# HEAVIER ALKALI METALS
## ANNUAL SURVEY COVERING THE YEAR 1976

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CONTENTS

## 1. REVIEWS AND BOOKS

The current state of research on solvated electrons has been discussed in a recent nine-chapter book [1].

Reviews devoted at least in part to heavier alkali metals included:

- Distinguishing between concerted and nonconcerted reactions [2].
- The acyloin condensation [3].
- Annulation [4].
- The Robinson annelation and related reactions [5].
- Pericyclic synthesis and study of select π-Frames [6].
- Name reactions in organosulfur chemistry [7].
- Metalloboranes derived from $B_3H_8^-$, and $B_9H_{14}^-$ [8].
- Organic derivatives of niobium (V) and tantalum (V) [9].
- Silylation of organic compounds [10].
- Organotin phosphines, arsines, stibines, and bismuthines [11].

## 2. PHYSICAL ORGANIC CHEMISTRY

Acidities of organic acids continued to be studied in 1976. Thus, the acidity constants of a large number of compounds ranging from polynitrodiphenylamines to substituted fluorenes in DMSO-water have been determined using ionization ratio measurements employing small amounts of base [12]. A determination of the equilibrium acidities of 2-, 2,7-, and 2,9-substituted fluorenes revealed that the effect of a second functional group, for example, cyanide, is substantially less than additive by 0.5-0.3 pK units [13]. Such results are ascribed to a resonance saturation effect even when the substituents are widely separated so that steric inhibition to resonance can not prevail. In the case of 9-thioalkylfluorenes, 1, G = S, the order of acidities is t-BuS > i-PrS > EtS > MeS, the same as that found with sulfonyl (1, G = $SO_2$) and alkylmethylene (1, G = $CH_2$) substituents [14]. These results are in marked contrast to 2 where the order of acidities is Me > Et > i-Pr > t-Bu.

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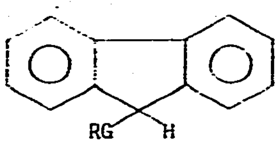
Annual Survey covering the year 1975 see J.Organometal. Chem., 130(1977) 133-155.



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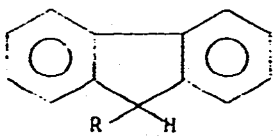
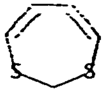


2

A new method to determine ion pair equilibrium acidities has been described involving competition of two carbon acids for phenylsodium chelated by a diamine in hydrocarbon solvents [15]. The procedure is thus less limited by the acidity of the solvent than earlier ones.

The pKa of cyclopentadiene in water has been determined to be 16.0 by dissolving the hydrocarbon in this solvent and ionizing it with sodium hydroxide [16]. This value is compared to that of 16.65 established using cesium cyclohexylamide in cyclohexylamine. The latter system was also employed to determine the equilibrium acidities of several fluorinated bicycloheptanes and bicyclooctanes [17]. Kinetic acidities of these hydrocarbons were also obtained using sodium methoxide catalyzed tritium exchange in methanol.

Both the thermodynamic and kinetic acidities of 3, 4 and 5 were determined in an effort to determine if the anion 6 from 3 is aromatic [18]. The enhanced acidities of 3 suggest that 6 represents a $10\pi$-heteroaromatic system though the degree of aromaticity is probably small.



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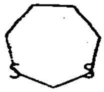

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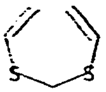

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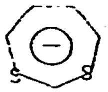
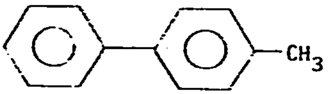


6

That the cesium salt of 7 but not the cesium salts of 8 and diphenylmethane react with hydrogen in cyclohexylamine has been taken as evidence that the acidity of hydrogen is intermediate between 7 and 8 [19]. It is suggested that the pKa of hydrogen is approximately 38. Similar results were obtained using potassium salts [20].



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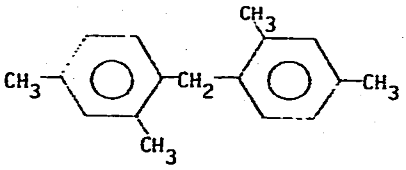

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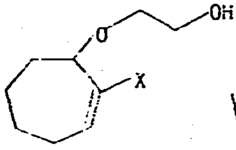
Acidities have also been determined for α-heteroatomic monosubstituted acetylenes [21], certain phosphorus-containing compounds [22], and substituted α-phenylsulfinylacetophenones [23].

A large number of papers were concerned with metalation or ionization of carbon-hydrogen bonds and the subsequent chemistry derived from this. Thus, seven fluoroethanes have been reacted with strong bases in the gas phase to afford products from elimination and proton transfer as determined by ion cyclotron resonance [24]. The amount of proton transfer decreased relative to elimination as the base strength was decreased.

Cycloheptatriene has been found to be the major product in the reaction of 9 with potassium t-butoxide in DMSO or THF [25]. Compounds 10-12 are proposed as intermediates in the process. Other products as well as related chemistry of a similar bicyclooctane are discussed.



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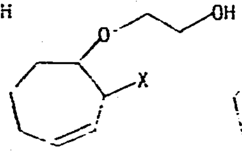
(X=Br,Cl)



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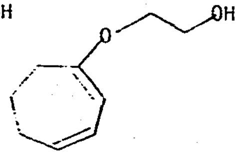

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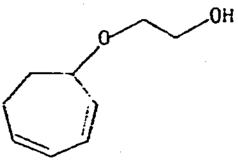

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Deuterium labeling studies have been performed on bicyclic 13 to demonstrate that, upon treatment with potassium t-butoxide, the formation of fulvene 14 occurs via hexatriene 15 without skeletal rearrangement [26]. In a second paper, the pKa of 15 has been estimated as being approximately 40-41, slightly less than that of benzene [27].

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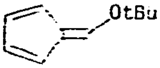

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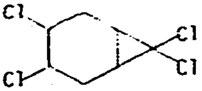
The dehydrohalogenation of 16 by potassium t-butoxide has been reinvestigated and the structure of the product said to be 17 rather than the previously suggested 18 [28]. Also, a birdcage alcohol has been found to undergo ring opening by this same base to a ketone with retention of configuration, not by the previously predicted inversion of configuration [29].



