HEAVIER ALKALI METALS

ANNUAL SURVEY COVERING THE YEAR 1975

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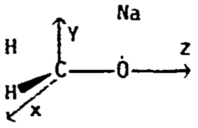
CONTENTS

1. PHYSICAL ORGANIC CHEMICAL ASPECTS

The sodium-formaldehyde ion pair has been studied by an ab initio MO SCF UHF procedure, the results of which suggest the presence of one minimum corresponding to I [1]. These results are not only in contrast to those obtained with the lithium-formaldehyde ion pair where two stable species of the ion-pair exist, but also do not agree with earlier explanations concerned with spectroscopy of certain sodium ion-ketyls ion-pairs. The discrepancies are reconciled by differences in bonding and solvation, respectively.



I

Kinetic and conductometric studies on ethereal solutions of polystyrylsodium have led the authors to conclude that the carbanion is a naked one and

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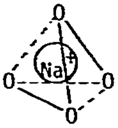
Annual Survey covering the year 1974 see J.Organometal.Chem., 103(1975)1-38.

that the cation in dimethoxyethane (DME) can be described by the kinetic entity $Na(DME)_2^+$(II) [2].



II

Several papers described additional work in the area of acidities of carbon acids. Thus, equilibrium acidities of certain sulfonyl-containing thio, phosphino, and phenyl-substituted molecules have been determined and compared with the kinetic acidities of several carbon-acids activated by these same functional groups [3]. The authors conclude that "...although kinetic acidities often give a rough guide to carbanion stabilities, conclusions regarding relative carbanion stabilities derived from kinetic measurements must be regarded as tentative, at best." The acidities of several nitriles and ketones in DMSO have been found to parallel and even approach those of the same compounds in the gas phase [4]. Such results are ascribed to the negative charge in these species being extensively delocalized. The results of the above two papers and other earlier ones are summarized in a full paper which describes the establishment of an absolute scale of acidities in DMSO using a spectrophotometric method [5]. Many earlier assigned pKa's have now been changed and different pKa values of certain compounds as a function of solvent are discussed. Indicators available to cover the pK range of 8.3 to 30.6 in DMSO are listed.

Another group of workers has presented experimental solvation enthalpies of a large number of anions derived from carbon, oxygen, and halogen acids in DMSO [6]. Both charge delocalization and steric hindrance to solvation are said to affect the solvation energies.

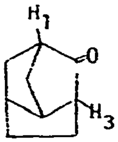
The trifluoromethylsulfonyl group has been found to lie between the nitro and benzoyl groups in its ability to activate α-hydrogen atoms towards ionization [7]. The use of this and other functional groups attached to methyl, isopropyl, and cyclopropyl moieties has provided quantitative data which allow an estimate to be made of the extent to which cyclopropyl anions are strained and thus destabilized. Both in the cyclic and acyclic systems, it is concluded that the SO_2CF_3 group exerts a large conjugative effect with carbanions.

Equilibrium-acidities have also been studied using cesium salts and a variety of hydrocarbons and other compounds in DMSO [8], and cesium salts and a variety of substituted dithianes in cyclohexylamine [9]. Finally, in an unrelated study, the kinetic acidity of III has been found to be greater than that of tritiated triphenylmethane indicating that alpha-trimethylsilyl groups stabilize carbanions substantially [10].

$$(\equiv Si)_3C^3H$$

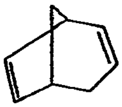
III

The bridgehead hydrogen H_3, shown in structure IV, has been found to undergo exchange in deuterated methanol using sodium methoxide at the remarkably low temperature of 25° [11]. In contrast, H_1 in IV fails to exchange under these conditions. These results along with those on other ring systems have led the authors to state that enolate stability in such polycyclics is enhanced at the side of bridged boat forms but not at their bows. The stability of similar enolates in locked chain forms is diminished considerably.

