was synthesized from 592 and appropriate metal chlorides.



592

Niobium-containing compounds 593 and 594 have been obtained from 595 and 596 [467] and various cyclopentadienyl anions and niobium(V) and (IV) chlorides [468], respectively.

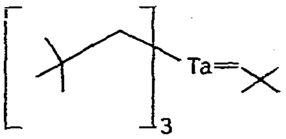
$Cp_2NbC_9H_9$ 593

$(RC_5H_4)_2NbCl_2$ 594

Cp_2NbCl_2 595

LiC_9H_9 596

Neopentylidene complex 597 has been prepared from 598 and two equivalents of lithio-2,2-dimethylpropane apparently via 599 [469]. The corresponding niobium compound is also described. Additional chemistry of 597 and a related cyclopentadiene derivative is described [470,471].



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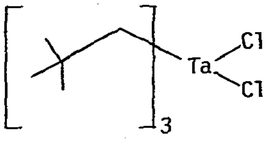

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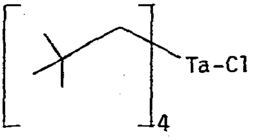
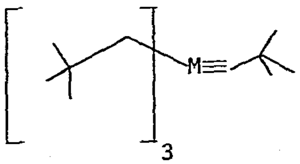


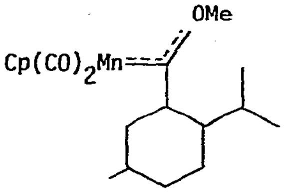
599

Chemistry similar to the above has been employed to synthesize tungsten and molybdenum complexes 600 [472].

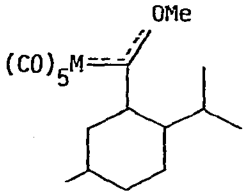


600

Several optically active carbene and carbyne complexes have been prepared using (+)-menthyllithium and metal carbonyls and then characterized by IR, ^{1}H-, and ^{13}C-NMR spectroscopy, and by polarimetry [473,474]. The compounds listed include 601 [473], 602 [M = Cr,W) [474], and 603 (M = Cr,W) [473].



601



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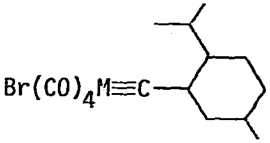
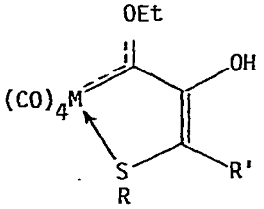


603

Carbene complexes 604 and 605 (M = Cr,W) have been synthesized from the metal hexacarbonyls and 606 [475]. The R groups of 606 were Me, Ph, SPh, and $(CH_2)_3S$. Another paper presented a full disclosure about the preparation and reactions of alkyl- and arylpentacarbonyltungsten anions [476].



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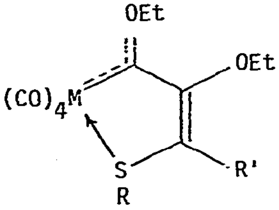

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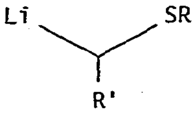


606

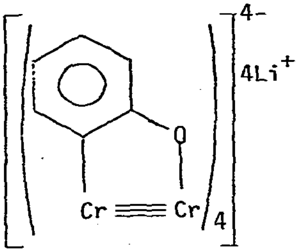
In an effort to determine if metal-metal metathesis in the chemistry of triple bonds between molybdenum and tungsten were possible, a mixture of WCl_6 and $MoCl_5$ was treated with lithium dimethylamide [477]. That only 607-609 but not 610 were formed along with other experiments suggested that such metal-metal triple bonds are not ruptured.