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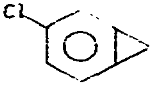

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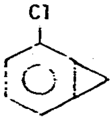
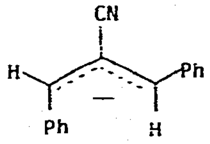


18

Topomerization between 19 and 20, formed by ring opening of cyclopropyl derivative 21, occurs via bond rotation through 22, not by ring closure to 21 [30]. This conclusion is supported by MINDO/3 and STO-3G calculations, absence of a metallic cation effect in the nmr spectra, and $\Delta G^{\ddagger}$ values. Anion 22 has been trapped with acenaphthene. Incidentally, isomerization of non-cyanide containing cyclopropanes 23 and 24 effected by potassium t-butoxide proceed via a protophilic mechanism [31].



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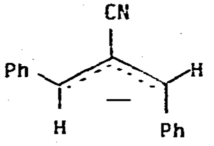

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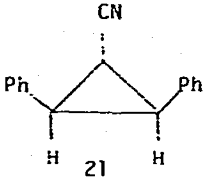

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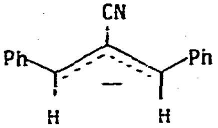

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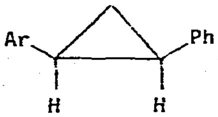

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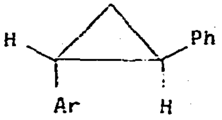

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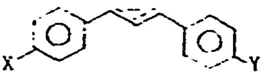
A wide variety of 1,3-diarylpropenes have been converted to their anions (25,26) in liquid ammonia and studied as a function of X and Y by uv, proton nmr, $^{13}C$ nmr, and by kinetically controlled protonations with methanol or ammonium chloride [32-34]. It was found that contact ion pairs are not formed in ammonia and that the systems consisted of more 25 than 26. The barrier to rotation of a phenyl group, 10.9 kcal/mole, is virtually independent of the metallic cation. Protonation of such ions gives mixtures of olefins which can be correlated with the local charges on the benzylic positions.



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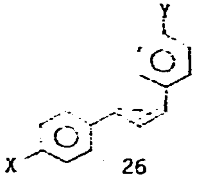
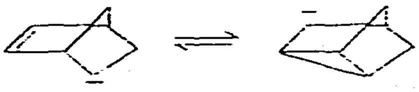


26

Reduction of norbornadiene by sodium in ammonia-$d_3$ and methanol-O-d at -33° has led to the conclusion that intermediate carbanions in this system are best described as equilibrating anions 27 and 28 rather than nonclassical anion 29 [35]. Similar conclusions are reached in the case of the related benzonorbornene.



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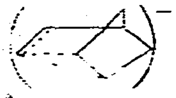
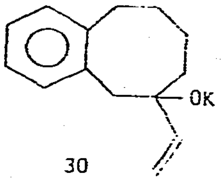


29

Several isomerization studies were described including the conversion of cis- to trans-dienoic esters by potassium t-butoxide/transition metals in HMPA [36], the equilibria between α,β- and β,γ-unsaturated ketones [37], and between certain monoacetylenes [38] using potassium t-butoxide and dimsyl carbanion, respectively, and the conversion of acetylenic alcohols to alkyn-1-ols using potassium 3-aminopropylamide [39,40]. The first [1,3] shifts of oxy-Cope systems occurring at room temperature were also discussed [41]. The process is illustrated by the rearrangement of 30 to 31.



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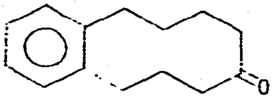

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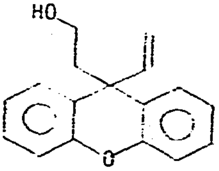
Dialkylation of sodioxanthene unexpectedly gave alcohol 32 apparently via 33 and 34 [42]. Related vinyl migrations were observed in the corresponding thioxanthene and N-methylacridine systems.



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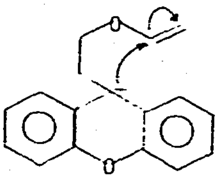

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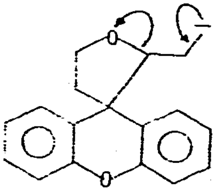
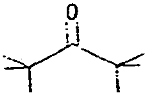


34

The first examples of skeletal rearrangements through homoenolizable methyl groups have now been reported [43]. The process is illustrated by the conversion of 35 to 37 via 36 effected by potassium t-butoxide. In another study, camphor (38), 39, and 40 have been interconverted by the above base at 185-250° demonstrating that homoenolates can be formed even in the presence of enolizable protons [44]. The interconversion of 39 and 40 shows that epimerization can be realized at a homoenolic site . Other examples are listed.



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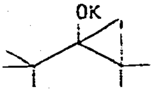

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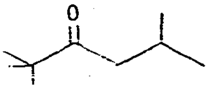

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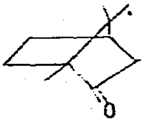

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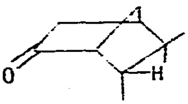

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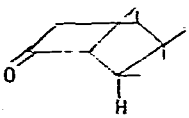

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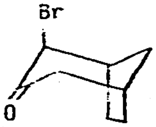
The concentration of base and the choice of solvent have been shown to be critical in the Favorskii rearrangement of bromoketone 41 [45,46]. Thus, the use of 0.089 M sodium methoxide in DME gave only the Favorskii product 42 [45]. In contrast, the use of 0.089-0.1 M sodium methoxide in methanol afforded mostly [45] or exclusively [46] axial substitution product 43. Finally, the use of

2.2 and 2.0 M sodium methoxide in methanol seems contradictory since such concentrations are said to afford mostly axial product 43 [45] and equitorial product 44 [46], respectively. Both papers describe similar chmeistry on other bromoketones. Additional papers in this area discuss the trapping of α'-enolates in such reactions by molecular oxygen [47] and the mechanism of the conversion of 1,1,1-trichloro-2-penten-4-one to 5-chloro-2,4-pentadienoic acid effected by hydroxide ion [48].



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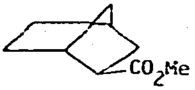

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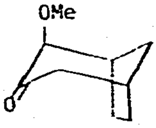

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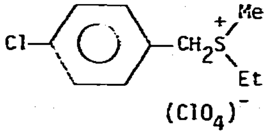
44

Asymmetric induction was observed in the Sommelet rearrangement of sulfonium salt (+)-45 to 46 and (+)-47 [49].



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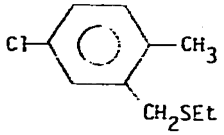

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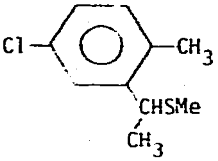

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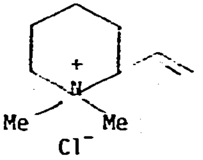
The Sommelet-Hauser rearrangement of 48 to 49 has been effected by sodium amide [50]. The related reaction of smaller ring system 50 proceeds similarly but in lower yield.



