

HEAVIER ALKALI METALS

ANNUAL SURVEY COVERING THE YEAR 1980 *

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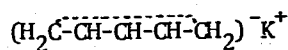
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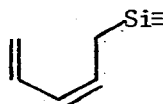
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1. PHYSICAL ORGANIC CHEMISTRY

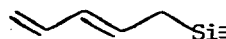
The structure of alkali derivatives of pentadiene continued to be actively studied in 1980 [1]. Thus, potassium reagent 1 in THF was found by ^1H - and ^{13}C -NMR spectroscopy to be U-shaped where the proton-proton coupling constant, J_{23} , of the 1,1,5,5-tetradeutero compound was 8.7Hz at temperatures below -30° . The results were supported by silylation of 1 to afford 2. Interestingly, 1 appears to exist in the W form in the solid state since silylation under these conditions gives 3.



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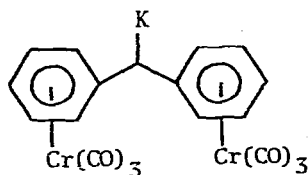
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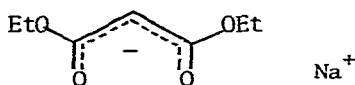
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*Previous survey see J. Organometal. Chem., 203 (1980) 149 - 181.

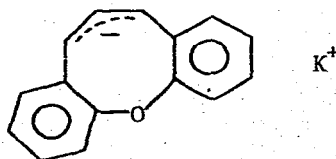
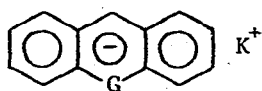
Both ^1H - and ^{13}C -NMR spectroscopy have been employed to demonstrate that chromiumdiphenylmethyl system 4 is stabilized by delocalization of the negative charge onto the carbonyl groups [2]. Direct interaction between the α -carbon atom and the chromium seems to be absent.



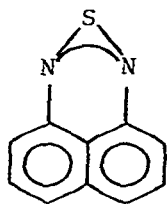
The ^1H -NMR chemical shifts of the remaining methynyl proton of *p*-substituted sodioethyl phenylacetates have been correlated using σ and σ^- substituent constants [3]. Similar correlations were realized by plotting the carbonyl stretching vibrations against these same constants. Another paper described the use of ^1H -NMR spectroscopy to determine that a variety of sodiodiethyl malonates exist in the *Z,Z*-conformation 5 ($\text{R}=\text{H}, \text{Me}, \text{Et}, \text{n-Pr}, \text{n-Bu}, \text{i-Bu}, \text{s-Bu}$) in DMSO [4]. IR data for these compounds were also reported.



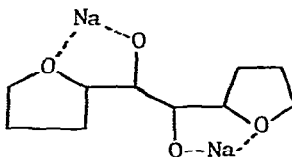
Potassium salts 6 ($\text{G}=\text{O}$) [5], ($\text{G}=\text{NMe}$ and S) [6] have been generated by treatment of the parent compounds with potassium amide in liquid ammonia and their ^1H and ^{13}C -NMR spectra obtained to reveal the existence of stable $4n\pi$ -systems. In contrast, a similar study on oxocinide ion 7 suggested that this species is a non-aromatic $(4n+2)\pi$ system where the negative charge is primarily localized in the allylic moiety [7].



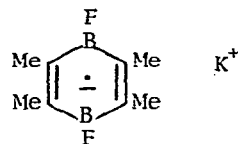
Papers in 1980 discussing ESR spectroscopy were concerned with contact ion pairs of mesitylene, m-xylene, and toluene with potassium in the neat hydrocarbons with a small amount of crown ether [8], ion pair formation of the alkali triphenylene radical anion [9], the radical anions of 5,5'-and 6,6'-biazulenyl [10], radical anions of syn- and anti-anthracenophanes [11], ^{14}N - and ^1H -ENDOR and triple resonance on azaaromatic radicals such as pyridine [12], radical anions of thiadiazines such as 8 [13], alkali metal cryptates of the 9-fluorenone radical anion [14], the sodium hyperfine splitting constant of disodiofuryl radical triple ion (9) [15], crown complexed semiquinone ion pairs in THF [16], ion pairing in cyclic 1,2-semidiones [17], the radical anion of 1,4-diborabenzene 10 and 11 [18], substituent effects of benzene and naphthalene radical anions substituted with Me_3M ($\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) [19], and radical species 12 [20].



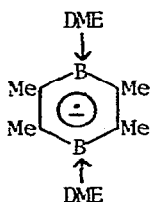
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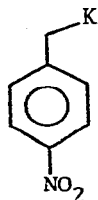
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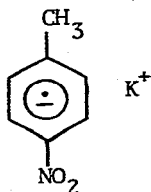
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Alkali metals have been found to dissolve in 12-crown-4 to afford blue solutions whose optical absorptions were measured to reveal the presence of Na^- and K^- anions [21]. Potassium solutions also gave a band ascribed to solvated electrons. The blue color was too short lived to be measured in the cases of rubidium and cesium in this ether though spectra due to Rb^- , Rb^\cdot , and solvated electrons were observed in THF-dicyclohexyl-18-crown-6 [22].

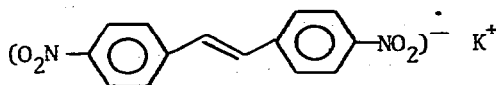
The intermediates in the reaction of p-nitrotoluene with a variety of potassium bases in different solvents have been studied using UV spectroscopy [23]. The authors suggest that 13 is formed which then decays via reaction with parent p-nitrotoluene to produce 14. Radical anion 15 is also a major species in such reactions.



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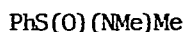
Other papers concerned with spectroscopy discussed the IR spectra of $\text{Cs}^+ \text{OCF}_3^-$ [24] and $\text{Cs}[(\text{CF}_3)_2 \text{BF}_2]$ [25], and the Raman spectra of potassium cyclooctatetraenide in THF [26].