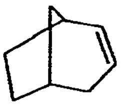


IV

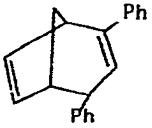
In contrast to the corresponding non-phenylated systems V and VI, the αhydrogens of VII and VIII are exchanged with deuterium at virtually the same rate suggesting that the phenyl groups in VII cause the elimination of charge delocalization from C_4 to the double bond at $C_{6,7}$ previously observed in V [12]. The results are discussed in relation to earlier described carbonium ion chemistry.



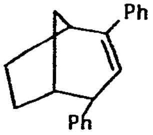
V



VI

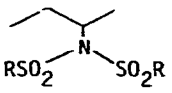


VII



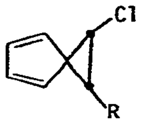
VIII

The influence of ionic association in β-elimination reactions has been reviewed [13]. Other papers in this area have addressed the question of hydrogen tunneling in the elimination of certain 2-phenylethyl systems [14], the olefin distribution from E_2 reactions of five secondary alkyl bromides [15], and the orientation of similar reactions of 2-butyl-N,N-disulfonimides (IX) [16]. The latter reactions are noteworthy in that such eliminations afforded only 1-butene.

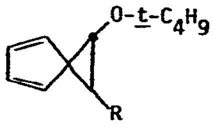


IX

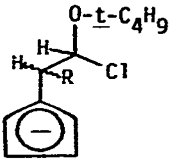
A new type of 1,3-dehydrohalogenation has been proposed to account for the conversion of species like X to XI effected by potassium t-butoxide [17]. The reactions presumably proceed via ring-opened intermediates XII which stereospecifically eliminate potassium chloride to afford trans-products.



X

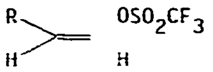


XI

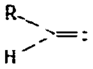


XII

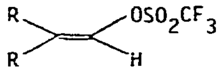
Three more papers appeared describing additional aspects of the preparation and reactions of unsaturated carbenes or acetylenes from vinyl trifluoromethanesulfonates. In the case of acetylene formation from XIII and base, it has now been shown by deuterium labelling that such products arise via α-elimination [18]. Carbenes from XV have now been shown to exist in the singlet state [19] as free carbenes, not as carbenoids [20].



XIII



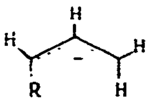
XIV



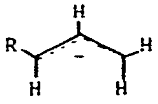
XV

1-Butene has been isomerized by potassium metal without a support to give trans-2- and cis-2-butene in ratios of 0.1-0.2 and about one at temperatures of 20-40° and 90-140°, respectively [21].

Considering the area of spectroscopy applied to organoalkalies, neopentylallylsodium has been synthesized and its proton NMR recorded to reveal the presence of cis- and trans-forms XVI and XVII (R = neopentyl) [22]. The former isomer predominates as confirmed by hydrolysis, and the results are related to those obtained with neopentylallyllithium. Isomers XVI and XVII are in a dynamic equilibrium that is slow on the NMR time scale.



XVI



XVII

Carbon-13 shift values have now been reported for allylpotassium, pentadienylpotassium, 1-phenylallylpotassium, benzylpotassium, and triphenylmethylpotassium [23]. The relationship between chemical shifts and π-density is discussed.

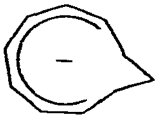
The proton NMR of phenylcyclopentadienide anion has been obtained at

100 MHz [24]. In conjugation with the NMR spectra of phenyltropylium cation, the authors conclude that the proportionality constant of 10 ppm/unit charge is open to question.

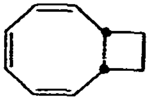
Conformational mobility in the potassium salt of *cis*,*cis*,*cis*,*trans*-[9]-annulene has been studied by proton NMR [25]. The spectra at various temperatures are interpreted in terms of rotation of the *trans*-bond about the neighboring bonds leading to a dynamic equilibrium between nine topomers. Such topomerization is demonstrated chemically.

Protonation of sodium naphthalene, sodium anthracene, and sodium pyrene with water or two alcohols has been found to occur directly rather than via a disproportionation sequence as evidenced by CIDNP at 60-G [26]. Interestingly, such CIDNP is not observed at a higher field of 5000-G.

