Journal of Organometallic Chemistry, 47 (1973) 225–280

ALKALI METAL ADDITIONS TO UNSATURATED SYSTEMS

V. KALYANARAMAN and M. V. GEORGE*
Department of Chemistry, Indian Institute of Technology, Kanpur-16 (India)
(Received June 2nd, 1972)

CONTENTS

---

* To whom enquiries may be addressed.

I. INTRODUCTION

A. Alkali metal additions

Alkali metals add to a variety of organic substrates containing double and triple bonds and the synthetic utility of this method of reduction has been well studied. Excellent reviews are available on various aspects of the reduction of organic substrates by alkali metal solutions in liquid ammonia[1] or low molecular weight amines[2]. Addition of alkali metals to multiple bonds such as C=C, C=O and C=N and the reduction of acetylenes to olefins were known quite early[3,4]. Reduction of organic compounds by alkali metal solutions in hexamethylphosphoramide (HMPA) has also been examined in recent years, extensively by Normant and coworkers[5].

Alkali metals tend to add to unsaturated systems giving rise to radical anion intermediates and some of these radical anions are relatively stable in solutions. Radical anions are intensely coloured and can be readily characterized by spectroscopic methods. Structural features of radical anion intermediates have been extensively investigated using ESR techniques and the results of these studies are well documented in the literature. Radical anions may take up an additional electron to form dianions, which are diamagnetic and are generally in the singlet state. Both the radical anions and dianions show characteristic absorption bands. A comprehensive review on the electronic spectra of radical anions and dianions and the various equilibria associated with these species has been published by us recently[6]. In recent years, radical anions have also been postulated as intermediates in a variety of organic reactions[7-10]. In the following pages, a brief review of the addition of alkali metals to different unsaturated systems is presented.

B. Scope

This review is limited to those reactions of unsaturated systems with alkali metals (Li, Na, K, Rb and Cs) in aprotic ether solvents. Halogen-metal interconversion reactions[11], metalation reactions[12], use of organolithium compounds in synthesis[13] and synthetic applications of organosodium and -potassium compounds[14] are excluded from consideration. However, some reactions where the distinction is one of degree rather than of kind, are also discussed. In the present review, we have included some of the results of spectroscopic studies, which show evidence of some chemical transformations. The literature survey for this review is covered up to the end of 1971.

II. HYDROCARBONS

A. Aromatic hydrocarbons

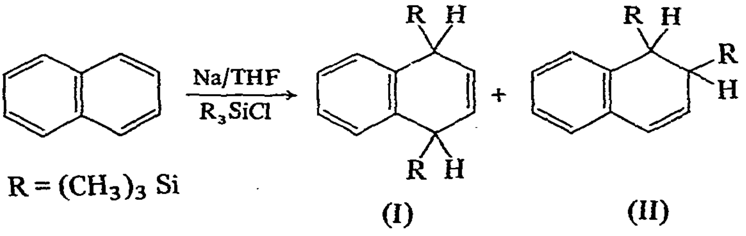
Addition of alkali metals to benzene gives rise to an unstable radical anion intermediate[15], which has been trapped by treatment with halosilanes to give 3,6-disilyl-substituted 1,4-cyclohexadienes[16]. Toluene and anisole, on similar treatment, give 30 to 50% yields of 1-methyl- and 1-methoxy-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene, respectively[16].

Benzene is converted to a mixture of naphthalene, biphenyl and biphenylene, on treatment with alkali metals in HMPA, as evidenced by ESR studies[17]. Na, K or Li reacts with *p*-cymene in a mixture of HMPA and tetrahydrofuran (THF) and this product mixture is used as a catalyst in the preparation of polybutadiene oils[18].

As early as 1867, Berthelot[19] reported the formation of a black addition product on fusing naphthalene with potassium. Alkali metals add to naphthalene which can be converted to 1,2- or 1,4-dihydro derivatives, by either carboxylation or hydrolysis[20-24]. The formation of a dilithium adduct of naphthalene, in contrast to a monosodium adduct, may be cited as an example of the strong reducing power of lithium[25]. The kinetics of the reaction of sodium naphthalenide with water has also been studied recently[26]. Alkali metal adducts of naphthalene abstract hydrogen atoms from solvents such as 1,2-dimethoxyethane (DME) and methyltetrahydrofuran (MTHF) to give dihydronaphthalenes and ether-cleavage products[27,28].

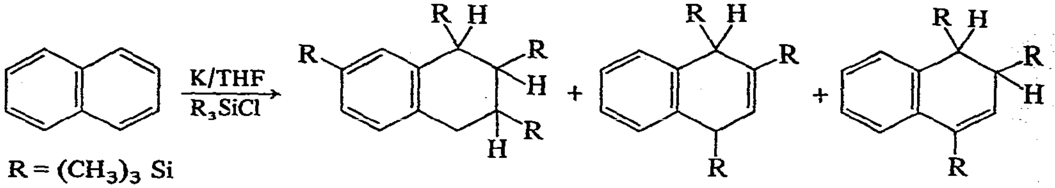
The reaction of alkyl, vinyl and aryl halides with naphthalene radical anion has received much attention[29-44]. Both electron transfer and nucleophilic displacement mechanisms have been suggested for these reactions. The reaction of sodium naphthalenide with alkyl halides (RX) in DME yields a mixture of aliphatic hydrocarbons (RH), dimeric products (R–R), alkylated dihydronaphthalenes, alkylnaphthalenes, naphthalene and traces of alkenes, in some cases. Chlorides and bromides give much diminished yields of the dimeric products. In a series of primary, secondary and tertiary iodides, the yields of RH and alkylation products increase while the dimer formation decreases. Reductions of haloolefins[37] and halocyclopropanes[42] have been accomplished by sodium naphthalenide. Garst and coworkers[31] reported that the reaction of sodium naphthalenide with 5-hexenyl halide in DME gives 1-hexene, small amounts of a dimeric hydrocarbon (C_{12}) and methylcyclopentane. On the other hand, reaction with cyclopentylmethyl bromide gives only methylcyclopentane. Reaction with α,ω-dihalo compounds results in the formation of polycyclic hydroaromatic hydrocarbons[41]. Treatment of sodium naphthalenide with halobenzenes in THF, for example, gives a mixture of products consisting of benzene, biphenyl, terphenyls, phenylnaphthalenes and a dimer of THF[44]. The formation of these products has been explained in terms of free radical as well as ionic mechanisms[39,44].

Alkali metal naphthalenides react with monohalosilanes to give a mixture of 1,2- and 1,4-disilyldihydronaphthalenes, which undergo aromatization through the loss of both hydrogen and a silyl fragment[45]. Recently, it has been shown that the reaction of naphthalene with trimethylchlorosilane and sodium in THF gives rise to 1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene (I) and the 1,2-derivative (II) (Scheme 1)[46]. On the other hand,



Scheme 1

the reaction with potassium gives mainly 1,2,3,7-tetrakis(trimethylsilyl)-1,2,3,4-tetrahydronaphthalene (III), besides, 1,2,4-tris(trimethylsilyl)-1,4-dihydronaphthalene (IV) and 1,2,4-tris(trimethylsilyl)-1,2-dihydronaphthalene (V) (Scheme 2)[46].



(III) (IV) (V)

Scheme 2

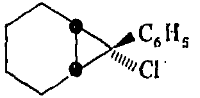
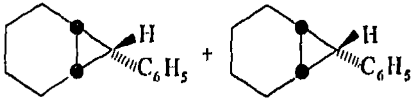
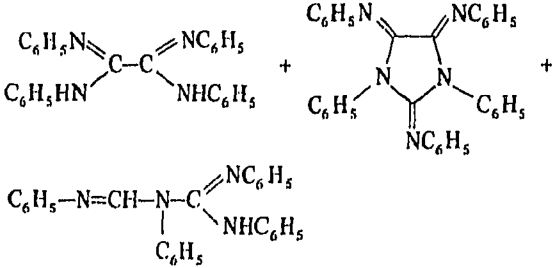
The reaction of triphenylsilyl halides with sodium naphthalenide, however, yields mainly hexaphenyldisilane and a small amount of 1,4-disubstituted 1,4-dihydronaphthalene[47]. The yield of silylated products increase if an excess of free naphthalene is present and an electron transfer mechanism to produce a triphenylsilyl radical has been proposed for the initial step. When sodium naphthalenide in THF is added to a premixed solution of benzyl chloride and trimethylsilyl chloride, a 90% yield of benzyltrimethylsilane is obtained[48]. Benzyl chloride alone is reduced by sodium naphthalenide to give bibenzyl, benzylated dihydronaphthalenes and traces of toluene.

Naphthalene radical anion, generated by reaction with sodium in THF reacts with hydrogen[49] or sulfur dioxide to give back naphthalene[50]. Sodium naphthalenide is converted to a mixture of 1,2- and 1,4-dihydronaphthalene in an autoclave pressurized with hydrogen[51]. The other products formed in the reaction with sulfur dioxide are sodium dithionate, sulfite and thiosulfate[50]. Naphthalene radical anion has been used as a catalyst in initiating polymerization reactions[52-55]. A few reactions with inorganic complexes have also been studied[56-58].

Sodium naphthalenide in THF has been successfully employed in several alkylation[59-64] and cyclization reactions[59,65-66], and in reactions of this type, naphthalene acts as a metal carrier. Sodium naphthalenide in THF constitutes a good metalating agent for compounds containing active methylene groups and is thus effective in Claisen condensation and in the synthesis of several other organic compounds[59,60]. *N*-Alkylation of amines[37,37a], α-ethylation of naphthalene[61,62], and dimerization and trimerization of nitriles[65,66], carbodiimide[67] and phenylisocyanate[67], have been brought about by lithium naphthalenide. Some of these reactions are tabulated in Table 1. Coates and coworkers[69] have reported that solutions of triphenylstannylsodium could be prepared by the action of sodium naphthalenide on hexaphenyldistannane or tetraphenylstannane. The use of lithium naphthalenide in the reductive bis-alkylation of a bis-sulfoxide such as (VI) to the cyclooctatriene derivative (VII) has been reported recently (Scheme 3)[70]. Lithium naphthalenide in THF is an excellent reagent for the ethynylation of α,β-unsaturated ketones[59,71-73], for the dimerization of conjugated dienes[74-79] and for the synthesis of certain terpene alcohols[80,81] (Table 1). Sodium naphthalenide promotes the cleavage of trifluoroethyl ethers. Regeneration of amines in excellent yields from different sulfonamides can be achieved by treatment with sodium naphthalenide in DME[83,84]. Reaction of sodium naphthalenide with alkyl toluene-

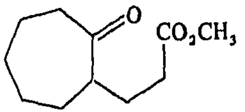
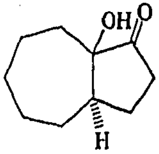
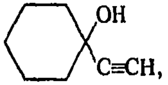
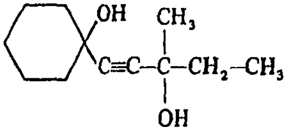
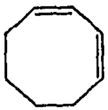
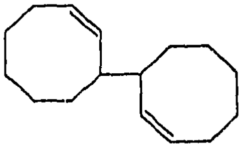
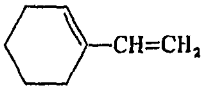
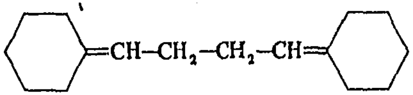
TABLE 1

SOME REACTIONS OF ALKALI METAL NAPHTHALENIDES

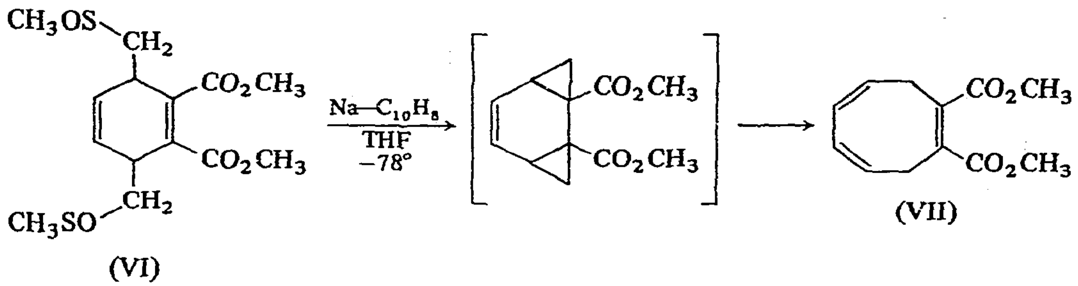
Alkali metal	*Solvent*	*Reactant*	*Products*	*Reference*
Li or Na	E[a]	n-BuBr	1-Butylnaphthalene, dibutylnaphthalene and octane	29
Na	THF	H_2O	Dihydronaphthalenes, naphthalene, and tetralin	30
Na	DME	5-Hexenyl halide	1-Hexene, methylcyclopentane, and C_{12} hydrocarbon	31
Na	DME	R-I, R = iso-C_5H_{11}	R–R, R–H, 1-pentene, 2-pentene, alkylated naphthalenes, mono- and di-alkylated dihydronaphthalenes	32, 33
Na	DME	1,4-Diiodobutane	Cyclobutane and alkylation products	33
Na	THF-DMF	*cis*- or *trans*-3-Chloro-3-hexene	Mixture of *cis*- and *trans*-hexenes	37
Na	THF	Chlorobenzene	Benzene, biphenyl, *o*-terphenyl, *m*-terphenyl, *p*-terphenyl, α-phenylnaphthalene, β-phenylnaphthalene and THF dimer	44
Li, Na, K	THF	Halosilanes	See Schemes 1 and 2	45, 46, 47
Na	THF	Benzylchloride + trimethylchlorosilane	Benzyltrimethylsilane	48
Li	–	Diethyldichlorosilane	Polymers containing Et_2Si, dihydronaphthalene and chlorine units	53
Na	THF			42
Na	THF	Diphenylmethane, CO_2	Diphenylacetic acid	59
Na	THF	Hexyne, CO_2	1-Hexyne-1-carboxylic acid	59
Na	THF	Camphor, CO_2	Camphor-3-carboxylic acid	59
Na	THF	Ethyl acetate	Ethyl acetoacetate	59
Li	THF	Dibenzylamine, n-butyl bromide	Dibenzylbutylamine	61
Li	THF	Methylvinyl ether	α-Ethylnaphthalene	63
Na	D	Bis(β-cyanoethyl)amine, HCl	3-Cyano-4-piperidone	65
Na	THF	Diphenylcarbodiimide		67

(*continued*)

(*Table continued*)

Alkali metal	*Solvent*	*Reactant*	*Products*	*Reference*
Na	THF	Phenylisocyanate	Cyclic trimer	67
Na, K	THF		 and *cis*-isomer	68
Na	DME	Hexaphenyldistannane, diphenyl disulfide	Hexaphenyldistannane, triphenyl(phenylthio)tin, and sodium phenylmercaptide	69
Li	THF	Acetylene, *β*-ionone	Ethynyl-*β*-ionol	72
Li	THF	Acetylene, benzalacetone	3-Methyl-3-hydroxy-5-phenyl-4-pent-1-yne	72
Li	THF	 $CH_3–CH_2–CO–CH_3$		73
Li				75
Li	THF			75
Li	THF	Isoprene	2,6-Dimethyl-2,6-octadiene and 2,7-dimethyl-2,6-octadiene	78
Li	THF	Isoprene	Mixture of dimer, trimer, tetramer and hexamer	79
Li	THF	Isoprene O_2, CH_3OH	Mixture of terpene alcohols (8 major and 3 minor constituents)	80
Na	DME	*N*-Ethyl-*N*-phenyl-*p*-toluene sulfamide	Toluene and ethylaniline	84

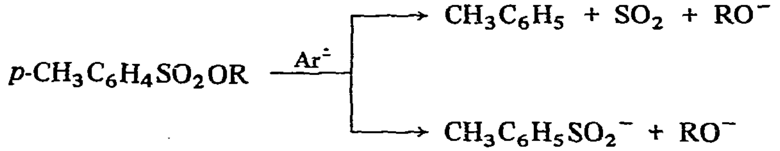
[a] E = diethyl ether, D = dioxane, THF = tetrahydrofuran, DMF = dimethoxyethane.



Na—$C_{10}H_8$ = Sodium naphthalenide

Scheme 3

sulfonates in THF constitutes an ideal procedure for regenerating the corresponding alcohols (Scheme 4)[85]. Competitive C-O and S-O bond cleavages in reactions of alkyl alkanesulfonates with arene radical anions have also been studied[86]. Using naphthalene radical anion, van Tamelen and coworkers[87] have recently reported a novel method for the fixation of atmospheric nitrogen. Molecular nitrogen, on treatment with a mixture of any titanium alkoxide and sodium naphthalenide followed by treatment with a protic solvent generates hydrazine or ammonia depending upon the concentration of the reactants (Scheme 5). The reaction is not successful with other transition metals like Co, Mo, W, Cr, Ni or Fe. Under high pressure, nitrogen reacts with the dilithio adduct of naphthalene to give a mixture of ammonia and 1-aminonaphthalene[88].



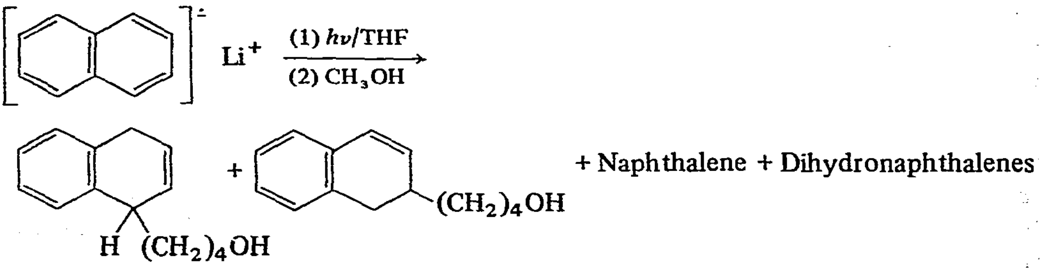
R = phenyl, cyclopentyl, cyclohexyl etc.
Ar = naphthalene, phenanthrene, anthracene

Scheme 4

$$\begin{tikzcd}
\mathrm{Ti(OR)_4} \arrow[r, "\mathrm{NaNp}"] & {[\mathrm{Ti(OR)_2}]_x} \arrow[r, "N_2"] & {[\mathrm{Ti(OR)_2}\cdot N_2]} \arrow[r, "\mathrm{4NaNp}"] & {} \\
 & & {[\mathrm{Ti(OR)_2}\cdot N_2]_x^{4-}} \arrow[r, "\mathrm{2NaNp}"] \arrow[d, "4H^+"'] & {[\mathrm{Ti(OR)_2}\cdot N_2]_x^{6-}} \arrow[d, "6H^+"'] \\
 & & N_2H_4 & 2NH_3
\end{tikzcd}$$

Scheme 5

The ESR and electronic spectra of the radical anion of naphthalene-d_8 in tetrahydrofuran-d_8 are exactly similar to those of alkali metals dissolved in amines[89], and the similarities in the spectra can be explained in terms of an ion-pair interaction between the metal cation and the solvent. The photochemical reaction of lithium naphthalenide in THF gives rise to a mixture of 4-hydroxybutyldihydronaphthalenes (VIII) and (IX) (Scheme 6)[90,91]. It is interesting to note that sodium naphthalenide does not undergo this reaction.



(VIII) (IX)

Scheme 6

Numerous examples of the addition of alkali metals to polycyclic aromatics have been reported in the literature. Thus, the alkali metals add to halonaphthalenes[92,93], 1-methylnaphthalene[94], 1-phenylnaphthalene[95], 1,4-diphenylnaphthalene[95], anthracene[96-103], 9,10-alkylated derivatives of anthracene[104,105], pyrene[106-108], naphthacene[109,110], 1,2,3,4-tetrahydronaphthacene[111], pentacene[112], acenaphthene[113], phenanthrene[110,113], chrysene[114] and 1,2-benzanthracene[96] to give radical anion and dianion intermediates. Quenching the reaction products with water, ammonium chloride or alcohol gives the dihydroaromatic derivatives[115]. It is found that the sites which carry the highest electron density are most easily protonated. Thus, anthracene produces 9,10-dihydroanthracene and not the 1,4-dihydro derivative[115]. 9,10-Diethylanthracene is reduced to give *cis*- and *trans*-isomers of 9,10-dihydro-9,10-diethylanthracene[105]. Stereospecific control of this reduction is possible, by the proper choice of the alkali metal and solvents. Thus, sodium metal and a solvent mixture (3/2) of HMPA and THF gives exclusively the *cis*-isomer whereas lithium metal and a 1/4 mixture of the same solvent leads to the isolation of the pure *trans*-isomer. The dianions of naphthalene, anthracene, tetracene and pyrene, on protonation with either stearyl alcohol or the dihydro compounds of the corresponding hydrocarbons give the respective carbanions[116].

The dimetal adducts undergo a variety of reactions such as deuterolysis, hydrogen exchange, hydrogen abstraction, carbonation, alkylation and silylation reactions (Table 2). The reactions of various aromatic radical anions with a number of difunctional alkylating agents such as 1,4-dichlorobutane, have been examined[36,117]. In general, three types of products, namely, the 1,2-dihydro fused ring systems, the 1,4-dihydro bridged ring systems and alkylated aromatics are obtained in these reactions. The formation of alkali metal adducts has been used in the study of electron affinities of hydrocarbons[9,110,118]. In the presence of alkali metals, even side-chain alkylation of aromatics becomes possible.

TABLE 2

SOME REACTIONS OF HYDROCARBON-ALKALI METAL ADDUCTS

Metal	*Solvent*	*Hydrocarbon*	*Reactant*	*Products*	*Reference*
NaK		1-Methylnaphthalene	C_2H_4	1-n-Propylnaphthalene	94
Na	DME	1-Phenylnaphthalene	CO_2	1-Phenylnaphthalene-3,4-dicarboxylic acid	95
Na	DME	1,8-Diphenylnaphthalene	CO_2	1,8-Diphenylnaphthalene-3,4-dicarboxylic acid	95
Na	E-C_6H_6 mixture	Anthracene	CH_3I	9,10-Dihydro-9,10-dimethylanthracene, 9-methylanthracene, anthracene, methane, ethane and ethylene	96
Na	E-C_6H_6	1,2-Benzanthracene	CH_3I, sulfur	9,10-Dimethyl-1,2-benzanthracene and 10-methyl-1,2-benzanthracene	96
LiNa	E[a]	Anthracene	RCl (R = ethyl, n-butyl, s-butyl, isoamyl)	9,10-Dialkylated derivatives of 9,10-dihydroanthracene	97, 98 104
Li	E	Pyrene	CO_2	4,9-Dihydropyrene-4,9-dicarboxylic acid and/or 3,10-dihydropyrene-3,10-dicarboxylic acid	106
Na	E	Pyrene	H_2O	1,2-Dihydropyrene	107
Li	–	Pyrene	$C_6H_5CH_2Cl$	4-Benzylpyrene	108
Li	E	Naphthacene	CH_3OH	6,11-Dihydronaphthacene	109
Li	E	Naphthacene	CH_3Cl	6,11-Dimethyl-6,11-dihydronaphthacene	109
Li	E	Naphthacene	Chromic acid	6,11-Naphthacenequinone	109
Li	DME	1,2,3,4-Tetrahydronaphthacene	CH_3OH	1,2,3,4,6,11-Hexahydronaphthacene	111
Li	–	Pentacene	RCl (R = CH_3, s-butyl, $Si(CH_3)_3$, cyclohexyl)	6,13-Disubstituted 6,13-dihydropentacene derivatives	112
Li	E	Biphenyl	n-Hexyl bromide	4-Hexyl-1,4-dihydrobiphenyl and 1,4-dihexyl-1,4-dihydrobiphenyl	124a
Li	–	Biphenyl	RBr (R = n-Bu, C_6H_{13}, $C_{10}H_{21}$)	3-Alkyl- and 3,6-dialkyldihydrobiphenyls	126
Li	E	Biphenyl	C_6H_5Br	Benzene, biphenyl, *o*- and *p*-terphenyls	127
Li	THF	Biphenyl	n-C_3H_7OH	Phenylcyclohexane	130

[a] E = diethyl ether.

Thus, in the sodium- and potassium-catalysed reactions of 1-methylnaphthalene with ethylene under pressure, all the hydrogen atoms of the α-carbon of the side-chain can be replaced by ethyl groups[94]. Quite early, Schlenk and Bergmann[119,120] have reported the formation of dimeric products in the addition of alkali metals to several unsaturated compounds. The reactions of radical anions derived from fluorescent compounds with various oxidizing agents represent a very general type of chemiluminescent reactions[121-123] 9,10-Diphenylanthracene, for example, undergoes a luminescent reaction with benzoyl peroxide.

The addition of lithium to biphenyls has been reported to give 1,4-dilithio-1,4-dihydrobiphenyl[119,124]. However, there seems to be some doubt concerning the points of attachment of the metal atoms in the adduct. Thus, it has been stated that the addition takes place not at the 1,4-positions but at the 3,6- and also at the 2,5-positions[125-127]. The effect of different solvents on the formation of radical anions from biphenyl has also been investigated[128]. Shatenshtein and coworkers[128c] tested the effect of several ethers for solvation effects in the formation of sodiobiphenyl. While 2,5-dimethoxytetrahydrofuran failed to show any anion formation, DME, diglyme etc. were more effective than THF. While steric factors appear to be effective on solvation of the cation, there is no relation between the solvating ability and the number of oxygen atoms in an ether molecule.

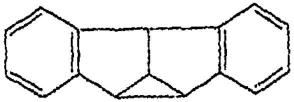
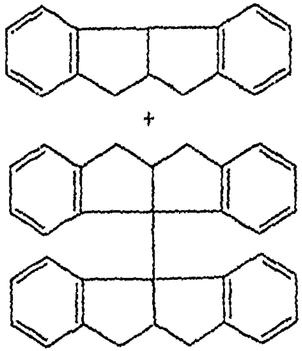
Alkali metal adducts of biphenyl can bring about different types of reactions which do not occur when alkali metals alone are used[129-135]. Thus, a 1/2-adduct of lithium and biphenyl in THF acts as a metalating agent toward pseudo-acidic hydrocarbons. Eisch and coworkers[129-131] have suggested a modified Birch-type reduction, by the use of biphenyl-lithium adducts. Selective reduction of the 1,2-double bond in $\Delta^{1,4}$-3-oxo steroids[132] and reductive ring opening of bridged polycyclic compounds have been described[133]. Biphenyl-dilithium adducts bring about the cleavage reactions of several organic compounds which are immune to cleavage by lithium alone (see Table 3). 1,1-Binaphthyl radical anion, generated from tris(1-naphthalene)phosphine by the action of alkali metals in THF or DME, undergoes cyclodehydrogenation to give perylene radical anion, in the presence of lithium metal deposited on silica[136].

Hydrocarbons such as diphenylmethane[137], cyclopentadiene[140,141], indene[142], substituted indenes[143,144], fluorene[130,141,142,145-151], substituted fluorene derivatives[143,150-153], and fluoranthene[154] react with alkali metals giving rise to metalation products probably arising through radical anion intermediates. The mechanism of the reaction of alkali metals with fluorene has been the subject of considerable investigation. A green coloured radical anion is formed at low temperatures (−90°) whereas at higher temperatures, the orange coloured carbanion is formed. In the absence of hydrogen evolution and metal hydride formation, the formation of the carbanion can be explained only by disproportionation reactions. Carbanions of fluorene, substituted fluorenes and condensed fluorenes undergo reduction, cleavage, dimerization and suitable displacement reactions[140,142,143,145,146,148-151].