Acidity scales continued to be studied. Thus, a new scale has been developed in the dipolar aprotic solvent *N*-methylpyrrolidin-2-one where absolute acidities are about one pKa unit lower than in DMSO [27]. The paper reports acidity constants for 48 weak acids in the pKa range 2 to 31 in this new solvent. Also discussed were the equilibrium acidities in DMSO of indene and several of its mono-, di-, and triphenyl derivatives [28], and of certain sulfoximines and related oxosulfonium cations [29]. For example, 16 is more acidic than 17 by 19 pKa units. The authors continued the discussion about carbanions GCH_2^- being planar or nearly planar when $\text{G}=\text{RSO}_2$, RSO_2NR , RSO , Ph_2PO , and $(\text{RO})_2\text{PO}$. They also conclude that "the preferential generation of chiral, rather than achiral, planar α -sulfonyl carbanions is a consequence of a preferred kinetic pathway rather than an inherent greater thermodynamic stability".

Linear Brønsted-type plots have been obtained for five families of 9-substituted fluorenyl anions 18 ($\text{G}=\text{CN}, \text{CO}_2\text{Me}, \text{SO}_2\text{Ph}, \text{SPh}, \text{Ph}, \text{OPh}, \text{CH}_2\text{Ph}, \text{Me}, \text{t-Bu}$) and benzyl chloride where the basicity of the anions was changed by remote substitution [30].

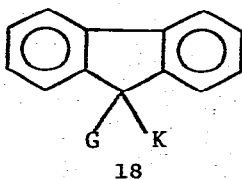


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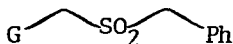
Based on the series of parallel lines obtained with slopes (β_{Nu}) near 0.3, it is concluded that the extent of carbon-carbon bond making in the transition states is essentially constant. Hammett and Brønsted plots for 18 and ring-substituted benzyl chlorides were also reported [31].



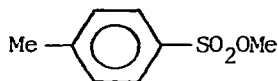
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The rates of exchange of protium of methyl and the rings of 6,6-dimethylfulvene effected by NaOMe-MeOD and KO-t-Bu-t-BuOH have been found to be of the same order of magnitude [32]. An unexpected rate ratio for k_{OTs}/k_{Cl} of 0.0011 was observed in 1,3-eliminations of 19 (G=OSO₂C₆H₄Me and Cl, respectively) in KO-t-Bu-t-BuOH [33]. The use of NaOMe-MeOH in such reactions failed to effect 1,3-elimination and, in the case of the tosylate, reacted at the sulfonate sulfur to afford 20 and benzenesulfonic acid.

Additional studies on the determination of partial rate coefficients were described for the reaction of ammonium ions 21 with sodium methoxide [34]. Three

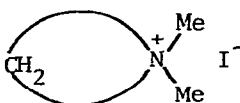


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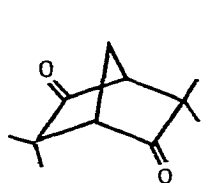
second-order parallel reactions are observed leading to demethylation, ring-opening substitution, and ring-opening olefin-forming elimination. Another paper concerned with base cleavage of arylsilanes by sodium methoxide discussed the results obtained with silyl derivatives of certain thiophenes and furans [35]. The authors state that such heterocycles stabilize a carbanion more effectively than a phenyl moiety.



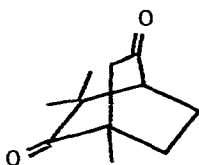
21

Homoenolization of 22 by potassium *t*-butoxide to afford 23 apparently occurs via 24 and other alkoxypropylcyclopropanes [36]. A similar intermediate is proposed in the unusually rapid H-D exchange of the bridgehead methyl protons of 23 [37]. Such intermediates are supported by the homoketonization of silyl derivatives of cyclopropanols such as 25 with this same base to give 26 [38]. Another paper discussed the directive effect of a β -carbonyl versus the corresponding ketal on the regiochemistry of homoketonization of 1,3-bishomocubane acetates [39].

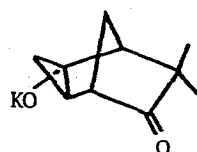
Cyclopropyl derivative 27 (R=Me,Ph) has been opened by potassium *t*-butoxide in



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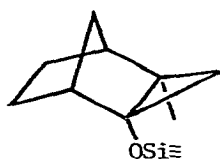


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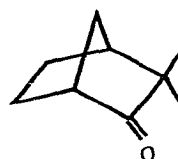


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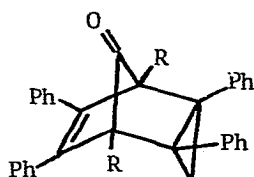
DMSO to 28 and acrylic acids 29 presumably via 30 [40]. Similar treatment of alcohol 31 with this base yielded 32 via disrotatory opening of a cyclopropyl intermediate.



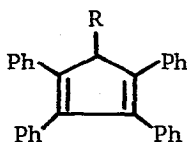
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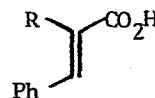
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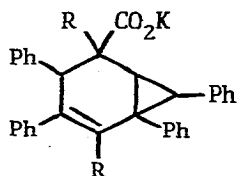
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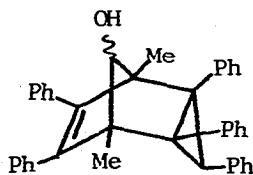
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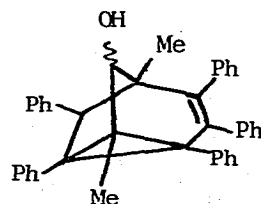
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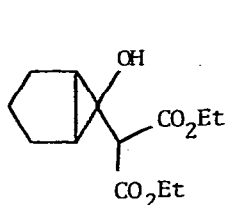
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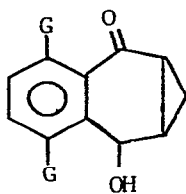
32

Favorskii-type intermediate 33 has now been obtained in the reaction of 2-chloro-cyclohexanone with sodiodiethyl malonate [41]. Other examples are cited. Earlier condensations of such reagents to afford SN_2 -products had been run at higher temperatures. Cyclopropyl derivatives 34 ($G=H, OMe$) have been realized upon treatment

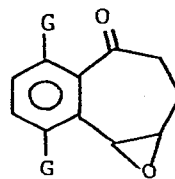
of epoxyketones 35 with sodium isopropoxide [42]. An unrelated full paper disclosed that the conversion of alkanones 36 to 37 by sodium methoxide occur via intermediates such as 38 [43].