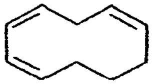
The cyclodecatrienyl anion XVIII has been prepared by reaction of triene XIX with potassium and by proton abstraction of XX by potassium amide [27]. The NMR spectrum of XVIII at -65° indicates the presence of a symmetrical species; this compound undergoes electrocyclization at -41°.



XVIII



XIX



XX

A full paper appeared which discussed the results of a detailed examination of the homoenolization of fenchone (XXI) [28]. That deuterium exchange occurs at the five β-positions was demonstrated by ^{13}C and ^{2}H NMR spectroscopy.

XXI

Other papers describing NMR spectra of carbanions and related compounds included the following: ^{13}C NMR of the sodium salts of several diethyl alkylmalonates [29], ^{1}H NMR of the sodium enolates of certain β-diketones and β-ketoesters [30], the ^{1}H NMR of the oxanonatetraenyl anion [31], and the ^{1}H NMR of an alkoxide adduct of a carboxamide [32]. Finally, ^{39}K NMR and ^{87}Rb NMR experiments have been effected on certain inorganic species in the presence of dibenzo-18-crown-6 [33].

Electron transfer processes as measured by ESR spectroscopy have been chosen as a tool to investigate the dynamic flexibility of certain chains which contain a radical anion of a hydrocarbon on one end and the corresponding hydrocarbon on the other end as illustrated by XXII (n = 3 to 20) [34]. It has been determined that the shape of the ESR spectra of such systems is a function of the frequency of intramolecular electron transfer between the aromatic moieties which, in turn, is a function of n and temperature. The processes are treated as if they were bimolecular exchanges. Three other papers used the above technique to investigate peculiarities in systems XXII where n = 3 and 4 [35], to study electron transfer between N-*n*-butylphthalimide radical anion and its parent [36], and to investigate electron transfer in XXII where Ar = phthalimide [37].

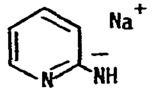
$$\text{Ar}\text{—}(\text{CH}_2)_n\text{Ar}^{\overset{\cdot}{-}}$$

XXII

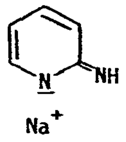
The following species have been prepared and their ESR spectra recorded: benzyl radical [38], toluene radical anion [38, 39, 40], benzene radical anion [39, 40], mesitylene radical anion [40], 2,3-naphthobarrelene radical anion [41], 2,3-naphthobarrelane radical anion [41], *cis*- and *trans*-1,2-*bis*(diphenylphosphinyl)ethylene radical anions [42], several hindered alkylbiphenyl radical anions [43], radical anions of certain triptycene and [2.2]-paracyclophane derivatives [44], and radical anions of a variety of ring substituted silyl-anilines [45, 46, 47].

Ultraviolet spectroscopy has been employed to obtain the first direct evidence for carbanion ion pairing in methanol [48]. Specifically, though solutions of potassium or lithium fluoradenide in this solvent exhibited spectra attributed only to hydrogen bonded, free ions, the spectra from solutions of this carbanion with tetramethylammonium methoxide or of potassium fluoradenide in the presence of 18-crown-6 suggested the presence of contact ion pairs. UV spectroscopy has also been used to study the effect of THF and dioxane on the kinetics of electron photoejection from disodiotetraphenylethylene effected by a 530-nm pulse [49]. It was found that the excited state behaved differently in the two solvents, the bleached state persisting longer in THF than in dioxane. These results were rationalized by the relative tightness of the aggregates in the respective media.

Two other papers in this area of spectroscopy deserve brief mention. First, a variety of N-sodioamino-N-heteroaromatics have been studied by infrared spectroscopy; the authors conclude that in the crystalline state, such compounds exist in the amino forms like XXIII, not in the tautomeric imino forms as in XXIV [50]. Second, microwave spectroscopy has been employed to demonstrate that the hydrogen exchange reaction between propylene and deuterated DMSO in the presence of base proceeds via a π-allyl intermediate [51].



