LITHIUM

ANNUAL SURVEY COVERING THE YEAR 1979 *

EDWIN M. KAISER

Department of Chemistry
University of Missouri-Columbia
Columbia, Missouri 65211, USA

TABLE OF CONTENTS

---

* Lithium; Annual Survey covering the year 1978 see J. Organometal. Chem., Vol. 183 (1979) p. 1-105

1. REVIEWS AND BOOKS

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

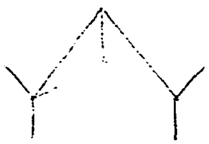
- Coordination chemistry of alkali and alkaline earth cations [1].
- Carbon-hydrogen acids [2].
- Absorption spectroscopy, emission spectroscopy, and photochemical reactions of alkali metal salts of organic anions [3].
- Stereochemistry and mechanism of ketone reductions by hydride reagents [4].
- Organometallic intramolecular-coordination compounds containing a nitrogen donor ligand [5].
- The use of organolithium reagents in organic synthesis [6,7].
- Heteroatom-facilitated lithiations [8].
- Methods of reactivity unpolung [9].
- Alkylation and related reactions of the metal enolates of ketones and aldehydes [10].
- Aldol and related reactions [11].
- Synthesis of aldehydes, ketones, and carboxylic acids from lower carbonyl compounds by carbon-carbon coupling reactions [12].
- Asymmetric carbon-carbon bond forming reactions using lithiooxazolines and lithioenamines with alkyl halides, and by reaction of chiral electrophilic oxazolines with organolithium reagents [13].
- Recent advances in asymmetric synthesis [14].
- New alternatives to oxidative phenolic coupling in natural products total synthesis by the use of quinoid precursors [15].
- Isocyanides and organometallic reagents in organic synthesis [16,17].
- Manipulation of fuctional groups using organoselenium reagents [18].
- Substitutions, additions, oxidative additions, and insertions of metal complexes with organic materials [19].
- A fourty year history of reductions effected by hydride reagents [20].
- A survey of novel and useful reactions discovered through research on prostaglandins [21].
- Synthesis of heterocyclopolyaromatic compounds from organometallic linkage of heteroaromatic compounds [22].
- Inorganic chemistry in liquid ammonia [23].
- Alkylidene complexes of niobium and tantalum [24].
- Organic synthesis by electrophilic substitution of organosilicon compounds [25].
- Synthetic methods for the preparation of aryl- and heteroaryltrimethylsilanes [26].

2. PREPARATION OF CARBANIONS

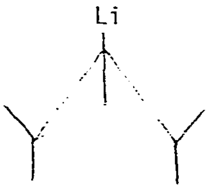
A. Metalation at sp^3 Carbon

Although it has been known for many years that a by-product in the alkali metal reductions of unsaturated substances in ammonia and low molecular weight amines is the corresponding alkali amide, only recently has the emphasis in such reactions been placed on the preparation of such bases [27]. Thus, lithium diethyl- and diisopropylamides may be conveniently prepared by reduction of isopropenylbenzene or phenanthrene in THF-ethyl ether and the amine. Such reductions are much slower in ethyl ether alone. Metalation of 14 different active hydrogen compounds by lithium diethylamide prepared in the above manner is described.

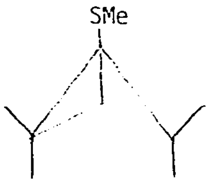
Additional examples of the lithiation of strained ring systems were disclosed in 1979. For example, treatment of bicyclobutane 1 with n-butyllithium·TMEDA gave 2 as evidenced by subsequent condensation with dimethyl disulfide to afford 3 [28]. A similar reaction on 3 itself yielded a 2:1 mixture of 4 and 5.



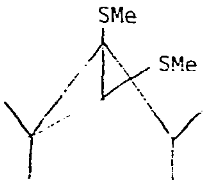
1



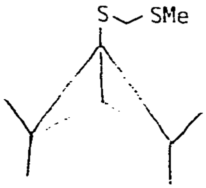
2



3

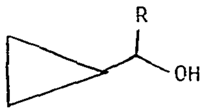


4

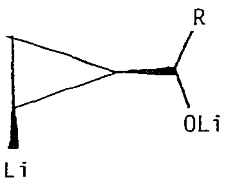


5

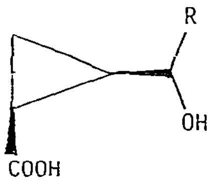
Metalation of cyclopropanes has been found to be enhanced when such rings are substituted with hydroxy groups [29]. For example, treatment of 6(R=Me, c-Pr, i-Pr, t-Bu) with i-propyllithium gave mostly or exclusively 7 since subsequent carbonation yielded 8 (73-100%).



6

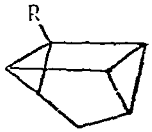


7

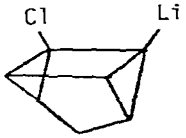


8

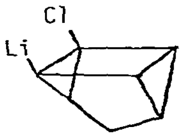
Quadricyclane 9(R=H) has been lithiated by n-butyllithium·TMEDA to give 9(R=Li) which, in turn, has been converted to the chloro derivative 9(R=Cl) by p-toluenesulfonyl chloride [30]. Subsequent treatment of the latter chloride with n-butyllithium to afford butyl derivative 9(R=n-Bu) presumably proceeds via 10 and 11 and the related bridgehead olefins as evidenced by trapping experiments with methyl bromide and with anthracene.



9



10



11

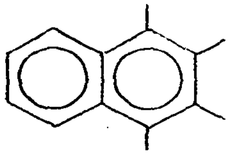
Turning to other types of compounds, sterically-crowded 1-hydryl-F-neopentane (12) has been metalated by methyllithium·lithium bromide to yield 13 which has been halogenated with molecular iodine and bromine to give 14(X=I,Br) [31].

$(F_3C)_3CCF_2H$ 12

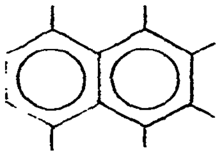
$(F_3C)_3CCF_2Li$ 13

$(F_3C)_3CCF_2X$ 14

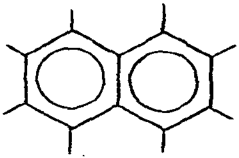
Polymethylnaphthalenes 15-17 have been interacted with excess n-butyllithium-TMEDA and the resulting metalated derivatives trapped with chloromethylsilane or methyl iodide [32]. Despite MO calculations to the contrary, each of the hydrocarbons gave substantially more of the 2-lithiomethyl than of the 1-lithiomethyl derivatives. The results are discussed in terms of the relative coplanarities of the alkyl groups with the aromatic ring, and peri interactions with the bulky metalating agent. Not surprisingly, polymethylnapthalene 18 underwent metalation more slowly than 15-17.



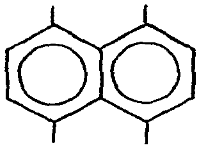
15



16

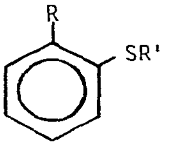


17

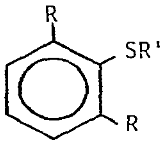


18

Further work on the metalation of certain alkylthiobenzenes was described this past year [33]. Thus, compounds 19(R=Me,Et; R'=Me,i-Pr) and 20(R=Me,Et; R'=Me,i-Pr) were treated with n-butyllithium both in the presence and absence of TMEDA, then carbonated to afford appropriate carboxylic acids. It was found that while metalation occurred on the ring methyl, thiomethyl, and hydrogen atom ortho to the sulfur (when present) in ether alone, mostly thiomethylic or ring metalation were realized in the presence of TMEDA.

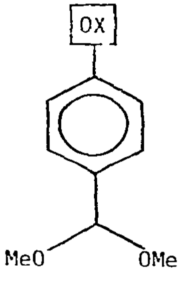


19

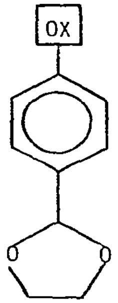


20

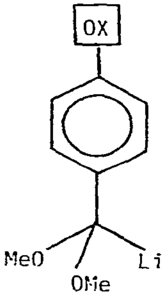
2-Arylacetals 21 and 22 have been metalated by n-butyllithium in THF to afford 23 and 24, respectively as evidenced by quenching with methanol-O-d [34]. Lithio salt 24 was also condensed with several alkyl halides and carbonyl compounds. In contrast, similar reaction of acetal 25(R=Ph) resulted only in the formation of aryllithium 26(R=Ph) while 25(R=H) gave 70% ring- and 30% lateral products. It is concluded that the acetal proton may be removed in such systems provided it can occupy an "equatorial-like" conformation [35].



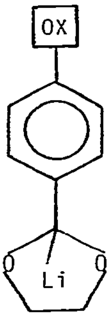
21



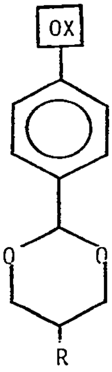
22



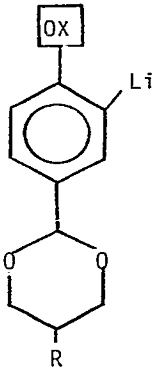
23



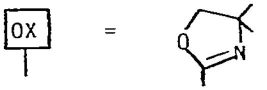
24



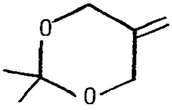
25



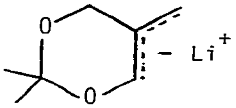
26



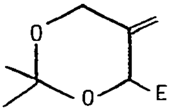
Regioselective lithiation of methylidene-1,3-dioxane 27 at the 4-position has been effected by sec-butyllithium in THF at low temperature [36]. The resulting allyl carbanion 28 has been condensed with certain electrophiles to give 29 and/or 30 usually in excellent yields.



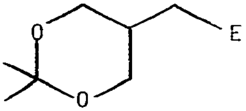
27



28



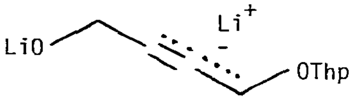
29



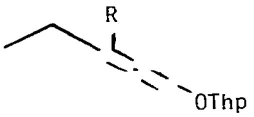
30

Lithium 4-(2-tetrahydropyranyloxy)-2-butynolate (31) has been metalated by t-butyllithium to give 32, alkylation of which yields 33 [37]. Subsequent lithiation of 33 to give 34 followed by a second alkylation, then cyclization has been shown to constitute an excellent preparation of substituted furans.

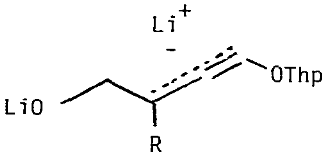
31



32

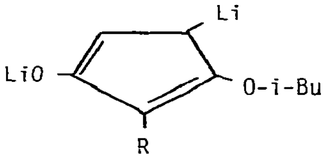


33

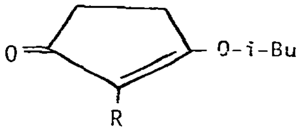


34

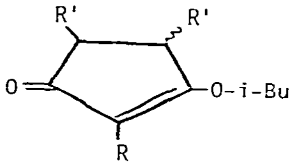
Allyloxy carbanions 35 have been similarly generated from the parent compounds 36(R=H,Me,Et) and LDA or lithium bis(trimethylsilyl)amide, then condensed with methyl iodide or formaldehyde to afford products such as 37 [38].



35

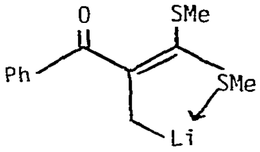


36

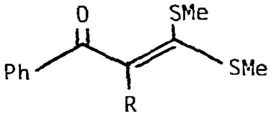


37

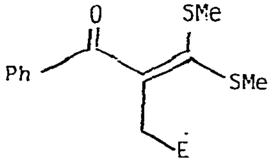
Allyl anion 38 in which the charge is stabilized by sulfur has been prepared from the parent compound 39(R=Me) and LDA [39]. The anion was condensed with a variety of electrophiles to give 40. Interestingly, metalation of 39 when R≠Me (for example, Et,H,OMe) gave rise to dipole stabilized anions 41 which underwent cyclization to thiophene derivatives [39,40]. An unrelated paper discussed the conversion of the previously reported dilithioallyl mercaptan derivative 42 and the related methallyl system to Grignard reagents by means of magnesium bromide etherate [41].



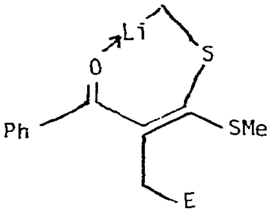
38



39



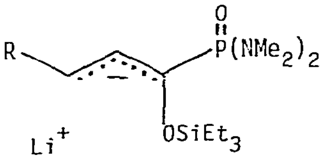
40



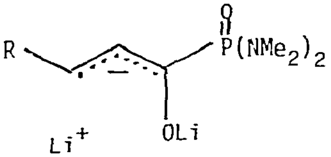
41

42

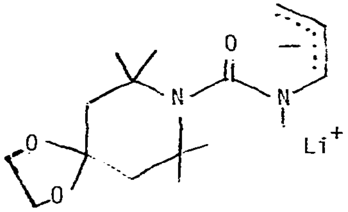
Other allylic carbanions stabilized by resonance into functional groups or through dipole interactions which were prepared in 1979 by metalation included 43(R=Ph, CH_3) [42], 44(R=Ph,Me,H) [42], 45 [43], 46 [44], and 47 [45]. Condensations of each of these anions with electrophiles are described.



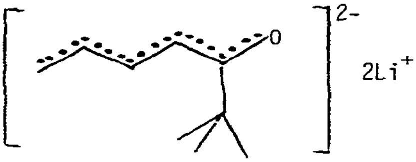
43



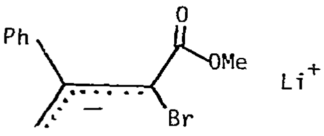
44



45



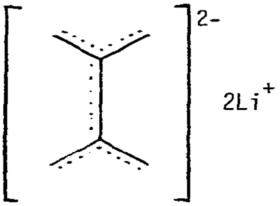
46



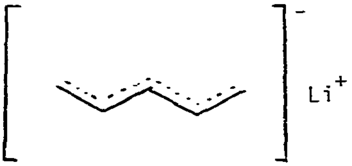
47

Allyl anions themselves continued to be investigated. Thus, a general method has been presented for the preparation of dienyl anions from both conjugated and non-conjugated dienes using alkali metals in THF in the presence of triethylamine or TMEDA [46]. The procedure allowed the isolation of eight different open-chain or cyclic crystalline dienyl anions. The presence of the amines inhibits polymerization, sometimes completely, in such reactions. The results of hydrolyses and methylations of the anions are discussed.

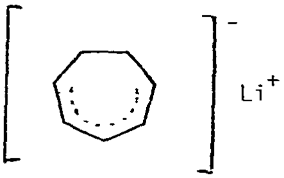
The above mentioned polymerization has also been avoided in the preparations of 48, 49 and 50 by metalating the parent 1,3-dienes by n-butyllithium-potassium t-butoxide [47].



48



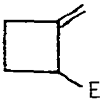
49



50

Methylenecyclobutane has been metalated by n-butyllithium·TMEDA to afford 51 [48]. Subsequent condensations of 51 with various electrophiles to give mixtures of 52 and 53 have been employed in the synthesis of various natural products.

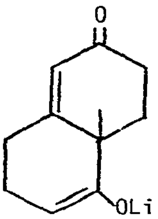
51



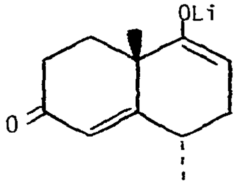
52

53

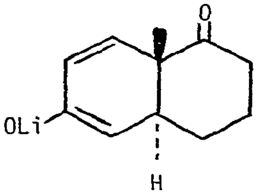
Turning to the area of carbanions stabilized by functional groups other than unsaturated hydrocarbons, three enolates, 54, 55, and 56, have been prepared under kinetic conditions (LDA in THF) from 57, 58, and 59, respectively [49]. Several condensations of the enolates are described. It should be noted that 54-56 possess a carbonyl unit in addition to the one providing delocalization to the anions.



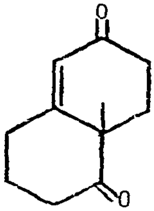
54



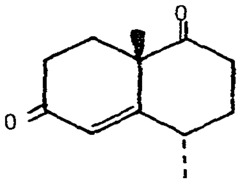
55



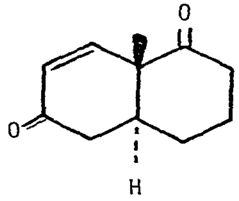
56



57

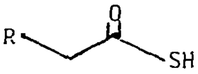


58

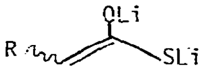


59

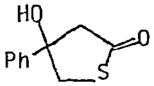
Interaction of thioacetic acids 60(R=H,Me) with two equivalents of LDA in THF has provided the first examples of dilithio derivatives 61(R=H,Me) [50]. Such reagents have been combined with aldehydes, ketones, and chloroketones, generally in excellent yields. The use of the latter electrophiles provides a convenient route to thiolactones illustrated by 62.



60

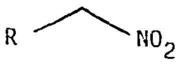


61

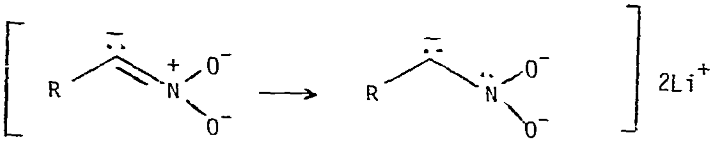


62

Several full papers appeared in 1979 which discussed two-fold lithiation of certain aliphatic nitro compounds by butyllithium in THF in the presence of HMPA [51,52,53]. Thus, 63($R=H,Et,i\text{-}Pr,n\text{-}C_5H_{11},Ph,SPh$) is converted to 64 via 65; the acidity of the α-proton of 65(R=i-Pr) is estimated to be similar to that of diisopropylamine. A very large number of condensations of 64 are described. Similarly, β-arylnitroethanes 66 are dilithiated to afford 67 [53]. While condensations of 64 give products such as 68, those of 67 yield β-substituted materials 69.

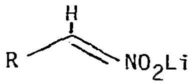


63



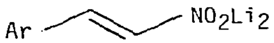
64

As a part of the synthesis of functional phosphines with an optically active phosphorus, 70 has been metalated by n-butyllithium·TMEDA to give 71 which has been condensed with several esters, benzophenone, and benzonitrile to yield 72 [54]. Esters 73(R=Et,i-Pr; R'=H,Me) have been converted to 74 by LDA, then combined with aldehydes and ketones to afford 75 (48-68%) [55]. The R' and R" of 75, originally part of the aldehyde or ketone, were hydrogen, aliphatic and aromatic.

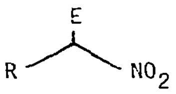


65

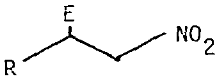
66



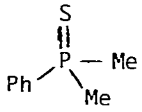
67



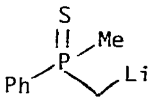
68



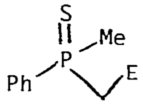
69



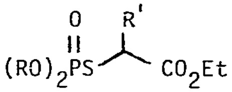
70



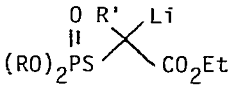
71



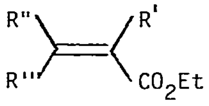
72



73

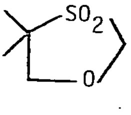


74

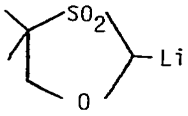


75

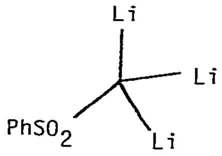
1,3-Oxathiolane 76 has been found to serve as a useful carbonyl equivalent because it can be conveniently metalated to 77 by n-butyllithium in THF, alkylated or condensed with aldehydes or ketones, and demasked to the substituted formyl moiety under thermal rather than hydrolytic conditions [56]. Another paper reports trilithiation of methyl phenyl sulfone and methyl naphthyl sulfone to give organometallics such as 78 [57].



76

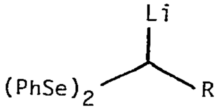


77

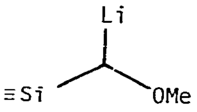


78

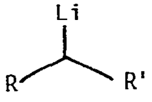
1,1-Bis(phenylseleno)alkyllithiums 79(R=Me,c-Hx) have been prepared by metalation of the parent compounds with lithium tetramethylpiperidide in HMPA/THF [58]. Several condensations are described. Reagents 80 [59] and 81(R=R'=$PbPh_3$,$SnPh_3$, $SbPh_2$, and combinations) [60] have been prepared similarly using s-butyllithium and lithium cyclohexylamide, respectively. Reagent 80 combines with aldehydes and ketones to ultimately afford aldehydes. Finally, phosphonate 82, synthesized from the parent compound and LDIPA, has been found to constitute a α-hydroxybenzyl anion equivalent since acylations of it eventually lead to α-hydroxyketones [61].



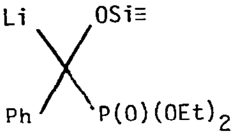
79



80



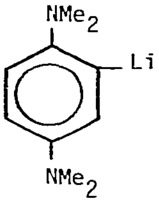
81



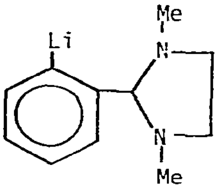
82

B. Metalation at sp^2 Carbon

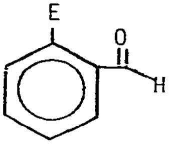
Heteroatom facilitated lithiations on substituted aromatic systems continued to be studied in 1979. Thus, o- and p-phenylenediamines have been converted to o-lithio derivatives illustrated by 83, then condensed with benzophenone or used to effect polymerization reactions [62]. Similar results were achieved on 1,3-dimethyl-2-phenylimidazolidine to give 84 [63]. The latter reagent was combined with a variety of electrophiles to yield, after hydrolysis, substituted benzaldehydes 85. Metalation of the related o-tolylimidazoline resulted in side-chain lithiation.



83

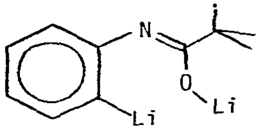


84

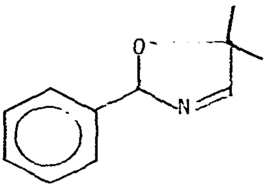


85

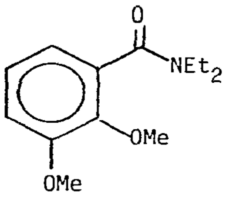
Several N-pivaloylanilines have likewise been o-lithiated with n-butyllithium to afford, for example, 86 [64]. Lateral metalation was realized on the related o-tolyl derivative. Two other studies described competition effects between two different functional groups with respect to their ability to direct such metalations. In the first one, disubstituted benzenes were treated with s-butyllithium·TMEDA to show that the tertiary amide function is superior to sulfonamide, oxazoline, methoxy, dimethylaminomethyl, chloro, carboxyl, and methyl [65]. The N-lithio-N-methylamide group was found to be a somewhat better director than the N,N-diethyl moiety. In the second study, an intermolecular one, equimolar amounts of phenyl oxazoline and various amides and sulfonamides were allowed to compete for only one equivalent of n-butyllithium [66]. It was found that the oxazoline group in 87 does not compete effectively with the other functional groups. However, it was also shown that the o-lithio derivative of 87 can itself metalate certain of the other materials, for example, benzenesulfonamide. All of the above o-lithio derivatives were combined with appropriate electrophiles. Similar ring metalation adjacent to the amide group of 88 has been employed as part of a convergent route to several phthalideisoquinoline alkaloids [67].



86

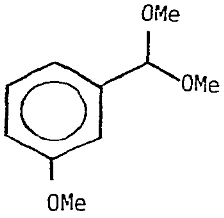


87

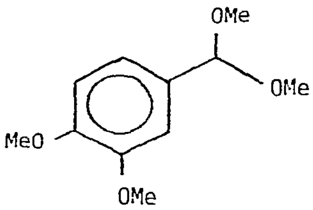


88

Benzaldehydes substituted in the 2,3- and 2,3,4-positions have been obtained by o-lithiation of dimethyl acetals such as 89 and 90, respectively followed by condensation and hydrolysis [68]. Several examples are listed though the metalation failed when the acetals were already substituted in one of the ortho positions. In another paper, the relative directive abilities of alkoxy versus alkylthio moieties has been reexamined to show that the former have a stronger orientating effect than the latter [69].

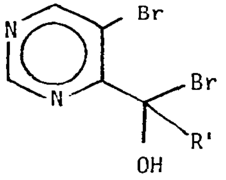


89

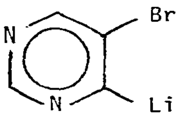


90

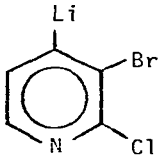
5-Bromopyrimidine has been directly lithiated by LDA/ether in the presence of carbonyl compounds to afford 91 via 92 [70]. In another study, the pyridine ring of 3-bromo-2-chloropyridine has been found to similarly undergo metalation by n-butyllithium to yield 93 [71]. Possible pathways leading to the latter material are discussed.



91

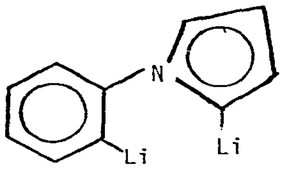


92

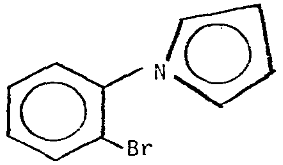


93

Dilithiopyrrole 94 has been prepared from 95 and two equivalents of n-butyllithium in ether [72]. Though a two-fold condensation with benzophenone was realized, reactions of 94 with other electrophiles were not as successful. A very thorough study of the lithiation of six N-alkylpyrroles by n-butyllithium under various conditions has also been described [73]. As the size of the N-alkyl group was increased, the total yield of lithiopyrroles decreased while the ratio of 2,4- to 2,5-dilithio derivatives increased. The effect of a variety of solvents is discussed.

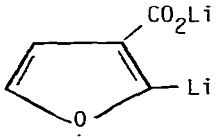


94

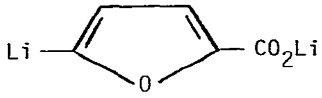


95

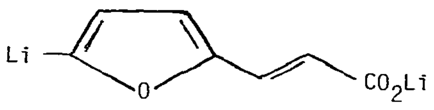
Dilithio derivatives 96, 97, and 98 have been generated from 3-furoic acid, 2-furoic acid, and 2-furylacrylic acid, respectively, and LDA [74]. Condensations of each of the dianions with electrophiles are described. Similar metalation of 5-ethoxyoxazole 99 with n-butyllithium has been found to lead to ring-opened isocyanoacetic acid derivative 100 [75]. The latter has been alkylated by several alkyl halides to yield 101.



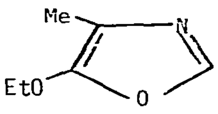
96



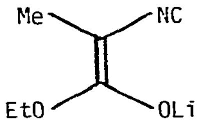
97



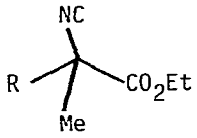
98



99

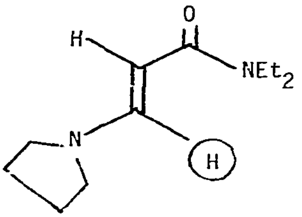


100

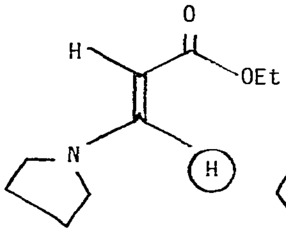


101

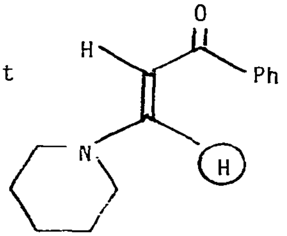
Turning to lithiation of non-aromatic systems, acrylic acid derivatives 102-105 with t-butyllithium and/or LDA have been shown to undergo metalation predominately at the β-hydrogen, that is the circled hydrogen atom [76]. In contrast, 106 is metalated at the β- and α-hydrogens at -113° and -76°, respectively while acrylonitriles 107 and 108 are lithiated mostly alpha to the cyanide [76,77]. Finally, sulfoxide 109(R presumably = Et) is metalated alpha to the sulfinyl moiety [77]. The results of some ab initio and semi-empirical calculations are presented to explain the experimental results [76]. A separate paper described several condensations of the α-lithio derivative of 107 [78].



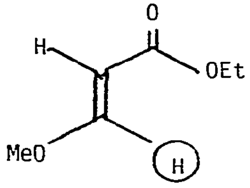
102



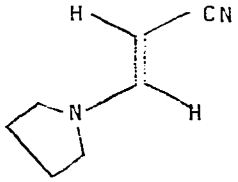
103



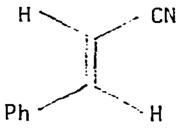
104



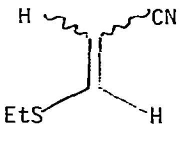
105



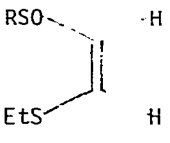
106



107

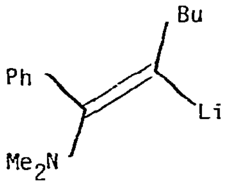


108

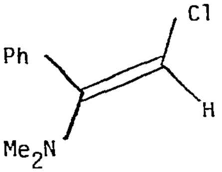


109

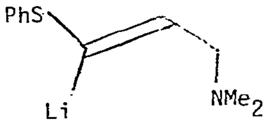
Other vinyllithium reagents prepared by vinyl metalation of the parent compounds were 110 from 111 [79], 112 [80], 113 [81], 114 [82], 115(R=Ph,Me) [83], 116 and related polylithio derivatives [84], and pyrans 117(R=H,Me) [85]. Dilithio salt 114 was also synthesized by dilithiation of epoxysulfone 118 [82]. Simple alkyllithiums or LDA were employed in each case except that of 117 where butyllithium-potassium t-butoxide was employed. Condensations of each of the anions with electrophiles are described.



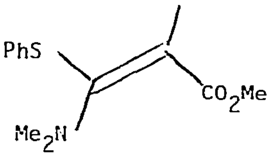
110



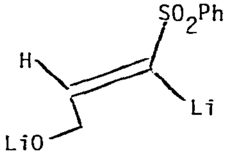
111



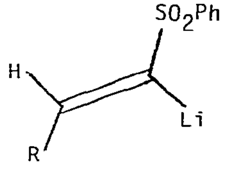
112



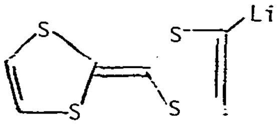
113



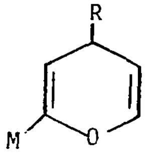
114



115



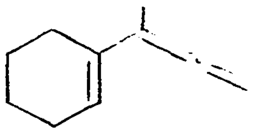
116



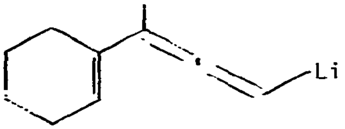
117

118

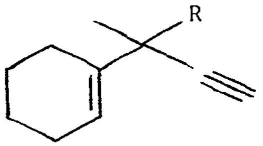
Lithiation of allenes also continued to be studied last year. Thus, two papers discussed the preparation and reactions of five different vinylallenyllithiums, prepared from the parent compounds and n-butyllithium [86,87]. The investigation is illustrated by the conversion of 119 to 120, alkylation of which afforded 121-123. In most cases, the major products corresponded to 123.



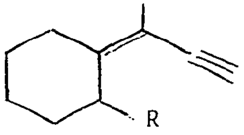
119



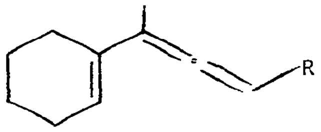
120



121

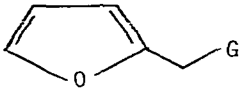


122

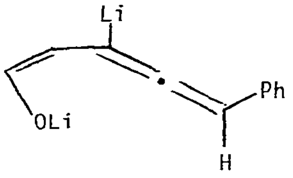


123

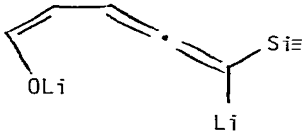
Additional studies have been performed on the ring-opening reactions of furfuryl carbanions [88]. Thus, treatment of 124(G=Ph,$SiMe_3$) with two equivalents of n-butyllithium has been shown to afford 125 and 126 as evidenced by trapping experiments with chlorotrimethylsilane. Intermediates 125 and 126 arise from secondary metalation of the β- and δ-hydrogen atoms, respectively, of 127, the initial ring-opened product obtained from 128. Trianionic enolates derived from such furans have also been proposed. For example, 124, three equivalents of n-butyllithium, and excess chlorotrimethylsilane give 129 (92%). Condensations of the carbanions with other electrophiles are discussed.



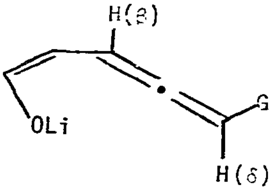
124



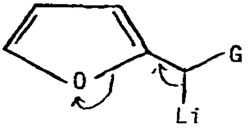
125



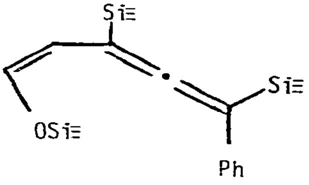
126



127

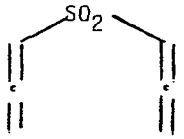


128

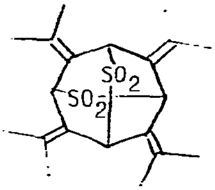


129

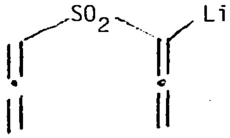
Diallenyl sulfone 130 has been converted to dithiaadamantane 131 by n-butyllithium [89]. The reaction which presumably proceeds via 132 appears to represent the first reported example of a base-catalyzed cyclodimerization of an allenic system.



130

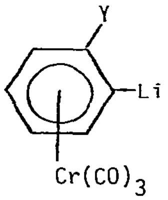


131

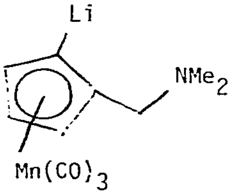


132

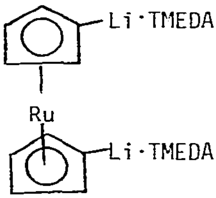
Finally, in this section, several transition metal organometallics have been metalated by n-butyllithium then combined with electrophiles to afford appropriate derivatives. Among those reported were 133(Y=H,OMe,F,Cl) [90,91] and 134 [92]. Lithiation of ruthenocene in the presence of TMEDA gave mostly 1,1'-dilithio derivative 135 accompanied by some monolithio and 1,1',3-trilithio derivatives [93].



133



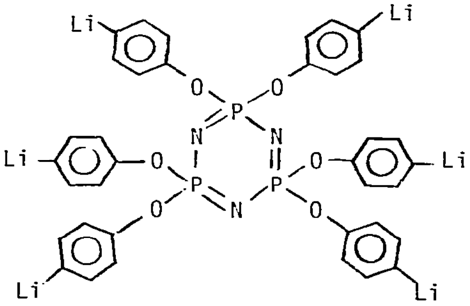
134



135

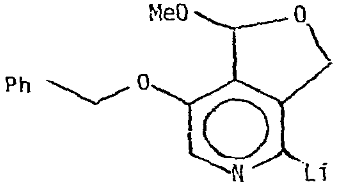
C. Lithium-Halogen Exchange

Hexalithiocyclotriphosphazene 136 has been obtained from the corresponding hexabromo derivative and n-butyllithium at -40° [94]. The organometallic was combined with electrophiles including carbon dioxide, chlorodiphenylphosphine, and chlorotriphenylstannane.

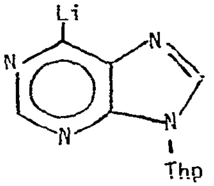


136

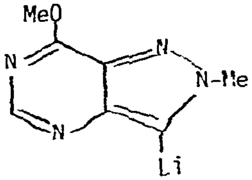
Lithium-halogen exchange has been employed on several heterocyclic rings themselves. Thus, 137 [95], 138 [96], 139 [97], and 140 [97] were obtained upon interaction of n-butyllithium with the corresponding bromo (for 137, 139, and 140) or iodo (for 138) derivatives. Temperature effects were observed in the formation of 138 since it underwent isomerization to 141 when the reaction was allowed to warm from -130° to -78° [96]. Each of the above anions was combined with electrophiles.



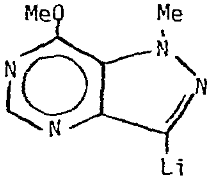
137



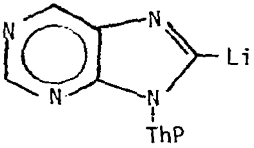
138



139

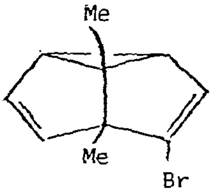


140

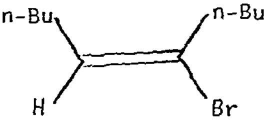


141

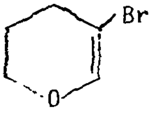
The following vinyl halides have similarly been converted to vinyllithium reagents by t- or n-butyllithium, then condensed with certain electrophiles to afford derivatives. Of course, 145 and related compounds give dilithio salts upon such treatment.



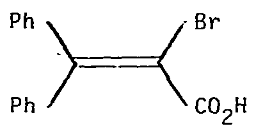
142 [98]



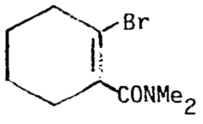
143 [99]
(and E-isomer)



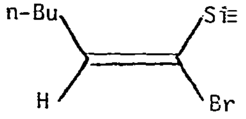
144 [100]



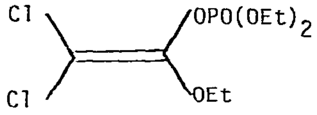
145 [101]



146 [102]

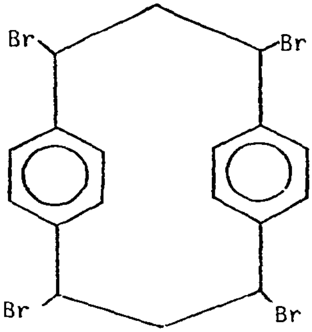


147 [103]
(and E-isomer)



148 [104]

Finally, lithium-bromine exchange on 149 has been employed in the preparation of [1:2,9:10]bismethano[2:2]paracyclophane [105].

