SODIUM AND POTASSIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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Two works containing reviews of the structures of alkali metal compounds have been published in the past year [1,2].

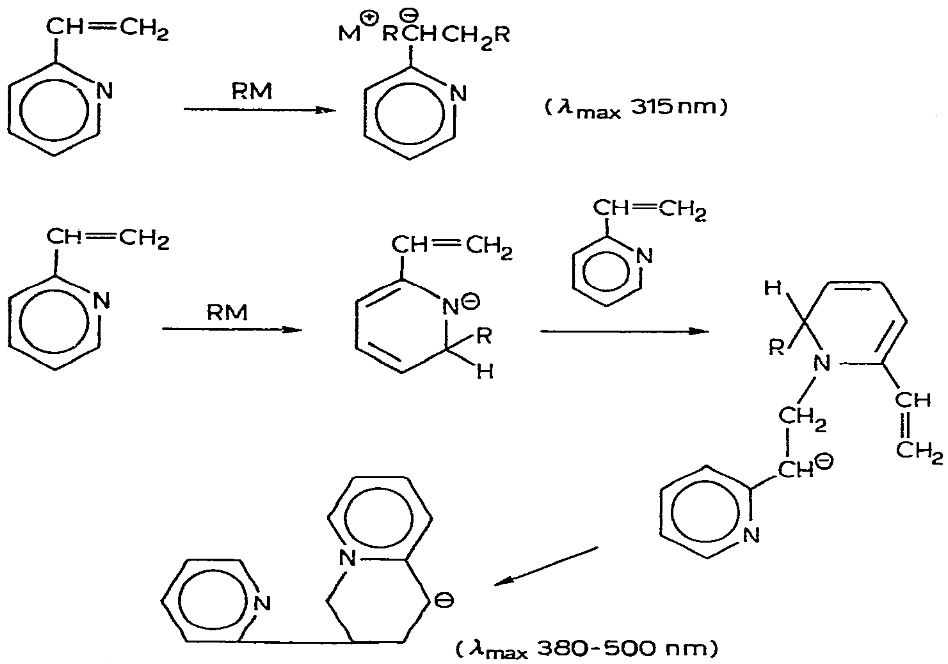
Jackman and coworkers have analyzed the ^{1}H NMR spectra of triphenylmethyl-, fluorenyl-, and indenyl-alkali metal compounds in donor solvents [3]. The principal features of the spectra were interpreted in terms of contact and solvent-separated ion pair equilibria. Dutch workers also have examined the indenyl system in THF and DME with similar interpretation of the spectra. In THF the preferred position of the Na^+ and K^+ in the contact pairs was taken to be over the five, rather than the six membered ring [4].

Smid has reviewed the properties of delocalized organoalkali compounds such as fluorenylsodium in donor solvents including polyglycol ethers [5]. Smid and coworkers also have determined that fluorenylalkali compounds obey Beers Law in THF and in the presence of some crown ethers [6]. Thus, spectrophotometry may be used for the quantitative determination of such compounds in dilute solution.

The compounds fluorenylcesium, indenylcesium and triphenylmethylcesium have been studied by spectrophotometry in cyclohexylamine (CHA) or CHA-diethylamine solvents [7]. Thermodynamic constants for ion pair equilibria were obtained from the variation of the spectra with temperature. As expected, the cesium salts of these carbanions are largely in the form of contact-ion pairs.

A similar spectrophotometric study of the alkali metal-triphenylene anion radicals has appeared [8]. In 2-methyltetrahydrofuran, one may identify contact and solvent-separated ion pairs as well as free ion spectra.

A long-wavelength shoulder in the spectrum of poly-2-vinylpyridine anions has been explained in terms of a secondary reaction product I, rather than in terms of ionic equilibria [9]. The same authors have presented electric conductivity data on this system ($M = Na^+$, K^+ and Cs^+ in THF) [10]. Especially for the smaller cations, the dissociation of these salts is much less than that of the corresponding polystyrylmetal salts.



I

The ^1H NMR spectra of the alkali metal derivatives of 1- and 2-methylnaphthalene have been reported [11,12]. The authors conclude that the term $[1 - 1/(3.5\ R_{M^+})]$, where R_{M^+} is the radius of the cation, may be interpreted as the fractional C-M bond delocalization in the contact ion pair. Thus, in THF the percentages delocalization for the Li, Na and K salts were concluded to be 58, 71 and 79% respectively.