$MO_2(NMe_2)_6$	$W_2(NMe_2)_6$	$W(NMe_2)_6$	$MoW(NMe_2)_6$
607	608	609	610

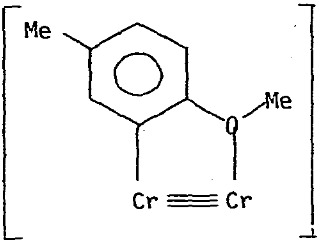
Now σ-alkyl systems 611 [478] and 612 [479] have been prepared by treatment of 613 with methyl- and ethyllithium, respectively.

$Me_2Mo_2(NMe_2)_4$	$(CH_3CH_2)_2Mo_2(NMe_2)_4$	$Cl_2Mo_2(NMe_2)_4$
611	612	613

Several new species containing chromium-chromium and molybdenum-molybdenum quadruple bonds have been prepared from o-lithiophenyl ethers or phenoxides and dichromium and dimolybdenum tetraacetates [480-482]. The compounds are illustrated by 614 and 615. Similar compounds have been obtained from lithio-2-amino-6-methylpyridine [483].

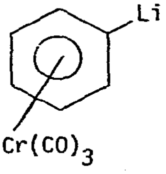


614



615

Finally, in this family, novel lithium derivative 616 has been prepared from the corresponding organomercurial, then combined with a variety of electrophiles to afford 617 [484]. An unrelated paper describes the preparation of 618 (R,R' = alkyl, aryl) from the chloromolybdenum tricarbonyl and lithioamidines [485].



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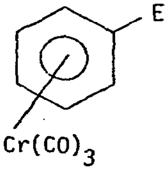

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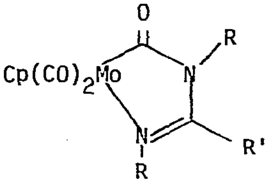
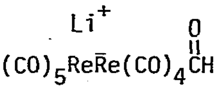


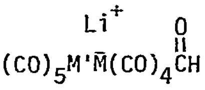
618

Binuclear formyl complex 619 has been obtained by reaction of lithium triethylborohydride with dirhenium decacarbonyl [486]. The kinetically less stable 620 (M,M' = Re,Mn) has been similarly prepared from 621. Both 619 and 620 are potent hydride donors.



$\mathrm{Li}^+\ (CO)_5Re\bar{R}e(CO)_4\overset{\overset{O}{\|}}{C}H$

619



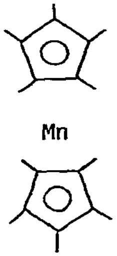
$\mathrm{Li}^+\ (CO)_5M'\bar{M}(CO)_4\overset{\overset{O}{\|}}{C}H$

620

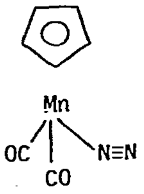
$ReMn(CO)_{10}$

621

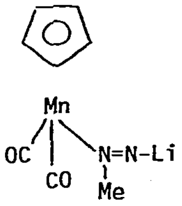
Manganese derivative 622 has been prepared from lithiopentamethylcyclopentadiene and manganese(II) chloride [487]. Compound 622 was converted to the first isolable metallocene anion by sodium naphthalenide. Manganese derivative 623 has been converted to alkyldiazene complex 624 by methyllithium which was then methylated to give azo derivative 625 [488].



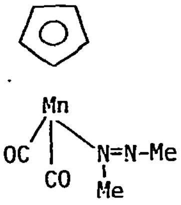
622



623



624

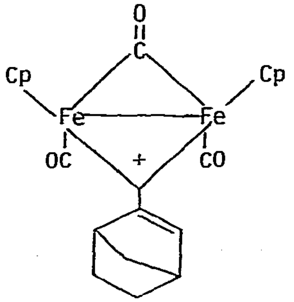


625

Iron reagent 626 but not the corresponding sodio salt combines with exo-norborene oxide to afford, after acidification with fluoroboric acid, bridged carbyne complex 627 [489]. The proposed intermediates in a similar reaction of 626 and cyclopentene oxide are outlined in detail.