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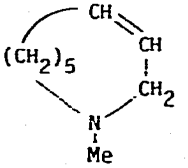

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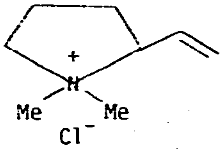

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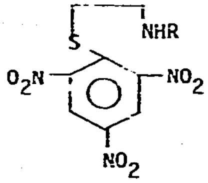
Finally, in work related to the Smiles rearrangement, a rather remarkable solvent effect has been observed in the reaction of 51 with potassium t-butoxide [51]. Thus, the use of t-butyl alcohol and THF results in the formation of 52 and 53, respectively. The choice of base in these reactions is also important. The existence of spiro-complex 54 in the presence of potasium t-butoxide has been demonstrated by nmr.



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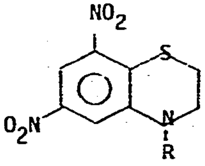

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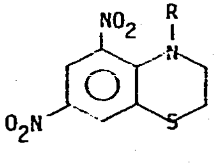

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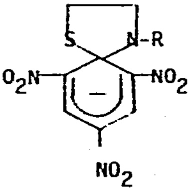
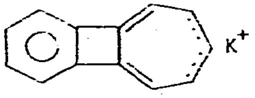


54

Turning to the area of spectroscopy itself, 'H nmr along with charge density calculations using the HMO ω-technique have been investigated for anion 55 [52]. The authors conclude that 55 behaves as both a peripheral 4n+2 and as a local 4n π-system and thus displays properties characteristic of both aromatic and anti-aromatic π-electron systems. The 'H nmr spectra of alkali aryl acetylenes [53] and of acetylacetonate anions [54] have also been described. In the former case, this spectroscopy confirms that such propargylic anions are delocalized approximately half into aryl rings and half at the terminal acetylenic carbon atom. In the latter case, various conformations are observed as a function of cation and solvent.



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The stereochemistry of 1-alkylallylpotassium reagents 56 (Z) and 57 (E) was studied by $^{13}C$ nmr [55]. Only 56 was observed when R = Me while only 57 was present when R = t-Bu. Similar spectra have also been recorded for dianions 58 (G = CN, H, and/or $CO_2CH_3$) [56], Meisenheimer complexes derived from a furazan and a furoxan [57] and certain anisoles [58], hetero[9]annulene 59 [59], and various mono- and dianions of isomeric diphenylcarboranes [60]. Dianion 58 has been oxidized to its radical-anion and its esr spectrum recorded [61].

56

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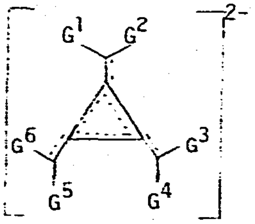

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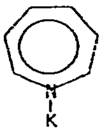

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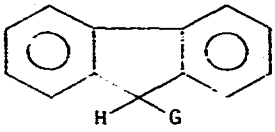
Four other papers describing nmr should be of interest to organometallic chemists even though the papers do not deal with carbon-metal bonds. Thus, $^{23}Na$-nmr has been employed to establish tetracoordination of $Na^+$ in mixtures of ether and alcohols [62], to confirm the presence of single bicyclic intermediates in the competition of glyme ethers with tetrahydrofuryl alcohol [63], and to determine interactions between sugars and sodium cations [64]. Complexes between cesium cation and crowns and cryptates have been studied using $^{133}Cs$ nmr [65].

Equilibria between the radical anion and dianion of cyclooctatetraenes [66,67], the p-nitrobenzene anion radical and its neutral molecule [66], and 2,4-di-t-butylbenzoquinone anion radical and its neutral molecule [68] have been studied with the aid of esr spectroscopy. In the first two pairs of compounds, electron transfer was decreased by the addition of potassium iodide in HMPA and was related to ion pair dissociation constants.

Spin-lattice relaxation times have been measured for alkali tetracyanoethylenes and the neutral olefin [69,70]. In one paper, the authors conclude the "observed electron spin-lattice relaxation time is the same as the intrinsic electron spin-lattice relaxation time of the radical ion" [69]. Hyperfine splittings have been studied for the above radical anions in the presence of crowns and cryptates [70].

The species responsible for esr hyperfine structure from solutions of alkali metals in ethylamine and THF are said to be the same ones responsible for new transient optical bonds obtained by pulse radiolysis of such solutions [71].

Treatment of fluorene derivatives 60 with potassium methoxide and aromatic nitro compounds has afforded a variety of compounds, including dimers 61, nitrones, azoxy compounds, and others [72]. The reactions have been shown to proceed via fluorenyl radicals.



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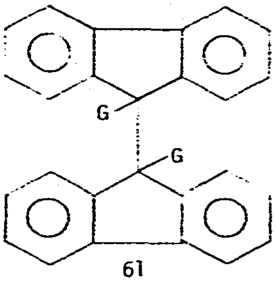

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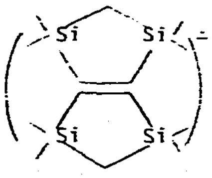
A variety of aromatic polyradical anions and the radical anions of their monomers have been prepared in DME by reduction with potassium in order to study the decomposition products of such compounds [73]. The authors indicated that in nearly all cases, the ultimate reaction mixtures displayed epr signals of the parent hydrocarbon ring systems. A few of the systems studied were biphenyl, 4-vinylbiphenyl, and poly(4-vinylbiphenyl).

Other systems derived from aromatics and studied by esr included the radical anion of benzo[b]biphenylene as a test for HMO models of biphenylene and its derivatives [74], ring inversion in the radical anions of peri-bridged naphthalenes and singly bridged biphenyls [75], racemization of the radical anions of 1,1'-binaphthyl and 9,10-dihydro-3,4;5,6-dibenzophenanthrene [76], ion pairs from the radical anion of [2.2] paracyclophane and the potassium cation [77] and the $\pi$-spin distribution in this compound and some of its symmetric benzo derivatives [78], and radical anions derived from alkylpyrazines [79], 2,7-diazapyrene [80], thiadiazolothiadiazole and related sulfur-nitrogen heterocycles [81], and of [16]annulene [82].

Esr spectra have also been recorded for tetrasilyethylene 62 [83], phenylcyclobutadienequinone (63) [84], and the radical anions of several alkylbenzophenones [85], thioxanthen S,S-dioxide and its 9-substituted derivatives [86], transition metal complexes like 64 (M = Cr, Mo, and W) [87], and metallepins like 65 and related compounds [88].