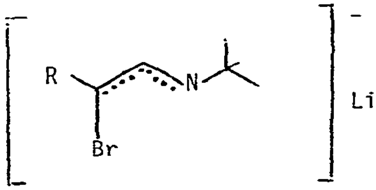


149

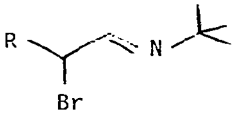
D. Miscellaneous Methods

The attention of those chemists who read Japanese is directed to an article which discusses the synthesis and properties of organoalkali compounds [106]. The same issue also contains articles on a wide variety of other organometallics.

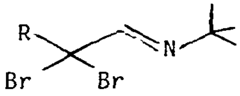
Bromoimine anions 150(R=H,Me,Et,n-Am) have been prepared from 151 and LDA and from 152 and n-butyllithium [107]. Alkylations of 150 were realized on the carbon atom bearing the bromine.



150

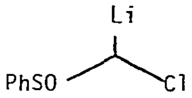


151

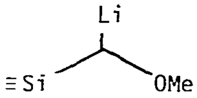


152

Other carbenoids prepared included 153 from chloromethyl phenyl sulfoxide and LDA [108] and 154 from methoxymethyltrimethylsilane and s-butyllithium [109]. The former reagent was alkylated while the latter one was combined with aldehydes and ketones.

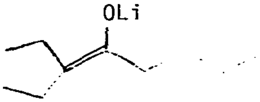


153

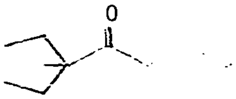


154

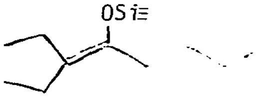
Diethylketene has been converted to directed enolate 155 by n-butyllithium, then methylated to give 156 [110]. Silylation of 155 by chlorotrimethylsilane afforded mostly 157.



155

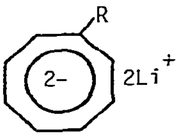


156

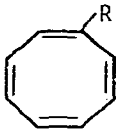


157

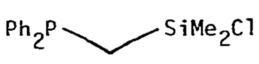
Provided that oxygen is rigorously excluded, treatment of cyclooctatetraene with a variety of alkyl- and phenyllithiums has been shown to yield dilithio salt 158 [111]. Subsequent treatment with molecular oxygen affords the corresponding 159 (45-76%). Another addition reaction involving 160, cyclopentadienyllithium, and n-butyllithium gives 161, a compound capable of directed attachment to various transition metal centers [112].



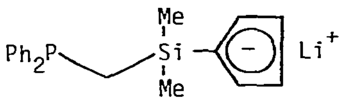
158



159

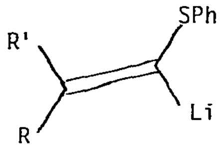


160

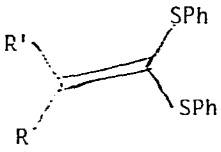


161

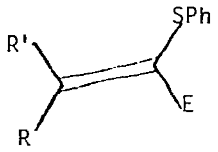
Sulfur-stabilized vinyllithiums such as 162(R=aliphatic) have been obtained from 163 by reduction with lithium naphthalenide, then combined with a variety of electrophiles to afford 164 [113]. Reduction has also been employed in a simple preparation of t-butyllithium from the chloride and lithium containing 1-2% of sodium [114].



162



163



164

1,5-Dichloropentane and other similar materials have been converted to dilithio derivatives using lithium vapor under conditions milder than used previously [115]. Deuteration of the 1,5-dilithiopentane revealed the presence of a variety of products including but not limited to C_2D_2 (28%), C_3D_4 (19%), and $DCH_2(CH_2)_3CH_2D$ (31%).

Hexalithioethane, Li_6C_2, has been obtained in high yield in a purity of 99% from lithium vapor and diethylmercury [116]. The authors speculate that C_2Li_6 as well as C_2Li_4 are probably formed by a combination of two lithium substituted methyl radical or carbenoid species.

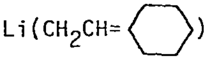
Two full papers appeared in 1979 which discussed the preparation of a variety of allyllithium reagents including 165-169 from tin compounds and alkyllithiums [117,118]. A similar transmetalation was employed to synthesize 170 [119]. Each of the allyllithiums was combined with a variety of electrophiles.

$Li(CH_2CHCHC_6H_{13})$

165

$Li(CH_2CHCHPh)$

166



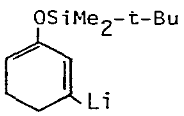
167

$Li(CH_2CMeCHEt)$

168

$Li(F_2CCH_2CH_2)$

169



170

3. STRUCTURAL STUDIES

Structural investigations of organolithiums were few in number in 1979. Figure I shows the structure of bis(lithium-N,N,N',N'-tetramethylethylenediamine)—(all-trans-1,5,9-cyclododecatrienenickel) in which the trigonal bipyramidal geometry of the nickel atoms and the centers of three olefinic double bonds in the trigonal plane and lithium atoms in apical positions are distorted [120]. Such distortion is not significant in the structure of tris(N,N,N',N'-tetramethyl-2-butene-1,4 -diamine)dilithium nickel, the numbering system of which is shown in Figure II [120]. The nickel-olefinic carbon bond lengths in the two compounds average 1.99 and 2.000 Å, respectively.

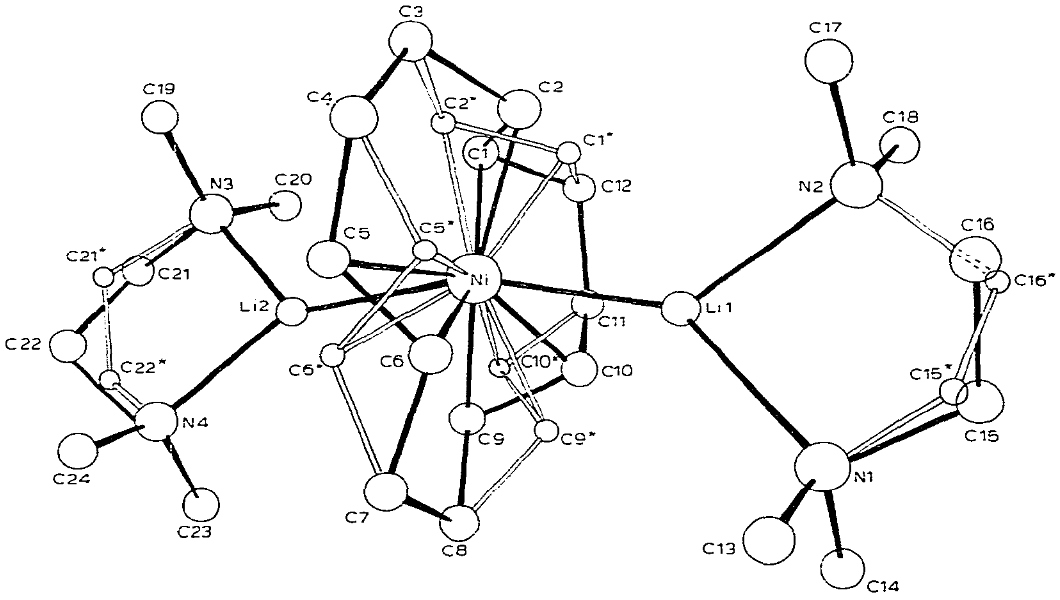
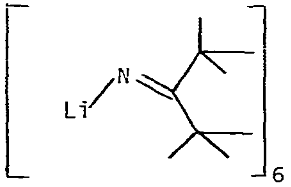


Figure I

An x-ray study of 171 revealed the presence of a folded chair arrangement of lithium atoms held together by triply bridged amino groups [121]. Such bonding is believed to represent the first example of electron-deficient bridging through nitrogen atoms of organonitrogen ligands. Two possible orientations of the lithium atoms of the hexameric structure are shown in the paper.



171

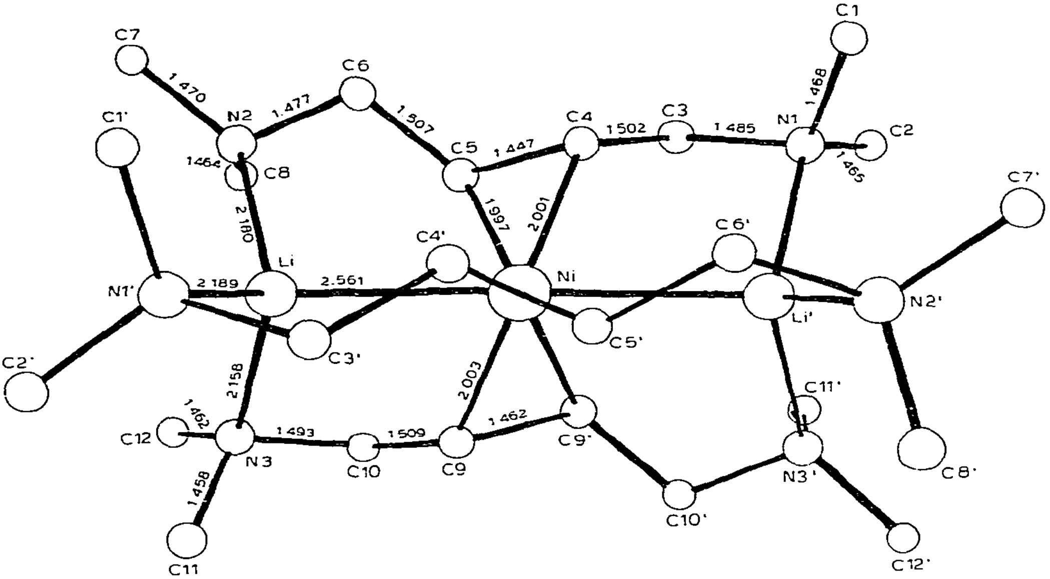


Figure II

4. APPLICATION OF MOLECULAR ORBITAL THEORY

In contrast to the previous section, a large number of papers discussed the results of MO calculations applied to a variety of organolithiums. Thus, the optimum geometries of 172-177, lithium cluster species observed in the fragmentations of ethyl- and t-butyllithium, were computed and the STO-3G energies (a.u.) were found to be 172: -146.604; 173: -107.460, 174: -68.326; 175: -53.634; 176: -46.244; 177: -92.897 [122]. The ΔE's are listed for possible pathways through which the optically excited parent 178 could be transformed into products.

$Li_4Me_3^+$ 172

$Li_4Me_2^+$ 173

Li_4Me^+ 174

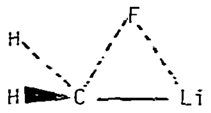
Li_2Me^+ 175

$LiMe^+$ 176

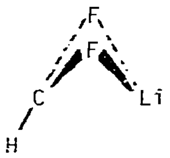
Li_2Me_2 177

Li_4Me_4 178

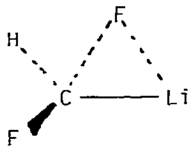
While ab initio Gaussian calculations on CH_2F anion revealed that it is much more stable in the pyramidal form than in the planar form [123], complete geometry optimization of a variety of structures for CH_2FLi revealed three local minima, the most stable of which is represented by 179 [124]. This structure in which all valencies of carbon extend into a single hemisphere (umbrella-shape) is best interpreted in terms of an intimate ion pair between F^- and CH_2Li^+. Several isomers have also been found for CHF_2Li [125] and for CCl_3Li [126], the most stable of which are represented by 180-183. While 180 and 182 can be considered lithiocarbanions, 181 and 183 are analogous to 179 since they may be pictured as carbocations bonded to halide ions.



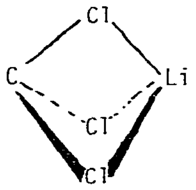
179



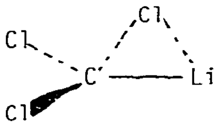
180



181



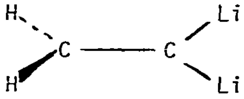
182



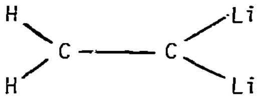
183

The geometries, force constants, charges, and gas phase acidities of mono-, di-, and trinitromethanes as well as their anions have been studied employing both ab initio STO-3G and CNDO/2 methods in an effort to compare the two methods [127]. While the methods closely paralleled each other, agreement with experimental quantities in absolute terms favored ab initio in some instances and CNDO/2 in others

Additional calculations on 1,1-dilithioethene using state-of-the-art levels of reliability were reported in 1979 [128]. The authors conclude that the compound has a twisted triplet ground state (184) which lies ∿ 1.4 kcal lower than the planar triplet conformation 185.

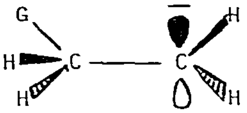


184

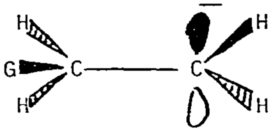


185

The usual retention of stereochemistry in nucleophilic vinylic substitutions via addition-elimination has been ascribed to hyperconjugation in intermediates such as 186 [129,130]. Though hyperconjugation is at a maximum in 186, it is zero in 187 where the interacting orbitals are perpendicular. The barriers to rotation in the intermediates, calculated using STO-3G methods, were found to be in the order $G=Cl>>OMe\sim OH>F\sim SH>CN\sim CF_3>NH_2\sim PH_2>Me>H\sim SiH_3>BH_2$ [130].



186



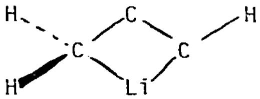
187

MO calculations have also been applied to the stereochemistry of alkene-forming elimination reactions [131]. The authors conclude that "the feasibility of both syn and anti modes of elimination is enhanced by maximizing the overlap of the developing carbanionic orbital at C_β with the C_α-leaving group σ^* orbital." They also suggest that "the less favored mode of syn elimination occurs by the concerted process of leaving-group expulsion at C_α and the concomitant inversion of configuration at C_β."

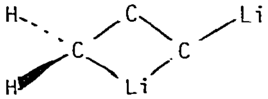
A very thorough paper described the results of calculations applied to hypothetical isolated monomers of lithioallenes, -propynes, and -cyclopropenes [132]. Although a large number of structures are listed, the most favorable ones energetically are as follows: C_3H_3Li - 188 and 189; $C_3H_2Li_2$ - 190; C_3HLi_3 - 191; and C_3Li_4 - 192. In most cases, classical structures based on the corresponding hydrocarbons were much less stable than other arrangements which could better utilize the multicenter bonding capabilities of lithium. Because of the latter, 1,2-dilithiocyclopropene is said to be better represented by 193.

$Li\text{-}C{\equiv}C\text{-}CH_3$

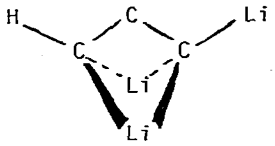
188



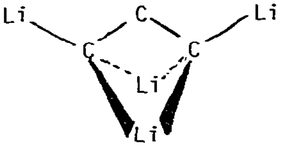
189



190



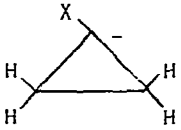
191



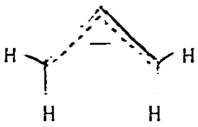
192

193

The relative energies of planar and bent 194(X=H,F,Cl) have been obtained to demonstrate substantial barriers to inversion of the atoms X about the plane of the rings [133]. Such findings are consistent with configurational retention in these ions. The authors indicate that α-substitution of halogen for hydrogen does not appear to stabilize such species. Another paper discusses the construction of state correlation diagrams for the interconversion of 194(X=H) and 195 as well as for the analogous aziridine, diaziridine, and oxaziridine systems [134].



194



195

An ab initio study of the cyclohexadienyl anion using a more diffuse set than 4-31G has indicated in agreement with earlier semiempirical predictions that the greatest portion of the negative charge is located in the 4-position of the molecule [135]. The same authors also published similar work on monofluorocyclohexadienyl anions [136].

Other papers in this area were concerned with homocyclooctatetraene dianion [137], the deprotonation energies of polycyclic benzenoid methylarenes and methylazaarenes [138], and the effect of the polarity of the medium and alkali metal cations on the rate of propagation in anionic polymerizations [139].

5. SPECTROSCOPIC DETERMINATIONS

A. NMR Spectroscopy

Several invited lectures at a recent symposium on ions and ion pairs in honor of Prof. Michael Szwarc were concerned with NMR and have now been published. Among them were papers dealing with optical and NMR investigations on alkali ion pairs of carbanions and nitranions [140], multinuclear NMR studies of alkali ions in nonaqueous solvents [141], ion pairing and reactivity of β-ketoenolates [142], and stereochemical effects of ion pairing in anionic vinyloligomerization and related carbanion reactions [143]. Another paper was concerned with the structure of sodium, potassium, and rubidium biphenyl ion pairs in solution and in the solid state and is listed here for completeness [144].

Confirmation of the earlier proposal that splitting due to ^{13}C, ^{7}Li coupling is often not observed in the ^{13}C-NMR spectra of alkyllithiums because of an averaging of ^{13}C, ^{7}Li coupling by a combination of C-Li bond exchange and ^{7}Li quadrupole relaxation has been achieved by obtaining appropriate NMR spectra of n-propyllithium variously enriched in ^{13}C (on C_1) and ^{6}Li [145]. Specifics are listed for the spectra of 196-199.

$H_3C-CH_2-CH_2-Li$

196

$H_3C-CH_2-{}^{13}CH_2-Li$

197

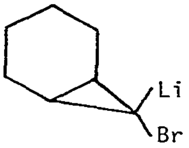
$H_3C-CH_2-{}^{13}CH_2-{}^{6}Li$

198

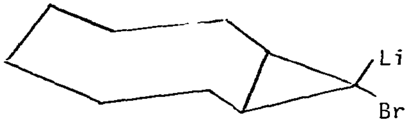
$H_3C-CH_2-CH_2-{}^{6}Li$

199

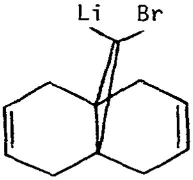
Experimental evidence for the presence of carbenoids of structures 179, 181, and 183 [124-126] has possibly been provided by the ^{13}C NMR spectra of ^{13}C enriched species 200-204 [146,147]. The ^{13}C-NMR signals appeared at unexpectedly low field. Moreover, the spectra were noteworthy for their usually large $^{13}C-{}^{7}Li$ but small $^{13}C-{}^{13}C$ coupling constants. The NMR spectrum of 203 is said to constitute the first proof of non-ionized organolithium compounds which are monomeric on the NMR time scale.



200



201



202

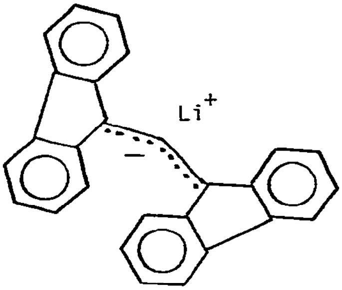
Br_3CLi

203

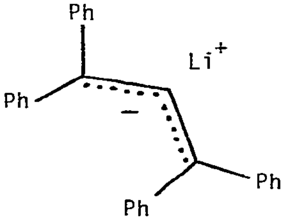
H_3C-CBr_2Li

204

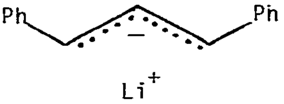
Barriers to rotation ($\Delta G^{\pm}$ in kcal mol^{-1}) of a variety of allyl systems have been obtained using ^{13}C-[148] and ^{1}H-[149,150] NMR spectroscopy. Among the large number listed were 205: 13.62; 206: 13.265; allylithium: 10.7; allylpotassium: 16.7; allylcesium: 18.0; and 207: 17.0. The value for allylcesium is said to set a new lower limit for the barrier of the allyl anion in solution [149]. Needless to say, each paper devoted much discussion to the conformations of such systems.



205

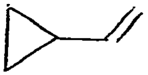


206

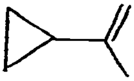


207

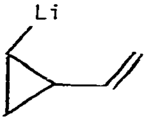
In addition to expected allylic anions, lithiation of 208 and 209 by one and two equivalents of n-butyllithium·TMEDA has been shown by ^{1}H-NMR and by alkylation to afford 210 and 211, respectively [151]. Such ring lithiations are apparently facilitated by the vinyl group. The NMR spectra of the other lithiated species are also reported.



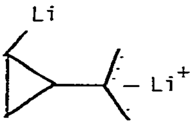
208



209



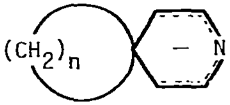
210



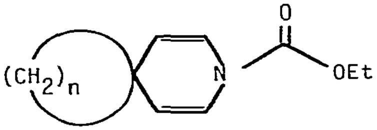
211

Two full papers have discussed the results of studies on variable temperature ^{13}C-NMR magnetic resonance of alkali derivatives of triphenylmethane [152], fluorenes [152,153], diphenylmethanes [152], toluene [152], indene [153], and a variety of mono- and dimethylindenes [153]. Discussions center around chemical shifts as a function of metallic cations, solvents, and temperature. The entropies and enthalpies of solvation are listed for several of the anions. Another paper examined the complex character of the temperature dependence of the ^{1}H-NMR chemical shifts of indenyllithium and -sodium [154]. The proton shifts were discussed in terms of polarization of the C-H bonds influenced by the electric field along the bonds and by the π-electron distribution.

Spirodihydroaromatic anions illustrated by 212 have been prepared from the corresponding urethanes 213 and dimethylmagnesium and butyllithium [155]. The NMR spectra of the anions indicated that they contain conjugated anions largely *unperturbed by counterion and n. When n = 2 or 3, such treatment of the urethanes* with the organometallics afforded ring-opened products as a result of strain in the smaller rings.

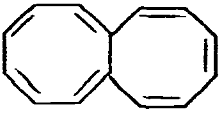


212

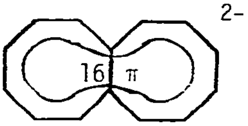


213

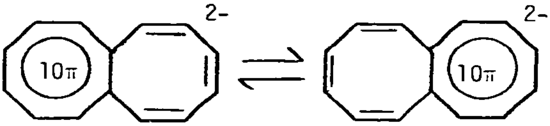
Octalene (214) has been reduced by lithium in THF-d_8 to dianion 215 or 216, then to tetraanion 217 as evidenced by 'H- and ^{13}C-NMR spectroscopy [156]. Compound 217 is said to be analogous to naphthalene.



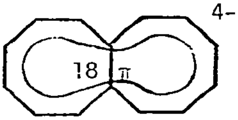
214



215

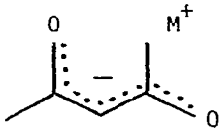


216

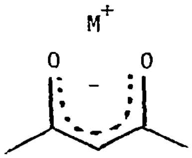


217

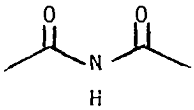
Earlier investigations on the equilibrium of acetylacetonate species using 'H-NMR spectroscopy have been extended to ^{13}C-NMR work [157]. As before, addition of lithium ion to sodioacetylacetone causes a shift from the E,Z form 218 to the Z,Z isomer 219. Data are also presented for the alkali salts of 2,4-hexanedione, 3-methyl-2,4-pentanedione, and 3-ethyl-2,4-pentanedione. Similar results using 'H-NMR have been realized with diacetamide (220) [158].



218

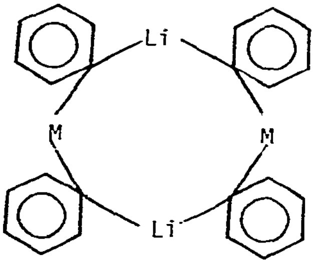


219



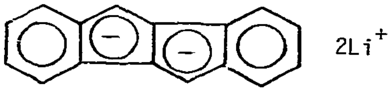
220

Both 'H- and ^{13}C-NMR have been employed to elucidate the structures of $Ar_4M_2Li_2$ *where M = Ag [159,160], Cu [160], and Au [160].* Both papers suggest that the structures may be represented by 221.



221

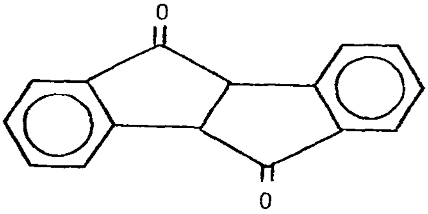
Finally, 'H-NMR spectra have been reported for a variety of anions of benzannelated [9]- and [13] annulenes [161], and for two dianions of pentalenes illustrated by 222 [162].



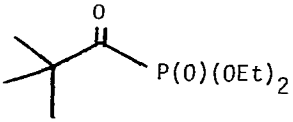
222

B. Other Spectroscopy

ESR, ENDOR, and TRIPLE-resonance measurements have been reported for fluorenone ketyl and all alkali cations [163]. Also studied were the related ketyls derived from [9-^{13}C]perdeuterio-9-fluorenone and [10-^{17}O]perdeuterio-9-fluorenone. Resonances from ^{7}Li, ^{23}Na, ^{85}Rb, and ^{133}Cs were detected including all hyperfine coupling constants including their signs. Hyperfine interactions of ^{13}C and ^{17}O proved to be sensitive local probes of the electron structure in ion pair complexes. The results of similar studies on dione 223 [164], α-ketophosphonates such as 224 [165], and [6]helicene [166] were also reported. The α-ketophosphonates were shown to yield semidiones.



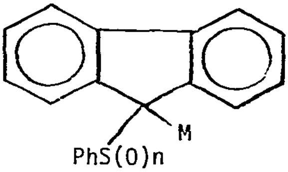
223



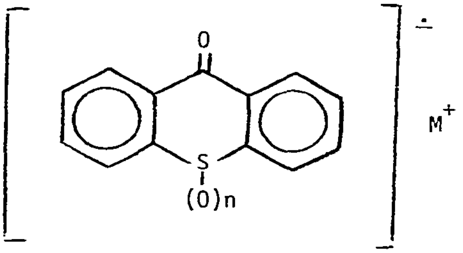
224

UV-visible spectroscopy has been employed to confirm conclusions about the nature of alkali derivatives of tri- and diphenylmethane in solution previously obtained from their NMR spectra [167,168]. Thus, contact and solvent-separated ion pairs were observed depending upon the cation and the solvent. In addition, the current study revealed the presence of two types of contact ion pairs in the diphenylmethide system, one unsolvated, the other partially solvated [168]. Thermodynamic parameters are discussed for both systems.

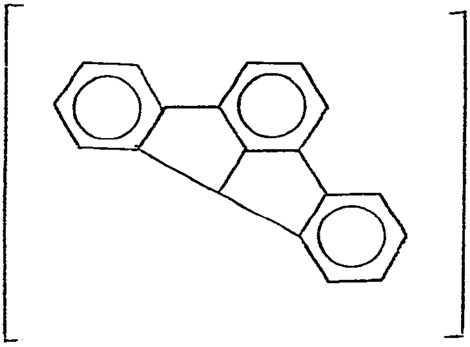
Other compounds whose UV-visible spectra were reported included 225(n=0,1,2) [169], 226(n=0,1,2) [170], 227 [171], and 228 [172]. Ion-pairing effects in 225 and 226 were also studied by 'H-NMR and ESR spectroscopy, respectively.



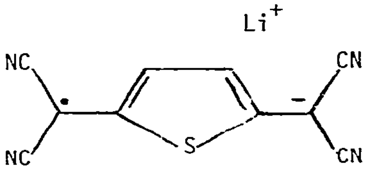
225



226

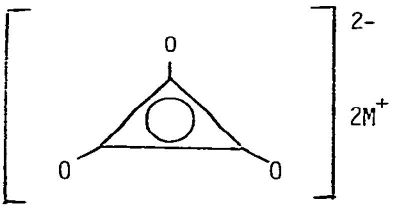


227

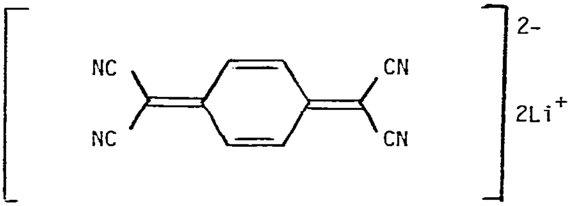


228

Infrared spectra have been described for complexes of n- and s-butyllithium with THF, dimethyl ether, and trimethylamine [173], and for mono- and dialkali derivatives of anthracene [174]. Both IR and Raman spectra of deltate ion 229 (M=Li,K) [175] as well as the Raman spectrum of 230 [176] were also reported in 1979.



229



230

A quadrupole mass spectrometer has been employed to observe CLi_3, formed from permeation of gaseous lithium through a graphite membrane [177]. Its ionization potential was found to be 4.6 ± 0.3 eV.

The chemistry of Li^+, Na^+, Fe^+, Co^+, and Ni^+ with alkyl halides and alcohols in the gas phase has been studied by ion cyclotron resonance (ICR) spectroscopy [178]. For example, Li^+ and n-propyl chloride give $Li(C_3H_6)^+$ and HCl while this cation with t-butyl alcohol affords $Li(C_4H_8)^+$, water, $Li(OH_2)^+$, and C_4H_8.

Other papers discussing ICR results may be of interest to the reader even though alkali cations were not involved. Thus, papers were published which dealt with a scale of acidities in the gas phase from methanol to phenol [179], substituent and solvation effects on gas phase acidities [180], generation of specific isomeric carbanions such as 231 and 232 from trimethylsilyl derivatives in the gas phase [181], gas phase reactions of carbanions with triplet and singlet molecular oxygen [182], electron photodetachment spectra of the cyclooctatetraenyl and perinaphthenyl anions [183], and gas phase nucleophilic displacement reactions of negative ions with carbonyl compounds [184].

$H_3C\text{-}C\equiv\overline{C}$

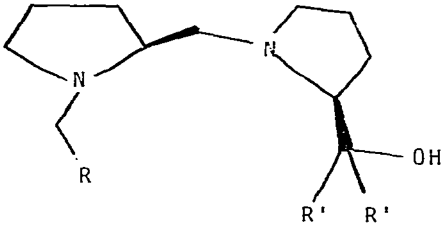
231

$H_2\overline{C}\text{-}C\equiv CH$

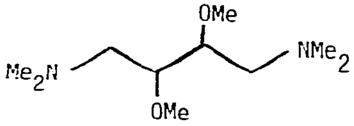
232

6. STEREOCHEMICAL ASPECTS

Enantioselective condensation of achiral organolithium reagents and aldehydes and ketones continue to be effected in the presence of chiral reagents such as 233(R=H,Me,t-Bu; R'=H,Me,Et,n-Pr,n-Bu) derived from (S)-proline [185], and 234 as well as others obtained from tartaric acid [186,187,188]. For example, n-butyllithium, benzaldehyde, and 233(R=R'=H) in dimethyoxymethane-dimethyl ether at -123° affords 1-phenyl-1-pentanol (77%) with an optical purity of 95% [185]. Such condensations are described for a large number of organolithiums [185,186] including conjugate additions of organocuprates [188].

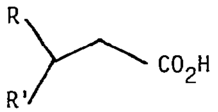


233

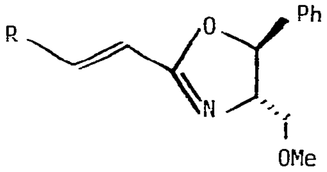


234

3-substituted alkanoic acids 235 have been obtained in >90% enantiomeric excess by stereoselective addition of organolithiums to chiral oxazolines 236 followed by hydrolysis [189]. Either enantiomer of 235 can be obtained depending upon the order of addition of R and R'. Incidentally, a separate paper discusses the separation of diastereomeric oxazolines using preparative liquid chromatography [190].



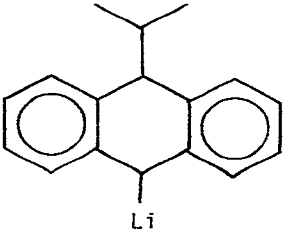
235



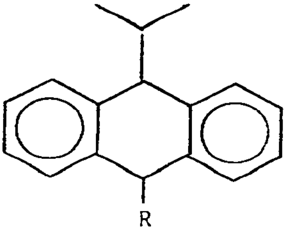
236

A method has been described for determining the enantiomeric purities of γ-, δ-, and ε-lactones to within ±3% [191]. The procedure involves addition of methyllithium to the lactone followed by NMR examination of the resulting diol in the presence of a chiral shift reagent such as $Eu(tfc)_3$.

Additional research concerned with the stereoselectivity of alkylations of 237 appeared in 1979 [192]. The nature of the solvent, the leaving group, and the temperature were shown to be important. For example, treatment of 237 with methyl iodide in ether, cyclohexane/TMEDA, THF, and HMPA gave the following amounts of cis-238, respectively: 42%, 86%, 90%, and 90%. Moreover, ethyl iodide and 237 afforded more cis-238 than did ethyl chloride. The results are ascribed to electrophilic assistance by cation for the contact ion pairs.

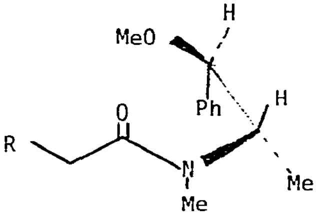


237



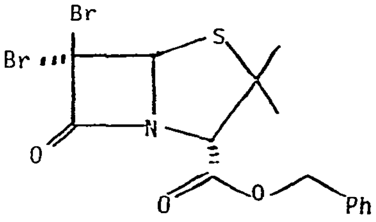
238

Turning to carbanions stabilized by carbonyls, a full paper discussed asymmetric alkylations of chiral lithium N,N-disubstituted amides 239(R=Me,Et,n-Bu) [193]. The parent amides are conveniently prepared from anhydrides and ℓ- or d-ephedrine. Treatment of the alkylated amide with methyllithium yields methyl ketones. The overall procedure was employed to prepare (S)-(+)-4-methyl-3-heptanone in 81% enantiomeric excess.

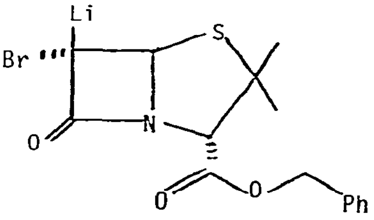


239

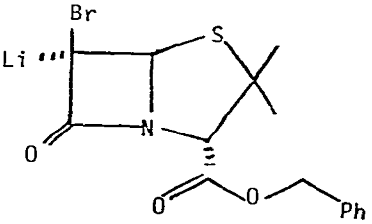
Lithiation of penicillinate 240 by t-butyllithium in toluene gives a 60:40 mixture of 241 and 242 as evidenced by protonation with acetic acid [194]. Interestingly, addition of THF to 241-242 prior to acid quenching causes isomerization to a mixture containing at least 90% of 241. While treatment of the 60:40 mixture of 241-242 with acetaldehyde gives rise to four isomeric adducts, pretreatment of 241-242 with $ZnCl_2$ in THF affords only one of the adducts, namely 243 (40%). The results are interpreted in terms of "a non-planar β-lactam 'enolate' whose stereochemistry appears to be mediated by metal ion solvation as well as conformational analysis of aldol transition states."



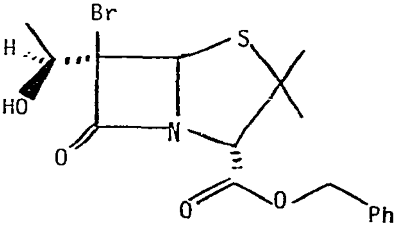
240



241

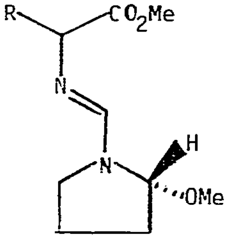


242

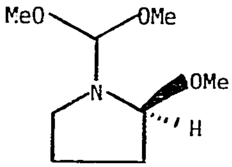


243

Chiral α-alkyl α-amino acids have been obtained (50-80%) by lithiation of 244 by LDA, alkylation, and hydrolysis [195]. Reagent 244 is synthesized from appropriate α-amino acids and pyrrolidine 245.

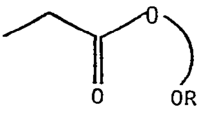


244

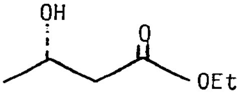


245

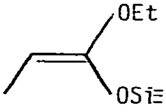
High threo to erythro ratios in condensations of several different types of ester derivatives with electrophiles have been reported. Thus, lithiation of 246(R=Me,CH_2OMe, etc.) and dilithiation of 247 followed by the addition of aldehydes and alkyl halides affords threo-3-hydroxy-2-methylcarboxylic esters [196] and threo-2-alkyl derivatives [197], respectively. Threo-3-hydroxy-2-methylcarboxylic acid esters have also been obtained by reactions of aldehydes with 248 and 249 in the presence of $TiCl_4$ [198]. Reagents 248 and 249 are synthesized from ethyl propanoate, LDA, and chlorotrimethylsilane in THF in the presence and absence of 23% HMPA, respectively.



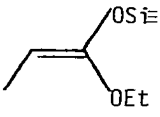
246



247

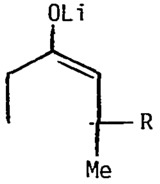


248

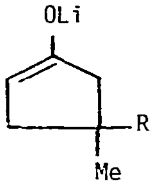


249

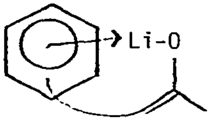
A full paper presented details on the directing effects of aryl groups on the regiochemistry of formation of ketone enolates [199]. Thus, for example, larger amounts of 250 and less of 251 were obtained from the parent ketone and LDA in THF at 25° as evidenced by trapping with chlorotrimethylsilane when R = p-MeOPh than when R = phenyl itself. In contrast more of 251 than 250 was realized when R = p-O_2NPh and n-Bu. Similar results were found with cyclohexanones and certain acyclic systems. Such regiochemistry, ascribed to π-coordination illustrated by 252, was supported by 'H- and ^{13}C-NMR spectroscopy. While enolates such as 250 were alkylated by alkyl halides to afford mixtures of mono- and dialkyl derivatives, such alkylations in the presence of copper salts not only yielded diminished amounts of dialkyl products, but the monoalkyl derivatives were the less thermodynamically stable cis-products illustrated by 253. Explanations for the above are suggested.