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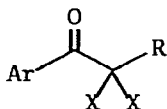


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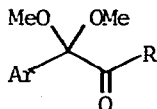


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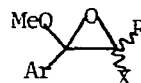
Rearrangements of 1,5-diene alkoxides have been shown to proceed in a concerted fashion mostly via chair transition states [44]. The study was performed on substrates such as 39 to afford diastereoisomeric ketones such as 40 and 41. The authors indicate that the use of alkoxide rather than hydroxyl increases the rates



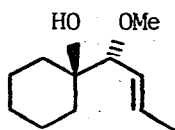
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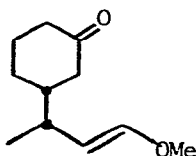
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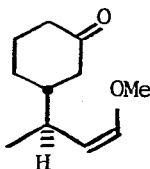
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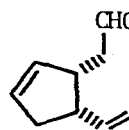
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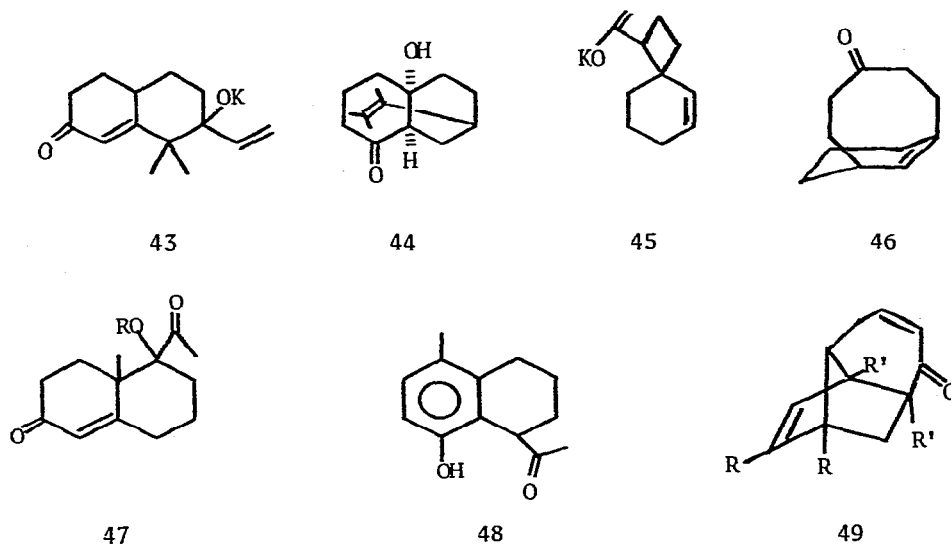
41



42

of such reactions without changing the reaction mechanism. Similar rearrangements of the potassium salts of *cis*-2,4,7-cyclonatrienol have been found to give quantitative amounts of 42 thus allowing a stereocontrolled synthetic entry to the primary prostaglandins from butadiene [45]. Heating of the parent *cis*-2,4,7-cyclonatrienol yielded only small amounts of 42 (20%) accompanied by *cis*-3,7-cyclonadienone (80%).

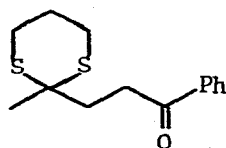
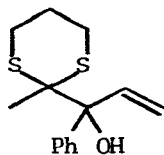
Oxy-Cope rearrangements have also been effected on 43 to afford transannular product 44 [46], and on 45 to give 46 as part of a model study on pleuromutilin [47]. Related studies have been reported for the conversion of 47 (R=H, COMe) by potassium hydroxide to 48 [48] and the transformations of 49 by potassium hydride to non-twistane derivatives [49].



A full paper discussed the details of the conversion of 1,2-adducts such as 50 to 1,4-derivatives illustrated by 51 effected by potassium hydride in HMPA/THF [50]. The methodology has been applied to the synthesis of dL-muscone.

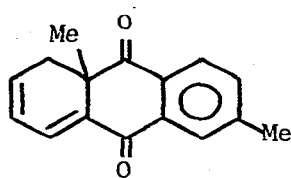
1,2-Alkyl shifts have been realized in a blocked aromatic anion [51]. For example, 52 affords 53 upon treatment with potassium t-butoxide in HMPA. Another paper disclosed the formation of 54 from 55 and one equivalent of potassium t-butoxide in DMF [52]. The cyclization apparently proceeds via enolate 56.

Sulfonium ylide 57, prepared from the parent compound and sodium methoxide, rearranges to 58 (78%) [53]. A [2,3] sigmatropic rearrangement of selenium system

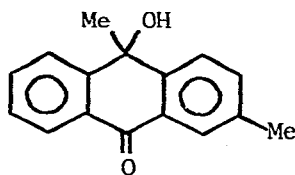


59 to 60 was also reported [54].

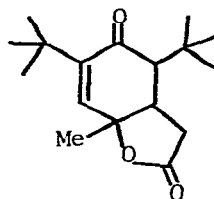
Other papers concerned with rearrangements disclosed additional studies on nitrogenous ylides [55-60], the Smiles rearrangement [61-63], and participation of oligochlorobenzenes in the base-catalyzed halogen dance [64].



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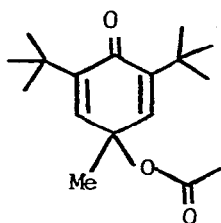
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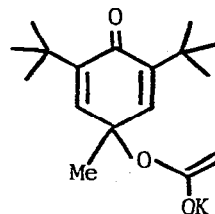
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The controversy surrounding the reaction of sodium naphthalenide with water continued in 1980. It has now been disclosed that this radical anion reacts with water and ethanol in liquid ammonia by two pathways to afford naphthalene, hydrogen, and sodium hydroxide in one and dihydronaphthalene, naphthalene, and sodium hydroxide in the other [65]. The first route was the dominant one.

Dicyclohexylphosphine has been found useful as a free radical trap to estimate the electron-transfer contributions in reactions of alkyl bromide with (trimethyltin)-

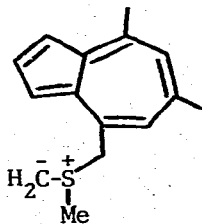


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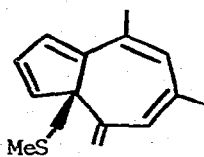


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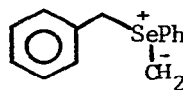
sodium [66]. For example, these reagents with cyclohexyl bromide give increasing amounts of cyclohexane and decreasing amounts of cyclohexyltrimethyltin, cyclohexene, and dicyclohexyl as the phosphine concentration is increased.