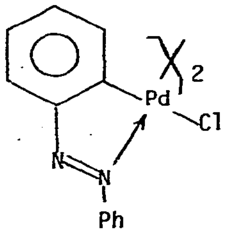
$CpFe(CO)_2Li$

626



627

Organopalladium complexes 628, 629, and 630 have been converted to 631, 632, and 633, respectively, by RLi (R = alkyl, aryl, vinyl) [490]. Products 633 were accompanied by the corresponding amines in which the imine had been reduced. An unrelated paper described the preparation of several different nickelocyclopentanes containing a variety of phosphine ligands [491].



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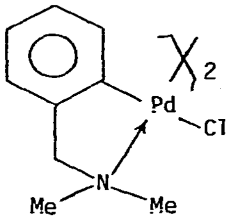

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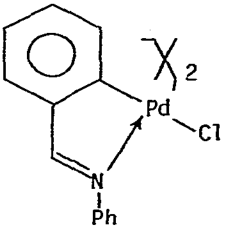
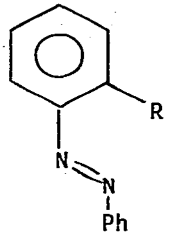


630

Ether and pentane solutions of lithium di-n-butylcuprate-n-butyllithium have been studied by ^1H NMR spectroscopy [492]. The authors suggest that while species such as 634 and 635 are apparently present in ether, 1:1 and 1:2 complexes of n-



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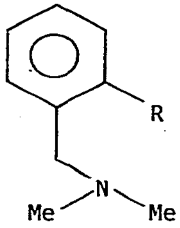

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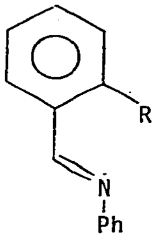


633

butylcopper(I) with n-butyllithium are found in pentane. Results are also described for tri-n-butylphosphine and lithium iodide complexes of certain cuprates.

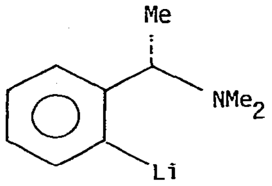
$(R_2CuLi)_2$

634

R_4CuLi_3

635

Chiral 636 has been combined with appropriate copper or gold reagents followed by dibromomethylphenylstannane to afford 637 [493]. Similar copper and gold derivatives derived from 587 have been reacted with $Cl(CO)_2Rh$ dimer to give 638 [494]. Gold complexes 639 have been obtained from the corresponding chloro species and organolithium or magnesium reagents [495].



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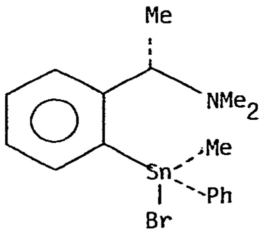

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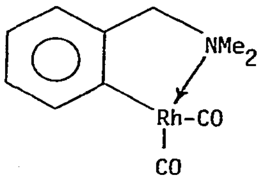
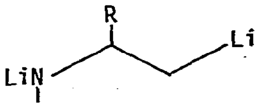


638

$RAuPR'_3$

639

β-Lithioamides 640 (R = H,Ph) and β-lithioalkoxide 641 have been prepared from the corresponding carbon-mercury systems and lithium metal [496]. Such reagents are stable at -78° and have been dideuterated with D_2O.



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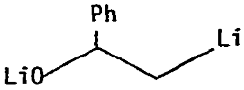
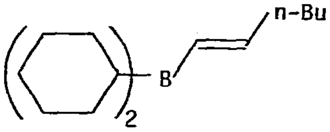


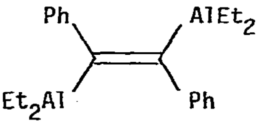
641

Turning to Group IIIb, the scope and limitations of the preparation of lithium organoborates from tri-n-butyl, tri-n-hexyl-, and dicyclohexyl-(E)-hex-1-enylborane (642) have been studied by IR and by ^1H and ^{13}C NMR spectroscopy [497]. Though the complexation has been found to be somewhat general, weaker, resonance delocalized carbanions do not form such borates under the conditions studied.