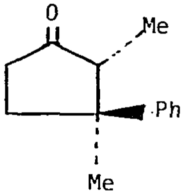
250



251

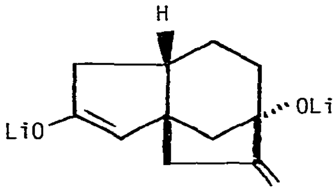


252

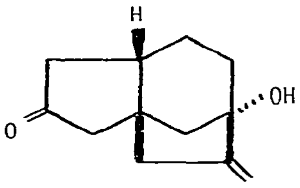


253

Enolate 254 has been produced regiospecifically from 255 using LDA in THF at -20° [200]. Such regiochemistry is ascribed to overlap of the $C_3\beta$ hydrogen with the carbonyl in the enolization transition state. Condensations of 254 are described.

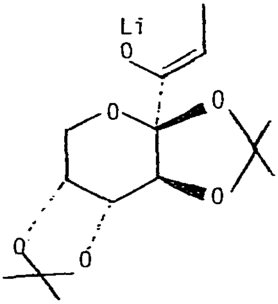


254

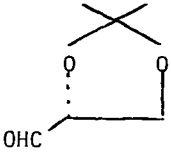


255

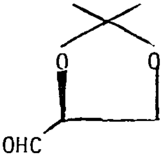
The principle of double stereodifferentiation (double asymmetric induction) has been illustrated by certain condensations of chiral 256 with aldehydes 257 and 258 [201]. Thus, while 256 and 257 gave three aldols in a ratio of 5.5:2.5:1 the major product of which was 259, 256 and 258 afforded only two stereoisomers in a ratio of 13:1. In the latter case, the major product was 260. A second paper described the use of 261 in related condensations to yield 3-hydroxy-2-methylcarboxylic acids from chiral aldehydes [202].



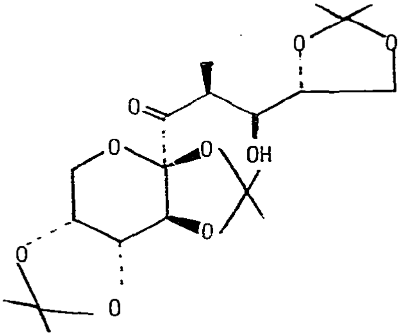
256



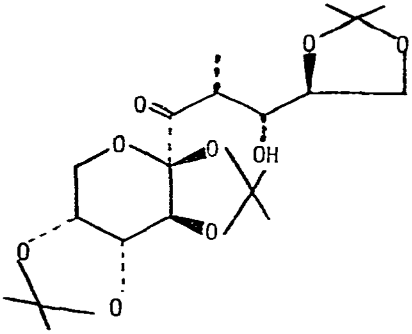
257



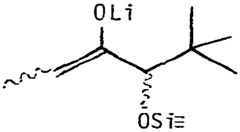
258



259

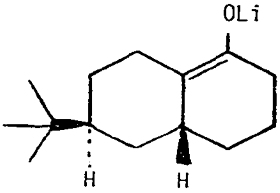


260

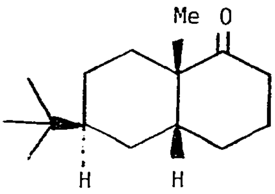


261

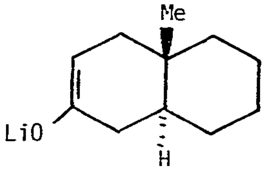
Enolate 262, prepared from the related silyl enolate and methyllithium has been methylated by methyl iodide to form predominately 263 [203]. It is suggested that the favored conformations of 262 are twist-boats which are shown in the paper. It is also suggested that formation of cis-263 is consistent with an early, reactant-like transition state rather than a late, product-like one that resembles the geometry of the products. Another paper discusses the effect of olefinic double bonds on the stereochemistry of alkylations of enolates of reduced naphthalene derivatives [204]. For example, methylation of 264 and 265(R=H) gives equatorial and axial alkyl derivatives, respectively. Similar reaction of 265(R=Me) gives 1:1 axial-equatorial mixtures. The results are discussed in terms of secondary orbital interactions.



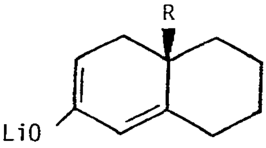
262



263



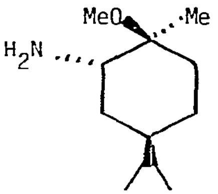
264



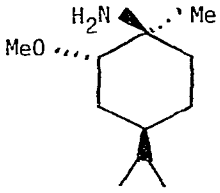
265

The effect of a variety of lithium, aluminum, and magnesium salts on the stereochemistry of addition of organolithiums, dimethylmagnesium, and trimethylaluminum to several cyclic ketones has been reported [205]. For example, the amount of axial alcohol from methyllithium and 4-t-butylcyclohexanone increases from 65 to 92% in the absence and presence of $LiClO_4$, respectively. Such changes in stereochemistry are attributed to prior complexation of the ketone with the salt followed by addition of the RLi.

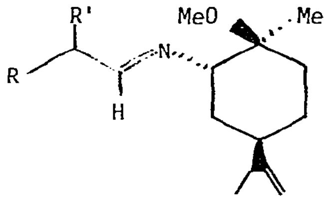
Although the factor responsible for the preferential syn stabilization of lithioaldimines has not yet been identified, its magnitude has been calculated to be at least 18 kJ mol^{-1} [206]. Lithiation, alkylation, and hydrolysis of aldimines derived from secondary carbinamines such as 266 have been shown to afford chiral aldehydes with greater enantiomeric excess than that obtained from related derivatives made from tertiary carbinamines illustrated by 267 [207]. Incidentally, the amount of enantiomeric excess of such aldehydes may be conveniently determined by the 'H-NMR spectra of the aldimine proton prior to hydrolysis of derivatives such as 268 [208]. Chiral aldehydes and acids have similarly been obtained by lithiation and alkylation of α-phenethylimines such as 269 [209] and lactim ether 270 [210].



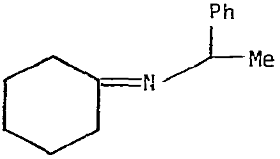
266



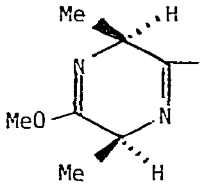
267



268

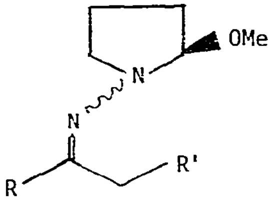


269

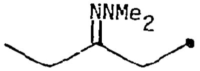


270

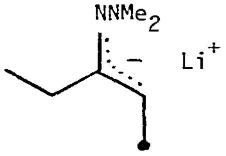
Several more papers concerned with the metalation of hydrazones appeared in 1979. A full paper discussed lithiation of chiral hydrazones 271 and subsequent alkylations to ultimately afford chiral aldehydes and ketones (51-80%) in high to complete enantioselectivity [211]. The method has been employed in the synthesis of an ant pheromone [212] and gingeral [213]. The stereochemistry of such lithiations and alkylations was studied by 'H- [214] and ^{13}C- [215,216] NMR. For example, treatment of 271(R=H,R'=Me) with LDA in THF or LDA in THF in the presence of HMPA gave the E_{C-C},Z_{C-N} (>98%) and the Z_{C-C},E_{C-N} (>95%) lithiohydrazones, respectively [214]. Deprotonation in such reactions is said to be more stereospecific than the subsequent alkylations. The ^{13}C-NMR results are illustrated by the conversion of ^{13}C-enriched 272 to 273 (72%) and 274 (28%) by LDA in THF [215]. These authors conclude that "once formed, facile isomerization apparently occurs in these lithio anions at 0°C within 0.5 hour since we only observe Z C=N alkylated product" [215]. Other authors conclude that "the ease of inversion at the nitrogen of ketone dimethylhydrazones via base-catalysis prevents the determination of the stereochemistry of the deprotonation step" though they suggest that syn deprotonation occurs faster than anti lithiation [216].



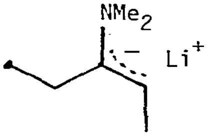
271



272

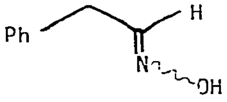


273

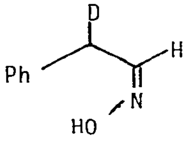


274

Another paper concerned with dilithiation of oximes and subsequent condensations with electrophiles reenforced earlier conclusions about such systems [217]. For example, treatment of a mixture of syn- and antioximes 275 with two equivalents of LDA in THF at 0° followed by D_2O yielded only syn-isomer 276.

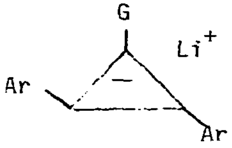


275

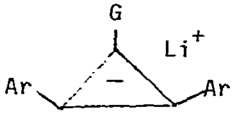


276

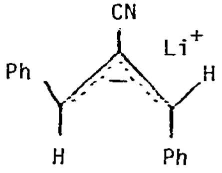
Further studies on the ring opening of substituted 2,3-diarylcyclopropyllithiums to 1,3-diarylallyllithiums have been reported [218]. Thus, 277 was found to undergo such reaction when Ar = phenyl, G = CN, SOPh, SO_2Ph and when Ar = p-MeOPh and G = CN but not when Ar = Ph and G = NC, SPh, and H. Similar ring opening was observed on 278 when Ar = Ph and G = CN or SO_2Ph. That only the thermodynamically most stable endo, exo-279 is obtained from 277 or 278(Ar=Ph, G=CN) is ascribed to the fact that the isomerization reactions of the allyl anions are faster than the valence isomerizations of 277 and 278(Ar=Ph, G=CN). MO calculations are described which confirm the high barrier of the conrotatory cyclopropyl anion ring opening and the small barrier of the allyl anion isomerization.



277

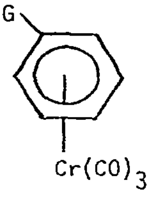


278

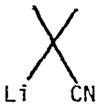


279

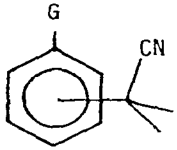
Another paper describing the addition of carbanions to arenechromium tricarbonyl complexes was concerned with the regiochemistry in such reactions [219]. For example, while 280(G=Cl and NMe_2) with 281 followed by oxidation with iodine affords mostly meta-282, similar reaction of 280(G=$SiMe_3$) gives mostly the para isomer. The nature of the carbanion is also important since tertiary and secondary carbanions derived from esters with 280(G=Cl) yield meta-282 and a mixture of ortho- and meta-282, respectively. Results with di- and trisubstituted arene systems as well as with naphthalene are also presented. The reactions are discussed in terms of polar effects and HOMO-LUMO interactions. Substituted 3-cyclohexanones have been obtained from 280(G=OMe), 281, and acid [220].



280

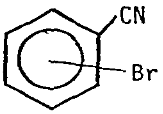


281

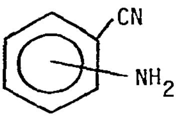


282

The influence of the cyano group on the orientation of amide ion to arynes has been studied [221]. Thus, either ortho- or meta-283 with two equivalents of $LiNH_2$, $NaNH_2$, or KNH_2 gives mostly meta-284. Similar reaction of para-283 affords 284 in a ratio of 80:20 para/meta, respectively. The results are in agreement with inductive effect arguments usually presented in such reactions.

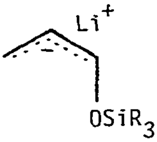


283

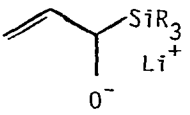


284

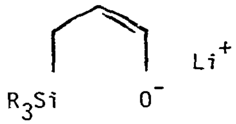
The regioselectivity in the reactions of the equilibrating system 285-287 with electrophiles has been found to change with the nature of the leaving group of the silylating agent [222]. For example, treatment of 285-287 with fluoro- and iodotrimethylsilane gives 288 and 289 as 65%/35% and 15%/85% mixtures, respectively in THF/HMPA; only 289 is obtained, though, in the absence of HMPA or in the presence of zinc chloride and HMPA. Another paper discussed additional examples of inversion of configuration in reactions of certain chiral silylfluorides with organolithiums [223].



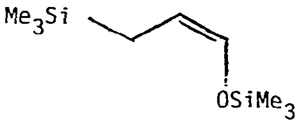
285



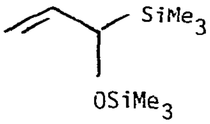
286



287

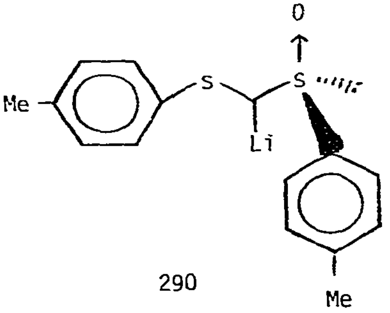


288

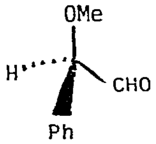


289

Lithio derivative 290, derived from the parent chiral compound and n-butyllithium, has been combined with benzaldehyde to ultimately afford chiral 291 [224].

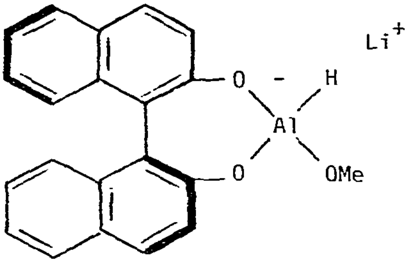


290

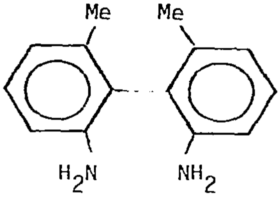


291

Other papers of interest in this section were concerned with the stereochemistry of nucleophilic substitution at cyclopropanes [225], inversion at the cyclopropyl ring of 7-exo-bromobicyclo[4.1.0]heptan-3-endo-ol to afford a THF ring [226], stereochemistry of elimination reactions of halohydrins with butyllithium [227], stereochemical equilibration of dilithiodiols [228], the stereochemistry and mechanism of the base-induced loss of thiophenol from 1,1,3-tris-(phenylthio)alkanes to give cyclopropanone dithioketals [229], and stereoselective aldol condensations using boron enolates [230]. Four papers discussed reductions of ketones by complex reducing agents. They included evidence for a linear combination of steric strain and product stability control in the stereochemical course of the addition reactions of LAH (and methyllithium) to ketones [231], orbital control in the stereochemistry of substituted cyclohexanones by $LiAlH(t\text{-}OBu)_3$ [232], and enantioselective reductions of ketones by chiral reagents such as 292 [233] and ones derived from 293 and LAH [234].



292

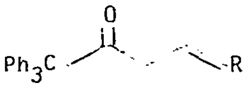


293

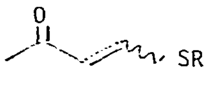
As in 1978, a rather large number of papers appeared in 1979 which discussed 1,2- or 1,4-addition reactions of organolithiums to α,β-unsaturated system. They included:

a. 1,4-Addition of alkyl-, aryl- and 1,3-dithian-2-yllithiums to 294(R=H, Me,Ph) and a related α,β-unsaturated amide [235].

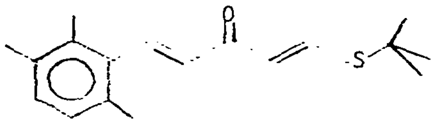
b. 1,2-Additions of alkyl- and acetyleniclithium reagents to sulfur-containing systems such as 295 [236] and 296 [237] as part of the synthesis of conjugated aldehydes.



294



295



296

c. 1,2-Addition of p-tolyllithium to 6-methyl-3,5-heptadien-2-one in ether as part of a preparation of (±)-β-curcumene [238].

d. 1,4-Addition of lithiocyanoenamines 297 to a variety of α,β-unsaturated ketones in THF [239].

e. Kinetically controlled 1,4-additions of lithionitriles and -thio systems to cyclohexenone [240].

f. 1,4-Addition of lithionitriles to α,β-unsaturated aldehydes and imines [241].

g. Kinetic (1,2) versus thermodynamic (1,4) control in the additions of lithionitriles to α,β-unsaturated aldehydes [242].

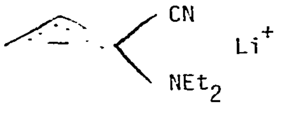
h. Temperature and solvent effects in the 1,2- versus 1,4-additions of 298 to cycloalkenones [243].

i. Induced 1,4-addition by HMPA of α-lithiothio ethers to α,β-unsaturated aldehydes [244] and ketones [245].

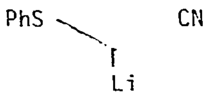
j. Condensations of a variety of lithium carbanions stabilized by sulfur with α,β-unsaturated ketones [246,247].

k. 1,4-Additions of sulfinates to α,β-unsaturated ketones [248].

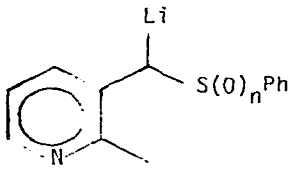
l. Reaction of sulfur-containing carbanions such as 299(n=1,2) with ethyl 4-bromocrotonate to afford cyclopropanecarboxylates illustrated by 300(n=1,2) [249].



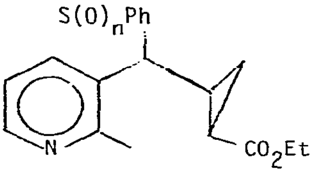
297



298



299



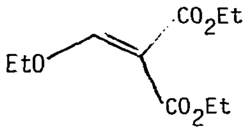
300

m. 1,4-Additions of aryllithiums with 301 as part of a synthesis of coumarins [250].

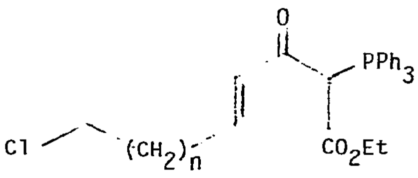
n. 1,4-Additions of lithium enolates to α,β-unsaturated thioamides [251].

o. Formation of 5- and 6-membered rings by 1,4-addition of organolithiums to 302(n=2,3) [252].

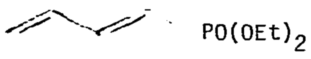
p. Conjugate additions of a variety of enolates with phosphonate 303 [253, 254].



301



302



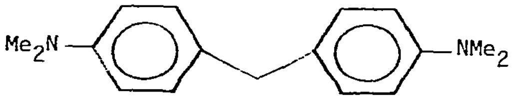
303

7. OTHER PHYSICAL-ORGANIC CHEMISTRY

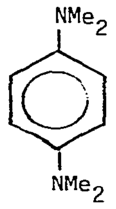
The ion pair equilibrium between the lithium and cesium salts of 9-t-butylfluorene and pentafluorobenzene has been studied in cyclohexylamine [255]. While the equilibrium has almost zero entropy for the cesium salts, a high entropy change of 21.5 e.u. has been found for the lithium derivatives. Both of the pentafluorophenyl systems exist primarily as contact ion pairs in this amine. The alkali derivatives of cyclohexylamine have also been employed to study the deuterium isotope exchange between molecular hydrogen and the parent amine, a very fast reaction even at -15° [256]. Activation parameters and kinetic isotope effects are listed.

The anomaly in the acidities of nitroalkanes has been shown to be largely a consequence of earlier work done with protic solvents as evidenced in the reactions of substituted arylnitromethanes and alkali benzoates in DMSO at 25° [257]. The study demonstrated that ionization of such compounds is subject to a large kinetic solvent effect and that proton transfer is not accelerated by strong mesomeric electron-withdrawing groups to the extent expected from their effect on Ka.

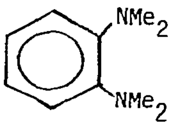
The influence of aromatic tertiary diamines 304-306 on the kinetics of polymerization of isoprene effected by n-butyllithium in hexane has been reported [258]. The initiation rate was found to increase in the order 304<305<<306 which corresponds to the ability of the amines to complex with n-butyllithium. Another paper discussed activation of alkali hydrides by cryptands in the formation of enolates of cyclohexanone [259]. Such cryptands also activated the enolates to the point that they abstracted protons from the ethereal solvents.



304



305

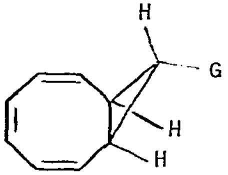


306

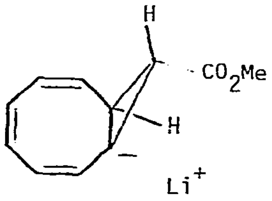
On the basis of kinetic studies, it has been determined that lithiotriphenylmethane and lithiodiphenylmethane react with neopentyl iodide and bromide as well as with benzyl fluoride by a normal S_N2 mechanism [260]. Rate constants are listed. Another paper discussed the kinetics of the solvolysis of alkyl p-hydroxybenzoates in fused alkali acetates [261].

N-Lithioethylenediamine in excess ethylenediamine has been found to be an effective base for the double bond isomerization of stigmasterol, 3α,5-cyclo-6β-methoxystigmast-22-en, and fucosterol [262]. Such isomerizations led to mixtures containing larger amounts of the more highly substituted alkenes. Potassium t-butoxide in DMSO and potassium 3-aminopropylamide in 1,3-diaminopropane were ineffective in promoting such transformations.

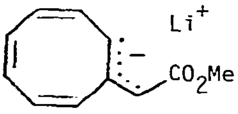
Rather than the expected ionization alpha to the ester group, metalation of 307(G=CO_2Me) by LDA has been found to afford bridgehead anion 308 which opens to allyl system 309 [263]. In contrast, similar reaction of 307(G=CN) leads to α-anion 310 which quickly rearranges to 311. MO calculations for the conversion of 310 to 311 are discussed.



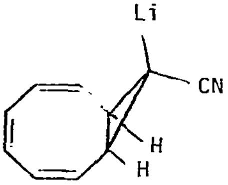
307



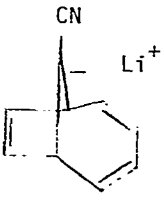
308



309

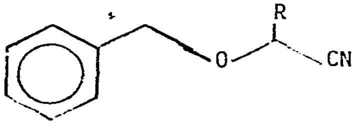


310

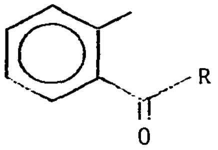


311

Benzylic ethers of cyanohydrins (312; R=Me,Pr,Bu) have been subjected to 2,3-sigmatropic rearrangements by LDA to yield ketones 313 [264]. The starting ethers themselves were prepared from the cyanohydrins and benzyl bromide using phase transfer catalysis.

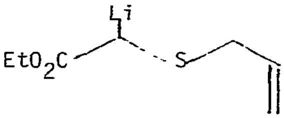


312

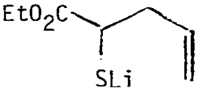


313

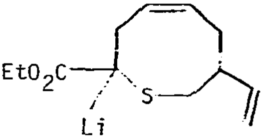
While anion 314, prepared from the corresponding parent ethyl (allylthio)-acetate and LDA, underwent 2,3-sigmatropic rearrangement at -22° to afford 315, anions 316, 317, and 318 failed to do so even under forcing conditions (e.g., 50°) though double bond migration was realized on 317 and 318 [265]. The S-methyl derivative of 317 was, though, converted by potassium t-butoxide to 319. The failure of certain of the cyclic systems to undergo the sigmatropic rearrangements is ascribed to "conformational and transannular destabilization of the necessary bicyclic transition states."



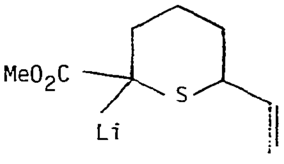
314



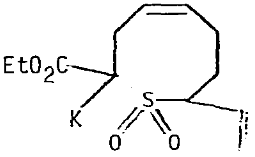
315



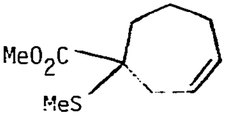
316



317

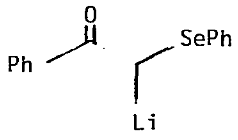


318

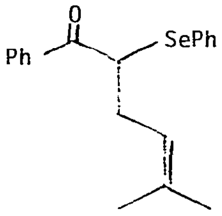


319

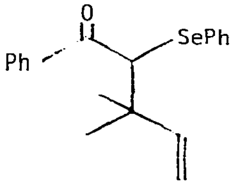
Alkylation of lithium derivative 320 by prenyl iodide has been shown to afford 321 and 322 [266]. Though 321 arises from an S_N2 process, 322 is formed via prior alkylation at selenium to give ylide 323 followed by a 2,3-sigmatropic rearrangement. Other examples of similar reactions are presented.



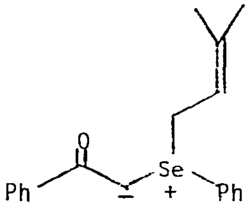
320



321

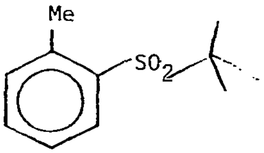


322

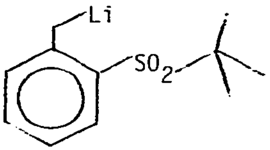


323

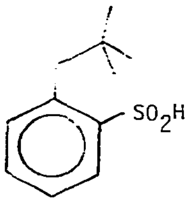
The first example of the migration of an alkyl rather than aryl group has been recorded in a Truce-Smiles rearrangement [267]. Thus, treatment of 324 with butyllithium at -78° gave 325 which rearranged upon reflux to yield, after hydrolysis, sulfinic acid 326. The results are explained by an electron transfer-radical anion pathway.



324

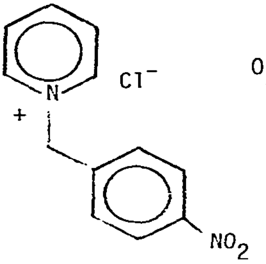


325

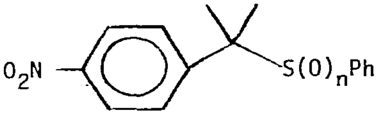


326

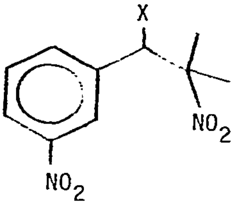
Several other papers were also concerned with electron transfer processes. Among the reactions occurring by intermediate radicals and radical anions were 2-lithio-2-nitropropane with 327 and 328(n=1,2) to afford coupling products [268], 2-lithio-2-nitropropane with m-nitro-α,α-dichloro(bromo)toluene to give 329 and 330 along with other products [269], and a variety of lithionitriles and -dithianes with 331(X=Cl,Br,NO_2) to yield dimers of the carbanions [270]. In contrast to the above dimerizations, combination of a number of lithium acetylides with 331(X=Cl,NO_2) gave coupling products such as 332 by a non-radical chain mechanism [270]. Reagent 331(X=Cl) has been shown to serve as a ketone equivalent since primary and secondary enolates combine with it to yield products of a controlled crossed aldol condensation [271]. For example, lithiocyclohexanone and 331(X=Cl) afford, under photolysis, 333 and 334; the latter arises by elimination of lithium nitrite from the former. Finally, phenylation of 335, previously thought to be 9,10-diphenyl-10-thiaanthracene, has been discussed [272].



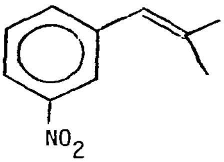
327



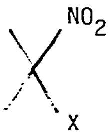
328



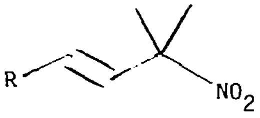
329



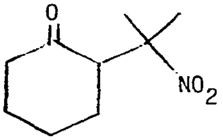
330



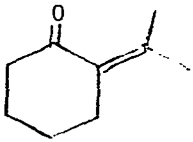
331



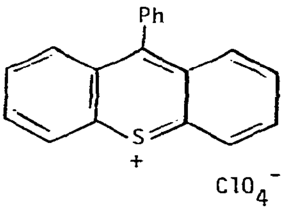
332



333

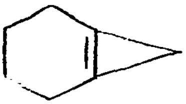


334

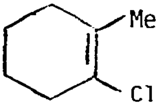


335

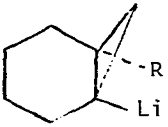
Strained cyclopropene 336 has been proposed as an intermediate in the reactions of excess organolithiums with 337 to afford 338(R=Ph,n-Bu,Me) as evidenced by deuteration [273].



336

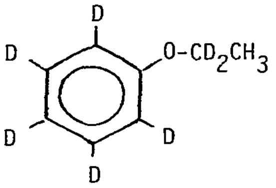


337

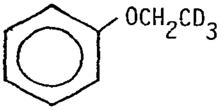


338

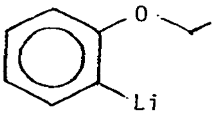
The metalation of ethoxybenzene by ethyllithium-d$_5$ has been studied in an effort to ascertain which of several mechanisms may have been operating [274]. Interesting, while β-elimination was realized on 339, α-elimination was observed on 340. The major reaction on both 339 and 340, though, was o-metalation. Interesting reactions of 341 with ethylene and with itself are reported to yield ring-alkylated derivatives and 342, respectively.



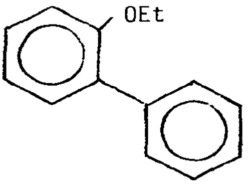
339



340

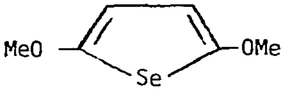


341

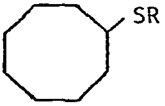


342

A variety of products arising from selenophene 343 and butyl- and phenyllithium has been rationalized by initial attack directly on the selenium by the organolithium [275]. Other papers discussed the formation of cis-cyclooctene from carbanions derived from alkyl cyclooctyl thioethers 344 and butyllithium [276], new evidence using deuterium labeling that a fast and reversible transition between betaines and oxaphosphetanes occurs in Wittig reactions [277], and stereoselectivity in the reactions of dilithiocarboxylates and aldehydes [278,279].



343



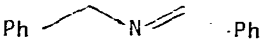
344

Finally, in this section, the enthalpies of reaction for alkali cyclooctatetraene dianions and sodioanthracene dianion with water have been measured calorimetrically [280]. Other papers of interest included discussions of the voltammograms of lithiotriphenylmethanes in DME [281], conductivity studies of polybutadienyl- and polyisoprenyllithium in THF and DME [282], and conductances of lithium picrate in 2-butanone [283] and THF [284].

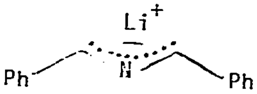
8. ADDITION AND SUBSTITUTION REACTIONS

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

Another method has been described for simple determination of organolithiums using 345 [285]. The resulting crimson anion 346 is then titrated with s-butyl alcohol in xylene or benzoic acid in THF.

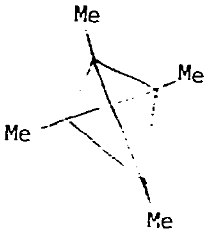


345



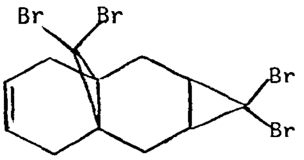
346

Tetralithio derivative C_4Li_4, prepared in 1978 from the photolysis of dilithioacetylene, has been treated with methyl iodide to afford tetramethyltetrahedrane (347) [286]. The authors believe the reaction represents a promising synthetic method for the synthesis of tetrahedrane derivatives.

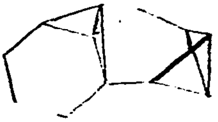


347

Treatment of tetrabromide 348 with methyllithium has been shown to yield 349 by regiospecific two-fold intramolecular carbene insertion [287]. The conversion is part of a convenient synthesis of heptalene.

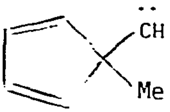


348

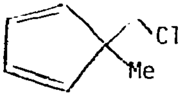


349

In a related paper, the carbene (350) derived from 351, n-butyllithium, and potassium t-butoxide has been shown to undergo a stereospecific intramolecular 1,4-addition to afford 1-methylbenzvalene (352) [288].



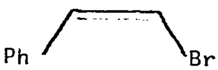
350



351

352

Alkenes may be prepared stereoselectively by the coupling of a variety of organolithiums with alkenyl halides in the presence of zerovalent palladium compounds [289]. For example, 353 with methyllithium in the presence of 354 gives 355 (88%) with an isomeric purity of 99%.



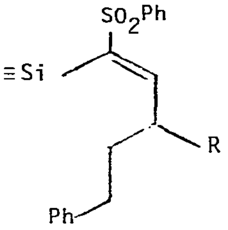
353

$Pd(PPh_3)_4$

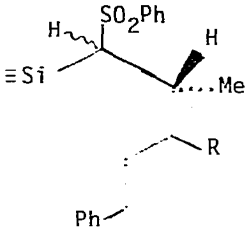
354

355

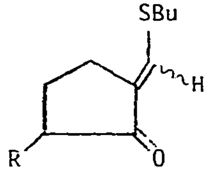
Addition of methyllithium to 356(R=methoxyethoxymethoxy) has been found to yield 357 with >99% threo formation [290]. The system has been employed in the synthesis of maytansine. Similar addition of methyllithium to 358 has been employed as a part of the synthesis of 1-formyl-2-methyl-3-alkylcyclopent-1-enes [291].



356

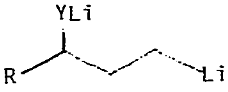


357



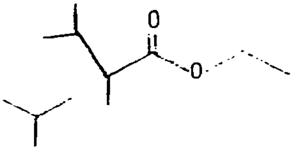
358

A full paper appeared in 1979 which described the preparation of dilithioalkoxides and -amides 359(Y=O,N) by transmetalation of C-mercury reagents [292]. Condensations with a variety of electrophiles to afford 1,2- and 1,3-diols, 1,2- and 1,3-amino alcohols, β-hydroxy and β-amino esters, and β-hydroxy- and β-aminosilanes are described.



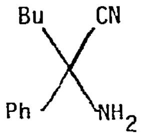
359

Condensation of n-propyllithium with hindered esters such as 360 has been shown to constitute an excellent method of dealkylation of such reagents to give the parent carboxylic acids [293]. Some of the reactions proceed by β-elimination while others occur by alkyl-oxygen cleavage.

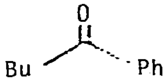


360

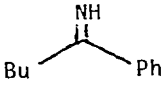
Successive addition of two equivalents of an organometallic or one equivalent each of two different organometallics to cyanogen has been shown to afford mixtures of glycinonitriles, ketones, imines, nitriles, and tertiary alcohols [294]. For example, cyanogen, n-butylmagnesium bromide, and phenyllithium give 361 (12%), 362 (38%), and 363 (50%).



361

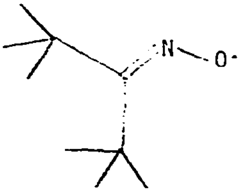


362

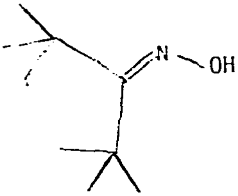


363

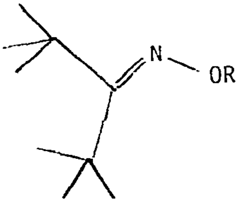
As above, reaction of various organolithiums (RM) with iminoxy radical 364 gives several products, the major ones of which are 365 and 366 [295]. Grignard reagents react similarly.



364

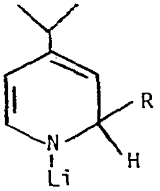


365

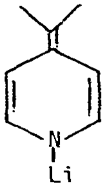


366

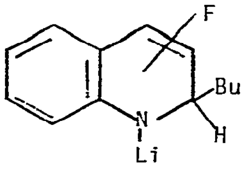
While treatment of 4-isopropylpyridine with n-butyl-, methyl-, or t-butyllithium affords mostly σ-complex 367 as evidenced by ¹H-NMR and benzylation, the use of phenyllithium on this heterocycle gives about a 1.8:1 mixture of 367(R=Ph) and metalated derivative 368 [296]. Similar additions were realized on 3-, 5-, 6-, 7-, and 8-fluoroquinolines with n-butyllithium to yield 369 [297]. In contrast, the use of LDA on the heterocycles resulted in the formation of derivatives ring-lithiated adjacent to the fluorine atoms. Both additions and metalations were also realized on 370 [298]. In another paper, metalation of 1,3-dimethylisoquinoline and its 6,7-dimethoxy derivative was reported to afford only the 1-lithiomethyl derivatives 371(R=H,OMe) regardless of the choice of metalating agent [299]. Condensations of 371 with a variety of electrophiles are described.



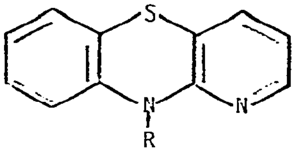
367



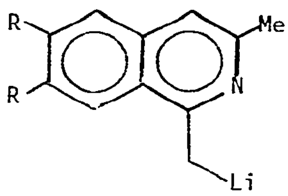
368



369

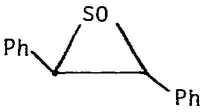


370

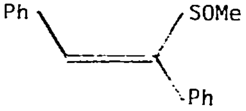


371

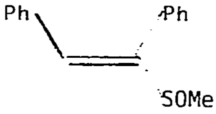
Treatment of trans-stilbene episulfoxide (372) with two equivalents of n-butyllithium to give trans-stilbene (97%), di-n-butyl sulfide (95%), and, after methylation, 373-374 has been ascribed to initial attack on the sulfur by the butyllithium [300]. Similar results but with lower yields were realized on cis-stilbene episulfoxide.