In the presence of excess metal (generally potassium), further reduction of the hydrocarbon dianions is possible. Thus, the carbanion of dibenzoylmethane[155] Koelsch's radical[156], 4,5-methylenephenanthrene[156,157], fluorene[158,159] and 9-phenylfluorene[156] form radical dianions, which can be reduced further even to the trianions in certain cases[155]. ESR studies have shown that the g values of these radicals increase with an increase in the negative charge[156] and that the unpaired electron interacts with one counter ion only[157]

TABLE 3

SOME REACTIONS OF LITHIUMBIPHENYL ADDUCTS

Ratio of the biphenyllithium adduct	*Solvent*	*Reactant*	*Product*	*Reference*
1/1	THF	N_2	Ammonia and 2- and 4-aminobiphenyls	88
1/1	THF	Fluorene	Fluorenyllithium	129
1/1	THF	Triphenylmethane	Triphenylmethyllithium	129
2/1	THF	THF	n-Butyl alcohol	130
2/1	THF	Carbazole	Ammonia	130
2/1	THF	C_6H_5F, CO_2	Benzoic acid, and 2-phenylbenzoic acid (trace)	130
2/1	THF	Anisole	Phenol	130
2/1	THF	*N,N*-Dimethylaniline	*N*-Methylaniline	130
2/1	THF	$(C_6H_5)_3N$	$(C_6H_5)_2NH$, and $C_6H_5NH_2$	130
2/1	THF	1,1,1-Triphenylethane, CO_2	Triphenylacetic acid	130
2/1	THF	1,1,1,2-Tetraphenylethane, CO_2	Triphenylacetic acid, and phenylacetic acid	130
2/1	THF	1,1,2,2-Tetraphenylethane, CO_2	Diphenylacetic acid	130
2/1	THF	Dibenzothiophene	3,4-Benzothiocoumarin	130
Na-Adduct	DME	, H$_2$O, O$_2$		133
Na-adduct	DME	Cholesteryl chloride	5-Cholestene	134
Na-adduct	DME	*β*-Cyclocholestanyl chloride	3α,5α-Cyclocholestane	134
Na-adduct	DME	*exo-* or *endo-*Dehydronorbornyl chloride	Norbornene and nortricyclene	135
Na-adduct	DME	Nortricyclylchloride	Norbornene and nortricyclene	135

Hydrocarbons also undergo few interesting transformations in the presence of alkali metals. Thus, the conversions of 1,1-binaphthyl radical anion to perylene radical anion (counter ion Li^+)[136], benzylsodium to stilbene dianion[160], dinaphthylenecyclobutane to acenaphthylene radical anion (counter ion Na^+)[161], biphenylene to dibenzonaphthacene (by Li)[162] and 1,1,3-triphenylindene to 1-sodio-1,2,3-triphenylindene[144] have been reported. In the photolysis of aryllithiums, coupling reactions have been observed and the radical anions have been postulated as intermediates[163,164].

Triptycene undergoes ring cleavage on treatment with potassium in ether to give 9-phenyl-9,10-dihydroanthracene, on protonation[165,166]. Many substituted triptycenes behave similarly. Benzocyclobutene, a valence isomer of *o*-xylylene, was reported to give *o*-xylylene radical anion, on treatment with sodium–potassium alloy in THF or DME at −80°. However, there exists some controversy concerning this electrocyclic ring opening[167,168].

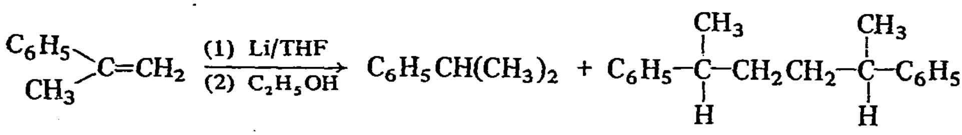
Syntheses and reactions of the dianions of [14]-, [16]-, and [24]annulenes have been reported[169-171]. It seems that the non-planar annulenes are converted to the planar form of dianions[169]. The aromatic radical anions act as neighbouring groups in the electron-transfer and nucleophilic substitution reduction reactions of optically active aromatic hydrocarbons[172,173]. Paracyclophanes[174-176] and paracyclonaphthanes[176] form radical anions on treatment with potassium in DME or THF, but they are finally cleaved to the arylmethide anions. The ESR spectrum of adamantane radical anion observed in THF–DME mixture after reduction by Na–K alloy is identical to that of benzene radical anion[177]. Decacyclene can be reduced up to the trianion stage by sodium in MeTHF[178]. Spiropentane and 1-methyladamantane form radical anions with Na–K alloy in THF–DME mixture[179]. It might be noted that the ESR signal obtained for a solvated electron in DME is not quenched by the addition of varying amounts of compounds like cyclopropane, and adamantane[180,181].

B. Olefinic compounds

Although alkali metals do not add to simple olefins, they readily yield addition products with phenyl-substituted olefins. The addition of alkali metals to different olefinic compounds such as 1,1-diphenylethylene, tetraphenylethylene and tetraphenylbutene gives radical anions and dianions or products derived from them[119,120,182-190]. The disproportionation reaction of tetraphenylethylene radical anion ($TPE^{\dot{-}}$) to form the dianion and neutral molecule has been extensively studied as a function of the cation, solvent and temperature[183-186].

$$2\,TPE^{\dot{-}} \rightleftharpoons TPE^{2-} + TPE$$

The reaction of α-methylstyrene (X) with lithium in THF, gives rise to a mixture of cumene (XI) and 2,5-diphenylhexane (XII) (Scheme 7)[191]. Lithium adds to styrene in an

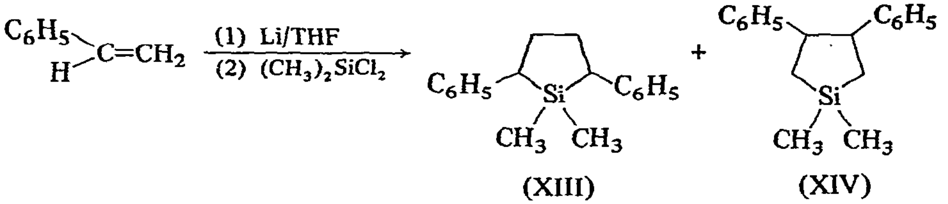


$$(C_6H_5)(CH_3)C{=}CH_2 \xrightarrow[(2)\ C_2H_5OH]{(1)\ Li/THF} C_6H_5CH(CH_3)_2 + C_6H_5{-}\underset{H}{\overset{CH_3}{C}}{-}CH_2CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}C_6H_5$$

(X) (XI) (XII)

Scheme 7

aprotic solvent such as THF to give the radical anion intermediate which then dimerizes to give a dianion intermediate[192,193]. This dianion intermediate has been trapped through its reaction with dimethyldichlorosilane to give products such as 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (XIII) or 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane (XIV), depending on the reaction conditions (Scheme 8)[192,193]. Disilacyclohexanes and polymers have



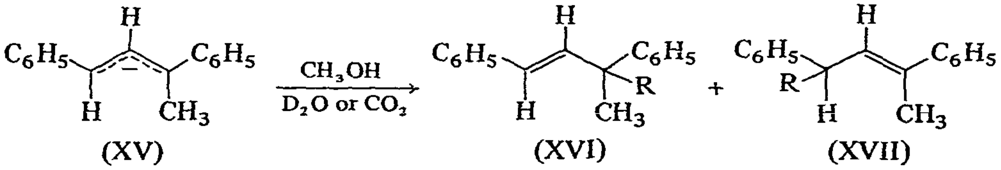
Scheme 8

also been prepared, employing the treatment of the appropriate dianionic species with different chlorosilanes[193-196]. The side-chain aralkylation of alkyl pyridines with styrene, α-methylstyrene etc., is catalysed by alkali metals[197].

Alkali metals add to stilbene to give the dimetal adducts, which on methylation, give a diastereoisomeric mixture of 2,3-diphenylbutanes[120,198,199]. The solvent appears to play a role in this reaction as, asymmetry can be induced by the use of optically active 2,3-dimethoxybutane as solvent. Several other reactions of the disodium adduct of stilbene have been studied[200,201]. It also catalyses the trimerizations of benzonitrile to *s*-triazine and phenylisocyanate to *s*-triazinetriones.

Addition of lithium followed by alcohol to α-(9-phenanthryl)stilbene gives α-(9-phenanthryl)dibenzyl and other unidentified products, one of which appears to be a fluorene derivative[202].

Direct reactions between alkali metals and ether solutions of 1,3-diphenyl-1-butene give the allylic anion (XV) which with CH_3OH, D_2O or CO_2, give mixtures of (XVI) and (XVII) (Scheme 9). Compound (XV) is present in solution in three distinct solvation



R = H, D or CO_2H
Scheme 9

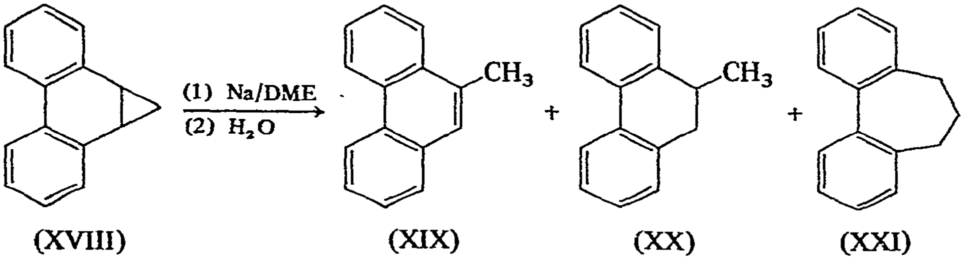
states, namely, the solvated contact ion-pair, the solvent-separated ion-pair and the free ion. The absorption maxima of the solvent-separated ion-pair has been found to be independent of the nature of the cation. The solvent-separated ion-pairs, in this case fluoresce in ether solvents at low temperatures.

Alkali metals bring about the cleavage of carbon–carbon bonds as well as C–H bonds in certain specific cases[206,207]. When 1,1-diphenyl-2-cyclopropylethylene is treated with Na-K alloy in THF, the cyclopropyl ring is cleaved to give, after hydrolysis, a mixture of *trans*-1,1-diphenylpent-2-ene and 1,1-diphenylpent-1-ene[206]. Action of lithium on 1,1,3,3,3-pentaphenylpropylene, gives a mixture of triphenylmethane and 1,1,4,4-tetraphenylbut-2-ene after hydrolysis[207]. Skinner and coworkers[208] have reported that 1-alkenes on refluxing in the presence of lithium results in the formation of lithium hydride and alkynyllithium compounds.

$$RCH{=}CH_2 + 4Li \rightarrow RC{\equiv}CLi + 3LiH$$

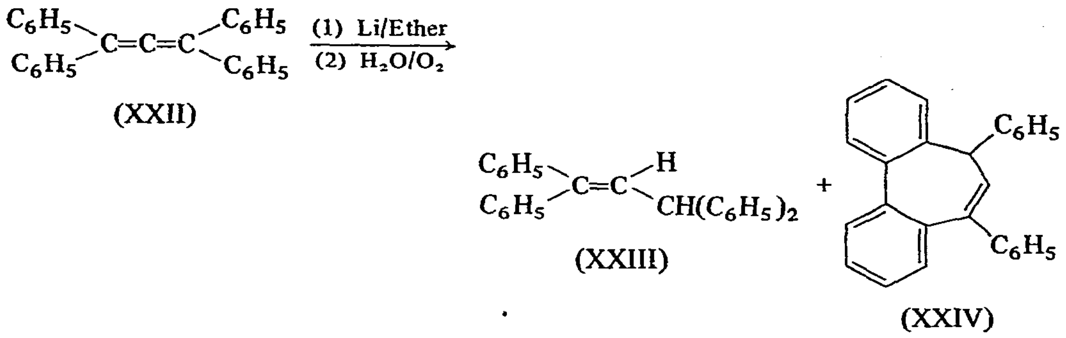
Olefins and dienes undergo geometric isomerization in the presence of their radical anions. Possibly, the double bond character is reduced by the presence of the unpaired electron and hence free rotation around this bond becomes possible. Thus, *cis*-stilbene is isomerized to *trans*-stilbene in THF solution[209]. Similarly, *cis,cis*- or *cis,trans*-tetraphenylbutadiene is isomerized to the *trans,trans*-isomer in THF by lithium or sodium[209].

Treatment of certain dienes with alkali metals results in the formation of high molecular weight polymeric compounds[210,211]. Weyenberg and coworkers[212] have reported that in the addition of alkali metals to conjugated dienes like butadiene, isoprene and 2,3-dimethylbutadiene in THF and subsequent silylation reactions, lithium gives 1,4-disilyl-substituted *trans*-olefins, whereas sodium gives the corresponding *cis*-olefins. Metallic sodium reduces nonconjugated olefins and polyalkylated aromatic derivatives to their saturated derivatives in HMPA-t-butanol[213]. Behaviour of compounds such as norbornadiene and dibenzocyclobutadiene with alkali metals has been investigated and some cleavage products have been identified[214-218]. Thus, norbornadiene reacts with lithium to give a mixture of norbornene, nortricyclene, 3-vinyl-1-cyclopentene and other unidentified products[214]. The products of reduction of dibenzonorcaradiene (XVIII) with sodium metal in DME are 9-methylphenanthrene (XIX), 9-methyl-9,10-dihydrophenanthrene (XX) and the cycloheptene derivative (XXI) (Scheme 10)[216]. The reactions of few allenes with alkali metals have been reported to give the corresponding acetylenes or propenes[219-224]. In the reaction of tetraphenylallene (XXII) with lithium in ether, besides the expected propene derivative (XXIII), the cycloheptatriene (XXIV), is also isolated (Scheme 11). However, reduction by Na–K alloy leads to the isolation of 1,1,3,3-tetraphenylpropane[224].



Scheme 10

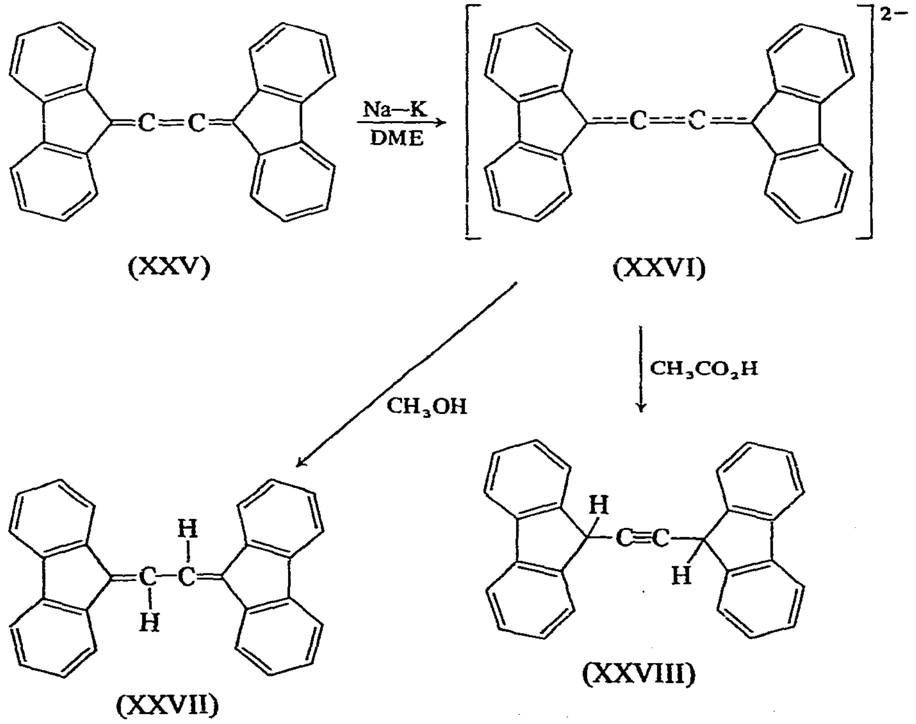
Addition of alkali metals to few trienes has also been studied[225-229]. Thus, the triene, bis(biphenylene)butatriene (XXV) reacts with Na–K alloy to give the dianionic intermediate (XXVI) which gives (XXVII) or a mixture of (XXVII) and (XXVIII) when methanol and acetic acid respectively, are used for protonation (Scheme 12). Protonation studies of the dianions derived from several trienes reveal that all these undergo 1,4-addition initially. The



Scheme 11

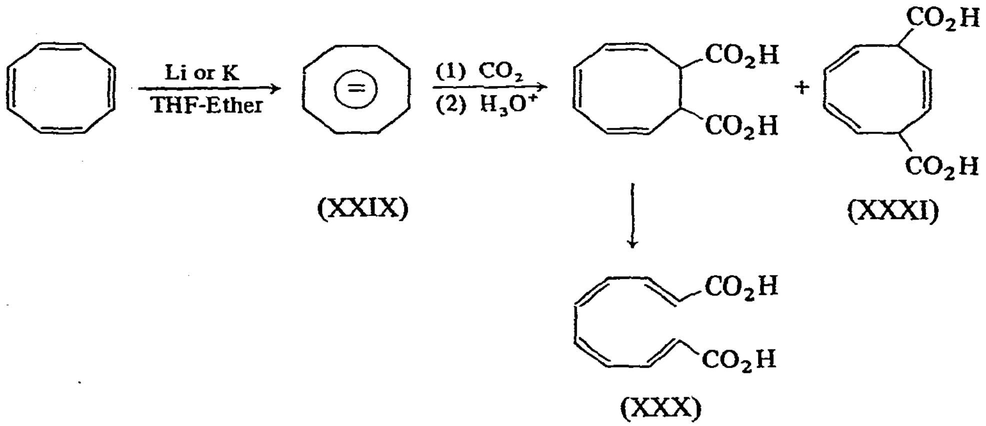
1,4-dihydro compounds, which are kinetically favoured, rearrange to the thermodynamically more stable 1,2-dienes and finally to the even more stable conjugated dienes[228]. In the case of carbonation and methylation reactions, the required hydrogen for the prototropic changes is absent and therefore products corresponding to (XXVIII) are obtained.

Formation of both tropenide anion[230,231] and a radical dianion[232,233] has been observed in the reaction of tropyl ethers with sodium in THF. Cyclooctatetraene dianion (XXIX) is a highly resonance-stabilized species and reacts with a number of substrates such as proton donors, carbon dioxide, aldehydes, ketones and halogen containing compounds to give a



Scheme 12

variety of products accompanied by interesting valence isomerizations[234-246]. The carboxylation of (XXIX) for example, gives chiefly 2,4,6,8-decatetraene-1,10-dioic acid (XXX) accompanied by minor amounts of 2,5,7-cyclooctatriene-1,4-dicarboxylic acid (XXXI) (Scheme 13). When (XXIX), generated by potassium reduction in THF, is irradiated in presence of weakly acidic proton donors, cyclooctatrienyl anion is obtained[247]. Protonation studies have also been carried out with certain alkali metal cyclooctatetraenides, containing fused benzene rings[248,249]. Reactions of cyclononatrienide, cyclononatetraenide and the dianions of monohomocyclooctatetraene[136] and bicyclononatrienes[137,138] have also been studied[250-257].

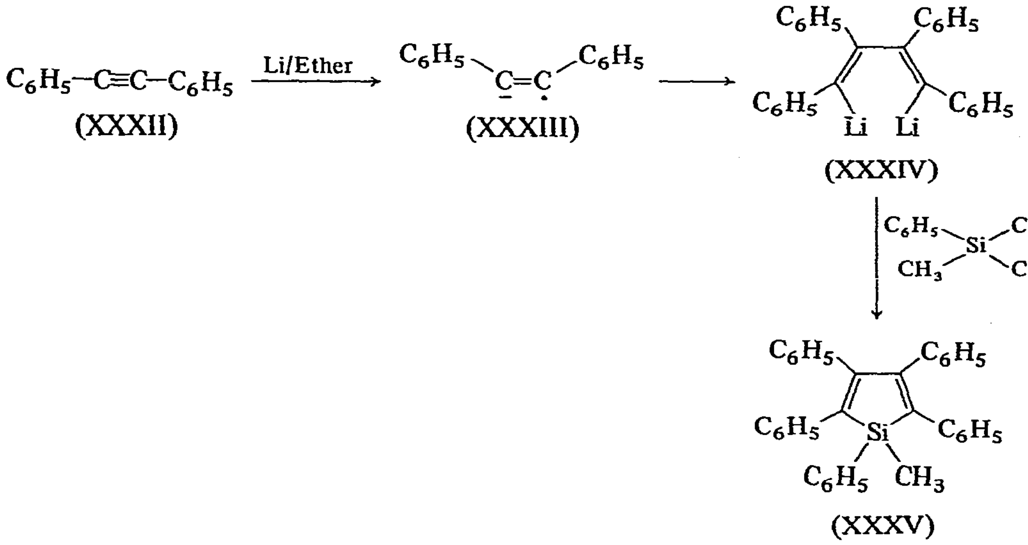


Scheme 13

C. *Acetylenic compounds*

Among acetylenic compounds, the reaction of tolan towards alkali metals has been investigated by several groups of workers[258-267]. By the action of lithium or sodium on tolan in ether solvents and subsequent hydrolysis, products such as 1,2,3,4-tetraphenylbutadiene and 1,2,3-triphenylnaphthalene were obtained[119,258,259,264]. Addition of alkali metals to tolan proceeds through a radical anion intermediate which can undergo dimerization to a dianion intermediate. Several interesting cyclopentadiene derivatives have been prepared by the treatment of these dianions with different substrates[262,265,268-282]. Thus, in the addition of lithium to tolan, the radical anion intermediate (XXXIII) is formed which dimerizes to give 1,4-dilithiotetraphenylbutadiene (XXXIV) (Scheme 14). The reaction of (XXXIV) with methylphenyldichlorosilane gives 1-methyl-1,2,3,4,5-pentaphenylsilacyclopentadiene (XXXV)[280]. The geometric configuration of (XXXIV) has not been fully established but it appears to be the *cis,cis*-isomer, as evidenced by the ease of formation of cyclic derivatives[262].

Addition of alkali metals to substituted acetylenes gives rise to the corresponding radical anions, dianions and dimerization products, whereas acetylene gives simple acetylides[283-287]. Interestingly enough, the dianion of methylphenylacetylene is protonated by methylphenylacetylene itself, yielding an allene and a carbanion intermediate[285].

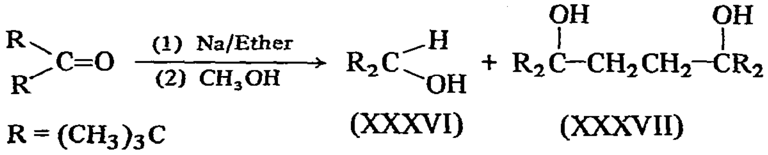


Scheme 14

III. CARBONYL COMPOUNDS

A. Aliphatic ketones

The reactions of several aliphatic ketones such as acetone[288], isobutyrone[289] and hexamethylacetone[290,291] with sodium in ether were studied quite early. Hydrolysis of these alkali metal derivatives gives a mixture of products consisting mainly of the starting ketone, glycol and alcohols. Hexamethylacetone, for example, yielded a red adduct with sodium, which on exposure to air and subsequent hydrolysis gave hydrogen peroxide, the starting ketone, di-t-butylmethanol and tetra(t-butyl)ethylene glycol. The reduction of this ketone with sodium in diethyl ether has been reinvestigated and the structure of the product, assumed earlier to be tetra(t-butyl)ethylene glycol, is shown to be 1,1,4,4-tetra(t-butyl)-butane-1,4-diol (XXXVII)[292,293]. In addition, di(t-butyl)carbinol (XXXVI) could also be isolated (Scheme 15). In the absence of diethyl ether, the product (XXXVII) is not formed, thereby suggesting that the solvent participates in this reaction.



$$R_2C{=}O \xrightarrow[(2)\ CH_3OH]{(1)\ Na/Ether} R_2CH(OH) + R_2C(OH){-}CH_2CH_2{-}C(OH)R_2$$

$R = (CH_3)_3C$

Scheme 15

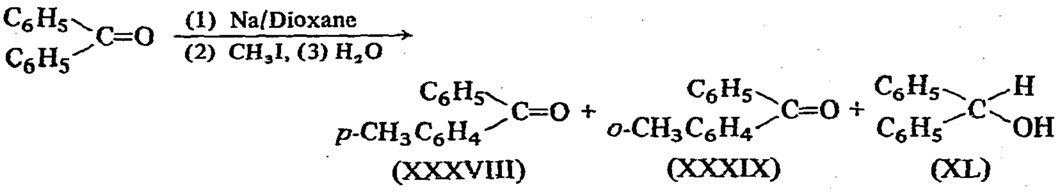
Pinacols and pinacolones react with sodium or potassium in ether to give ketyls and ultimately ketones and the corresponding secondary alcohols[294-300]. In several instances, some of the products formed in these reactions remain unidentified. In a few cases olefins have also been detected.

B. Aromatic ketones

Beckmann[301] in 1891 had shown that sodium reacts with benzophenone to give a blue coloured product presumably due to benzophenone ketyl. Extensive investigations of ketyls, formed from aromatic aldehydes and ketones have been carried out by different workers[302-314] and it is now assumed that these ketyls exist in equilibrium with several species such as the monomeric and dimeric radical anion intermediates and the dianions[308-312]. The stability of aromatic ketyls is increased by delocalization of the unpaired electron, whereas, in the aliphatic series the uncoupled electron is localized on the carbon of the carbonyl group and their stability can be enhanced by steric effects[315-319]. The ketyl systems are marked by the presence of several species such as paramagnetic monomer, paramagnetic dimer, diamagnetic dimer, different types of ion pair and ionic aggregates. The various equilibria associated with these species and their electron exchange reactions have been well established mainly from ESR and electronic spectral studies[6,312]. Substituent effects are also well correlated in these studies[312,316,319]. The sodio derivatives of ketones are converted by magnesium halides to halomagnesium pinacolates[320]. According to Bachmann[307], hydrolysis of the dimetal derivatives of aryl ketones by dilute acids gives nearly quantitative yields of pinacol; if water alone is used for hydrolysis, then the pinacol rapidly decomposes by the alkali to a mixture of ketone and secondary alcohol. In spite of this generalization, hydrogen evolution has been noticed, when the carbon adjacent to the carbonyl contains labile hydrogens which also partake in the reduction[306]. Further, kinetic data support the electron transfer mechanism for the dismutation of ketyls and aromatic pinacols in alkaline media to the corresponding ketones and secondary alcohols[299] Autoxidation of the dimetal derivatives of benzophenone gives back the ketone and the superoxides or peroxides of the alkali metals[221,322]. Ketyls such as benzophenone ketyl induce the decomposition of benzoyl peroxide also[323,324].