Young and coworkers have continued to investigate the ^{1}H NMR [13] and visible-uv absorption spectra [14] of phenylallyl anions [AS 71; 3, 66]. Equilibrium constants and thermodynamic values for ion pair equilibria are obtained by both methods which are in reasonable agreement with each other.

Other workers have studied the absorption spectra of a series of alkali derivatives of nitrogen heterocyclics in liquid ammonia [15]. Some Hückel MO calculations were used to correlate the observed spectra. Substituent effects were also considered.

Absorption and fluorescence spectra have been analyzed for lithium and potassium derivatives of the carbanions of fluorene, 4,5-methylenephenanthrene and indene, and nitranions of carbazole, 4,5-iminophenanthrene and indole [16]. Of particular interest was the observation that the fluorescence spectra of the carbanions were insensitive to the nature of the alkali ion. The authors conclude that contact ion pairs are converted into solvent-separated ion pairs in the first excited state.

Also reported in the past year were photoionization spectra of alkali metal-pyrene and -biphenyl compounds [17]. Infrared spectra of the carbanions of 2- and 4-methylpyridine, 2- and 4-methylquinoline, methylquinoline, 2,4- and 2,6-lutidine, and other nitrogeneous heterocycles have been reported [18]. Infrared spectra of tetracene and pentacene anions and dianions have also been reported [19].

The crystal structure of $[Na(THF)_2]_2[Al(CH_3)_2C_{14}H_{10}]_2$, where

$C_{14}H_{10}$ = 9,10-dihydro-9,10-anthrylene, has been determined by x-ray crystallography [20]. Although the compound would not be viewed as an organosodium compound, the structure does illustrate the nature of Na^+-solvent-carbanion interactions in the solid state.

Streitweiser and coworkers have determined the pK's of more weak carbon acids by measuring the extent of reaction (1) in cyclohexylamine solvent [21]:

$$R_1H + R_2^-Cs^+ \rightleftharpoons R_2H + R_1^-Cs^+ \qquad (1)$$

Bank and Bockrath have utilized the stopped flow kinetic method for the study of the reaction between sodium anthracene and water [22, AS 71; 70]. The study was complicated due to the fact that the anthracene dianion is the major species formed from sodium and anthracene in THF. The observed rate law is $-d[\text{Anth}^{\dot{-}}]/dt = 2k[\text{Anth}^{\dot{-}}][H_2O]$. The anthracene anion is less reactive to water than the naphthalene anion. Also reported the past year were the kinetics of the reaction of $K^+\text{Naph}^{\dot{-}}$ with Ph_2CH_2, Ph_3CH and fluorene [23].

Schulz and coworkers have reviewed the kinetics of carbanionic polymerizations with particular attention to propagation of polystyrylsodium ions and ion pairs [24].

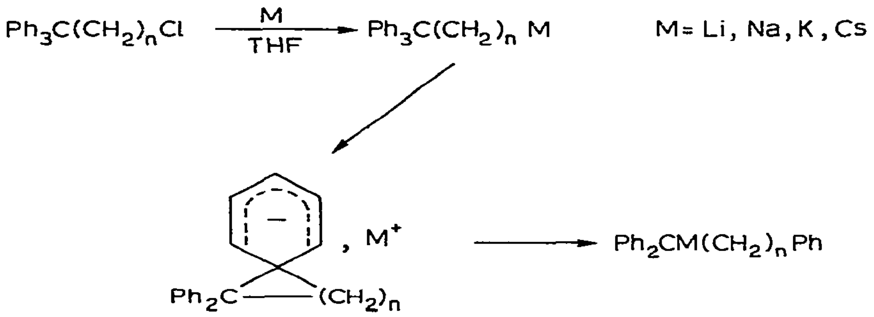
The use of large electric fields to augment polymerization kinetics studies has been exploited by Ise and coworkers [25, AS 70; 260]. The propagation kinetics of poly(o-methylstyrene) have been studied with Li^+, Na^+, K^+ and Cs^+ cations in 2-methyltetrahydrofuran. The rates are lower in general than for polystyrene, and the order of reactivity ($Li^+ > Na^+ > K^+ > Cs^+$) parallels the degree of dissociation of the ion pairs. The authors attribute these effects to the steric repulsion of the o-methyl substituent which prevents highly solvated cations from association with the carbanion center. The same group has studied the kinetics of polymerization of styrene, m-methylstyrene, p-isopropylstyrene and p-methylstyrene in THF with Cs^+ gegenion [26]. Whereas the ion pair-free ion dissociation constants were found to be invariant for this series, the free ion and ion pair rate constants increased in the order p-methoxy-<p-methyl-∿m-methyl<styrene. (The p-methoxy data were obtained in earlier work and the p-isopropyl data were excluded due to the presence of an impurity in that system.)