372

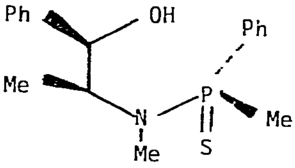


373

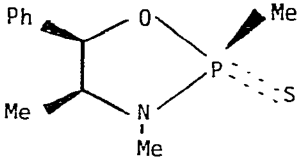


374

Chiral phosphinothioic acid derivatives such as 375 have been obtained from an unexpected P-O bond cleavage of 376 with phenyllithium [301]. The reaction occurs with retention of configuration at phosphorus.

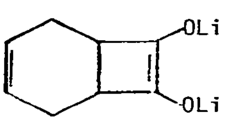


375

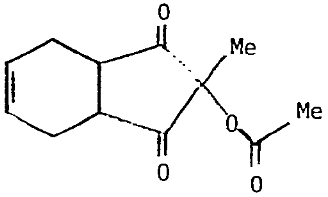


376

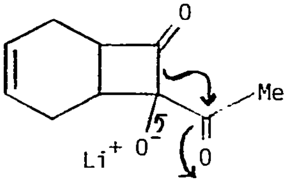
Acetylation of 377, obtained from the bis(trimethylsilyl) enol ether and methyllithium, has been shown to afford the novel ring-enlarged product 378 [302]. Alkoxides 379 and 380 are proposed as intermediates.



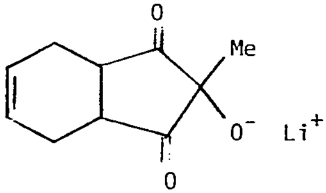
377



378

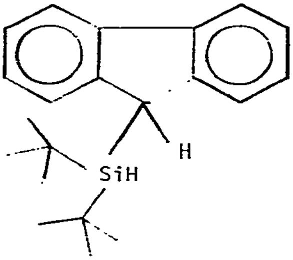


379

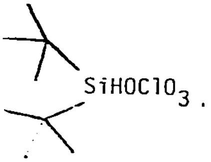


380

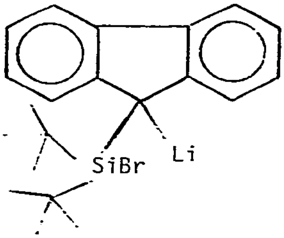
That perchlorate can act as an excellent leaving group during alkylations on silicon has been demonstrated by the rapid formation of 381 (75%) from 382 and 9-lithiofluorene [303]. In contrast, 381 was formed from the corresponding fluorosilane in a yield of only 25% after a 24 hour reflux period. The successful formation of α-halosilyl carbanion 383 by metalation of the parent compound by t-butyllithium in THF is ascribed to steric bulk.



381

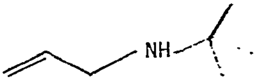


382

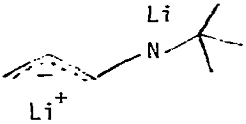


383

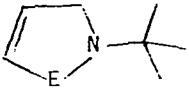
Allyl amines such as 384 have been converted to dianions illustrated by 385 by dimetalation with n-butyllithium·TMEDA [304]. Subsequent condensations of 385 with electrophiles have given cyclic products 386($E=Me_2Sn, t\text{-}Bu_2Sn, Me_2Si$, and PhP).



384

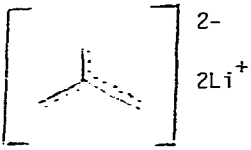


385

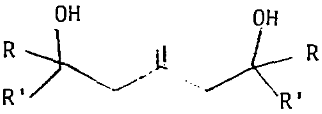


386

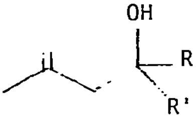
Additional chemistry of 2-methylenallyl dianion (387) was described in 1979 [305]. Thus, 387 was combined with aldehydes, ketones, ethylene oxide, and allyl chloride to give diadducts (49-76%) and monoadducts illustrated by 388 and 389, respectively. Sequential addition of two different electrophiles to afford a mixed diadduct failed.



387

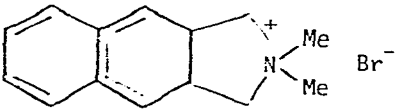


388

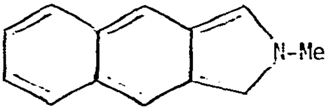


389

Turning to aryllithiums, the belief that reaction of isoindolium salt 390 with phenyllithium gives isoindole 391 has been confirmed by trapping the latter using the more reactive dienophile N-phenylmaleimide [306].

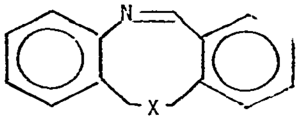


390

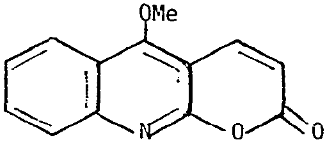


391

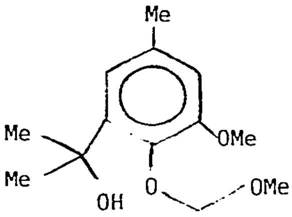
Directed lithiation of a variety of aromatic compounds followed by condensation with appropriate electrophiles has been utilized to synthesize several anthraquinone natural products [307], dibenzoazepine systems 392(X=O,S,NH) [308], pyranoquinolines such as 393 [309], 3-phenylcoumarins and their benzo derivatives [310], and 394 [311].



392

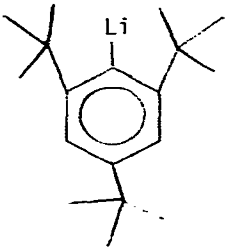


393

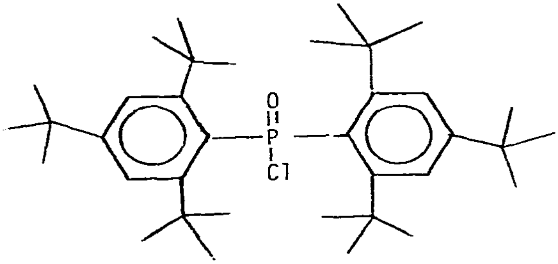


394

Lithium reagent 395, prepared by metal-bromine exchange with butyllithium, has been combined with phosphorus oxychloride to afford the sterically crowded phosphinic chloride 396 and 2,4,7-tri-t-butylchlorobenzene [312].

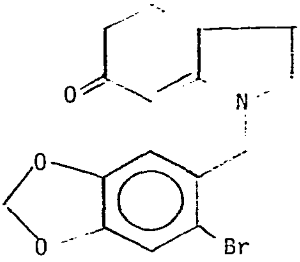


395

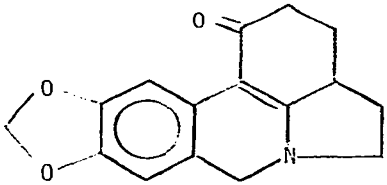


396

Several halo enaminones have been cyclized upon treatment with lithium diethylamide probably via benzyne intermediates [313]. The process is illustrated by the conversion of 397 to 398 which was, in turn, ultimately converted to γ-lycorane.

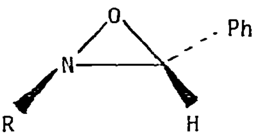


397

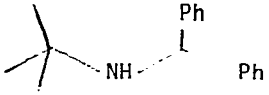


398

Phenyllithium has been found to react with oxaziridines 399(R=CMe$_3$,SO$_2$Ph) to afford phenol and 400 [314]. In contrast, phenylmagnesium Br and 399 (R=CMe$_3$) gave only biphenyl. Possible mechanisms for the transformations are discussed.

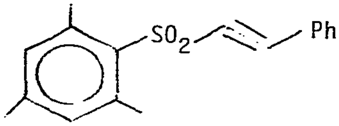


399



400

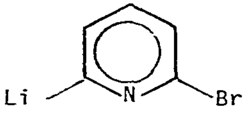
Aryl- and alkyllithiums combine with arylsulfonylacetylenes to yield higher acetylenes and arylsulfinate salts [315]. For example, 401 and phenyllithium give 402 (81%).



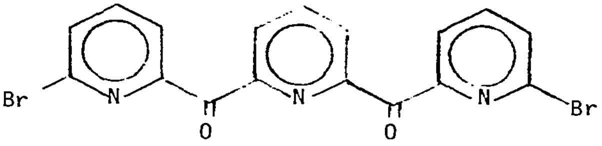
401

402

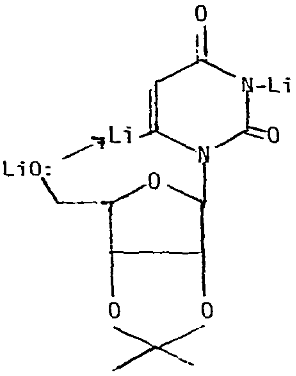
6-Lithio-2-bromopyridine (403) has been combined with methyl 2,6-pyridinedicarboxylate to afford 404 as part of the syntheses of spiro and ketonic heteromacrocycles [316]. Dilithiouridine 405, prepared by metalation of the parent compound with LDA, has been alkylated by alkyl halides to give 406(R=Me,Et,Pr,Bu) [317]. The products in such reactions were not contaminated by 5-, N^3-, or 5'-O-alkyl derivatives.



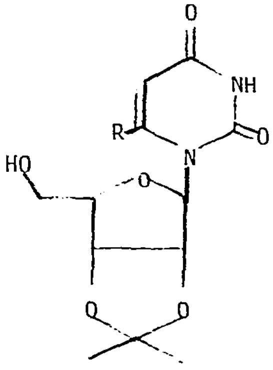
403



404

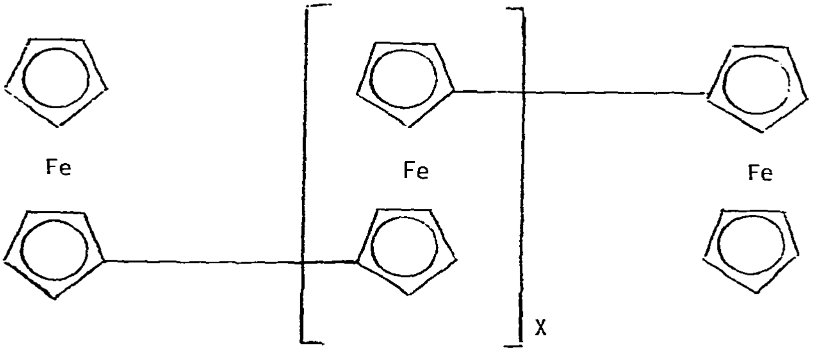


405

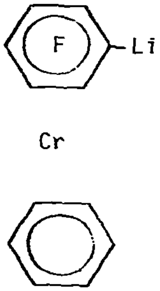


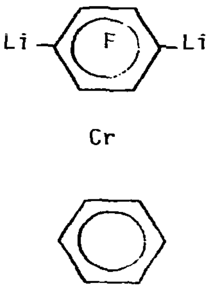
406

Poly(ferrocenylenes) 407 have been prepared from 1,1'-dilithioferrocene chelated with TMEDA and 1,1'- diiodoferrocene [318]. Another paper discussed condensations of 408 and 409 with several derivatives of carboxylic acids and other electrophiles [319].



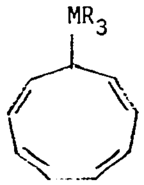
407





408 409

Cyclononatetraenes 410($M=Si,R=H$; $M=Ge,R=H$; $M=Sn,R=Me$) have been synthesized from the corresponding lithio or potassio derivatives and appropriate halogen-containing compounds [320]. The electrocyclic ring closures of 410 are discussed.



410

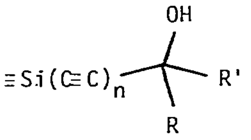
Selective desilylation of 411($n=1,2$) by methyllithium to afford 412 followed by the addition of aldehydes and ketones to give 413 has been reported [321]. Similar desilylations with KF-18-crown-6 are described.

$\equiv Si(C\equiv C)_nSi\equiv$

411

$\equiv Si(C\equiv C)_nLi$

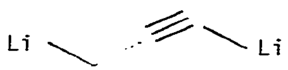
412



$\equiv Si(C\equiv C)_nC(OH)RR'$

413

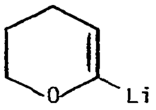
Additional chemistry of dilithiopropyne 414 was described in 1979 [322]. Thus, treatment of this dianion with n-butyl bromide followed by one equivalent of a second electrophile gives 415. Monolithioacetylenes have also been converted to 1-chloro derivatives [323] and highly branched alkynes [324].



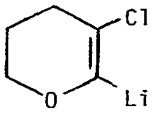
414

415

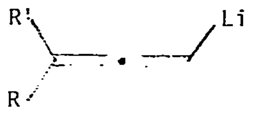
Finally, additional examples of condensations of 416 [326], 417 [326], and [327] with electrophiles were reported last year.



416



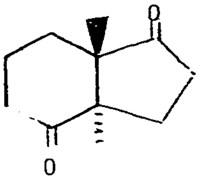
417



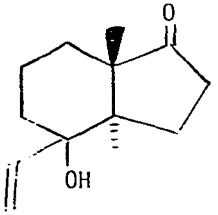
418

B. Carbanions Stabilized by Carbonyls

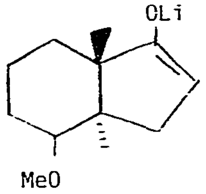
The relative reactivities of the two carbonyls of 419 towards nucleophiles has been studied [325]. Thus, while 419 gave 420 with vinyllithium, additions to the other carbonyl could not be effected by this or other related reagents. Instead, enolization was realized in several cases to afford species such as 421. When 421 was generated from 422 and lithium ethoxyacetylene, 423 was obtained in high yield.



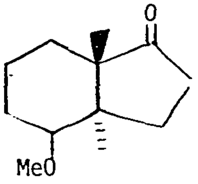
419



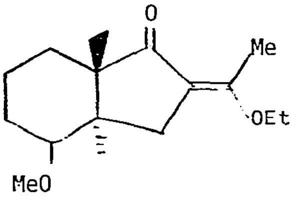
420



421

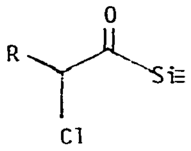


422

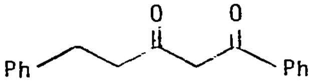


423

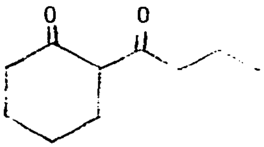
In the area of additions and substitutions involving enolates, unsymmetrically substituted 1,3-dicarbonyl compounds may be conveniently prepared by combination of ketone and ester enolates with 424(R=benzyl,Et) [328]. For example, lithioacetophenone and 424(R=benzyl) gives 425 (87-98%). The reactions obviously involve an interesting rearrangement of silyl group, presumably after loss of chloride ion. 1,3-Diketones have also been prepared from ketone enolates and acyl cyanides [329]. For example, lithiocyclohexanone and butyryl cyanide yield 426 (94%).



424

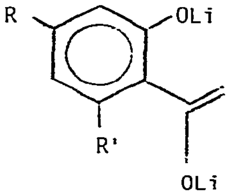


425

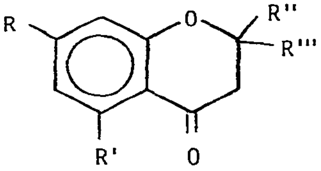


426

Simple additions of dilithio derivatives of o-hydroxyacetophenones (427, R and R'=H and/or OMe) to aliphatic ketones followed by acid-catalyzed cyclization has been shown to afford chromanones 428 (68-90%) [330]. An unrelated paper described a large number of condensations of ketone and aldehyde enolates with 429 to give Mannich adducts [331].



427

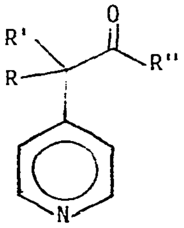


428

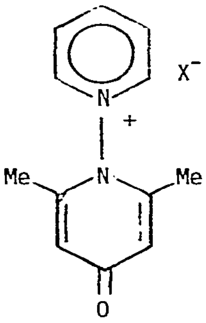
$\overset{+}{Me_2N{=}CH_2}\quad X^-$

429

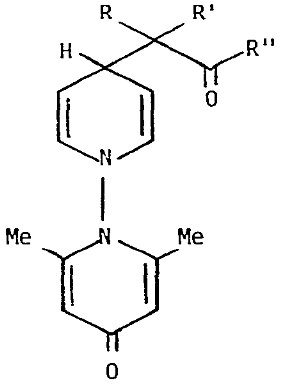
4-Substituted pyridines such as 430 have been prepared in excellent yields by treatment of 431 with a variety of lithium ketone enolates [332]. The reactions proceed via 432 which are converted to 430 by refluxing in carbon tetrachloride in the presence of azobis(isobutyronitrile).



430

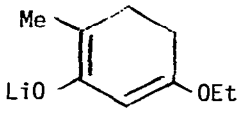


431

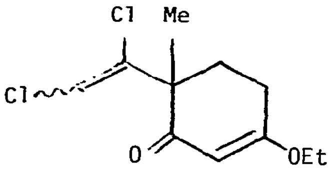


432

Several ketone enolates have been dichlorovinylated by trichloroethylene as illustrated by the conversion of 433 to 434 [333].

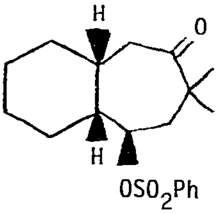


433

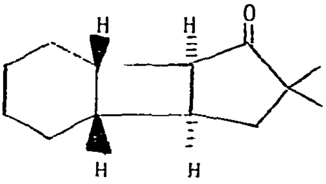


434

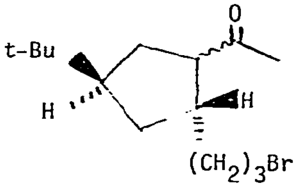
Additional examples of intramolecular cyclizations of ketone enolates were described in 1979. Thus, 435 and LDA were shown to give 436 [334] while 437 with this base yielded cis and trans 438 [335]. Three diastereoisomers of 435 were also studied [334].



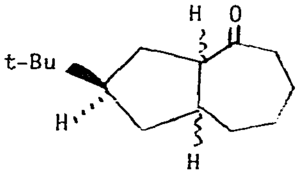
435



436

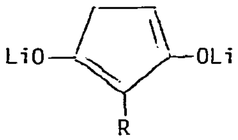


437

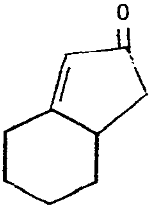


438

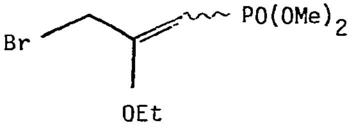
4-Substituted cyclopentane-1,3-diones have been prepared directly by alkylation of dilithio salts 439 [336]. 2-Cyclopenten-1-ones such as 440 have been obtained by alkylation of ketone enolates with 441 followed by hydrolysis of the enol ether moiety and cyclization with sodium hydride [337]. Lithium enolates have also been converted to dihydroarene oxides by the use of 442 [338]. For example, lithiocyclohexanone and 442 afford 443.



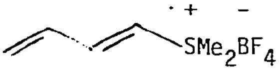
439



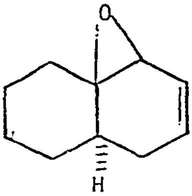
440



441

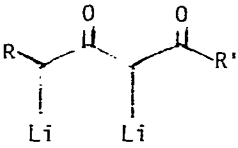


442

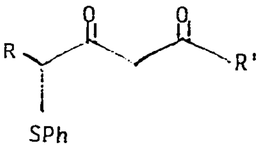


443

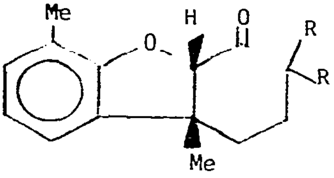
Among the sulfenylations of ketone enolates reported in 1979 were the conversions of 444 to 445 [339], 446 to 447 [340], and 448 to 449 [341]. Silyl enolate 450, obtained from 451 and chlorotrimethylsilane, has been found useful in the preparation of both 7- and 5-membered ring systems [342].



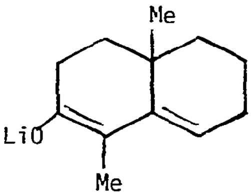
444



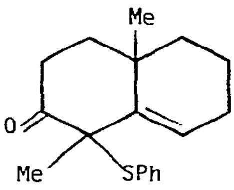
445



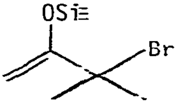
446(R=H)
447(R=SPh)



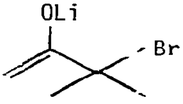
448



449

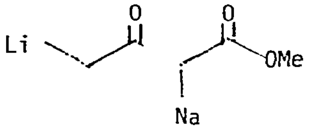


450

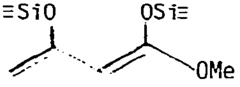


451

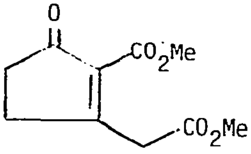
Lithiosodiomethyl acetoacetate (452) has been employed as part of the synthesis of luciferin [343] and of mokupalide [344]. The reactivity of 452 has been compared with a synthon of itself, namely 453 [345]. The synthon has been found to be more selective than 452 and is particularly effective in the synthesis of cyclopentenones such as 454.



452

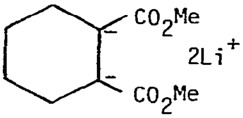


453

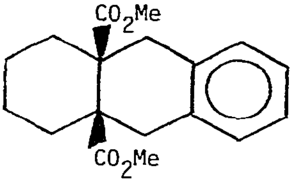


454

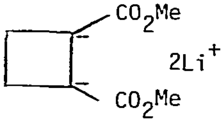
Dilithium diester 455, prepared by metalation of the parent compound with LDA in THF/HMPA, has been combined with α, ω-dihalides to afford annelated products such as 456 [346]. Additional condensations of the related dilithio salt 457 were also described [347].



455

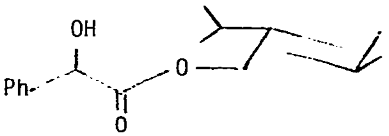


456

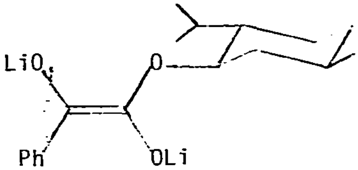


457

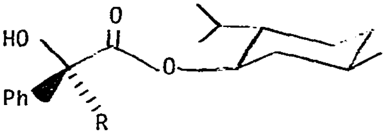
Two-fold metalation of 458, prepared from ℓ-menthol, has given enediolate 459 [348]. Alkylation of this material afforded 460 with up to 50% enantiomeric excess.



458

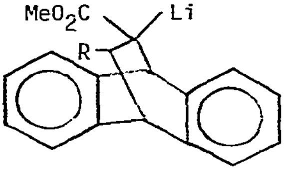


459

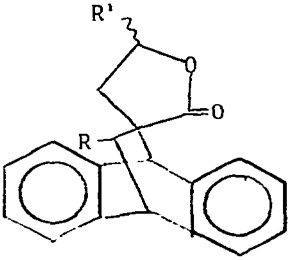


460

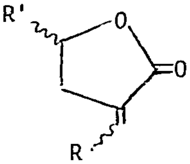
That anion 461 (R=H,CO_2Me) is a masked acrylate system has been demonstrated by treatment with ethylene oxide or propylene oxide to afford 462 (R'=H,Me), pyrolysis of which gives methylene lactones 463 [349]. Acrylates 464 have been prepared from a similar retro Diels-Alder reaction of 465, synthesized by condensation of 466 with a variety of alkyl halides [350].



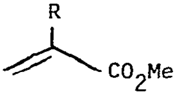
461



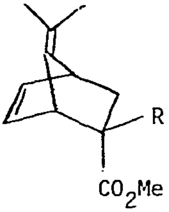
462
(cis and trans)



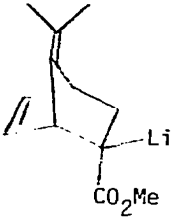
463
(cis and trans)



464

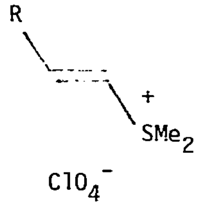


465

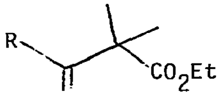


466

Acrylates have also been obtained from certain ester enolates and 467(R=Ph, i-Pr) [351]. For example, lithioethyl isobutyrate and 467 give 468. In contrast, the condensation of less sterically demanding enolates (for example, lithioethyl acetate) with 467 affords cyclopropanes. Similar results were realized with lithionitriles. Another paper discussed the reactions of certain lithio enolates of diesters and β-ketoesters with 469-472 to yield unsaturated sulfinyl derivatives [352]. For example, 473 and 469 or 472 give cis- and trans-474.

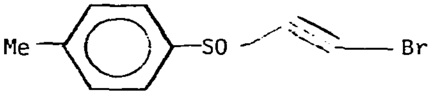


467



468

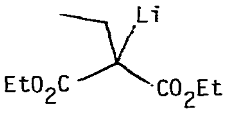
469
(cis and trans)



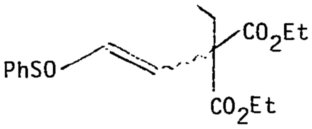
470

471

472

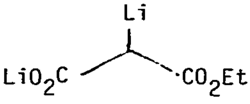


473

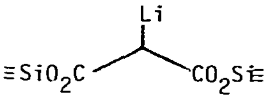


474
(cis and trans)

β-Keto esters or acids have been prepared from lithioacetates and succinic anhydrides [353], from 475 and acid chlorides [354], and from 476 and acid chlorides [355].

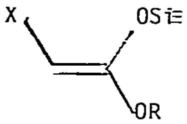


475

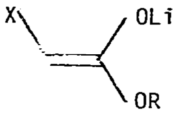


476

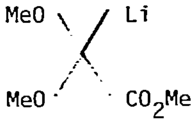
Silylated ketene acetals 477(X=OMe,OSiMe$_3$,OPh,SMe; R=Me,SiMe$_3$), reagents useful for the preparation of α-hydroxy-, α-alkoxy-, and α-methylthioketones, have been obtained by silylation of enolates 478 [356]. An unrelated paper revealed that 479 has now been alkylated by a variety of alkyl halides [357].



477

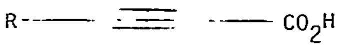


478



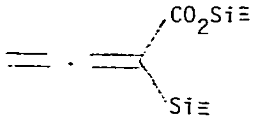
479

The choice of metalating agent employed on certain alkynoic acids has been found important in determining the nature of the products in subsequent alkylations with alkyl halides and chlorotrimethylsilane [358-361]. Thus, silylation of dilithio-2-butynoic acid, prepared by reaction of 480(R=Me) with butyllithium·TMEDA and LDA·CuI, gave 481 and 482, respectively [358]. While similar treatment of 480(R=Et,*i*-Pr) with butyllithium·TMEDA afforded cleavage products arising from attack at the carboxyl carbonyl group, the use of LDA promoted the formation of 483 and 484 [359]. Interestingly, in a study of 485 and 486, while butyllithium·TMEDA caused the rearrangement of the lithio derivative of 485 to that of 486, the opposite was realized with LDA [360]. A fourth paper was concerned with LDA as a base, nucleophile, and electron transfer agent on derivatives of 480(R=Me) and related compounds [361].

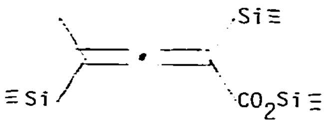


480

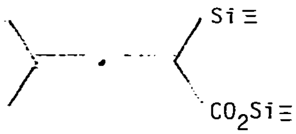
481



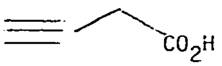
482



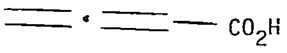
483



484

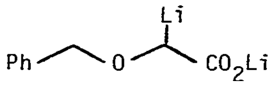


485

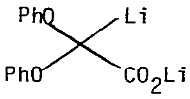


486

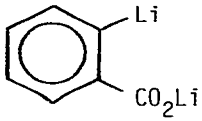
Other papers concerned with dilithiocarboxylates discussed the preparation of enol ethers and ketene diphenyl acetals from 487 [362] and 488 [363], respectively, the use of 489 in the preparation of shihunine and dihydroshihunine [364], and the effect of temperature upon alkylation of the dilithio derivative of 490 [365].



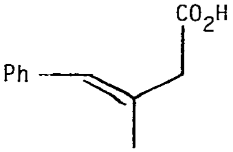
487



488

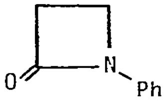


489

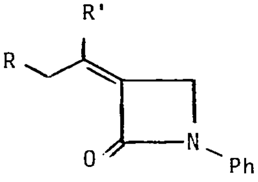


490

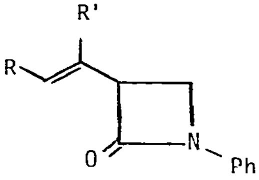
As part of the synthesis of α,β-unsaturated γ-butyrolactones, lactam 491 has been converted to 492 by LDA, chlorotrimethylsilane, and ketones, then isomerized to 493 by additional LDA [366]. A variety of aliphatic amides have been silylated by chlorotrimethylsilane·lithium [367].



491

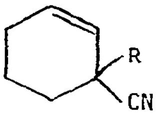


492

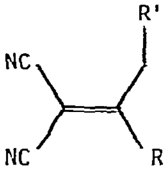


493

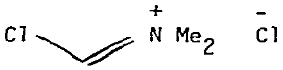
1-Cyanocyclohexene has been lithiated by LDA in THF·HMPA, then alkylated to afford 494(R=Me,i-Pr,CH_2=CMe_2) [368]. Dinitriles 495(R,R'=H, aliphatic, aromatic) have similarly been metalated, then combined with 496 to give 497 [369]. Other lithionitriles have been combined with thirene 1,1-dioxides to form products such as 498 and 499 [370] and with chromium complex 500 to yield adducts such as 501 [371].



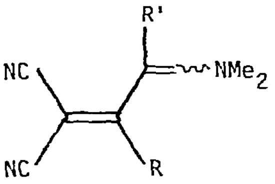
494



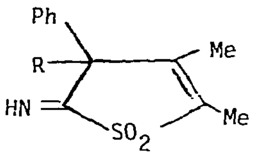
495



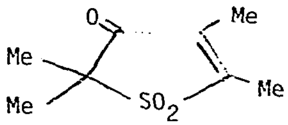
496



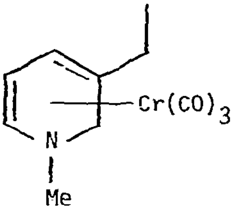
497



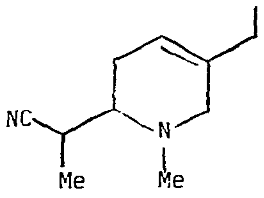
498



499

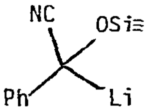


500

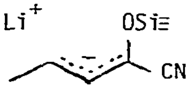


501

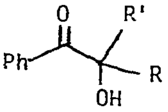
Anions 502 [372] and 503 [373] have been combined with ketones to afford α-hydroxyketones 504 and adducts such as 505, respectively. The latter materials provide a useful entry to cyclopentenones as illustrated by the conversion of 505 to 506 by means of p-toluenesulfonic acid. Related anion 507 has been condensed with anhydrides to give β-ketonitriles [374].



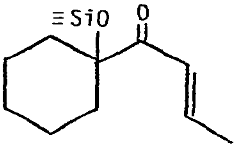
502



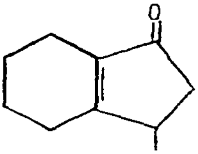
503



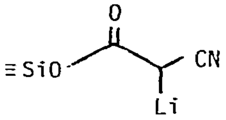
504



505

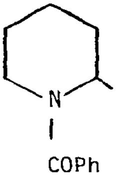


506

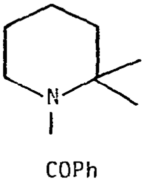


507

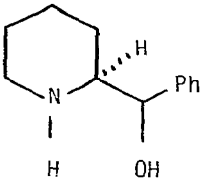
Lithio derivatives of α-aminonitriles have now been employed to introduce α-substituents in tertiary amines [375] and in the synthesis of enamines and dieneamines [376]. The first process is illustrated by the conversion of 508 to 509 by LDA, then to 510 by benzaldehyde followed by sodium borohydride [375]. Intermediates for the above transformation are proposed and other examples are listed. In the second case, aminonitriles 511, obtained by alkylation of the carbanion, have been shown to undergo dehydrocyanation to affort 512 in refluxing toluene or benzene in the presence of KOH or potassium t-butoxide despite the fact that α-phenyl moieties are absent [376].



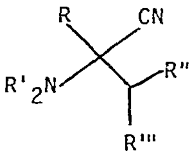
508



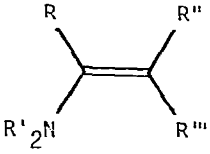
509



510



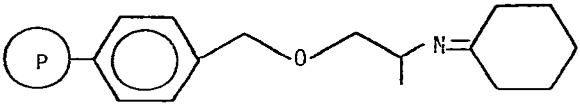
511



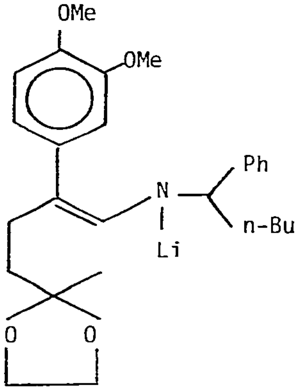
512

C. Amines, Imines, Ethers, and Related Compounds

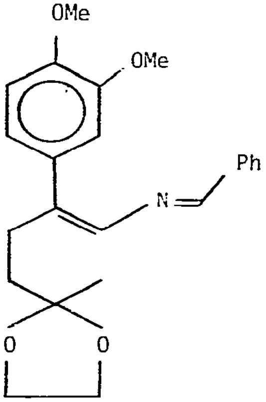
(S)-2-Methylcyclohexanone has been obtained in 95% optical yield and 80% chemical yield by lithiation and methylation of polymer-supported imine 513 followed by hydrolysis [377]. Similar results were realized with the propyl derivative though the optical purity was less. Key steps in a new method of preparing alkaloids involved condensation of lithioenamine 514, obtained by addition of n-butyllithium to 515, with a bromoester, and reaction of 516 with a ketone [378]. A reagent related to 516, 517 has been employed in Horner-Wittig synthesis of enamines [379]. For example, 517 and benzophenone afford 518 (90%). 4-substituted 1,2-4H-diazepines (519, R=E) have been obtained from 519(R=H), LDA, and a variety of electrophiles [380].



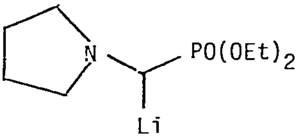
513



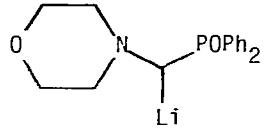
514



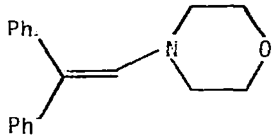
515



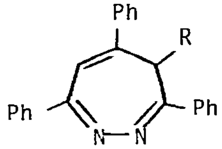
516



517

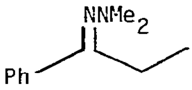


518

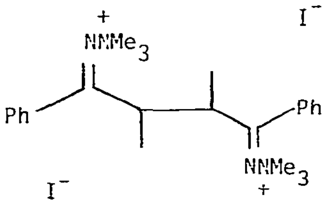


519

As part of an unsuccessful synthesis of a bi(2H-azirine) system, hydrazone 520 has been lithiated by LDA then treated with copper(I) chloride and methyl iodide to give 521 [381]. In other papers, dilithiooximes have been condensed with epoxides to ultimately yield 1,4-diketones [382], and substituted γ- and δ-ketoaldehydes have been obtained from lithioimines and haloacetals [383].

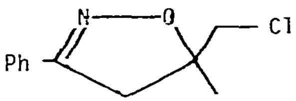


520

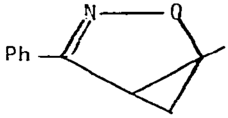


521

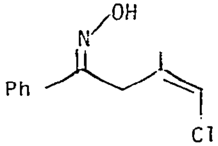
The reaction of 5-chloromethylisoxazoline 522 with organolithiums has been shown to afford cyclopropyl derivatives or unsaturated oximes illustrated by 523 and 524, respectively [384]. Thus, while 522 and n-butyllithium give mostly 524, this heterocycle and LDA·HMPA yields 523 exclusively. The related isoxazoline-5-one 525 has been converted to lithium derivative 526 by a variety of bases [385]. Condensation of 526 with a variety of electrophiles gives 527. Metalation and subsequent condensations of ethyloxazine 528 were also reported [386].



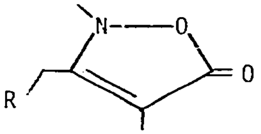
522



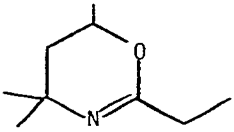
523



524

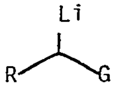


525(R=H)
526(R=Li)
527(R=E)

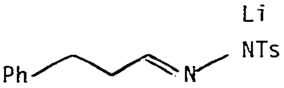


528

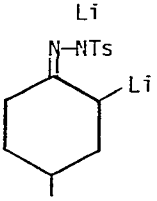
Alkenes including terminal ones may be synthesized via a convenient alternative to the Wittig reaction by condensation of lithiotosylhydrazones derived from aldehydes and non-sterically hindered lithium reagents 529(G=SO$_2$R,CN) [387]. For example, 530 and lithiodimethylsulfone afford 4-phenyl-1-butene (73%). Dilithiotosylhydrazones derived from ketones have been sulfenylated by dimethyl disulfide, relithiated by n-butyllithium, and hydrolyzed to represent a one-pot, three-step, 1,2-carbonyl transposition [388]. The process is illustrated by the sequence 531——>532——>533. Another paper disclosed that syn-dilithio derivatives of tosylhydrazones such as 534 are regiostable [389]. Decomposition of 534 leads exclusively to (Z)-2-lithio-2-octene.