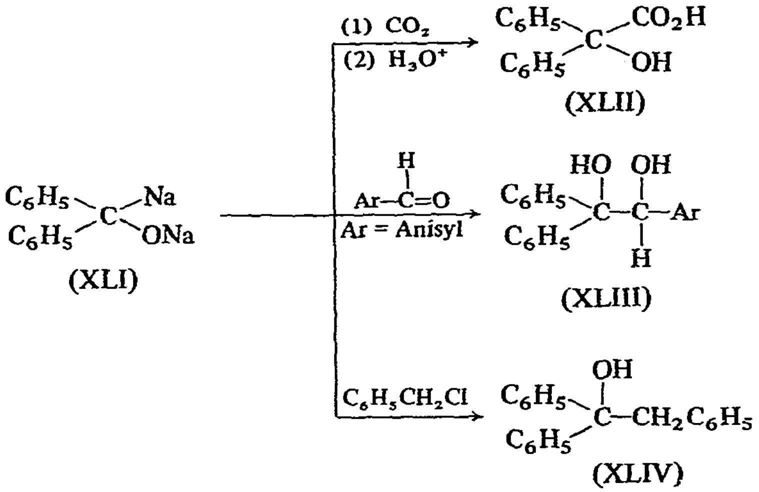
Samuel and Setton[325] have made the interesting observation that in the absence of solvents, the reaction between acetophenone and alkali metals gives a variety of linear and cyclic condensation products, depending on the nature of the alkali metals. Alkylations of the radical anions and dianions of aryl ketones have been studied by different workers[302,305,310,314,326-330]. The disodio derivative of benzophenone in liquid ammonia gives a mixture of diphenylmethyl carbinol and benzhydryl methyl ether, on treatment with methyl iodide[331]. The relative ratios of carbon and oxygen alkylation products depend on the nature of the alkali metal, the alkyl halides and the leaving groups. A one-step alternative to the Grignard reaction has been suggested recently where a mixture of the carbonyl compound and an alkyl halide is added to a suspension of lithium in THF to give a tertiary alcohol ultimately[332]. Both organolithium and radical anion intermediates have been suggested for this reaction. Sodium benzophenone ketyl reacts with methyl iodide in ether solvents to give, in addition to the normal methylation product, ring-substituted products also[333]. Thus, both 4-methylbenzophenone (XXXVIII) and 2-methylbenzophenone (XXXIX) were isolated from this reaction, besides the expected carbinol (XL) (Scheme 16).

The disodio adduct of aryl ketones serve as useful synthetic intermediates[67,334]. Benzophenone disodio adduct (XLI) in DME, for example, reacts with carbon dioxide and water to give benzilic acid (XLII). Reaction of (XLI) with anisaldehyde gives the glycol (XLIII)



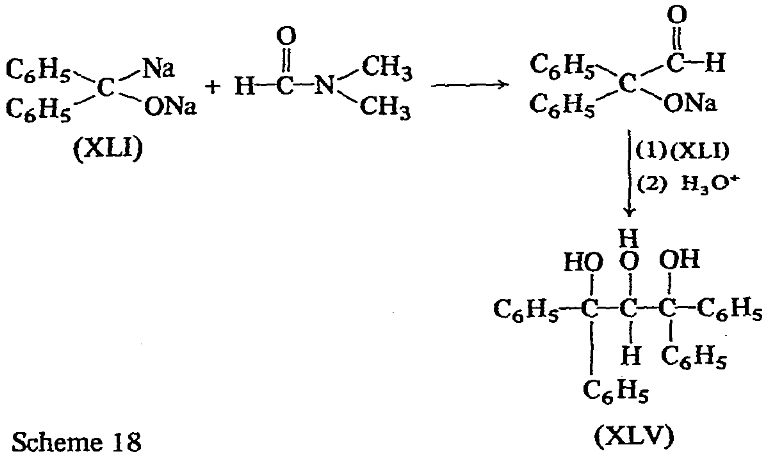
Scheme 16

and the reaction with benzyl chloride results in the formation of the corresponding benzyl derivative (XLIV) (Scheme 17). Several other reactions of ketyls in liquid ammonia and in hydrocarbon solvents have also been reported[335-337]. Aminomethylation and intramolecular alkylation of ketyls are also known[336,337].



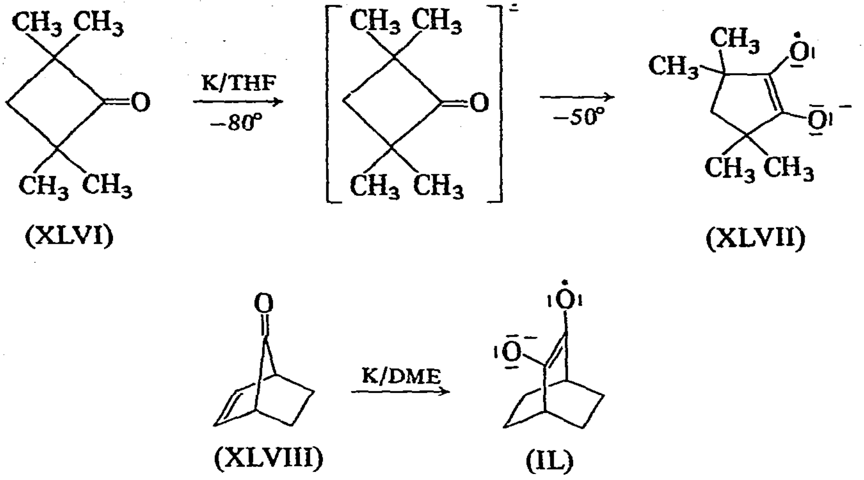
Scheme 17

Several interesting reactions of benzophenone dianion have been reported in recent years. Benzophenone dianion reacts with dimethylformamide in a mixture of ether and ammonia to yield a 83% yield of 1,1,3,3-tetraphenylglycerol (XLV) (Scheme 18)[338]. When



Scheme 18

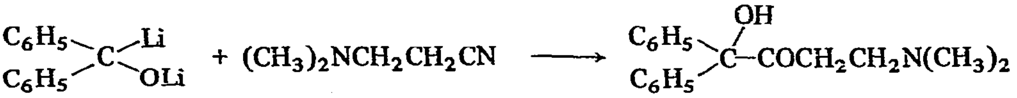
attempts were made to prepare the ketyls of cyclic compounds, a carbonyl insertion reaction was observed[338,339]. Thus, 2,2,4,4-tetramethylcyclobutanone (XLVI) forms a radical anion with potassium in THF at –80°; upon warming this solution to –50°, the ketyl decomposes to give 3,3,5,5-tetramethylcyclopentane-1,2-semidione (XLVII) (Scheme 19)[338]. Similarly, the reaction of 7-norbornenone (XLVIII) with potassium in DME gives the semidione (IL) (Scheme 19)[339]. A possible explanation for this carbonyl insertion reaction is that the strained ketyl decomposes to yield K^+ and $CO^{\dot{-}}$, which can undergo an insertion reaction with the ketone or ketyl. Such a behaviour is not observed in the case of cyclic ketones containing 5, 6 or 7 carbon atoms but is noticed in 9-benzonorbornenone system[338,339]



(XLVI) (XLVII) (XLVIII) (IL)

Scheme 19

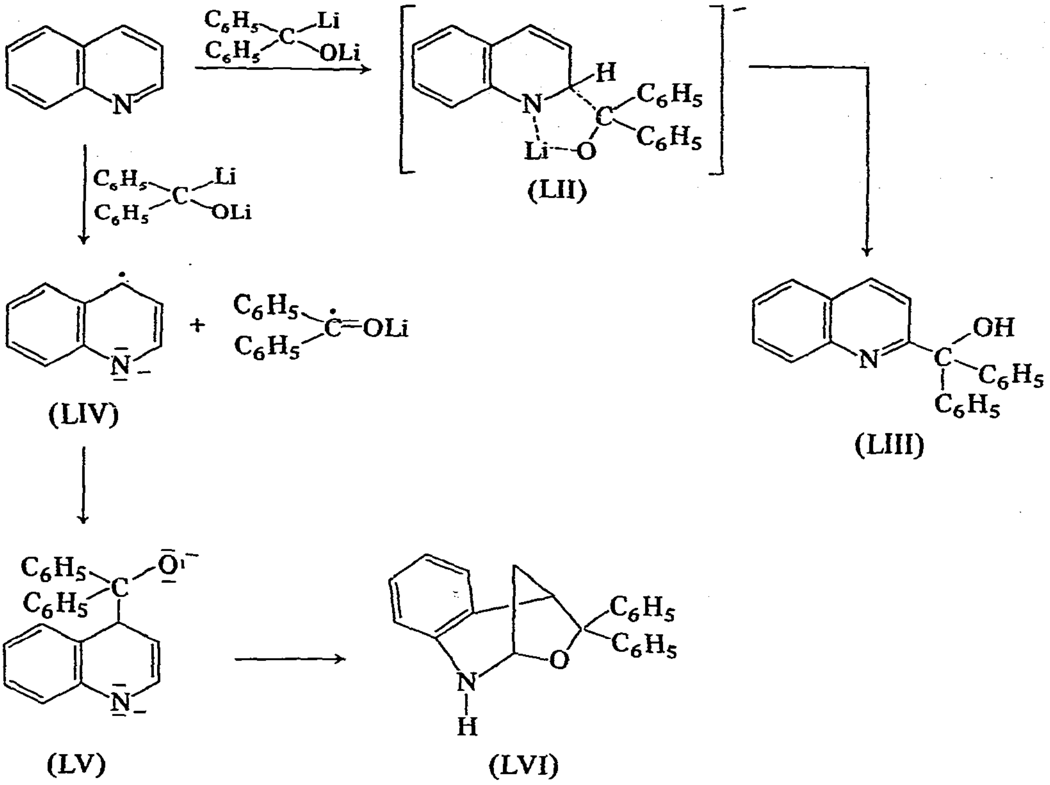
The addition of benzophenone dilithium adduct to the nitrile (L) gives the substituted carbinol (LI) after hydrolysis (Scheme 20)[340]. Treatment of pyridine and benzopyridines with benzophenone and lithium (1/2), in boiling ether provides a convenient route to the preparation of α-substituted alcohols and benzoxazepines[341]. Quinoline, for example, on treatment with a mixture of benzophenone and lithium yields the alcohol (LIII) and the benzoxazepine (LVI) (Scheme 21). A cyclic intermediate (LII) is assumed, to account for the formation of the exclusively α-substituted derivative (LIII). Single electron transfer to quinoline may also result in the formation of (LIV) which can couple with the ketyl to give (LV). The formation of (LVI) can be visualized by the protonation of (LV), followed by an internal Michael addition. Treatment of benzophenone ketyl with titanium tetrachloride and aqueous ammonia results in the formation of hydrogen peroxide, titanium dioxide and tetraphenylethylene[342]. Aryl ketyls have also been used as grafting agents in polymerization reactions[343,344].



$$(C_6H_5)_2C(Li)OLi + (CH_3)_2NCH_2CH_2CN \longrightarrow (C_6H_5)_2C(OH)COCH_2CH_2N(CH_3)_2$$

(L) (LI)

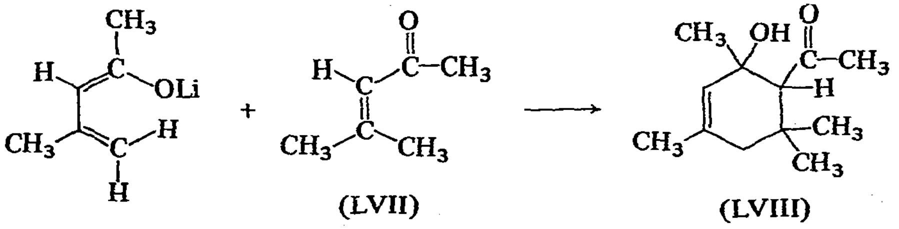
Scheme 20



Scheme 21

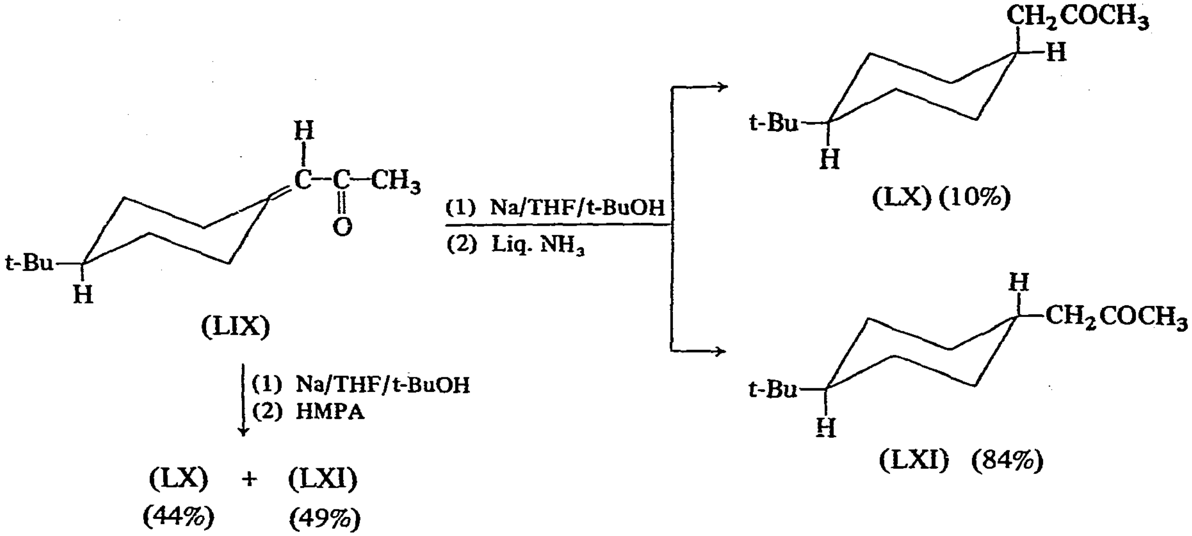
C. α,β-Unsaturated ketones

Mesityl oxide (LVII) dimerizes under the influence of lithium in ether, to give 2-acetyl-1,3,3,5-tetramethylcyclohex-5-en-1-ol (LVIII), besides other products (Scheme 22)^{345,346}. This reaction can be regarded as a diene addition between one molecule of mesityl oxide, acting as a dienophile and another in the form of the enolate, acting as diene. The reduction of α,β-unsaturated ketones to the corresponding saturated ketones by alkali metals dissolved in HMPA has also been investigated$^{347-349}$. House and coworkers^{348,349} have reduced a large number of enones to give monomeric and dimeric reduction products. Generally, a

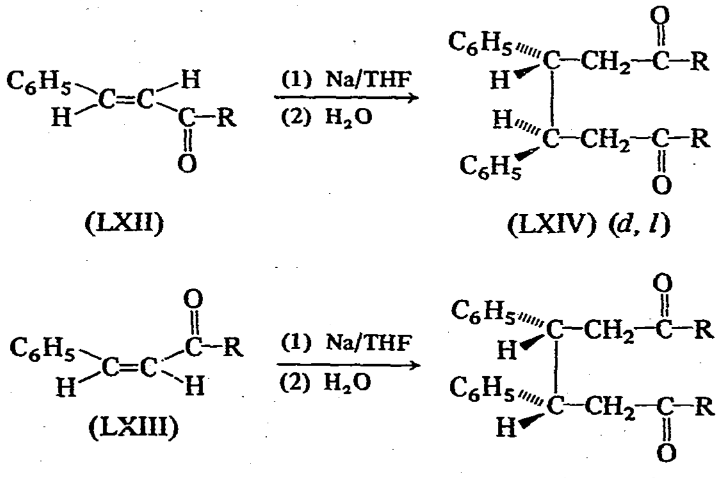


Scheme 22

greater percentage of the less stable epimer is formed in the reduction of cyclohexenone by lithium or sodium, when a mixture of HMPA/THF/t-butanol is used as the solvent. In the absence of proton donors (t-butanol), polymeric materials and unchanged ketone are obtained. Thus, when (LIX) is reduced with Na/THF/t-butanol, in liquid ammonia a 10% yield of (LX) and 84% yield of (LXI) are obtained; using HMPA, the yields of (LX) and (LXI) are 44% and 49%, respectively (Scheme 23)[349]. Sodium in THF alone, favours the conversion of enones such as (LXII) and (LXIII) to their corresponding dihydrodimers (LXIV) and (LXV) in a process that is at least partially stereospecific (Scheme 24). Coreduction of acetone with olefins like styrene[350a], and butadiene[350b] by sodium in ether solvents, results in the formation of several condensation products.



Scheme 23

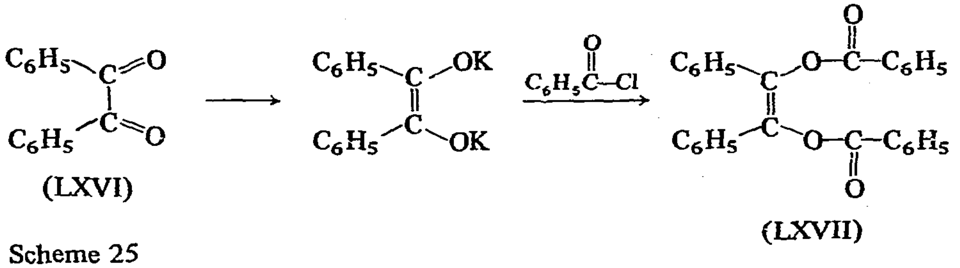


Scheme 24

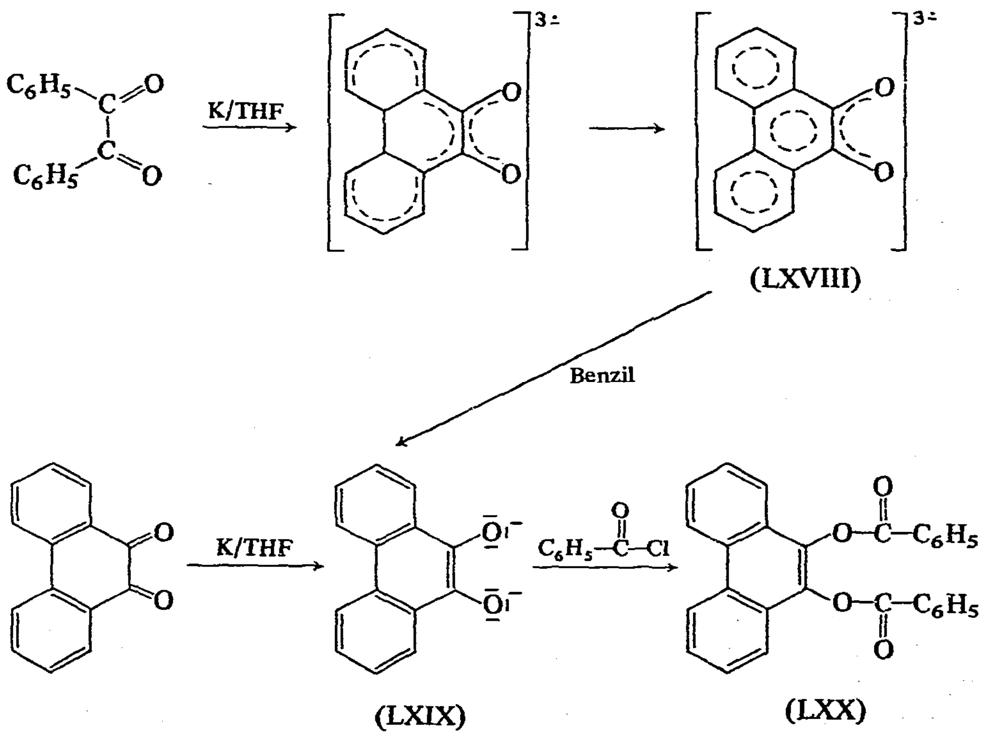
(LXV) (*meso*)

D. Diketones

The addition of alkali metals to diketones exhibits a pronounced *cis*-stereochemistry[351,352]. Potassium adds to benzil (LXVI) in THF to give an adduct which on benzoylation gives stilbenediol dibenzoate (LXVII) (Scheme 25). Benzil radical anion undergoes disproportionation to the corresponding dianion and the neutral molecule[353]. With excess of potassium in boiling THF, benzil dianion forms a trianion radical, which undergoes cyclodehydrogenation to give phenanthrenequinone trianion radical (LXVIII)[354]. Addition of benzil to (LXVIII) gives the dianion (LXIX) which on benzoylation gives the dibenzoyl derivative (LXX) (Scheme 26). The spectral properties of (LXVIII) synthesized from either

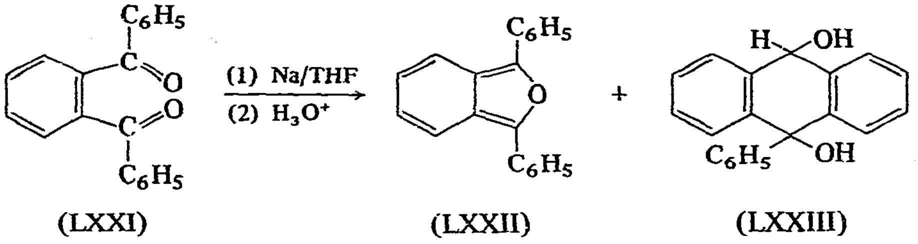


Scheme 25



Scheme 26

phenanthrenequinone or benzil are similar. Alkylation products of dimetal adducts of substituted benzils have been identified[355]. When diketones separated by four carbon atoms are reduced by lithium in ether, a mixture of cyclic and linear diols is obtained, arising through intramolecular condensations[356]. The reaction of *o*-dibenzoylbenzene (LXXI) with sodium in THF gave, on protonation, a mixture of products consisting chiefly of 1,3-diphenylisobenzofuran (LXXII) and 9,10-dihydroxy-10-phenyl-9,10-dihydroanthracene (LXXIII) (Scheme 27)[200,201,357-360]. Lithium reduction of biacetyl



Scheme 27

and perfluorobiacetyl gives rise to *cis*- and *trans*-isomers of semidiones with a slow equilibration rate[361]. An ether solution of dipivaloylmethane extracts and binds lithium ions selectively under alkaline conditions. Thus, separation of lithium from other alkali metal ions can be achieved by this procedure[362].

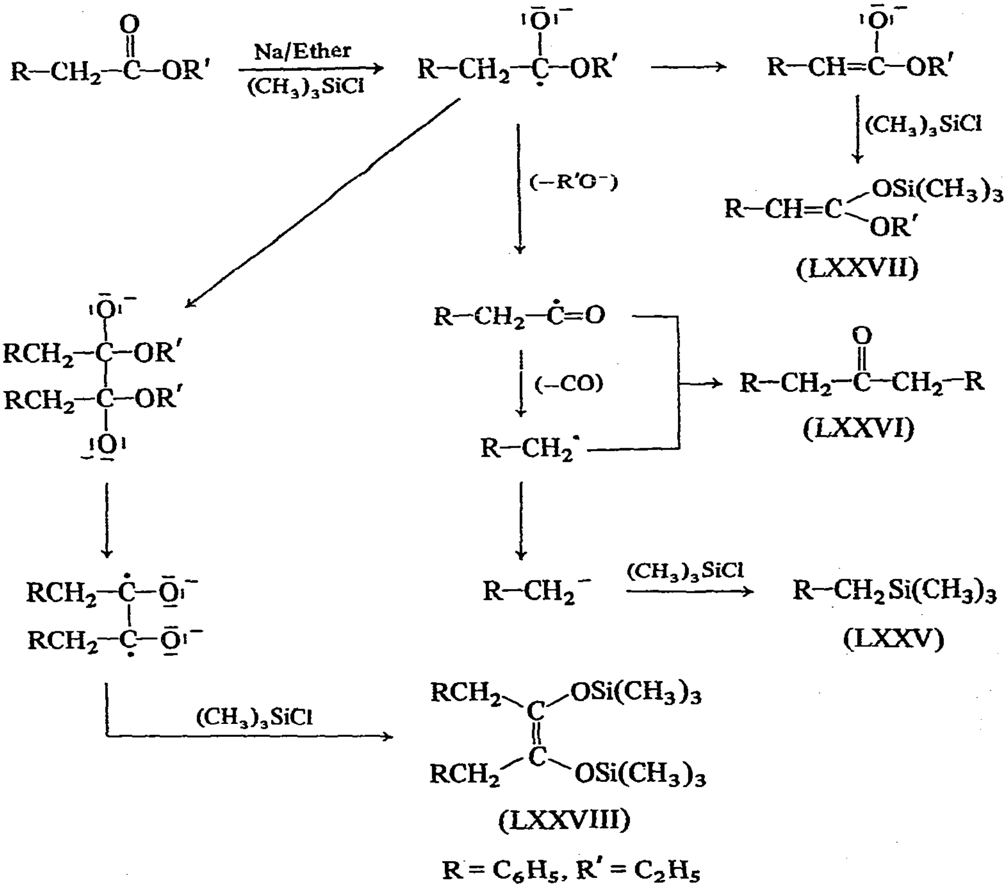
E. Quinones

Semiquinone salts are formed on treatment of quinones with alkali metals in ether solvents[306,363-366]. Substituted *o*-semiquinone salts undergo quantitative disproportionation in acid solution to give the dimetal salt and the hydroquinone. The semiquinone salts react with alkyl halides to give the dialkyl derivatives of the hydroquinone. They also react with diazonium salts to give quinone salts substituted with aryl groups in the α-position[363]. Tetrabromo-*o*-benzoquinone, phenanthrenequinone, bromanil, anthraquinone, and 1,2-naphthoquinone react with sodium amalgam in ether to give the dimetal salts, which can be isolated as the diacetyl or dibenzoyl derivatives of the corresponding hydroquinone[364]. This reaction fails with *p*-benzoquinone, 1,4-naphthoquinone, 1-chloroanthraquinone, 2-chloroanthraquinone and chloranil. In such cases, the dimetal salts can be prepared from the sodium metal adducts of nitrobenzene or azobenzenes by electron transfer reactions[364,365].

F. Esters

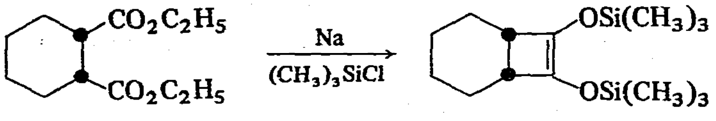
The reactions of esters with alkali metals have been studied long back. The behaviour of esters is quite varied and may warrant a systematic investigation. Phenyl benzoate, for example, reacts with one equivalent of sodium in ether solution to give a radical anion which then couples with a similar species, followed by the spontaneous loss of phenoxide ions to give benzil[367]. Phenyl benzoate also reacts with two equivalents of sodium to give an adduct, which on treatment with bromobenzene gives sodium phenoxide and benzophenone[367]. Wiemann and coworkers[368] have studied the comparative ease of reduction of the carbonyl group of ketones, aldehydes and esters by sodium. The reaction of phenyl acetate with alkali metals, gives a variety of products including pyrone, chromone and xanthone derivatives[369-371]. On the other hand, the reaction of ethyl diphenylacetate with sodium in ether gives *sym*-tetraphenylacetone, while that of ethyl β,β-diphenylpropionate gives a mixture of hexane-3,4-dione and its derivatives[372].

The reduction of esters by alkali metals may proceed through radical anion intermediates. In the absence of hydroxylic solvents, dimerization of the radical anion is observed. Thus, aliphatic esters react with alkali metals in ether to give acyloins. With excess of the ester, however, acetoacetic ester type of condensation takes place[373,374]. The reaction of potassium with ethyl acetate gives also paraffinic compounds[375] which are not formed when sodium is used. The reaction of ethyl phenylacetate (LXXIV) with sodium and trimethylchlorosilane in ether yields benzylsilane (LXXV), dibenzylketone (LXXVI), the keten-acetal (LXXVII), and the bis-siloxyalkene (LXXVIII) (Scheme 28)[376].