Other papers have appeared pertaining to the polymerization with alkali metal initiators of the following monomers: methyl methacrylate [27], isoprenyl-substituted heterocyclic compounds [28], various fluoromethyl-substituted styrenes [29], methacrylic esters [30], and 1,1-bis(trifluoromethyl)-1,3-butadiene [31]. Also reported was the coupling of acrylonitrile with living polybutadienes [32], and the cleavage of polyphenyl ethers with sodium in HMPA [33].

Absorption spectra of the living polymer of 2-vinylpyrene have been observed and compared with corresponding spectra of polystyrylpotassium and other arylmethide ions [34].

The microstructure of anionically initiated polyisoprene using different solvents and gegenions has been interpreted in terms of free ion and ion pair propagation mechanisms [35]. The authors conclude that the influence of the alkali gegenion is important only when contact ion pairs are the principal kinetic species, and they propose alternate mechanisms to account for 1,4- and 1,2-addition.

Grovenstein and coworkers have continued to examine aryl migrations in carbanionic systems [AS 70; 286]. In recent work, this group has shown that 4-chloro-1,1,1-triphenylbutane and 5-chloro-1,1,1-triphenylpentane show evidence of 1,4- and 1,5-phenyl migration in the presence of alkali metals in THF [36]. The yields are not comparable with those obtained when 1,2-aryl migration is possible (n=1 in the following equation):

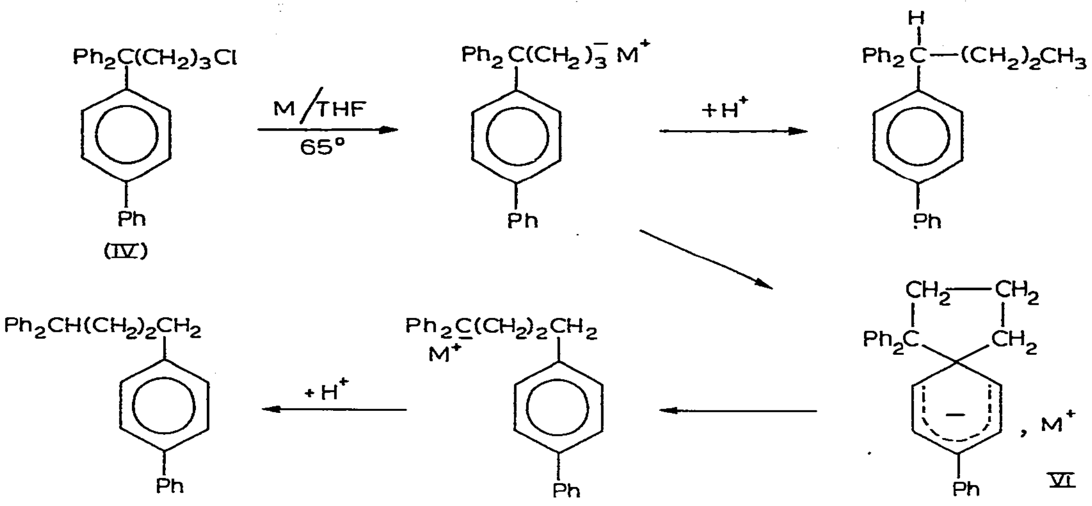


Of particular interest is the use of cesium alloys which allow work at rather low temperatures. The cesium and potassium salts of II were found to undergo 1,2-(p-biphenyl) migration [37]. The yields of III and IV were quite dependent on the metal and temperature

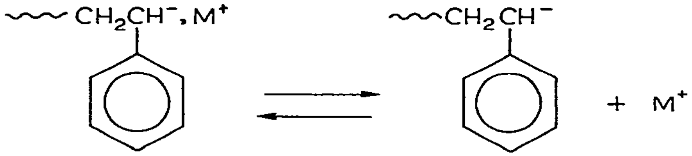
$$\underset{(II)}{p\text{-}PhC_6H_4CH_2CD_2Cl} \xrightarrow[2)\ H_2O]{1)\ Cs\ or\ K} \underset{(III)}{p\text{-}PhC_6H_4CH_2CD_2H} + \underset{(IV)}{p\text{-}PhC_6H_4CD_2CH_3}$$

used. Surprisingly, 1,4-(p-biphenyl) migration is the major process observed when V is treated with potassium or cesium in THF at reflux [38]. The spiro intermediate VI was proposed.