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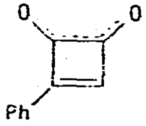

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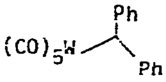

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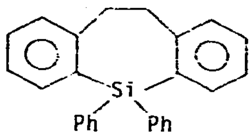
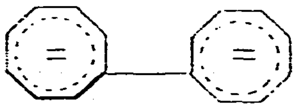


65

Other spectral investigations of carbanions were concerned with photoionization of dialkali cyclooctatetraene to give triple ions $2M^+$ and $COT^-$ which were further converted to $M^+$ $COT^-$ ion pairs and free $COT^-$ ions [89], ir studies of alkali salts of ethylene- and butadiene-methacrylic acid copolymers [90] and for m- and p-substituted alkaliphenylacetonitriles [91], voltammetry of tetranion 66 [92] and of reduction products of 67 (M = Si, Ge, Sn) [93], the pulse radiolytic formation of Na anion from alkali metal-sodium cation solutions in ethylamine [94], the magnetic circular dichroic spectra of diphenylmethide [95], and the use of esca spectroscopy to study the Lewis base properties of potassium-graphite [96].



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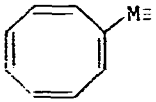

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The results of studies of gas phase ion-molecule equilibria of alkali cations-acetonitrile (Eq. 1) [97] and alkali cations-ammonia, amines, water, and ethers (Eq. 2) [98] were described. In each case, free energies, enthalpies, and entropies were calculated. For low values of n, acetonitrile gives stronger binding than does water.

$$M^+(CH_3CN)_{n-1} + CH_3CN = M^+(CH_3CN)_n \qquad (1)$$

$$M^+(GR_2)_{n-1} + GH_2 = M^+(GR_2)_n \qquad (2)$$

$$(G = O,\ N;\ R = H \text{ or carbon})$$

The free energies and free energies of activation for ion pairing of potassium p-cyanonitrobenzene radical anion and for hydrogen bonding of this species with methanol have been determined [99]. It was found that the $\Delta G°$ is smaller and the rate of formation faster for the ion pair than for the hydrogen bonded species.

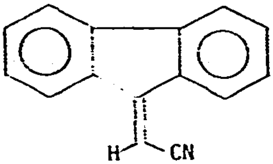
The disproportionation of sodium tetracenide ($Na^+Te^{\dot{-}}$) has been studied and the equilibrium found to be represented by Eq. 3 where n is probably 2 [100]. The disproportionation constant is dramatically affected by THF being 400 at low THF concentration and $10^{-5}$ in THF alone. The kinetics are also described.

$$2Te^{\dot{-}}, Na^+, (THF)_n \rightleftarrows Te + Te^{=}, 2Na^+, (THF)_{2n-2} + 2THF \qquad (3)$$

n-Hexyl iodides, bromides, and chlorides have now been reduced by a larger number of radical anions, namely those derived from biphenyl, naphthalene, pyrene, anthracene, fluoranthracene, and perylene [101]. That plots of the log of the rates versus reduction potentials and versus carbon-halogen bond strength are not linear is ascribed to changes in the position of the transition state in proceeding from highly exothermic to less exothermic reactions.

The activation volume of a series of second order elimination reactions have been determined as a means of differentiating between $E_2$ and $E_{1cb}$ mechanisms [102]. It was found that $\Delta V^*$ is negative for the former and positive for the latter, respectively.

Nitriles 68 and 69 have been treated with sodium ethoxide in ethanol-O-d to afford recovered nitriles containing vinyl deuterium atoms [103,104]. Such compounds are said to arise via vinyl carbanions rather than by an addition-elimination mechanism. Nitrile 69 also gave some addition product as well as trans-cis isomerization, the latter process occurring via addition-elimination. The H-D exchange process is faster than the addition reaction. Other rates are discussed.



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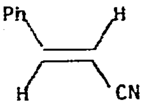
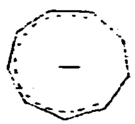


69

Other kinetic studies considered elimination reactions of 2-aryl-1-haloethanes by alkali t-butoxides complexed with 18-crown-6 [105], the formation of 1,4-dihydropyridines from acylpyridinium salts and certain carbanions [106], the preparation of Meisenheimer complexes from 1,3,5-trinitrobenzene and carbanions [107], C-arylation of sodio-N,N-dimethylcyanoacetamide with halonitrobenzenes [108], alkylation of sodioethyl acetoacetate in the presence of 18-crown-6 and a cryptate [109], autoxidation and Michael addition to several α,β-unsaturated esters of sodiofluorenes [110], and intramolecular condensations in aromatic ketoesters [111].

Protonation and alkylation of 70, 71 and 72 have been found to occur at the 3- and 5-positions which are the sites of highest electron density [112]. For example, methylation of 72 afforded a mixture of 73 and 74. Stereo- and regioselectivities in these systems is discussed. In a different paper, enolate 75 has been alkylated with certain ethylating agents and the amount of

C versus O alkylation studied as a function of the presence or absence of certain cryptates [113]. The enolate reacts with ethyl iodide mostly as free ion and with ethyl tosylate both as free ion and as ion pair.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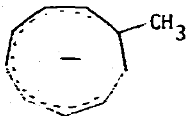
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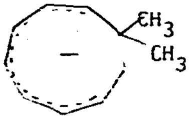
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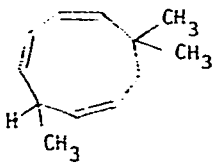
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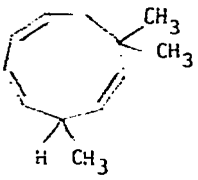
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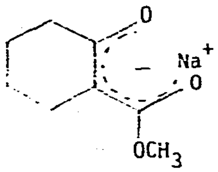
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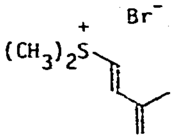
Potassiodimethyl malonate has been reacted with sulfonium salt 76 to give vinylcyclopropane 77 [114]. The reaction is said to occur via 78. Another example of heterophilic addition has been reported in the reaction of thiofluorenone (79) to yield 80 and 81 [115].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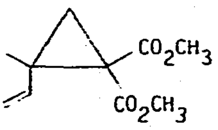
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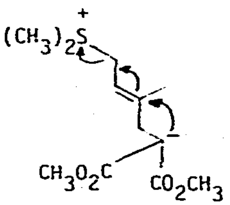
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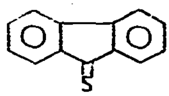
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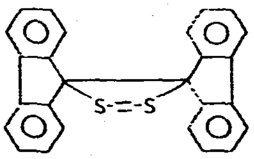
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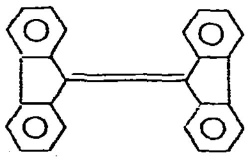
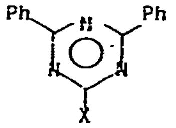