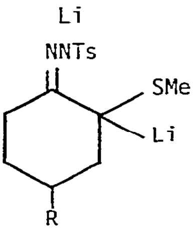
529



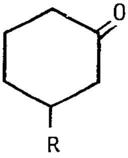
530



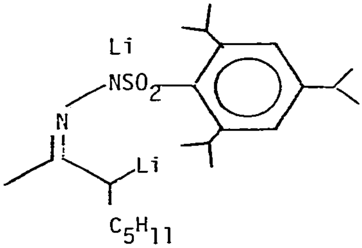
531



532



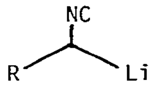
533



534

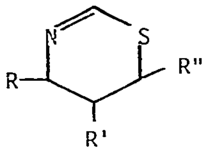
Manipulations using lithio-N-nitrosamines as synthetically useful nucleophiles have been made safer by the disclosure that after completion of condensations with appropriate electrophiles, the nitroso group can be reduced completely by LAH in the same reaction pot [390]. The resulting hydrazine is then conveniently converted to the desired substituted amine by Raney nickel.

Three more papers appeared last year which were concerned with the reactions of lithiated isocyanides. Thus, 535(R=Ph,H) and episulfides 536(R',R"=H,aliphatic, $CH(OEt)_2$) have been combined to ultimately give thiazines 537 [391]. o-Tolyl isocyanide has been lithiated as in the past, then combined with certain esters to afford 538 or 539 upon subsequent treatment with copper(I) oxide and acid, respectively [392]. While cyclization of o-tolyl isocyanide by two equivalents of LDA followed by alkylation was previously reported to yield 1-alkylindoles 540, it has now been found that addition of magnesium iodide to the system prior to the alkyl halide results in the formation of 3-alkylindoles 541 [393].

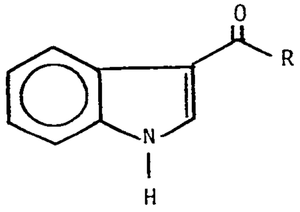


535

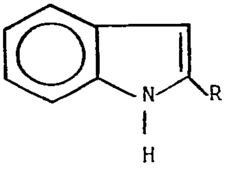
536



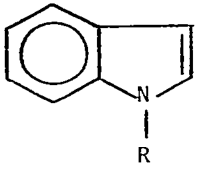
537



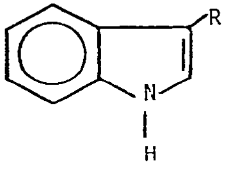
538



539



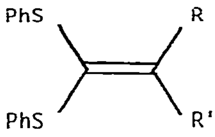
540



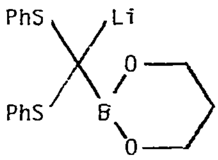
541

D. Carbanions Stabilized by Sulfur and Other Heavier Atoms

Ketene thioacetals 542 have been synthesized from boron-sulfur substituted anions such as 543 and ketones [394].

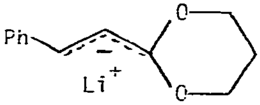


542

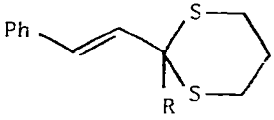


543

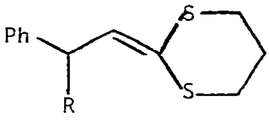
The site of alkylation of lithioketene thioacetal 544 to afford 545 and/or 546 has been studied in terms of the HSAB theory [395]. The authors found that the ratio of 545/546 increased with increasing hardness of the leaving group of the alkylating agent, that the hard electrophiles chlorotrimethylsilane and D_2O gave only 545, and that 545 was usually trans. Exclusive γ-allylation of non-arylated 544 was realized in the presence of copper(I) iodide·trimethyl phosphite [396].



544

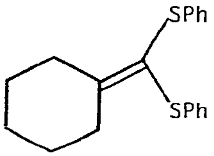


545

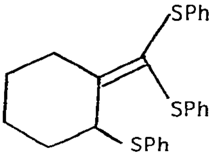


546

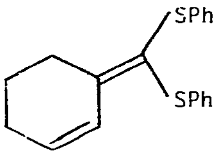
Ketene thioacetal 547, prepared from cyclohexanecarboxylic acid and $Al(SPh)_3$, has been sulfenylated by s-butyllithium·TMEDA and diphenyl disulfide to afford 548, subsequently converted to 549, then treated with n-butyllithium to give 550 [397]. The more simple ketene thioacetal 551 has been combined with sulfur-stabilized anions such as 552 to yield cyclopropanone phenylthioketals such as 553 [398]. Another paper described the conversion of 547 into 554 by lithium napththalenide followed by condensations with electrophiles to afford 555 [399]. Similar results with other ketene thioacetals are included.



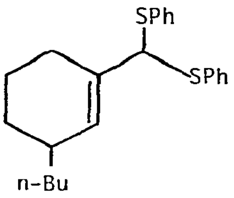
547



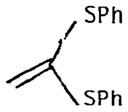
548



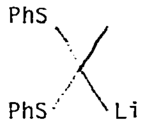
549



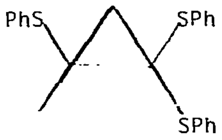
550



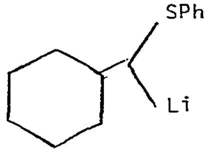
551



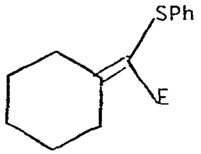
552



553

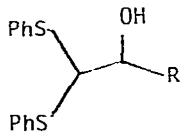


554

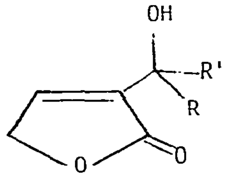


555

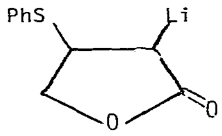
A full paper appeared in 1979 which disclosed details of the conversion of α-hydroxybis(phenylthio)acetals 556, prepared in the usual manner, to simple ketones and α-(phenylthio)ketones by trifluoroacetic acid and p-toluenesulfonic acid, respectively [400]. 2-Substituted 2-buten-4-olides 557 have been prepared by condensation of 558 with aldehydes and ketones followed by elimination of the phenylsulfur moiety as its sulfoxide [401].



556

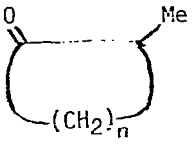


557

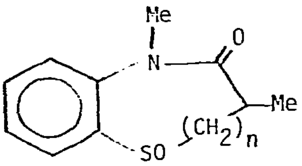


558

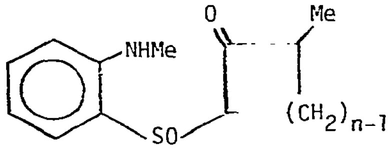
Medium-sized rings 559(n=5-9) may now be synthesized in excellent yields by treatment of 560 with LDA to give 561 [402]. The rings 559 themselves are freed from the sulfoxides by reduction with aluminum amalgam. Similar results were obtained with the related sulfones and potassium t-butoxide.



559

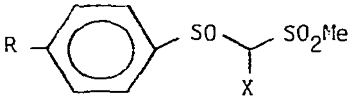


560

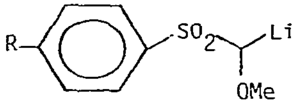


561

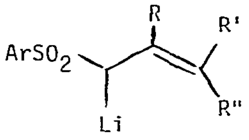
Sulfinylsulfones 562 have been metalated by n-butyllithium, then alkylated to afford 563 [403]. These carbanions have also been condensed with formaldehyde and secondary amines to yield Mannich adducts. Similarly prepared and condensed were 564 [404] and 565 [405]. The latter reagents are useful for the preparation of allylic alcohols. Condensation of lithiomethyl aryl sulfones with chiral 566 has afforded chiral agents 567 ($\geq$97% ee) [406].



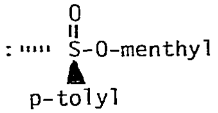
562(X=H)
563(X=R')



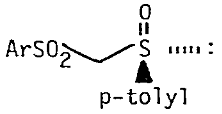
564



565

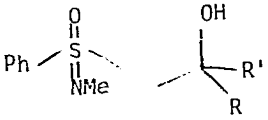


566



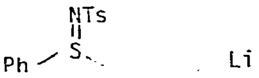
567

Alkenes have been prepared by reductive elimination of 568, prepared from 569 and aldehydes and ketones [407]. In contrast, condensation of 570 with these electrophiles gives oxiranes (71-100%) [408].



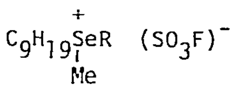
568

569



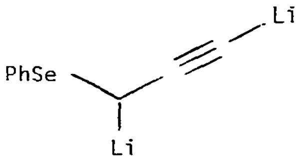
570

Two full papers discussed details about selenium stabilized carbanions. The first one described deprotonation of a variety of selenides by LDA and LiTMP and compared the kinetic acidities of selenides and sulfides [409]. For example, aryl methyl sulfides are kinetically about four times as acidic as the corresponding selenides. Surprisingly, the trimethylsilyl group reduces the kinetic acidity of $ArSeCH_2SiMe_3$ toward LiTMP but has the opposite effect towards LDA. Extensive examples of the condensations of α-lithioselenides with aldehydes and ketones to afford β-hydroxy selenides are presented as well as their anti-reductive-elimination to give olefins. The formation of alkenes by selenoxide syn-elimination is also discussed. The second paper devotes more attention to the preparation of α-lithioselenoxides and their condensations with aldehydes and ketones as well as alkyl halides and esters [410]. The second paper assumes more importance when it is recalled that α-lithioselenoxides are more easily prepared than the α-lithioselenides by simple deprotonation. The preparation of allyl alcohols, enones, and olefins from the selenium reagents are described. Other papers in this area describe a high yield synthesis of terminal alkenes from alkyl halides, $RSeCH_2Li$, CH_3SO_3F, and potassium t-butoxide where 571 is an intermediate [411], the use of 572 in the synthesis of epi-7-hydroxymyoporone where reagent 572 is equivalent to 573 [412], and conversion of the adducts derived from 574 and aldehydes to vinyl selenides, vinyl silanes, vinyl bromide, and others [413].

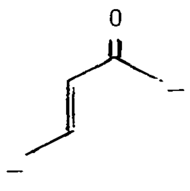


$C_9H_{19}\overset{+}{\underset{Me}{Se}}R\ (SO_3F)^-$

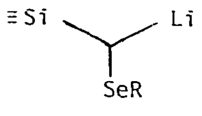
571



572

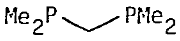


573

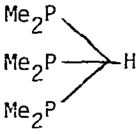


574

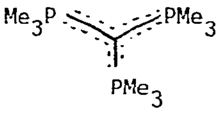
Metalation of bisphosphane 575 followed by addition of chlorodimethylphosphine has been shown to yield 576 [414]. Metalation of the latter with t-butyllithium followed by quaternization with three equivalents of methyl iodide has given 577, the first symmetrical resonance-stabilized phosphorus ylide derivative [415].



575

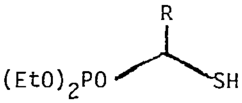


576

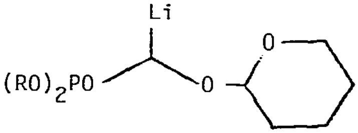


577

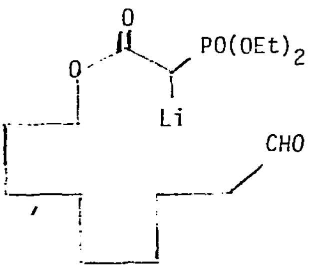
Lithium phosphonate carbanions have been combined with elemental sulfur to afford α-phosphoryl thiols such as 578 [416]. Related reagents such as 579 [417] and 580 [418,419] have been employed in the synthesis of enol ethers and macrocycles, respectively.



578

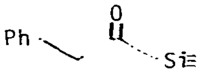


579

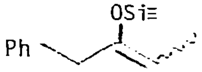


580

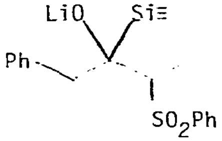
Silyl enol ethers have been prepared from acylsilanes and certain organolithium reagents [420]. For example, 581 and α-lithioethyl phenyl sulfone afford 582 via rearrangement of 583 to 584. A similar rearrangement of 585, prepared from the allyl alcohol and butyllithium, to 586 also yielded silyl enol ethers [421]. Metalation of 587 by LDA provided an equilibrium mixture of 588 and 589 which favored 588 when R was large (for example, isopropyl) and at 25^c [422]. Alkylation of the mixture (R=H,Me,Et,n-Hp,Ph) at 25° gave 590.



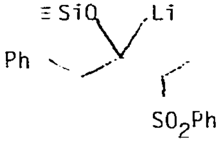
581



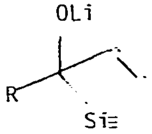
582



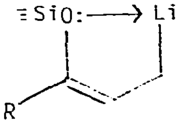
583



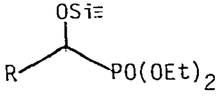
584



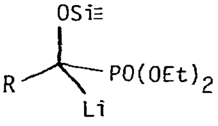
585



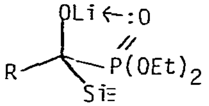
586



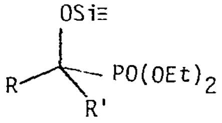
587



588

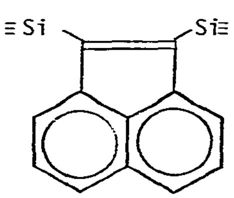


589

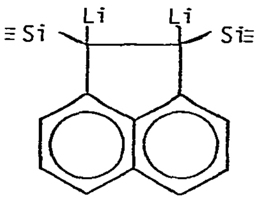


590

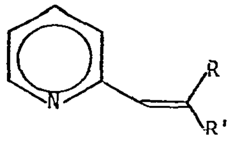
Silyl derivatives such as 591 have been obtained from 592 and $CdCl_2$ [423]. Alkenylpyridines 593 have been synthesized directly from 594 and aldehydes and ketones [424].



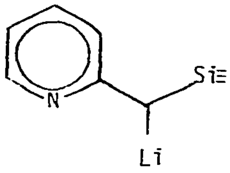
591



592

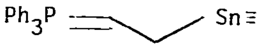


593

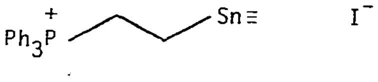


594

A full paper described the preparation of allyl tin compounds by Wittig reactions of 595, prepared by reaction of 596 with LDA or lithium bis(trimethylsilyl)amide, but not phenyllithium [425].



595

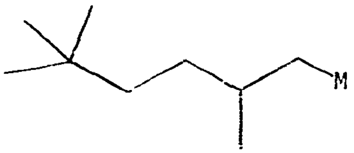


596

E. Polymerization

Activation of n-butyllithium-promoted polymerization of ethylene by TMEDA, tetraethylethylenediamine (TEEDA), and pentamethyldiethylenetriamine (PMDT) has been studied [426]. Consistent with the NMR determination that the α-hydrogens of n-butyllithium are shifted more by TEEDA than the others, kinetics reveal the polymerization to be faster in the presence of this amine.

The active centers in the anionic polymerization of isoprene have been studied in ethyl ether by the use of model compound 597 using UV and NMR spectroscopy [427]. The system shows a preference for the cis configuration though some trans structure is present with lithium as the counterion. The percentages of the 1,4- , 1,2-, and 3,4-isomers are shown as a function of the metallic cation.

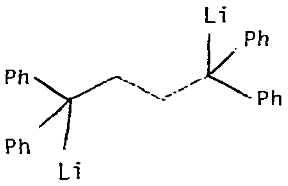


597

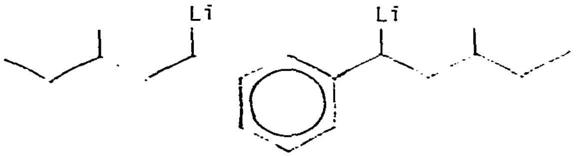
A new N-lithium initiator, N-lithiomorpholine, has been found to polymerize 1,3-butadiene but not isoprene [428]. Though this initiator afforded similar amounts of 1,2-content of the polybutadiene as obtained with lithium diethylamide, the percentage of such material was increased by the presence of alkali t-butoxides.

The propagating species in the polymerization of 1-phenyl-1,3-butadiene effected by n-butyllithium was concluded to be the 4,1-anion as evidenced by ^{13}C- and 'H-NMR spectroscopy [429]. Lithiated 1-phenyl-2-butene was used as a model compound.

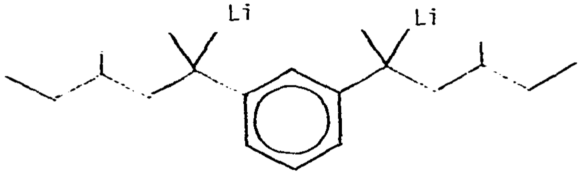
A note with reference to 32 earlier papers briefly discussed organodilithium initiators for polymerizations [430]. The authors concluded that the initiators must possess carbon-lithium bonds of equal reactivity, be completely soluble in hydrocarbon media, and must be able to initiate the polymerization quickly relative to the subsequent propagation step. They suggest that 598-600 and the difunctional adducts from 2,4-hexadiene isomers meet the above criteria. Two other papers were also concerned with this area. While one indicated that 601 polymerized styrene [431], the other suggests that 599 may not be suitable as a catalyst because the dilithium adduct is not formed quantitatively from n-diisopropenylbenzene and s-butyllithium [432].



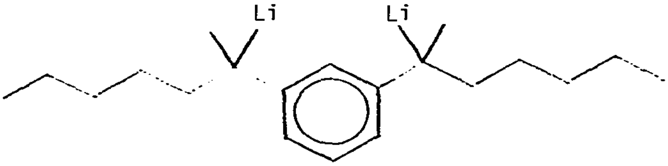
598



599

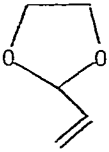


600

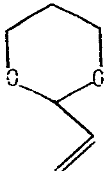


601

Other papers in this area were concerned with an NMR study of low-molecular weight stereoregular polymers of 2-vinylpyridine prepared with lithium salts as initiators in THF [433], the reactivity of monomers in the anionic copolymerization of α-methylbenzyl methacrylate and trityl methacrylate effected by n-butyllithium [434], the equilibrium anionic polymerization of β-methoxycarbonylpropionaldehyde by monolithium benzophenone in THF [435], anionic block copolymerization of ε-caprolactam [436], anionic polymerizations of 602 and 603 by n-butyllithium and other bases [437], and reaction of poly(dichlorophosphazene) (604) with phenyllithium to afford chain cleavage and chlorine substitution products [438].



602



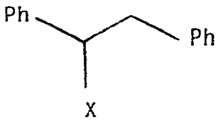
603

$[-N=P(Cl_2)-]_x$

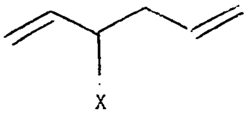
604

F. Carbenoids

The formation of α-lithiobenzyl chloride and bromide resurfaced in 1979 when it was shown that 605(X=Cl,Br) was obtained from benzyl chloride or bromide with a half equivalent of LDA [439]. While similar results were realized with allyl bromide, such treatment of allyl chloride with LDA followed by allyl bromide gave 606(X=Cl,Br) and 607. Another paper described condensations of allyl system 608(R=Me) with epoxides to afford vinyl epoxides [440]. For example, 608 and benzophenone yield 609 (71%). Allyl system 608(R=Cl) has been combined with simple alkenes to give chlorovinylcyclopropanes 610(R's=H or Me) [441].



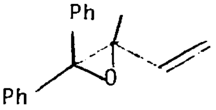
605



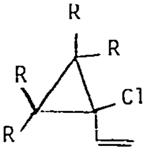
606

607

608

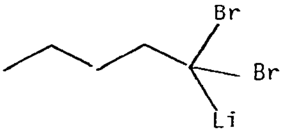


609

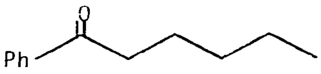


610

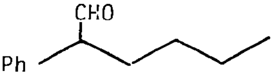
1,1-Dibromoalkyllithiums have been combined with aldehydes and ketones to afford ketones and homologues of ketones, respectively [442]. For example, benzaldehyde and 611 yields 612 (81%) and 613 (19%). The addition of lithiodibromomenthane to a cyclopentanone was a key step in the synthesis of (±)-nootkatone [443].



611

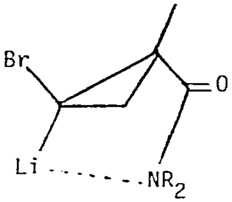


612

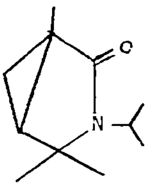


613

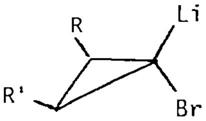
Cyclopropylamides 614(R=i-Pr,Me) have been obtained from the corresponding 1,1-dibromo systems and methyllithium [444]. Trapping experiments with D_2O and benzaldehyde as well as conversion to 615 are described. Carbenoids 616(R and R'=H, aliphatic, aromatic) ahve been converted to 617 by Eschenmoser's reagent, then to 618 by butyllithium and dimethyl carbonate, and finally to α-methylene-lactones 619 by iodotrimethylsilane and heat [445].



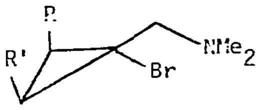
614



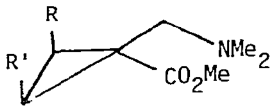
615



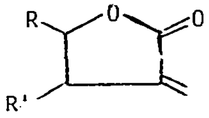
616



617

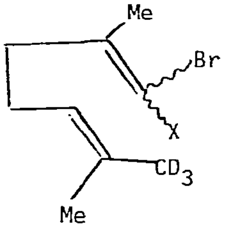


618



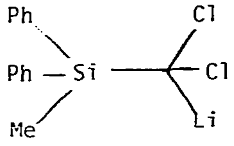
619

As part of the study of the mechanism of the dimerization of bicyclo[3.1.0]-hex-1-ene, 620 has been converted to 621 by methyllithium [446].

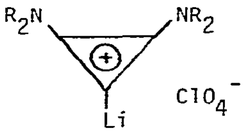


620(X=Br)
621(X=Li)

Other papers in this area discussed alkylation of lithiodichloromethane and the conversion of the alkylated derivatives to acetylenes by n-butyllithium [447], the formation and alkylations of silyl derivatives of lithiodichloromethanes such as 622 [448], and reactions of carbenoid 623 with 624 and with tetrachlorocyclopropene [449].



622



623

$\equiv SiOSO_2CF_3$

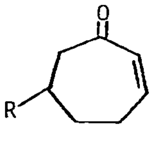
624

9. LITHIUM ATE COMPLEXES

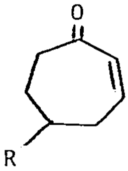
A. Cuprates

An article in Japanese described a variety of procedures for highly selective organic synthesis using ate complexes derived from lithium, copper, boron, aluminum, and palladium [450].

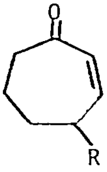
A systematic study of the stereochemistry of cuprate addition to alkylcycloheptenones has been reported [451]. The best stereoselectivity was realized with lithium dimethylcuprate and 626, 627, and 630 to afford mostly trans adducts, with lithium di-t-butylcuprate and 625 and 628 to give mostly cis adducts, and with the latter cuprate and 629 to yield the trans product.



625(R=Me)
626(R=t-Bu)

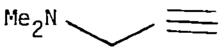


627(R=Me)
628(R=t-Bu)

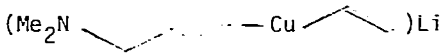


629(R=Me)
630(R=t-Bu)

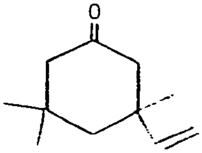
Amino acetylene 631 has been found to be a convenient precursor for versatile mixed cuprates because of its commercial availability, the ease of work-up, and the fact that complexing agents are not necessary for cuprates derived from it such as 632 [452]. Thus, 632 adds to isophorone to afford 633 (52-58%).



631

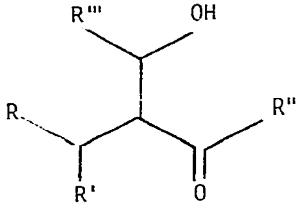


632



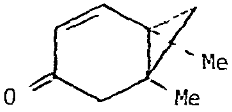
633

A large number of conjugate additions to α,β-unsaturated ketones by dialkylcuprates followed by the addition of aldehydes to give adducts such as 634 has been successful provided the latter condensations are effected in the presence of zinc chloride [453].

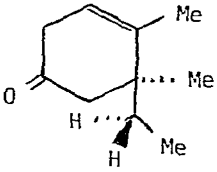


634

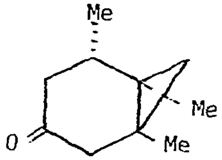
The high stereoselectivity in the cyclopropyl ring opening of 635 by lithium dimethylcuprate to yield 636 has been interpreted in terms of a direct nucleophilic attack at the cyclopropyl carbon rather than via a radical anion process [454]. Adduct 637 arising from conjugate addition was also present as a product. Cyclopropyl ring opening was also realized in the conversion of 638 to 639 by lithium dimethylcuprate as part of the synthesis of dl-7,8-epialantolactone [455].



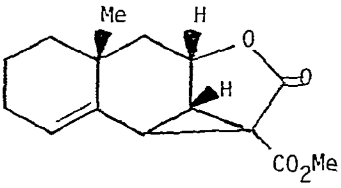
635



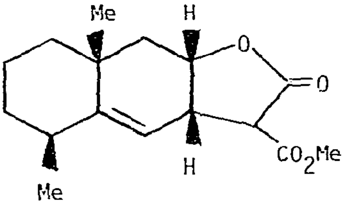
636



637

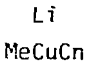


638



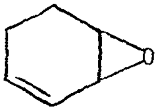
639

A simple route to 4-alkylcyclohexenols and -cycloheptenols has been achieved by condensation of cycloalkene epoxides with mixed alkylcyanocuprates 640, [456, 457]. For example, 640 and 641 at either -78° or 0° yields only 642. The above regioselective reactions coupled with hydroxyl directed epoxidations has provided a general methodology for the functionalization of five carbon atoms of a six carbon unit [457].

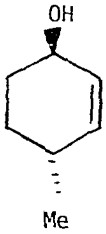


$\overset{Li}{MeCuCn}$

640

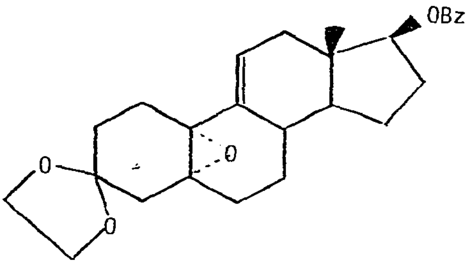


641

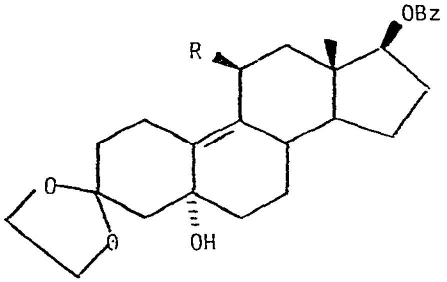


642

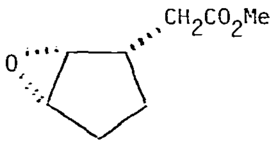
Regio- and stereospecific syntheses of 11β-substituted-19-norsteroids such as 644 have been achieved by treatment of epoxides such as 643 with cuprates [458]. Another paper described an SN' anti process in the reaction of 645 with lithium di-n-butylcuprate to afford 646 and 647 [459]. Reactions of this cuprate with several allyl halides are also discussed.



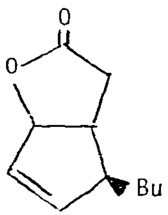
643



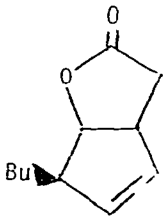
644



645

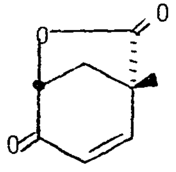


646

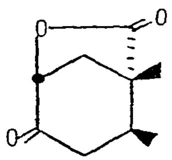


647

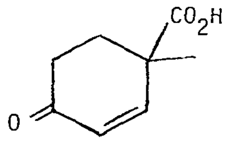
The imposition of a rigid conformation upon cyclohexenones by a lactone function has allowed steric control at the β-carbon in their reactions with cuprates [460]. For example, 648 and lithium dimethylcuprate give 649 (51%) and 650 (39%). The method has been used to prepare trans-fused ring systems. Interestingly, the amount of reductive cleavage observed is a function of the stereochemistry of the starting enone lactone since 651 and lithium dimethylcuprate yield 652 (60%) (after treatment with diazomethane) and 653 (9%) [461].



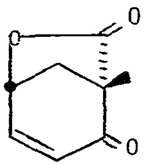
648



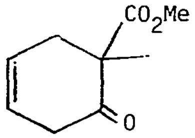
649



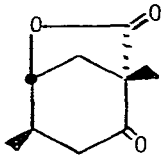
650



651

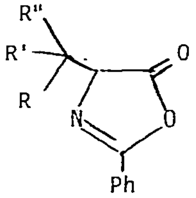


652

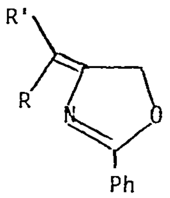


653

Oxazolinones 654 have been synthesized from 655 and lithium phenylthio(alkyl)cuprates [462]. The oxazolinones can be conveniently converted to α,α-disubstituted γ-diketones.



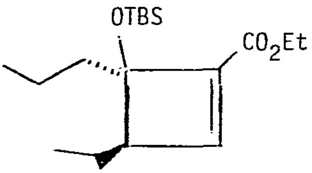
654



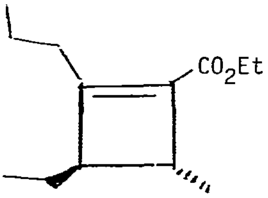
655

Another paper appeared which describes a test to determine whether nucleophilic additions occur by a single electron transfer pathway [463]. Thus, this mechanism is suggested to be in operation when the E- and Z-isomers of a chiral α,β-unsaturated ester give products of the same absolute configuration with organometallics such as cuprates.

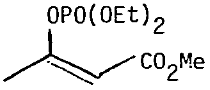
Lithium dimethylcuprate has been added to a variety of cyclobutenyl esters as illustrated by the conversion of 656 to 657 [464]. Cuprates have also been added to enol phosphates of β-keto esters to afford β-substituted α,β-unsaturated esters [465]. For example, 658 and lithium dimethylcuprate give 659.



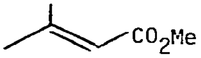
656



657



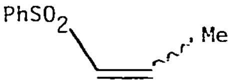
658



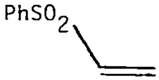
659

Several papers were concerned with cuprates and halounsaturated carbonyls and related compounds. Thus, while α-fluoro-α,β-unsaturated carbonyls afford mixtures of 1,2- and 1,4-addition products, β-monosubstituted α-chloro-α,β-unsaturated ketones and esters give 1,4-adducts [466]. Reactions of lithium dimethylcuprate with sulfones 660 have been found to afford 661 (cis and trans) and/or 662 as a function of the stereochemistry of 660 and the halogen [467]. For example, cis and trans 660 (X=Br) give mostly 662 and 661 (trans), respectively. In contrast, cis and trans 660 (X=Cl) give mixtures of 661 (cis) and 662, and 661 (trans), respectively.

660

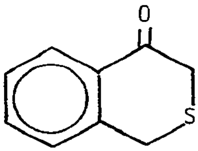


661

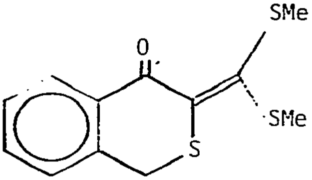


662

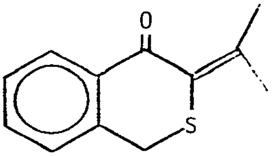
The t-butyl group has been introduced indirectly onto 663 by addition-elimination of lithium dimethylcuprate to 664 to afford 665 followed by addition of another equivalent of the cuprate to yield the final product [468].



663



664

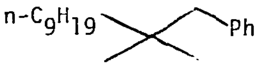


665

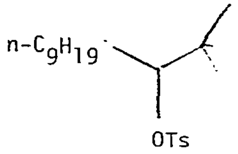
Polymer supported cuprates have been obtained from polymer-bound iodo(triarylphosphine)copper and two equivalents of organolithiums [469]. Such cuprates have been utilized in alkylations and conjugate additions. A major advantage of these systems is the fact that one or more equivalents of tertiary phosphine or phosphite is not necessary.

While primary neopentylic tosylate 666 and lithium diphenylcuprate afford 667 by displacement, 666 and lithium dimethylcuprate yield 2,2-dimethylundecane by an unknown mechanism [470]. In contrast, secondary neopentylic tosylates such as 668 with either cuprate reagent give olefins such as 669 (77-80%). Skeletal rearrangements are observed in such dehydrosulfonations when anti-eliminations are not possible.

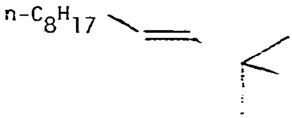
666



667

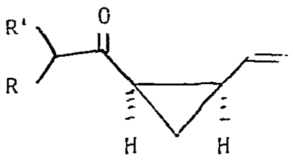


668

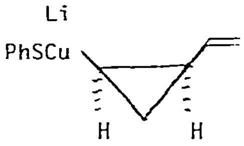


669

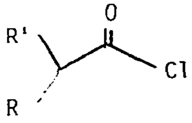
2-Vinylcyclopropyl ketones 670 have been synthesized from cuprate 671 and acid chlorides 672 [471]. Ketones 670 proved to be useful intermediates in the preparation of 4-cycloheptenones.



670

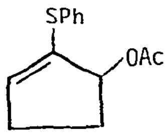


671

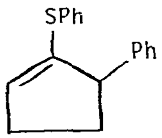


672

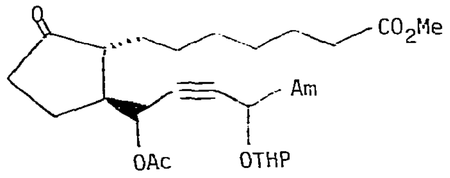
Acetoxyvinyl sulfides such as 673 have been combined with cuprates to afford coupled products illustrated by 674 (86%) [472]. Products such as 674 may be conveniently converted to a variety of cyclopentene derivatives. Similar displacement of propargylic acetates with cuprates has been employed to prepare new allenic prostanoids as illustrated by the conversion of 675 to 676 [473].



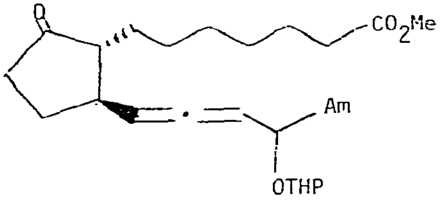
673



674

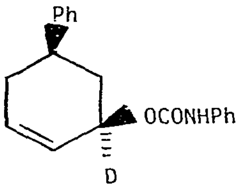


675

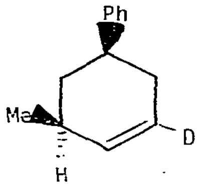


676

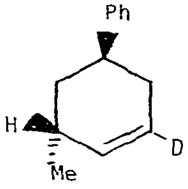
Treatment of cis-carbamate 677 with lithium dimethylcuprate has been shown to afford mostly 678 while the corresponding trans-carbamate gives mostly 679 [474]. Such formal syn S_N2' reactions are possibly a consequence of a preferred concerted process perhaps occurring by an electron-transfer mechanism. Other esters including formates, acetates, benzoates, $EtOCO_2$-, and $Me(Ph)NCO_2$- give mixtures of anti SN_2' and SN_2' products with this cuprate.



677

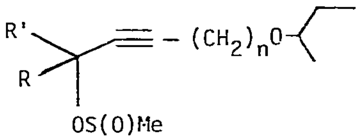


678

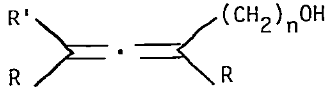


679

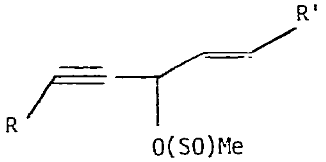
Reaction of 680 (R and R'=H, aliphatic; n=1 or 2) with RCuBr·MgX·LiBr followed by simple hydrolysis gives α- or β-allenic alcohols 681 (n=1 or 2, respectively) (60-90%) [475]. Similar condensations of E-682 with such reagents yields 683 or 684 as a function of the size of R and R' [476]. For example, 683 is obtained when R=H and R'=t-Bu while 684 is the sole product (mostly Z isomer) when R =t-Bu and R'=H.



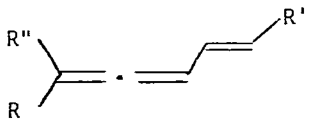
680



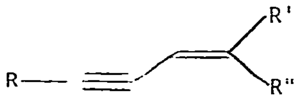
681



682

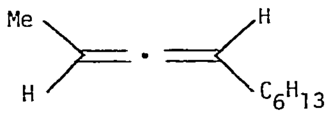


683

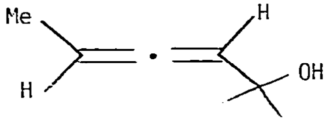


684

Chiral allenes 685 and 686 have been racemized by lithium di-n-butylcuprate in ether or THF at low temperature (-30°) persumably via radical anion intermeidates [477]. While 686 was also racemized by methylmagnesium iodide, it was unchanged by lithium aluminum hydride even after 17 hours.

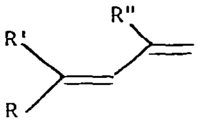


685

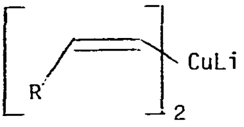


686

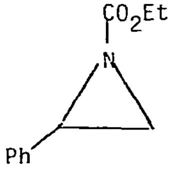
Other aliphatic cuprates have been added to 1,1-disubstituted 1,2,3-butatrienes to afford mostly 687 [478], to acetylene to give Z-dialkenylcuprates 688 [479], and to aziridines such as 689 to yield 690 [480].



