

SODIUM AND POTASSIUM

ANNUAL SURVEY FOR THE YEAR 1971

WILLIAM H. GLAZE

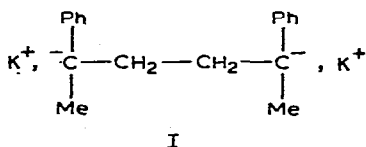
Department of Chemistry, North Texas State University, Denton,
Texas 76203 (U.S.A.)

Some organopotassium compounds have been prepared by metal exchange between alkyllithium compounds and potassium (-)(IR)-menthoxide in hydrocarbon solvents [1]:

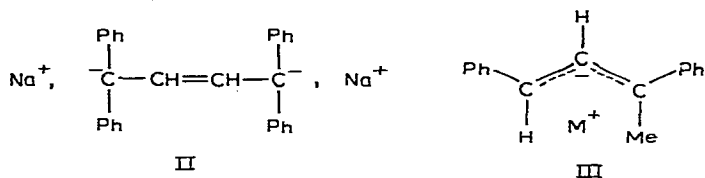


The potassium alkyls (R = n-C₄H₉, n-C₆H₁₃, n-C₁₂H₂₅) precipitate from solution in yields of 55-90%. t-Butyllithium gives only potassium hydride and isobutylene, however. With excess RLi, complexes of the type 1.65 RLi·RK were formed which metalated benzene, toluene and cumene. The infrared spectrum of n-BuK, which is unstable, was also reported.

PMR spectra of the potassium α-methylstyrene dimer (I) and cumylpotassium have been reported [2, see reference in Lithium Annual Survey]. Both compounds show large amounts of electronic charge delocalized onto the phenyl rings.



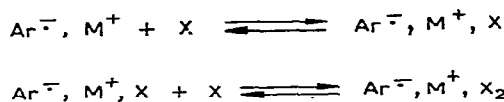
PMR data also have been used to estimate ring charge densities in the dianion of 1,1,4,4-tetraphenylbutadiene (II) [3]:



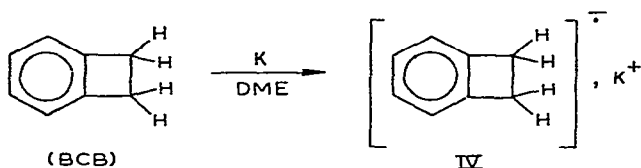
Electronic and PMR spectra of the alkali metal salts of 1,3-diphenyl-1-butene (III) have been reported in more detail [4]. The relative importance of various ionic species were discussed for Na, K and Cs salts in several solvent systems.

Several reports have appeared concerning alkali metal-organic radical ion pairs. These include an NMR investigation of alkali salts of naphthalene [5] and ESR studies of alkali-benzene [6], alkali-anthracene [7] and alkali-1-phenyl-2-trimethylsilylacetylene [8]. Also reported were ESR studies of alkali-radical ions with azobenzene and some azonaphthalenes [9]. Alkali metal hyperfine splittings were observed in each of these systems, and in most cases equilibria between various ionic forms was discussed.

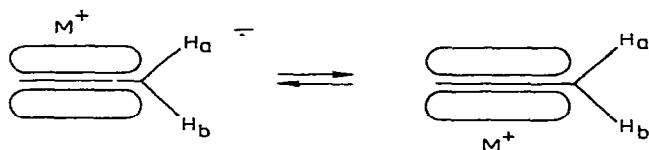
Szwarc and coworkers have examined the systems metallic sodium-biphenyl-tetrahydropyran (THP), metallic sodium-naphthalene-THP in the presence and absence of dimethoxyethane and tetraglyme, metallic sodium-naphthalene-Et₂O/THF, and metallic potassium-naphthalene-Et₂O/THF [10]. Spectrophotometric and ESR studies were used to obtain equilibrium constants for the following reactions. The constants and the corresponding ΔS and ΔH values were interpreted in terms of solvent-cation interactions:



Potassium reduction of benzocyclobutene yields the radical anion (IV) [11]. At low temperatures in dimethoxyethane the



spectrum is that of a mixture of two species with metal hyperfine splitting constants of 5.20 and 5.67 G. Moreover, the methylene protons were shown to be nonequivalent. The authors interpret their results in terms of equilibria involving free ions and two types of ion pairs, with the metal ion above and below the plane of the BCB π system:



Extended Hückel calculations for MeNa, MeK and MeRb have been reported [12]. The spectra of several cyclopentadienyl metal compounds, including alkali metals, have been interpreted in terms of the extent of s-character of the bonding orbitals [13].

