HEAVIER ALKALI METALS

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

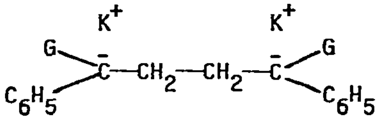
I. Physical Organic Chemical Aspects

Equilibrium acidities of a variety of ketones, sulfones, and sulfoxides have been related in DMSO by the same hydrocarbon indicators including diphenylyldiphenylmethane, 9-phenylxanthene, 1,1,3-triphenylpropene, and fluorene [1]. For example, either of the first two indicators can be used to compare such acidities of phenyl methyl sulfone and benzyl methyl sulfoxide where the negative charges of the carbanions are largely localized on carbon and delocalized in a benzene ring, respectively. This study of the equilibrium concentrations of dissociated ions complements earlier investigations of ion aggregates in ether, benzene, and cyclohexylamine.

The benzyl carbanion both in its free state and in its sodium ion paired state has been prepared in THF by subjecting dibenzylmercury to an electron pulse in the absence or presence of sodium ion, respectively [2]. Absolute rate constants were determined not only for the formation of the carbanions but also for their proton transfer reactions with various alcohols and water. Since submicrosecond periods were involved, this chemistry was studied by the pulse radiolysis method.

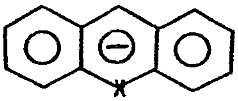
Electron transfer to nitrobenzene or oxygen vs. proton capture by alcohol of triphenylmethide ions, generated from triphenylmethane and potassium t-butoxide [3] and from the base-induced cleavage of benzopinacolone and benzoylazotriphenylmethane [4], has been studied. The efficiency of the electron transfer processes relative to protonation is a function of the extent of ion pairing of the carbanion, tight ion pairing increasing or decreasing the efficiency of reaction with nitrobenzene and oxygen, respectively.

Several papers have described the NMR spectra of certain carbanions. Thus, the natural abundance ^{13}C NMR spectra of 1,1-diphenylethylene and α-methylstyrene dimer dianions (I, G = C_6H_5 and CH_3, respectively) revealed that the charge shifts appear mostly at the o- and p-carbon atoms and slightly at the β- and the methyl carbon, but not at the m-carbon [5]. Also, the α-carbon exhibits strong deshielding. Though the chemical shifts of the two o-carbons are equivalent to one another in I (G = C_6H_5), they are non-equivalent for I (G = CH_3).



I

The proton NMR spectra of the sodium salts of 9,10-dihydroanthracene (II, X = CH_2), xanthene (II, X = O), and thioxanthene (II, X = S) suggest a strongly increasing paramagnetic ring current in the central ring in the order X = CH_2 < X = S < X = O [6]. Similar ring currents in the central rings of the sodium salts of III (X = CH, N) were also suggested by their respective proton NMR spectra [7].



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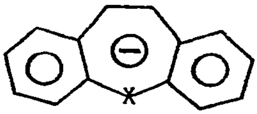
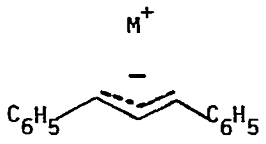


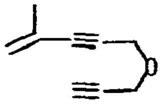
III

Finally, the proton decoupled ^{13}C NMR spectra of the sodium salt of trans, trans-1,3-diphenylallyl anion (IV) at various temperatures in liquid ammonia has been studied [8]. The signal in such spectra due to the o-carbons splits into two peaks at ≤-40° and corresponds to a barrier to phenyl rotation of $\Delta G = 10.9$ kcal/mol. That similar results are obtained with the corresponding lithium and potassium salts seems to eliminate the possibility of contact ion pairs.

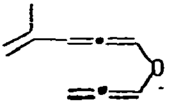


IV

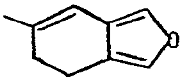
Anions derived from acetylenes and olefins continue to elicit interest. For example, treatment of ether V with two equivalents of potassium t-butoxide in t-butyl alcohol apparently affords bis-allene VI which undergoes an intramolecular cycloaddition ($\pi^4 + \pi^2$) to give isobenzofuran VII in a yield of 45% [9]. Other related systems have been similarly cyclized.



V



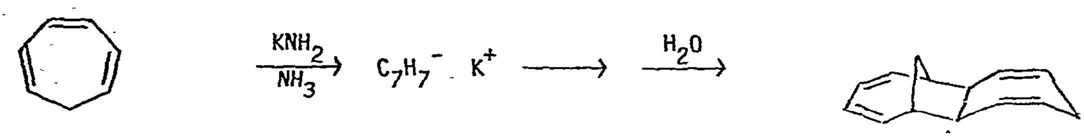
VI



VII

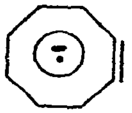
Reduction of 3-hexyne by sodium in HMPA-THF has been systematically studied by varying the amounts of sodium and t-butyl alcohol as well as the reaction times and temperatures [10]. Though cis- and trans-2- and 3-hexenes were formed, only trans-3-hexene was observed in every reaction; in fact, this compound was obtained in a yield of 95% in one case. Reductions of 3-chloro-cis-3-hexene and 1-hexyne were similarly investigated. Reaction pathways for the reactions are discussed.

Evidence has been presented to demonstrate that cycloheptatriene is converted to the cycloheptatrienyl anion (VIII) by potassium amide in liquid ammonia [11]. The major product in this reaction, dimer IX, is obtained in a yield of 81%.



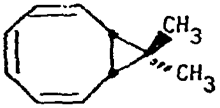
VIII IX

A new radical anion, that of cyclooctatrienyne [X], has apparently been observed by esr spectroscopy [12]. Compound X was formed by treatment of bromocyclooctatetraene with a potassium mirror in THF-HMPA at -100°. Esr parameters of the radical anions of four substituted cyclooctatetraenes have also been reported [13]. The compounds studied were derived from reduction of phenyl-d_5-, 1,3,5,7-tetramethyl-, t-butoxy-, and ethylcyclooctatetraene by potassium in HMPA.

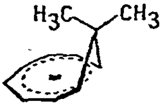


X

Several cis-bicyclo[6.1.0]nona-2,4,6-trienes have been reduced to the corresponding monohomocyclooctatetraene dianions by alkali metals in liquid ammonia-d_3 or ammonia; for example, XI affords XII as evidenced by pmr spectroscopy [14]. All of the dianions so formed underwent deuteration but at different rates depending on the substitution. Thus, in the case of the parent compound, deuteration was so rapid that only the monodeuterated cyclononatrienyl monoanion was observed. Quenching studies and alkylations were performed in some cases.

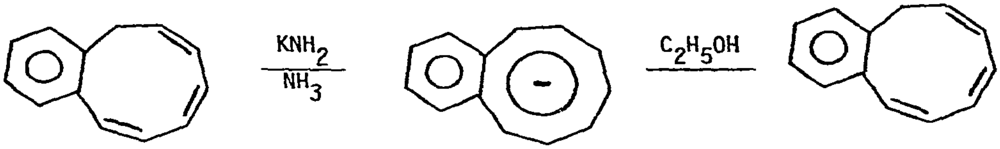


XI



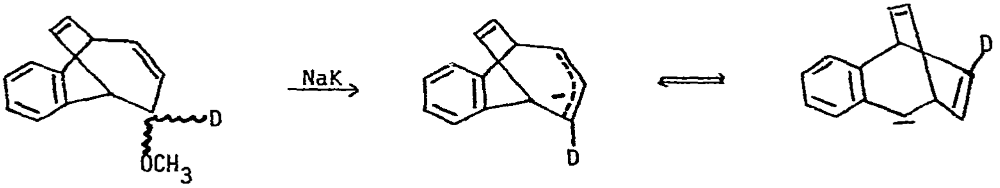
XII

To assess the effect of perturbation of benzenoid fusion on the π-delocalization in a 10π monocycle, the benzocyclononatetraenyl anion (XIV) was prepared from triene XIII and potassium amide in ammonia [15]. Consideration of the NMR spectrum of XIV led the authors to classify the molecule as an aromatic best viewed as a 14π unit rather than as a benzannelated 10π system. Ethanolysis of XIV gave the new triene XV.