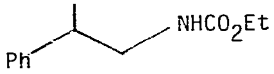
687



688

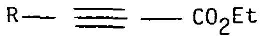


689

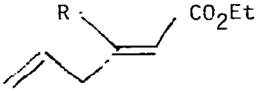


690

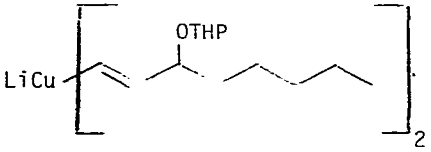
Turning to allylic cuprates, lithium diallylcuprate has been found to add stereoselectively at -90° to 691 (R=n-Bu,Me) to afford 692 (100%) [481]. Mixtures of products were obtained at higher temperatures or when allyl groups with additional substituents were employed. Cuprates such as 693 have been added to certain cyclopentenones as part of the synthesis of prostaglandin analogs modified at the 10- and 11-positions [482].



691



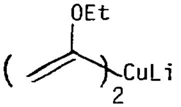
692



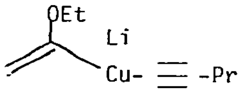
693

Conditions have been described for the alkylation of 688 where both alkenyl groups are used [483]. The success of the reactions is ascribed to the use of HMPA.

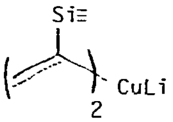
Full details were published in 1979 on the preparation, conjugate additions, and demasking of synthonic cuprates 694, 695, and 696 [484]. A comparison of the reactivities, stabilities, and demasking characteristics of the reagents is listed.



694

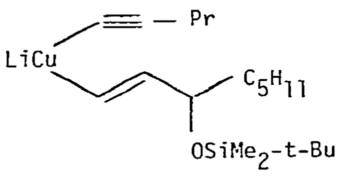


695

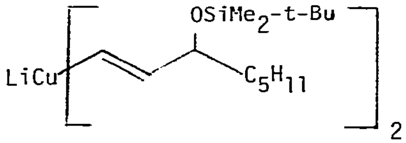


696

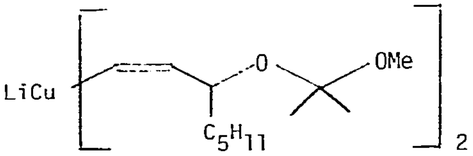
Certain prostaglandins continued to by synthesized using various cuprates. Thus, the preparation of prostaglandin-A_2 [485], 9-deoxa-9,10-dehydroprostaglandin-D_2 [486], and (±)-prostaglandin-$F_{2\alpha}$ [487] utilized 697, 698, and 699, respectively. Reagent 697 has also been combined with an epoxybicyclo[3.2.0]heptanone [488].



697

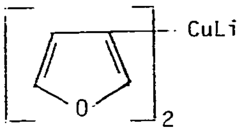


698



699

Styrene and n-butyl acrylate have now been arylated by lithium and halomagnesium diphenylcuprates in the presence of $PdCl_2$ to afford trans-stilbene and butyl cinnamate, respectively [489]. 3-Substituted furans have been conveniently prepared from 700 and acid chlorides, ketones, alkyl halides, and epoxides [490].



700

Direct carbamoylations may now be effected by 701, prepared from 702 and carbon monoxide [491]. For example, 703 is obtained from 701 and allyl bromide in yields of up to 76%.

$(Et_2NCO)_2CuLi$

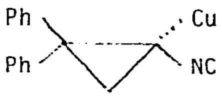
701

$(Et_2N)_2CuLi$

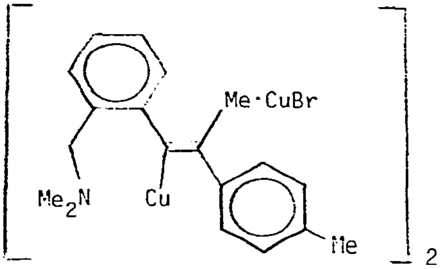
702

703

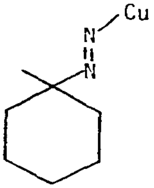
Several organocopper reagents themselves have been prepared using organolithiums. Among them were 704 [492], 705 [493], 706 [494], and 707 [495,496]. Subsequent condensations of most of the above are discussed.



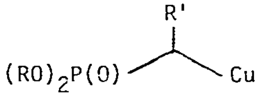
704



705



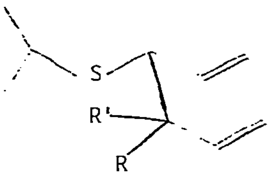
706



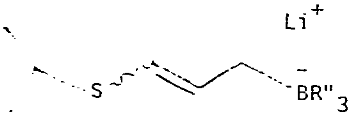
707

B. Boron, Aluminum, and Silver

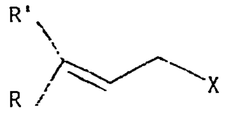
Head-to-tail 1,5-dienes 708 (R and R'=Me or H) have been prepared from 709 and allyl halides 710 (X=Cl,Br) [497]. The ate complexes 709 were obtained from isopropylthioallyllithium and trialkylboranes.



708

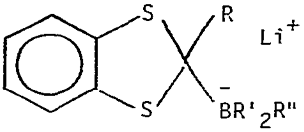


709

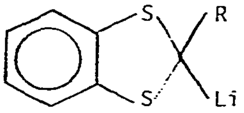


710

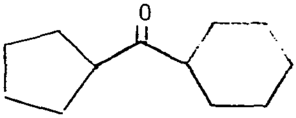
Boron ate complexes 711, prepared from 712 and trialkylboranes, have been oxidized by hydrogen peroxide [498] or treated with $HgCl_2$ (or methyl fluorosulfonate), then oxidized [499] to afford ketones or tertiary alcohols, respectively. For example, 712 (R=cyclohexyl) with tricyclopentylborane gives 713 (78%) and 714 (67%), respectively. Other examples are listed including several with mixed trialkylboranes.



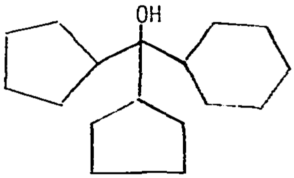
711



712

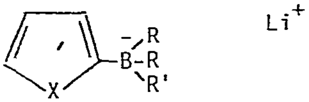


713



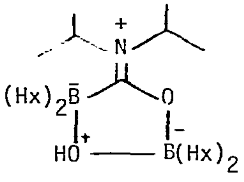
714

2-lithiofurans [500,501] and 2-lithio-N-methylpyrrole [501] have been converted to 2-alkyl derivatives by trialkylboranes and iodine [500] or N-chlorosuccinimide [501]. Ate complexes 715 are intermediates.

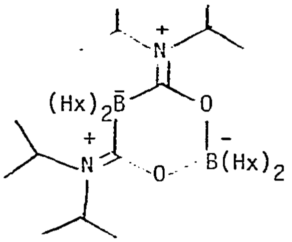


715 (X=O or NMe)

Reaction of $LiCON\text{-}i\text{-}Pr_2$ with di-n-hexylbromoborane has been shown to afford cyclic products 716 and 717 [502]. The crystal structure of 717, a compound resistant to oxidation by 50% hydrogen peroxide and base, is described.



716



717

Of the voluminous number of papers describing the use of complex borohydrides and aluminum hydrides, only a few are included here. Thus, $[Co(CO)_4]Li$, $[(C_5H_5)Mo(CO)_3]Li$, $[Mn(CO)_5]Li$ and $[(C_5H_5)Fe(CO)_2]Li$ have been conveniently prepared by reduction of the corresponding metal carbonyl dimers by $LiEt_3BH$, $Li\text{-}s\text{-}Bu_3BH$ and $K\text{-}s\text{-}Bu_3BH$ [503]. The paper lists several condensations of each of the above anions.

Lithium trialkylborohydrides may be obtained in quantitative yields from trialkylboranes and lithium trimethoxyaluminohydride in THF [504] and trialkylboranes and lithium aluminum hydride·TED in ether [505]. Such borohydrides may be used directly in subsequent reactions without removal of the aluminum methoxide side products. Similar reactions of trialkylboranes with lithium tri-t-butoxyaluminohydride in THF result in conversion of the solvent to 1-butanol [506]. However, the latter reactions can be effected in tetrahydropyran thus allowing the use of ^{11}B-NMR to follow such reactions.

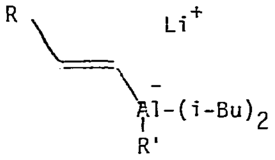
Asymmetric alkylations of benzaldehyde and acetophenone have been effected by lithium and sodium complexes 718 in which the R' group contained (-)-N-methylephedrin, (-)-quinine, and (+)-cinchronine [507].

$$R_3\overset{-}{\text{Al}}\text{OR}' \qquad M^+$$

718

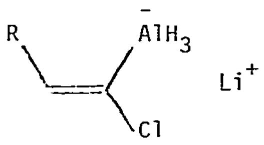
Ate complexes such as 719 (R'=Me) have been found to transfer only the vinyl moiety to cyclopentenones in a 1,4-fashion [508]. No 1,2-adducts were observed. This technique has been applied to the preparation of several prostaglandins. Reagents 719 (R'=n-Bu) have also been combined with allyl thiosulfonates

720 to give allyl vinyl thioethers, precursors for the thio-Claisen rearrangement [509]. Chloroalanates 721, prepared by treatment of chloroacetylenes with lithium aluminum hydride, have been methanolyzed to yield (E)-1-chloro-1-alkenes [510].



719

720



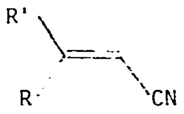
721

Finally, alkylargentates 722 have been added to 723 (R'=Ph,cyclohexenyl) at low temperature to afford, after hydrolysis, 724 [511]. Mixtures of 724 and their stereoisomers are obtained if the reaction mixtures are allowed to warm before hydrolysis.

$R_2AgMgX \cdot 2LiBr$

722

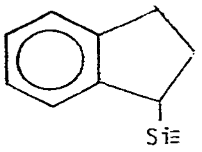
723



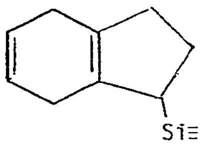
724

10. REDUCTIONS AND RADICAL IONS

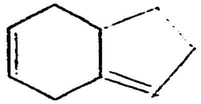
A large number of benzylsilanes have been converted to dihydro derivatives by lithium/ammonia/alcohol, then protodesilylated with aqueous hydrochloric acid to give olefins [512]. For example, 725 affords 726 (70%), then 727 (98%).



725

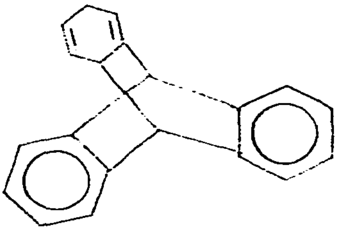


726

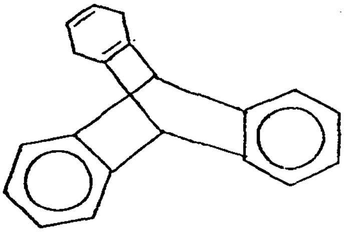


727

In contrast to ring opening with potassium in THF, lithium/ammonia/t-butyl alcohol reduction of triptycene has been shown to yield 728 accompanied by 729 [513]. Similar reductions of derivatives of this hydrocarbon are reported.

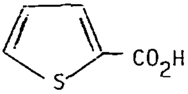


728

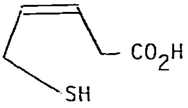


729

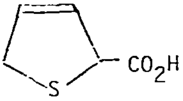
Lithium/ammonia/methanol reduction of 730 using five equivalents of the metal affords 731 [514]. Similar reduction of 730 using only three equivalents of lithium gives 731 accompanied by 732, 733, and 734. Another paper described the preparation of 735 from the parent hydrocarbon and lithium/ammonia as part of the synthesis of metabolites of 7-methylbenz[a]anthracene [515].



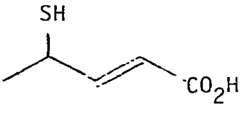
730



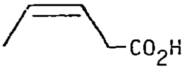
731



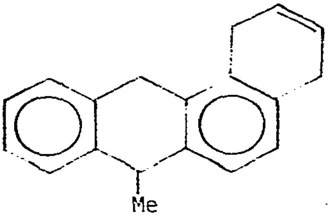
732



733



734

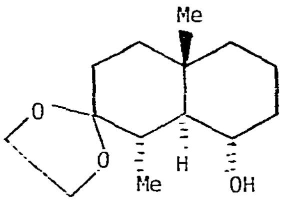


735

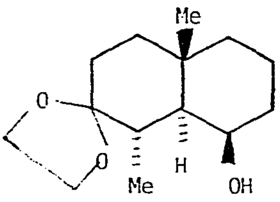
A very thorough paper discussed the chemistry of alkali metal adducts of α,β-unsaturated organosilanes obtained by reduction of the parent compounds by lithium or potassium in donor solvents at -78° [516]. Among the compounds studied were vinyl-, phenyl-, allyl-, 1,3-alkadienyl-, 1-alkynyl-, and cyclopropylsilanes as well as triphenylvinyl derivatives of silicon, germanium, and tin. Reductions, bimolecular couplings, cleavages, and isomerizations are described.

The reduction of camphor by lithium, sodium, and potassium in liquid ammonia has been reinvestigated and the ratio of epimeric alcohols found to be insensitive to the choice of metal [517]. Relative rates and yields in the reductions of several cyclohexanones and bicyclic ketones were determined both in the presence and absence of ethanol. Thus, while the bicyclic ketones are reduced more rapidly than the cyclohexanones in the presence of this alcohol, the relative rates of the reductions are more nearly equal in its absence. Yields of alcohols and pinacols from reductions of pairs of such ketones are listed. Incidentally, pinacols are often the major product in the reactions of aryl ketones and aldehydes with n-butyllithium in the presence of [Fe$_4$S$_4$(SPh)$_4$](n-Bu$_4$N)$_2$ or iron(III) chloride [518].

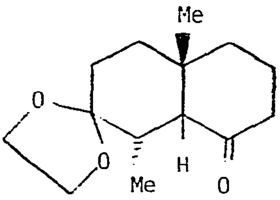
Additional examples of the effect of different conditions upon the stereochemistry of the products in lithium/ammonia reductions of ketones have been described [519]. For example, 736 and 737 are obtained from 738 in such a reduction in a ratio of 1.2:1 when the addition of acid (NH$_4$Cl) is delayed. In contrast, the alcohols are obtained in a ratio of 1:5.6 when the acid is present throughout the reaction.



736

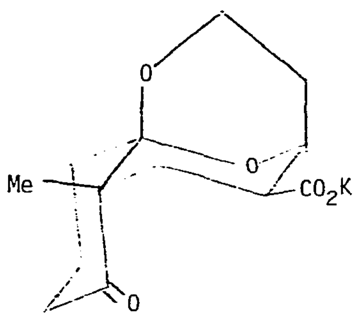


737

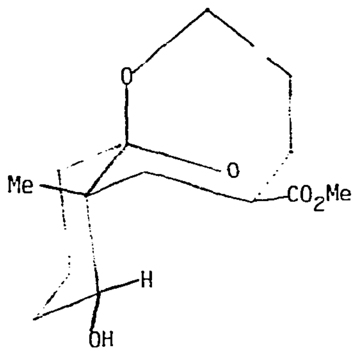


738

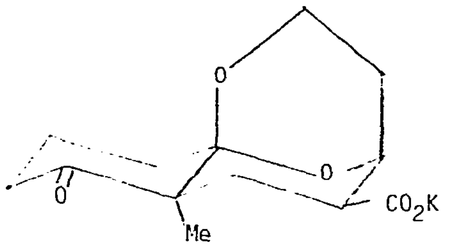
While lithium/ammonia reduction of cis-739 followed by esterification with diazomethane affords equitorial 740, similar reaction of trans-741 unexpectedly gives axial 742 [520]. Similar results were realized on other carboxylates, prepared in situ from esters, related to 739 and 741. The results are interpreted in terms of chelation and steric effects.



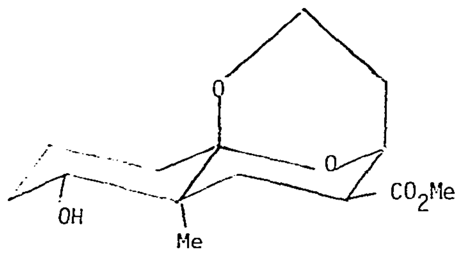
739



740

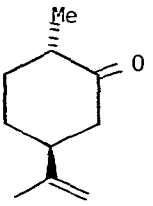


741

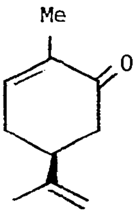


742

The amount of ketone obtained from lithium/ammonia reductions of α,β-unsatruated ketones may be increased by the presence of iron(III) chloride [521]. For example, the amount of 743 in the reduction of 744 is increased from 60% to 90% by the use of this salt.

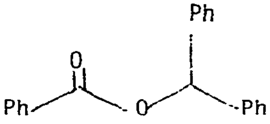


743

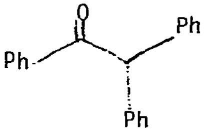


744

Several benzhydryl esters illustrated by the parent 745 have been converted to benzhydryl ketones such as 746 by the use of lithium naphthalenide in THF [522]. Another paper discussed the reductive cleavage of certain benzoate and pivalate esters of primary and secondary alcohols using lithium or sodium in liquid ammonia [523].



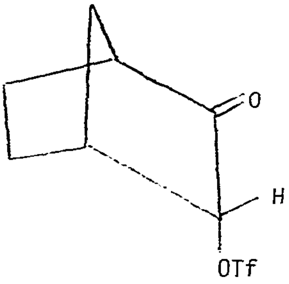
745



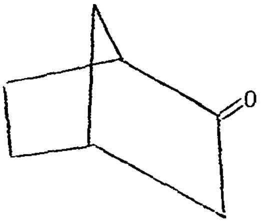
746

A full paper appeared in 1979 which discussed Markownikoff two-step lithiation of α-olefins involving addition of mercaptans to alkenes followed by reduction of the resulting sulfides by lithium in THF or lithium naphthalenide [524]. The process is illustrated by the conversion of 1-heptene to 2-lithioheptane (78%).

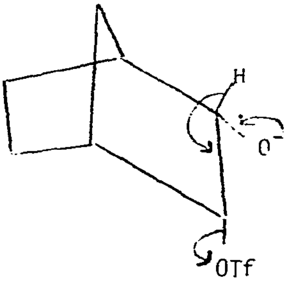
While keto triflate 747 undergoes β-elimination of trifluoromethanesulfinic acid with LiTMP or potassium t-butoxide, it surprisingly is reduced by LDA to tive 748 apparently via 749 [525]. Ketone 748 was accompanied by a dimer.



747

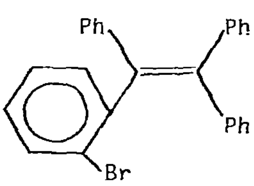


748

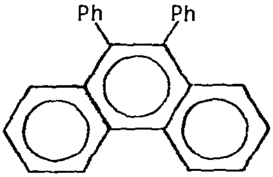


749

Other papers in this area were concerned with reductions of cyanosulfonates and related compounds by lithium/ammonia or sodium naphthalenide to afford cycloalkenes stereoselectively [526], the conversion of 750 to 751 by lithium or sodium naphthalenide [527], and lithium/methylamine reductions of carboxamides to yield different products depending upon the order of addition of the reactants [528].



750



751

II. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

As in the past, this section will be divided according to families from left to right in the periodic table except for an increasingly large number of compounds derived from Groups IIIb, IVb, and/or Vb which will be presented between IIIb and IVb.

Trimethylsilylmethyllithium has been combined with lutetium(III) chloride in ether to afford 752 [529]. The latter compound decomposes slowly to give tetramethylsilane and 753.

$[(Me_3SiCH_2)_4Lu][Li(Et_2O)_4]$

752

$[(Me_3SiCH_2)_2Lu(CHSiMe_3)]Li$

753

1,1'-Di-n-butyluranocene has been prepared in 50% yield from dilithium n-butylcyclooctatetraenide and uranium(IV) chloride in ether [530]. Six cyclopentadienyl derivatives of uranium(IV) have been obtained from organolithiums and uranium chlorides [531]. For example, two equivalents of 754 and 755 yielded 756, a compound shown by ^{1}H-NMR spectroscopy to possess magnetic non-equivalence for the ring protons and the protons of the methyl groups. The latter has been ascribed to the prochirality of the uranium atom. Other compounds prepared using similar chemistry were 757 and 758 from the related chloro derivatives and methyllithium [532], and 759 from the corresponding dichloride and t-butyllithium [533]. Several other methods for the synthesis of 759 which do not involve organolithium chemistry were also presented.

$(C_5H_4\text{-}i\text{-}Pr)^-Li^+$

754

$C_5H_5UCl_3$

755

$C_5H_5(C_5H_4\text{-}i\text{-}Pr)_2UCl$

756

$MeTh[N(SiMe_3)_2]_3$

757

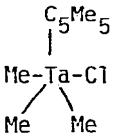
$MeU[N(SiMe_3)_2]_3$

758

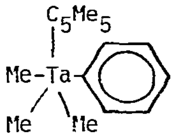
$[(C_5Me_5)_2UCl]_3$

759

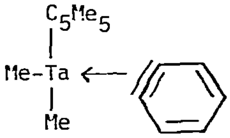
Addition of phenyllithium to 760 gives 761 which is decomposed at 120° for 30 min to afford benzyne complex 762 [534]. The niobium analogue of 762 has been prepared similarly.



760



761



762

Molybdenum complex 763 has been obtained from molybdenum(V) chloride and phenyllithium in ether [535]. The 'H-NMR spectrum of the compound obtained at low temperature is reported. Tetramesityl molybdenum compound 764 has similarly been prepared from molybdenum(III) chloride and mesityllithium [536]. A full paper disclosed the details of the preparation of molybdenum-containing compounds such as 765 ($R=CH_2SiMe_3$, CH_2Ph, Me) [537].

$(C_6H_4)_2Mo(C_6H_5Li\cdot OC_4H_{10})_4$

763

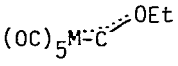
$LiMo(C_9H_{11})_4$

764

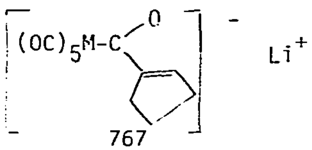
$[(n-C_5H_5)MOR]_2[\mu-(\eta-C_5H_4-\eta-C_5H_4]$

765

Condensation of 1-lithiocyclopentene with the hexacarbonyls of chromium, molybdenum, and tungsten followed by triethyloxonium fluoroborate affords carbene complexes 766 via 767 [538]. Similar reaction of hexacarbonyltungsten with 768 (n=1,2,3) followed by methylation with methyl fluorosulfonate gives 769 [539]. Methyllithium has been added to 770 to yield the binuclear complex, 771 [540].



766



767

$LiSiMe_nPh_{3-n}$

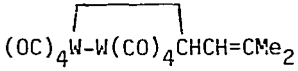
768

$(OC)_5WC(OMe)SiMe_nPh_{3-n}$

769

$EtOCMe{=}W(CO)_5$

770



$(OC)_4W{-}W(CO)_4CHCH{=}CMe_2$

771

Several papers discussed the preparation of compounds containing multiple bonds between chromium, molybdenum, and tungsten. Thus, a series of σ-alkyl complexes 772 (M=Mo,W; R=Me,Et,CH_2CD_3,n-Bu,i-Pr,CH_2-t-Bu,CH_2SiMe_3, and t-Bu) have been prepared from the respective organolithiums and the dichlorotetrakis(dimethylamino) derivatives [541]. Reactions of 772 with carbon dioxide and t-butyl alcohol are discussed. Quadruple bonds were the subject of the following manuscripts, all full papers except for the first one which was a communication: Cr to Cr in a tetracarboxamidato compound [542], Cr to Cr and Mo to Mo in tetraacetanilido systems [543], Cr to Cr in a tetraamidinato compound [544], Cr to Cr and Mo to Mo in 1,3-diphenyltriazine complexes [545], Mo to Mo in [N-(2-pyridyl)acetamido-N,N']dimolybdenum [546], and W to W in a mixed ligand complex involving N,N'-diphenylacetamidinato and 2,4-dimethyl-6-hydroxypyrimidinato groups [547]. Crystallography data are reported for each of the compounds.

$R_2M_2(NMe_2)_4$

772

Condensations of $LiN(SiMe_3)_2$ with "active" manganese(II) chloride and with $ReOCl_4$ has afforded 773 [548] and 774 [549], respectively. Triacylmetalate dianions 775 have been prepared from 776 (R=Me,i-Pr,$PhCH_2$, $(CH_2)_n$ where n = 5 or 6) and two equivalents of methyllithium [550].

$Mn[N(SiMe_3)_2](THF)$

773

$ReO[N(SiMe_3)_2]_3$

774

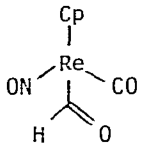
$[fac\text{-}(OC)_3Re(RCO)(CH_3CO)_2]^{2-}2Li^+$

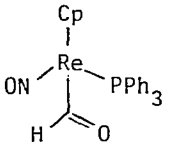
775

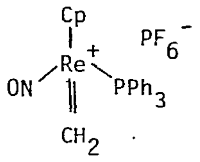
$RC(O)Re(CO)_5$

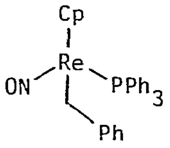
776

Formyl complexes 777 and 778 have been prepared by reduction of the fluoroborate salts of the corresponding di- and mono-carbon monoxide derivatives, respectively using $LiBHEt_3$ [551]. Phenyllithium has been added to 779 to afford 780 [552].


777


778


779


780

Metalation of the parent metal hydrides with n-butyllithium·pentamethyldiethylenetriamine(PMDT) has been shown to afford 781 and 782 [553]. Organometallic 781 has been alkylated to give 783 (R=Et,Pr), and combined with 784 (M=Mo,W) to yield mixed-metal bimetallic species. Another paper described the synthesis of 785 from manganese(II) chloride and lithiopentamethylcyclopentadiene [554]. Oxidation of 785 by $(Cp_2Fe)^+PF_6^-$ afforded 786, the first cationic derivative of such manganese metallocenes.

$Cp_2ReLi \cdot PMDT$

781

$Cp_2MoHLi \cdot PMDT$

782

Cp_2ReR

783

$CpM(CO)_3Cl$

784

$(Me_5Cp)_2Mn$

785

$[(Me_5Cp)_2Mn]^+PF_6^-$

786

Lithium acyltetracarbonylferrates have been arylated using diaryliodonium salts in THF-pentane to afford aryl ketones and aryl iodides [555]. X-ray diffraction studies on 787 with $[Na(THF)_2]^+$, $[(Ph_3P)_2N]^+$, and $[Li(THF)_3]^+$ counter ions have enabled a direct assessment of the type and extent of ion pairing of alkali metal ions with metal acyl carbonylate anions in the solid state [556].

$[Fe_2(CO)_5(C(O)R)(\mu_2\text{-}PPh_2)_2]^-$

787

Ethylene complex 788 [557] and 1,5-cyclooctadiene (COD) complex 789 [558] have been obtained by treating ferrocene with ethylene and COD, respectively in the presence of lithium sand. Reaction of 788 with two equilvalents of COD affords 790 isolated as crystalline DME and TMEDA salts [557].

$(C_2H_4)_4FeLi_2(TMEDA)_2$ 788

$CpFe(COD)Li$ 789

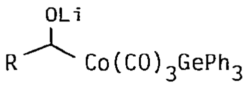
$(COD)_2FeLi_2$ 790

Condensation of lithioferrocene with tri-n-butylborane or boron trifluoride gives 791 which, upon oxidation, yields the mixed valence zwitterion 792 [559]. Another paper discusses the conversion of $Os_3(CO)_{12}$ and other metal carbonyls to spectroscopically detectable formyl complexes [560].

$Li^+ \ B(Fc)_4^-$ 791

$Fe^+ \ B(Fc)_3^-$ 792

Acyl anions 793 (R=Me,Et,n-Pr,n-Bu,Ph) have been obtained by addition of organolithiums to 794, then trapped with triethyloxonium fluoroborate or tetraethylammonium chloride [561].



793

$(OC)_4CoGePh_3$

794

One of the products in the lithiation of 795 has been shown to be 796, where the $C_{12}H_{18}$ moiety is all-trans-1,5,9-cyclododecatriene [562]. Another paper discussed the preparation and chemistry of the "lithium hydride" complex 797 [563].

$C_{12}H_{18}Ni^{0}$ $\quad$ $Ni(C_{12}H_{17}NiLi)_2(THF)_4$ $\quad$ $(COD)_{1.5}NiLi_2H_2(THF)_x$

795 796 797

Several new methylidene trinickel cluster complexes illustrated by 798 (R=t-Bu,$SiMe_3$,etc.) have been prepared from nickelocene and organolithiums, and by reaction of 799 with n-butyllithium in the presence of nickelocene [564].

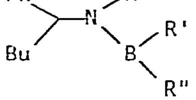
$RCNi_3Cp_3$ $\quad$ $CpNi(CH_2R)(PPh_3)$

798 799

Other papers in the nickel triad were concerned with reaction of Me_5C_5Li with $Ni(CO)_4$ to afford $[(Me_5C_5)Ni(CO)]_2$ [565], the preparation and characterization of monocyclopentadienyl mononeopentylidene complexes of niobium and tantalum [566], and a simple preparation of bis(tetraphenylcyclobutadienyl)nickel from $Ph_4C_4NiBr_2$ and 1,2,3,4-tetraphenyl-1,4-dilithiobutadiene [567].

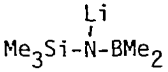
Organosilver(I) compounds have been stabilized by lithium bromide to such an extent that they have been added to conjugated enynes to afford allenes in synthetically useful yields [568]. Finally, in this portion, gold compounds RAuL, RAuL-LAuR, and AuR_2Li have been obtained from ClAuL and organolithiums [569,570]. While R was a fluoro- or polyfluorophenyl group, L was PPh_3, $AsPh_3$ and related materials.

Mono-, bis-, and trisaminoboranes 800 (R=aryl; R'=Me,Ph,NMe_2,NEt_2; R"=Me, Ph,NMe_2, NEt_2) have been prepared (60-70%) from the corresponding lithioamines and R'R"BX [571]. Similarly synthesized were 801 (R=$SiMe_3$,t-Bu) from $Me_2S{\cdot}BH_2Br$ and $LiNR(SiMe_3)$ [572] and 802 from $Me_2BNMeLi$ and tin(II) chloride [573]. A similar condensation of 803 with tin(II) chloride, though, gave diazastannaboretidine 804.



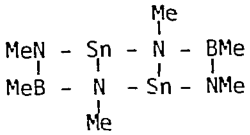
$R(Me_3Si)NBH_2$ $\quad$ $Sn(NMe\text{-}BMe_2)_2$

800 801 802



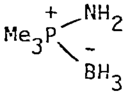
$\mathrm{Me_3Si\text{-}\overset{Li}{N}\text{-}BMe_2}$

803

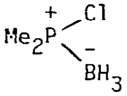


804

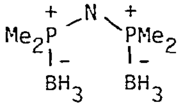
N-Lithiation of 805 with n-butyllithium followed by addition of 806 affords 807 which itself, has been further metalated to give 808 [574]. Salts 809 [575] and 810 [576] have also been obtained by metalation of the parent compounds. Cyclizations using 810 and haloboranes to give products such as 811 are reported. Related heterocycles have also been obtained from 812, prepared by metalation of 813 [576].



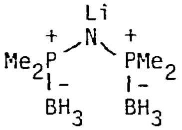
805



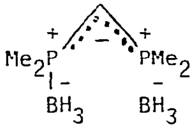
806



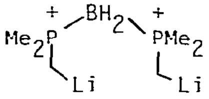
807



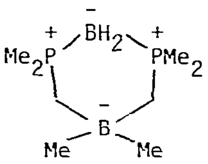
808



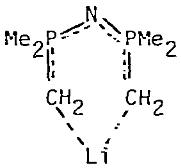
809



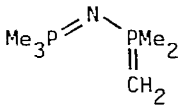
810



811

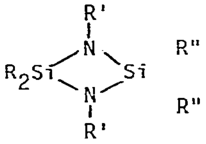


812

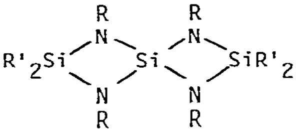


813

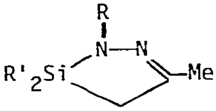
Tri-t-butylsilylamine has been converted to N-methyl- and N,N-dimethyl derivatives by methyllithium and dimethyl sulfate [577]. Full papers described ring systems such as 814 [578], 815 [579], and 816 [580], prepared from appropriate N-lithio systems and halosilanes.



814



815

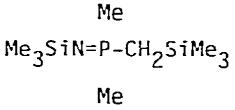


816

A full paper describing the conversion of systems such as 817 to 818 by n-butyllithium appeared in 1979 [581]. The preparation of several other silylmethyl- [581] and silylaminophosphinimines [582] was discussed.

$[(Me_3Si)_2NPMe_3]I$

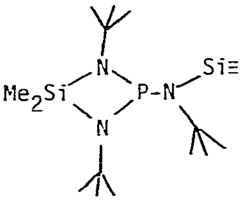
817



$Me_3SiN{=}\underset{Me}{\overset{Me}{P}}{-}CH_2SiMe_3$

818

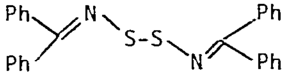
Related chemistry has been employed to prepare 819, a system consisting of two rotamers which have been resolved [583]. Finally, a large number of nitrogen-sulfur compounds have been obtained from 820 and SCl_2, S_2Cl_2, $SOCl_2$, SO_2Cl_2, and $(NSCl)_3$ [584]. For example, 820 and S_2Cl_2 gives 821.



819

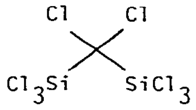
Ph_2CNLi

820

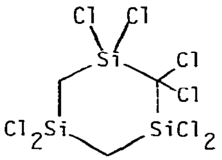


821

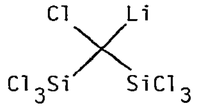
Turning to Group IVb, metal-halogen exchange reactions on polychlorinated bis-silylmethyl systems with n-butyllithium have been effected regiospecifically at -100° [585]. For example, 822 and 823 yield 824 and 825, respectively as evidenced by subsequent methylation and silylation. An unrelated paper described silylations of trisyllithium (826) to afford 827 (R=Cl,Me,OMe,Et) [586].



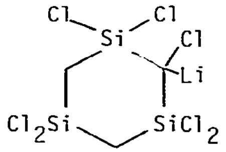
822



823



824



825

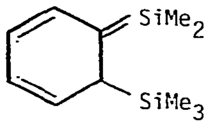
$(Me_3Si)_3CLi$

826

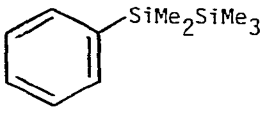
$(Me_3Si)_3CSiR_2X$

827

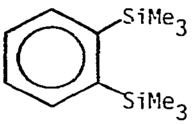
The silicon-carbon double bonded compound 828, postulated to be an intermediate in the photolysis of 829, has been trapped by methyllithium and methylmagnesium bromide to give 830 and the corresponding m-isomer [587].



828

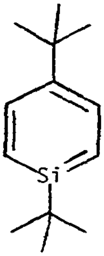


829

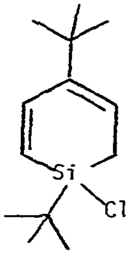


830

1,4-Di-t-butylsilabenzene (831), prepared from 832 and LDIPA, has been trapped by a variety of 1,3-dienes [588].



831

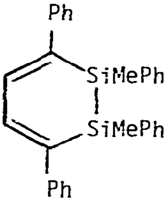


832

1,4-Dilithio-1,4-diphenylbutadiene has been combined with 833 to afford 834 as part of a study about the double bond character of the Si=Si system [589]. The above dilithio derivative has also been condensed with 835 to give 836 as part of a study of 1,5-sigmatropic migrations of the trimethylsilyl group from silicon to carbon [590]. Related cyclizations using 837 to prepare cyclic silanes [591] and germanes [592] were also reported. A variety of plumboles derived from 838-840 have also been prepared [593].

FMePhSi-SiPhMeF

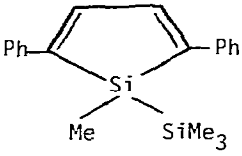
833



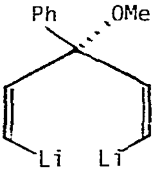
834

$Cl_2MeSi-SiMe_3$

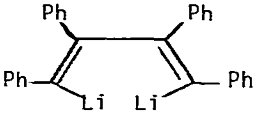
835



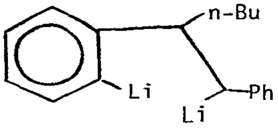
836



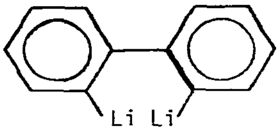
837



838



839



840

Lithium tetrakis(trimethylsilyl)aluminate (841) has been obtained from chlorotrimethylsilane, aluminum, and lithium [594]. This reagent has been combined with zinc chloride and cadmium chloride to afford 842 (M=Zn,Cd) [595].

$LiAl(SiMe_3)_4$

841

$M(SiMe_3)_2$

842

Finally, in this family, a variety of pentamethylcyclopentadienyltin compounds has been obtained from organolithiums and chlorostannanes [596].

In Group V, several lithioamides have been carbonylated by carbon monoxide to afford carbamoyllithiums [597] and N-lithio(alkyl)formamides [598]. For example, 843 gives 844 and, upon hydrolysis, 845.

t-BuNDLi

843

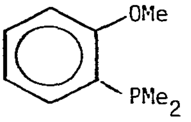
$\text{t-BuND}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{Li}$

844

$\text{t-BuNH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{D}$

845

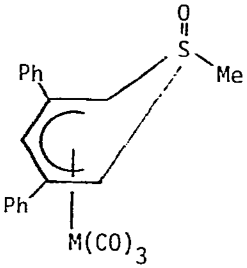
Lithiophosphines have been combined with electrophiles as follows: lithiodimethylphosphine with o-bromoanisole to yield 846 [599], lithiodi-t-butylphosphine with MCl_3 (M=Y,Ho,Cr,Tm,Yb,Lu) to afford 847 [600], and lithiodiphenylphosphine with 848 (M=Cr,Mo,W) to give 849 and methyldiphenylphosphine [601].