PMR spectra of alkali metal salts of indole have been interpreted in terms of solvent-separated ion pairs for Li and contact pairs for Na and K [14].

Several kinetic studies have been published this year, most of which relate to polymer-forming reactions. Kinetics

of the propagation of styrene in THF with potassium as counter ion have been combined with conductivity measurements to yield specific rate constants for free ions and ion pairs [15]. Also reported was the effect of HMPA on the same system [16]. As expected, HMPA leads to increased reactivity of polystyryl-potassium. However, it was found that the specific rate constant for propagation involving free ions was less than that of solvent-separated ion pairs in the presence of small quantities of HMPA.

In dioxane, propagation of polystyrylsodium was found to involve mainly contact ion pairs [17].

Ion pair dissociation constants and propagation rate constants for polystyrylalkali metal compounds (sodium, potassium, and cesium) and poly-p-methoxystyrylalkali metal compounds have been compared [18]. The dissociation constants for the latter are smaller and the reactivities less than for polystyrene, presumably due to the electron-donating tendency of the p-methoxy substituent. The same group has examined the effect of certain impurities on the rate of styrene polymerization [19].

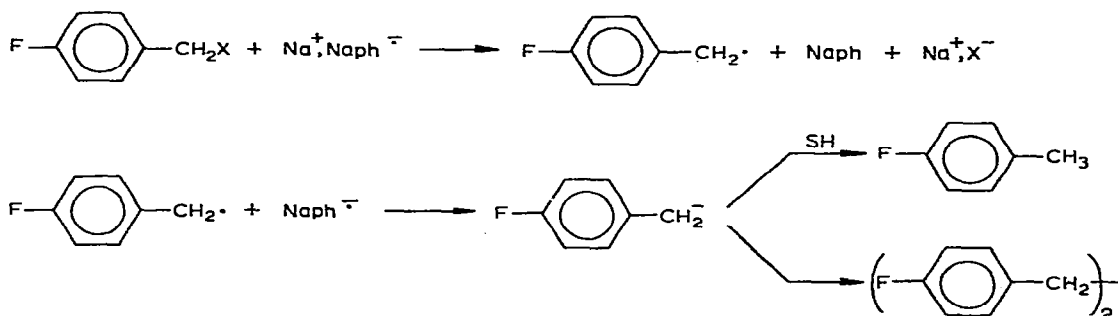
Podolsky and coworkers have published more on their proposed mechanism for anionic polymerizations [20, 21, AS 69; 61]. These authors reject the ion-ion pair concepts of Szwarc and Schulz, and propose instead a mechanism involving an active complex of the organometallic compound with the monomer. Further data on the propagation of α -methylstyrylsodium in THF is presented to support the latter mechanism.

The use of n-butylnsodium for the initiation of butadiene polymerization was reported to yield relatively low molecular

weight polymer, presumably due to chain termination by elimination of NaH or Na metal [22]. However, the use of mixtures of *n*-BuNa with *t*-BuOK or *t*-BuOLi dramatically stabilizes the living polymer. *t*-BuONa has no effect.