81

Several papers discussed reactions involving nucleophilic aromatic substitution. Those involving stimulation by light or alkali metals ($S_{RN}1$ mechanism) included the reaction of 1-halonaphthalenes with nucleophiles [116], arylation of ketone enolates [117], an esr study of the kinetics of the interaction of aryl halides with potassium [118], arylations of cyanomethide [119], and reactions of halothiophenes with acetone enolate and amide ions [120]. Others dealt with the occurrence of the $S_N$(ANRORC) mechanism in the amination of triazines 82 [121], the presence of didehydropyridazine 83 in the amination of 84 [122], and evidence for the intermediacy of 85 in the reaction of 86 with potassium t-butoxide [123].



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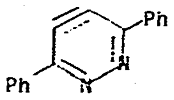

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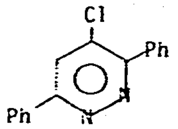

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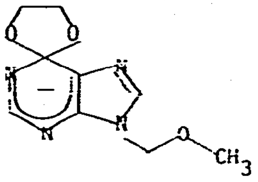

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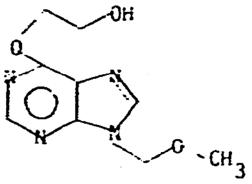
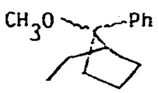


86

In the area of polymer chemistry, the use of a cryptate in the anionic polymerization of styrene by alkali metals gives $\bar{M}n$ values higher than expected from the concentration of $e^-$ and $M^-$ in solution [124]. Stereoregularity in the synthesis of polystyrenes effected by alkali naphthalenes has been studied by $^{13}C$ nmr as a function of cation, solvent, and temperature [125]. The kinetics of the anionic polymerization of α-methylstyrene [126], the solvent and metallic cation effects in the polymerization of α,α-disubstituted β-propiolactones [127], and the polymerization of methyl methacrylate using disodio oligomeric α-methylstyrene [128] have also been discussed.

Other papers appropriate for this section include structural determinations on bis(diacetamide)(perchlorato)sodium (I) [129], potassium amide [130], and cyclopentadienylsodium-TMEDA [131], the heats of formation of disodio- and dipotassiocyclooctatetraenide [132,133], a room temperature retro-Dels-Alder reaction of 87 by NaK in DME to afford 88 [134], bridged radicals in the reactions of sodium naphthalene with dichlorodiphenylmethane and 9,9-dichlorofluorene [135], and the demonstration of the presence of carbanions and carbenes in the reactions of chloromethanes with trimethylstannylsodium [136].



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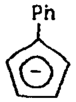
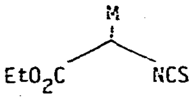


88

## 3. SYNTHESIS

Several papers described additional examples or more specifics in the chemistry of α-metalated α-isothiocyanatoesters 89. That 89 acts like 2-aza-allyl anions has been demonstrated by alkylation with several alkyl halides to give 90 and 91 [137]. Condensations of 89 with aldehydes and ketones affords thioxo-oxazolidines 92 [138] which have also been converted into 93 [139], 94 [140], and 95 [141]. Preparation of systems like 96 (G = $CO_2Me$) from 97 are also described [142]. Metalated ethyl isocyanoate has been employed to synthesize a pregnatetraene [143].



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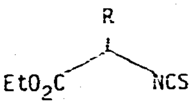

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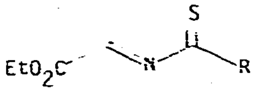

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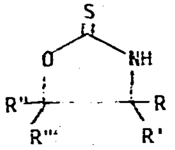

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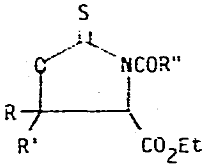

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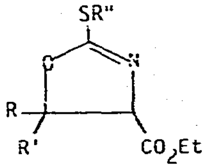

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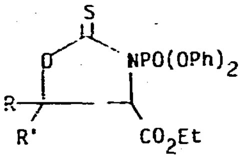

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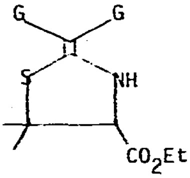

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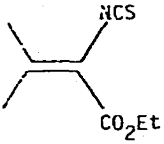
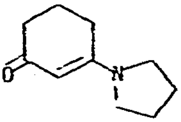


97

Several vinylogous amides like 98 have been alkylated using potassium hydride to give γ-products like 99 [144]. Similar reactions on 100 where G= O and S yield α,α,α',α'- and α,α-polyalkylated products, respectively.



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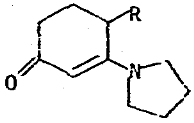

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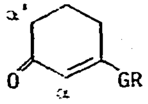
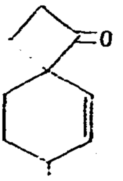


100

Several cyclobutanones have been bissulfenylated by diphenyl disulfide in the presence of sodium methoxide; the latter reagent cleaves the ketones in situ to esters [145]. The process is illustrated by the conversion of 101 to 103 via 102.



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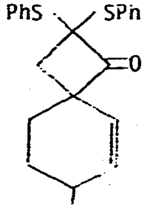

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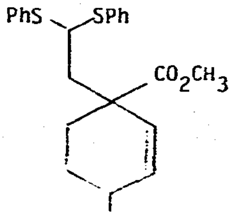
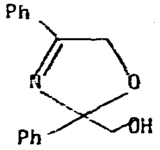


103

The interaction of α-chloroketones with sodium or lithium amide in ammonia affords oxazolines [146]. For example, phenacyl chloride gives 104 perhaps via 105 and 106.



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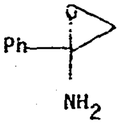

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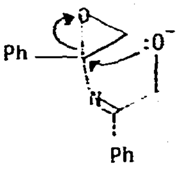
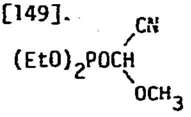


106

Other species metalated then condensed with electrophiles have included organomethylphosphonates like 107 to prepare α-alkoxyacrylonitriles [147], 3-coordinate phosphorous-containing easters like 108 to synthesize O-silyl and germyl phosphineesters [148], and dithioacetate 109 as a source of α-ketoesters [149].