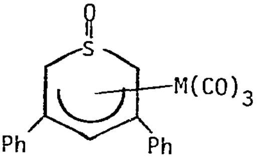
846

$M[P(i\text{-}Bu)_2]_3$

847



848



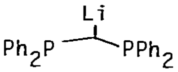
849

Reductive cleavage of bis(phosphines) such as 850 by lithium metal in THF has been shown to afford 851-853 and phenyllithium by fission of the P-C-P sequence rather than by elimination of a phenyl moiety as evidenced by trapping experiments with chlorotrimethylsilane [602]. Anion 852, also generated by metalation of the parent compound with n-butyllithium·TMEDA, has been found to react with chlorodialkylphosphanes to give products such as 854 which arise from the phosphorus rather than the carbon of 852 serving as the nucleophile [603]. Another paper reported that ylides such as 854 slowly rearrange to tris(phosphineo)methanes such as 855 unless the R' group is large (for example, t-butyl) [604]. A variety of other lithiomono-, bis- and tris(phosphino)methanes have also been obtained by direct metalation of the parent phosphines [605].

850

Ph_2PLi

851



852

$PhMePLi$

853

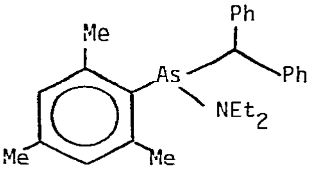
$Ph_2P\text{-}CH{=}P(Ph)_2PR'_2$

854

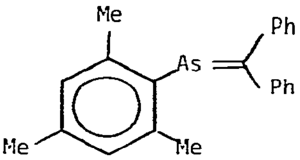
$(Ph_2P)_3CH$

855

Arsenic compound 856 has been obtained from the corresponding chloroarsane and lithiodiphenylmethane as a part of the synthesis of methylenearsane 857 [606].

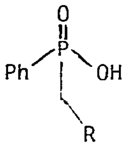


856

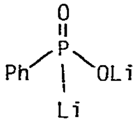


857

P-Derivatization of phenyl phosphinic acid to give 858 has been achieved by alkylation of dilithio salt 859, obtained by simple metalation of the parent compound by n-butyllithium [607].

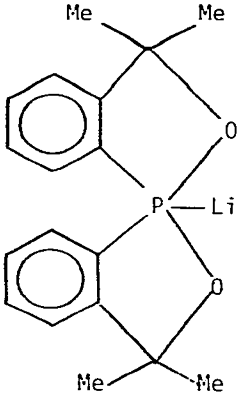


858

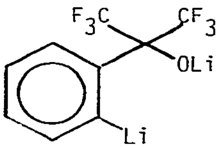


859

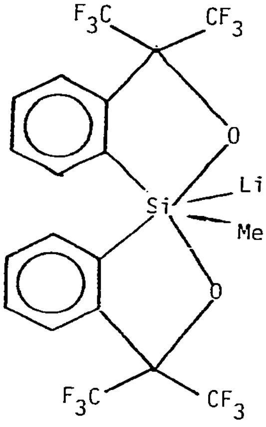
Full details about the preparation of 860 and related compounds appeared in 1979 [608]. Dilithio derivative 861 has been shown to be a useful intermediate in the synthesis of siliconates 862 as well as hypervalent sulfur and phosphorus derivatives [609].



860



861

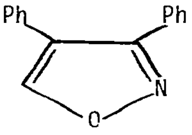


862

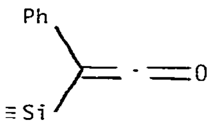
Finally, lithium alkynolate 863, obtained from isoxazole 864 and n-butyllithium or lithium dialkylamides, has been found to react with electrophiles at carbon to afford products such as 865 [610]. Condensation of 863 with aldehydes and ketones gives β-lactones.

$(\text{Ph-}\overset{\cdots\cdots}{\text{C=C-O}})^{-}\text{Li}^{+}$

863



864



865

12. REFERENCES

1. N. S. Poonia and A. V. Bajaj, Chem. Rev., 79 (1979) 389.
2. O. A. Reutov, I. P. Beletskaya, and K. P. Butin, "CH-Acids", Pergamon Press, Elmsford, N.Y., 1979.
3. M. A. Fox, Chem. Rev., 79 (1979) 253.
4. D. C. Wigfield, Tetrahedron, 35 (1979) 449.
5. I. Omae, Chem. Rev., 79 (1979) 287.
6. John C. Stowell, "Carbanions in Organic Synthesis", John Wiley & Sons, Inc., New York, N.Y., 1979.
7. E. Negishi, "Organometallics in Organic Synthesis", Vol. 1, Wiley-Interscience, New York, N.Y., 1979, Chapter 4.
8. H. Gschwend and R. Rodriquez, Org. Reactions, 26 (1979) 1.
9. D. Seebach, Angew.Chem. Int. Ed. Engl., 18 (1979) 239.
10. D. Caine in "Carbon-Carbon Bond Formation", R. L. Augustine, Ed., Marcel Dekker, Inc., 1979, Chapter 2.
11. Z. G. Hajos in "Carbon-Carbon Bond Formation", R. L. Augustine, Ed., Marcel Dekker, Inc., 1979, Chapter 1.
12. S. F. Martin, Synthesis, (1979) 633.
13. A. I. Meyers, Pure & Appl. Chem., 51 (1979) 1255.
14. J. W. ApSimon and R. P. Seguin, Tetrahedron, 35 (1979) 2797.
15. D. A. Evans, D. J. Hart, P. M. Koelsch, and P. A. Cain, Pure & Appl. Chem., 51 (1979) 1285.
16. U. Schöllkopf, Pure & Appl. Chem., 51 (1979) 1347.
17. M. P. Periasamy and H. M. Walborsky, Org. Prep. and Procedures Int., 11 (1979) 293.
18. H. J. Reich, Acc. Chem. Res., 12 (1979) 22.
19. R. P. Houghton, "Metal Complexes in Organic Chemistry", Cambridge University Press, New York, N.Y., 1979.
20. H. C. Brown and S. Krishnamurthy, Tetrahedron, 35 (1979) 567.
21. M. P. L. Caton, Tetrahedron, 35 (1979) 2705.
22. T. Kauffmann, Angew. Chem. Int. Ed. Engl., 18 (1979) 1.
23. D. Nicholls, "Inorganic Chemistry in Liquid Ammonia", Elsevier Scientific Publ. Co., Amsterdam/Oxford/New York, 1979.

24. R. R. Schrock, Acc. Chem. Res., 12 (1979) 98.

25. T. H. Chan and I. Fleming, Synthesis, (1979) 761.

26. D. Häbich and F. Effenberger, Synthesis, (1979) 841.

27. F. Gaudemar-Bardone and M. Gaudemar, Synthesis, (1979) 463.

28. P. G. Gassman and M. J. Mullins, Tetrahedron Lett., (1979) 4457.

29. G. W. Klumpp, M. Kool, M. Schakel, R. F. Schmitz, and C. Boutkan, J. Am. Chem. Soc., 101 (1979) 7065.

30. J. Harnisch, O. Baumgärtel, G. Szeimies, M. Van Meerssche, G. Germain, and J.-P. Declercq, J. Am. Chem. Soc., 101 (1979) 3370.

31. J. L. Adcock and E. B. Renk, J. Org. Chem., 44 (1979) 3431.

32. E. Dunkelblum and H. Hart, J. Org. Chem., 44 (1979) 3482.

33. S. Cabiddu, S. Melis, P. P. Piras, and F. Sotgiu, J. Organomet. Chem., 178 (1979) 291.

34. A. I. Meyers and A. L. Campbell, Tetrahedron Lett., (1979) 4155.

35. A. I. Meyers, A. L. Campbell, A. G. Abatjoglou, and E. L. Eliel, Tetrahedron Lett., (1979) 4159.

36. A. P. Kozikowski and K. Isobe, Tetrahedron Lett., (1979) 833.

37. M. Stähle and M. Schlosser, Angew. Chem., 91 (1979) 938; Angew. Chem. Int. Ed. Engl., 18 (1979) 875.

38. M. Koreeda, Y. Liang, and H. Akagi, J. Chem. Soc., Chem. Comm., (1979) 449.

39. J. P. Marino and J. L. Kostusyk, Tetrahedron Lett., (1979) 2489.

40. J. P. Marino and J. L. Kostusyk, Tetrahedron Lett., (1979) 2493.

41. M. Pohmakotr, K.-H. Geiss, and D. Seebach, Chem. Ber., 112 (1979) 1420.

42. D. A. Evans, J. M. Takacs, and K. M. Hurst, J. Am. Chem. Soc., 101 (1979) 371.

43. T. Hassel and D. Seebach, Angew. Chem., 91 (1979) 427; Angew. Chem. Int. Ed. Engl., 18 (1979) 399.

44. D. Seebach and M. Pohmakotr, Helv. Chim. Acta, 62 (1979) 843.

45. R. V. J. Chari and J. Wemple, Tetrahedron Lett., (1979) 111.

46. H. Yasuda, Y. Ohnuma, M. Yamauchi, H. Tani, and A. Nakamura, Bull. Chem. Soc. Japan, 52 (1979) 2036.

47. J. J. Bahl, R. B. Bates, and B. Gordon III, J. Org. Chem., 44 (1979) 2290.

48. S. R. Wilson, L. R. Phillips, and K. J. Natalie, Jr., J. Am. Chem. Soc., 101 (1979) 3340.

49. P. A. Grieco, S. Ferrino, and T. Oguri, J. Org. Chem., 44 (1979) 2593.

50. A. M. Sarpeshkar, G. J. Gossick, and J. Wemple, Tetrahedron Lett., (1979) 703.

51. D. Seebach and F. Lehr, Helv. Chim. Acta, 62 (1979) 2239.

52. F. Lehr, J. Gonnermann, and D. Seebach, Helv. Chim. Acta, 62 (1979) 2258.

53. D. Seebach, R. Henning, and J. Gonnermann, Chem. Ber., 112 (1979) 234.

54. F. Mathey and F. Mercier, J. Organomet. Chem., 177 (1979) 255.

55. M. Baboulene and G. Sturtz, J. Organomet. Chem., 177 (1979) 27.

56. G. W. Gokel, H. M. Gerdes, D. E. Miles, J. M. Hufnal, and G. A. Zerby, Tetrahedron Lett., (1979) 3375.

57. A. Roggero, T. Salvatori, A. Proni, and A. Mazzei, J. Organomet. Chem., 177 (1979) 313.

58. D. Van Ende, A. Cravador, and A. Krief, J. Organomet. Chem., 177 (1979) 1.

59. P. Magnus and G. Roy, J. Chem. Soc., Chem. Comm., (1979) 822.

60. T. Kauffmann, B. Altpeter, K. J. Echsler, J. Ennen, A. Hamsen, and R. Joussen, Tetrahedron Lett., (1979) 501.

61. T. Hata, A. Hashizume, M. Nakajima, and M. Sekine, Chem. Lett., (1979) 519.

62. G. Friedmann, P. Linder, M. Brini, and A. Cheminat. J. Org. Chem., 44 (1979) 237.

63. T. D. Harris and G. P. Roth, J. Org. Chem., 44 (1979) 2004.

64. W. Fuhrer and H. W. Gschwend, J. Org. Chem., 44 (1979) 1133.

65. P. Beak and R. A. Brown, J. Org. Chem., 44 (1979) 4463.

66. A. I. Meyers and K. Lutomski, J. Org. Chem., 44 (1979) 4464.

67. S. O. deSilva, I. Ahmad, and V. Snieckus, Can. J. Chem., 57 (1979) 1598.

68. H. P. Plaumann, B. A. Keay, and R. Rodrigo, Tetrahedron Lett., (1979) 4921.

69. S. Cabiddu, S. Melis, P. P. Piras, and F. Sotgiu, J. Organomet. Chem., 182 (1979) 155.

70. T. J. Kress, J. Org. Chem., 44 (1979) 2081.

71. M. Mallet and G. Queguiner, Tetrahedron, 35 (1979) 1625.

72. G. W. H. Cheeseman and S. G. Greenberg, J. Organomet. Chem., 166 (1979) 139.

73. D. J. Chadwick and I. A. Cliffe, J. Chem. Soc., Perkin I, (1979) 2845.

74. D. W. Knight, Tetrahedron Lett., (1979) 469.

75. P. A. Jacobi, S. Ueng, D. Carr, J. Org. Chem., 44 (1979) 2042.

76. R. R. Schmidt, J. Talbiersky, and P. Russegger, Tetrahedron Lett., (1979) 4273.

77. R. R. Schmidt, H. Speer, and B. Schmid, Tetrahedron Lett., (1979) 4277.

78. R. R. Schmidt and H. Speer, Synthesis, (1979) 797.

79. L. Duhamel and J.-M. Poirier, J. Org. Chem., 44 (1979) 3585.

80. J. J. Fitt and H. W. Gschwend, J. Org. Chem., 44 (1979) 303.

81. K. Isobe, M. Fuse, H. Kosugi, H. Hagiwara, and H. Uda, Chem. Lett., (1979) 785.

82. J. J. Eisch and J. E. Galle, J. Org. Chem., 44 (1979) 3277.

83. J. J. Eisch and J. E. Galle, J. Org. Chem., 44 (1979) 3279.

84. D. C. Green, J. Org. Chem., 44 (1979) 1476.

85. M. Schlosser and P. Schneider, Angew. Chem., 91 (1979) 515; Angew. Chem. Int. Ed. Engl., 18 (1979) 489.

86. R. Baudouy, F. Delbecq, and J. Gore, Tetrahedron Lett., (1979) 937.

87. R. Baudouy, F. Delbecq, and J. Gore, J. Organomet. Chem., 177 (1979) 39.

88. K. Atsumi and I. Kuwajima, J. Am. Chem. Soc., 101 (1979) 2208.

89. S. Braverman, D. Reisman, M. Sprecher, D. Rabinovich, and F. Frolow, Tetrahedron Lett., (1979) 901.

90. M. F. Semmelhack, J. Bisaha, and M. Czarny, J. Am. Chem. Soc., 101 (1979) 768.

91. M. D. Rausch, G. A. Moser, and W. A. Lee, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 357.

92. N. M. Loim, N. A. Abramowa, Z. N. Parnes, and D. N. Kursanow, J. Organomet. Chem., 168 (1979) C33.

93. L. Bednarik and E. Neuse, J. Organomet. Chem., 168 (1979) C8.

94. T. L. Evans, T. J. Fuller, and H. R. Allcock, J. Am. Chem. Soc., 101 (1979) 242.

95. Y. Yamada, T. Hayashi, Y. Fusho, and H. Okada, Tetrahedron Lett., (1979) 2603.

96. N. J. Leonard and J. D. Bryant, J. Org. Chem., 44 (1979) 4612.

97. T. E. Stone, E. J. Eustace, M. V. Pickering, and G. D. Daves, Jr., J. Org. Chem., 44 (1979) 505.

98. R. Askani and R. Kirsten, Tetrahedron Lett., (1979) 1491.

99. R. B. Miller and G. McGarvey, Synth. Comm., 9 (1979) 831.

100. J. Ficini, P. Kahn, S. Falou, and A. M. Touzin, Tetrahedron Lett., (1979) 67.

101. D. W. Boykin and W. E. Parham, J. Org. Chem., 44 (1979) 424.

102. W. R. Baker and R. M. Coates, J. Org. Chem., 44 (1979) 1022.

103. R. B. Miller and G. McGarvey, J. Org. Chem., 44 (1979) 4623.

104. F. Karrenbrock and H. J. Schäfer, Tetrahedron Lett., (1979) 2913.

105. E. A. Truesdale and R. S. Hutton, J. Am. Chem. Soc., 101 (1979) 6475.

106. T. Hiyama, J. Syn. Org. Chem., Japan, 37 (1979) 982.

107. L. Duhamel and J.-Y. Valnot, Tetrahedron Lett., (1979) 3319.

108. V. Reutrakul and P. Thamnusan, Tetrahedron Lett., (1979) 617.

109. P. Magnus and G. Roy, J. Chem. Soc., Chem. Comm., (1979) 822.

110. T. T. Tidwell, Tetrahedron Lett., (1979) 4615.

111. J. T. Miller, C. W. DeKock, and M. A. Brault, J. Org. Chem., 44 (1979) 3508.

112. N. E. Schore, J. Am. Chem. Soc., 101 (1979) 7410.

113. T. Cohen and R. B. Weisenfeld, J. Org. Chem., 44 (1979) 3601.

114. C. Giancaspro and G. Sleiter, J. Prakt. Chem., 321 (1979) 876.

115. L. A. Shimp and R. J. Lagow, J. Org. Chem., 44 (1979) 2311.

116. L. A. Shimp and R. J. Lagow, J. Am. Chem. Soc., 101 (1979) 2214.

117. D. Seyferth and R. E. Mammarella, J. Organomet. Chem., 177 (1979) 53.

118. D. Seyferth and K. R. Wursthorn, J. Organomet. Chem., 182 (1979) 455.

119. E. Piers and H. E. Morton, J. Org. Chem., 44 (1979) 3437.

120. D. J. Brauer, C. Kruger, and J. C. Sekutowski, J. Organomet. Chem., 178 (1979) 249.

121. H. M. M. Shearer, K. Wade, and G. Whitehead, J. Chem. Soc., Chem. Comm., (1979) 943.

122. W. McLean, J. A. Schultz, L. G. Pedersen, and R. C. Jarnagin, J. Organomet. Chem., 175 (1979) 1.

123. J. Burdon, D. W. Davies, and G. del Conde, J. Chem. Soc., Perkin II, (1979) 1205.

124. T. Clark and P. von R. Schleyer, J. Chem. Soc., Chem. Comm., (1979) 883.

125. T. Clark and P. von R. Schleyer, Tetrahedron Lett., (1979) 4963.

126. T. Clark and P. von R. Schleyer, J. Am. Chem. Soc., 101 (1979) 7747.

127. H. M. Niemeyer, Tetrahedron, 35 (1979) 1297.

128. W. D. Laidig and H. F. Schaefer, III, J. Am. Chem. Soc., 101 (1979) 7184.

129. F. Texier, O. Henri-Rousseau, and J. Bourgois, Bull. Soc. Chim. France, Ser. II, (1979) 86.

130. Y. Apeloig and Z. Rappoport, J. Am. Chem. Soc., 101 (1979) 5095.

131. R. D. Bach, R. C. Badger, and T. J. Lang, J. Am. Chem. Soc., 101 (1979) 2845.

132. E. D. Jemmis, J. Chandrasekhar, and P. von R. Schleyer, J. Am. Chem. Soc., 101 (1979) 2848.

133. J. Tyrrell, V. M. Kolb, and C. Y. Meyers, J. Am. Chem. Soc., 101 (1979) 3497.

134. J. Sauer, Tetrahedron, 35 (1979) 2109.

135. J. Burdon, I. W. Parsons, and E. J. Avramides, J. Chem. Soc., Perkin I, (1979) 1268.

136. J. Burdon, I. W. Parsons, and E. J. Avramides, J. Chem. Soc., Perkin II, (1979) 1201.

137. R. C. Haddon, J. Org. Chem., 44 (1979) 3608.

138. W. Förster, P. Birner, and C. Weiss, Tetrahedron, 35 (1979) 1615.

139. S. Miertus, O. Kysel, and P. Majek, Macromolecules, 12 (1979) 418.

140. N.H. Velthorst, Pure & Appl. Chem., 51 (1979) 85.

141. A. I. Popov, Pure & Appl. Chem., 51 (1979) 101.

142. E. M. Arnett, V. DePalma, S. Maroldo, and L. S. Small, Pure & Appl. Chem., 51 (1979) 131.

143. W. L. Jenkins, C.-F. Tien, and T. E. Hogen-Esch, Pure & Appl. Chem., 51 (1979) 139.

144. E. deBoer, A. A. K. Klaassen, J. J. Mooij, and J. H. Noordik, Pure & Appl. Chem., 51 (1979) 73.

145. G. Fraenkel, A. M. Fraenkel, M. J. Geckle, and F. Schloss, J. Am. Chem. Soc., 101 (1979) 4745.

146. D. Seebach, H. Siegel, K. Mullen, and K. Hiltbrunner, Angew. Chem., 91 (1979) 844; Angew. Chem. Int. Ed. Engl., 18 (1979) 784.

147. H. Siegel, K. Hiltbrunner, and D. Seebach, Angew. Chem., 91 (1979) 845; Angew. Chem. Int. Ed. Engl., 18 (1979) 785.

148. H. Bauer, M. Angrick, and D. Rewicki, Org. Mag. Resonance, 12 (1979) 624.

149. T. B. Thompson and W. T. Ford, J. Am. Chem. Soc., 101 (1979) 5459.

150. G. Boche, K. Buckl, D. Martens, and D. R. Schneider, Tetrahedron Lett., (1979) 4967.

151. W. A. Beavers, S. E. Wilson, B. Gordon, III, R. B. Bates, and A. R. Romano, Tetrahedron Lett., (1979) 1675.

152. D. H. O'Brien, C. R. Russell, and A. J. Hart, J. Am. Chem. Soc., 101 (1979) 633.

153. U. Edlund, Org. Mag. Resonance, 12 (1979) 661.

154. C. Gooijer and N. H. Velthorst, Org. Mag. Resonance, 12 (1979) 684.

155. S. Q. A. Rizvi, J. Foos, F. Steel, and G. Fraenkel, J. Am. Chem. Soc., 101 (1979) 4488.

156. K. Mullen, J. F. M. Oth, H.-W. Engels, and E. Vogel, Angew. Chem., 91 (1979) 251; Angew. Chem. Int. Ed. Engl., 18 (1979) 229.

157. M. Raban and D. P. Haritos, J. Am. Chem. Soc., 101 (1979) 5178.

158. M. Raban, R. A. Keintz, and E. A. Noe, Tetrahedron Lett., (1979) 1633.

159. J. Blenkers, H. K. Hofstee, J. Boersma, and G. J. M. van der Kerk, J. Organomet. Chem., 168 (1979) 251.

160. G. van Koten and J. G. Noltes, J. Am. Chem. Soc., 101 (1979) 6593.

161. M. Rabinovitz, I. Willner, A. Gamliel, and A. Gazit, Tetrahedron, 35 (1979) 667.

162. I. Willner, J. Y. Becker, and M. Rabinovitz, J. Am. Chem. Soc., 101 (1979) 395.

163. W. Lubitz, M. Plato, K. Mobius, and R. Biehl, J. Phys. Chem., 83 (1979) 3402.

164. P. Furderer, F. Gerson, J. Heinzer, S. Mazur, H. Ohya-Nishiguchi, and A. H. Schroeder, J. Am. Chem. Soc., 101 (1979) 2275.

165. V. Cerri, M. Boyer, and P. Tordo, Tetrahedron Lett., (1979) 1437.

166. H. J. Fey, H. Kurreck, and W. Lubitz, Tetrahedron, 35 (1979) 905.

167. E. Buncel and B. C. Menon, J. Org. Chem., 44 (1979) 317.

168. E. Buncel, B. C. Menon, and J. P. Colpa, Can. J. Chem., 57 (1979) 999.

169. S. Nishi and M. Matsuda, J. Am. Chem. Soc., 101 (1979) 4632.

170. T. Aruga, O. Ito, and M. Matsuda, J. Am. Chem. Soc., 101 (1979) 7585.

171. R. D. Guthrie and N. S. Cho, J. Am. Chem. Soc., 101 (1979) 4698.

172. N. F. Haley, J. Chem. Soc., Chem. Comm., (1979) 1030.

173. V. M. Sergutin, V. N. Zgonnik, and K. K. Kalninsh, J. Organomet. Chem., 170 (1979) 151.

174. S. Konishi, Y. Morioka, and I. Nakagawa, Chem. Phys. Lett., 64 (1979) 266.

175. R. West, D. Eggerding, J. Perkins, D. Handy, and E. C. Tuazon, J. Am. Chem. Soc., 101 (1979) 1710.

176. R. P. Van Duyne, M. R. Suchanski, J. M. Lakovits, A. R. Siedle, K. D. Parks, and T. M. Cotton, J. Am. Chem. Soc., 101 (1979) 2832.

177. C. H. Wu and H. R. Ihle, Chem. Phys. Lett., 61 (1979) 54.

178. J. Allison and D. P. Ridge, J. Am. Chem. Soc., 101 (1979) 4998.

179. J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., J. Am. Chem. Soc., 101 (1979) 6046.

180. J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., J. Am. Chem. Soc., 101 (1979) 6056.

181. C. H. DePuy, V. M. Bierbaum, L. A. Flippin, J. J. Grabowski, G. K. King, and R. J. Schmitt, J. Am. Chem. Soc., 101 (1979) 6443.

182. R. J. Schmitt, V. M. Bierbaum, and C. H. DePuy, J. Am. Chem. Soc., 101 (1979) 6443.

183. R. Gygax, H. L. McPeters, and J. I. Brauman, J. Am. Chem. Soc., 101 (1979) 2567.

184. O. I. Asubiojo and J. I. Brauman, J. Am. Chem. Soc., 101 (1979) 3715.

185. T. Mukaiyama, K. Soai, T. Sato, H. Shimizu, and K. Suzuki, J. Am. Chem. Soc., 101 (1979) 1455.

186. D. Seebach and W. Langer, Helv. Chim. Acta, 62 (1979) 1701.

187. D. Seebach, G. Crass, E.-M. Wilka, D. Hilvert, and E. Brunner, Helv. Chim. Acta, 62 (1979) 2695.

188. W. Langer and D. Seebach, Helv. Chim. Acta, 62 (1979) 1710.

189. A. I. Meyers, R. K. Smith, and C. E. Whitten, J. Org. Chem., 44 (1979) 2250.

190. A. I. Meyers, J. Slade, R. K. Smith, E. D. Mihelich, F. M. Hershenson, and C. D. Liang, J. Org. Chem., 44 (1979) 2247.

191. I. J. Jakovac and J. B. Jones, J. Org. Chem., 44 (1979) 2165.

192. M. Daney and R. Lapouyade, J. Organomet. Chem., 172 (1979) 385.

193. M. Larcheveque, E. Ignatova, and T. Cuvigny, J. Organomet. Chem., 177 (1979) 5.

194. J. A. Aimetti and M. S. Kellogg, Tetrahedron Lett., (1979) 3805.

195. M. Kolb and J. Barth, Tetrahedron Lett., (1979) 2999.

196. A. I. Meyers and P. J. Reider, J. Am. Chem. Soc., 101 (1979) 2501.

197. G. Frater, Helv. Chim. Acta, 62 (1979) 2825.

198. T. H. Chan, T. Aida, P. W. K. Lau, V. Gorys, and D. N. Harpp, Tetrahedron Lett., (1979) 4029.

199. G. H. Posner and C. M. Lentz, J. Am. Chem. Soc., 101 (1979) 934.

200. G. Stork, W. C. Still, and J. Singh, Tetrahedron Lett., (1979) 5077.

201. C. H. Heathcock and C. T. White, J. Am. Chem. Soc., 101 (1979) 7076.

202. C. H. Heathcock, M. C. Pirrung, C. T. Buse, J. P. Hagen, S. D. Young, and J. E. Sohn, J. Am. Chem. Soc., 101 (1979) 7077.

203. H. O. House, W. V. Phillips, and D. VanDerveer, J. Org. Chem., 44 (1979) 2400.

204. C. Agami, J. Levisalles, and B. Lo Cicero, Tetrahedron, 35 (1979) 961.

205. E. C. Ashby and S. A. Noding, J. Org. Chem., 44 (1979) 4371.

206. R. R. Fraser and J. Banville, J. Chem. Soc., Chem. Comm., (1979) 47.

207. A. I. Meyers, Z. Brich, G. W. Erickson, and S. G. Traynor, J. Chem. Soc., Chem. Comm., (1979) 566.

208. A. I. Meyers and Z. Brich, J. Chem. Soc., Chem. Comm., (1979) 567.

209. R. R. Fraser, F. Akiyama, and J. Banville, Tetrahedron Lett., (1979) 3929.

210. U. Schöllkopf, W. Hartwig, and U. Groth, Angew. Chem., 91 (1979) 922; Angew. Chem. Int. Ed. Engl., 18 (1979) 863.

211. D. Enders and H. Eichenauer, Chem. Ber., 112 (1979) 2933.

212. D. Enders and H. Eichenauer, Angew. Chem., 91 (1979) 425; Angew. Chem. Int. Ed. Engl., 18 (1979) 397.

213. D. Enders, H. Eichenauer, and R. Pieter, Chem. Ber., 112 (1979) 3703.

214. K. G. Davenport, H. Eichenauer, D. Enders, M. Newcomb, and D. E. Bergbreiter, J. Am. Chem. Soc., 101 (1979) 5654.

215. D. E. Bergbreiter and M. Newcomb, Tetrahedron Lett., (1979) 4145.

216. M. E. Jung and T. J. Shaw, Tetrahedron Lett., (1979) 4149.

217. M. Bellassoued, F. Dardoize, Y. Frangin, and M. Gaudemar, J. Organomet. Chem., 165 (1979) 1.

218. G. Boche, K. Buckl, D. Martens, D. R. Schneider, and H.-U. Wagner, Chem. Ber., 112 (1979) 2961.

219. M. F. Semmelhack, G. R. Clark, R. Farina, and M. Saeman, J. Am. Chem. Soc., 101 (1979) 217.

220. M. F. Semmelhack, J. J. Harrison, and Y. Thebtaranouth, J. Org. Chem., 44 (1979) 3275.

221. E. R. Biehl, W. Stewart, A. Marks, and P. C. Reeves, J. Org. Chem., 44 (1979) 3674.

222. P. W. K. Lau and T. H. Chan, J. Organomet. Chem., 179 (1979) C24.

223. C. Breliere, R. J. P. Corriu, A. DeSaxce, F. Larcher, and G. Royo, J. Organomet. Chem., 164 (1979) 19.

224. L. Colombo, C. Gennari, C. Scolastico, G. Guanti, and E. Narisano, J. Chem. Soc., Chem. Comm., (1979) 591.

225. D. Seebach, R. Dammann, H. J. Lindner, and B. Kitschke, Helv. Chim. Acta, 62 (1979) 1143.

226. D. Seebach, H. Neumann, and R. Dammann, Helv. Chim. Acta, 62 (1979) 1162.

227. T. Sugita, J. Nakagawa, K. Nishimoto, Y. Kasai, and K. Ichikawa, Bull. Chem. Soc. Japan, 52 (1979) 871.

228. C. E. Slemon and P. Yates, Can. J. Chem., 57 (1979) 304.

229. T. Cohen and J. R. Matz, J. Org. Chem., 44 (1979) 4816.

230. D. A. Evans, E. Vogel, and J. V. Nelson, J. Am. Chem. Soc., 101 (1979) 6120.

231. M.-H. Rei, J. Org. Chem., 44 (1979) 2760.

232. C. Agami, M. Fadlallah, A. Kazakos, and J. Levisalles, Tetrahedron, 35 (1979) 969.

233. R. Noyori, I. Tomino, and Y. Tanimoto, J. Am. Chem. Soc., 101 (1979) 3129.

234. H. Suda, M. Motoi, M. Fujii, S. Kanoh, and H. Yoshida, Tetrahedron Lett., (1979) 4565.

235. D. Seebach and R. Locher, Angew. Chem., 91 (1979) 1024; Angew. Chem. Int. Ed. Engl., 18 (1979) 957.

236. S. Akiyama, S. Nakatsuji, T. Hamamura, M. Kataoka, and M. Nakagawa, Tetrahedron Lett., (1979) 2809.

237. S. Akiyama, S. Nakatsuji, S. Eda, M. Kataoka, and M. Nakagawa, Tetrahedron Lett., (1979) 2813.

238. J. S. R. Zilenovski and S. S. Hall, Synthesis, (1979) 698.

239. B. Lesur, J. Toye, M. Chantrenne, and L. Ghosez, Tetrahedron Lett., (1979) 2835.

240. L. Wartski, M. El-Bouz, J. Seyden-Penne, W. Dumont, and A. Krief, Tetrahedron Lett., (1979) 1543.

241. M. El-Bouz, M.-C. Roux-Schmitt, and L. Wartski, J. Chem. Soc., Chem. Comm., (1979) 779.

242. L. Wartski, M. El-Bouz, and J. Seyden-Penne, J. Organomet. Chem., 177 (1979) 17.

243. N. Wang, S. Su, and L. Tsai, Tetrahedron Lett., (1979) 1121.

244. C. A. Brown and A. Yamaichi, J. Chem. Soc., Chem. Comm., (1979) 100.

245. J. Lucchetti, W. Dumont, and A. Krief, Tetrahedron Lett., (1979) 2695.

246. R. A. J. Smith and A. R. Lal, Aust. J. Chem., 32 (1979) 353.

247. F. E. Ziegler and C. C. Tam, Tetrahedron Lett., (1979) 4717.

248. H. W. Pinnick and M. A. Reynolds, J. Org. Chem., 44 (1979) 160.

249. E. Ghera and Y. Ben-David, Tetrahedron Lett., (1979) 4603.

250. G. A. Kraus and J. O. Pezzanite, J. Org. Chem., 44 (1979) 2480.

251. Y. Tamaru, T. Harada, and Z. Yoshida, J. Am. Chem. Soc., 101 (1979) 1316.

252. M. P. Cooke, Jr., Tetrahedron Lett., (1979) 2199.

253. S. D. Darling, F. N. Muralidharan, and V. B. Muralidharan, Tetrahedron Lett., (1979) 2757.

254. S. D. Darling, F. N. Muralidharan, and V. B. Muralidharan, Tetrahedron Lett., (1979) 2761.

255. A. Streitwieser, Jr. and C. C. C. Shen, Tetrahedron Lett., (1979) 327.

256. E. A. Symons, M. F. Powell, J. B. Schnittker, and M. J. Clermont, J. Am. Chem. Soc., 101 (1979) 6704.

257. J. R. Keeffe, J. Morey, C. A. Palmer, and J. C. Lee, J. Am. Chem. Soc., 101 (1979) 1295.

258. A. Cheminat, G. Friedmann, and M. Brini, J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 2865.

259. R. Le Goaller, H. Handel, M. A. Pasquini, and J. L. Pierre, Tetrahedron, 35 (1979) 1437.

260. H. E. Zieger and D. Mathisen, J. Am. Chem. Soc., 101 (1979) 2207.

261. E. H. Braue, Jr., V. T. Alexander, L. L. Burton, T. I. Crowell, and C. P. Devlin, J. Am. Chem. Soc., 101 (1979) 5303.

262. E. Ayanoglu, A. Chan, and C. Djerassi, Tetrahedron, 35 (1979) 1591.

263. G. Boche and D. Martens, Chem. Ber., 112 (1979) 175.

264. B. Cazes and S. Julia, Tetrahedron, 35 (1979) 2655.

265. E. Vedejs, M. J. Arnost, and J. P. Hagen, J. Org. Chem., 44 (1979) 3230.

266. H. J. Reich and M. L. Cohen, J. Am. Chem. Soc., 101 (1979) 1307.

267. D. M. Snyder and W. E. Truce, J. Am. Chem. Soc., 101 (1979) 5432.

268. G. A. Russell and J. M. Pecoraro, J. Am. Chem. Soc., 101 (1979) 3331.

269. R. K. Norris and R. J. Smyth-King, Aust. J. Chem., 32 (1979) 1949.

270. G. A. Russell, M. Jawdosiuk, and M. Makosza, J. Am. Chem. Soc., 101 (1979) 2355.

271. G. A. Russell, M. Jawdosiuk, and F. Ros, J. Am. Chem. Soc., 101 (1979) 3378.

272. M. Hori, T. Kataoka, and H. Shimizu, Tetrahedron Lett., (1979) 1603.

273. P. G. Gassman, J. J. Valcho, and G. S. Proehl, J. Am. Chem. Soc., 101 (1979) 231.

274. A. Maercker and R. W. Stumpe, Tetrahedron Lett., (1979) 3843.

275. S. Gronowitz, A. Hallberg, and T. Frejd, Tetrahedron, 35 (1979) 2607.

276. J.-F. Biellmann, H. d'Orchymont, and J.-L. Schmitt, J. Am. Chem. Soc., 101 (1979) 3283.

277. M. Schlosser and H. B. Tuong, Angew. Chem., 91 (1979) 675; Angew. Chem. Int. Ed. Engl., 18 (1979) 633.

278. J. Mulzer, A. Pointner, A. Chucholowski, and G. Bruntrup, J. Chem. Soc., Chem. Comm., (1979) 52.

279. J. Mulzer, G. Bruntrup, J. Frike, and M. Zippel, J. Am. Chem. Soc., 101 (1979) 7723.

280. G. R. Stevenson, J. Valentin, E. Williams, Jr., G. Caldwell, and A.E. Alegria, J. Am. Chem. Soc., 101 (1979) 515.

281. S. Bank, C. L. Ehrlich, and J. A. Zubieta, J. Org. Chem., 44 (1979) 1454.

282. L. V. Vinogradova, V. N. Zgonnik, N. I. Nikolaev, and K. B. Tsvetanov, Eur. Polym. J., 15 (1979) 545.

283. M. D. Jackson and W. R. Gilkerson, J. Am. Chem. Soc., 101 (1979) 328.

284. W. R. Gilkerson and M. D. Jackson, J. Am. Chem. Soc., 101 (1979) 4096.

285. L. Duhamel and J.-C. Plaquevent, J. Org. Chem., 44 (1979) 3404.

286. N. S. Zefirov, V. N. Kirin, N. M. Yur'eva, A. S. Koz'min, N. S. Kulikov, and Y. N. Luzikov, Tetrahedron Lett., (1979) 1925.