XXIII

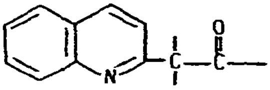


XXIV

Concerning mechanistic studies, the isomerization of *cis*- to *trans*-stilbene continued to be studied. The current investigation was centered around the use of sodium biphenylide on *cis*-stilbene where it was determined that the rate-determining step was the conversion of the *cis*- to the *trans*-stilbene radical anion [52].

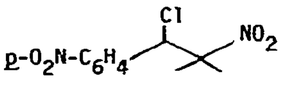
Two more papers appeared describing the reaction of certain alkyl halides with aromatic radical anions. In the first, sodium naphthalene and anthracene were reacted with n-hexyl bromide and chloride; among others, the authors conclude that the irreversible electron transfer "involves an early transistion state with little bond breaking and charge delocalization on the halide" [53]. The second paper studied similar reactions with n-hexyl fluoride carried out in various ethereal solvents [54]. These authors suggest that the negative charge in the transistion state is more localized in such reactions of fluorides relative to that of the naphthalene radical anion. The latter paper discusses the differences in shapes of the Arrhenius plots described in both papers.

Several potassium, but not lithium enolates have been found to react with 2-chloroquinoline to afford XXV provided the reactions are subjected to photostimulation [55]. Another paper concerned with this $S_{RN}1$ mechanism describes similar chemistry of iodobenzene and related compounds with certain thiolate anions [56]. Fragmentation products of intermediate radical anions are described and rationalized.

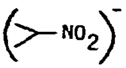


XXV

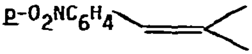
The term $E_{RC}1$ has been applied to a unimolecular radical anion-radical chain elimination process as illustrated by the light-stimulated reaction of XXVI with XXVII to afford styrene derivative XXVIII [57]. Several other examples are included.



XXVI

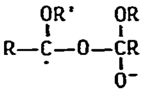


XXVII



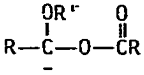
XXVIII

An alternative mechanism for the acyloin condensation has been presented which does not involve α-diketones [58]. Instead, the pathway proposed consists of a series of discrete steps differing one from the other by one electron. Structures XXIX-XXXI illustrate only three of the suggested intermediates.



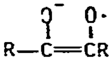
$\mathrm{R{-}\underset{\cdot}{\overset{OR'}{C}}{-}O{-}\underset{O^-}{\overset{OR'}{C}}R}$

XXIX



$\mathrm{R{-}\underset{-}{\overset{OR'}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}R}$

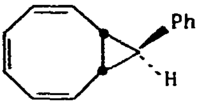
XXX



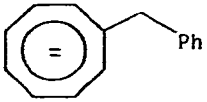
$\mathrm{R{-}\overset{O^-}{C}{=}\overset{O\cdot}{C}R}$

XXXI

Reduction of XXXII with potassium has been shown to afford dianion XXXIII [59]. These results are in marked contrast to similar reductions of alkylated rather than phenylated XXXII which previously have been shown to afford cyclononyl systems. Possible mechanisms are proposed for the current reaction.

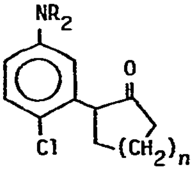


XXXII

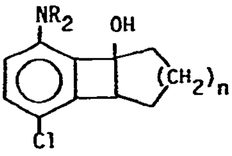


XXXIII

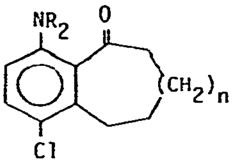
A variety of ketone enolates have been reacted with several dialkylaminochlorobenzenes in the presence of base to give products like XXXIV-XXXVII in varying yields depending upon choice of substrates and base [60]. Most of the products presumably arise via aryne intermediates. A second paper was concerned with the formation of benzofurans like XXXVII where it is demonstrated that species like XXXIV are intermediates in their formation [61].