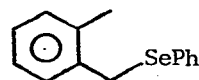
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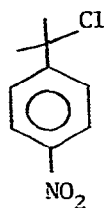


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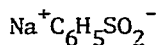


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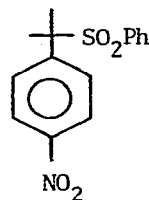
That only one of two possible products are realized in condensations of ambident nucleophiles via electron—transfer chain-substitution reactions has been ascribed to the instability of the products not formed in such systems [67]. For example, 61 and 62 give 63 but not 64. Interestingly, treatment of 64 with 62 yields 63 apparently via 65. The reaction is intermolecular as evidenced by cross-over experiments. Another paper reported C-benylation of certain 1-benzylpyridinium salts by hindered malonate systems [68]. Radical chains are not involved.



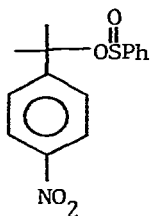
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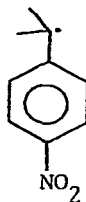
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63



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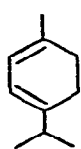
The reaction of resonance stabilized carbanions such as triphenylmethyl anion with methyl radicals, produced upon irradiation in DMSO, has been found to be governed more by the pKa of the conjugate acid of the carbanion than by the stability of the resulting radical anion [69]. The products in the above non-chain process are the radical anions of 1,1,1-triphenylethane and diphenylmethylene-6-methyl-1,4-cyclohexadiene [70].

Other papers of interest discussed the effects of leaving groups after they have left in $S_{RN}1$ reactions of halobenzenes, enolates, and solvated electrons [71,72], $S_{RN}1$ reactions of amide enolates with halobenzenes [73], two-fold $S_{RN}1$ condensations of p-dihalobenzenes [74], the $S_{N}ANRORC$ mechanism in the amination of 2-substituted purines with potassium amide in liquid ammonia [75], tele-amination in reactions of 6- and 8-substituted purines with potassium amide [76], ring transformations and amination in reactions of 3-halo-5-phenyl-1,2,4-triazines [77], and tele-substitution reactions in naphthalene derivatives [78].

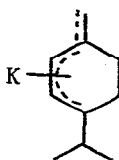
2. SYNTHETIC ASPECTS

Books and reviews of interest in this area were concerned with phase transfer catalysis [79], the preparation and reactions of cyclic α -nitroketones [80], and the synthesis and reactions of glutaconaldehyde [81].

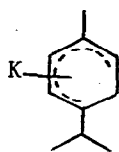
Metalation of α -terpinene (66) by *n*-butyllithium/potassium *t*-butoxide has been found to be non-selective since three products, 67-69, were obtained [82]. Treatment of 67 with fluorodimethoxyborane and hydrogen peroxide afforded the monoterpene alcohol 70. Potassiophenalene (71) has been photocyclized to 72 [83]. Tri- and diphenylmethanes have been metalated by sodium and potassium hydride in the presence of certain cryptands [84].



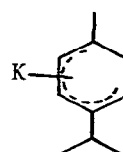
66



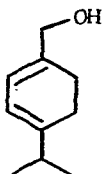
67



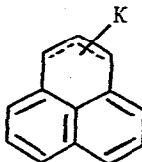
68



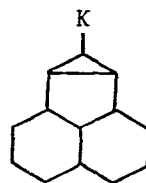
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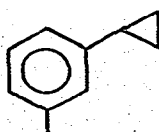


71

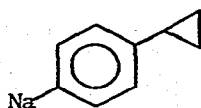


72

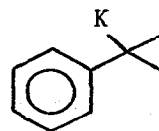
While phenylcyclopropane is metalated on the aryl ring by pentylsodium to afford 73 and 74, the use of butyllithium/potassium *t*-butoxide and trimethylsilyl potassium gives 75 [85]. The latter organometallic has been added to ethylene at -40° to yield the 1-ethyl derivative.



73



74



75

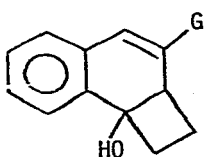
Isomerization of alkyn-1-ols to terminal acetylenes has now been effected by sodium 1,3-diaminopropane, prepared from the amine and sodium hydride [86,87]. Intermediate isomers were observed in such isomerizations of decyn-1-ols.

Enolates of α,β -unsaturated ketones combine with arynes leading to a variety of products [88]. For example, cyclohexenone enolates with benzyne afford 76. ($G = R, Ar, RO, ArO, RS, ArS$) which are converted to 77 and 78 with base. In contrast, acyclic enolates such as 79 give naphthalene derivatives such as 80. Additional examples of the synthesis of indoles from *o*-haloanilines and ketone enolates in ammonia under irradiation also were described in 1980 [89].

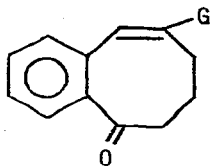
Terminal condensations of β -diketones with aromatic aldehydes and ketones have now been effected by potassium hydride [90]. For example, benzoylacetone and benzophenone with this base afford 81. Interestingly, the use of *p*-anisaldehyde and *p*-tolualdehyde instead of benzophenone give 82 ($R = OMe, Me$) apparently via novel hydride expulsion and a Michael reaction in which a dicarbanion adds to a monoanion. Another paper described an improved preparation of chalcones and related enones from ketones and aldehydes using sodium hydroxide in absolute ethanol [91].

While triketone 83 was aromatized to 84 in methanol by sodium methoxide, a similar conversion of 85 required the use of sodium hydride in benzene and DMF [92].