642

Several organoaluminum reagents have been interacted with lithium metal to give interesting products. Thus, 643 and lithium give 644 apparently via reduction of the carbon-carbon double bond, internal o,o'-metalation, and rearrangement of the diethylaluminum from the benzylic to the ortho positions [498]. Similar rearrangements were observed in the conversion of 645 to 646 [499]. Both 644 and 646 were trapped by typical electrophiles such as methyl iodide. Sandwich compound 647 has been obtained from 648, lithium, and nickel(II) bromide [500].



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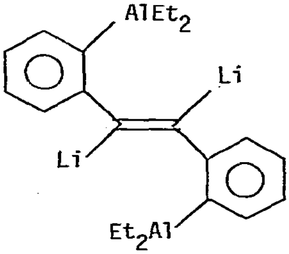

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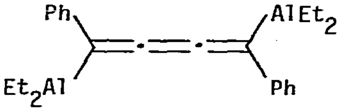

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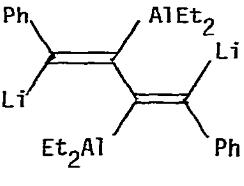

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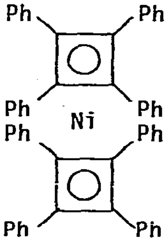

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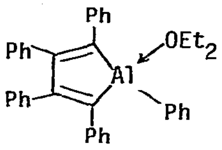


648

While 649, 650, and 651 all form boron ate complexes with methyllithium, only

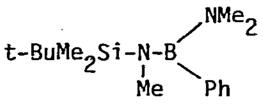
649 and 650 display proton acidity towards this reagent to give N-lithio derivatives [501]. The decomposition of the ate complexes is discussed.

$Me_2B\text{-}NH\text{-}NMe_2$ 649

$Me_2B\text{-}NH\text{-}SiMe_3$ 650

$Me_2B\text{-}NH\text{-}BMe_2$ 651

A large number of compounds containing boron, nitrogen, and silicon have been prepared usually from N-lithio reagents and halosilanes and -boranes. A few of the compounds included 652 [502], 653 [503], and 654 [504]. Phosphorus-boron system 655 has been obtained from 656 and butyllithium, then cyclized to 657 with MX_2 (M = Zn,Cd,Ni) [505].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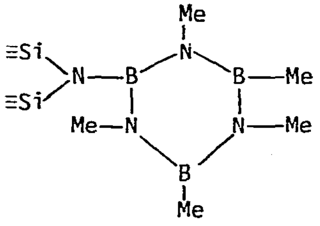
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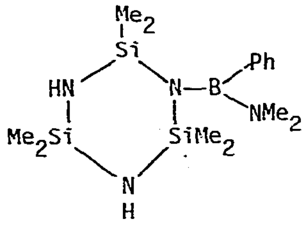
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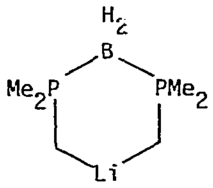
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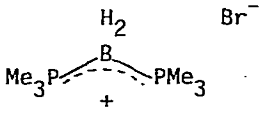
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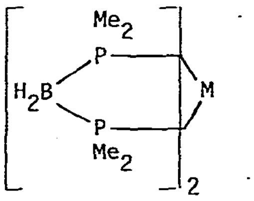
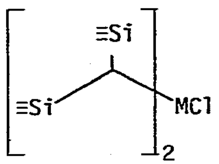

657

Boron and aluminum derivatives 658 (M = B,Al) have been obtained from the trichlorides and bis(trimethylsilyl)methyllithium [506]. The latter reagent has also been combined with the cadmium and mercury chlorides to give 659 (M = Cd,Hg).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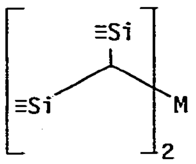
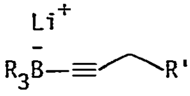
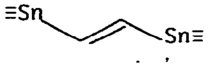