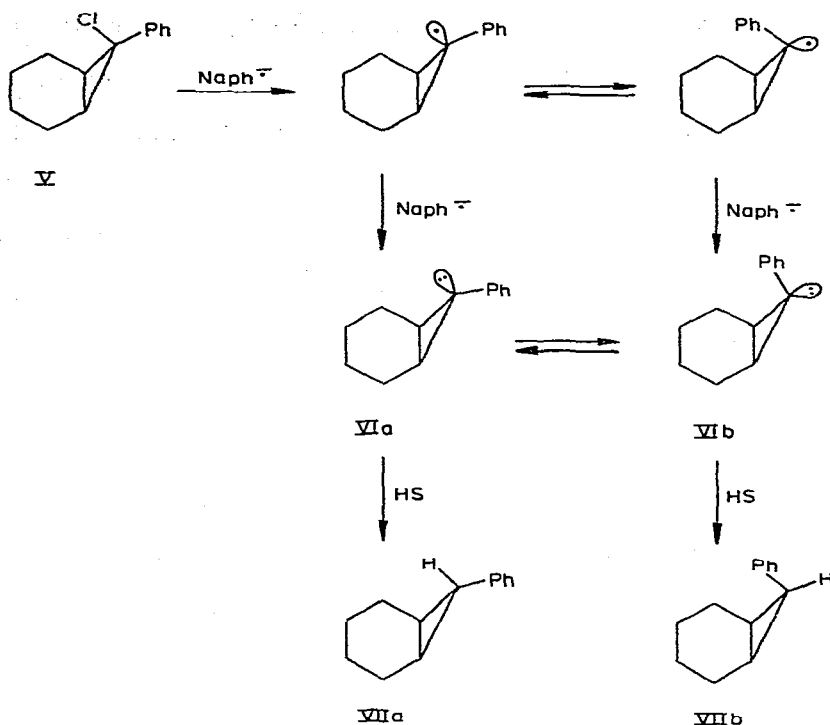
The equilibrium between monomer and living poly- α -methylstyrylpotassium has been studied in *p*-dioxane, and the results compared with those obtained in THF solvent [23, AS 70; 324]. Also reported was the bulk polymerization of α -methylstyrene with sodium naphthalene initiator [24].

Garst has reviewed work from his group on electron transfer reactions in the system sodium-naphthalene-alkyl halide [25, AS 70; 325]. In some related work, Rakshys [26] has shown by way of ^{19}F CIDNP measurements that benzyl halides react with sodium naphthalene by the same mechanism as do alkyl bromides and chlorides:



In the reaction of cyclopropyl halides with NaNaph, the intermediate cyclopropyl radical would be expected to invert so as to lose its stereochemical identity [27]. Thus, V would form carbanions VIa and VIb.

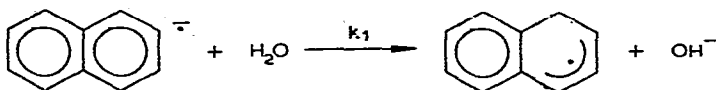
As expected, the ratio of protonated products (VIIa/VIIb) was found to be dependent on the temperature, the concentration of the reactants, and the solvent.



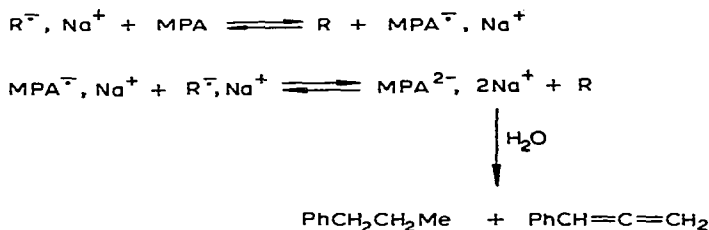
The effect of various solvents (Et_2O , THF, DME) on the products obtained from Wurtz-Fittig reactions was also reported this year [28].

The use of magnesium bromide to trap carbanions from reactions such as those described in reference [26] above was originally developed by Bank and Bank [AS 69; 63]. The procedure has been used by the same pair to generate several Grignard reagents when the traditional route is unsuccessful [29]. Also, reaction of NaNaph with a premixed solution of benzyl chloride and chlorotrimethylsilane yielded 90% benzyltrimethylsilane.