Chan and Smid have studied the kinetics of the reaction between polystyrylsodium, -potassium, and -cesium with triphenylmethane in THF and DME [39]. The reaction is self retarding due to

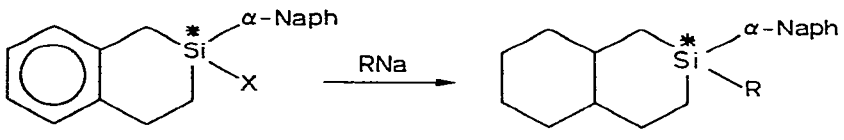


the fact that the $Ph_3C^-M^+$ product is more dissociated than the polystyryl salt, thus displacing the equilibrium (2) and reducing the concentration of reactive free ions:



(2)

The reactions of EtNa, BuNa, PhNa, $PhCH_2Na$ and $CH_2{=}CHCH_2Na$ with the cyclosilane derivatives VIIa-d were found to be stereoselective retention processes [40].

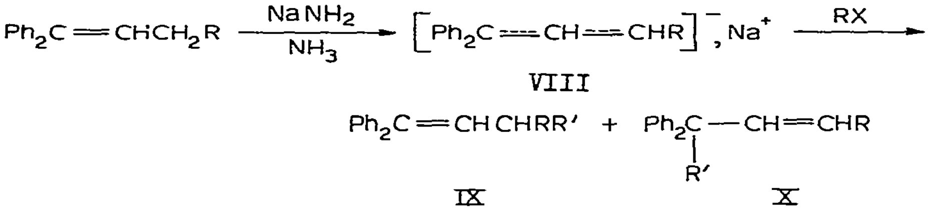


VII a (X = H)
b (X=Cl)
c (X=F)
d (X=OMe)

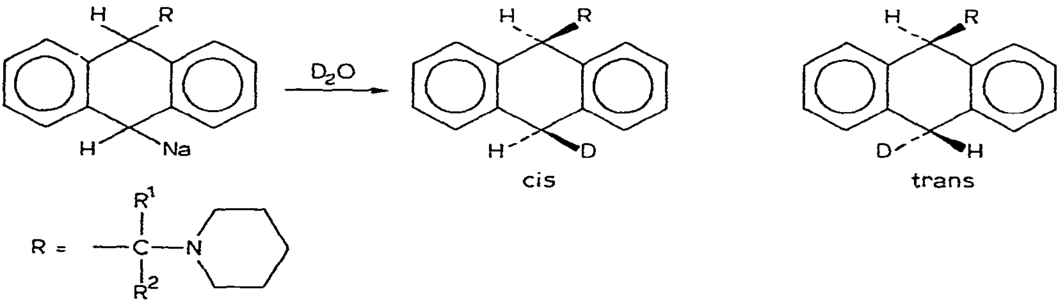
(60-98% retention)

These results, coupled with the observation that the addition of TMEDA causes an acceleration of the reaction between EtLi and VIIb and an increase in the per cent retention, have led the authors to suggest that metal assistance is not necessary for retention reactions

The distribution of alkylated product isomers from the reaction of VIII with alkyl halides has been rationalized in terms of Hine's principle of least motion [41]. Thus, the application of the principle suggests that product X will be favored over IX as was observed.