659

Acyclic trans-α,β-unsaturated ketones may now be prepared from 660, benzeneselenenyl chloride, trimethylamine N-oxide, and hydrogen peroxide [507]. Another paper described the conversion of gray elemental selenium to Li_2Se or Li_2Se_2 depending upon the stoichiometry by lithium triethylborohydride [508]. Such selenium species have been alkylated in situ to afford RSeR and RSeSeR, respectively.


660

Interaction of stannylethylene 661 with two equivalents of n-butyllithium and appropriate electrophiles to give 662 has been shown to proceed via sequential transmetalation-condensation rather than through the intermediacy of dilithioethylene 663 [509]. Another paper described the use of similar chemistry to prepare 664 from 665 and n-butyllithium [510]. In light of the previous paper, though, it is certainly possible that intermediate 666 could be trapped by electrophiles, then converted to organolithium species 667 by a subsequent transmetalation.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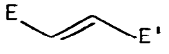
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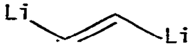
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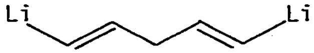
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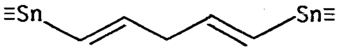
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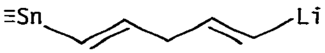
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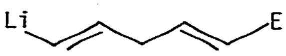
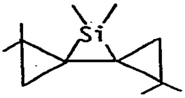

667

Reactions of silirane 668 with a variety of nucleophiles to afford ring-opened products have been reported [511]. Of interest in this review are condensations of 668 with lithium diethylamide and methyl- and phenyllithium to apparently give intermediates 669 and 670, respectively. LDIPA is suggested to yield an intermediate similar to 669 which is eventually converted to a disilazane.



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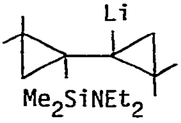

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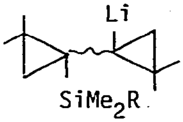
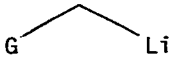


670

A variety of α-lithio compounds 671 (G = Ph_3Pb,Ph_3Sn,Ph_2Sb,Ph_2As,Ph_2P,PhTe, PhS) have been combined with aldehydes and ketones to afford hydroxy derivatives which have been converted to H_2C=CRR' by heat or acid [512]. The best yields were realized with the lead and tin compounds. Silyl sulfonium salt 672 has been converted to its ylide by s-butyllithium, then combined with α,β-unsaturated ketones to give cyclopropanes such as 673 [513].



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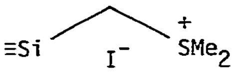

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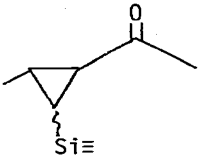
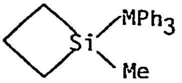


673

Silyl-, germyl-, and stannyllithium reagents continued to be employed in 1978. Such compounds were thus used to synthesize 674 (M = Si,Ge,Sn) from 1-chloro-1-methylsilacyclobutane [514], β-silylketones such as 675 from α,β-unsaturated ketones which can be desilylated to regenerate unsaturation by copper(II) bromide [515], acylsilanes 676 from acid chlorides [516], chiral germanium transition metal compounds such as 677 by displacement of carbonyl ligands [517], and α-alkoxylithium derivatives such as 678 by transmetalation of the related tribuyltin reagents, prepared themselves from tributylstannyllithium and aldehydes [518].