$(\mathrm{EtO})_2\mathrm{POCH}(\mathrm{CN})(\mathrm{OCH_3})$

107

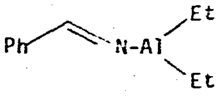
$R_2PCH_2CO_2R'$

108

$(\mathrm{EtS})_2\mathrm{CHCO_2CH_3}$

109

*In the area of nitranions*, imine 110 has been reduced to 111 by potassium metal in the presence of a catalytic amount of naphthalene [150]. Subsequent treatment with lithium bromide, electrophiles, and acid results in a convenient synthesis of amines 112 where E is derived from alkyl halides, aldehydes, ketones, carbon dioxide, epoxides, nitriles, and iodine.



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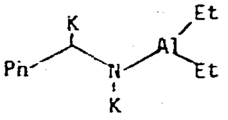

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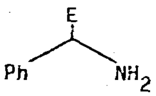
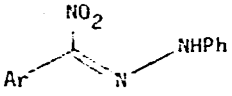


112

A variety of phenylhydrazones 113 have been converted to nitro derivatives 114 by several base systems and n-propyl nitrate [151]. Potassium ethylnitrosolate (115) and aralkyl halides have been found to afford oxadiazole-4-oxides 116 [152]. Certain potassiodinitroalkanes have been thermally decomposed to $\Delta^2$-isoxazolines 117 and potassium nitrate [153]. Sodio salt 118 has been concondensed with aldehydes and ketones to give oxiranes in good yields [154].

113



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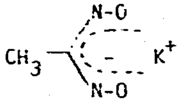

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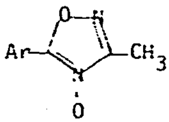

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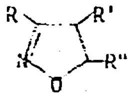

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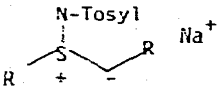
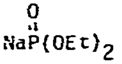


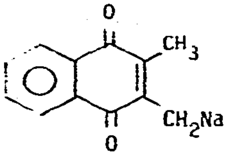
118

A new olefin synthesis has been described in which 119 is condensed with aromatic aldehydes to afford stilbenes [155]. Additional chemistry of carbanion 120 has been reported wherein this compound has been added to 2,6-dimethyl-1,4-benzoquinone [156]. Alkali diphenylmethides have been added to several α,β-unsaturated esters including methyl acrylate to give diarylated esters [157]. Thiosquarate anions like 121 and 122 readily undergo alkylation at sulfur to yield alkylthio substituted cyclobutenediones [158].



$NaP(O)(OEt)_2$

119



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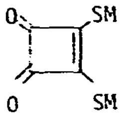

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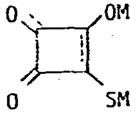
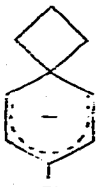


122

Carbanions 123 and 124, synthesized by cleavage of open-chain alkyl chlorides using Cs-K-Na alloy, have been trapped by carbon dioxide to afford 125 and 126, respectively [159]. At -75° in THF, the half-lives of the carbanions are 13 min. and 22 min., respectively. In an unrelated paper, it has been disclosed that aromatic $S_{RN}1$ reactions may be effected in DMSO, acetonitrile, and t-butyl alcohol as well as in the more commonly employed liquid ammonia [160].



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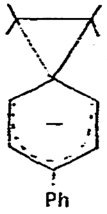

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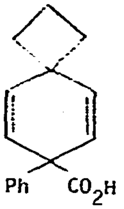

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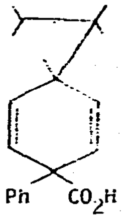
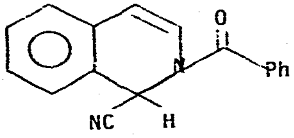


126

Several papers discussed the incorporation of Reissert compounds (127) into polymers by condensing their sodio salts with poly(vinylbenzyl chloride) [161, 162] and with polymeric aldehydes [162,163]. Ring-unsubstituted $\lambda^2$-phospha- (129, E = P) and arsabenzenes (129, E = As) have been prepared by treatment of the corresponding quaternary salts (128) with dimsylsodium [164].



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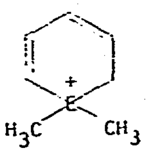

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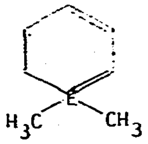
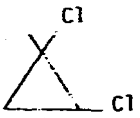


129

Several other papers involving breakage of carbon-hydrogen bonds include the use of trimethylsilylpotassium and other reagents to ionize allylic, benzylic, vinyl and cyclopropyl hydrogens [165], the preparation of lithium salt-free ylides using sodium bis(trimethylsilyl)amide [166], the synthesis of potassium and sodium derivatives of various alkylbenzenes using phenylpotassium [167] and n-pentylsodium·TMEDA [168], respectively, and the reactions of certain halonaphthyridines with potassium amide in liquid ammonia [169,170]. Certain dihalocyclopropanes like 130 have been converted to 131 apparently via the intermediacy of 132 [171,172]. Additional results in the conversion of acyclic vinyl bromides to alkylidenecarbenes [173] and cyclic vinyl halides to cycloalkynes and cycloallenes [174,175] have been described.



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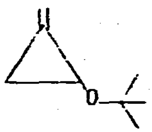


131

132

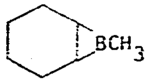
Finally, in the area of reductions, potassium-graphite combinations have been used as catalysts in the conversion of alkenes to alkanes [176] and in the dimerization of benzene to biphenyl [177]. A practical technique for effecting laboratory Birch reductions has been disclosed [178].

## 4. INORGANIC AND ORGANOMETALLIC COMPOUNDS

Methylborylene (133) has been generated from methylboron dibromide and a suitable form of potassium like $NaK_5$ and $C_8K$ [179]. Among other products, boracyclopropane 134 was obtained from 133 and cyclohexene. Cyclic boron-containing systems 135 [180] and 136 [181] have been obtained by alkali metal reduction of 137 and 138, respectively. The reaction of dibutylchloroborane with NaK and benzoyl chloride has been reinvestigated and the products identified as 139 and benzyl benzoate [182]. The authors express doubts about the formation of the previously reported 140. A variety of 9-borylfluorenes (141) have been prepared from 9-sodiofluorene and haloboranes [183].