XIII XIV XV

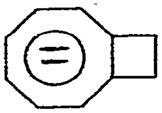
Reductive cleavage of ether XVI by NaK gave the benzo-6,7-bicyclo[3.2.2]-nonatrienyl anion XVII whose ^{13}C NMR spectrum gradually changed suggesting a rearrangement via XVIII [16]. The rearrangement which consisted of a degenerate seven-carbon scrambling has been used to probe the relative stabilities of benzylic and allylic carbanions.



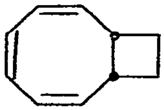
XVI XVII XVIII

Bicyclo[6.2.0]decatetraene dianions like XIX have been prepared by proton abstraction from XX, XXI, and XXII with potassium amide in ammonia [17]. The subsequent chemistry of such dianions constitutes a useful method of synthesizing substituted cyclooctatetraenes. A different paper describes the synthesis of the bicyclo[3.3.2]decatrienyl dianion XXIII by reduction of bullvalene by

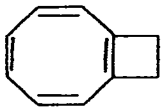
NaK in THF or DME [18]. Thus, synthesis of the longicyclic trio of XXIII, the 7-norbornadienyl cation, and the bicyclo[3.2.2]nonatrienyl anion has now been completed.



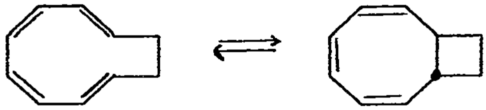
XIX



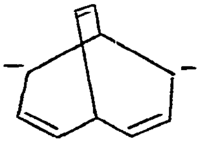
XX



XXI

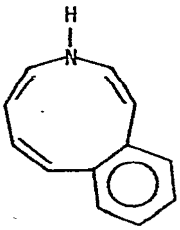


XXII

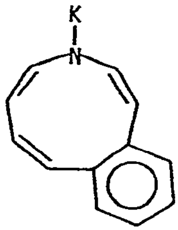


XXIII

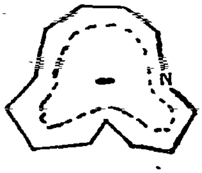
Finally, two large ring systems containing nitrogen have been studied. First, based on NMR, neither 3H-3-benzazonine (XXIV) nor its corresponding potassium salt XXV, prepared from XXIV and potassium amide in ammonia, are aromatic [19]. This result is in marked contrast to the aromatic character observed in the iso-π-electronic carbocycle XIV. Second, the anion of aza[13]annulene (XXVI) has been prepared by treatment of XXVII by potassium t-butoxide [20]; the anion of aza[17]annulene is synthesized similarly. NMR studies of the anions suggest that the species are configurationally labile and that the magnetic field induces a diamagnetic ring current.



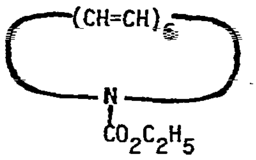
XXIV



XXV

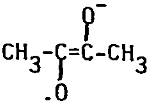


XXVI

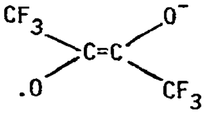


XXVII

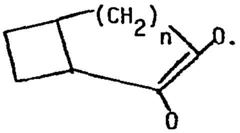
Many papers in 1974 dealt with the subject of radical anions. The series of papers by Russell and co-workers concerned with aliphatic semidiones has been continued. Included are discussions about acylic dialkyl-1,2-semidiones like XXVIII [21], perfluorobiacetyl radical anions (XXXIX) [22], bicyclo[n.2.0]alkane-2,3-semidiones like XXX [23], bicyclo[n.2.1]alkane-2,3-semidiones like XXXI [24], 1,4-semidiones in $C_5 - C_7$ carbocyclic systems like XXXII [25], and radical anions from bicyclo[4.n.0]alk-3-ene-2,5-diones like XXXIII [26].



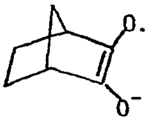
XXVIII



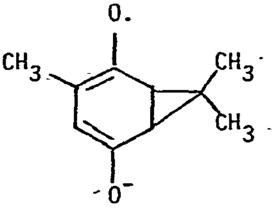
XXIX



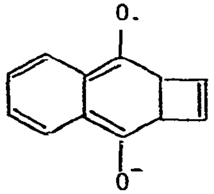
XXX



XXXI



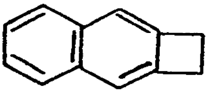
XXXII



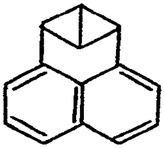
XXXIII

The kinetics of electron transfer from sodium anthracenide and sodium pyrenide to *cis*-stilbene have been studied [27]. The isomerization of *cis*- to *trans*-stilbene that is observed apparently occurs via the dianion rather than the radical anion of the former compound. In a different paper, esr evidence is presented for the ion-pair formation between the tetracyanoethylene radical anion and the cesium counterion in THF [28]. The broad linewidths from the compound are ascribed to the unresolved hyperfine splitting of the cesium atom.

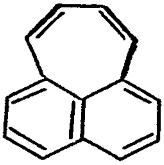
Reduction of naphtho[b]cyclobutene (XXXIV) by sodium and potassium in a variety of ethereal solvents has been investigated [29]. Thus, reduction with potassium in DME and DME-HMPA and sodium in DME gave the free ion while sodium in THF and ether afforded ion pairs as evidenced by esr spectroscopy. Similar reduction of naphthobicyclobutane XXXV by NaK in 2-methyltetrahydrofuran-DME at -110° gave the corresponding radical-anion whose esr spectrum did not change below -60° [30]. Above this temperature, the esr spectrum revealed the presence of the radical anion of pleiadiene (XXXVI). If this conversion is concerted, it presumably represents the first report of a $\sigma 2a + \sigma 2a$ cyclo-reversion reaction occurring in a radical anion.



XXXIV



XXXV



XXXVI

Disproportionation of the alkali salts of the anthracenide and perylenide radical anions in DME and THF has been studied [31]. The disproportionation constant of eq. 1 of the potassium anthracenide or perylenide in DME is much greater than those for the lithium and sodium salts. In THF, the constant increases as lithium is replaced by sodium. Finally, disproportionation is favored more for the anthracenide compared to the perylenide radical anion and is more extensive in THF than in DME. In an unrelated study, the rather stable radical anion of 2-phosphanapthalene has been prepared by reduction of the parent compound by potassium in THF; the esr spectrum is reported [32].