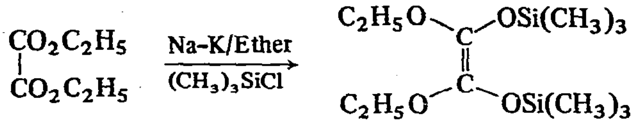
Scheme 28

Many abnormal acetoacetic ester type of condensations have also been reported in the reaction of unsaturated esters with alkali metals[377,378]. Several esters of dicarboxylic acids are known to undergo a variety of condensation reactions[373-379]. The reaction of several dicarboxylic esters with sodium in the presence of trimethylchlorosilane leads to 1,2-bis-(trimethylsiloxy)olefins in high yields[380-383]. Under these conditions, cyclobutane ring systems can be successfully synthesized. Thus, the cyclization of 1,2-dicarbethoxycyclohexane (LXXIX) leads to (LXXX) (Scheme 29)[383]. Similar reduction of diethyl oxalate, leads to a *cis*- and *trans*-mixture of 1,2-diethoxy-1,2-bis(trimethylsiloxy)ethylene (LXXXI) (Scheme 30). On the other hand, disubstituted malonates (LXXXII), which on treatment with methanol gives the ester (LXXXIV) and the ether (LXXXV) (Scheme 31). This provides a mild dealkoxycarbonylation procedure for malonic esters. The reactions of alkali metals with both acid anhydrides and acid chlorides have also been studied[384-387].



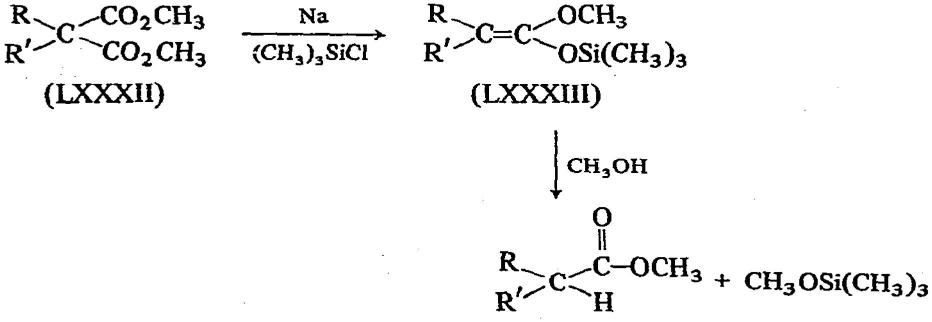
(LXXIX) (LXXX)

Scheme 29



(LXXXI)

Scheme 30



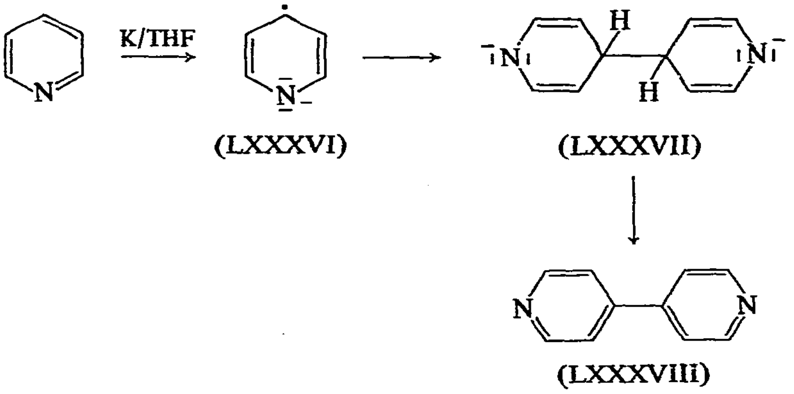
(LXXXIV) (LXXXV)

Scheme 31

IV. HETEROCYCLIC COMPOUNDS

A. *Azaaromatics*

Addition of alkali metals to nitrogen containing heterocyclic compounds yields a wide variety of products. Several workers have examined the reaction of pyridine with alkali metals and found that both monomeric and dimeric reduction products are formed, depending upon the reaction conditions. Pyridine reacts with sodium in presence of protic solvents to give piperidine and partially hydrogenated derivatives of pyridine[388-391]. Anderson[392] first noticed the reaction between sodium and pyridine to give a dark green compound, whereas the formation of 4,4′-bipyridyl was noticed by several workers[393-400]. Formation of a mixture of bipyridyls was reported by few workers, and in some cases these reports were supported by spectroscopic evidences[400-406]. Smith[401,402] had isolated several isomers of bipyridyls and partially hydrogenated mixture of bipyridyls, especially when the reaction was carried out at higher temperatures. The evolution of hydrogen gas has also been observed in these reactions[407,408], while Kuwata and coworkers[409] have reported the evolution of methane when the reaction between pyridine and sodium was carried out in DME. We have observed that the reaction of pyridine in THF with Li, Na or K even at room temperature gives rise to a mixture of products consisting of 2,2′- and 4,4′-bipyridyls, partially hydrogenated bipyridyls and polymeric materials[270,410]. The formation of 4,4′-bipyridyl (LXXXVIII) may be rationalized through the dimerization of pyridine radical anion (LXXXVI) leading to tetrahydrobipyridyl dianion (LXXXVII) which then loses hydride ions to give (LXXXVIII). The formation of other mixed bipyridyls can be explained by the delocalization of the electron in (LXXXVI) and by the disproportionation of (LXXXVII).

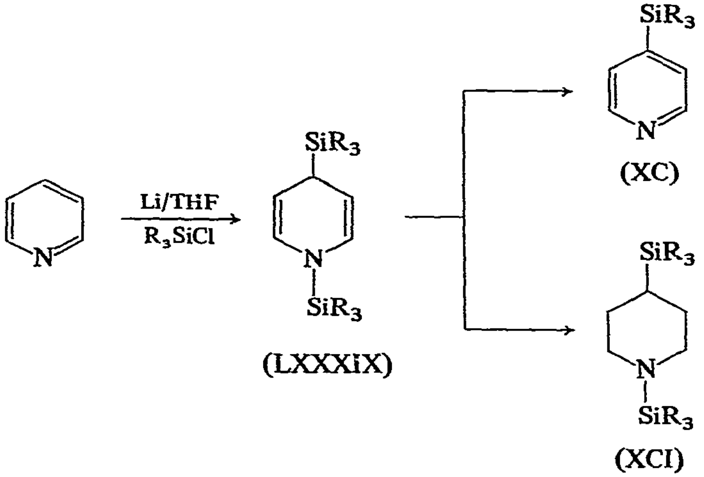


(LXXXVI)
(LXXXVII)
(LXXXVIII)

Scheme 32

Analogous coupling reactions to give dimers of quinoline[411], isoquinoline[412], acridine[413,414] phenazine[413], pyrimidine[415] and pyridazine[415], have been observed, when the corresponding compounds are treated with alkali metals. Under these conditions, however, the radical anions of pyrazine and 3,5-lutidine do not dimerize[416]. Recent work shows that pyrazine radical anion also gives a dimer which is stable in the dark but decays slowly in presence of light[417]. Szwarc and coworkers[418,419] have reported that using HMPA as solvent, the dimerization reaction could be prevented. When an alkyl substituent is present in the 3- or 4-position of the pyridine nucleus, the radical anion appears to be stable, with K^+ as the counter ion in THF solution. Thus, 3- and 4-picoline undergo dimerization[410]. Similarly, the radical anions of quinoline and isoquinoline, do not show any evidence of dimerization[410,420,421]. Recent reports show that 2-methylquinoline and 2,6-dimethylquinoline are reduced to dimeric products by lithium in THF[422]. Reactions of bipyridyls, and 2,4,6-triphenylpyridine with alkali metals in THF give dark coloured crystalline adducts, containing solvent molecules[423,424].

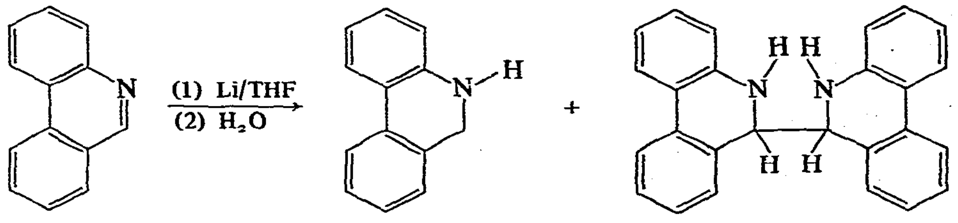
Sodium and potassium catalysed additions of pyridine to olefins have been described in the literature[425,426]. The reductive silylation of pyridine leads to (LXXXIX), from which (XC) and (XCI) can be obtained (Scheme 33)[427]. Pyridinium salts give the corresponding pyridinyl radicals, on treatment with potassium in DME or dioxane[428]. Pyridine-*N*-oxide undergoes deoxygenation in the presence of alkali metals to give pyridine and bipyridyls[410,429], while 4-nitropyridine-1-oxide[410,430] and 2,2'-bipyridyldi-*N*-oxide[280] are quite stable. It is thus apparent that alkali metals cannot be used for deoxygenating pyridine-*N*-oxides.



Scheme 33

Phenanthridine (XCII) reacts with lithium in THF to yield, 5,6-dihydrophenanthridine (XCIII) and the dimeric product (XCIV), on hydrolysis (Scheme 34)[431]. The formation of dimers, on the other hand, is not observed with 6-substituted phenanthridine. Dimetal adducts of phenazine[432] and dibenzopyridazine[433-435] are good nucleophiles in substitution reactions. Phthalocyanin[436], tetrazine[437] and phenanthroline[438] also form alkali metal adducts.

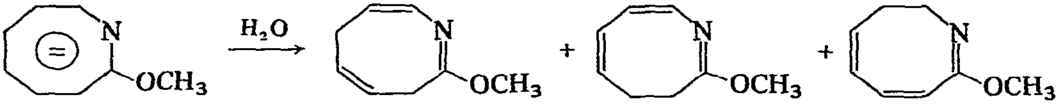
When 2-methoxyazocine and a number of its methylated derivatives are treated with potassium in THF or DME, their conversion to azocinyl dianion takes place[439,440]. On



(XCII) (XCIII) (XCIV)

Scheme 34

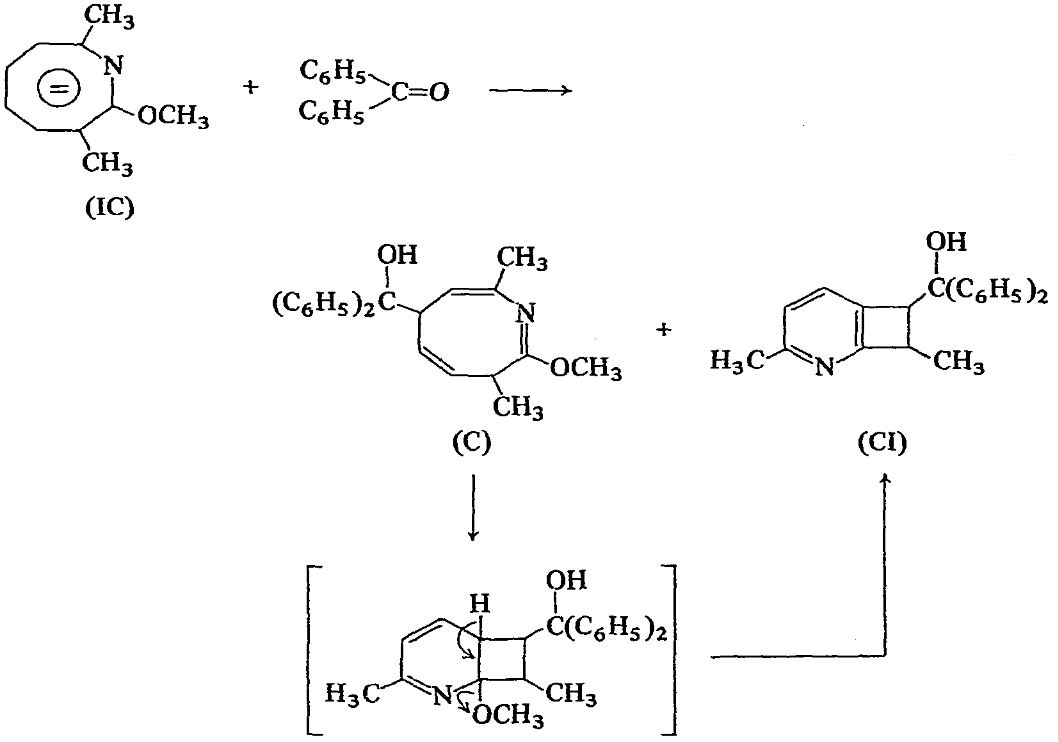
protonation, both 3,4- and 3,6-dihydroazocine (XCVI, XCVII) are formed in preference to (XCVIII) (Scheme 35). Treatment of the dianion (IC) of the azocinyl derivative with



(XCV) (XCVII) (XCVI) (XCVIII)

Scheme 35

benzophenone gives the C_6-monoalkylation product (C) together with the 2,3-pyridocyclobutane derivative (CI) (Scheme 36)[441].

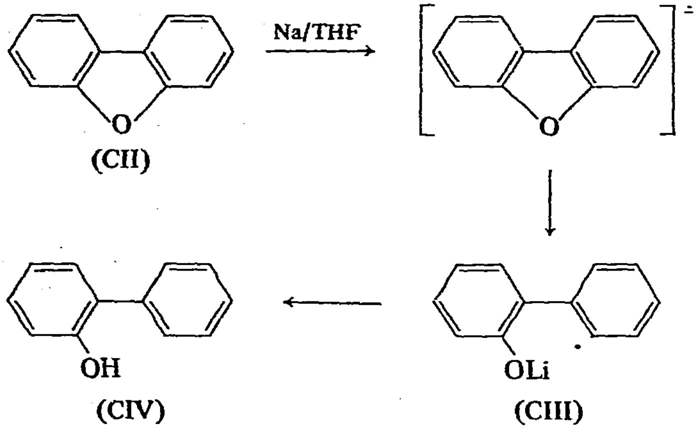


(IC) (C) (CI)

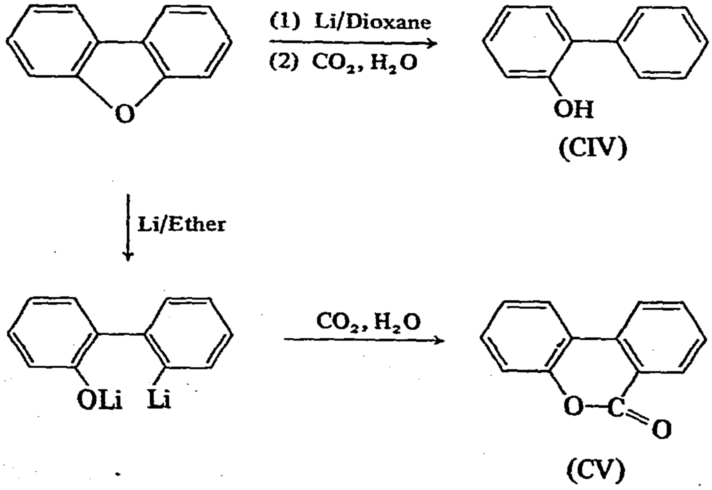
Scheme 36

B. Oxygen heterocyclics

Alkali metals bring about the cleavage of several oxygen containing heterocyclic compounds[442-444]. Cleavage of dibenzofuran (CII) gives 2-hydroxybiphenyl (CIV) which arises through the protonation of the intermediate (CIII) (Scheme 37). Among the different alkali metals, lithium brings about this cleavage more readily. The cleavage of (CII) by lithium in dioxane yields only (CIV), after carbonation and hydrolysis, while 3,4-benzocoumarin (CV) is obtained when the reaction is carried out in ether (Scheme 38). The alkali metal reduction of oxepins by potassium in THF-NH_3 does not lead to the formation of their dianions but cleaves them to carbonyl derivatives[445].



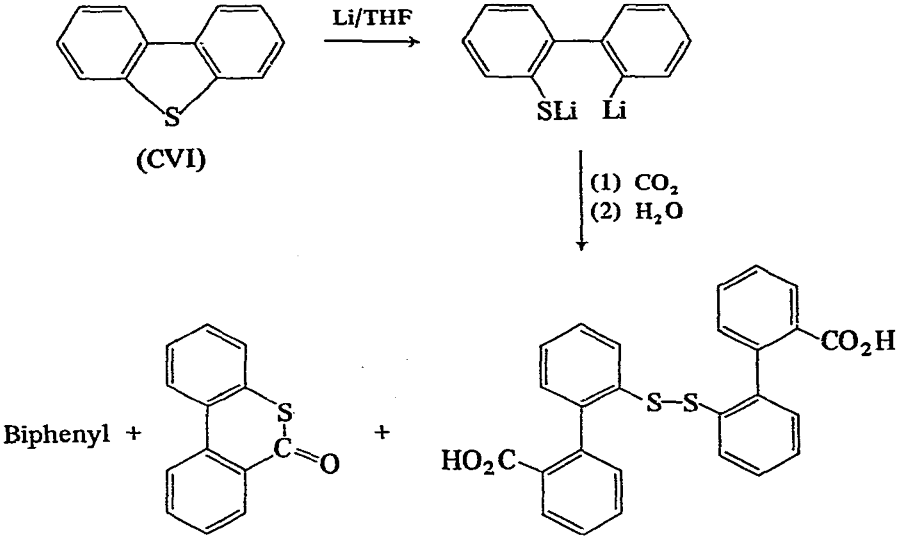
Scheme 37



Scheme 38

C. Sulfur heterocyclics

Alkali metals bring about certain desulfurization reactions of heterocyclic sulfur compounds[446,447]. The cleavage of dibenzothiophene (CVI) by lithium is markedly affected by the choice of the solvent medium and refluxing conditions. Thus, it is unaffected in ether but yields biphenyl and 2-mercaptobiphenyl, after hydrolysis or carbonation[444]. On the other hand, 3,4-benzothiocoumarin (CVII), the disulfide (CVIII) and trace of biphenyl have been isolated after carbonation in THF medium (Scheme 39). A novel desulfurization and dealkylation reaction is observed when 12-methylbenzo[*a*]phenothiazine (CIX) is refluxed with lithium in boiling THF to give benzo[*a*]carbazole (CX) (Scheme 40)[447].

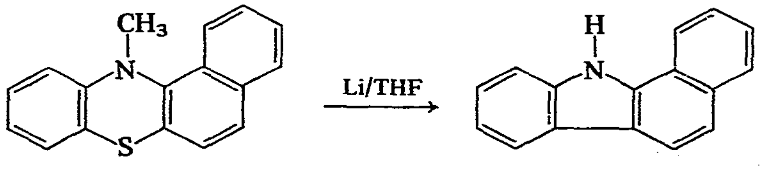


(CVI)

(CVII)

(CVIII)

Scheme 39

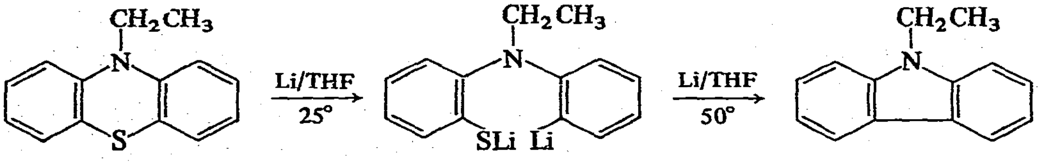


(CIX)

(CX)

Scheme 40

Normal cleavage of *N*-ethylphenothiazine (CXI) by lithium in THF at 25° leads to (CXII) whereas, ring closure occurs at 50°, eliminating lithium sulfide to give *N*-ethylcarbazole (CXIII) (Scheme 41)[448].



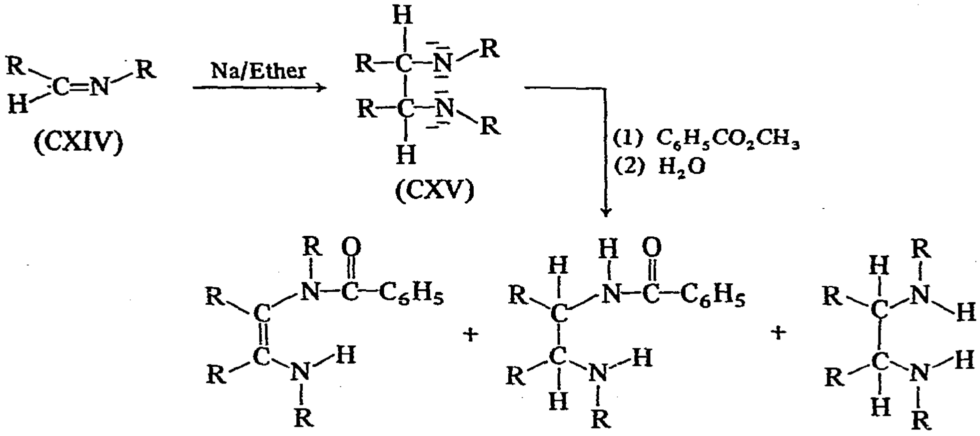
(CXI) (CXII) (CXIII)

Scheme 41

Vinyl-substituted thiophene, furan and pyridine derivatives also give radical anion intermediates, on treatment with sodium in THF and these adducts are used in polymerization reactions[449].

V. ANILS AND AZINES

Schlenk and coworkers[119,327,413] were the first to study the addition of sodium to compounds containing C=N system, such as anils and azines of aldehydes and ketones. Recent work shows that these systems do not give rise to simple adducts, as was formulated by earlier workers[119,327,413,450,452]. *N*-Benzylideneaniline (CXIV), for example, gives rise to a monosodium adduct, which immediately dimerizes to give (CXV) (Scheme 42)[327,453,454]. Treatment of (CXV) with methyl benzoate gives a mixture of optically active *N*,*N*′-1,2-tetraphenylethylenediamine (CXVI), its monobenzoyl derivative (CXVII) and *N*-benzoyl-*N*,*N*′-diphenylstilbenediamine (CXVIII) (Scheme 42)[453]. The sodium adduct of *N*-benzylidene-



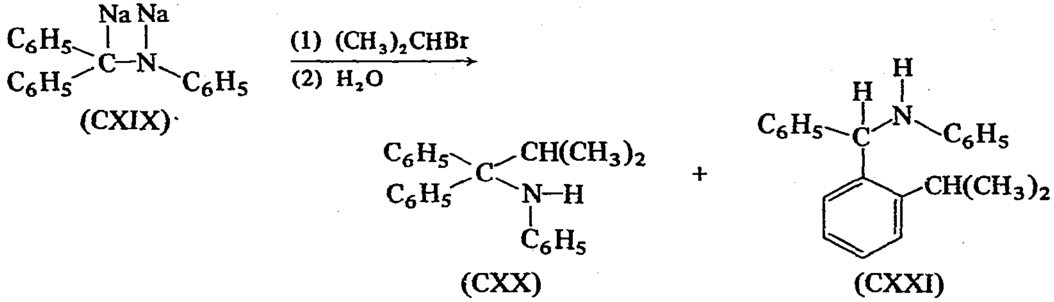
(CXIV) (CXV)

(CXVIII) (CXVII) (CXVI)

Scheme 42

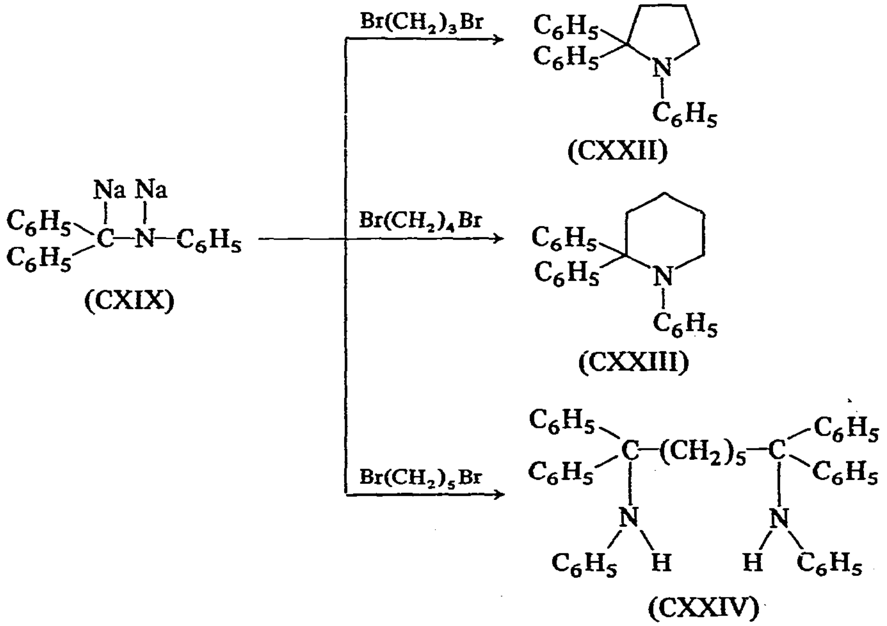
aniline, on protonation, gives the optical isomers of (CXVI) and the influence of solvent polarity and the nature of alkali metals in determining the ratios of optical isomers have been discussed[454]. It appears that the dimerization of (CXIV) can be prevented, if the metal adduct is prepared by electron transfer from indenylsodium[455].

Disodium adduct of benzophenone anil (CXIX) gives mainly *C*-alkylation products[251], on treatment with alkyl halides[456]. Substantial amounts of alkylation also occur in the aromatic ring attached to the benzylic carbon atom, to give (CXXI), in addition to the normal product (CXX) (Scheme 43)[457,458]. A series of transformations resulting in the formation of aniline and 1,1-diphenylethylene have been reported in the reaction of (CXIX) with methyl iodide[459]. In the reaction of (CXIX) with polymethylene dibromides, carbon alkylation occurs first whereas further alkylation occurs on nitrogen[456]. Thus, treatment of (CXIX) with 1,3-dibromopropane and 1,4-dibromobutane gives rise to the pyrroline derivative (CXXII), and the piperidine derivative (CXXIII), respectively. But the reaction with 1,5-dibromopentane results in the formation of the linear diamine (CXXIV), instead of the expected homopiperidine derivative (Scheme 44).



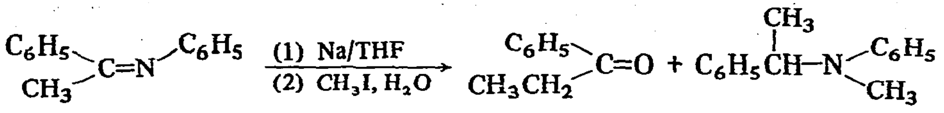
Scheme 43

Contrary to previous reports, the reaction between acetophenone anil (CXXV) and



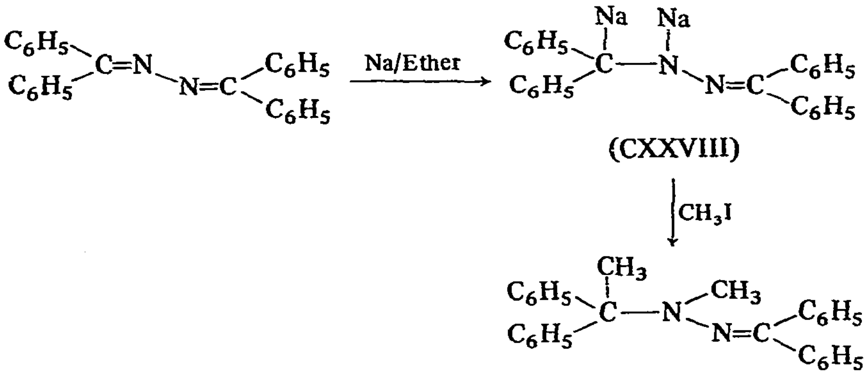
Scheme 44

sodium produces a mixture of mono-sodio adducts which on methylation gives propiophenone (CXXVI) and the tertiary amine (CXXVII) (Scheme 45)[460].