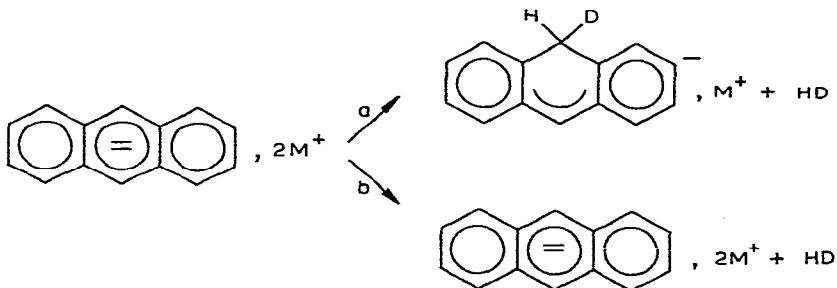
The reaction of water with NaNaph in THF has been followed using a stopped-flow kinetic apparatus [30]. The reaction is mixed second order, the observed rate constant being equal to $2k_1$:



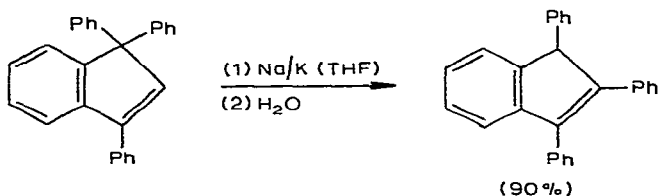
Electron transfer reactions of radical anions with diphenylacetylene [31] and methylphenylacetylene (MPA) [32] have been shown to involve very reactive dianions, albeit their concentration is very low in the reaction mixture:



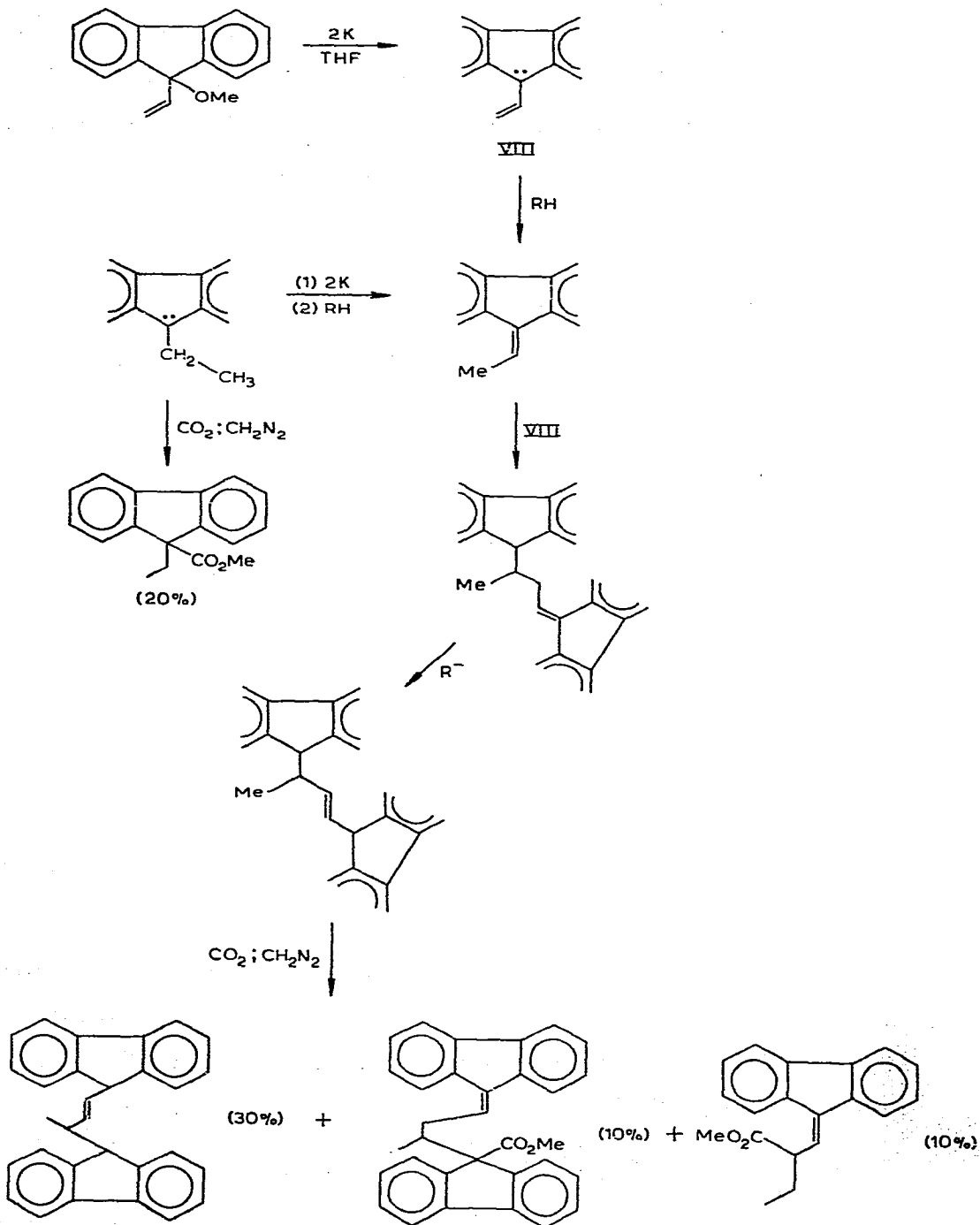
Further evidence on the reaction of dianions with molecular deuterium [33, AS 69; 63] indicates that lithium- and sodium-anthracene react via path a while the potassium and cesium compound react via path b:



1,2-Phenyl migrations have been observed when 1,1-disubstituted indenenes were treated with Na/K alloy in ethereal solvents [34]. Methyl migrations were not found, however. It

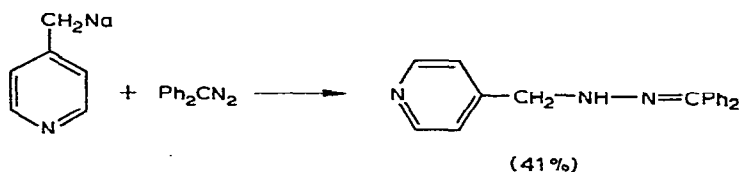


is not clear whether the migration occurs in the radical anion or dianion species.

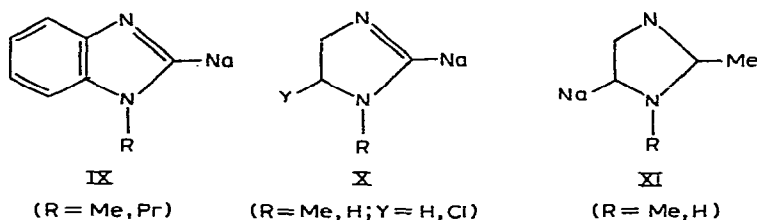


Reductive cleavage of 9-methoxy-9-vinylfluorene with Na/K alloy does not occur as expected [35]. Several products were observed some of which could be accounted for by the mechanism shown on page 72.

The reaction of 4-sodiummethylpyridine with diphenyldiazomethane in liquid ammonia was one of several hydrazone-forming reactions explored in a recent communication [36]:



Sodium derivatives of imidazoles (IX-XI) were condensed with ethylene oxide, aldehydes and ketones to yield several new compounds [37, 38]:



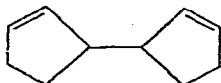
Several alkali metal carbenoids were prepared by the reaction of polyhalomethanes with alkali metal amides [39]. The carbenoids were condensed with chlorotrimethylsilane to yield the following compounds: $\text{Me}_3\text{SiCHBr}_2$, $\text{Me}_3\text{SiCHClBr}$, $\text{Me}_3\text{SiCH}_2\text{Cl}$, $\text{Me}_3\text{SiCBr}_3$ and $(\text{Me}_3\text{Si})_2\text{CBr}_2$.

Also prepared were carbenoids from the reaction of $\text{R}(\text{CH}_3)_2\text{SiCH}_2\text{Cl}$ ($\text{R} = \text{vinyl, allyl, 3-butenyl, 2,3-dimethyl-3-butenyl, 4-pentenyl, and 5-hexenyl}$) [40]. In several cases intramolecular addition of the carbene to the olefin linkage

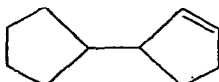
occurred.

Direct metalation of $(EtO)_2P(O)CH_2CN$ with K or Na in 1:1 Et_2O -dioxane, followed by reaction with alkyl or acyl halides yielded 10-44% C-alkyl or C-acyl derivatives [41].

The photolysis of cyclopentadienylsodium in 20% *t*-BuOH - 80% THF, which yields XII and XIII, has been described in more detail [42].



XII



XIII

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