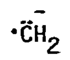
$$2\ \mathrm{Ar}^{\dot{-}},\ \mathrm{M}^{+} \rightleftharpoons \mathrm{Ar} + \mathrm{Ar}^{2-},\ 2\ \mathrm{M}^{+} \qquad (1)$$

Several papers have described further interactions of sodium napthalene with alkyl halides. Thus, such a reaction with primary alkyl fluorides like 5-hexenyl fluoride in DME affords 1-hexene and methylcyclopentane apparently via radical intermediates like XXXVII (eq. 2) [33]. Rate constants for the above reaction as well as those effected by lithium and potassium naphthalene are given; the reaction fails with cesium naphthalene.

XXXVII

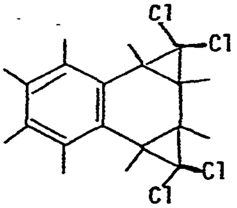
Reactions of sodium naphthalene with 1,4- and 1,5-dihaloalkanes afford cycloalkanes, olefins, and alkylated naphthalene derivatives but dimeric or polymeric residues of the dihaloalkanes are absent [34]. Since initially formed alkyl radicals do not couple, the authors conclude that alkyl dimers from monoiodoalkanes and sodium naphthalene probably arise from reaction of such alkyl iodides with alkyl anions.

Methylene halides (X = Cl, Br, and I) with sodium naphthalene have been shown to give mostly (>70%) a mixture of methane, ethylene, ethane, and propane and only <1% of norcarane [35]. The authors suggest that the reactions proceed via the intermediacy of the methylene radical anion (XXXVIII). In a related study, reaction of gem-dichloro compound XXXIX with four equivalents of sodium naphthalene in THF at <-50° afforded mostly XL in a yield of 75% [36]. This reaction represents the first example of a substituent shift to a neighboring cyclopropylidene function. At higher temperatures, the latter reaction gave various benzocyclooctatetraenes, benzocycloheptadienes, and some starting material; however, XL was absent.

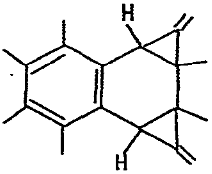


$\cdot\overset{-}{\ddot{C}}H_2$

XXXVIII

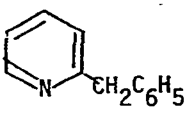


XXXIX

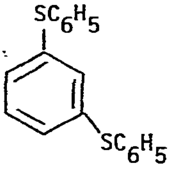


XL

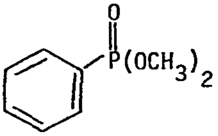
A variety of papers have discussed the reactions of nucleophiles with aryl halides to give substitution products. Thus, the 2- and 4-picolyl anions have been arylated by chlorobenzene and other benzene derivatives to afford compounds like XLI by the $S_{RN}1$ mechanism [37]. A similar pathway is thought to be operational in the reactions of aryl iodides with arenethiolate ions to give diaryl sulfides [38], of several dihalobenzenes with thiophenoxide to afford disubstituted products like XLII [39], and of iodides with potassium dialkyl phosphites to give dialkyl arylphosphonates like XLIII [40]. Also, various substituted benzenes are cleaved by potassium in ammonia [41].



XLI



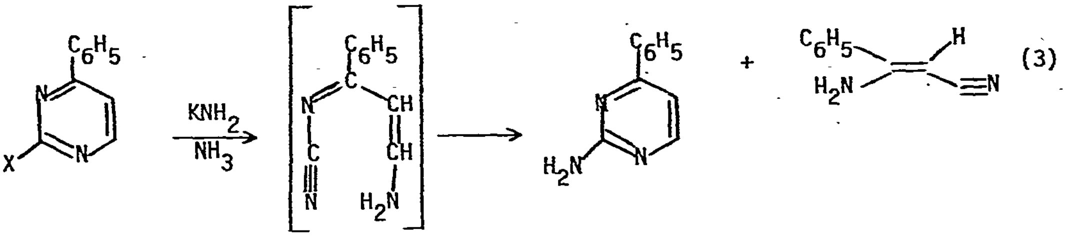
XLII



XLIII

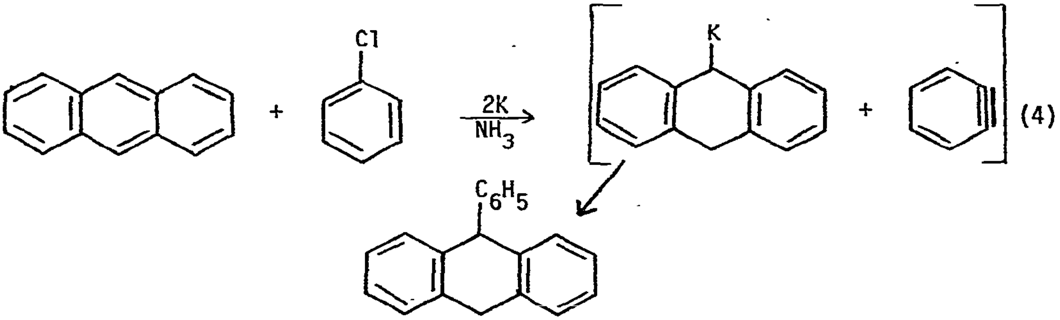
In contrast to the above, reactions of 2-halo-4-phenylpyrimidines (X = F, Cl, Br, and I) with potassium amide in liquid ammonia to afford 2-amino-4-phenylpyrimidine (XLIV) proceed by the SN(ANRORC) mechanism (eq. 3) as evidenced by the use of halopyrimidines labeled with ^{15}N [42]. A mechanistic pathway leading to XLV, a by-product in most of these reactions, is presented.

Anthracene and naphthalene have been reductively phenylated by treatment of the hydrocarbons with sodium or potassium followed by halobenzenes; for example, anthracene gives 9-phenyl-9,10-dihydroanthracene in good yield (eq. 4) [43]. The

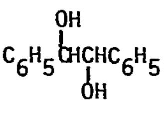


XLIV XLV

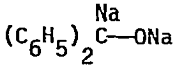
reactions are thought to proceed via a benzyne rather than an $S_{RN}1$ mechanism.



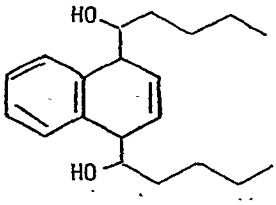
Sodium naphthalene has been employed in reactions with aromatic aldehydes and ketones to give 1,2-diols and alcohols, respectively [44]. For example, benzaldehyde and benzophenone afford 1,2-diphenyl-1,2-ethanediol (XLVI) and benzhydrol in yields of 88% and 90%, respectively. The latter reduction presumably proceeds via the 1,2-dianion XLVII. Similar reactions of aliphatic aldehydes and ketones afford naphthalene derivatives like XLVIII.


$C_6H_5\overset{OH}{C}H\underset{OH}{C}HC_6H_5$

XLVI

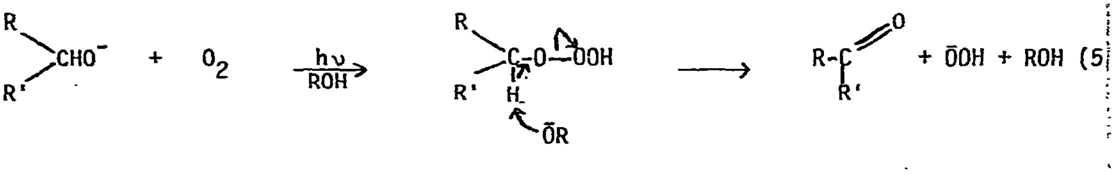

$(C_6H_5)_2\overset{Na}{C}\text{—}ONa$

XLVII



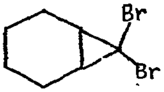
XLVIII

Primary and secondary alkoxides in the corresponding alcohol can be photooxidized by oxygen in the presence of dye-sensitizers like Rose Bengal to give the corresponding aldehydes or ketones, respectively (eq. 5) [45]. A mechanism via XLIX is proposed.