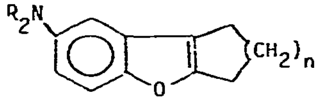
XXXIV



XXXV



XXXVI

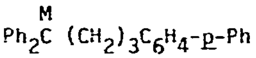


XXXVII

1,4-Rearrangement of XXXVIII, prepared from the corresponding chloride and alkali metals, has been realized to afford XXXIX as evidenced by carbonation, protonation, and NMR spectroscopy [62]. This 1,4-migration is much less facile than related 1,2-rearrangements and increases in the order Li<<Na<<K, Cs. Evidence could not be garnered to demonstrate the presence of non-classical ion XL.

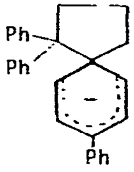
$\underline{p}$-Ph-$C_6H_4C(Ph)_2(CH_2)_3M$

XXXVIII



$\overset{M}{Ph_2C}\ (CH_2)_3C_6H_4$-$\underline{p}$-Ph

XXXIX



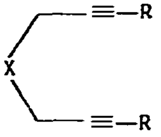
XL

Other studies of rearrangements that deserve mention include the mechanism of the Stevens rearrangement [63], a quantitative CIDNP study in the latter [64], allowed and forbidden sigmatropic pathways in the latter [65], base-catalyzed rearrangements of 3-(α-haloacyl)indoles [66], Favorskii reactions of equatorial and axial 2-bromobenzo[6,7]bicyclo[3.2.1]-oct-6-en-3-one [67], and the Favorskii reaction of certain dichlorinated methylketones [68].

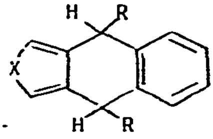
2. SYNTHETIC ASPECTS

A warning about another explosion involving perchloryl fluoride and an organometallic has been published [69]. The current explosion occurred with a mixture of benzocyclobutene, potassium $\underline{t}$-butoxide, $\underline{n}$-butyllithium, and perchloryl fluoride. The desired 3-fluorobenzocyclobutene has been prepared by a safer route.

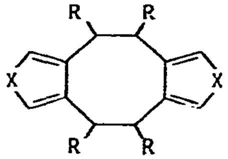
Another strong potassium base, that of 3-aminopropylamide, has been described [70] and employed in the facile contrathermodynamic isomerization of internal to terminal acetylenes [70, 71]. In another study, a variety of bis-propargyl compounds (XLI, G = O, N, S) have been reacted with potassium t-butoxide or KOH to afford XLII, XLIII, or XLIV depending upon the base and the group R [72]. The reactions are postulated to proceed via diallene intermediates.



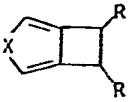
XLI



XLII

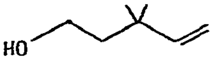


XLIII

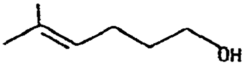


XLIV

Metalation of 3-methyl-1-butene by trimethylsilypotassium followed by addition of ethylene oxide has been found to afford a mixture of XLV (28%) and XLVI (37%) [73].

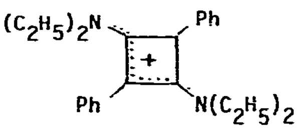


XLV

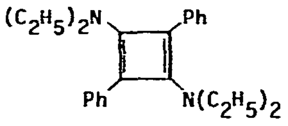


XLVI

Several new, stable cyclobutadienes have been described, the last step of their synthesis being proton abstraction by strong bases [74]. The process is illustrated by the conversion of XLVII to XLVIII.



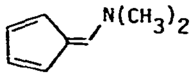
XLVII



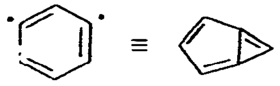
XLVIII

Double dehydrobromination of XLIX by potassium t-butoxide followed by addition of dimethylamine has been found to give 6-dimethylaminofulvene (L) [75]. The authors suggest that the reaction proceeds via m-benzyne LI.