(CXXV) (CXXVI) (CXXVII)

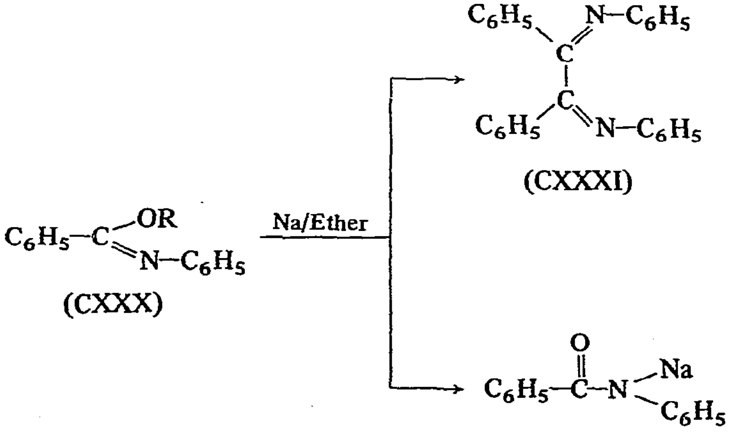
Scheme 45

Sodium or potassium reacts with benzophenone azine to give a 1,2-dimetal adduct (CXXVIII) which on methylation, gives *N*-(1,1-diphenylethyl)-*N*-methylbenzophenone hydrazone (CXXIX) (Scheme 46)[120,413,461]. When lithium is used, it brings about extensive reduction and cleavage. The phenylimido ester (CXXX) has been reported to react with sodium to yield benzil dianil (CXXXI) and the sodium salt of benzanilide (CXXXII) (Scheme 47)[462]. Syntheses of a few macrocyclic compounds by the reaction of alkali metals


(CXXVIII)

(CXXIX)

Scheme 46

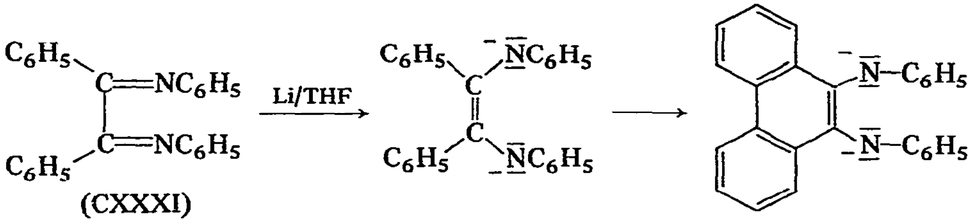

(CXXXI)

(CXXX)

(CXXXII)

Scheme 47

with dianils and imido esters have also been reported[463-466]. Benzil dianil (CXXXI) undergoes cyclodehydrogenation with lithium in THF to produce the dianion of 9,10-dianilinophenanthrene (CXXXIII) and lithium hydride (Scheme 48)[467,468].



(CXXXI)

(CXXXIII)

Scheme 48

Benzophenone phenylhydrazone adds to sodium, but the addition product decomposes to give a mixture of products, on treatment with ethanol[413].

VI. NITRILES

The addition of alkali metals to nitriles in ether solvents has not received much attention. Sodium adds to pivalonitrile to give an adduct, which on hydrolysis yields hexamethylacetone[469]. Dimerization of tetracyanoethylene radical anion[470], cross hydrodimerization of acrylonitrile and its derivatives[471] and elimination of a nitrile group from α-aminonitriles[472] have been brought about by alkali metals in a variety of solvents. When benzonitrile is treated with sodium[473] or the disodio adduct of stilbene, it undergoes cyclization to *s*-triphenyltriazine.

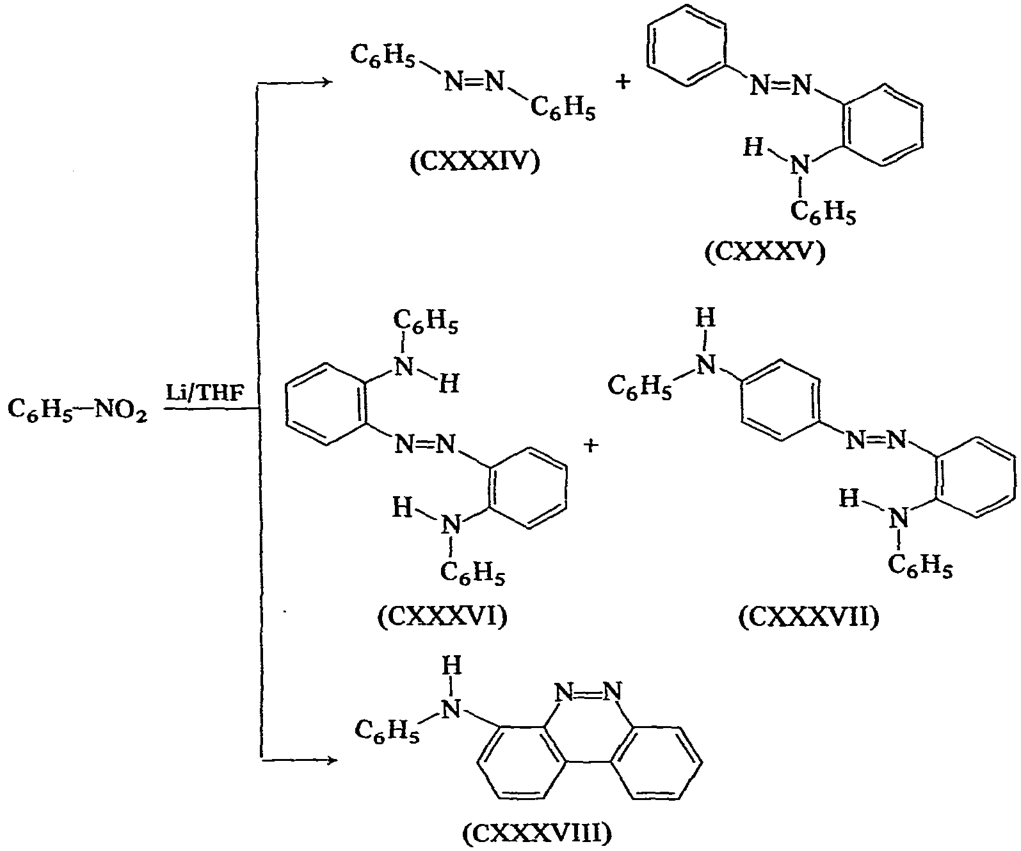
VII. NITRO AND NITROSO COMPOUNDS

A. Nitro compounds

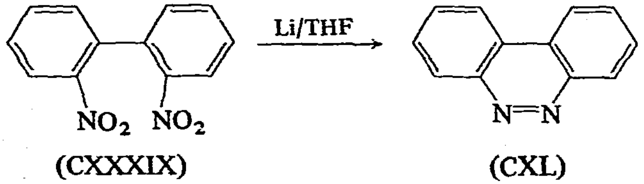
Aromatic nitro compounds readily form radical anion intermediates, on reaction with alkali metals. Although both ESR and electronic spectral data of these radical anion intermediates are available, the products formed in these reactions have not yet been studied in detail. Nitrobenzene radical anion decomposes in aqueous solution to give nitrobenzene and phenylhydroxylamine[474]. Reduction with potassium in THF of nitrobenzene gives a radical anion which is oxidized by air to nitrobenzene and potassium superoxide[475]. Lukashevich first reported the formation of disodio adducts of nitro compounds on treatment of aromatic nitro compounds with sodium[476,477].

Aromatic nitro compounds are reported to be selectively reduced to nitroso, azoxy, azo and hydrazo stages by metal amalgams, although the details of these reactions are not available[478,479].

The decomposition of nitrobenzene radical anion, generated by alkali metal reduction becomes apparent by its change of colour with time[280,480-482]. The reaction of nitrobenzene with lithium in THF under nitrogen atmosphere gives a mixture of azobenzene (CXXXIV), 2-anilinoazobenzene (CXXXV), 2,2′-dianilinoazobenzene (CXXXVI), 2,4′-dianilinoazobenzene (CXXXVII), anilinodibenzopyridazine (CXXXVIII) and unidentified polyazo compounds (Scheme 49)[280,483]. The reaction involves the immediate formation of nitrobenzene radical anion and it goes through the nitroso and azoxy stages. Nitrobenzenes containing substituents like CH_3, OCH_3 and $N(CH_3)_2$ behave in a fashion similar to that of nitrobenzene.but no reaction occurs when the substituent group is either NH_2 or $NHCOCH_3$. 2,2′-Dinitrodiphenyl (CXXXIX) undergoes reductive cyclization to give dibenzopyridazine (CXL) in presence of lithium or sodium in THF or DME (Scheme 50)[280,483]. It may be mentioned in this connection that the ESR spectrum observed on



Scheme 49



Scheme 50

prolonged treatment of (CXXXIX) with alkali metals in ether solvents, corresponds to that of (CXL)[484].

Reactions of aliphatic tertiary nitro compounds with sodium in ether solvents have been studied[485-488]. The initially formed radical anions of these compounds cleave giving rise to both the nitrite anion and the corresponding free radical. Subsequent reactions of these free radicals, however, lead to a variety of products such as alkanes, alkenes, nitroxide and alkoxides.

B. Nitroso compounds

Formation of the disodio adduct of nitrosobenzene was first noticed by Lukashevich[476,477]. Treatment of aromatic nitroso compounds with sodium in ether gives rise to a radical anion intermediate, which dimerizes to give azoxy compounds[489]; with excess sodium, however, they form dimetal adducts and give phenylhydroxylamine derivatives, on hydrolysis.

Treatment of nitrosobenzene with lithium in THF gives azobenzene and 2-anilinoazobenzene as products[280,483]. In addition, the reaction mixture contains several constituents quite similar to the type of products formed in the nitrobenzene reaction.

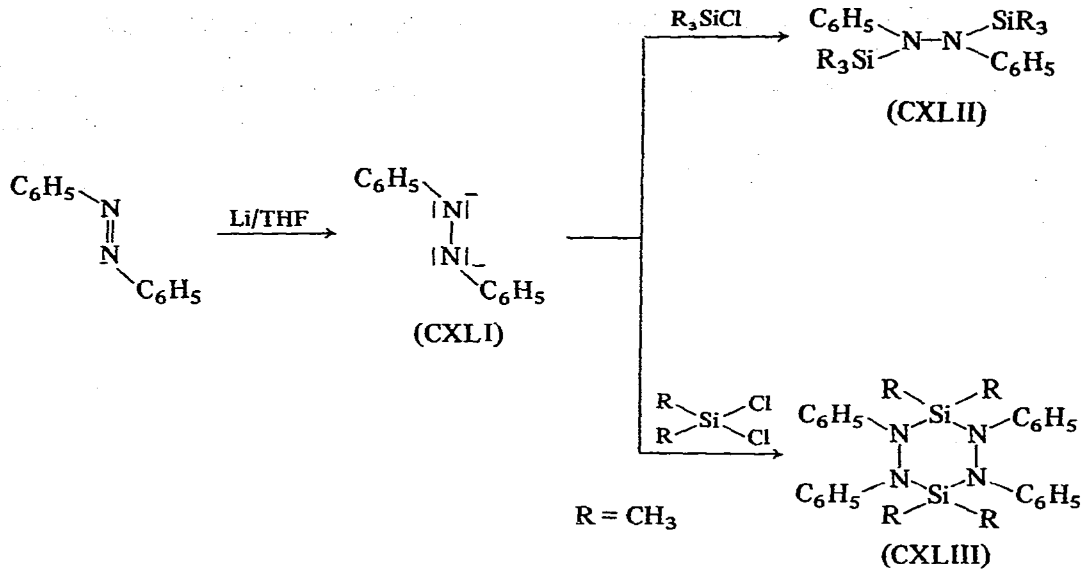
VIII. AZOXY AND AZO COMPOUNDS

A. Azoxy compounds

Alkali metals bring about deoxygenation of azoxy compounds to give the corresponding azo compounds. Thus, lithium in THF deoxygenates azoxybenzene and 4,4′-azoxyanisole to azobenzene and 4,4′-azoanisole, respectively, in almost quantitative yields[280,483]. The alkali metal adduct of azoxybenzene gives azobenzene, after protonation followed by air oxidation[490]. The reaction of α-4-bromoazoxybenzene gives only a poor yield of azobenzene, suggesting thereby that a debromination step is also involved[280,483].

B. Azo compounds

Addition of alkali metals to azobenzene was first reported in 1928 by Schlenk and Bergmann[413]. The disodio adduct of azobenzene on benzoylation gives either the dibenzoyl derivative or benzanilide, depending on the reaction conditions. The formation of the dimetal adducts was also studied by other workers[491-494]. Azobenzene radical anion is green in colour and it can be reduced further to the dianion which is yellow. This radical anion disproportionates to the dianion and neutral molecule and the equilibrium is governed by the choice of the alkali metal, solvent and temperature[280,493,495]. George and coworkers[435,495-501] have studied the nucleophilic displacement reactions of azobenzene dianions on halosilanes, for the syntheses of several silylhydrazines and disilatetraazacyclohexanes. Azobenzene dianion (CXLI) for example, reacts with trimethylchlorosilane to give *N,N*′-diphenyl-*N,N*′-bis(trimethylsilyl)hydrazine (CXLII) or with dimethyldichlorosilane to give 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (CXLIII) (Scheme 51). Treatment of the dianions of aromatic azo compounds with methanol constitutes a quick method for the synthesis of the corresponding hydrazo compounds[280,501].



Scheme 51

Recently, azobenzene complexes of nickel have been synthesized from its dianion[502]. Addition of sodium and potassium to diethyl azodicarboxylate in DME to give both mono and dimetal adducts and also several reactions of these intermediates have been reported[503].

Diazomethane undergoes decomposition on treatment with sodium in ether solvents[504]. Sodium adds to diazofluorene and diphenyldiazomethane to give the corresponding radical anion intermediates[505]. Diazofluorene radical anion exists in equilibrium with its dimer and the hydrolysis of this mixture yields both bifluorenylidene and fluorenone azine.

Phenyl azide reacts with sodium in ether to give a free-radical intermediate, which gives hydroazobenzene, on hydrolysis. Prolonged treatment of phenylazide with sodium, however, gives aniline as one of the products[505].

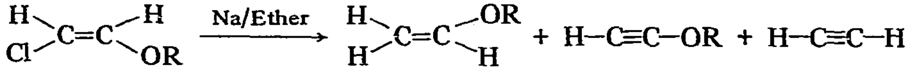
IX. MISCELLANEOUS COMPOUNDS

In this section, the reactions of several organic compounds toward alkali metals are discussed under the appropriate headings. Some of the systems present clear evidence of alkali metal additions across the double bond, whereas in some cases, there is evidence for the formation of radical anion intermediates at least in the initial stages, if the reaction is performed at low temperatures. In most of the reactions discussed in this section, bond cleavage takes place and the mechanism is not known with certainty. Based on analogies, we feel that several of these reactions may proceed through radical anion intermediates and hence are included in this review.

A. Ethers

Ethers are reported to be cleaved on treatment with alkali metals[506]. Thus, it is not advisable to purify high boiling ethers by distilling over sodium[507-509]. Alkali metal treatment of ethers gives rise to a number of cleavage products. Diphenyl ether, for example, when refluxed with sodium, gives a mixture of benzene, biphenyl, phenol and polymeric materials. Analysis of the products and ESR spectra indicate that the reaction proceeds through a heterocyclic cleavage of the aryl C–O bond of the dianion intermediate[509]. However, benzyl ethers undergo a rearrangement to give secondary alcohols[510]. Thus, when benzyl methyl ether is boiled with sodium in nitrogen atmosphere, a mixture of toluene and phenyl methyl carbinol is obtained[511]. On the other hand, Gilman and coworkers[512] have reported that the action of lithium in the cold, on a solution of benzyl methyl ether in THF results in the formation of lithium methoxide and benzyllithium. Cleavage of allyl phenyl ether by lithium in THF is a convenient method for the preparation of allyllithium[513] and its derivatives[513,514].

Various degradation and dimerization reactions of ethers and ketals by alkali metals have been studied[515-517]. 9-Phenyl-10-methoxyanthracene reacts with sodium in ether to give a bianthryl derivative[515] or the disodio adduct of 9-phenylphenanthrene[516]. Several β-dialkenyl ethers are readily converted to aliphatic dienes by treatment with alkali metals[518]. In the reaction of β-chlorovinyl ether (CXLIV), with sodium in ether, no Wurtz type of products are formed but the vinyl and alkynyl ethers (CXLV) and (CXLVI), respectively have been isolated in addition to sodium butoxide, sodium chloride, acetylene and unidentified products (Scheme 52)[519].



(CXLIV) (CXLV) (CXLVI)

Scheme 52

Several phenyl ethers and *m*-polyphenyl ethers cleave to give biphenyl radical anion, on treatment with potassium in THF or DME[520,521]. Anisole is cleaved by potassium and when the reaction is quenched by heavy water, deuterium is found to enter into the resulting biphenyl[522].

Reaction of epoxides to give diols[523] and cleavage of THF, MeTHF, DME and cyclic ethers of ferrocene during the formation of organometallic compounds[409,524,525] have been reported. Treatment of tropyl methyl ether with sodium in THF results in the formation of cycloheptatrienide dianion radical[233].

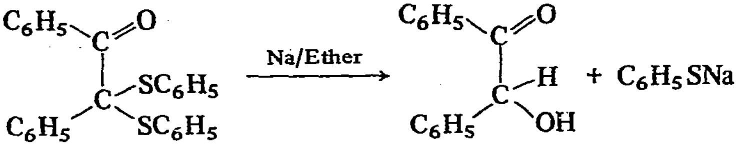
B. Sulfur compounds

Most disulfides react very readily with alkali metals to give the corresponding mercaptides[526]. Diphenyl sulfide, thioanisole etc. are cleaved by potassium in DME with the initial formation of the phenoxide ion and the corresponding aryl or alkyl radical[527]. Thioanisole (CXLVII) reacts with sodium in ether and after carboxylation yields phenylthioglycolic acid (CXLVIII) and thiophenol (CXLIX) (Scheme 53)[528]. Thioacetals appear to be very resistant to alkali metals but sodium reacts with the mercaptole (CL), to give benzoin (CLI) and thiophenoxide (Scheme 54)[529]. Action of alkali metals on sulfoxides has been studied[530-532]. Dimethylsulfoxide reacts with sodium or potassium to give methane

$$C_6H_5{-}S{-}CH_3 \xrightarrow[(2)\ CO_2,\ H_2O]{(1)\ Na/Ether} C_6H_5{-}S{-}CH_2CO_2H + C_6H_5{-}SH$$

(CXLVII) (CXLVIII) (CXLIX)

Scheme 53



(CL) (CLI)

Scheme 54

sulfenate, methyl sulfinyl carbanion, methane and dimethyl sulfone. Diaryl sulfones form radical anions with potassium in DME and their ESR spectra are closely related to the corresponding hydrocarbons[533]. The dianion of thiobenzophenone generated by alkali metals, induces the polymerization of vinyl monomers[534]. In the preparation of tetrathiaadamantane dianion, cleavage of the C-S bond is observed[535]. The sulfur analogue of azoxybenzene is believed to be formed when aniline sulfate is treated with sodium in boiling toluene[536].

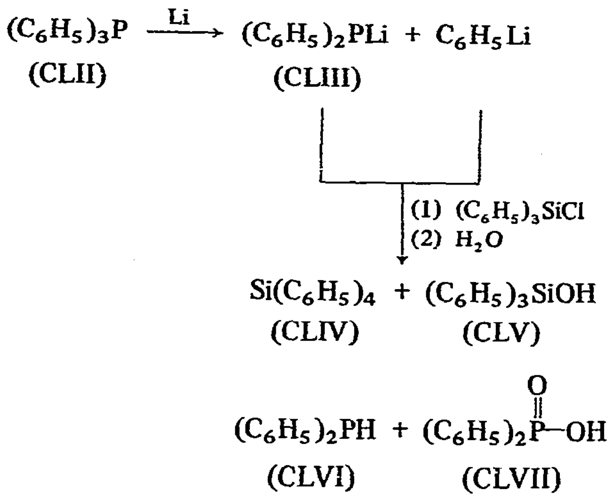
C. Amines

The tendency of the alkali metals to cleave the C-N bond in amines, is generally less than that in the case of ethers[537]. The cleavage is very facile, however, in the case of polyaryl amines[537-540]. Triphenylamine, for example, reacts with Li, Na and K in THF to give biphenyl, aniline and diphenylamine[540]. The use of lithium metal in place of n-butyllithium as a reagent in the direct butylation of *N,N*-dimethylaniline has been studied[541]. Sodium reacts with *N,N*-dimethylformamide in protic and aprotic solvents to give an equal mixture of dimethylaminomethoxide and dimethylformamidylsodium[542].

D. Phosphorous compounds

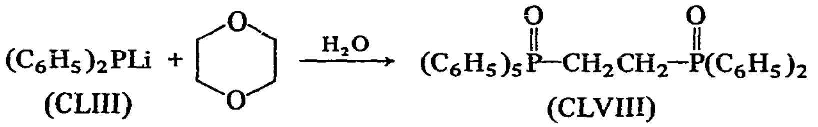
The cleavage of tertiary phosphines by alkali metals to give metalloorganophosphides and organometallics is well known[539,543-545]. Issleib[543] had suggested that the dimetallophosphorane, (R_3PM_2) which is formed initially, dissociates further to give the cleavage products. In mixed tertiary phosphines, the most electronegative group is ejected and the alkali metal phosphide contains at least one aromatic group.

In the reaction of triphenylphosphine (CLII) with alkali metals, the initial reaction is a phenyl cleavage rather than the formation of a negative ion[539,546,547]. The alkali metal diphenyl phosphide (CLIII) gives a radical anion on further treatment. When the cleavage products are treated with a halosilane and subsequently hydrolysed in presence of air, a mixture of products (CLIV-CLVII) are formed but no stable compound containing a Si-P bond has been isolated (Scheme 55).



Scheme 55

Lithium in THF cleaves phosphines containing unsaturated groups also[548]. Preparation of (CLIII) from unsaturated phospines, di-tert-phosphine and from tetraalkyldiphenylphosphine disulfide[549] have been reported. Cleavage of solvents like dioxane by (CLIII) to give ethylenebis(diphenylphosphineoxide) (CLVIII) has been observed (Scheme 56)[550].



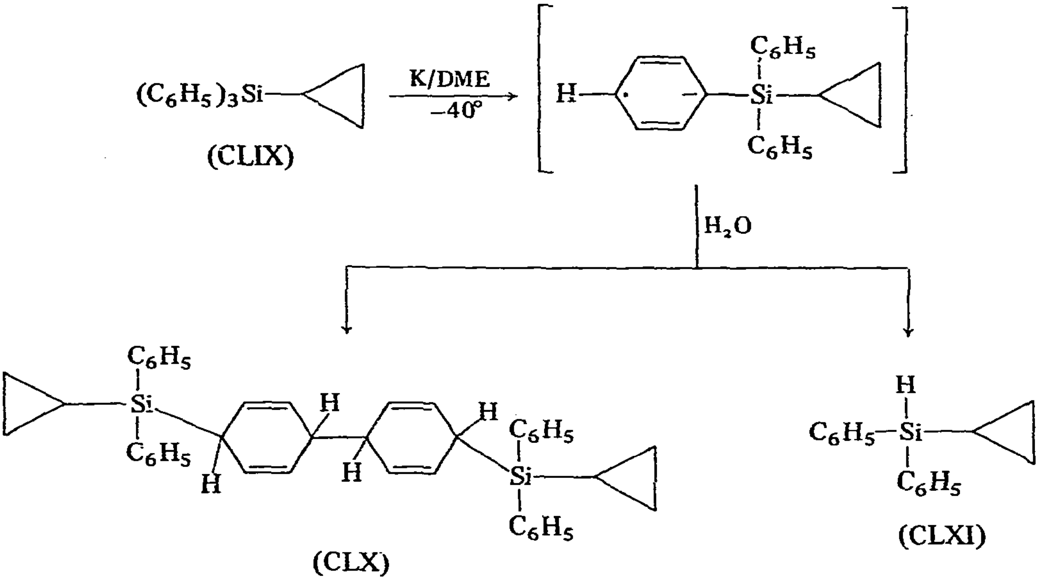
Scheme 56

Several other reactions of alkali metal phosphides have been reported[539,543,551-555]. The ESR spectrum of biphenyl radical anion is observed when triphenylphosphine is treated with alkali metals in ether solvents[546,556], whereas the formation of biphenyl radical anion and "ylides" are observed in the case of phosphineoxides[557]. The reactions of phenyldichlorophosphine[553], phosphorous esters[558,559] and phosphonium bromides[560] with alkali metals have been studied. Reesor and Wright[561] have found that each of the polymeric forms of phosphorobenzene is converted by treatment with sodium in dioxane to its disodio adduct which can be methylated or benzoylated to give air-sensitive compounds.

E. Silicon compounds

The preparation of silylmetallic species by the reaction of alkali metals with polysilanes in ether solvents is well established and has been reviewed[562-565]. While lithium, potassium, rubidium and cesium derivatives are easily obtained, the corresponding sodium compounds are difficult to prepare[566]. However, they can be prepared from the corresponding disilane in THF using metallic sodium and a little naphthalene[567,568]. The triarylsilyl potassium or lithium readily undergoes a variety of reactions such as protonation, alkylation and silylation[569-572].

Hexaalkyldisilanes are not cleaved by alkali metals but readily by bromine. A possible explanation for the failure of alkali metal cleavage may be due to the lack of resonance stabilization of the trialkylsilyl fragment, as compared to the triphenylsilyl or diphenylsilyl groupings[573]. Treatment of an optically active disilane with lithium has been reported to give an optically active silyllithium compound[574]. A radical anion intermediate is formed when cyclopropyltriphenylsilane (CLIX) is treated with alkali metals[575]. Depending on the reaction temperature, both reductive coupling to give (CLX) and phenyl cleavage to give (CLXI) are observed (Scheme 57). Silyllithium compounds were found to react with cyclic and linear ether solvents to give glass-like resins or silyl substituted carbinols[576]. The cleavage reactions of alkali metals on linear polysilanes, cyclic polysilanes and silaoxaphenanthrenes have been reported[577-579]. Both sodium and potassium cleave methyltrimethoxysilane to give a mixture of substituted silanes and alkali metal oxides[580].



Scheme 57

Compounds containing olefinic groups attached to silicon, undergo two types of reactions with alkali metals. Seyferth and coworkers[581] found that propenyltrimethylsilane undergoes isomerization by the action of lithium in THF to give the *trans*-isomer, whereas no isomerization occurred in ether. This reaction, as well as the formation of 1,4-bis(triphenylsilyl)butane from triphenylvinylsilane by lithium can be rationalized in terms of a radical anion intermediate which subsequently undergoes either isomerization or reductive coupling[581,582]. Addition of lithium to 1-trialkylsilylnaphthalene gives a dilithio adduct which has good nucleophilic properties[583]. Further silylation results in the formation of 1,5-bis(trialkylsilyl)-1,4-dihydronaphthalene or 1,4,5-tris(trialkylsilyl)-1,4-dihydronaphthalene (compare with Scheme 2). Formation of radical anions and dianions of a few silacyclopentadiene derivatives[280,584-586] has been observed. Chemiluminescence has also been observed, when these solutions are exposed to air[586].