XLIX

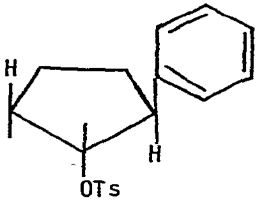
In the final paper concerned with free radicals to be mentioned herein, it is suggested that reduction of gem-dibromocyclopropanes like L by sodium borohydride to afford the corresponding monobromo compounds occurs by a free radical process [46]. Evidence is included to support the proposal and the results are compared with those obtained by other reducing agents.



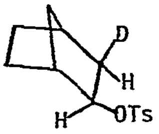
L

The effect of base strength and size on the orientation in β-eliminations of 2-iodobutane has been studied [47]. The bases employed included various alkali metal phenoxides, alkoxides, anilides, and methide bases in DMSO. Sensitivity of positional orientation to base strength decreases in the order O>N>C. Two other papers have described the effects of base association and strength upon base-promoted eliminations of trans-2-arylcyclopentyl tosylates (LI) [48] and exo-2-norbornyl-exo-3d tosylate (LII) [49]. The latter paper demonstrates the previously unrecognized importance of such association upon the stereochemistry of these β-eliminations.

Evidence has been presented that electrophilic aromatic substitution of 2,4,6-tribromobenzene by t-butyl hypobromite proceeds via a carbanion mechanism

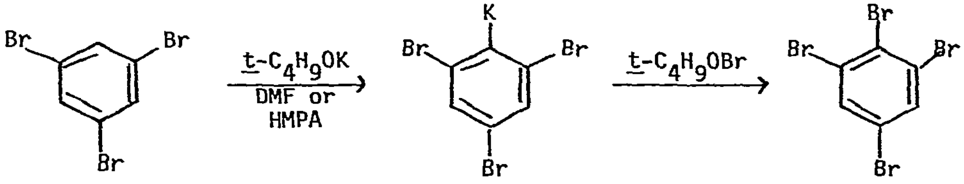


LI



LII

(eq. 6) [50]. Thus, the reaction to give LIII occurs in the presence of potassium t-butoxide but not in its absence.



(6)

LIII

Homocuneone (LIV) and the isomeric homocubanone (LV) are cleaved with potassium t-butoxide to afford esters [51]. That cleavage of LIV is complete in 30 seconds compared to a necessary 24 hour reaction period for LV is ascribed not only to strain release but also to the intermediacy of bishomoaromatic anion LVI.

LIV

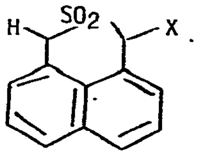
LV

LVI

Four papers described additional investigations on the Ramberg-Bäcklund reaction. Thus, α-chlorine atoms have been found to facilitate deuterium exchange of the α'-hydrogen in LVII [52]. Solvent and substituent effects on the rates of such dehydrohalogenations [53], the reaction of diastereoisomeric α-halo sulfones with base [54], and dehydrohalogenation of LVIII have been studied [55]. Each of these papers provides additional evidence that such reactions proceed via a two-stage (carbanion) mechanism

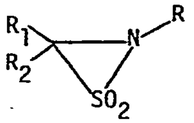
$(CH_3)_2CHSO_2CHClC_6H_5$

LVII

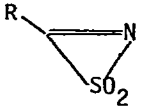


LVIII

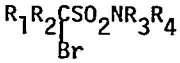
In an attempt to prepare three-membered ring systems LIX and LX, a variety of α-halosulfonamides (LXI) have been treated with potassium $\underline{t}$-butoxide or sodium [56]. Instead of the desired products though, LXI ($R_1 = R_2 = R_3 = H$, $R_4 = \underline{t}\text{-}C_4H_9$) gave LXII, and LXI ($R_1 = C_6H_5$, $R_2 = H$, $R_3 = \underline{t}\text{-}C_4H_9$, $R_4 = Cl$) gave LXIII.



LIX

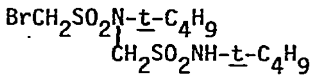


LX



$R_1R_2\underset{Br}{C}SO_2NR_3R_4$

LXI



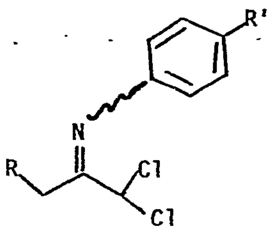
$BrCH_2SO_2\underset{CH_2SO_2NH\text{-}\underline{t}\text{-}C_4H_9}{N}\text{-}\underline{t}\text{-}C_4H_9$

LXII

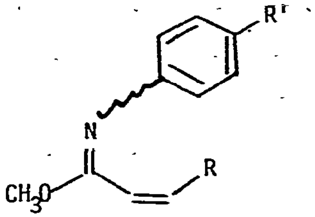
$C_6H_5CH_2SO_2NH\text{-}\underline{t}\text{-}C_4H_9$

LXIII

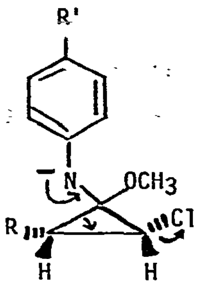
Finally, treatment of aniline LXIV with sodium methoxide and other alkoxides not only results in displacement of the chlorine atoms by methoxyl but also gives LXV via a Favorskii rearrangement [57]. A mechanism for the formation of LXV is proposed which involves the intermediacy of LXVI.



LXIV



LXV

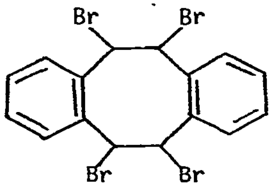


LXVI

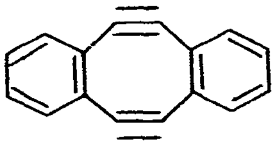
II. Synthetic Aspects

The use of potassium t-butoxide in synthesis has been reviewed [58]. Included are discussions about alkylations, arylations, acylations, aldol and aldol-like condensations, eliminations, isomerizations, rearrangements, and redox reactions.

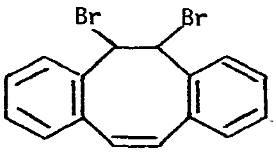
Several papers have described synthetically useful elimination reactions. Thus, dehydrobromination of LXVII with potassium t-butoxide gives the stable diyne LXVIII in a yield of 48% [59]. A similar reaction of LXIX affords the less stable LXX. NMR spectra for LXVIII, LXX, and the dianion of LXX are reported.



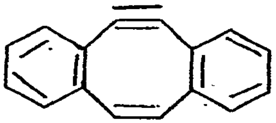
LXVII



LXVIII

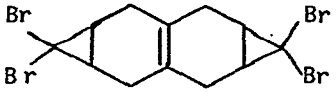


LXIX

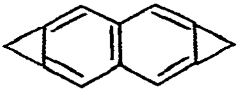


LXX

Dehydrobromination of cis or trans- LXXI with excess potassium t-butoxide affords the highly strained hydrocarbon LXXII [60]. It is estimated that LXXII has a destabilization energy of >100 kcal/mole; it is thus not surprising that it undergoes explosive decomposition at 132-133°.