XLIX

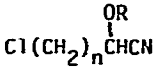


L



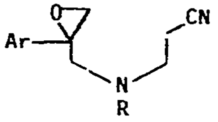
LI

Cyclopropane and cyclobutanone cyanohydrins have been prepared by cyclization of chlorocyanohydrins LII (n = 2 or 3) effected by sodiohexamethyldisilazane [76]. Similar cyclizations have been carried out on certain aminocyanoepoxides like LIII to afford pyrrolidines like LIV (G = NH, O or H_2) [77]. The subject of ring size in such cyclizations has been discussed [77, 78]. Other cyclizations described in 1975 include the preparation of epoxides from β-hydroxyalkylselenonium salts [79] and of naphthyridines from dinitriles [80].

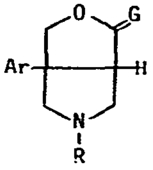


$Cl(CH_2)_n\overset{OR}{\overset{|}{C}}HCN$

LII

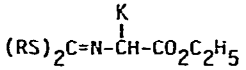


LIII



LIV

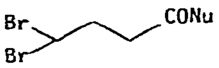
Alkylation and subsequent oxidation of LV has been found to constitute a convenient synthesis of chain-extented and α-branched α-amino acids; several examples are listed [81].



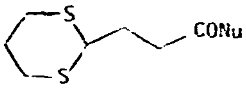
$(RS)_2C{=}N{-}\overset{K}{C}H{-}CO_2C_2H_5$

LV

Cyclobutanones containing α,α-dibromo or α,α-trimethylenedithio substituents are readily cleaved by basic reagents (NuM) to afford γ-substituted systems like LVI or LVII, respectively [82, 83]. In conjunction with earlier described spiroannelations, the method represents reductive alkylation or geminal alkylation of a carbonyl group. The nucleophiles used to date include hydroxide, alkoxide, and methyllithium to give acids, esters, and ketones, respectively.

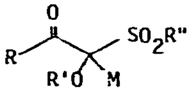


LVI

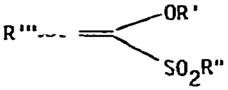


LVII

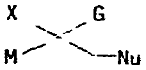
Other studies in this area that deserve mention include the condensation of LVIII with non-enolizable aldehydes to afford enol ethers of hypothetical α-ketosulfones (LIX) [84], the generation of Darzens intermediates LX (G = carbonyl-containing functional group or cyanide) by conjugate addition of a nucleophile to a vinyl halide [85], and a discussion of the formation of cyclopropanes versus epoxides from the reactions of α-haloacrylic acid derivatives, carbonyl compounds, and base [86].



LVIII



LIX



LX

Several papers discussed aliphatic semidiones. Systems specifically covered included bicyclo[3.2.0]hep-2-ene-6,7-semidiones [87], cycloheptane-1,2-

-emidiones [88], alkenyl and cycloalkyl substituted 1,2-semidiones [89], and certain carbocyclic conjugated unsaturated 1,2-semidiones [90].

Finally, the preparations of naphthalene cesium and phenylpyridine cesium have been described [91].

3. REACTIONS WITH INORGANIC AND ORGANOMETALLIC COMPOUNDS

Eight examples of complexes LXI and LXII have been observed in reactions of alkali metal hydrides with certain magnesium alkyls and aryls [92]. For example, potassium hydride and di-n-butylmagnesium afford LXI in benzene; similarly, this hydride and diphenylmagnesium give LXII in ether. Both solvent and metallic cation are important in determining which complex is formed; for example, no reaction was observed in the case of lithium hydride and dimethylmagnesium in ether.

$MMgR_2H$ LXI

MMg_2R_4H LXII

A review discussing certain aspects of metallocarborane chemistry has been published [93]. The synthesis and crystal structure of a new ferracarborane, $(C_5H_5)_2Fe_2C_2B_6H_8$, has been described [94]. The compound was prepared by a polyhedral expansion of 4,5-$C_2B_7H_9$ with sodium cyclopentadienide and ferrous chloride. Metallocarborane complexes of titanium, zirconium, and vanadium have been synthesized by treatment of certain closo carboranes with sodium, then transistion metal halides [95]. Four isomers of the mixed-metal bimetallocarborane, $(C_5H_5)_2CoNiCB_7H_8$ have been prepared. Some of their chemistry has been presented including novel thermal polyhedral rearrangements in which the metal atoms migrate to adjacent polyhedral vertices [96]. The synthesis of several nickelaboranes has also been discussed [97, 98].