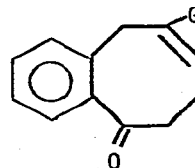
Potassioethyl acetoacetate and sodium β -naphthoxide undergo mostly C-ethylation and O-ethylation on alumina and in THF in the presence of polymer supported HMPA,



76



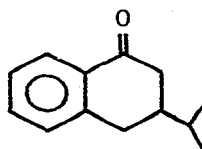
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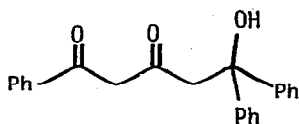


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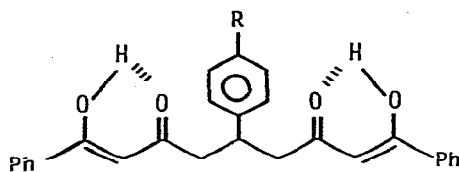


80

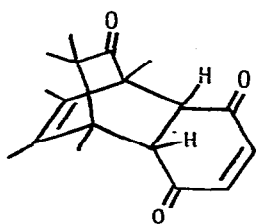
respectively [93]. α,β -Unsaturated ketoesters such as 86 have been obtained from the disodium salt 87 and aldehydes and ketones [94].



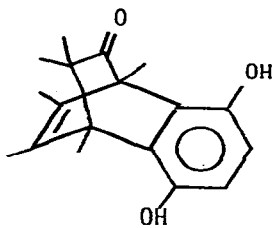
81



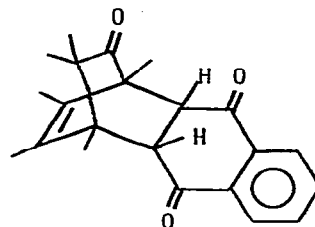
82



83

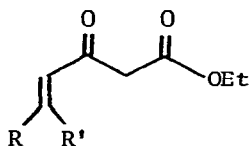


84

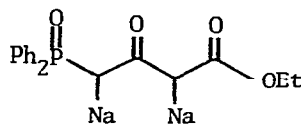


85

Cyclic ketals of α,β -unsaturated ketones illustrated by 88 give dienol ethers such as 89 and 90 upon treatment with sodium hydride in DMSO [95]. The alcohols were converted to benzyl ethers in certain cases.



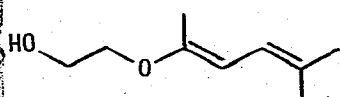
86



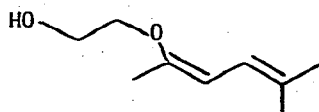
87

Sodiodiethyl malonate and related carbanions have been added in a 1,4-fashion to quinone monoacetals such as 91 to afford 92 [96]. The adducts have been aromatized to derivatives illustrated by 93.

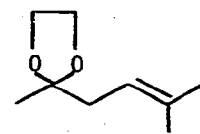
Carbanions alpha to esters were also involved in unidirectional Dieckmann cyclizations of resin supported alkyl pimelates [97] and the preparation and reactions of 94 and related nitriles [98].



88



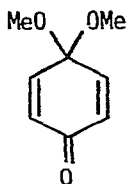
89



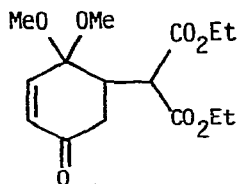
90

Potassium diisopropylamide has been found to be a more reliable base than butyllithium or LDA for metalation of oxime ethers and dimethylhydrazones [99]. The resulting organometallics were converted to cuprates, then added in a 1,4-fashion to cyclohexenones. The process is illustrated by the conversion of 95 to 96.

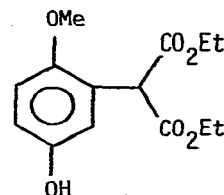
Sodium salt 97 (R=Me, i-Pr) has been generated by addition of alkoxides to 98, by metalation of the parent cyclopropane by alkoxide in the presence of crown ether, and by carrying out the latter deprotonations in the absence of crown ether [100]. The stereochemistry of the protonation revealed the presence of a free carbanion, a hydrogen-bonded carbanion which exhibits some retention of configuration, and a hydrogen-bonded carbanion which affords equal amounts of retention and inversion, respectively.



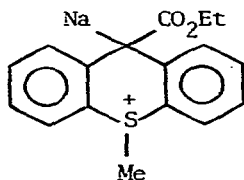
91



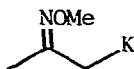
92



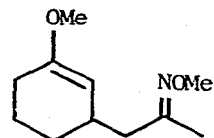
93



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95



96

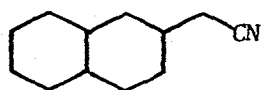
Nitriles with α -hydrogen atoms have been converted to carboxylic acids with one less carbon atom using potassium *t*-butoxide and oxygen [101]. For example, 99 gives 100 (93%) probably via 101. An unrelated paper reported the convenient synthesis of aminomalononitrile from sodiomalononitrile and *O*-mesitylenesulfonylhydroxylamine [102].



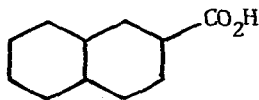
97



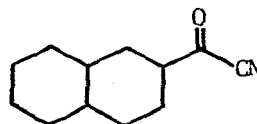
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99

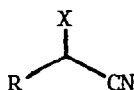


100

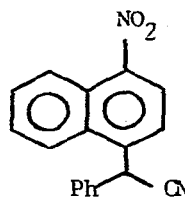


101

Vicarious substitution of hydrogen in aromatic nitro compounds has now been effected by acetonitrile derivatives 102 ($R = H, Ph; X = Cl, OPh, SPh, \text{ others}$) in the presence of sodium hydroxide in DMSO [103]. The process is illustrated by the preparation of 103 from phenoxyphenylacetonitrile and 1-nitronaphthalene.

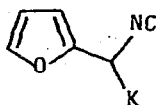


102

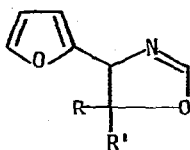


103

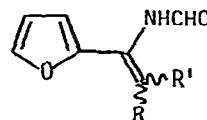
α -Potassiofurfuryl isocyanide 104, prepared from the parent compound and potassium *t*-butoxide, has been combined with aldehydes and ketones to afford oxazolines 105 [104]. The preparation of formamides 106 from 104 with benzaldehyde, cinnamaldehyde, and benzophenone is also reported.