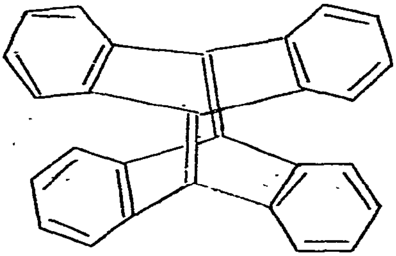


LXXI



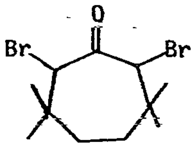
LXXII

The novel, highly strained dianthracene derivative LXXIII has been synthesized by dehydrobromination of 9,10'-dibromodianthracene with potassium t-butoxide [61]. Because of facile addition of the base to the olefinic linkages of LXXIII, the olefin had to be trapped with azide ion which was converted to the N-aminotriazoline; the olefin was regenerated by treatment with lead tetraacetate in the absence of base.



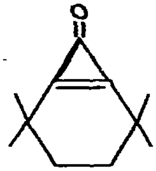
LXXIII

Similar dehydrobromination of LXXIV [62] and dehydrochlorination of LXXV [63] with potassium t-butoxide have given the strained molecules LXXVI and LXXVII in yields of 41% and 80%, respectively.

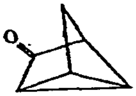


LXXIV

LXXV

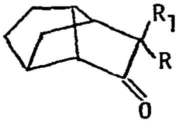


LXXVI

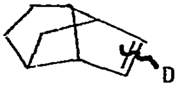


LXXVII

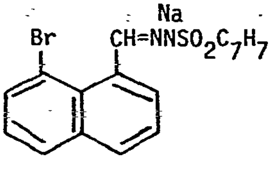
Thermolysis of the sodiotosylhydrazone of ketones like LXXVIII to give olefins like LXXIX is taken as evidence that the ease of rearrangements in thermal Bamford-Stevens reactions depends on geometry [64]. This same reaction has been employed in the conversion of LXXX to the strained 1,8-methanonaphthalene LXXXI in a yield of 46% [65]. Also, ketones can now be regenerated from tosylhydrazones by treatment with sodium hypochlorite in good to excellent yields [66].



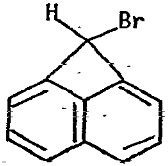
LXXVIII



LXXIX

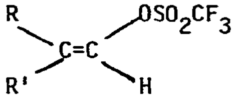


LXXX

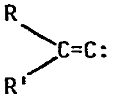


LXXXI

Finally, dialkyl vinyl triflates (LXXXII) have been found to serve as progenitors of vinylidene carbenes (LXXXIII) [67]. Thus, treatment of such species with potassium _t_-butoxide in olefinic solvents gave methylenecyclopropanes in excellent yields. Similar reactions of triflates containing β-aryl or β-hydrogens though gave only acetylenes. Reaction of 1-bromo-1,2-dienes (LXXXIV) with potassium _t_-butoxide likewise gave vinylidene carbenes [68]. These species were found to undergo insertion into the Si-H bond of triethylsilane and into the C-H bond alpha to oxygen in primary alcohols and 2,5-dimethyltetrahydrofuran.



LXXXII

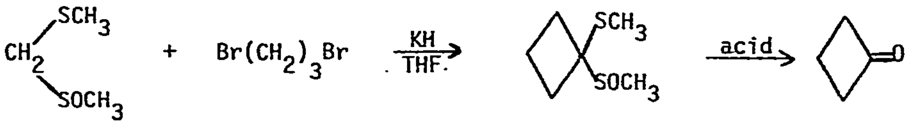


LXXXIII

$RCH{=}C{=}CHBr$

LXXXIV

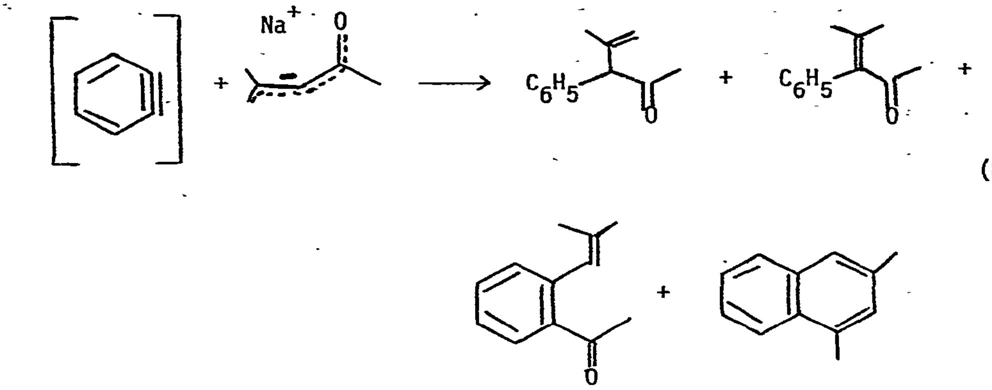
Metalations of organic compounds continue to be synthetically useful. A full paper has described the use of potassium hydride for ionization of ketones, sulfoxides, certain acidic hydrocarbons, and other compounds [69]. This reagent has been employed to effect the synthesis of cyclobutanones as illustrated by eq. 7 [70].



(7)

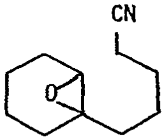
Enolates of α, β-unsaturated ketones have been condensed with benzyne as illustrated by eq. 8 [71]. Mechanisms are proposed to explain the products.

Two papers have described the preparation of ring systems using epoxynitrile cyclization [72,73]. For example, treatment of LXXXV with potassium amide in ammonia affords LXXXVI which has, in turn, been converted to a lactone, hydroxyketone, and diol. Steric control at three asymmetric centers is

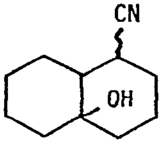


(8)

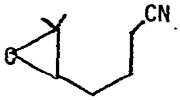
established in the cyclization. Six- and even four-membered rings are formed more easily than cyclopentane systems. Thus, LXXXVII conveniently gives LXXXVIII in a yield of 70%.



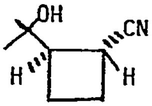
LXXXV



LXXXVI



LXXXVII

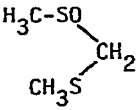


LXXXVIII

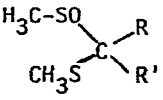
Alkylation of alkali sulfinyl esters like LXXXIX in HMPA followed by heating affords a new one-pot synthesis of α, β-unsaturated esters [74]. In an unrelated study, methyl thiomethylsulfoxide (XC) now can be dialkylated with n-alkyl bromides to give XCI, acidic hydrolysis of which affords ketones [75]. Compound XC thus serves as a carbonyl synthon.

$C_6H_5SO\underset{Na}{C}HCO_2CH_3$

LXXXIX

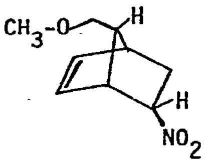


XC

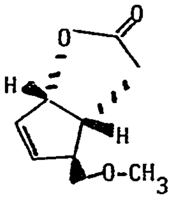


XCI

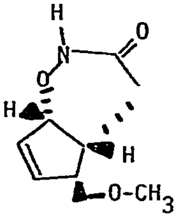
A novel preparation of prostaglandin intermediates starting with nitro compounds like XCII has been described [76]. For example, conversion of XCII to its sodium salt with sodium hydroxide followed by treatment with hydrochloric acid gives XCIII and hydroxamic acid XCIV in yields of 32% and 33%, respectively. The latter compound is easily converted to the former one with nitrous acid. Such a preparation of XCIII represents the simplest entry to the prostanoid A nucleus.