In the alkali metal adducts of some organosilicon compounds, conjugation of aromatic ring systems through a silicon atom has also been observed[587]. Electron delocalization even in some permethylpolysilanes suggest that electron mobility is not limited to conjugated molecules, but can also be observed in systems not normally considered as unsaturated[588]. The possible implications of this phenomenon for preparing organic conductors and super conductors have been described[588,589]. A novel organosilicon cyclophane and its radical anion which is fully delocalized through transannular interaction have also been described[589].

Radical anions of trimethylsilyl and trimethylgermyl substituted polyphenyls and naphthalenes have been generated and studied[590]. Seyferth et al.[581] found that propenyltrimethylgermane isomerizes to a mixture of 92% *trans*- and 8% *cis*-isomers, by the action of lithium in THF.

Tetraethylgermane is remarkably stable to lithium[591] but tetraphenylgermane can be cleaved in DME to give triphenylgermyllithium[592]. Hexaalkyldigermanes can be cleaved by lithium and other alkali metals in HMPA but not in ether, THF or DME[593].

F. Boron compounds

Sodium reacts with diborane in ether solution to give sodium borohydride and triborohydride[594]. Formation of alkali metal complexes has been reported in the reactions with trialkyl boron[595], triphenyl boron[596] and trialkyl borates[597]. Tri-1-naphthylborane is reduced to the radical anion and dianion intermediates by treatment with sodium amalgam in DME. The dianion decomposes to give naphthalene radical anion and 1,1′-binaphthyl radical anion[598]. Similarly, prolonged reaction of the radical anion of triphenylboron with sodium in DME degrades it to biphenyl radical anion[599,600].

G. Other systems

Reaction between lithium and the phenyl derivatives of the elements of Groups II, III, IV and V of the periodic table have been studied[601]. Some of these cleave to give phenyllithium in ether solution. The reaction of arsenobenzene with sodium in DME gives di- and tetra-sodium adducts, resulting finally in the cleavage of the As–As bond[602].

Lithium isomerizes *cis*- and *trans*-propenyltrimethyltin in ether solution to a mixture of *trans* and *cis* isomers, in each case. However, in THF, compounds like propenyllithium, trimethylstannyllithium and methyllithium are obtained[581]. When tetra-*cis*- and tetra-*trans*-propenyltin (CLXII) are treated with lithium in ether, metal displacement reaction occurs to give propenyllithium (CLXIII), which can be silylated (Scheme 58). In addition, the tetrapropenyltin recovered in this reaction, is found to be a mixture of both *cis* and *trans*

$$\underset{\text{(CLXII)}}{(\mathrm{CH_3CH{=}CH})_4\mathrm{Sn}} \xrightarrow{\text{Li/Ether}} \underset{\text{(CLXIII)}}{\mathrm{CH_3CH{=}CHLi}} + \begin{array}{l}\text{tetra-}\textit{cis}\text{ and}\\ \text{tetra-}\textit{trans}\text{ forms}\\ \text{of (CLXII)}\end{array}$$

Scheme 58

isomers. It is interesting to note that while the propenyl derivatives of silicon, germanium and tin are isomerized, no isomerization occurred with the corresponding carbon compounds. Crotyltrimethyltin also undergoes a similar isomerization[603].

Cleavage reactions of organolead compounds are known[604,605]. Trialkylaluminum reacts with sodium in the presence of naphthalene in THF to give solid derivatives of dihydronaphthalenealuminates containing sodium and THF in their molecular compositions[606-609]. Lithium displaces mercury from divinylmercury to give vinyllithium in high yields[610]. Similarly, bis(triethylgermyl)- and bis(triethylsilyl)-mercury react with lithium to yield triethylgermyllithium and triethylsilyllithium, respectively[611]. Lithium causes the isomerization of propenyl derivatives of mercury also, as in the case of propenyl derivatives of other Group IV elements[612].

ACKNOWLEDGEMENT

The authors thank Mr. K. B. Sukumaran for his help in preparing this manuscript.

REFERENCES

1 For some comprehensive reviews, see, (a) H. Smith in R.L. Augustine (Ed.), *Reduction Techniques and Applications in Organic Syntheses*, Marcel Dekker Inc., New York, 1968, pp. 95–170; (b) P. Grabbe, *Ingr. Chimist*, 38 (1956) 119; *Chem. Abstr.*, 52 (1958) 1934; (c) A.J. Birch, *Quart. Rev.*, 4 (1950) 69; (d) A.J. Birch and H. Smith, *Quart. Rev.*, 12 (1958) 17; (e) G.W. Watt, *Chem. Rev.*, 46 (1950) 317; (f) H. Smith, *Organic Reactions in Liquid Ammonia Chemistry in Non-aqueous Ionizing Solvents, Vol. I, part 2*, John Wiley and Sons, New York 1963; (g) R.G. Harvey, *Synthesis*, 4 (1970) 161.
2 (a) D. Sedzik-Hibner and Z. Chaubudzinski, *Wiad. Chem.*, 23 (1969) 809; *Chem. Abstr.*, 72 (1970) 89397; (b) R.A. Benkeser and C.A. Tincher, *J. Org. Chem.*, 33 (1968) 2727 and the earlier papers in the series; (c) R.A. Benkeser and E.M. Kaiser, *J. Org. Chem.*, 29 (1964) 955.
3 C.B. Wooster, *Chem. Rev.*, 11 (1932) 1.
4 K.N. Campbell and B.K. Campbell, *Chem. Rev.*, 31 (1942) 77.
5 (a) H. Normant and M. Larcheveque, *C.R. Acad. Sci. Paris*, 260 (1965) 5062; (b) H. Normant, T. Cuvigny, J. Normant and B. Angelo, *Bull. Soc. Chim. Fr.*, (1965) 3441; (c) H. Normant, *Angew. Chem. Intern. Ed.*, 6 (1967) 1046; (d) H. Normant, *Bull. Soc. Chim. Fr.*, (1968) 791; (e) M. Larcheveque, *Ann. Chim.*, 5 (1970) 129.
6 C.N.R. Rao, V. Kalyanaraman and M.V. George, *Appl. Spect. Rev.*, 3 (1970) 153.
7 L.L. Miller, *J. Chem. Educ.*, 48 (1971) 168.
8 N.L. Holy and J.D. Marcum, *Angew. Chem. Intern. Ed.*, 10 (1971) 115.
9 M. Szwarc, in A. Streitwieser, Jr. and R.W. Taft (Eds.), *Progr. Phys. Org. Chem., Vol. 6*, Interscience Publ., New York, 1968, pp. 323.
10 B.J. MacClelland, *Chem. Rev.*, 64 (1964) 301.
11 R.J. Jones and H. Gilman, *Org. Reactions*, 6 (1951) 339.
12 H. Gilman, *Org. Reactions*, 8 (1959) 258.
13 (a) G. Wittig in *Newer Methods of Preparative Organic Chemistry*, Interscience, New York, 1948, p. 570; (b) H. Gilman and J.J. Eisch, *Sci. Am.*, 208 (1963) 88; (c) G. Wittig, *Bull. Soc. Chim. Fr.*, (1963) 1352; (d) D. Seyferth, M.A. Weiner, L.G. Vaughan, G. Raab, D.E. Welch, H.M. Cohen and D.L. Alleston, *Bull. Soc. Chim. Fr.*, (1963) 1364; (e) G. Kobrich, *Angew. Chem. Intern. Ed.*, 6 (1967) 41.
14 M. Schlosser, *Angew. Chem. Intern. Ed.*, 3 (1964) 287, 362.
15 R.W. Fessenden and S. Ogawa, *J. Amer. Chem. Soc.*, 86 (1964) 3591.
16 D.R. Weyenberg and L.H. Topercer, *J. Amer. Chem. Soc.*, 84 (1962) 2848.
17 J. Dubois and G. Dodin, *Tetrahedron Lett.*, (1969) 2325.
18 H. Naarmann, *German Patent, 1,302,121* (1970); *Chem. Abstr.*, 72 (1970) 67455.
19 M. Berthelot, *Ann. Chim.*, 12 (1867) 155.
20 (a) N.D. Scot, *U.S. Patent, 2,019,832* (1936); *Chem. Abstr.*, 30 (1936) 490; (b) N.D. Scot, *U.S. Patent 2,027,000* (1936); *Chem. Abstr.*, 30 (1936) 1393.

21 T.M. Lyssy, *J. Org. Chem.*, 27 (1962) 5.
22 L.H. Slaugh, *U.S. Patent 3,278,620* (1966); *Chem. Abstr.*, 66 (1967) 2414.
23 C. Fabre and Z. Welvart, *Tetrahedron Lett.*, (1967) 3801.
24 E. de Boer, *Advan. Organometal. Chem.*, 2 (1964) 115.
25 J. Smid, *J. Amer. Chem. Soc.*, 87 (1965) 655.
26 S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, 93 (1971) 430.
27 N.D. Scot, J.F. Walker and V.L. Hansley, *J. Amer. Chem. Soc.*, 58 (1936) 2442.
28 K.H.J. Buschow and G.J. Hoijtink, *J. Chem. Phys.*, 40 (1964) 2501.
29 D.N. Andreev, *J. Gen. Chem. (USSR)*, 17 (1947) 1645; *Chem. Abstr.*, 42 (1948) 2595.
30 S. Bank and W.D. Clossen, *Tetrahedron Lett.*, (1965) 1349.
31 J.F. Garst, P.W. Ayers and R.C. Lamb, *J. Amer. Chem. Soc.*, 88 (1966) 4260.
32 G.D. Sargent and G.A. Lux, *J. Amer. Chem. Soc.*, 90 (1968) 7160.
33 J.F. Garst and J.T. Barbas, *Tetrahedron Lett.*, (1969) 3125.
34 S. Bank and J.F. Bank, *Tetrahedron Lett.*, (1969) 4533.
35 J.F. Garst and F.E. Barton, *Tetrahedron Lett.*, (1969) 587.
36 G.D. Sargent, J.N. Cron and S. Bank, *J. Amer. Chem. Soc.*, 88 (1966) 5363.
37 G.D. Sargent and M.W. Browne, *J. Amer. Chem. Soc.*, 89 (1967) 2788.
38 J.F. Garst, J.T. Barbas and F.E. Barton, *J. Amer. Chem. Soc.*, 90 (1968) 7159.
39 G.D. Sargent, *Tetrahedron Lett.*, (1971) 3279.
40 J.W. Rakshys, Jr., *Tetrahedron Lett.*, (1971) 4745.
41 D. Lipkin, F.R. Galiano and R.W. Jordan, *Chem. Ind.*, (1963) 1657.
42 D.B. Ledlie, R.L. Thorne and G. Weiss, *J. Org. Chem.*, 36 (1971) 2186.
43 J.F. Garst, R.H. Cox, J.T. Barbas, R.D. Roberts, J.I. Morris and R.C. Morrison, *J. Amer. Chem. Soc.*, 92 (1970) 5761.
44 T.C. Cheng, L. Headley and A.F. Halasa, *J. Amer. Chem. Soc.*, 93 (1971) 1502.
45 D.R. Weyenberg and L.H. Topercer, *J. Org. Chem.*, 30 (1965) 943.
46 L. Birkofer and N. Ramadan, *Chem. Ber.*, 104 (1971) 138.
47 F.W.G. Fearon and J.C. Young, *J. Chem. Soc. (B)*, (1971) 272.
48 S. Bank and J.F. Bank, *Tetrahedron Lett.*, (1971) 4581.
49 (a) S. Bank and T.A. Lois, *J. Amer. Chem. Soc.*, 90 (1968) 4505; (b) S. Bank, T.A. Lois and M.C. Prislopski, *J. Amer. Chem. Soc.*, 91 (1969) 5407.
50 S. Bank and D.A. Noyd, *Tetrahedron Lett.*, (1969) 1413.
51 L.H. Slaugh, *U.S. Patent, 3,278,620* (1966); *Chem. Abstr.*, 66 (1967) 2414.
52 P. Rempp, *Bull. Soc. Chim. Fr.*, (1968) 1605.
53 K.A. Andrianov, A.I. Nogaideli, R.Sh. Tkeshelashvili and D.Sh. Akhobadze, *Soobshch. Akad. Nauk Gruz. SSR.*, 56 (1969) 569; *Chem. Abstr.*, 72 (1970) 111549.
54 Y. Yamashita and S. Nunomoto, *Makromol. Chem.*, 58 (1962) 244.
55 S. Moriwacki, S. Kusabayashi and H. Mikawa, *Chem. Commun.*, (1971) 607.
56 R.B. King and A. Efraty, *J. Organometal. Chem.*, 24 (1970) 241.
57 A.N. Nesmeyanov, N.A. Vol'kenau and L.S. Shilovtseva, *Dokl. Akad. Nauk SSSR*, 190 (1970) 354; *Chem. Abstr.*, 72 (1970) 132929.
58 G.W. Watt, L.J. Baye and F.O. Drummond, Jr., *J. Amer. Chem. Soc.*, 88 (1966) 1138.
59 H. Normant and B. Angelo, *Bull. Soc. Chim. Fr.*, (1960) 354.
60 H. Normant and B. Angelo, *Bull. Soc. Chim. Fr.*, (1961) 1988.
61 K. Suga, S. Watanabe, T. Fujita and T.P. Pan, *Bull. Chem. Soc. Japan*, 42 (1969) 3606.
62 K. Suga, S. Watanabe, T.P. Pan and T. Fujita, *Chem. Ind.*, (1969) 78.
63 K. Suga, S. Watanabe and I. Torii, *Chem. Ind.*, (1967) 360.
64 K. Suga, S. Watanabe and T.P. Pan, *Aust. J. Chem.*, 21 (1968) 2341.
65 G.B. Bachman and R.S. Barker, *J. Amer. Chem. Soc.*, 69 (1947) 1535.
66 L. Horner and H. Gusten, *Ann.*, 652 (1962) 99.
67 T. Tsuzuki and Y. Iwakura, *J. Org. Chem.*, 30 (1965) 2665.
68 C.D. Gutsche, I.Y.C. Tao and J. Kozma, *J. Org. Chem.*, 32 (1967) 1782.
69 D. Blake, G.E. Coates and J.M. Tate, *J. Chem. Soc.*, (1961) 618.
70 H.W. Whitlock Jr. and P.F. Schatz, *J. Amer. Chem. Soc.*, 93 (1971) 3837.
71 K. Suga, S. Watanabe and K. Takahasti, *Chem. Ind.*, (1961) 1748.
72 K. Suga, S. Watanabe and T. Suzuki, *Can. J. Chem.*, 46 (1968) 3041.
73 S. Watanabe, K. Suga and T. Suzuki, *Can. J. Chem.*, 47 (1969) 2343.
74 K. Suga and S. Watanabe, *Tetrahedron Lett.*, (1966) 2527.
75 K. Suga, S. Watanabe and K. Kamma, *Can. J. Chem.*, 45 (1967) 933.
76 S. Watanabe, K. Suga, K. Kamma and I. Torii, *Can. J. Chem.*, 46 (1968) 1154.

77 K. Suga and S. Watanabe, *Bull. Chem. Soc. Japan*, 40 (1967) 1257.

78 K. Suga, S. Watanabe, T. Watanabe and M. Kuniyoshi, *J. Appl. Chem.*, 19 (1969) 318.

79 K. Suga, S. Watanabe, H. Kikuchi and T. Watanabe, *Can. J. Chem.*, 46 (1968) 2619.

80 S. Watanabe and K. Suga, *Aust. J. Chem.*, 24 (1971) 1301.

81 S. Watanabe, K. Suga and T. Watanabe, *Chem. Ind.*, (1970) 1145.

82 G.D. Sargent, *J. Amer. Chem. Soc.*, 93 (1971) 5268.

83 S. Ji, L.B. Gortler, A. Waring, A. Battisti, S. Bank, W.D. Closson and P. Wriede, *J. Amer. Chem. Soc.*, 89 (1967) 5311.

84 W.D. Closson, S. Ji and S. Schulenberg, *J. Amer. Chem. Soc.*, 92 (1970) 650.

85 W.D. Closson, P. Wriede and S. Bank, *J. Amer. Chem. Soc.*, 88 (1966) 1581.

86 T.R. Ganson, S. Schulenberg and W.D. Closson, *Tetrahedron Lett.*, (1970) 4397.

87 (a) E.E. van Tamelen, G. Boche, S.W. Ela and R.B. Fechter, *J. Amer. Chem. Soc.*, 89 (1967) 5707; (b) E.E. van Tamelen, G. Boche and R. Greeley, *J. Amer. Chem. Soc.*, 90 (1968) 1677; (c) E.E. van Tamelen, R.B. Fechter and S.W. Schneller, *J. Amer. Chem. Soc.*, 91 (1969) 7196; (d) E.E. van Tamelen, *Acc. Chem. Res.*, 3 (1970) 361.

88 M.E. Vol'pin, A.A. Belyi, N.A. Katkov, R.V. Kudryavtsev and V.B. Shur, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 2858; *Chem. Abstr.*, 72 (1970) 78745.

89 T.R. Tuttle, Jr. and P. Graceffa, *J. Phys. Chem.*, 75 (1971) 843.

90 K. Suga, S. Watanabe and T. Fujita, *Chem. Ind.*, (1970) 402.

91 T. Fujita, K. Suga and S. Watanabe, *Aust. J. Chem.*, 24 (1971) 2705.

92 V. Vesley and F. Stursa, *Collect. Czech. Chem. Commun.*, 4 (1932) 139.

93 H.L. Hsieh, *J. Organometal. Chem.*, 7 (1967) 1.

94 B. Stipanovic and H. Pines, *J. Org. Chem.*, 34 (1969) 2106.

95 H.O. House and R.W. Bashe, *J. Org. Chem.*, 32 (1967) 784.

96 B.M. Mikhailov, *Izv. Akad. Nauk SSSR. Otdel. Khim. Nauk* (1946) 619; *Chem. Abstr.*, 42 (1948) 6350.

97 B.M. Mikhailov and A.N. Blokhina, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1949) 164; *Chem. Abstr.*, 44 (1950) 2962.

98 A.I. Nogaideli and N.N. Skhirtladze, *Soobsch. Akad. Nauk Gruz. SSR*, 29 (1962) 151; *Chem. Abstr.*, 58 (1963) 5594.

99 C. Fabre, H. Ali and Z. Welvart, *Chem. Commun.*, (1970) 1149.

100 M. Ichikawa and K. Tamaru, *J. Amer. Chem. Soc.*, 93 (1971) 2079.

101 M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, 63 (1967) 997, 1215, 2012.

102 V.C. Bien and L.E. Lyons, *Aust. J. Chem.*, 23 (1970) 261.

103 W. Muench, L. Notarbartolo, G. Silvestri and V. Ruoti, *U.S. Patent, 2,948,762* (1960); *Chem. Abstr.*, 55 (1961) 5446.

104 R. Gerdil and E.A.C. Lucken, *Helv. Chim. Acta.*, 44 (1961) 1966.

105 R. Lapouyade, P. Labandibar and H. Bouas-Laurent, *Tetrahedron Lett.*, (1971) 979.

106 E. Bergmann and E. Bograchov, *J. Amer. Chem. Soc.*, 62 (1940) 3016.

107 O. Neunhoeffer and H. Woggon, *Ann.*, 600 (1956) 34.

108 R.O.C. Norman, G.A. Thompson and W.A. Waters, *J. Chem. Soc.*, (1958) 175.

109 B.M. Mikhailov and A.D. Chinaeva, *Sbornik Statei Obshchei Khim. Akad. Nauk SSSR*, 1 (1953) 626; *Chem. Abstr.*, 49 (1955) 993.

110 D.E. Paul, D. Lipkin and S.I. Weissman, *J. Amer. Chem. Soc.*, 78 (1956) 116.

111 B.M. Mikhailov and A.D. Chinaeva, *Zh. Obshch. Khim.*, 22 (1952) 162; *Chem. Abstr.*, 46 (1952) 11070.

112 N.N. Skhirtladze and A.I. Nogaideli, *Soobshch. Akad. Nauk Gruz. SSR*, 58 (1970) 337; *Chem. Abstr.*, 73 (1970) 66326.

113 A.N. Pudovick and A.A. Muratova, *Referat. Zh. Khim.*, (1954) No. 42864; *Chem. Abstr.*, 49 (1955) 14429.

114 A.G. Evans and J.C. Evans, *J. Chem. Soc.*, (1963) 6036.

115 G.J. Hoijtink and J. van Schooten, *Rec. Trav. Chim.*, 72 (1953) 691.

116 N.H. Velthorst and G.J. Hoijtink, *J. Amer. Chem. Soc.*, 87 (1965) 4529.

117 D. Lipkin, G.J. Divis and R.W. Jordan, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, 13 (1964) D 10; *Chem. Abstr.*, 72 (1970) 3262.

118 G. Briegleb, *Angew. Chem. Intern. Ed.*, 3 (1964) 617.

119 W. Schlenk and E. Bergmann, *Ann.*, 463 (1928) 1.

120 W. Schlenk and E. Bergmann, *Ann.*, 463 (1928) 98.

121 E.A. Chandross and F.I. Sonntag, *J. Amer. Chem. Soc.*, 88 (1966) 1089.

122 E.A. Chandross and F.I. Sonntag, *J. Amer. Chem. Soc.*, 86 (1964) 3179.

123 E.A. Chandross, *Trans. N.Y. Acad. Sci.*, 31 (1969) 571.

124 (a) E.P. Kaplan, Z.I. Letina and A.D. Petrov, *Zh. Obshch. Khim.*, 26 (1956) 1243; *Chem. Abstr.*, 50 (1956) 14656; (b) A.D. Petrov, E.P. Kaplan, Z.I. Letina and Yu.P. Egorov, *Zh. Obshch. Khim.*, 28 (1958) 608; *Chem. Abstr.*, 52 (1958) 17168.

125 Yu. P. Egorov, E.P. Kaplan, Z.I. Letina, V.A. Shlyapochnikov and A.D. Petrov, *Zh. Obshch. Khim.*, 28 (1968) 3258; *Chem. Abstr.*, 53 (1959) 12232.

126 A.D. Petrov, E.P. Kaplan and Z.I. Letina, *Tr. Vses. Soveshch. Po Khim. Pererabotke. Neft. Uglevodorodov v Poluprod. dlya. Sinteza Volokoni Plast. Mass. Baku*, (1957) 295; *Chem. Abstr.*, 57 (1962) 14970.

127 E.P. Kaplan, Z.I. Kazakova and A.D. Petrov, *Dokl. Akad. Nauk SSSR*, 137 (1963) 606; *Chem. Abstr.*, 55 (1961) 21044.

128 (a) A.I. Shatenshtein, E.A. Yakovleva and E.S. Petrov, *Zh. Obshch. Khim.*, 32 (1962) 1350; *Chem. Abstr.*, 58 (1963) 1537; (b) E.S. Petrov, E.A. Yakovleva and A.I. Shatenshtein, *Zh. Obshch. Khim.*, 33 (1963) 107; *Chem. Abstr.*, 59 (1963) 416; (c) A.I. Shatenshtein, E.S. Petrov, M.I. Belousova, K.G. Yanova and E.A. Yakovleva, *Dokl. Akad. Nauk SSSR*, 151 (1963) 353; *Chem. Abstr.*, 59 (1963) 8769.

129 J.J. Eisch and W.C. Kaska, *J. Org. Chem.*, 27 (1962) 3745.

130 J.J. Eisch and W.C. Kaska, *Chem. Ind.*, (1961) 470.

131 J.J. Eisch, *J. Org. Chem.*, 28 (1963) 707.

132 P. Wieland and G. Anner, *Helv. Chim. Acta*, 51 (1968) 1698.

133 S.J. Cristol, P.R. Whittle and R.A. Dahl, *J. Org. Chem.*, 35 (1970) 3172.

134 S.J. Cristol and R.V. Barbour, *J. Amer. Chem. Soc.*, 88 (1966) 4262.

135 S.J. Cristol and R.W. Gleason, *J. Org. Chem.*, 34 (1969) 1762.

136 M.H. Hnoosh and R.A. Zingaro, *J. Amer. Chem. Soc.*, 92 (1970) 4388.

137 S.P. Solodovnikov, Yu.B. Zaks, S.I. Ioffe and M.I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1969) 1675; *Chem. Abstr.*, 70 (1969) 28235.

138 H.O. House and V. Kramar, *J. Org. Chem.*, 27 (1962) 4146.

139 H. Gilman and B.J. Gaj, *J. Org. Chem.*, 28 (1963) 1725.

140 W. Schlenk and E. Bergmann, *Ann.*, 464 (1928) 1.

141 G.L. Bitman, I. Skorokhodov and G. Perevalova, *Teor. Eksp. Khim.*, 6 (1970) 418; *Chem. Abstr.*, 73 (1970) 119892.

142 P. Pfeiffer and E. Lubbe, *Chem. Ber.*, 63 (1930) 762.

143 C.F. Koelsch, *J. Amer. Chem. Soc.*, 56 (1934) 1605.

144 K. Ziegler and F. Crossman, *Chem. Ber.*, 62 (1929) 1768.

145 H.F. Tseou and T.S. Chow, *J. Chinese Chem. Soc.*, 7 (1939) 27; *Chem. Abstr.*, 34 (1940) 1985.

146 G.W.H. Scherf and R.K. Brown, *Can. J. Chem.*, 38 (1960) 697, 2450.

147 K.A. Bilevick, N.N. Bobhov, V.V. Bukhtiyarov and O.Y. Okhlobystin, *Dokl. Akad. Nauk SSSR*, 174 (1967) 594; *Chem. Abstr.*, 67 (1967) 116286.

148 K.L. Kugel, W.G. Hodgson and H.R. Allcock, *Chem. Ind.*, (1962) 1649.

149 E.J. Greenhow, E.N. White and D. McNeil, *J. Chem. Soc.*, (1951) 2848.

150 H. Gilman and R.D. Gorsich, *J. Org. Chem.*, 23 (1958) 550.

151 W. Schlenk and E. Bergmann, *Chem. Ber.*, 62 (1929) 745.

152 D. Casson and B.J. Tabner, *J. Chem. Soc. (B)*, (1970) 1560.

153 D. Casson and B.J. Tabner, *J. Chem. Soc. (B)*, (1970) 1565.

154 A. Streitwieser and S. Suzuki, *Tetrahedron*, 16 (1963) 153.

155 (a) N.L. Bauld and M.S. Brown, *J. Amer. Chem. Soc.*, 89 (1967) 5413; (b) N.L. Bauld, *J. Amer. Chem. Soc.*, 86 (1964) 2305.