$CH_3B:$

133



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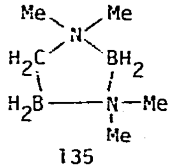

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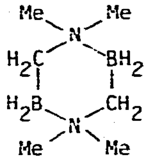


136

$[(Me_3N)_2BH_2]^+I^-$

137

$Me_3NBH_2Br$

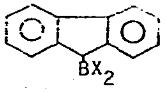
138

$(C_4H_9)_2BOCH_2Ph$

139

$(C_4H_9)_2BM$

140



141

The previously described reaction of $NaB_5H_8$, $CoCl_2$, and $NaC_5H_5$ has been shown to provide additional products, e.g., $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ [184]. Decaborane has been reacted with dihalophosphines in the presence of sodium hydride to give $7\text{-}B_{10}H_{12}PR$ (R = alkyl, aryl) [185]. Condensation of $B_5H_9$ with iron pentacarbonyl has given $B_5H_9Fe(CO)_3$ [186]. The anion of the latter species was prepared using potassium hydride at -78°.

Carboranes synthesized in 1976 included $(C_5H_5Ni)_3CB_5H_6$ [187], $(C_5H_5Ni)_3\text{-}CB_5H_5R$ (R = H or Me) [188], $(Me_2C_2B_4H_4)_2FeH_2$ [189], $Me_4C_4B_8H_8$ [189], $(C_5H_5)_2\text{-}Fe_2Me_4C_4B_8H_8$ [190], $6,6\text{-}(R_3P)_2\text{-}6\text{-}H\text{-}6,2,3\text{-}RuC_2B_7H_9$ [191], $6,6\text{-}(R_3P)_2\text{-}6,2,3\text{-}RuC_2B_7H_9$ [191], $1,1\text{-}(Ph_3P)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}IrC_2B_8H_{10}$ [191], $CB_8H_{14}$ [192], and $[M^{II}(C_2B_{10}H_{10}Me_2)_2]^{2-}$ where M = a variety of transition metals [193].

Tetraisobutyldialuminum (142) has been synthesized from diisobutylaluminum and potassium [194]. The authors discuss the stability of the aluminum-aluminum bond in terms of steric, +M, and +I effects.

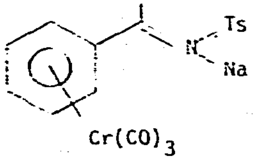
$$(i\text{-}C_4H_9)_2Al{-}Al(i\text{-}C_4H_9)_2$$

142

The first carbonyl derivatives of zirconocene and hafnocene, $(C_5H_5)_2Zr(CO)_2$ and $(C_5H_5)_2Hf(CO)_2$, respectively, have been synthesized by sodium amalgam reduction of the corresponding dichloro sandwich compounds in the presence of carbon monoxide [195]. Titanium-containing compounds prepared included $(di\text{-}\eta^5\text{-}C_5H_4(CH_2)_3C_5H_4)Ti(\eta^1\text{-}C_5H_5)_2$ from the bridged titanium dichloride and $NaC_5H_5$ [196], $(C_5H_5)_3(C_5H_4)Ti_2$ by reduction of $(C_5H_5)_2TiCl_2$ with potassium naphthalene [197], and μ-(1-3η:2-4η-trans,trans-1,4-diphenylbutadiene)-bis-(bis(η$^5$-methylcyclopentadienyl)titanium by reaction of $(CH_3C_5H_4)_2TiCl$ with $PhC{\equiv}CNa$ [198].

"Superreduced" $V(CO)_5^{3-}$ has been prepared by sodium/ammonia reduction of $V(CO)_6^-$ as evidenced by trapping experiments with triphenyltin and lead chlorides [199]. In another paper, certain carbonyl anions of V, Nb, and Ta have been synthesized by reduction of triphenylstannyl derivatives using sodium amalgam [200]. Several π-allylcarbonyl vanadium compounds, for example, $\pi\text{-}C_3H_5V(CO)_5$, have been prepared by reaction of $Na[V(CO)_6]$ with allyl halides [201]. Certain cyclopentadienylmetal carbonyls have been reduced by sodium in HMPA where the products obtained depend upon the transition metal [202]. For example, $C_5H_5V(CO)_4$ affords $C_5H_5V(CO)_3^{2-}$ while $C_5H_5Mn(CO)_3$ gives $Mn(CO)_4^{3-}$. Several cyclooctatetraene derivatives of niobium and tantalum have been synthesized from $C_8H_8K_2$ and metal chlorides [203]. For example, $Nb(C_8H_8)_2Ph$ is obtained from $C_8H_8K_2$, $NbCl_5$, and PhLi.

Transition metal carbyne complex, $(CO)_5Re\text{-}Mo(CO_4){\equiv}CPh$, has been prepared by reaction of $(CO)_5ReNa$ and $BrMo(CO)_4{\equiv}CPh$ [204]. Alkanes ($RCH_3$) and alkynes ($RC{\equiv}CH$) have been identified as products from the reaction of $(CO)_5WNa_2$ and $RCH_2COCl$ [205]. Reagents $C_5H_5M(CO)_3Na$ have been condensed at the metal with alkyl halides (M = W) [206], chloroaldehydes and chloroketones (M = Mo, W) [207], benzaldimines (M = Mo, W) [208], and phosphorus trichloride (M = Cr, Mo, W) [209]. The related compounds $C_5H_5W(CO)_2(P{\equiv})Na$ [210] and $C_5H_5Mo(CO)_2(CNR)Na$ (R = $CH_3$ [211] and Ph [212]) have also been alkylated at the transition metal. Other papers concerned with this family described the reactions with α,β-unsaturated ketones, aldehydes, and nitriles by $NaHCr_2(CO)_{10}$ [213], the thermolysis of sodium salt 143 to give carbene 144 and products derived from it [214], the preparation of five-membered rings containing molybdenum and arsenic [215], and the use of cyclopentadienylsodium and phenylethylsodium as co-catalysts with $WCl_6$ in homogeneous olefin metatheses [216].



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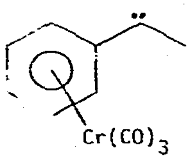
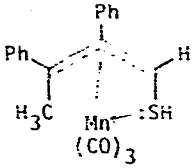


144

Alkalimanganese pentacarbonyl has been condensed with 145 and methyl iodide to afford 146 [217] and with thiobenzophenones to give $[Ar_2CHSMn(CO)_4]_2$ [218]. Species $(Mn(CO)_4CNCH_3)Na$ has been alkylated on the manganese by a variety of alkyl and group IV halides [219].