104

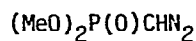


105

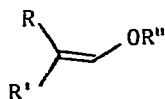


106

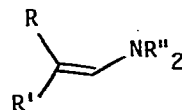
Condensations of 107 with non-aryl ketones in alcohols or amines as solvent in the presence of potassium *t*-butoxide give enol ethers 108 and enamines 109 respectively [105]. The use of allyl alcohols in the reaction affords allyl vinyl ethers [106]. The process involves diazoethene intermediates.



107



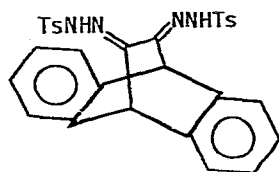
108



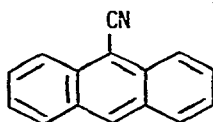
109

Unusual ring-opened products have been realized with certain bis-tosylhydrazones and potassium hydroxide at high temperatures [107]. For example, 110 yields 111 (51%). Sulfonyl hydrazide 112 has been successfully employed in the McFadyen-Stevens synthesis of aromatic aldehydes effected by potassium carbonate in boiling methanol in the presence of hydrazine [108].

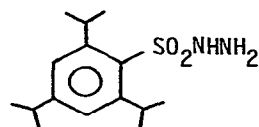
Benzylic alcohols have been transformed to 2-nitropropyl derivatives in an interesting example of the $\text{S}_{\text{RN}}1$ -reaction [109]. The synthesis is illustrated by the conversion of 113 to 114 by sodio-2-nitropropane.



110

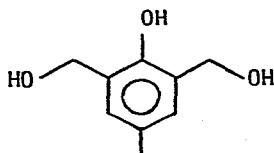


111

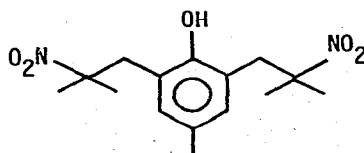


112

C-Alkylations of 115 to afford 116 have been realized using benzyl halides and primary alkyl iodides [110]. γ -Alkylations of α,β -unsaturated ketones have been effected by using γ -arylsulfonyl groups as regioselective control elements [111]. For example, methylation of 117 gives 118 and 119 in a ratio of about 10:1; subsequent treatment of 118 with zinc/acetic acid yields 120. A part of the synthesis of steroids and other cyclic systems involved alkylation of α -potassio-sulfones [112].

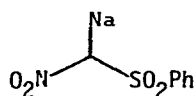


113

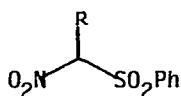


114

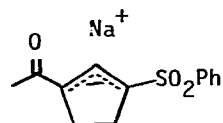
Cyclization via intramolecular epoxidation has been realized on ketosulfonium ylides [113,114]. One of the many examples cited involves the conversion of 121 to



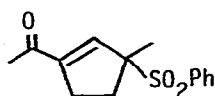
115



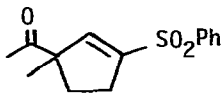
116



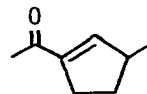
117



118



119

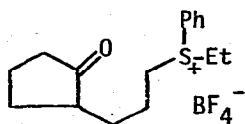


120

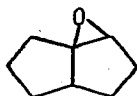
122 by potassium *t*-butoxide. The first stable ylide in the thiazulene system, 123, has been prepared from the parent compound and sodium hydride [115]. Rearranged products from 123 as well as the *S*-ethyl and *n*-propyl analogs are reported.

The anomalous behavior of tosylates in elimination reactions effected by alkali amides has been ascribed to metalation of the *p*-methyl group as evidenced by the conversion of 124 to 125 (70%) by potassium amide and methyl iodide [116]. Elimination reactions have been employed in the conversion of 126 to 127 [117], the transformation of 128 to 129 [118], the preparation of benzyne adduct 130 from 131, potassium amide, and furan [119], the synthesis of alkadienylidenecarbenes 132 [120] and 133 [121] from triflates, and the conversion of 134 to 135 by sodium bis(trimethylsilyl)amide [122].

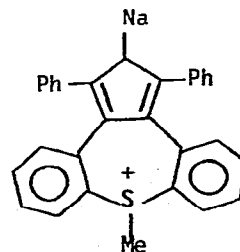
Vinyl monomers such as 2-vinylpyridine, methyl methacrylate, and methacrylonitrile have now been polymerized by complex bases comprised of sodium amide/sodium alkoxides [123]. Such bases appear to be general anionic initiators in THF as well



121



122



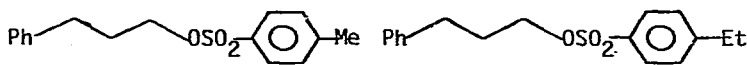
123

as in toluene. Two other papers discussed the use of solutions of alkali metals in dicyclohexyl-18-crown-6 to polymerize methyl methacrylate [124], butadiene [125], and isoprene [125].

Symmetrical conjugated dienes such as 136 have been obtained at 0° from alkenylboranes 137 and the related cyclohexyl derivatives, sodium methoxide, and copper(I) bromide complexed with dimethylsulfide [126]. The intermediate alkenylcopper reagents have been trapped at -15° with alkyl halides to afford 1,4-dienes [127]. The latter procedure is illustrated by the conversion of 137 with allyl bromide to give 138 (92%).

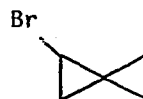
Turning to the area of reductions, non-solvated intercalates KC_8 , RbC_8 , and CsC_8 have been prepared from the metals, flake graphite, and catalysts such as monoolefintris(trialkylphosphane)cobalt(0) complexes in pentane [128].

Cleavage of both sp^3-sp^3 and sp^2-sp^3 bonds in alkanes has been effected by sodium potassium alloy in glyme-triglyme as evidenced by alkylation with methyl iodide [129]. For example, 1,1-diphenylethane affords ethylbenzene and 2,2-diphenylpropane. The intense blue solutions obtained from eutectic mixtures of sodium potassium alloy in THF at 0° in the presence of 18-crown-6 and *t*-butyl alcohol have been used to reduce acetylenes to mixtures of *cis*- and *trans*-olefins, and benzoic acid to cyclohexanecarboxylic acid (86%) [130]. Another paper demonstrated that reduction of six alkyl-substituted butadienes by sodium in liquid ammonia prefers to occur by the 1,4-route through *cisoid* conformations [131].