XCII

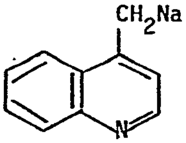


XCIII

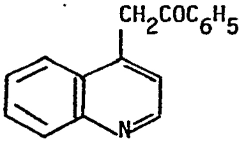


XCIV

Sodium hydride has been found to be a very efficient base to effect acylations of methylated heterocycles [77]. For example, acylation of XCV with methyl benzoate gives XCVI in a yield of 98%. The rates of these reactions are dependent upon both the concentration and polarity of the carbonyl group of the ester.

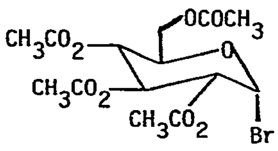


XCV

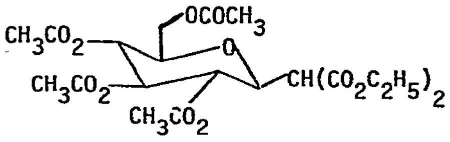


XCVI

Two full papers appeared that described $S_{N}2$-like alkylations of halogenated carbohydrates [78,79]. For example, reaction of XCVII with sodiodiethyl malonate affords XCVIII. The reactions are often complicated in the case of D-ribofuranosyl halides.



XCVII

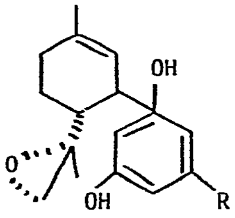


XCVIII

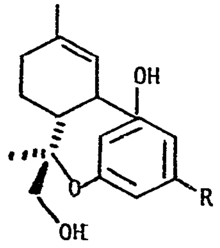
Carboxylic acids containing ^{14}C-carboxyl carbon atoms have been obtained using the known exchange reaction between sodium or potassium carboxylates and carbon dioxide (eq. 9) [80]. The reactions are run in sealed tubes at high temperatures.

$$\mathrm{RCOOM} + {}^{14}\mathrm{CO}_2 \rightleftharpoons \mathrm{R{-}{}^{14}COOM} + \mathrm{CO}_2 \tag{9}$$

Several syntheses of new and biologically active cannabinoids have been effected by a stereospecific intramolecular epoxide cleavage by phenolate anion [81]. The process is illustrated by the conversion of XCIX to C by sodium hydroxide; dihydrobenzofuran and tetrahydrobenzoxepin ring systems may also be prepared.



XCIX

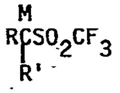


C

A survey of the reactivity and synthetic utility of triflones has been presented [82]. Included are examples of the triflinate anion CI as a nucleophile to give sulfones and as a leaving group to afford olefins, of triflone α-carbanions like CII, and of additions to vinyl triflones.

KSO_2CF_3

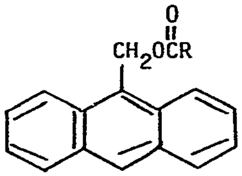
CI



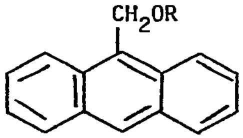
$R\overset{M}{\underset{R'}{C}}SO_2CF_3$

CII

The 9-anthrylmethyl system has been found useful as a protecting group for carboxylic acids, phenols, thiophenols, and mercaptans [83]. Carboxylic acids are protected as esters like CIII which are conveniently deblocked with sodiomethyl mercaptan. The other functional groups are protected as ethers like CIV or thioethers

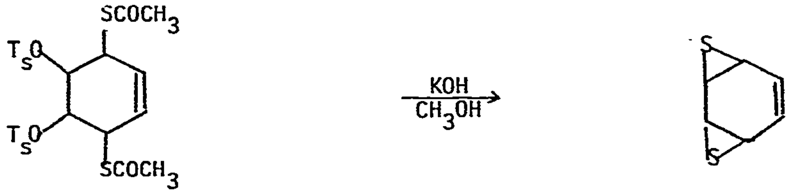


CIII



CIV

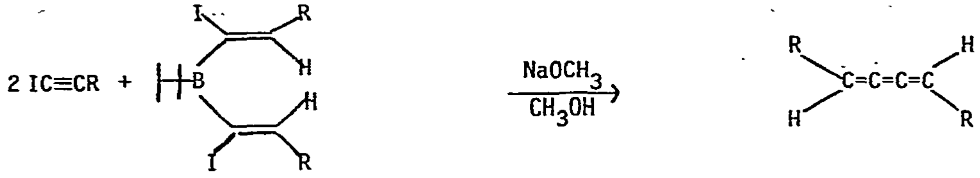
syn-Benzene bisepisulfide (CV) has been prepared as shown in eq. 10 [84]. Compound CV is the first arene episulfide to have been synthesized.



(10)

CV

Partially substituted 1,2,3-butatriene derivatives CVII may be synthesized stereoselectively by hydroboration [85]. An example is shown in eq. 11 where hydroboration of 1-iodo-1-alkynes gives boranes like CVI treatment of which by sodium methoxide gives CVII.



(11)

CVI

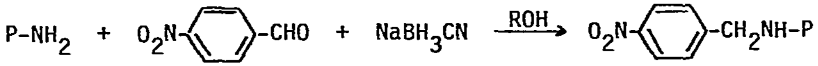
CVII

Primary aromatic and heteroaromatic amines can be N-monoalkylated by trialkyl orthocarboxylates and sodium borohydride as illustrated in eq. 12 [86].

$$ArNH_2 + HC(OC_2H_5)_3 \xrightarrow{acid} ArN{=}CHOC_2H_5 \xrightarrow{NaBH_4} ArNHCH_3 \qquad (12)$$

Though sodium hydride is seldom noted for its ability to act as a reducing agent, this reagent has been found to reduce several aliphatic azides to the corresponding primary amines in fair yield [87]. A mechanism is proposed for such transformations.

Reductive alkylations of amines by borohydride have been reported. Thus, treatment of proteins with substituted nitrobenzaldehydes and sodium cyanoborohydride gives alkylated amino acids as illustrated in eq. 13 [88]. Reaction of indole with sodium borohydride in neat carboxylic acids reduces the double bond and alkylates the nitrogen to give N-alkylindolines (CVIII) in fair to excellent yields (eq. 14) [89]. The reagents also alkylate primary and secondary amines; for example, aniline, acetic acid, and sodium borohydride affords N-ethylaniline in a yield of 88%.



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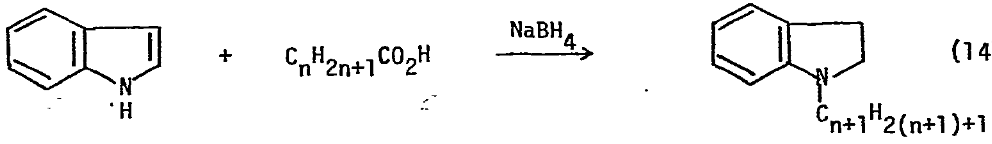
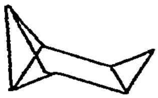


(14)

CVIII

Two new isomers of cycloheptatrienes, CIX and CX, have been prepared by sodium/ammonia reduction of certain halogenated derivatives of these compounds [90].