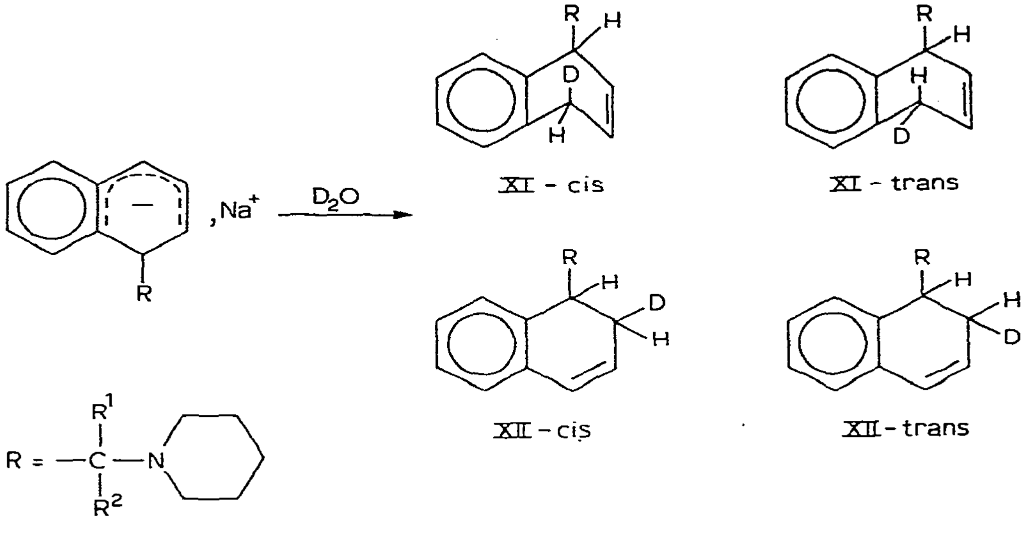


Welvart and coworkers have studied the stereochemistry of the protonation of 9-aminoalcoyl-10-sodio-9,10-dihydroanthracenes [42] and 1-aminoalcoyl-sodio-1,4-dihydronaphthalenes [43]. In the case of the former, reaction with D_2O gave predominately the <u>trans</u> isomer, whereas the lithium analog gave a 50/50 mixture of <u>cis</u> and <u>trans</u> isomers. Similarly, the naphthalene anion gave almost equal

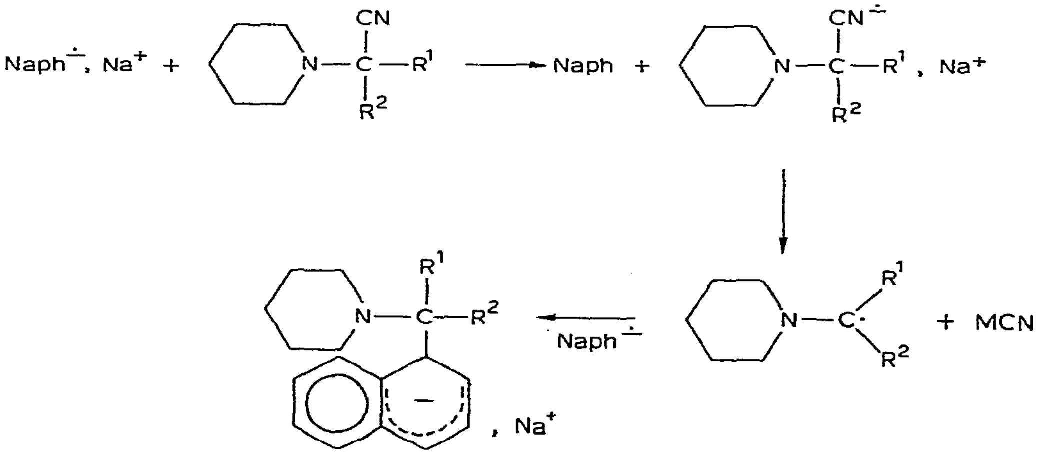


cis

trans

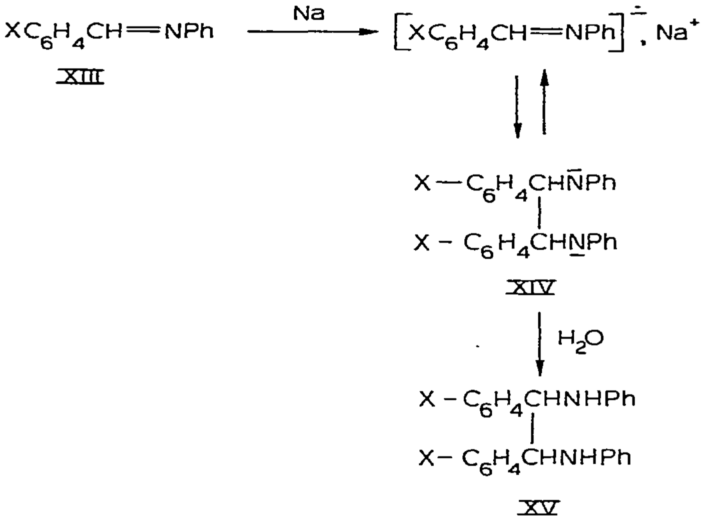


quantities of XI and XII, but only the trans isomer of each was found. When the lithium analog was used, XII was the predominant product ($\sim$ 80%), but both cis and trans isomers were formed. These results were discussed in terms of ion pairs for the sodium compounds and "ate" complexes ($Li^+R_2Li^-$) for the lithium analogs. In another paper, this group also reported conditions used for the preparation of 1-aminoalcoyl-1, 4-dihydronaphthalene anions by the following reaction scheme [43]:

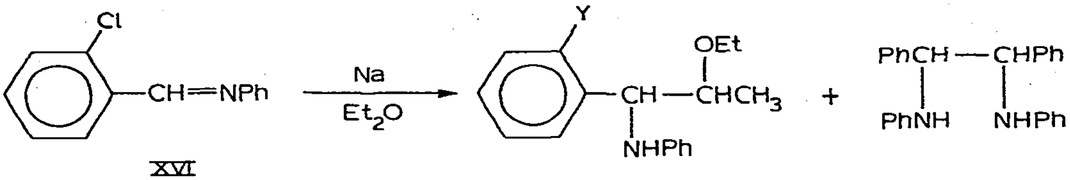


Hydrolysis of the adduct obtained from Na-K alloy and biphenyl has been shown to yield a complex mixture of products, principally phenylcyclohexane and isomeric phenylcyclohexenes and phenylcyclohexadienes [45].

Dimerization of N-benzalanilines XIII has been shown previously to yield only one diastereomer of the dimer XV, the *dl*-form. Lately, Smith and Ho have shown that isomerization to the thermocynamically favored *dl*-form occurs by the following mechanism [46]:



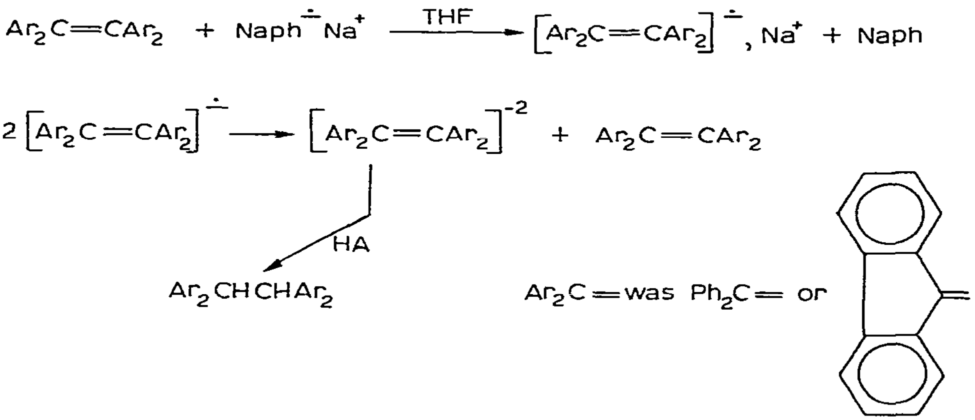
To establish this, these workers treated a mixture of *meso*-XV (X = H) and *meso*-XV (X = o-Me) with disodium-*cis*-stilbene complex to generate the corresponding dianions XIV. Mixing occurred to give the same products as produced from a mixture of the Schiff bases XIII (X = H and o-Me). This group has also investigated the dehalogenation of XVI in diethyl ether [47]. A mechanism was proposed to account for the solvent-derived product XVII. Other workers have isolated dimers, tetramers and hexamers from 1,4-



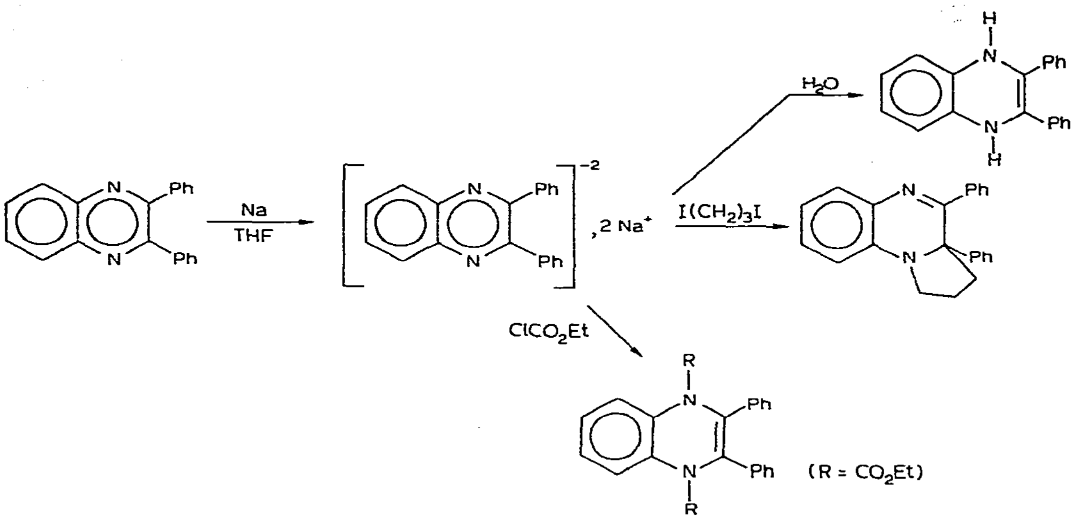
XVI

XVII (Y = H, Cl)