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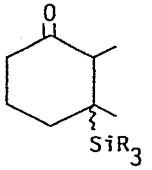

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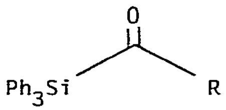
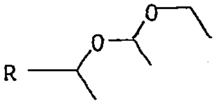


676

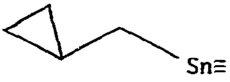
$Cp(CO)_2FeGePh_3$

677



678

A very thorough study of the reactions of trimethylstannyllithium, -sodium, and potassium with certain cyclohexyl and cyclopropylcarbinyl halides and tosylates has led the author to conclude that such reactions proceed by at least two competing pathways, one of which is free radical in nature [519]. For example, the tin reagents and cyclopropylcarbinyl bromide and iodide yield 679 and 680. An unrelated paper disclosed that triethyl- and triphenylgermyllithium directly displace the halogens of iodo- and bromotoluenes to afford triethyltolyl- and triphenyltolylgermanes such as 681 [520]. In contrast, chloro- and fluorotoluenes give cine substitution products with these reagents.



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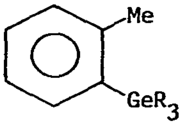
680

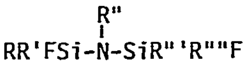


681

A rather large number of papers appeared again in 1978 which discussed compounds prepared from Groups IVB and VB of the periodic table. Among the many types of compounds prepared involving silicon and nitrogen were 682 from s-BuSiF$_3$ and LiNRR' [521], 683 from 684 and difluorosilanes [522], silylamidines 685 from lithio derivatives related to 684 and 686 [523], isocyanates such as 687 from lithiosilylhydrazides and phosgene [524], four-membered ring compounds 688 from 684 [525-527], and a variety of spiro compounds illustrated by 689 [528] and 690 [529] from N-

s-BuSiF$_2$NRR'

682

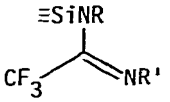


$RR'FSi\text{-}\overset{R''}{N}\text{-}SiR'''R''''F$

683

RR'FSiNR"Li

684



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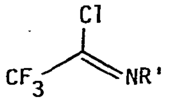
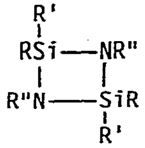


686

[(≡Si)$_2$NNCO]$_2$

687



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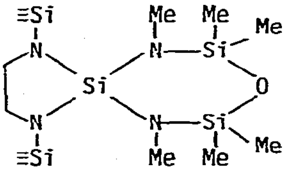

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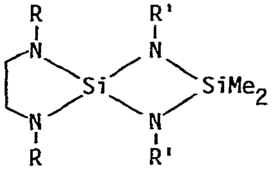

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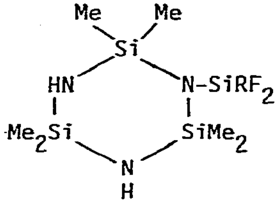
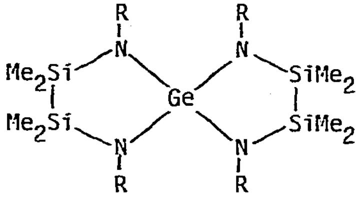


691

lithio species and halosilanes. Trisilazane 691, prepared by silylation of the lithio derivative of the parent heterocycle [530], has been found to undergo substitution of the side-chain fluorine, N-metalation, and ring coupling with lithiated amines [531].

Cyclic germanium compounds illustrated by 692 [532-534] and stannanes such as 693 as well as related spiro systems [535] have been prepared using N-lithio reagents with germyl- and stannylchlorides, respectively.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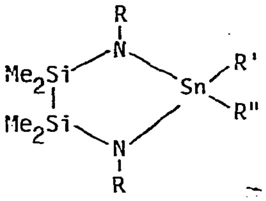

693

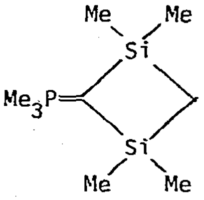
Silylphosphines 694 have been prepared from dilithiophosphines and chlorotrimethylsilane and from 695 and alkyl halides [536]. Cyclic derivative 696 has been synthesized from 697 and 698 [537]. Another paper described the preparation of a variety of cyclic silylphosphines illustrated by 699 [538].