145



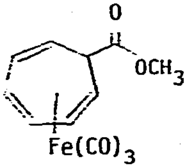
146

The crystal structure of disodium tetracarbonylferrate complexed with 1.5 dioxane has been determined and the anion found to be significantly distorted from tetrahedral symmetry [220]. This species has been employed to convert aryl and thiolic esters to aldehydes [221] and aromatic aldehydes to esters [222]. $\alpha,\beta$-Unsaturated esters, ketones, and nitriles have been reduced to the saturated analogues by $NaHFe_2(CO)_8$ [223]. Acyl carbonylferrates (0), $RCOFe(CO)_4M$, have been found useful in the conversion of nitro compounds $R'NO_2$ to amides RCONHR' [224].

The complex $Os_6(CO)_{18}$ has been reacted with $Os_3(CO)_{11}HNa$ and methanolic potassium hydroxide to afford $HOs_3(CO)_{10}\cdot O_2C\cdot Os_6(CO)_{17}^-$ [225] and $Os_5(CO)_{15}^{2-}$ [226], respectively. Similarly, reaction of $Ru_3(CO)_{12}$ with $NaMn(CO)_5$ gives $NaHRu_6(CO)_{18}$ [227].

A large number of papers were concerned with $\eta^5$-$C_5H_5Fe(CO)_2Na$. The infrared spectra of this compound in ethers revealed the presence of three ion pair species due to sodium-iron and sodium-oxygen interactions and to a solvent separated system [228]. This compound has been converted to a variety of carbon-iron systems by condensations with cis-3,4-dichlorocyclobutene [229], adamantyl halides and carbonyl chloride [230], allyl halides and tosylates [231], 1,4-dichloro-2-butyne and the corresponding dibenzenesulfonate [232], $(CF_3)_2C{=}C{=}C(CF_3)_2$ [233,234], menthyl systems to give chiral iron alkyl complexes [235], chloroacetylferrocene [236], and carbon disulfide [237]. The iron reagent has also been reacted with halophosphines and tetraphenylphosphonium salts to give iron-phosphorus systems [238] and $PhFe(CO)_2C_5H_5$ [239], respectively.

Reduction of $\eta^3$-$C_3H_5Fe(CO)_2PPh_3Br$ by sodium amalgam gave the corresponding anion which is useful for the conversion of 1,2-dibromides to olefins [240]. In another paper, $C_7H_7Fe(CO)_3Na$ has been condensed with alkyl chloroformates to afford esters 147 and 148 [241].



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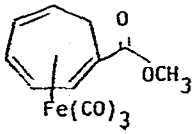
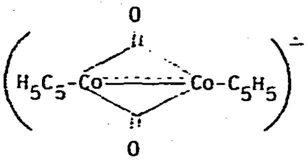


148

Treatment of $\eta^5$-$C_5H_5Co(CO)_2$ with sodium amalgam has been shown to give 149, a species with a cobalt-cobalt bond of order 1.5 [242]. The crystal and molecular structure, spectroscopic properties, and redox behavior of 149 have been reported [243].



149

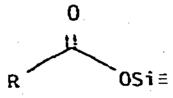
Reduction of $Ni(CO)_4$ with alkali metals under a variety of conditions has afforded $Ni_5(CO)_{12}^{2-}$ and $Ni_6(CO)_{12}^{2-}$ [244]. Reaction of the latter dianion with $Ni(CO)_4$ gives $Ni_9(CO)_{18}^{2-}$ [245]. Nickel (II) salts have been condensed with $R_2PCS_2K$ (R = alkyl, aryl) to yield $Ni(S_2CPR_2)_2$ [246]. Combination of cis-$[PtCl_2(PEt_3)_2]$ with 150 has afforded 151 [247].

150

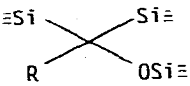
151

The first cyclopentadienylsilver compound, $\eta^5$-$C_5H_5Ag(PPh_3)$ has been prepared from cyclopentadienylsodium, $AgSO_3CF_3$, and triphenylphosphine [248]. Moreover, the first $\eta^8$-$C_8H_8$-containing derivatives of scandium, $C_8H_8ScCl\cdot$THF, $C_8H_8ScC_5H_5$, and $KSc(C_8H_8)_2$ have been synthesized from $ScCl_3$ and $K_2C_8H_8$, $C_8H_8ScCl\cdot$THF and cyclopentadienylsodium, and $C_8H_8ScCl\cdot$THF and $K_2C_8H_8$, respectively [249].

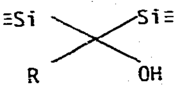
Epoxides have been deoxygenated with inversion of stereochemistry by trimethylsilylpotassium prepared in situ from hexamethyldisilane and potassium methoxide [250]. For example, trans-3-hexene epoxide affords >99% cis-3-hexene. Sterically hindered alcohols whose pKa values should lie between normal alcohols and amides have been synthesized by treating silyl esters with sodium in the presence of chlorotrimethylsilane [251]. For example, 152 gives 153 which is hydrolyzed to 154. Silicon, germanium, tin, and arsenic σ-bonded to a *monohapto-cyclonona-traenyl* system have been prepared by treating the ring carbanion with the respective metal chlorides [252]. Transition metal carbonyls bonded to germanium can be displaced by other transition metal carbonyls bonded to germanium can be displaced by other transition metal carbonyls [253]. For example, $R_3GeCo(CO)_4$ reacts with $NaMn(CO)_5$ to give $R_3GeMn(CO)_5$.



152

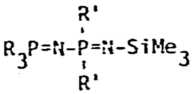


153



154

B-Nitrosamines have been synthesized by condensation of N-sodioamines with nitrosyl chloride [254]. Molecules like 155 (R = Me, Et; R' = alkyl, aryl) have been prepared by reaction of 156 with chlorophosphines, then trimethylsilylazide [255]. Diphosphine 157 has been obtained by addition of dineopentylphosphine to the β-olefinic carbon atom of dineopentylethenylphosphine (158) [256]. Alkali metal reduction of triphenylphosphine oxide in ethers has been shown to afford 159 (M = K, Rb) [257]. Finally, reaction of $C_5H_5Fe(CO)_2Na$ with $SbBr_3$ gives permetalated stibane 160 [258].



$R_3P{=}N{-}\overset{R'}{\underset{R'}{P}}{=}N{-}SiMe_3$

155

$R_3P{=}NLi$

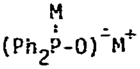
156

$[(Me_3CCH_2)_2P{-}CH_2{-}]_2$

157

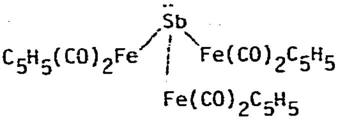
$(Me_3CCH_2)_2PCH{=}CH_2$

158



$(Ph_2\overset{M}{P}{-}O)^-M^+$

159



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