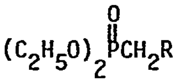
CIX

CX

The remaining papers in this section are mentioned since they provide additional examples of base-catalyzed reactions effected by phase transfer catalysis. Thus, the Wittig reaction between CXI and a variety of aldehydes has been effected in benzene with aqueous sodium hydroxide to give olefins mostly in fair to excellent yields [91]. Wittig-Horner syntheses using CXII have similarly been effected by aqueous sodium hydroxide in methylene chloride [92].

$(C_6H_5)_3\overset{+}{P}CH_2R\ \bar{X}$

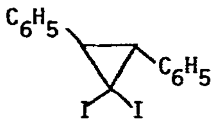
CXI



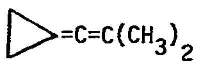
$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}CH_2R$

CXII

Previously nonisolable 1,1-diiodocyclopropanes like CXIII have now been prepared by interaction of olefins, iodoform, and sodium hydroxide in methylene chloride [93]. The products have been characterized, and their shelf-lengths are listed. Dimethylvinylidenecyclopropanes (CXIV) have been synthesized from CXV with sodium hydroxide in water-olefins in 20-40% higher yields than previously reported for single phase systems [94].



CXIII



CXIV

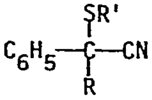
$(CH_3)_2C{=}C{=}CHBr$

CXV

Finally, organic thiocyanates have been found to be effective thiolating agents for carbanions generated in a similar two-phase system [95]. Such reactions on chloroform and alkylphenylacetonitrile give CXVI and CXVII, respectively.

$RSCCl_3$

CXVI



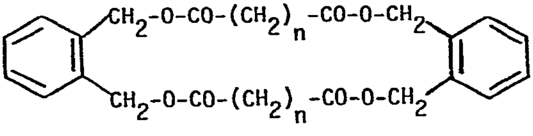
$C_6H_5-C(SR')(R)-CN$

CXVII

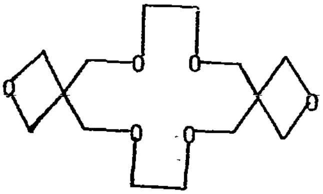
III. Alkali Metals and Cryptates

Since more and more papers in this rapidly expanding area have been appearing each year, it was decided to include those to be cited herein in a separate section.

A convenient preparation of 18-crown-6 from triethylene glycol and triethylene glycol dichloride in aqueous THF has been described in which the crown is purified via its acetonitrile complex [96]. Cyclic esters containing 16-32 members (CXVIII) have been synthesized from α,α-dibromo-o-xylene and the homologous series of dicarboxylic acids from oxalic to sebacic acid [97]. Polyethers bearing one or two spirooxetane rings like CXIX have been prepared from appropriate glycols and 3,3-bis(halomethyl)oxetanes [98]. Stability constants of these compounds with alkali thiocyanates and iodides are listed. Certain sulfur-containing systems have also been described.

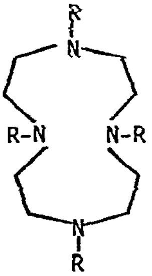


CXVIII

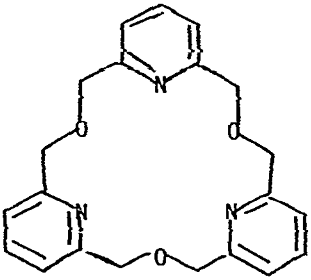


CXIX

The syntheses of various macrocyclic sulfides have been reviewed [99], and discussed in two other papers [100,101]. Nitrogen analogs of crowns like CXX containing up to 21 members have been synthesized by interacting preformed bissulfonamide sodium salts with compounds containing sulfonate ester leaving groups [102]. A variety of crowns containing pyridine units like CXXI have been prepared from bishydroxymethylpyridines and their corresponding dihalides [103]. The pKa's of the protonated crowns were determined and complexes with some of the host compounds were studied.

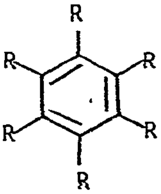


CXX



CXXI

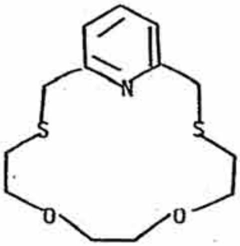
Molecules with long side-chains as illustrated by CXXII ($R = SCH_2CH_2-(OCH_2CH_2)_2OC_4H_9$) have been synthesized [104]. Such compounds have been appropriately called octopus molecules.



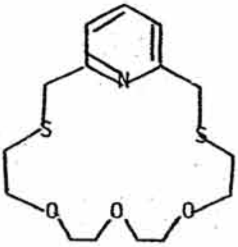
CXXII

Several novel ligand systems containing nitrogen, oxygen, and sulfur like CXXIII and CXXIV have been found which specifically complex alkali metal ions

[105]. For example, CXXIII solubilizes sodium permanganate but not potassium permanganate. Other examples are included. Isolation and chromatographic studies of alkali halides and thiocyanate with four benzo- and dibenzocrown ethers have also been studied [106].



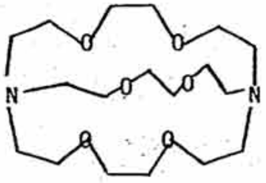
CXXIII



CXXIV

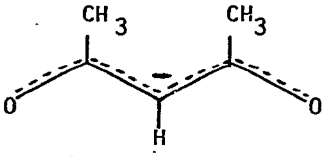
Reactions of potassium fluoride in 18-crown-6 [107] and of potassium halides in dicyclohexyl-18-crown-6 [108] have been described. The first paper discusses nucleophilic substitutions with solubilized fluoride ion while the second one delineates similar chemistry of potassium bromide and other salts. The synthesis of phenacyl esters from potassium carboxylates and α-bromoketones [109] and of acetates with potassium acetate and alkyl bromides [110] are facilitated by crowns. Nucleophilic substitutions have been effected in phase transfer systems using catalytic quantities of dicyclohexyl-18-crown-6 [111]. Phenacyl kojate has been compared with crown ethers [112].

A compound, $Na_2C_{18}H_{36}N_2O_6$, is formed from sodium/ethylamine and CXXV in which one of the sodium ions is trapped in the crypt and the other is outside [113,114]. The sodium outside the crypt is said to be a sodium anion. The crystal structure has been elucidated.

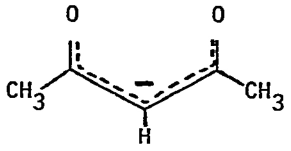


CXXV

The effect of 18-crown-6 on the conformational equilibrium of sodioacetylacetone has been studied by NMR [115]. Thus, while CXXVI and CXXVII are both present in pyridine-d_5, the amount of CXXVII is decreased as the amount of crown is increased. These data provide a measure of the relative affinities for sodium ion of the enolate anion and the crown.

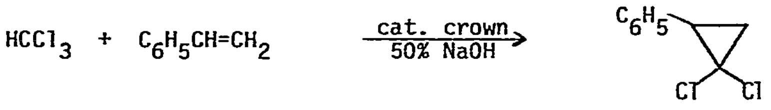


CXXVI



CXXVII

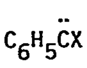
Dibenzo-18-crown-6 has been used in phase transfer reactions including alkylation of carbanions, reaction of carbanions with aromatic nitro compounds, in the Darzens condensation, and in carbene reactions [116]. An example of the latter is shown in eq. 15 in which CXXVIII is obtained in a yield of 87%.