$RP(Si\equiv)_2$

694

$(\equiv Si)_2PLi$

695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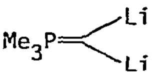
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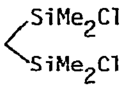
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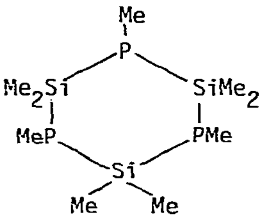

699

Pentaalkylstiboranes 700 (n = 0,1,2,3,4) have been synthesized by addition of methyllithium or lithiumtrimethylsilane to appropriate antimony halides [539].

Antimony compounds 701 and 702 (M = Si,Ge,Sn) have similarly been prepared from diphenyllithiumantimonide and metal chlorides [540].

$Me_nSb(CH_2SiMe_3)_{5-n}$

700

Ph_2SbMMe_3

701

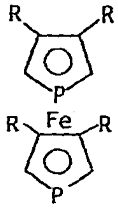
$(Ph_2Sb)_2MMe_2$

702

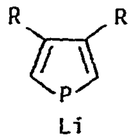
Four N-t-alkyl-O-t-butylhydroxylamines 703 have been synthesized from t-butyl peroxybenzoate and lithium amides (20-41%) [541]. Diphosphaferrocenes 704 have been obtained from 705 and iron(II) chloride [542]. Reagent 705 was prepared by reduction of the corresponding P-phenyl system by lithium metal.

t-RNHO-t-Bu

703

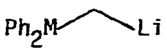


704



705

α-Lithio derivatives 706 (M = As,Sb) and 707 have been obtained by treatment of the corresponding bis(diphenylmetal)methanes with butyl- or phenyllithium [543, 544]. The carbanions have been alkylated and combined with aldehydes and ketones.



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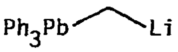
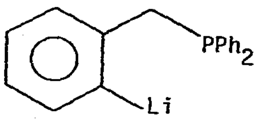


707

Other papers concerned with Group VB discussed the preparation of o-nickle, palladium, and platinum complexes derived from 708 and the metal chlorides [545], the synthesis of Et_3SbMe_2 from the corresponding dichloro antimony reagent and methyllithium [546], the condensations of 709 with propenyllithiums to afford monosubstituted products [547], and nucleophilic reactions of 710 with a variety of chlorine- and fluorine-containing electrophiles and unsaturated systems [548].



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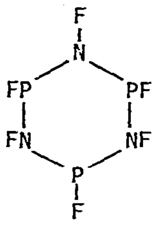
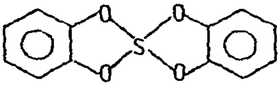


709

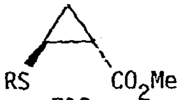
$(CF_3)_2S{=}NLi$

710

Papers dealing with the chemistry of chalcogen salts discussed the preparation of tetraoxysulfuranes such as 711 from lithium phenoxides and SF_4 [549], the stereochemical results in the reactions of lithium thiophenoxide and CF_3SLi with octahedral sulfur reagents such as $SF_4(OCF_3)_2$ [550], the synthesis of sulfur substituted cyclopropanes such as 712 from RSLi and methyl 4-bromocrotonate [551], the formation of 713 from RSLi and bromomethylidynetricobalt nonacarbonyl [552], the ring cleavage of cyclopropanes by PhSeLi illustrated by the conversion of 714 to 715 [553], and the preparation of 716 from PhSeLi, methyllithium, and chlorotrimethylsilane [554]. Reagent 716 has been added to a large number of aldehydes and ketones to afford products containing C-Se/O-Si bonds.



711

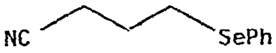


712

RSC(O)CCo$_3$(CO)$_9$

713

714



715

$PhSeSiMe_3$

716

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