287. L. A. Paquette, A. R. Browne, and E. Chamot, Angew. Chem., 91 (1979) 581; Angew. Chem. Int. Ed. Engl., 18 (1979) 546.

288. U. Burger and G. Gandillon, Tetrahedron Lett., (1979) 4281.

289. S.-I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, J. Org. Chem., 44 (1979) 2408.

290. M. Isobe, M. Kitamura, and T. Goto, Tetrahedron Lett., (1979) 3465.

291. P. R. Bernstein, Tetrahedron Lett., (1979) 1015 .

292. J. Barluenga, F. J. Fananas, and M. Yus, J. Org. Chem., 44 (1979) 4798.

293. C. Lion, J.-E. Dubois, J. A. MacPhee, and Y. Bonzougou, Tetrahedron, 35 (1979) 2077.

294. R. Gauthier and M. Chastrette, J. Organomet. Chem., 165 (1979) 139.

295. C. Schenk and T. J. de Boer, Tetrahedron, 35 (1979) 2119.

296. C.-S. Giam, T. E. Goodwin, K. F. Rion, and S. D. Abbott, J. Chem. Soc., Perkin I, (1979) 3082.

297. F. Marsais, E. Bouley, and G. Queguiner, J. Organomet. Chem., 171 (1979) 273.

298. F. M. Pasutto and E. E. Knaus, Can. J. Chem., 57 (1979) 2371.

299. E. M. Kaiser and J. R. McClure, J. Organomet. Chem., 175 (1979) 11.

300. B. F. Bonini, G. Maccagnani, G. Mazzanti, and P. Piccinelli, Tetrahedron Lett., (1979) 3987.

301. C. R. Hall, T. D. Inch, and I. W. Lawston, Tetrahedron Lett., (1979) 2729.

302. L. A. Carpino and J.-H. Tsao, J. Org. Chem., 44 (1979) 2564.

303. T. J. Barton and C. R. Tully, J. Organomet. Chem., 172 (1979) 11.

304. D. Hanssgen and E. Odenhausen, Chem. Ber., 112 (1979) 2389.

305. R. B. Bates, W. A. Beavers, B. Gordon III, and N. S. Mills, J. Org. Chem., 44 (1979) 3800.

306. J. Bornstein, S. E. Hunt, J. D. Mineck, and D. E. Remy, J. Org. Chem., 44 (1979) 805.

307. S. O. de Silva, M. Watanabe, and V. Snieckus, J. Org. Chem., 44 (1979) 4802.

308. N. S. Narisimhan and P. S. Chandrachood, Synthesis, (1979) 589.

309. N. S. Narisimhan and S. P. Bhagwat, Synthesis, (1979) 903.

310. N. S. Narasimhan, R. S. Mali, and M. V. Barve, Synthesis, (1979) 906.

311. T. A. Hase, L. Lahtinen, and E. R. Mamia, Acta Chem. Scand., B33 (1979) 587.

312. M. Yoshifuji, I. Shima, and N. Inamoto, Tetrahedron Lett., (1979) 3963.

313. H. Iida, Y. Yuasa, and C. Kibayashi, J. Org. Chem., 44 (1979) 1074.

314. F. A. Davis, P. A. Mancinelli, K. Balasubramanian, and U. K. Nadir, J. Am. Chem. Soc., 101 (1979) 1044.

315. R. L. Smorada and W. E. Truce, J. Org. Chem., 44 (1979) 3444.

316. G. R. Newkome, A. Nayak, J. D. Sauer, P. K. Mattschei, S. F. Watkins, F. Fronczek, and W. H. Benton, J. Org. Chem., 44 (1979) 3816.

317. H. Tanaka, I. Nasu, and T. Miyasaka, Tetrahedron Lett., (1979) 4755.

318. E. W. Neuse and L. Bednarik, Macromolecules, 12 (1979) 187.

319. N. Hao and M.J. McGlinchey, J. Organomet. Chem., 165 (1979) 225.

320. A. Bonny and S. R. Stobart, J. Chem. Soc., Dalton, (1979) 786.

321. A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, B. Akinde, and D. R. M. Walton, J. Chem. Soc., Chem. Comm., (1979) 840.

322. S. Bhanu and F. Scheinmann, J. Chem. Soc., Perkin I, (1979) 1218.

323. W. Verboom, H. Westmijze, L. J. de Noten, P. Vermeer, and H. J. T. Bos, Synthesis, (1979) 296.

324. F. Bernadou, D. Mesnard, and L. Miginiac, J. Chem. Research (S), (1979) 190.

325. J. C. Martin, J. S. Tou, and W. Reusch, J. Org. Chem., 44 (1979) 3666.

326. A. Lebouc, J. Delaunay, and O. Riobe, Synthesis, (1979) 610.

327. G. Balme, A. Doutheau, J. Gore, and M. Malacria, Synthesis, (1979) 508.

328. I. Kuwajima and K. Matsumoto, Tetrahedron Lett., (1979) 4095.

329. A. S. Howard, C. A. Meerholz, and J. P. Michael, Tetrahedron Lett., (1979) 1339.

330. A. Banerji and N. C. Goomer, Tetrahedron Lett., (1979) 3685.

331. H. Holy, R. Fowler, E. Burnett, and R. Lorenz, Tetrahedron, 35 (1979) 613.

332. A. R. Katritzky, H. Beltrami, J. G. Keay, D. N. Rogers, M. P. Sammes, C. W. F. Leung, and C. M. Lee, Angew. Chem., 91 (1979) 856; Angew. Chem. Int. Ed. Engl., 18 (1979) 792.

333. A. S. Kende, M. Benechie, Dp P. Curran, and P. Fludzinski, Tetrahedron Lett., (1979) 4513.

334. D. A. Clark and P. C. Fuchs, J. Am. Chem. Soc., 101 (1979) 3567.

335. H. O. House, C.-C. Yau, and D. Vanderveer, J. Org. Chem., 44 (1979) 3031.

336. M. Mellor and G. Pattenden, Syn. Comm., 9 (1979) 1.

337. E. Piers, B. Abeysekera, and J. R. Scheffer, Tetrahedron Lett., (1979) 3279.

338. M. E. Garst, J. Org. Chem., 44 (1979) 1578.

339. K. Hiroi, Y. Matsuda, and S. Sato, Synthesis, (1979) 621.

340. Y. K. Yee and A. G. Schultz, J. Org. Chem., 44 (1979) 719.

341. D. Caine and W. D. Samuels, Tetrahedron Lett., (1979) 3609.

342. H. Sakurai, A. Shirahata, and A. Hosomi, Angew. Chem., 91 (1979) 178; Angew. Chem. Int. Ed. Engl., 18 (1979) 163.

343. F. W. Sum and L. Weiler, Tetrahedron Lett., (1979) 707.

344. F. W. Sum and L. Weiler, J. Am. Chem. Soc., 101 (1979) 4401.

345. T.-H. Chan and P. Brownbridge, J. Chem. Soc., Chem. Comm., (1979) 578.

346. K. G. Bilyard, P. J. Garratt, A. J. Underwood, and R. Zahler, Tatrahedron Lett., (1979) 1815.

347. P. J. Garratt and R. Zahler, Tatrahedron Lett., (1979) 73.

348. T. Kaneko, D. L. Turner, M. Newcomb, and D. E. Bergbreiter, Tatrahedron Lett., (1979) 103.

349. Y. Jenkitkasemwong, Y. Thebtaranonth, and N. Wajirum, Tetrahedron Lett., (1979) 1615.

350. R. Kimura, A. Ichihara, and S. Sakamura, Synthesis, (1979) 516.

351. K. Takaki and K. Negoro, J. Chem. Soc., Perkin I, (1979) 1490.

352. I. Hori and T. Oishi, Tatrahedron Lett., (1979) 4087.

353. F.-P. Montforts and S. Ofner, Angew. Chem., 91 (1979) 656; Angew. Chem. Int. Ed. Engl., 18 (1979) 632.

354. W. Wierenga and H. I. Skulnick, J. Org. Chem., 44 (1979) 310.

355. J. W. F. K. Barnick, J. L. van der Baan, and F. Bickelhaupt, Synthesis, (1979) 787.

356. A. Wissner, J. Org. Chem., 44 (1979) 4617.

357. F. Huet, M. Pellet, and J. M. Conia, Synthesis, (1979) 33.

358. C. C. Shen and C. Ainsworth, Tetrahedron Lett., (1979) 83.

359. C. C. Shen and C. Ainsworth, Tetrahedron Lett., (1979) 87.

360. C. C. Shen and C. Ainsworth, Tetrahedron Lett., (1979) 93.

361. C. C. Shen and C. Ainsworth, Tetrahedron Lett., (1979) 89.

362. W. Adam and L. A. A. Encarnacion, Synthesis, (1979) 388.

363. W. Adam and H.-H. Fik, J. Org. Chem., 44 (1979) 356.

364. G. B. Bodem and E Leete, J. Org. Chem., 44 (1979) 4696.

365. E. S. Stratford and N. D. Aggerwal, J. Org. Chem., 44 (1979) 1570.

366. S. Kano, T. Ebata, K. Funaki, and S. Shibuya, J. Org. Chem., 44 (1979) 3946.

367. A. Ekouya, R. Calas, J. Dunogues, C. Biran, N. Duffaut, and P. Lapouyade, J. Organomet. Chem., 177 (1979) 137.

368. R. L. Cargill, D. F. Bushey, and J. J. Good, J. Org. Chem., 44 (1979) 300.

369. G. Ege, H. O. Frey, and E. Schuck, Synthesis, (1979) 376.

370. Y. Yoshida, M. Komatsu, Y. Ohshiro, and T. Agawa, J. Org. Chem., 44 (1979) 830.

371. J. P. Kutney, M. Noda, and B. R. Worth, Heterocycles, 12 (1979) 1269.

372. S. Hunig and G. Wehner, Chem. Ber., 112 (1979) 2062.

373. R. M. Jacobson and G. P. Lahm, J. Org. Chem., 44 (1979) 462.

374. C. Goasdoue and R. Couffignal, Tetrahedron Lett., (1979) 1586.

375. G. Stork, R. W. Jacobson, and R. Levitz, Tetrahedron Lett., (1979) 771.

376. H. Ahlbrecht, W. Raab, and C. Vonderheid, Synthesis, (1979) 127.

377. P. M. Worster, C. R. McArthur, and C. C. Leznoff, Angew, Chem., 91 (1979) 255; Angew. Chem Int. Ed. Engl., 18 (1979) 221.

378. S. F. Martin, T. A. Puckette, and J. A. Colapret, J. Org. Chem., 44 (1979) 3391.

379. N. L. J. M. Broekhoz, F. L. Jonkers, and A.van der Gen, Tetrahedron Lett., (1979) 2433.

380. L. Bemi, M. T. Thomas, and V. Snieckus, Synthesis, (1979) 130.

381. A. Padwa, T. J. Blacklock, P. H. J. Carlsen, and M. Pulwer, J. Org. Chem., 44 (1979) 3281.

382. M. Bellassoued, R. Dardoize, and M. Gaudemar, J. Organomet. Chem., 177 (1979) 35.

383. M. Larcheveque, G. Valette, and T. Cuvigny, Tetrahedron, 35 (1979) 1745.

384. H. Grund and V. Jager, J. Chem. Research (S), (1979) 54.

385. S. A. Tischler and L. Weiler, Tetrahedron Lett., (1979) 4903.

386. C. Alvarez-Ibarra, M. S. Arias-Perez, M. T. Garcia-Romo, M. T. Molina-Orden, S. Perez-Rubalcaba, and M. L. Quiroga, Tetrahedron, 35 (1979) 1767.

387. E. Vedejs, J. M. Dolphin, and W. T. Stolle, J. Am. Chem. Soc., 101 (1979) 249.

388. T. Nakai and T. Mimura, Tetrahedron Lett., (1979) 531.

389. A. R. Chamberlin and F. T. Bond, Synthesis, (1979) 44.

390. D. Seebach and W. Wykypiel, Synthesis, (1979) 423.

391. U. Schollkopf, R. Jentsch, and K. Madawinata, Liebigs Ann. Chem., (1979) 451.

392. Y. Ito, K. Kobayashi, and T. Saegusa, J. Org. Chem., 44 (1979) 2030.

393. Y. Ito, K. Kobayashi, N. Seko, and T. Saegusa, Chem. Lett., (1979) 1273.

394. A. Mendoza and D. S. Matteson, J. Org. Chem., 44 (1979) 1352.

395. W. S. Murphy and S. Wattanasin, Tetrahedron Lett., (1979) 1827.

396. F. E. Ziegler and C. C. Tam, J. Org. Chem., 44 (1979) 3428.

397. T. Cohen, R. E. Gapinski, and R. R. Hutchins, J. Org. Chem., 44 (1979) 3599.

398. T. Cohen, R. B. Weisenfeld, and R. E. Gapinski, J. Org. Chem., 44 (1979) 4744.

399. T. Cohen and R. B. Weisenfeld, J. Org. Chem., 44 (1979) 3601.

400. P. Blatcher and S. Warren, J. Chem. Soc., Perkin I, (1979) 1074.

401. M. Watanabe, K. Shirai, and T. Kumamoto, Bull. Chem. Soc. Japan, 52 (1979) 3318.

402. Y. Ohtsuka and T. Oishi, Tetrahedron Lett., (1979) 4487.

403. H. Böhme and B. Clement, Tetrahedron Lett., (1979) 1737.

404. K. Schank, F. Schroeder, and A. Weber, Liebigs Ann. Chem., (1979) 547.

405. P. J. Kocienski, Tetrahedron Lett., (1979) 441.

406. R. Annunziata, M. Cinquini, and F. Cozzi, Synthesis, (1980) 535.

407. C. R. Johnson and R. A. Kirchhoff, J. Am. Chem. Soc., 101 (1979) 3602.

408. C. R. Johnson, K. Mori, and A. Nakanishi, J. Org. Chem., 44 (1979) 2065.

409. H. J. Reich, F. Chou, and S. K. Shah, J. Am. Chem. Soc., 101 (1979) 6638.

410. H. J. Reich, S. K. Shah and F. Chou, J. Am. Chem. Soc., 101 (1979) 6648.

411. S. Halazy and A. Krief, Tetrahedron Lett., (1979) 4233.

412. H. J. Reich, P. M. Gold, and F. Chou, Tetradedron Lett., (1979) 4433.

413. W. Dumont, D. Van Ende, and A. Krief, Tetrahedron Lett., (1979) 485.

414. H. H. Karsch, U. Schubert, and D. Neugebauer Angew. Chem., 91 (1979) 518; Angew. Chem. Int. Ed. Engl., 18 (1979) 484.

415. H. H. Karsch, B. Zimmer-Gasser, D. Neugebauer, and U. Schubert, Angew. Chem., 91 (1979) 519; Angew. Chem. Int. Ed. Engl., 18 (1979) 484.

416. M. Mikolajczyk, S. Grzejszczak, A. Chefczynoka, and A. Zatorski, J. Org. Chem., 44 (1979) 2967.

417. A. F. Kluge and I. S. Cloudsdale, J. Org. Chem., 44 (1979) 4847.

418. G. Stork and E. Nakamura, J. Org. Chem., 44 (1979) 4010.

419. K. C. Nicolaou, S. P. Seitz, M. R. Pavia, and N. A. Petasis, J. Org. Chem., 44 (1979) 4011.

420. H. J. Reich, J. J. Rusek, and R. E. Olson, J. Am. Chem. Soc., 101 (1979) 2225.

421. I. Kuwajima and M. Kato, J. Chem. Soc., Chem. Comm., (1979) 708.

422. M. Sekine, M. Nakajima, A. Kume, and T. Hata, Tetrahedron Lett., (1979) 4475.

423. M. Laguerre, G. Felix, J. Dunogues, and R. Calas, J. Org. Chem., 44 (1979) 4275.

424. T. Konakahara and Y. Takagi, Synthesis, (1979) 192.

425. D. Seyferth, K. R. Wursthorn, and R. E. Mammarella, J. Organomet. Chem., 179 (1979) 25.

426. G. Crassous, M. Abadie, and F. Schue, Eur. Polym. J., 15 (1979) 747.

427. C. J. Dyball, D. J. Worsfold, and S. Bywater, Macromolecules, 12 (1979) 819.

428. T. C. Cheng, S. E. Oberster, and A. F. Halasa, J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 1847.

429. T. Suzuki, Y. Tsuji, Y. Watanabe, and Y. Takegami, Polym. J., (1979) 651.

430. L. J. Fetters, C. W. Kamienski, R. C. Morrison, and R. N. Young, Macromolecules, 12 (1979) 344.

431. E. A. Mushina, L. S. Muraviova, T. S. Samedova, and B. A. Krentsel, Eur. Polym. J., 15 (1979) 99.

432. G. G. Cameron and G. M. Buchan, Polymer, 20 (1979) 1129.

433. T. E. Hogen-Esch and C. F. Tien, J. Polym. Sci., Polym. Lett. Ed., 17 (1979) 431.

434. K. Ohta, Y. Okamoto, K. Hatada, and H. Yuki, J. Polym. Sci., Polym. Chem. Ed., 17(1979) 2917.

435. K. Hashimoto and H. Sumitomo, J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 2999.

436. D. Petit, R. Jerome, and P. Teyssie, J. Polym. Sci., Polym. Chem. Ed., 17 (179) 2903.

437. N. Yamashita, Y. Nishii, and T. Maeshima, J. Polym Sci., Polym. Lett. Ed., 17 (1979) 521.

438. H. R. Allcock and C. T.-W. Chu, Macromolecules, 12 (1979) 551.

439. E. Wenkert, P. Bakuzis, J. N. Dynak, and C. S. Swindell, Syn. Comm., 9 (1979) 11.

440. B. Mauze', J. Organomet. Chem., 170 (1979) 265.

441. R. A. Moss and R. C. Munjal, Synthesis, (1979) 425.

442. J. Villieras, P. Perriot, and J. F. Normant, Synthesis, (1979) 968.

443. T. Hiyama, M. Shinoda, and H. Nozaki, Tetrahedron Lett., (1979) 3529.

444. M. S. Baird and G. W. Baxter, J. Chem. Soc., Perkin I, (1979) 2317.

445. T. Hiyama, H. Saimoto, K. Nishio, M. Shinoda, H. Yamamoto, and H. Nozaki, Tetrahedron Lett., (1979) 2043.

446. R. F. Salinaro and J. A. Berson, J. Am. Chem. Soc., 101 (1979) 7094.

447. J. Villieras, P. Perriot, and J. F. Normant, Synthesis, (1979) 502.

448. G. L. Larson and O. Rosario, J. Organomet. Chem., 168 (1979) 13.

449. R. Weiss, M. Hertel, and H. Wolf, Angew, Chem., 91 (1979) 506; Angew. Chem. Int. Ed. Engl., 18 (1979) 473.

450. Y. Yamamoto and K. Maruyama, J. Syn. Org. Chem., Japan, 37 (1979) 641.

451. C. H. Heathcock, T. C. Germroth, and S. L. Graham, J. Org. Chem., 44 (1980) 4481.

452. D. B. Ledlie and G. Miller, J. Org. Chem., 44 (1979) 1006.

453. K. K. Heng and R. A. J. Smith, Tetrahedron, 35 (1979) 425.

454. C. P. Casey and M. C. Cesa, J. Am. Chem. Soc., 101 (1979) 4236.

455. A. G. Schultz, J. D. Godfrey, E. V. Arnold, and J. Clardy, J. Am. Chem. Soc., 101 (1979) 1276.

456. J. P. Marino and D. M. Floyd, Tetrahedron Lett., (1979) 675.

457. J. P. Marino and N. Hatanaka, J. Org. Chem., 44 (1979) 4467.

458. G. Teutsch and A. Belanger, Tetrahedron Lett., (1979) 2051.

459. C. B. Chapleo, M. A. W. Finch, T. V. Lee, S. M. Roberts, and R. F. Newton, J. Chem. Soc., Chem. Comm., (1979) 676.

460. G. Stork and E. W. Logusch, Tetrahedron Lett., (1979) 3361.

461. E. W. Logusch, Tetrahedron Lett., (1979) 3365.

462. G. Schulz, P. Gruber, and W. Steglich, Chem. Ber., 112 (1979) 3221.

463. D. Cabaret and Z. Welvart, J. Organomet. Chem., 177 (1979) 75.

464. R. D. Clark, Syn. Comm., 9 (1979) 325.

465. F.-W. Sum and L. Weiler, Can. J. Chem., 57 (1979) 1431.

466. C. Chuit, R. Sauvetre, D. Masure, and J. F. Normant, Tetrahedron Lett., (1979) 2645.

467. C. V. Maffeo, G. Marchese, F. Naso, and L. Ronzini, J. Chem. Soc., Perkin I, (1979) 92.

468. O. H. Johansen and K. Undheim, Acta Chem. Scand., B33 (1979) 460.

469. R. H. Schwartz and J. San Filippo, Jr., J. Org. Chem., 44 (1979) 2705.

470. G. H. Posner and K. A. Babiak, J. Organomet. Chem., 177 (1979) 299.

471. E. Piers and H.-U. Reissig, Angew. Chem., 91 (1979) 857; Angew. Chem. Int. Ed. Engl., 18 (1979) 791.

472. B. M. Trost and Y. Tanigawa, J. Am. Chem. Soc., 101 (1979) 4413.

473. P. Baret, E. Barreiro, A. E. Greene, J.-L. Luche, M.-A. Teixeira, and P. Crabbé, Tetrahedron, 35 (1979) 2931.

474. C. Gallina and P. G. Ciattini, J. Am. Chem. Soc., 101 (1979) 1035.

475. H. Kleijn, C. J. Elsevier, H. Westmijze, and P. Vermeer, Tetrahedron Lett., (1979) 3123.

476. H. Kleijn, H. Westmijze, K. Kruithof, and P. Vermeer, Recueil, 98 (1979) 27.

477. A. Claesson and L.-I. Olsson, J. Chem. Soc., Chem. Comm., (1979) 524.

478. H. Kleijn, H. Westmijze, A. Schaap, H.J.T. Bos, and P. Vermeer, Recueil, 98 (1979) 209.

479. A. Alexakis, G. Cahiez, and J. F. Normant, J. Organomet, Chem., 177 (1979) 293.

480. A. P. Kozikowski, H. Ishida, and K. Isobe, J. Org. Chem., 44 (1979) 2788.

481. P. Miginiac, H. Daviaud, and F. Gerard, Tetrahedron Lett., (1979) 1811.

482. A. G. Pernet, Tetrahedron Lett., (1979) 3933.

483. A. Alexakis, G. Cahiez, and J. F. Normant, Synthesis, (1979) 826.

484. R. K. Boeckman, Jr. and K. J. Bruza, J. Org. Chem., 44 (1979) 4781.

485. M. A. W. Finch, T. V. Lee, S. M. Roberts, and R. F. Newton, J. Chem. Soc., Chem. Comm., (1979) 677.

486. S. M. Ali, M. A. W. Finch, S. M. Roberts, and R. F. Newton, J. Chem. Soc., Chem. Comm., (1979) 679.

487. R. Davis and K. G. Untch, J. Org. Chem., 44 (1979) 3755.

488. R. J. Cave, C. C. Howard, G. Klinkert, R. F. Newton, D. P. Reynolds, A. H. Wadsworth, and S. M. Roberts, J. Chem. Soc., Perkin I, (1979) 2954.

489. N.-T. Luong-Thi and H. Riviere, Tetrahedron Lett., (1979) 4657.

490. Y. Kojima, S. Wakita, and N. Kato, Tetrahedron Lett., (1979) 4577.

491. T. Tsuda, M. Miwa, and T. Saegusa, J. Org. Chem., 44 (1979) 3734.

492. H. M. Walborsky and M. P. Periasamy, J. Organomet. Chem., 179 (1979) 81.

493. R. W. M. Ten Hoedt, G. Van Koten, and J. G. Noltes, J. Organomet. Chem., 179 (1979) 227.

494. S. H. Bertz, J. Org. Chem., 44 (1979) 4967.

495. P. Savignac, A. Breque, C. Charrier, and F. Mathey, Synthesis, (1979) 832.

496. P. Savignac, A. Breque, F. Mathey, J.-M. Varlet, and N. Collignon, Syn. Comm., 9 (1979) 287.

497. Y. Yamamoto, H. Yatagai, and K. Maruyama, J. Chem. Soc., Chem. Comm., (1979) 157.

498. S. Ncube, A. Pelter, and K. Smith, Tetrahedron Lett., (1979) 1893.

499. S. Ncube, A. Pelter, and K. Smith, Tetrahedron Lett., (1979) 1895.

500. I. Akimoto and A. Suzuki, Synthesis, (1979) 146.

501. E. R. Marinelli and A. B. Levy, Tetrahedron Lett., (1979) 2313.

502. A. S. Fletcher, W. E. Paget, K. Smith, K. Swaminathan, and M. J. Haley, J. Chem. Soc., Chem. Comm., (1979) 573.

503. J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, and J. C. Selover, Inorg. Chem., 18 (1979) 553.

504. H. C. Brown, S. Krishnamurthy, and J. L. Hubbard, J. Organomet. Chem., 166 (1979) 271.

505. H. C. Brown, J. C. Hubbard, and B. Singaram, J. Org. Chem., 44 (1979) 5004.

506. H. C. Brown, S. Krishnamurthy, J. L. Hubbard, and R. A. Coleman, J. Organomet. Chem., 166 (1979) 281.

507. G. Boireau, D. Abenhaim, and E. Henry-Basch, Tetrahedron, 35 (1979) 1457.

508. K. F. Bernady, M. B. Floyd, J. F. Poletto, and M. J. Weiss, J. Org. Chem., 44 (1979) 1438.

509. A. P. Kozikowski, A. Ames, and H. Wetter, J. Organomet, Chem., 164 (1979) C33.

510. G. Zweifel, W. Lewis, and H. P. On, J. Am. Chem. Soc., 101 (1979) 5101.

511. H. Westmijze,H. Kleijn, and P. Vermeer, Tetrahedron Lett., (1979) 3327.

512. D. J. Coughlin and R. G. Salomon, J. Org. Chem., 44 (1979) 3784.

513. P. W. Rabideau,.D. W. Jessup, J. W. Ponder, and G. F. Beekman, J. Org. Chem., 44 (1979) 4594.

514. W. G. Blenderman and M. M. Joullie, Tetrahedron Lett., (1979) 4985.

515. H. M. Lee and R. G. Harvey, J. Org. Chem., 44 (1979) 4948.

516. J. J. Eisch and G. Gupta, J. Organomet. Chem., 168 (1979) 139.

517. J. W. Huffman and W. W. McWhorter, J. Org. Chem., 44 (1979) 594.

518. H. Inoue, M. Suzuki, and N. Fujimoto, J. Org. Chem., 44 (1979) 1722.

519. P. A. Grieco, S. Burke, W. Metz, and M. Nishizawa, J. Org. Chem., 44 (1979) 152.

520. F. Jaisli, D. Sternbach, M. Shibuya, and A. Eschenmoser, Angew. Chem., 91 (1979) 673; Angew. Chem. Int. Ed. Engl., 18 (1979) 637.

521. G. S. R. Subba Rao and N. S. Sundar, J. Chem. Research (S), (1979) 282.

522. R. G. H. Kirrstetter, Chem. Ber., 112 (1979) 2804.

523. H. W. Pinnick and E. Fernandez, J. Org. Chem., 44 (1979) 2810.

524. C. G. Screttas and M. Micha-Screttas, J. Org. Chem., 44 (1979) 713.

525. X. Creary and A. J. Rollin, J. Org. Chem., 44 (1979) 1798.

526. J. A. Marshall, L. J. Karas, and R. D. Royce, Jr., J. Org. Chem., 44 (1979) 2994.

527. R. P. Quirk and F. H. Murphy, Tetrahedron Lett., (1979) 301.

528. A. O. Bedenbaugh, A. L. Payton, and J. H. Bedenbaugh, J. Org. Chem., 44 (1979) 4703.

529. H. Schumann and J. Muller, J. Organomet. Chem., 169 (1979) C1.

530. J. T. Miller and C. W. DeKock, Inorg. Chem., 18 (1979) 1305.

531. A. Dormond and C. Duval, J. Organomet. Chem., 178 (1979) C5.

532. H. W. Turner, R. A. Andersen, A. Zalkin, and D. H. Templeton, Inorg. Chem., 18 (1979) 1221.

533. J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day, and V. W. Day, J. Am. Chem. Soc., 101 (1979) 5075.

534. S. J. McLain, R. R. Schrock, P. R. Sharp, M. R. Churchill, and W. J. Youngs, J. Am. Chem. Soc., 101 (1979) 263.

535. B. Sarry, H. Singh, B. Hahn, and R. Schaffernicht, Z. anorg. allg. Chem., 456 (1979) 181.

536. W. Seidel and I. Burger, J. Organomet. Chem., 171 (1979) C45.

537. M. L. H. Green and S. J. Simpson, J. Organomet. Chem., 173 (1979) 287.

538. E. O. Fischer, W. R. Wagner, F. R.Kreissl, and D. Neugebauer, Chem. Ber., 112 (1979) 1320.

539. E. O. Fischer, H. Hollfelder, and F. R. Kreissl, Chem. Ber., 112 (1979) 2177.

540. J. Levisalles, H. Rudler, Y. Jeannin, and F. Dahan, J. Organomet. Chem., 178 (1979) C8.

541. M. H. Chisholm and D. A. Haitko, J. Am. Chem. Soc., 101 (1979) 6784.

542. A. Bino, F. A. Cotton, and W. Kaim, J. Am. Chem. Soc., 101 (1979) 2506.

543. A. Bino, F. A. Cotton, and W. Kaim, Inorg. Chem., 18 (1979) 3030.

544. A. Bino, F. A. Cotton, and W. Kaim, Inorg. Chem., 18 (1979) 3566.

545. F. A. Cotton, G. W. Rice, and J. C. Sekutowski, Inorg. Chem., 18 (1979) 1143.

546. F. A. Cotton, W. H. Ilsley, and W. Kaim, Inorg, Chem., 18 (1979) 2717.

547. F. A. Cotton, W. H. Ilsley, and W. Kaim, Inorg. Chem., 18 (1979) 3569.

548. B. Horvath, R. Moseler, and E. G. Horvath, Z. anorg. allg. Chem., 450 (1979) 165.

549. P. Edwards, G. Wilkinson, K. M. A. Malik, and M. B. Hursthouse, J. Chem. Soc., Chem. Comm., (1979) 1158.

550. D. T. Hobbs and C. M. Lukehart, Inorg. Chem., 18 (1979) 1297.

551. W. Tam, W.-K. Wong, and J. A. Gladysz, J. Am. Chem. Soc., 101 (1979) 1589.

552. W.-K. Wong, W. Tam, and J. A. Gladysz, J. Am. Chem. Soc., 101 (1979) 5440.

553. R. I. Mink, J. J. Welter, P. R. Young, and G. D. Stucky, J. Am. Chem. Soc., 101 (1979) 6928.

554. J. L. Robbins, N. M. Edelstein, S. R. Cooper, and J. C. Smart, J. Am. Chem. Soc., 101 (1979) 3853.

555. R. C. Cookson and G. Farquharson, Tetrahedron Lett., (1979) 1255.

556. R. E. Ginsburg, J. M. Berg, R. K. Rothrock, J. P. Collman, K. O. Hodgson, and L. F. Dahl, J. Am. Chem. Soc., 101 (1979) 7218.

557. K. Jonas, L Schieferstein, C. Kruger, and Y. Tsay, Angew, Chem., 91 (1979) 590; Angew. Chem. Int. Ed. Engl., 18 (1979) 550.

558. K. Jonas and L. Schieferstein, Angew. Chem., 91 (1979) 590; Angew. Chem. Int. Ed. Engl., 18 (1979) 549.

559. D. O. Cowan, P. Shu, F. C. Hedberg, M. Rossi, and T. J. Kistenmacher, J. Am. Chem Soc., 101 (1979) 1304.

560. R. C. Pruett, R. C. Schoening, J. C. Vidal, and R. A. Fiato, J. Organomet. Chem., 182 (1979) C57.

561. F. Carre, G. Cerveau, E. Colomer, R. J. P. Corriu, J. C. Young, L. Ricard, and R. Weiss, J. Organomet. Chem., 179 (1979) 215.

562. K. Jonas, C. Kruger, and J. C. Sekutowski, Angew. Chem., 91 (1979) 520; Angew. Chem. Int. Ed. Engl., 18 (1979) 487.

563. K. Jonas and K. R. Porschke, Angew. Chem., 91 (1979) 521; Angew. Chem. Int. Ed. Engl., 18 (1979) 488.

564. B. L. Booth and G. C. Casey, J. Organomet. Chem., 178 (1979) 371.

565. T. Mise and H. Yamazaki, J. Organomet. Chem., 164 (1979) 391.

566. C. D. Wood, S. J. McLain, and R. R. Schrock, J. Am. Chem. Soc., 101 (1979) 3210.

567. H. Hoberg and C. Frohlick, J. Organomet. Chem., 168 (1979) C52.

568. H. Westmijze, H. Kleijn, and P. Vermeer, J. Organomet. Chem., 172 (1979) 377.

569. R. Uson, A. Laguna, and P. Brun, J. Organomet. Chem., 182 (1979) 449.

570. R. Uson, A. Laguna, J. Garcia, and M. Laguna, Inorg. Chim. Acta, 37 (1979) 201.

571. A. Meller, W. Maringgele, and K. Hennemuth, Z. anorg. allg. Chem., 449 (1979) 77.

572. P. Wisian-Neilson and D. R. Martin, J. Inorg. Nucl. Chem., 41 (1979) 1545.

573. H. Fussstetter and H. Noth, Chem. Ber., 112 (1979) 3672.

574. H. Schmidbaur and E. Weiss, Angew. Chem., 91 (1979) 847; Angew. Chem. Int. Ed. Engl., 18 (1979) 781.

575. H. Schmidbaur, E. Weiss, and B. Zimmer-Gasser, Angew. Chem., 91 (1979) 848; Angew. Chem. Int. Ed. Engl., 18 (1979) 782.

576. H. Schmidbaur, H.-J. Fuller, G. Muller, and A. Frank, Chem. Ber., 112 (1979) 1448.

577. P. M. Nowakowski, and L. H. Sommer, J. Organomet. Chem., 178 (1979) 95.

578. U. Wannagat and S. Klemke, Mh. Chem., 110 (1979) 1089.

579. U. Wannagat, S. Klemke, D. Mootz, and H. D. Reski, J. Organomet. Chem. 178 (1979) 83.

580. U. Klingebiel and P. Werner, J. Organomet. Chem., 178 (1979) 409.

581. J. C. Wilburn and R. H. Neilson, Inorg. Chem., 18 (1979) 347.

582. J. C. Wilburn, P. Wisian-Neilson, and R. H. Neilson, Inorg. Chem., 18 (1979) 1429.

583. O. J. Scherer and M. Puttmann, Angew, Chem., 91 (1979) 741; Angew. Chem. Int. Ed. Engl., 18 (1979) 679.

584. A. J. Banister, J. A. Durrant, J. S. Padley, and K. Wade, J. Inorg. Nucl. Chem., 41 (1979) 1415.

585. G. Fritz and S. Wartanessian, J. Organomet. Chem., 178 (1979) 11.

586. S. S. Dua, C. Eaborn, D. A. R. Happer, S. P. Hopper, K. D. Safa, and D. R. M. Walton, J. Organomet. Chem., 178 (1979) 75.

587. M. Ishikawa, T. Fuchikami, and M. Kumada, J. Organomet. Chem., 173 (1979) 117.

588. G. Markl and P. Hofmeister, Angew. Chem., 91 (1979) 863; Angew. Chem. Int. Ed. Engl., 18 (1979) 789.

589. H. Sakurai, Y. Nakadaira, T. Kobayashi, J. Am. Chem. Soc., 101 (1979) 487.

590. T. J. Barton, W. D. Wulff, E. V. Arnold, and J. Clardy, J. Am. Chem. Soc., 101 (1979) 2733.

591. G. Markl, H. Baier, P. Hofmeister, F. Kees, and C. Soper, J. Organomet. Chem., 173 (1979) 125.

592. G. Markl and D. Rudnick, J. Organomet. Chem., 181 (1979) 305.

593. D. C. van Beelen, J. Wolters, and A. van der Gen, Recueil, 98 (1979) 437.

594. L. Rosch and G. Altnau, Chem. Ber., 112 (1979) 3934.

595. L. Rosch and G. Altnau, Angew. Chem., 91 (1979) 62; Angew. Chem. Int. Ed. Engl., 18 (1979) 60.

596. P. Jutzi and F. Kohl, J. Organomet. Chem., 164 (1979) 141.

597. V. Rautenstrauch and M. Joyeux, Angew. Chem., 91 (1979) 72; Angew. Chem. Int. Ed. Engl., 18 (1979) 83.

598. V. Rautenstrauch and M. Joyeux, Angew. Chem., 91 (1979) 73; Angew. Chem. Int. Ed. Engl., 18 (1979) 85.

599. W. Levason and K. G. Smith, J. Organomet. Chem., 169 (1979) 283.

600. H. Schumann and G.-M. Frisch, Z. Naturforsch., 34b (1979) 748.

601. L. Weber, Chem. Ber., 112 (1979) 99.

602. R. Appel, K. Geisler, and H.-F. Schöler, Chem. Ber., 112 (1979) 648.

603. R. Appel, M. Wander, and F. Knoll, Chem. Ber., 112 (1979) 1093.

604. H. H. Karsch, Z. Naturforsch., 34b (1979) 1171.

605. H. H. Karsch, Z. Naturforsch., 34b (1979) 1178.

606. T. C. Klebach, H. van Dongen, and F. Bickelhaupt. Angew. Chem., 91 (1979) 423; Angew. Chem. Int. Ed. Engl., 18 (1979) 395.

607. M. E. Garst, Synth. Comm., 9 (1979) 261.

608. I. Granoth and J. C. Martin, J. Am. Chem. Soc., 101 (1979) 4623.

609. E. F. Perozzi and J. C. Martin, J. Am. Chem. Soc., 101 (1979) 1591.

610. I. Hoppe and U. Schollkopf, Liebigs Ann. Chem., (1979) 219.