156 E.G. Janzen and J.G. Pacifici, *J. Amer. Chem. Soc.*, 87 (1965) 5504.

157 D. Casson and B.J. Tabner, *J. Chem. Soc. (B)*, (1971) 479.

158 E.G. Janzen and J.L. Gerlock, *J. Organometal Chem.*, 8 (1967) 354.

159 N.L. Bauld and J.H. Zoeller, Jr., *Tetrahedron Lett.*, (1967) 885.

160 F.J. Hopton and N.S. Hush, *Mol. Phys.*, 6 (1963) 209.

161 F. Gerson and B. Weidmann, *Helv. Chim. Acta*, 49 (1966) 1837.

162 I.B. Goldberg, R.F. Borch and R.J. Bolton, *Chem. Commun.*, (1969) 223.

163 E.E. van Tamelen, J.I. Brauman and L.E. Ellis, *J. Amer. Chem. Soc.*, 87 (1965) 4964.

164 E.E. van Tamelen, J.I. Brauman and L.E. Ellis, *J. Amer. Chem. Soc.*, 93 (1971) 6141.

165 W. Theilacker and E. Mollhoff, *Angew. Chem. Intern. Ed.*, 1 (1962) 596.

166 T.D. Walsh and R.T. Ross, *Tetrahedron Lett.*, (1968) 3123.
167 N.L. Bauld and F. Farr, *J. Amer. Chem. Soc.*, 91 (1969) 2788.
168 R.D. Rieke, S.E. Bales, P.M. Hudnall and C.F. Meares, *J. Amer. Chem. Soc.*, 92 (1970) 697.
169 F. Gerson, K. Mullen and E. Vogel, *Angew Chem. Intern. Ed.*, 10 (1970) 920.
170 R.H. Mitchell and V. Boekelheide, *Chem. Commun.*, (1970) 1557.
171 R.M. McQuilkin, P.F. Garrat and F. Sondheimer, *J. Amer. Chem. Soc.*, 92 (1970) 6682.
172 D.J. Cram and C.K. Dalton, *J. Amer. Chem. Soc.*, 85 (1963) 1268.
173 W. Bruning and S.I. Weissman, *J. Amer. Chem. Soc.*, 88 (1966) 373.
174 F. Gerson and W.B. Martin, Jr., *J. Amer. Chem. Soc.*, 91 (1969) 1883.
175 J.M. Pearson, D.J. Williams and M. Levy, *J. Amer. Chem. Soc.*, 93 (1971) 5478.
176 D.H. Eargle, *J. Amer. Chem. Soc.*, 86 (1964) 2567.
177 M.T. Jones, *J. Amer. Chem. Soc.*, 88 (1966) 176.
178 P. Brassem, R.E. Jesse and G.J. Hoijtink, *Mol. Phys.*, 7 (1963) 587.
179 K.W. Bowers, G.J. Nolfi, Jr., T.H. Lowry and F.D. Greene, *Tetrahedron Lett.*, (1966) 4063.
180 F. Gerson, E. Heilbronner and J. Heinzer, *Tetrahedron Lett.*, (1966) 2095.
181 K.W. Bowers and F.D. Greene, *J. Amer. Chem. Soc.*, 85 (1963) 2331.
182 W. Schlenk and E. Bergmann, *Ann.*, 479 (1930) 42, 78.
183 J.F. Garst and R.S. Cole, *J. Amer. Chem. Soc.*, 84 (1962) 4353.
184 J.F. Garst, E.R. Zabolotny and R.S. Cole, *J. Amer. Chem. Soc.*, 86 (1964) 2257.
185 J.F. Garst and E.R. Zabolotny, *J. Amer. Chem. Soc.*, 87 (1965) 495.
186 R.C. Roberts and M. Szwarc, *J. Amer. Chem. Soc.*, 87 (1965) 5542.
187 E. Bergmann and H. Weiss, *Ann.*, 480 (1930) 59.
188 E. Grovenstein, Jr., *J. Amer. Chem. Soc.*, 79 (1957) 4985.
189 R.F. Fuson, E.H. Hess and N.T. Mon, *J. Org. Chem.*, 26 (1961) 1042.
190 C.E. Frank, J.R. Leebrick, L.F. Moormeier, J.A. Scheben and O. Homberg, *J. Org. Chem.*, 26 (1961) 307.
191 D.R. Weyenberg, *J. Org. Chem.*, 30 (1965) 3236.
192 D.R. Weyenberg, L.H. Topercer and A.E. Bey, *J. Org. Chem.*, 30 (1965) 4096.
193 O.M. Nefedov, M.N. Manakov and A.D. Petrov, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1961) 1717; *Chem. Abstr.*, 56 (1962) 3504.
194 O.M. Nefedov, M.N. Manakov and A.D. Petrov, *Dokl. Akad. Nauk SSSR*, 154 (1964) 395.
195 C.L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, 66 (1962) 904.
196 T. Shimomura, J. Smid and M. Szwarc, *J. Amer. Chem. Soc.*, 89 (1967) 5743.
197 H. Pines and N.E. Sartoris, *J. Org. Chem.*, 34 (1969) 2113.
198 G.F. Wright, *J. Amer. Chem. Soc.*, 61 (1939) 2106.
199 G.S. Myers, H.H. Richmond and G.F. Wright, *J. Amer. Chem. Soc.*, 69 (1947) 710.
200 A.G. Brook, H.L. Cohen and G.F. Wright, *J. Org. Chem.*, 18 (1953) 447.
201 J.W.B. Reesor, J.G. Smith and G.F. Wright, *J. Org. Chem.*, 19 (1954) 940.
202 F. Bergmann, *J. Amer. Chem. Soc.*, 64 (1942) 69.
203 A. Alberola and M.F. Brana, *Ann. Real. Soc. Espan. Fis. Quim. Ser. B*, 63 (1967) 899; *Chem. Abstr.*, 67 (1967) 108389.
204 J.W. Burley and R.N. Young, *Chem. Commun.*, (1970) 1127, 1649.
205 J.W. Burley and R.N. Young, *J. Chem. Soc. B*, (1971) 1018.
206 A. Maercker, *Ann.*, 732 (1970) 151.
207 C.F. Koelsch and R.H. Bosenwald, *J. Amer. Chem. Soc.*, 59 (1937) 2170.
208 D.L. Skinner, D.J. Peterson and T.J. Logan, *J. Org. Chem.*, 32 (1967) 105.
209 M.A. Doran and R. Waack, *J. Organometal. Chem.*, 3 (1965) 94.
210 K. Ziegler, L. Jakob, H. Wollthan and A. Wenz, *Ann.*, 511 (1934) 64.
211 V.L. Hansley, C.E. Frank and J.F. Nobis, *U.S. Patent, 2,966,526* (1960); *Chem. Abstr.*, 55 (1961) 10393.
212 D.R. Weyenberg, L.H. Topercer and L.E. Nelson, *J. Org. Chem.*, 33 (1968) 1975.
213 G.M. Whitesides and W.J. Ehmann, *J. Org. Chem.*, 35 (1970) 3565.
214 G. Wittig and G. Klumpp, *Tetrahedron Lett.*, (1963) 607.
215 H. Hogeveen and E. de Boer, *Rec. Trav. Chim.*, 85 (1966) 1163.
216 L.L. Miller and L.J. Jacoby, *J. Amer. Chem. Soc.*, 91 (1969) 1130.
217 W.R. Moore, L.N. Bell and G.P. Daumit, *J. Amer. Chem. Soc.*, 92 (1970) 6680.
218 R. Waack, M.A. Doran and R. West, *J. Amer. Chem. Soc.*, 87 (1965) 5508.
219 W. Schlenk and E. Bergmann, *Ann.*, 463 (1928) 228.
220 D. Vorlander and C. Siebert, *Chem. Ber.*, 39 (1906) 1024.

221 A. Gulyaeva and T. Dauguleva, *Caoutchouc and Rubber (USSR)*, 1 (1937) 53; *Chem. Abstr.*, 32 (1938) 3754.
222 F. Bergmann and E. Bergmann, *J. Amer. Chem. Soc.*, 62 (1940) 1699.
223 P. Dowd, *Chem. Commun.*, (1965) 568.
224 P. Dowd, *J. Amer. Chem. Soc.*, 87 (1965) 4968.
225 R. Nahon and A.R. Day, *J. Org. Chem.*, 30 (1965) 1973.
226 R. Nahon, *Diss. Abstr.*, 25 (1965) 3846.
227 J.M. Edinger and A.R. Day, *J. Org. Chem.*, 36 (1971) 240.
228 J.M. Edinger, S.F. Sisenwine and A.R. Day, *J. Org. Chem.*, 36 (1971) 3614.
229 J.F. Sisenwine and A.R. Day, *J. Org. Chem.*, 32 (1967) 1770.
230 H.J. Dauben, Jr., and M.R. Rifi, *J. Amer. Chem. Soc.*, 85 (1963) 3041.
231 J.R. Bolton and G.K. Fraenkel, *J. Chem. Phys.*, 40 (1964) 3307.
232 N.L. Bauld and M.S. Brown, *J. Amer. Chem. Soc.*, 87 (1965) 4390.
233 N.L. Bauld and M.S. Brown, *J. Amer. Chem. Soc.*, 89 (1967) 5417.
234 V.D. Azatyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauk*, 17 (1964) 706; *Chem. Abstr.*, 63 (1965) 4323.
235 T.J. Katz and P.F. Garrat, *J. Amer. Chem. Soc.*, 88 (1964) 4876.
236 T.J. Katz and P.F. Garrat, *J. Amer. Chem. Soc.*, 88 (1964) 5194.
237 D.A. Bak and K. Conrow, *J. Org. Chem.*, 31 (1966) 3958.
238 T.S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, 89 (1967) 5868.
239 T.S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, 89 (1967) 5877.
240 T.S. Cantrell, *J. Amer. Chem. Soc.*, 92 (1970) 5480.
241 T.A. Antkowiak, *Diss. Abstr., B*, 30 (1969) 112.
242 F.J. Smentowski and G.R. Stevenson, *J. Amer. Chem. Soc.*, 89 (1967) 5120.
243 H.L. Strauss, T.J. Katz and G.K. Fraenkel, *J. Amer. Chem. Soc.*, 85 (1963) 2360.
244 F. Mares, K. Hodgson and A. Streitwieser, Jr., *J. Organometal. Chem.*, 24 (1970) C69.
245 F.J. Smentowski and G.R. Stevenson, *J. Amer. Chem. Soc.*, 91 (1969) 7401.
246 W. Roth, *Ann.*, 671 (1964) 25.
247 J.I. Brauman, J. Schwartz and E.E. van Tamelen, *J. Amer. Chem. Soc.*, 90 (1968) 5328.
248 T.J. Katz, M. Yoshida and L.C. Siew, *J. Amer. Chem. Soc.*, 87 (1965) 4516.
249 C.S. Baxter, P.J. Garrat and K.P.C. Vollhardt, *J. Amer. Chem. Soc.*, 91 (1969) 7784.
250 P. Radlick and G. Alford, *J. Amer. Chem. Soc.*, 91 (1969) 6529.
251 E.A. LaLencette and R.E. Benson, *J. Amer. Chem. Soc.*, 87 (1965) 1941.
252 M. Ogliaruso and S. Winstein, *J. Amer. Chem. Soc.*, 89 (1967) 5290.
253 M. Ogliaruso, *J. Amer. Chem. Soc.*, 92 (1970) 7490.
254 R. Rieke, M. Ogliaruso, R. McClung and S. Winstein, *J. Amer. Chem. Soc.*, 88 (1966) 4729.
255 T.I. Ito, F.C. Baldwin and W.H. Okamura, *Chem. Commun.*, (1971) 1440.
256 G. Moshuk, G. Petrowski and S. Winstein, *J. Amer. Chem. Soc.*, 90 (1968) 2179.
257 W.H. Okamura, T.I. Ito and P.M. Kellet, *Chem. Commun.*, (1971) 1317.
258 E. Bergmann and O. Zwecker, *Ann.*, 487 (1931) 155.
259 E. Bergmann and W. Schreiber, *Ann.*, 500 (1953) 118.
260 L.I. Smith and H.H. Hoehn, *J. Amer. Chem. Soc.*, 63 (1941) 1184.
261 F.C. Leavitt, T.A. Manuel and E. Johnson, *J. Amer. Chem. Soc.*, 81 (1959) 3163.
262 F.C. Leavitt, T.A. Manuel, F. Johnson, L.U. Matternas and D.S. Lehman, *J. Amer. Chem. Soc.*, 82 (1960) 5099.
263 G. Lewis, J. Jagur-Grodzinski and M. Szwarc, *J. Org. Chem.*, 35 (1970) 1702.
264 G. Levin, J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, 92 (1970) 2268.
265 H. Gilman, S.G. Cottis and W.H. Atweil, *J. Amer. Chem. Soc.*, 86 (1964) 1596, 5584.
266 D.A. Dadley and A.G. Evans, *J. Chem. Soc. B*, (1968) 107.
267 D. Dadley and A.G. Evans, *J. Chem. Soc. B*, (1967) 418.
268 V.Ya. Bogomol'nyi and B.A. Dolgoplosk, *Izv. Akad. Nauk SSSR Otdel. Khim. Nauk*, (1961) 1912; *Chem. Abstr.*, 56 (1962) 7494.
269 E.H. Braye, W. Hubel and I. Caplier, *J. Amer. Chem. Soc.*, 83 (1961) 4406.
270 K.W. Hubel, E.H. Braye and I. Caplier, *U.S. Patent, 3,151,140* (1964); *Chem. Abstr.*, 61 (1964) 16097.
271 R.A. Benkeser, R.F. Grossman and G.M. Stanton, *J. Amer. Chem. Soc.*, 84 (1962) 4723.
272 W.H. Atwell, D.R. Weyenberg and H. Gilman, *J. Org. Chem.*, 32 (1967) 885.
273 K. Ruehlmann, *Z. Chem.*, 5 (1965) 354.
274 K. Ruehlmann, V. Hagen and K. Schiller, *Z. Chem.*, 7 (1967) 353.

275 V. Hagen and K. Ruehlmann, *Z. Chem.*, 7 (1967) 462.

276 V. Hagen and K. Ruehlmann, *Z. Chem.*, 8 (1968) 262.

277 B. Resibois, C. Hode, B. Picart and J.C. Brunet, *Ann. Chim. (Paris)*, 4 (1969) 203.

278 M.D. Curtis, *J. Amer. Chem. Soc.*, 91 (1969) 6011.

279 B. Resibois and J.C. Brunet, *Ann. Chim. (Paris)*, 5 (1970) 199.

280 V. Kalyanaraman, *Ph.D. Thesis*, Indian Institute of Technology, Kanpur, 1971.

281 V. Kalyanaraman and M.V. George, unpublished results.

282 R. Balasubramanian and M.V. George, unpublished results.

283 H.E. Zimmerman and J.R. Dodd, *J. Amer. Chem. Soc.*, 92 (1970) 6507.

284 A.G. Evans, J.C. Evans, P.J. Emes and T.J. Phelan, *J. Chem. Soc. B*, (1971) 315.

285 G. Levin and M. Szwarc, *Chem. Commun.* (1971) 1029.

286 T.F. Rutledge, *J. Org. Chem.*, 22 (1957) 649.

287 R.J. Tedeschi and G.L. Moore, *U.S. Patent, 3,441,621* (1969); *Chem. Abstr.*, 71 (1969) 39137.

288 R.F. Bacon and P.C. Freer, *Philipp. J. Sci.*, 2 (1907) 67; *Chem. Abstr.*, 1 (1907) 1695.

289 I.N. Nazarov, *C.R. Acad. Sci. URSS*, 4 (1934) 288; *Chem. Abstr.*, 29 (1935) 2914.

290 (a) A.E. Favorskii and I.N. Nazarov, *C.R. Acad. Sci. Paris*, 196 (1933) 1229; (b) A.E. Favorskii and I.N. Nazarov, *Bull. Acad. Sci. URSS, Classe. Sci. Math. Nat.*, (1933) 1309; *Chem. Abstr.*, 28 (1934) 2673.

291 P.G. Stevens and J.H. Mowat, *J. Amer. Chem. Soc.*, 64 (1942) 554.

292 L. Eberson, *Acta Chem. Scand.*, 18 (1964) 1255.

293 P.D. Bartlett, T.T. Tidwell and W.P. Weber, *Tetrahedron Lett.*, (1970) 2919.

294 I.N. Nazarov, *C.R. Acad. Sci. URSS (N.S.)*, 1 (1934) 123; 2 (1936) 71; *Chem. Abstr.*, 28 (1934) 3713; 30 (1936) 5938.

295 H.J. Backer and H. Bos, *Rec. Trav. Chim. Pays Bas*, 57 (1938) 967.

296 T. John and S.T. Bowden, *J. Chem. Soc.*, (1940) 251.

297 L. Anschutz and A. Ungar, *J. Prakt. Chem.*, 156 (1940) 38.

298 M.K. Kalinowski, Z.R. Grabowski and B. Pakula, *Trans. Faraday Soc.*, 62 (1966) 918.

299 M.K. Kalinowski and Z.R. Grabowski, *Trans. Faraday Soc.*, 62 (1966) 926.

300 E.D. Venus-Danilova, *J. Gen. Chem. (USSR)*, 6 (1936) 917; *Chem. Abstr.*, 31 (1937) 665.

301 E. Beckmann and T. Paul, *Ann.*, 266 (1891) 1.

302 N. Nagai, A. Ogata and K. Takata, *J. Pharm. Soc. Japan*, No. 407 (1916) 3; *Chem. Abstr.*, 10 (1916) 1186.

303 F.F. Blicke, *J. Amer. Chem. Soc.*, 46 (1924) 2560.

304 O.L. Brady, *Sci. Progr.*, 19 (1925) 559.

305 W. Schlenk and T. Weickel, *Chem. Ber.*, 44 (1911) 1182.

306 W. Schlenk and A. Thal, *Chem. Ber.*, 46 (1913) 2840.

307 W.E. Bachmann, *J. Amer. Chem. Soc.*, 55 (1933) 1179.

308 N. Hirota and S.I. Weissman, *J. Amer. Chem. Soc.*, 86 (1964) 2538.

309 N. Hirota, *J. Amer. Chem. Soc.*, 89 (1967) 32.

310 E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, 62 (1966) 707.

311 J.F. Garst, R.A. Klein, D. Walmsley and E.R. Zabolotny, *J. Amer. Chem. Soc.*, 87 (1965) 4080.

312 E.T. Kaiser and L. Kevan, *Radical Ions*, Wiley-Interscience, New York, 1966.

313 E.L. Anderson and J.E. Casey, Jr., *J. Org. Chem.*, 30 (1965) 3959.

314 D.V. Ioffe, *Zh. Obshch. Khim.*, 34 (1964) 3900; 35 (1965) 185; *Chem. Abstr.*, 62 (1965) 904; 64 (1966) 3396.

315 V.M. Kazakova and Y.K. Syrkin, *Zh. Strukt. Khim.*, 3 (1962) 536; *Chem. Abstr.*, 58 (1963) 3022.

316 D.H. Eargle, Jr. and R. Emrich, *J. Org. Chem.*, 35 (1970) 3744.

317 N. Nazarov, *C.R. Acad. Sci. (URSS), (N.S.)*, 1 (1934) 325; *Chem. Abstr.*, 28 (1934) 4407.

318 A.A. Bothnerby, A.P. Krapcho and J.M. Van der Veen, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, 4 (1959) B17.

319 P.R. Jones and R. West, *J. Amer. Chem. Soc.*, 90 (1968) 6978.

320 W.E. Bachmann, *J. Amer. Chem. Soc.*, 55 (1933) 2827.

321 A.L. Berre and P. Goasguen, *Bull. Soc. Chim. Fr.*, (1963) 1838; *C.R. Acad. Sci. Paris*, 254 (1962) 1306.

322 G.A. Russell, A.G. Bemis, E.J. Geels, E.G. Janzen and A.J. Moye in *Oxidation of Organic Compounds*, Vol. I, American Chemical Society, Washington, 1968, p. 174.

323 J.F. Garst, D. Walmsley and W.R. Richards, *J. Org. Chem.*, 27 (1962) 2924.

324 W.F. Smith, Jr. and B.W. Rossiter, *Tetrahedron Lett.*, 25 (1969) 2059.

325 O. Samuel and R. Setton, *Bull. Soc. Chim. Fr.*, (1966) 1201.
326 P. Schorigin, *Chem. Ber.*, 41 (1908) 2711.
327 W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Chem. Ber.*, 47 (1914) 473.
328 W. Schlenk and E. Bergmann, *Ann.*, 464 (1928) 22.
329 P.J. Hamrick and C.R. Hauser, *J. Amer. Chem. Soc.*, 81 (1959) 493.
330 H.E. Bent and N.B. Keevil, *J. Amer. Chem. Soc.*, 58 (1936) 1367.
331 W.S. Murphy and D.T. Buckley, *Tetrahedron Lett.*, (1969) 2975.
332 P.J. Pearce, D.H. Richards and N.F. Scilly, *Chem. Commun.*, (1970) 1160.
333 G.O. Schenck and G. Mathias, *Tetrahedron Lett.*, (1967) 699.
334 S. Selman and J.F. Eastham, *J. Org. Chem.*, 30 (1965) 3804.
335 P. Yates, D.G. Farnum and G.H. Stout, *Chem. Ind.* (1956) 821.
336 H.E. Zaugg and R.J. Michaels, *J. Org. Chem.*, 33 (1968) 2167.
337 H.O. House, J. Riehl and C.G. Pitt, *J. Org. Chem.*, 30 (1965) 650.
338 G.A. Russell, D.F. Lawson and L.A. Ochrymowycz, *Tetrahedron*, 26 (1970) 4697.
339 J.P. Dirlam and S. Winstein, *J. Org. Chem.*, 36 (1971) 1559.
340 B.Z. Askinazi and D.V. Ioffe, *Zh. Org. Khim.*, 3 (1967) 367; *Chem. Abstr.*, 66 (1967) 115755.
341 C.E. Crawforth, C.A. Russell and O. Meth-Cohn, *Chem. Commun.*, (1970) 1406.
342 W. Heiber and R.E. Nitzschmann, *Z. Naturforsch, B*, 18 (1963) 413.
343 T. Takida and K. Noro, *Kobunshi Kagaku*, 22 (1965) 724; *Chem. Abstr.*, 64 (1966) 17726.
344 D. Brawn and I. Leoflund, *Makromol. Chem.*, 53 (1962) 219.
345 E.A. Braude, B.F. Gofton, G. Lowe and E.S. Waight, *J. Chem. Soc.*, (1956) 4054.
346 N. Bacon, S. Brewis, G.E. Usher and E.S. Waight, *J. Chem. Soc.*, (1961) 2255.
347 P. Angibeaud, M. Larcheveque, H. Normant and B. Tchoubar, *Bull. Soc. Chim. Fr.*, (1968) 595.
348 K.W. Bowers, R.W. Giese, J.N. Grimshaw, H.O. House, N.C. Kolodny, K. Kronberger and D.K. Roe, *J. Amer. Chem. Soc.*, 92 (1970) 2783.
349 H.O. House, R.W. Giese, K. Kronberger, J.P. Kaplan and J.F. Simeone, *J. Amer. Chem. Soc.*, 92 (1970) 2800.
350 T.K. Kochi, *J. Org. Chem.*, 28 (1963) 1960, 1968.
351 N.L. Bauld, *J. Amer. Chem. Soc.*, 84 (1962) 4345.
352 N.L. Bauld, *J. Amer. Chem. Soc.*, 87 (1965) 4788.
353 A.G. Evans, J.C. Evans and E.H. Godden, *Trans. Faraday Soc.*, 63 (1967) 136.
354 N.L. Bauld, *J. Amer. Chem. Soc.*, 86 (1964) 3894.
355 H. Kunimoto, *Nippon Kagaku Zasshi*, 83 (1962) 1282; *Chem. Abstr.*, 59 (1963) 11309.
356 J. Wiemann and A. Jacquet, *C.R. Acad. Sci. Ser. C*, 263 (1966) 313.
357 (a) B.J. Herold, *Tetrahedron Lett.*, (1962) 75; (*b*) *Rev. Port. Quim.*, 3 (1961) 101; *Chem. Abstr.*, 60 (1964) 13204.
358 B.J. Herold and M.E.N. Faustino, *Tetrahedron Lett.* (1968) 467.
359 B.J. Herold, *Rev. fac., Cienc. Univ. Lisboa, Ser. B*, 7 (1959–60) 155; *Chem. Abstr.*, 55 (1961) 19877.
360 B.J. Herold, A.F.N. Correia and J. dos Santos Veiga, *J. Amer. Chem. Soc.*, 87 (1965) 2661.
361 G.A. Russell, J.L. Gerlock and D.F. Lawton, *J. Amer. Chem. Soc.*, 93 (1971) 4088.
362 G.A. Guter and G.S. Hammond, *J. Amer. Chem. Soc.*, 78 (1966) 5166.
363 P. Mueller, F. Guenter, K. Scheffler, P. Ziemek and A. Riecker, *Ann.*, 688 (1965) 134.
364 V.O. Lukashevich and E.N. Dokunikhina, *Dokl. Akad. Nauk SSSR*, 167 (1966) 357; *Chem. Abstr.*, 64 (1966) 19511.
365 V.O. Lukashevich and E.N. Dokunikhina, *Dokl. Akad. Nauk SSSR*, 176 (1967) 837; *Chem. Abstr.*, 68 (1967) 78010.
366 T.L. Staples and M. Szwarc, *J. Amer. Chem. Soc.*, 92 (1970) 5022.
367 F.F. Blicke, *J. Amer. Chem. Soc.*, 47 (1925) 229.
368 J. Wiemann *et al.*, *Bull. Soc. Chim. Fr.*, (1954) 63.
369 W.H. Perkin, Jr., *J. Chem. Soc.*, 119 (1921) 1284.
370 R.I.E. Hall, *J. Chem. Soc.*, 125 (1924) 2266.
371 H. Scheibler and A.Z. Mahoub, *Chem. Ber.*, 60 (1927) 564.
372 (a) D. Vorlander and E. Rack, *Chem. Ber.*, 56 (1923) 1125; (b) D. Vorlander, E. Rack and W. Leister, *Chem. Ber.*, 56 (1923) 1131.
373 J.M. Snell and S.M. McElvain, *J. Amer. Chem. Soc.*, 53 (1931) 750.
374 For some reviews, see, (a) K.T. Finley, *Chem. Rev.*, 64 (1964) 573; (b) K.H. Kwart and K. King in S. Patai (Ed.), *The Chemistry of Carboxylic Acids and Esters*, Interscience, New York, 1969, pp. 341–373.