(15)

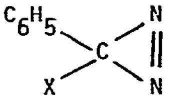
CXXVIII

Free phenylhalocarbenes like CXXIX can be generated not only by photolysis of phenylhalodiazirines like CXXX but also from CXXXI with potassium t-butoxide in the presence of 18-crown-6 [117]. In contrast, the latter reaction in the absence of crown does not afford a free carbene.



$C_6H_5\ddot{C}X$

CXXIX

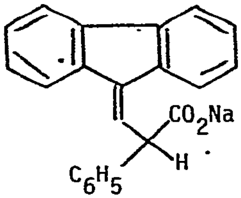


CXXX

$C_6H_5CHX_2$

CXXXI

Decarboxylation of CXXXII in THF is greatly accelerated by dibenzo-18-crown-6 [118]. Sodium and potassium dissolve in benzene and toluene in the presence of dicyclohexyl-18-crown-6 or CXXV [119]. The systems display esr spectra and should show enhanced reducing properties.



CXXXII

IV. Reactions with Inorganic and Organometallic Compounds

Metalloboroxanes and related compounds [120], and metalloboranes and metal-boron bonding [121] have been reviewed.

The first example of a selenium substituted borane has been described as shown in eq. 16 [122].

$$\begin{tikzcd} KSeCH_3 + B_2H_6 \arrow[r] & KCH_3Se(BH_3)_2 \arrow[d, "{}^1/_2\ I_2"] \\ \frac{1}{n}(CH_3SeBH_2)_n \arrow[r, shift left] & \mu\text{-}CH_3SeB_2H_5 \arrow[l, shift left] \end{tikzcd} \qquad (16)$$

Several papers described additional work in the area of metallocarborane Thus, polyhedral expansion of several such compounds by sodium in the presence of naphthalene followed by addition of sodiocyclopentadiene and cobalt(II) chloride has been employed to afford the first 11- and 13-vertex bimetallic and

[redacted]

Other new 13-vertex cobaltacarboranes like CXXXV have been prepared from CXXXVI with ethanolic potassium hydroxide in the presence of cyclopentadiene and metal salts [124]. Structures are shown. The crystal structure of CXXXVII has been determined [125].

$3,1,2\text{-}C_5H_5CoC_2B_9H_{11}$

CXXXIII

$(C_5H_5)_2Co_2C_2B_9H_{11}$

CXXXIV

$2\{4,5\text{-}(\eta\text{-}C_5H_5)_2\text{-}4,5\text{-}Co_2\text{-}1,8\text{-}C_2B_9H_{11}\}$

CXXXV

$(\eta\text{-}C_5H_5)CoC_2B_{10}H_{12}$

CXXXVI

$Cs^+[(C_5H_5)Co(CB_7H_8)]^-$

CXXXVII

Alcohols and borate esters have been obtained in good yields from alkylmercuric halides and sodium borohydride in DMF saturated with molecular oxygen [126]. The reaction is thought to involve free radicals and is illustrated by the conversion of CXXXVIII to CXXXIX.

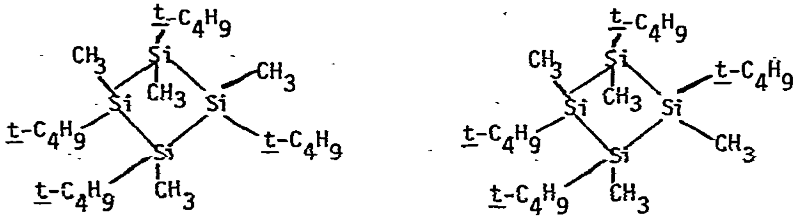
$C_5H_5C(CH_3)_2CH_2HgBr$

CXXXVIII

$C_6H_5C(CH_3)_2CH_2OH$

CXXXIX

The new, stable cyclotetrasilane CXL has been prepared by reductive coupling of t-butylmethyldichlorosilane with NaK in THF [127]. Compound CXL is inert to oxygen at 25°.



CXL

The first synthesis of a primary stannylamine, CXLI, has been accomplished as illustrated in eq. 17 [128]. All earlier attempts to prepare such compounds afforded only secondary or tertiary stannylamines.

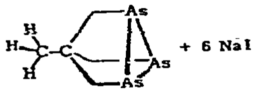
$$[(CH_3)_3C]_3SnC_6H_5 + KNH_2 \xrightarrow[0°]{NH_3} [(CH_3)_3C]_3SnNH_2 \qquad (17)$$

CXLI

Treatment of CXLII with sodium in THF has given the first described all-cis-organocyclotriarsine CXLIII [129].

$CH_3C(CH_2AsI_2)_3$

CXLII



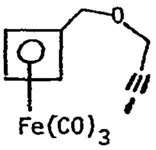
CXLIII

Sodium [N,N'-ethylenebis(salicylideneiminato)cobaltate(I)] (CXLIV) has been found to react reversibly with carbon dioxide to give CXLV (eq. 18) [130]. The compound is thus a reversible carbon dioxide carrier.

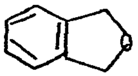
$$\text{Co(salen)Na} + CO_2 \overset{THF}{\rightleftharpoons} \text{Co(salen)}CO_2\text{Na} \qquad (18)$$

CXLIV CXLV

Cyclobutadiene has been found to react in an intramolecular fashion with attached dienophiles [131]. Thus, oxidation of CXLVI by ceric ion gives CXLVII in a yield of 50%.

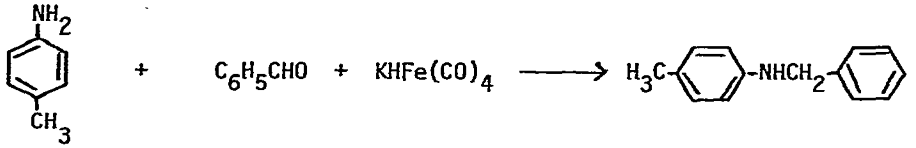


CXLVI



CXLVII

Amines and ammonia have been found to undergo facile alkylation and arylation by aldehydes in the presence of sodium or potassium iron carbonylates [132]. An example is shown in eq. 19.



(19)

Other carbonylates have been employed to synthesize other transition metal complexes. Thus, CXLVIII (M = Cr, Mo, W, Fe) react with dimethylchloroarsine to afford CXLIX [133] and with bromodimethylstibene to give CL [134]. Reaction of CXLVIII (M = Mo, Fe, Mn, Co) with CLI though gave CLII by cleavage of the C-Sn bond [135].

$[\pi\text{-}C_5H_5(CO)_nM]Na$

CXLVIII

$\pi\text{-}C_5H_5(CO)_nM\text{-}As(CH_3)_2$

CXLIX

$\pi\text{-}C_5H_5(CO)_nM\text{-}Sb(CH_3)_2$

CL

$(CH_3)_3SnCH_2I$

CLI

$(CH_3)_3SnM(CO)_n(C_5H_5)_m$

CLII

Finally, reaction of plutonium (III) iodide with sodium in liquid ammonia gave plutonium nitride of relative high purity [136]. This result is contrasted with similar reactions of other transition metal halides which normally give mixtures of metal, metal amide, and metal nitride.

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