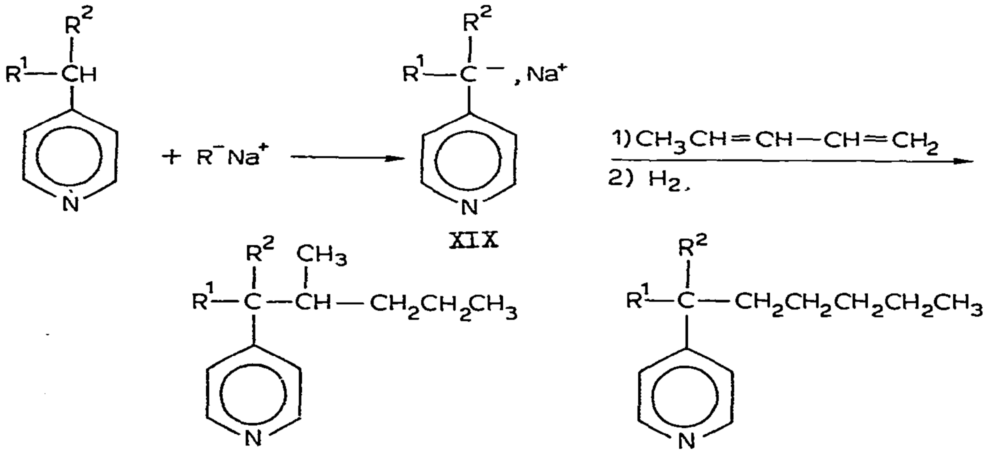
bis(1-phenylvinyl)benzene after treatment with Na, K or NaNaph [48]. Reduction of tetraphenylethylene and bifluorenylidene with NaNaph has been reported to yield the corresponding tetraarylethanes as shown in the following reaction sequence [49]. Yields were poor except when an excess of NaNaph was used.



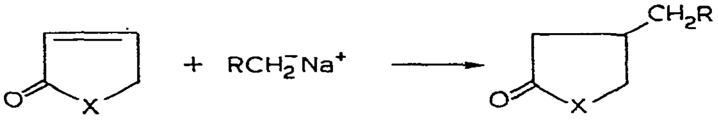
Reduction of 2,3-diphenylquinoxaline yields the dianion XVIII, several derivatives of which were prepared [50]:



Pines and coworkers have examined sodium-catalyzed side-chain alkenylations of γ-alkylpyridines with piperylenes [51]. The picolyl anion XIX adds to piperylene predominantly at the 4 or 1 positions with the <u>cis</u>- and <u>trans</u>-dienes giving quite different product distributions. It is also notable that the <u>cis</u>-isomer reacted about nine times faster than the <u>trans</u>-isomer.

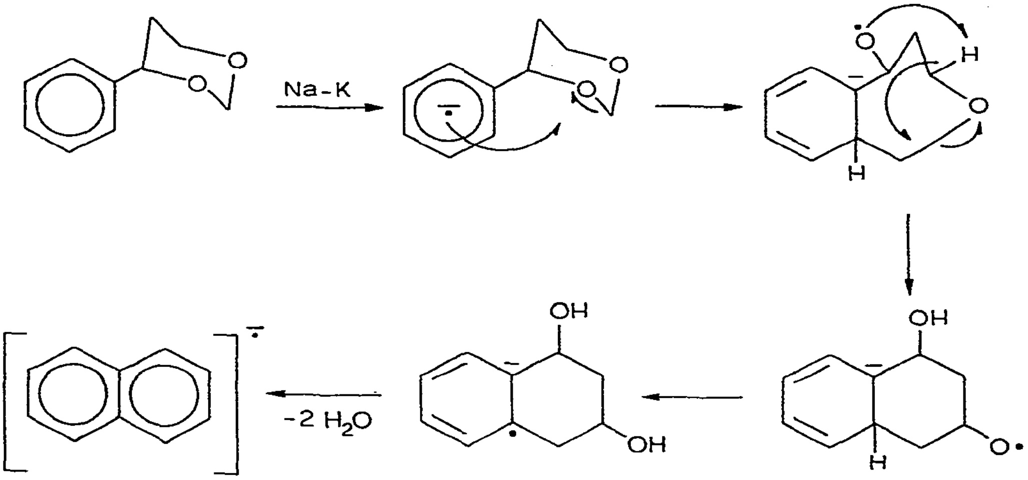


Picolylsodium reacts with α,β-unsaturated ketones by addition to the C=C bond [52]:



$X = O, CH_2$ $\quad$ R = 2 - and 4 - pyridyl

Reaction of 4-phenyl-1,3-dioxane with Na-K alloy produced the naphthalene radical anion [53]. The following mechanism was proposed:

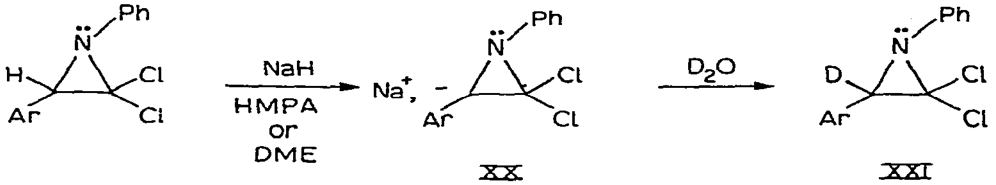


French workers have shown that potassium hydroxide may be used to metalate fluorene and diphenylmethane in HMPA [54]. The fluorenyl anion is stable in HMPA even in the presence of excess water.

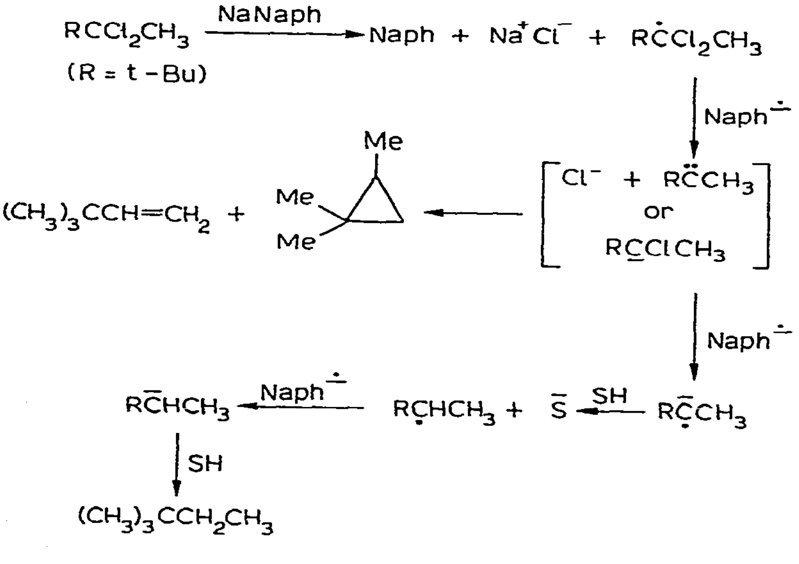
The reactivity of some alkenylsodium compounds with respect to metalation of olefins has been ordered in the following series:

2-sodio-1-alkene>trans-1-sodio-1-alkene>cis-1-sodio-1-alkene>trans-1-sodio-2-alkene [55].

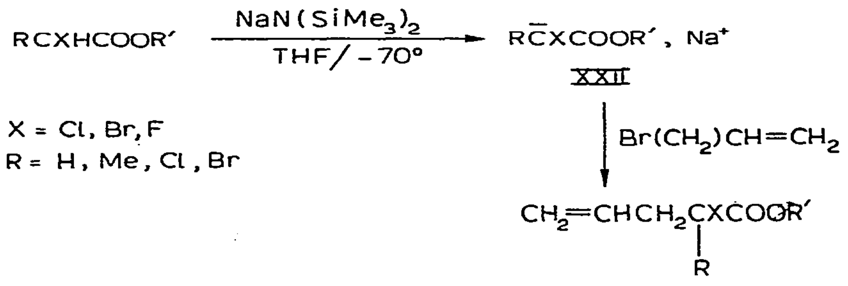
The aziridinyl carbanion XX has been prepared and shown to be quite stable [56]. After three days at -10° in HMPA, a 66% yield of XXI was obtained by D_2O quenching.



Geminal halides have been shown to react with sodium naphthalene to produce carbene (or carbenoid) intermediates [57]. The following mechanism was proposed to account for the data obtained:



Finally, we note the preparation of sodium derivatives of α-halogeno-esters such as XXII [58]:



Condensation of XXII with allyl bromide gave good yields of the product shown above. Other adducts were formed from XXII (R = Me, X = Cl) with alkyl halides, aldehydes, and acetic anhydride.

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