375 H. Scheiber, H. Ziegner and E. Peffer, *Chem. Ber.*, 55 (1922) 3921.
376 K. Ruhlmann, H. Seefluth, T. Kiriakidis, G. Michael, H. Jancke and H. Kriegsmann, *J. Organometal. Chem.*, 27 (1971) 327.
377 H.F. Tseou and Y.T. Wang, *J. Chinese Chem. Soc.*, 5 (1937) 224; *Chem. Abstr.*, 32 (1938) 530.
378 K. Bernhauer and R. Hoffmann, *J. Prakt. Chem.*, 149 (1937) 317.
379 M.A. Zakutskaya and R.A. Gudovich, *J. Gen. Chem. (USSR)*, 8 (1938) 216; *Chem. Abstr.*, 32 (1938) 5380.
380 Y. Kuo, F. Chen, C. Ainsworth and J.J. Bloomfield, *Chem. Commun.*, (1971) 136.
381 U. Schrapler and K. Ruhlmann, *Chem. Ber.*, 97 (1964) 1383.
382 K. Ruhlmann, H. Seefluth and H. Becker, *Chem. Ber.*, 100 (1967) 3820.
383 J.J. Bloomfield, *Tetrahedron Lett.*, (1968) 587.
384 I.F. Suknevich and N.F. Levkin, *J. Gen. Chem. (USSR)*, 7 (1937) 857; *Chem. Abstr.*, 31 (1937) 5760.
385 V.I. Egorova, *J. Russ. Phys. Chem. Soc.*, 60 (1928) 1199; *Chem. Abstr.*, 23 (1929) 2935.
386 A.G. Pearl, J.W. Evans and W.H. Dehn, *J. Amer. Chem. Soc.*, 60 (1938) 2478.
387 A.W. Ralston and W.M. Selby, *J. Amer. Chem. Soc.*, 61 (1939) 1019.
388 A. Marcusse and R. Wolffenstein, *Chem. Ber.*, 32 (1899) 2525.
389 E.C. Franklin and F.W. Bergstrom, *Chem. Rev.*, 35 (1944) 77.
390 H.H. Schlubach and H. Miedel, *Chem. Ber.*, 57 (1924) 1682.
391 J. Eisch and H. Gilman, *Chem. Rev.*, 57 (1957) 525.
392 T. Anderson, *Ann.*, 154 (1870) 270.
393 B. Emmert, *Chem. Ber.*, 47 (1914) 2598; 49 (1916) 1060; 50 (1917) 31.
394 B. Emmert and R. Buchert, *Chem. Ber.*, 54 (1921) 204.
395 J.W. Dodd, F.J. Hopton and N.S. Hush, *Proc. Chem. Soc.*, (1962) 61.
396 K. Holowiecki, J. Honk and M. Rozmarynowicz, *Lodz. Towarz. Nauk Wydzial III. Acta Chim.*, 9 (1964) 177; *Chem. Abstr.*, 62 (1965) 9100.
397 Imperial Chemical Industries, *Fr. Patent, 1,380,806* (1964); *Chem. Abstr.*, 62 (1965) 10418.
398 C.D. Schmulback, C.C. Hinckley and D. Wasmund, *J. Amer. Chem. Soc.*, 90 (1968) 6600.
399 M.H. Palmer, *The Structure and Reactions of Heterocyclic Compounds*, St. Martin's Press, New York, 1967, p. 57.
400 R.L. Ward, *J. Amer. Chem. Soc.*, 83 (1961) 3623.
401 C.R. Smith, *J. Amer. Chem. Soc.*, 46 (1924) 414.
402 C.R. Smith, *J. Amer. Chem. Soc.*, 53 (1931) 277.
403 K. Markau and W. Maies, *Z. Naturforsch. A*, 16 (1961) 1116.
404 H.S. Mosher in R.C. Elderfield (Ed.), *Heterocyclic Compounds, Vol. I*, Wiley, New York, 1950, p. 407.
405 A.A. Ziyaev, O.S. Otroshchenko, U.B. Leont'ev and A.S. Sadykov, *Zh. Organ. Khim.*, 1 (1965) 1884; *Chem. Abstr.*, 64 (1966) 3468.
406 P. Krumholz, *J. Amer. Chem. Soc.*, 73 (1951) 4449.
407 R. Setton, *C.R. Acad. Sci. Paris*, 244 (1957) 1205.
408 H. Schofield, *Hetero Aromatic Nitrogen Compounds-Pyrroles and Pyridines*, Butterworths, London, 1967.
409 K. Kuwata, T. Ogawa and K. Hirota, *Bull. Chem. Soc. Japan*, 34 (1961) 291.
410 V. Kalyanaraman, C.N.R. Rao and M.V. George, *J. Chem. Soc. B*, (1971) 2406.
411 H. Weidel, *Monatsh.*, 2 (1881) 491.
412 A. Ferman, *Monatsh.*, 14 (1893) 60.
413 W. Schlenk and E. Bergmann, *Ann.*, 463 (1928) 281.
414 S. Niizuma, M. Okuda and M. Koizumi, *Bull. Chem. Soc. Japan*, 41 (1968) 795.
415 A. Carrington and J. dos Santosveiga, *Mol. Phys.*, 5 (1962) 21.
416 N.M. Atherton, F. Gerson and J.N. Murrell, *Mol. Phys.*, 5 (1962) 509.
417 R.S. Hay and P.J. Pomery, *Aust. J. Chem.*, 24 (1971) 2287.
418 A. Cserhegyi, J. Chaudhuri, E. Franta, J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, 89 (1967) 7129.
419 J. Chaudhuri, S. Kume, J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, 90 (1968) 6421.
420 L. Lunazzi, A. Mangini, G.F. Pedulli and F. Taddei, *J. Chem. Soc. (B)*, (1970) 163.
421 M.J. Weiss, G.R. Allen, Jr., G.J. Gibs, C. Pidacks, J.F. Poletto and W.A. Remers in R.N. Castle (Ed.), *Topics in Heterocyclic Chemistry*, Wiley-Interscience, New York, 1969, pp. 178, 210.
422 A.M. Jones, C.A. Russell and O. Meth-Cohn, *J. Chem. Soc. (C)*, (1971) 2453.

423 S. Herzog and K. Luchder, *Z. Chem.*, 6 (1966) 474, 475, 476.

424 (a) K. Luehder, *Z. Chem.*, 7 (1967) 198; (b) K. Luehder and H. Langanke, *Z. Chem.*, 10 (1970) 74.

425 E. Proffit and F. Schneider, *Arch. Pharm.*, 289 (1956) 99.

426 W.M. Stalick and H. Pines, *J. Org. Chem.*, 35 (1970) 415.

427 R.A. Sulzback, *J. Organometal. Chem.*, 24 (1970) 307.

428 M. Itoh and S. Nagakura, *Bull. Chem. Soc. Japan*, 39 (1966) 369.

429 M. Itoh and T. Okamoto, *Chem. Pharm. Bull.*, 15 (1967) 435; *Chem. Abstr.*, 67 (1967) 43236.

430 M. Itoh, T. Okamoto and S. Nagakura, *Bull. Chem. Soc. Japan*, 36 (1963) 1665.

431 J.J. Eisch and R.M. Thompson, *J. Org. Chem.*, 27 (1962) 4171.

432 B.M. Mikhailov and A.N. Blokhina, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1950) 304; *Chem. Abstr.*, 44 (1950) 9452.

433 G. Wittig and O. Sticknoth, *Chem. Ber.*, 68 (1935) 928.

434 G. Wittig and A. Schumacker, *Chem. Ber.*, 88 (1955) 234.

435 S.S. Dua and M.V. George, *J. Organometal. Chem.*, 10 (1967) 219.

436 R. Taube and P. Meyer, *Angew. Chem. Internat. Ed.*, 5 (1966) 972.

437 H. Malkus, M.A. Battiste and R.W. White, *Chem. Commun.*, (1970) 479.

438 P.G. Grimes, *Diss. Abstr.*, 19 (1958) 454.

439 L.A. Paquette, T. Kakihana and J.F. Hansen, *Tetrahedron Lett.* (1970) 529.

440 L.A. Paquette, J.H. Hansen and T. Kakihana, *J. Amer. Chem. Soc.*, 93 (1971) 168.

441 L.A. Paquette and T. Kakihana, *J. Amer. Chem. Soc.*, 93 (1971) 174.

442 H. Gilman and D.L. Esmay, *J. Amer. Chem. Soc.*, 75 (1953) 2497.

443 A.G. Evans, P.B. Roberts and B.J. Tabner, *J. Chem. Soc. B*, (1966) 269.

444 H. Gilman and J.J. Dietrich, *J. Org. Chem.*, 22 (1957) 851.

445 L.A. Paquette and T. McCreadie, *J. Org. Chem.*, 36 (1971) 1402.

446 E. Lieber and S. Somasekhara, *Chem.Ind.*, (1958) 1367.

447 T.G. Jackson, S.R. Morris and B.W. Martin, *J. Chem. Soc.*, (C), (1969) 1728.

448 H. Gilman and J.J. Dietrich, *J. Amer. Chem. Soc.*, 80 (1958) 380.

449 K. Kuwata, H. Kawazura and K. Hirota, *Nippon Kagaku Zasshi*, 81 (1960) 1770.

450 A. Mathias and E. Warhurst, *Trans. Faraday Soc.*, 58 (1962) 943.

451 A.G. Evans and B.D. Phillips, *Chem. Ind.*, (1964) 1718.

452 S.M. Mikhailov and K.N. Kurdyumova, *Zh. Obshch. Khim.*, 25 (1955) 1734; *Chem. Abstr.*, 50 (1956) 5591.

453 J.G. Smith, *Can. J. Chem.*, 44 (1966) 59.

454 J.G. Smith and C.D. Veach, *Can. J. Chem.*, 44 (1967) 2497.

455 K. Ziegler and O. Schaffer, *Ann.*, 479 (1930) 150.

456 J.G. Smith and C.D. Veach, *Can. J. Chem.*, 44 (1966) 2245.

457 J.G. Smith, *Can. J. Chem.*, 46 (1968) 2271.

458 R. Turle and J.G. Smith, *Tetrahedron Lett.*, (1969) 2227.

459 B.M. Mikhailov and K.N. Kurdyumova, *Zh. Obshch. Khim.*, 26 (1956) 786; *Chem. Abstr.*, 50 (1956) 14656.

460 J.G. Smith and C.D. Veach, *Can. J. Chem.*, 45 (1967) 1785.

461 B.J. Macpherson and J.G. Smith, *Tetrahedron Lett.*, (1969) 3159; *Can. J. Chem.*, 48 (1970) 1904, 1915.

462 R. Jaunin and G. Sechaud, *Helv. Chim. Acta*, 37 (1954) 2088.

463 R. Jaunin and G. Sechaud, *Helv. Chim. Acta*, 39 (1956) 1257.

464 R. Jaunin and R. Holl, *Chimia*, 11 (1957) 312; *Chem. Abstr.*, 52 (1958) 6249.

465 R. Jaunin and R. Holl, *Helv. Chim. Acta*, 41 (1958) 1783.

466 R. Jaunin and J. Magnenat, *Helv. Chem. Acta*, 42 (1959) 328.

467 E.J. Macpherson and J.G. Smith, *Chem. Commun.*, (1970) 1552; *Tetrahedron*, 27 (1971) 2645.

468 E.J. Macpherson and J.G. Smith, *J. Org. Chem.*, 36 (1971) 2516.

469 V.L. Hansley, *U.S. Patent, 2,702,503* (1956); *Chem. Abstr.*, 50 (1956) 16830.

470 R. Chang, *J. Phys. Chem.*, 74 (1970) 2029.

471 H. Rosen, Y. Arad, M. Levy and D. Vosfi, *J. Amer. Chem. Soc.*, 91 (1969) 1425.

472 H. Thies, H. Schoenenberger and P.K. Qasba, *Arch. Pharm.*, 302 (1969) 803.

473 E.M. Smolin and L. Rapoport in A. Weissberger (Ed.), *The Chemistry of Heterocyclic Compounds, Vol. 13*, Interscience Publishers, New York, 1959, p. 151.

474 B. Kastening, *Electrochim. Acta*, 9 (1964) 241.

475 G.A. Russell and A.G. Bemis, *Inorg. Chem.*, 6 (1967) 403.

476 V.O. Lukashevich, *J. Gen. Chem. (USSR)*, 11 (1941) 1007; *Chem. Abstr.*, 40 (1946) 1150.
477 V.O. Lukashevich, *Ann.*, 521 (1936) 198.
478 S. Kobayashi and Y. Aoyoma, *Japan Patent, 4329* (1953); *Chem. Abstr.*, 49 (1955) 4712.
479 P.A.S. Smith, *Open Chain Nitrogen Compounds, Vol. II*, W.A. Benjamin Inc., New York, 1966, pp. 422-430.
480 A. Ishitani, K. Kuwata, H. Tsubomura and S. Nagakura, *Bull. Chem. Soc. Japan*, 36 (1963) 1357.
481 J.M. Gross, J.D. Barnes and C.N. Pillans, *J. Chem. Soc.*, (*A*), (1969) 109.
482 V. Kalyanaraman, C.N.R. Rao and M.V. George, *Tetrahedron Lett.*, (1969) 4889.
483 V. Kalyanaraman and M.V. George, in press.
484 J. Subramanian and P.T. Narasimhan, private communication.
485 A.K. Hoffmann, W.G. Hodgson and W.J. Jura, *J. Amer. Chem. Soc.*, 83 (1961) 4673.
486 A.K. Hoffmann and A.T. Henderson, *Belg. Patent 619,416* (1962); *Chem. Abstr.*, 59 (1963) 8593.
487 A.K. Hoffmann, A.M. Feldman, E. Gelblum and W.G. Hodgson, *J. Amer. Chem. Soc.*, 86 (1964) 639.
488 A.K. Hoffmann, W.G. Hodgson, D.L. Maricle and W.H. Jura, *J. Amer. Chem. Soc.*, 86 (1964) 631.
489 T. Kauffmann and S.M. Hage, *Angew. Chem. Intern. Ed.*, 2 (1963) 156.
490 T. Kauffmann, S.M. Hage and G. Buckleshauss, *Chem. Ber.*, 100 (1967) 1235.
491 J.W.B. Reesor and G.F. Wright, *J. Org. Chem.*, 22 (1957) 875.
492 G. Wittig, *Angew. Chem.*, 53 (1940) 241.
493 A.G. Evans, J.C. Evans and C.L. James, *J. Chem. Soc.* (*B*), (1967) 652.
494 A.G. Evans, J.C. Evans, P.J. Emes, C.L. James and P.J. Pomery, *J. Chem. Soc.* (*B*), (1971) 1484.
495 V. Kalyanaraman, S.S. Dua, C.N.R. Rao and M.V. George, *Tetrahedron Lett.*, (1968) 235.
496 D. Wittenberg, M.V. George, T.C. Wu, D.H. Miles and H. Gilman, *J. Amer. Chem. Soc.*, 80 (1958) 4532.
497 M.V. George, P.B. Talukdar and H. Gilman, *J. Organometal. Chem.*, 5 (1966) 397.
498 M.V. George, D. Wittenberg and H. Gilman, *J. Amer. Chem. Soc.*, 81 (1959) 361.
499 S.S. Dua and M.V. George, *J. Organometal. Chem.*, 9 (1967) 413.
500 S.S. Dua, *Ph.D. Thesis*, Indian Institute of Technology, Kanpur, 1967.
501 S. Sivaram, *M.Sc. Project*, Indian Institute of Technology, Kanpur, 1967.
502 H.F. Klein and J.F. Nixon, *Chem. Commun.*, (1971) 42.
503 A. Zweig and A.K. Hoffmann, *J. Amer. Chem. Soc.*, 85 (1963) 2736.
504 E. Muller and H. Disselhoff, *Naturwissenschaften*, 21 (1933) 661.
505 T. Kauffmann and S.M. Hage, *Angew. Chem. Intern. Ed.*, 2 (1963) 156 (a).
506 A. Luttringhaus and G.V. Suaf, *Angew. Chem.*, 51 (1938) 915.
507 P. Schorigin, *Chem. Ber.*, 56 (1923) 176; 57 (1924) 1627.
508 J. Durand, *C.R. Acad. Sci. Paris*, 172 (1921) 70.
509 D.H. Eargle, Jr., *J. Org. Chem.*, 28 (1963) 1703.
510 P. Schorigin, *Chem. Ber.*, 58 (1925) 2028; 59 (1926) 2510; 60 (1927) 2369.
511 D.R. Moore, *J. Org. Chem.*, 26 (1961) 3596.
512 H. Gilman, H.A. Mcninch and D. Wittenberg, *J. Org. Chem.*, 23 (1958) 2044.
513 J.J. Eisch and A.M. Jacobs, *J. Org. Chem.*, 28 (1963) 2145.
514 D. Seyferth and M.A. Weiner, *J. Org. Chem.*, 26 (1961) 4797.
515 W. Schlenk and E. Bergmann, *Ann.*, 464 (1928) 35.
516 C.F. Koelsch, *J. Amer. Chem. Soc.*, 56 (1934) 480.
517 D.H. Hunter and D.W. Moore, *Can. J. Chem.*, 49 (1971) 1665.
518 H. Dreyfus, F. Bryans and J.G.N. Drewitt, *U.S. Patent, 2,405,347* (1946); *Chem. Abstr.*, 41 (1947) 148.
519 M. Shostakovskii and F.P. Sidel'kovskaya, *Izv. Akad. Nauk. SSSR, Otdel. Khim. Nauk*, (1950) 641; *Chem. Abstr.*, 45 (1951) 8443.
520 A.N. Pravednikov, U.V. Kopylov, N.V. Eliseeva and N.V. Zakotova, *Zh. Org. Khim.*, 3 (1967) 776; *Chem. Abstr.*, 67 (1967) 43188.
521 D.H. Eargle and W.B. Moniz, *J. Org. Chem.*, 32 (1967) 2227.
522 J.K. Brown, D.R. Burnham and N.A.G. Rogers, *J. Chem. Soc.*, (*B*), (1969) 1149.
523 National Distillers and Chemical Corp., *Brit. Patent, 905,702* (1962); *Chem. Abstr.*, 58 (1963) 2406.
524 R.E. Goldsberry, D.E. Lewis and K. Cohn, *J. Organometal. Chem.*, 15 (1968) 491.

525 A.N. Nesmeyanov, E.G. Perevalova, Y.A. Ustynyuk, N.S. Prozorova, T.I. Tatashina and S.S. Churanov, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1966) 1646; *Chem. Abstr.*, 66 (1967) 65614.
526 C.G. Moses and E.E. Reid, *J. Amer. Chem. Soc.*, 48 (1926) 776.
527 R. Gerdil and E.A.C. Lucken, *J. Chem. Soc.* (1963) 2857, 5444; *Ann. Chim. (Rome)*, 53 (1963) 36.
528 H. Gilman and F.J. Webb, *J. Amer. Chem. Soc.*, 71 (1949) 4062.
529 A. Schonberg, E. Petersen and H. Kaltschmitt, *Chem. Ber.*, 66 (1933) 233.
530 A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, (1964) 108.
531 D.E. O'Connor and W.I. Lyness, *J. Org. Chem.*, 30 (1965) 1620.
532 K. Fuchs and P. Gross, *Chem. Ber.*, 63 (1930) 1009.
533 E.T. Kaiser, M.M. Urberg and D.H. Eargle, Jr., *J. Amer. Chem. Soc.*, 88 (1966) 1037.
534 Y. Minoura and S. Tsuboi, *J. Polymer. Sci., Part A, I*, 8 (1970) 125.
535 K. Olsson and S. Almqvist, B. Nygard and R. Anderson, *Acta Chem. Scand.*, 24 (1970) 3777.
536 G. Leandri and P. Rebora, *Experientia*, 13 (1957) 70.
537 E. Stoelzel, *Chem. Ber.*, 74 (1941) 982.
538 W. Krabbe and G. Grunwald, *Chem. Ber.*, 74 (1941) 1343.
539 D. Wittenberg and H. Gilman, *J. Org. Chem.*, 23 (1958) 1063.
540 A.D. Britt, M.M. Urberg and E.T. Kaiser, *J. Org. Chem.*, 31 (1966) 1661.
541 A.R. Lipley, V.C. Dohm and A.G. Giumanini, *J. Org. Chem.*, 34 (1969) 3042.
542 T.W. Sottery, *Diss. Abstr., B*, 27 (1967) 3469.
543 K. Issleib, *Z. Chem.*, 2 (1962) 163.
544 L. Maier in A. Cotton (Ed.), *Progr. Inorg. Chem., Vol. 5*, Interscience, New York, 1963, p. 27.
545 A.M. Aguiar, J. Beisler and A. Mills, *J. Org. Chem.*, 27 (1962) 1001.
546 A.D. Britt and E.T. Kaiser, *J. Phys. Chem.*, 69 (1965) 2775.
547 A.D. Britt and E.T. Kaiser, *J. Org. Chem.*, 31 (1966) 112.
548 A.M. Aguiar, H.J. Aguiar, T.C. Archibald and D. Daigle, *J. Organometal. Chem.*, 5 (1966) 205.
549 K. Issleib and A. Tzschach, *Chem. Ber.*, 93 (1960) 1852.
550 M.V. George, unpublished results.
551 A.M. Aguiar, J. Giacin and H.J. Greenberg, *J. Org. Chem.*, 28 (1963) 3545.
552 A.M. Aguiar, H.J. Greenberg and K.E. Rubenstein, *J. Org. Chem.*, 28 (1963) 2091.
553 P.R. Bloomfield and K. Parvin, *Chem. Ind.*, (1959) 541.
554 W. Kuchen and H. Buchwald, *Chem. Ber.*, 91 (1958) 2296.
555 R.E. Goldsberry, D.E. Lewis and K. Cohn, *J. Organometal. Chem.*, 15 (1968) 491.
556 K.S.V. Santhanam and A.J. Bard, *J. Amer. Chem. Soc.*, 90 (1968) 1118.
557 A.K. Hoffmann and A.G. Tesch, *J. Amer. Chem. Soc.*, 81 (1959) 5519.
558 H.H. Hamilton, Jr., *Diss. Abstr., B*, 30 (1969) 1035.
559 G.M. Kosolapoff and A.D. Brown, *Chem. Commun.*, (1969) 1266.
560 L.N. Parfent'ev and A.A. Shemshurin, *J. Gen. Chem. (USSR)*, 9 (1939) 865; *Chem. Abstr.*, 34 (1940) 392.
561 J.W.B. Reesor and G.F. Wright, *J. Org. Chem.*, 22 (1957) 385.
562 H. Gilman and H.J.S. Winkler, in H. Zeiss (Ed.), *Organometallic Chemistry*, Reinhold, New York, 1960, p. 270.
563 D. Wittenberg and H. Gilman, *Quart. Rev.*, 13 (1959) 116.
564 H. Gilman and G.L. Schwebke, *Advan. Organometal. Chem.*, 1 (1964) 90.
565 H. Gilman, W.H. Atwell and F.K. Cartledge, *Advan. Organometal. Chem.*, 4 (1966) 1.
566 A.G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 76 (1954) 278.
567 H. Gilman, F.W.G. Fearon and R.L. Hanell, Jr., *J. Organometal. Chem.*, 5 (1966) 592.
568 F.W.G. Fearon and H. Gilman, *J. Organometal. Chem.*, 9 (1967) 403.
569 R.A. Benkeser and R.G. Severson, *J. Amer. Chem. Soc.*, 73 (1951) 1424.
570 H. Gilman and T.C. Wu, *J. Org. Chem.*, 18 (1953) 753.
571 H. Gilman and G.D. Lichtenwalter, *J. Amer. Chem. Soc.*, 80 (1958) 608.
572 H. Gilman, K. Shiina, D. Aoki, B.J. Gaj, D. Wittenberg and T. Brennan, *J. Organometal. Chem.*, 13 (1968) 323.
573 H. Gilman, R.K. Ingham and A.G. Smith, *J. Org. Chem.*, 18 (1953) 1743.
574 L.H. Sommer and R. Mason, *J. Amer. Chem. Soc.*, 87 (1965) 1619.
575 J.J. Eisch and G. Gupta, *J. Organometal. Chem.*, 20 (1969) P9.
576 D. Wittenberg, D. Aoki and H. Gilman, *J. Amer. Chem. Soc.*, 80 (1958) 5933.
577 D. Wittenberg, M.V. George and H. Gilman, *J. Amer. Chem. Soc.*, 81 (1959) 4812.
578 H.J.S. Winkler and H. Gilman, *J. Org. Chem.*, 27 (1962) 254.

579 N.V. Eliseeva, T.L. Krasnova, A.N. Pravednikov and E.A. Chernyshev, *Teor. Eksp. Khim.*, 6 (1970) 420; *Chem. Abstr.*, 73 (1970) 120715.

580 J.W. Ryan, *Fr. Patent, 1,321,505* (1963); *Chem. Abstr.*, 59 (1963) 11562.

581 D. Seyferth, R. Suzuki and L.G. Vaughan, *J. Amer. Chem. Soc.*, 88 (1966) 286.

582 J.J. Eisch and R.J. Beuhler, *J. Org. Chem.*, 28 (1963) 2876.

583 E.A. Chernyshev and L.G. Kozhevnikova, *Dokl. Akad. Nauk SSSR*, 98 (1954) 419; *Chem. Abstr.*, 49 (1955) 12405.

584 (a) E.G. Janzen, J.B. Pickett and W.H. Atwell, *J. Organometal. Chem.*, 10 (1967) P6; (b) *J. Amer. Chem. Soc.*, 90 (1968) 2719.

585 M.N. Gudi and M.V. George, unpublished results.

586 E.G. Janzen, W.B. Harrison and J.B. Pickett, *J. Organometal. Chem.*, 20 (1969) 13.

587 R.D. Cowell, G. Urry and S.I. Weissman, *J. Amer. Chem. Soc.*, 85 (1963) 822.

588 R. West, *J. Polymer Sci. Part C*, No. 29 (1970) 65.

589 F. Wudl, R.D. Allendoerfer, J. Dimergian and J.M. Robbins, *Chem. Commun.*, (1971) 50.

590 A.L. Allred and L.W. Bush, *J. Amer. Chem. Soc.*, 90 (1968) 3352.

591 H. Gilman, M.B. Hughes and C.W. Gerow, *J. Org. Chem.*, 24 (1959) 352.

592 H. Gilman and C.W. Gerow, *J. Amer. Chem. Soc.*, 77 (1955) 4675.

593 E.J. Bulten and J.G. Noltes, *J. Organometal. Chem.*, 29 (1971) 397, 409.

594 Wm.A. Hough, L.J. Edwards and A.D. McElroy, *J. Amer. Chem. Soc.*, 78 (1956) 689; 80 (1958) 1828.

595 R.C. Pinkerton, *U.S. Patent, 3,187,014* (1965); *Chem. Abstr.*, 63 (1965) 7043.

596 H.E. Bent and M. Dorfman, *J. Amer. Chem. Soc.*, 57 (1935) 1259.

597 R.A. Bowie, O.S. Musgrave and H.R. Goldschmid, *J. Chem. Soc.* (C), (1970) 2228.

598 H.J. Shine. L.D. Hughes and P. Gesting, *J. Organometal. Chem.*, 24 (1970) 53.

599 J.E. Leffler, G.B. Watts, T. Tanigaki, E. Dolan and D.S. Miller, *J. Amer. Chem. Soc.*, 92 (1970) 6825.

600 J.E. Leffler, *U.S. Govt. Res. Develop. Rep.*, 69 (1969) 86.

601 T.V. Talalaeva and K.A. Kocheshkov, *J. Gen. Chem. (USSR)*, 8 (1938) 1831; *Chem. Abstr.*, 33 (1939) 5819.

602 J.W.B. Reesor and G.F. Wright, *J. Org. Chem.*, 22 (1957) 382.

603 D. Seyferth and T.F. Jula, *J. Organometal. Chem.*, 9 (1967) P13.

604 E. Bindschadler, *Iowa State Coll. J. Sci.*, 16 (1941) 33.

605 F. Hein and E. Nobe, *Chem. Ber.*, 75 (1942) 1744.

606 D.J. Brauer and G.D. Stuckey, *J. Amer. Chem. Soc.*, 92 (1970) 3956.

607 H. Lehmkuhl, *Angew. Chem. Intern. Ed.*, 4 (1965) 600.

608 H. Lehmkuhl, *Tetrahedron Lett.*, (1966) 2811, 2817.

609 H. Lehmkuhl, *Ann. Chim.*, 719 (1968) 20.

610 A.N. Nesmeyanov, A.E. Borisov, I.S. Savel'eva and E.I. Golebeva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1958) 1490; *Chem. Abstr.*, 53 (1959) 7973.

611 N.S. Vyazankin, G.A. Razuvaev, E.N. Gladyshev and S.P. Korneva, *J. Organometal. Chem.*, 7 (1967) 353.

612 D. Seyferth and L.D. Vaughan, *J. Organometal. Chem.*, 5 (1966) 580.