124

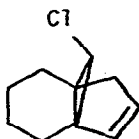
125



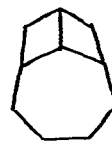
126



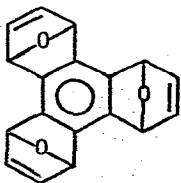
127



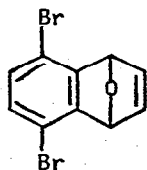
128



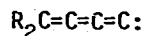
129



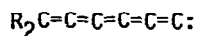
130



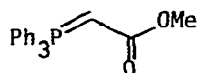
131



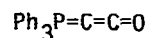
132



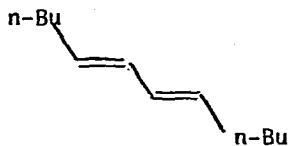
133



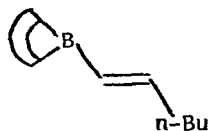
134



135



136

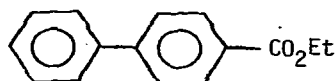


137

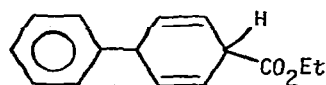


138

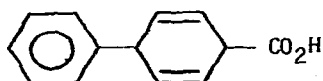
Aryl benzoates have been found to undergo clean reduction by sodium in ammonia in the presence of water [132]. For example, 139 gives 140. In contrast, the parent acid of 139 affords 141 and 142 [133]. In related work, polystyrene-bound anthracene has been converted to the corresponding radical anion by sodium naphthalenide [134]. Its chemistry is similar to that of soluble alkali aromatic radical anions.



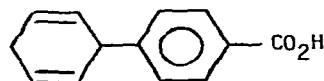
139



140



141

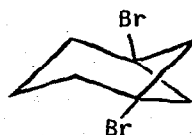


142

Other papers concerned with reductions discussed alkali metal induced transformations of *cis*-1,2-dibenzoylalkenes [135], reductive decyanation of alkylnitriles by potassium on alumina [136], and the preparation of [3.1.1]propellane (143) by treatment of 144 with sodium [137].



143

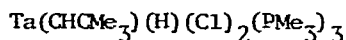


144

3. INORGANIC AND ORGANOMETALLIC COMPOUNDS

Combination of sodium cyclopentadienide with gadolinium (III) chloride in THF has given $\text{Cp}_3\text{Gd}\cdot\text{THF}$ [138]. The results of an X-ray study on this material are described.

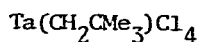
Neopentylidene complexes 145 and 146 have been prepared by sodium amalgam reduction of 147 and 148, respectively [139]. The only "d²" alkylidene complex which does not contain an olefin ligand, 149, was similarly obtained by reduction of 150. Each reaction was performed in the presence of trimethylphosphine.



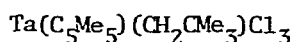
145



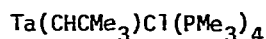
146



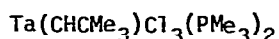
147



148

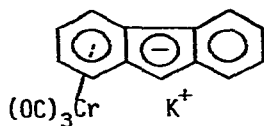


149

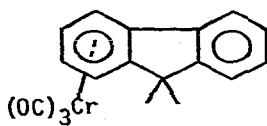


150

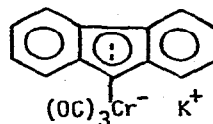
While chromium derivative 151, prepared from the parent compound and potassium t-butoxide, could be acylated at -30° to afford 152, it rearranged at temperatures above -20° to give 153 [140]. Several condensations of related indenyl complexes are discussed.



151

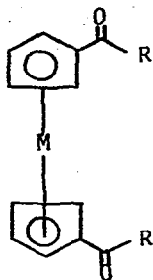


152

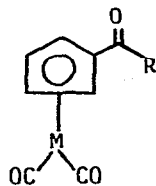


153

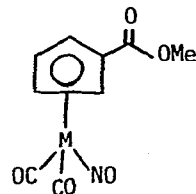
Functionally substituted η^5 -cyclopentadienyl metal compounds may now be obtained by in situ acylation of sodium cyclopentadienide followed by appropriate transition metal halides or carbonyls to yield derivatives such as 154 ($\text{M} = \text{Co}$ and Ni , $\text{R} = \text{Me}$ and OMe), 155 ($\text{M} = \text{Rh}$ or Co , $\text{R} = \text{H}$, Me , or OMe), 156 ($\text{M} = \text{Cr}$, Mo , W) and others [141]. Other VI A compounds prepared by simple condensations were 157 ($\text{M} = \text{Cr}$, Mo , W) from 158 and $\text{Me}_2\text{AsC}\equiv$ [142], 159 from 160 and KAsPh_2 [143], and 161 from the dichlorodipalladium derivative and $\text{NaMo}(\text{CO})_3\text{Cp}$ [144].



154

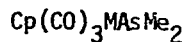


155

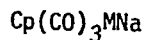


156

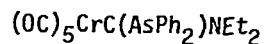
The completely unexpected 162 has been obtained from isocyanide reagent $\text{Mn}(\text{CO})_4(\text{CNMe})\text{Na}$ and methyl iodide [145]. Reaction of carbyne complex 163 with $\text{NaRe}(\text{CO})_5$ has been shown to afford 164, a new type of complex containing the phenylketenyl moiety as the bridging ligand [146]. The X-ray structure of both 162 and 164 are discussed.