Tetraborane has been deprotonated by potassium hydride or ammonia to afford the corresponding anion [99]. The preparation of $B_5H_8^-$, $B_6H_9^-$, $B_5H_{12}^-$, $B_6H_{11}^-$, and B_7H_{12} are also described. NMR and "B spectra have been reported for the above species. Mixed trialkylboranes have been synthesized in high yields by treatment of dialkylbromoboranes with sodium hydride in the presence of an alkene [100]. A new route to certain derivatives of borabenzene from bis-(borinato)cobalt complexes has been presented [101]. Finally, several alcoholates of aluminium chloride have been reacted with sodium cyclopentadienide to give corresponding π-cyclopentadiene compounds [102].

In the area of metal carbonyl anions, reviews have been published concerned with their reactivity patterns [103], and with their use in the syntheses of novel organometallic compounds [104]. Another review discusses disodium tetracarbonylferrate as a transition metal analog of Grignard reagents [105].

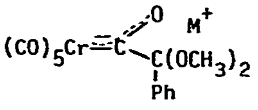
Convenient preparations of metal carbonyl anions have been effected by treatment of the corresponding metal carbonyls with alkali metal amalgams [106], with sodium-potassium alloy [107], and with C_8K [108]. Sodium-amalgam reduction of LXIII has afforded the new isonitrile-containing species LXIV which has been alkylated by a variety of alkyl and Group IV halides [109]. Reaction of pentacarbonyl[methoxy(phenyl)carbene]chromium(0) with base has given anion LXV; this species has been alkylated and its proton NMR recorded [110].

$(C_5H_5)Mo(CO)_2(CNCH_3)Cl$

LXIII

$(C_5H_5)Mo(CO)_2(CNCH_3)M$

LXIV



LXV

Reactions of metal carbonyl anions have been the subject of several papers. Thus, such species have been interacted with α-chloroenamines [111], fluoroaromatics [112], fluoroolefins [113], 1,2,3-tri-t-butylcyclopropenium cation [114], and methyl organometallics [115].

Carbonyl ferrate systems continue to be studied. For example, tetracarbonyl ferrates have been employed to couple aldehydes with ketones or other aldehydes [116], to prepare aldehydes and aldehydic acids from acid anhydrides [117], and to synthesize ethyl ketones from alkyl halides and ethylene [118]. Cyclopentadienyl carbonyl ferrates have been utilized in stereospecific deoxygenation of epoxides [119] and in the preparation of certain silicon containing compounds [120, 121].

With respect to sandwich compounds, ferrocenes substituted in the 1,1'-positions with cyanoalkyl groups have been cyclized by bases to afford ferrocenophanes [122]. Reaction of dipotassio-1,3,5,7-tetraphenylcyclooctatetraene with uranium tetrachloride has given bis-π-(1,3,5,7-tetraphenylcyclooctatetraene)uranium, an air stable uranocene [123]. Several negatively charged sandwich compounds involving niobium and tantalum with cyclooctatetraene [124] and vanadium with benzene [125] have been disclosed.

Finally, some miscellaneous papers deserve mention. The ability of sodium hydride to reduce certain carbon-halogen bonds has been enhanced by complexing it with nickel, cobalt, and copper salts [126]. Dipentadienylzinc complexed with THF has been prepared from pentadienylpotassium and zinc chloride [127]. Primary germylamine LXVI has been synthesized from chlorotriisopropylgermane and potassium amide [128]. Base-catalyzed additions of various mono- and disubstituted phosphines to certain vinylphosphorus derivatives have been reported to afford polyphosphines like LXVII and LXVIII [129, 130].

$(i\text{-}C_3H_7)_3GeNH_2$

LXVI

$RPHCH_2CH_2PH_2$

LXVII

$R_2PCH_2CH_2PR_2'$

LXVIII

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