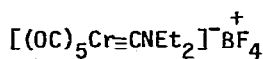
157



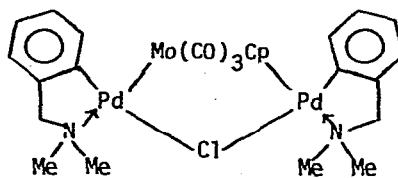
158



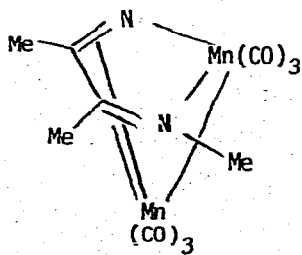
159



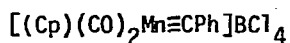
160



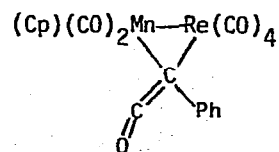
161



162

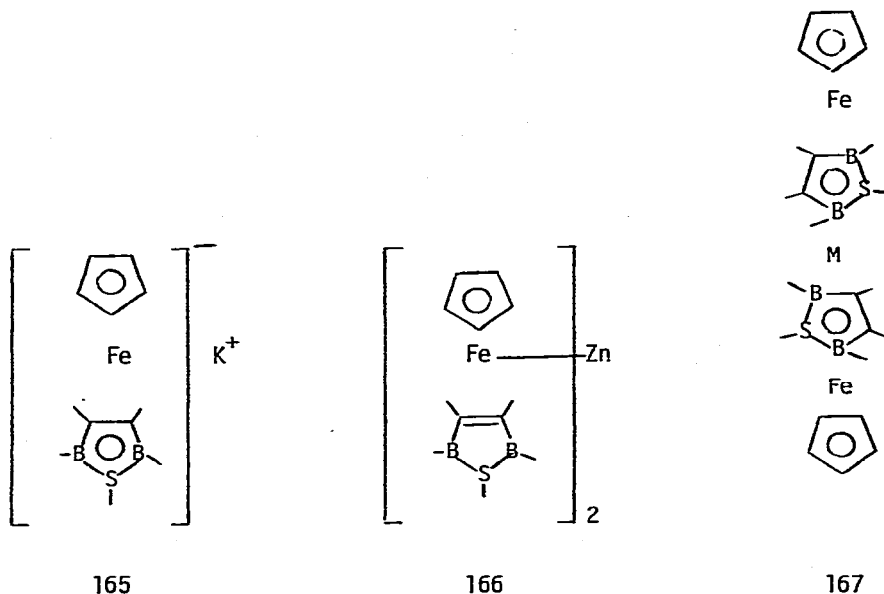


163

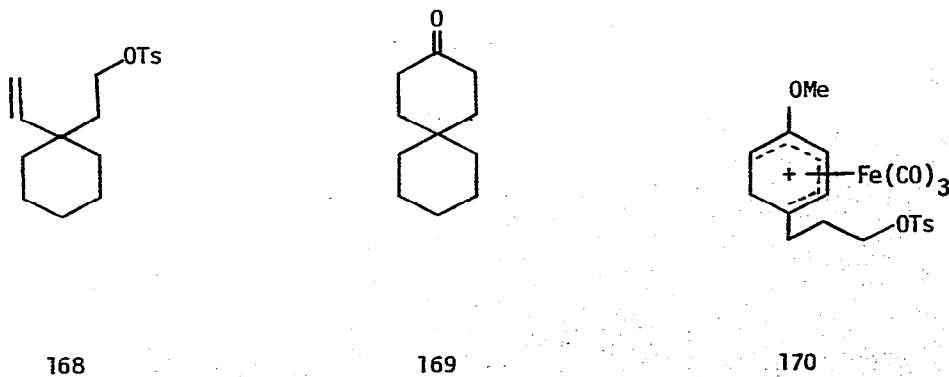


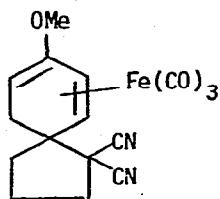
164

The long-sought anion 165 has been obtained from 166 and potassium metal, then combined with iron(II)chloride and cobalt(II)chloride to afford tetradecker sandwich complexes 167 (M = Fe, 53% and M = Co, 42%, respectively) [147]. The crystal structure of 167 (M = Fe) is described.

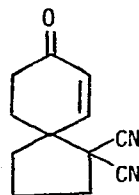


Cyclocarbonylations of monosubstituted olefinic tosylates by $\text{Na}_2\text{Fe}(\text{CO})_4$ have been found applicable to the synthesis of five-, six-, and seven-membered rings as well as spiro compounds [148]. For example, 168 leads to 169 (70%). Cyclizations are also realized on iron complexes illustrated by 170 [149]. Thus, its treatment with sodiomalononitrile in THF affords 171 which ultimately yields 172. α,β -unsaturated ketones have been obtained from allenes, $\text{Na}_2\text{Fe}(\text{CO})_4$, and alkyl halides [150].



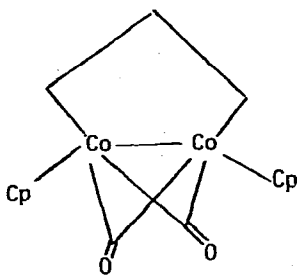


171

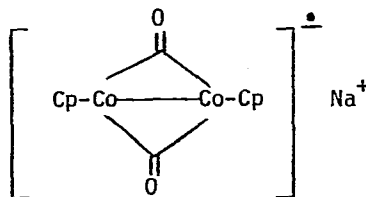


172

Metallacycle 173 containing two cobalt atoms in the ring has been obtained from 174 and 1,3-diiodopropane [151]. Several reactions of 173 are disclosed. New clusters $\text{HCoRu}_3(\text{CO})_{13}$, $\text{HCoRu}_2\text{Os}(\text{CO})_{13}$, $\text{HCoRuOs}_2(\text{CO})_{13}$, and $\text{HCoOs}_3(\text{CO})_{13}$ have been prepared from $\text{KCo}(\text{CO})_4$ and $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_2\text{Os}(\text{CO})_{12}$, $\text{RuOs}_2(\text{CO})_{12}$, and $\text{Os}_3(\text{CO})_{12}$, respectively, followed by protonation [152].

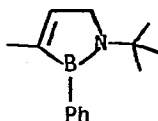


173

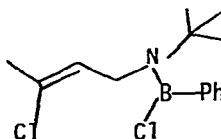


174

The first 1,2-azaboroline, 175, has been synthesized from 176 and potassium [153]. Attempts to convert 175 to its alkali metal salt have been unsuccessful to date.



175



176

Finally, alkali metal hydrides have been found capable of metalating Si-H [154], Ge-H [155], and Sn-H [155] bonds to afford the alkali silicon, germanium, and tin derivatives, respectively. For example, triethylsilane and potassium hydride give potassiotriethylsilane. Such derivatives can also be obtained by cleavage of silicon-silicon and tin-tin bonds using a mixture of potassium hydride/sodium hydride. Condensations of the alkali derivatives with electrophiles are discussed.

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