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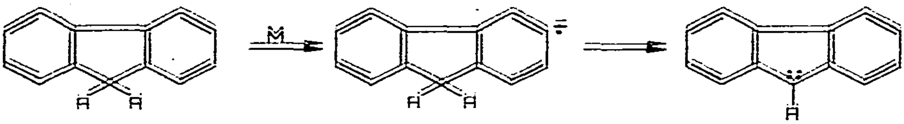
SHORT COMMUNICATIONS

On the metalation of fluorene

Introduction

The mechanism of the reaction of alkali metals with fluorene has been the subject of considerable discussion. In contrast to more acidic compounds like cyclopentadiene and indene, which form the organometallic compound with hydrogen evolution, the reaction of fluorene with lithium in ether solutions at room temperature does not produce hydrogen[1,2]. Eisch and Kaska[2] showed that lithium hydride also is not formed in the reaction of fluorene with lithium, but that reduction of the fluorene ring occurs simultaneously with the formation of fluorenyllithium. In an extensive study of the reaction of fluorene with alkali metals in various ethers Brown[3] has shown that the observed rate of reaction is in the order K > Li > Na. The reaction with sodium is least satisfactory for synthetic purposes, as has been found by previous workers[4]. With potassium, one or two equivalents of metal can be added to fluorene without difficulty[3,5]. No carbon–carbon bond cleavage or rearrangement takes place in the formation of the dipotassium adduct since reaction with alkyl halides gives dialkylfluorene derivatives. The preparation of disodium derivatives of fluorene also has been claimed from the reaction of fluorene with sodium and ammonia[6].

At lower temperatures (-90°), the reaction of fluorene with alkali metals produces a stable solution of fluorene radical anion[7]. The green solutions of potassium, sodium and lithium salts in tetrahydrofuran (THF) decompose at -50°, -40° and -20°, respectively to form the orange-colored carbanion:



It has been suggested that the reaction with alkali metals at room temperature also proceeds *via* reduction of fluorene to the radical anion and that further reactions of this radical lead to fluorenyl carbanion. In a continuation of our studies in the electron spin resonance of aromatic hydrocarbon dianion radicals formed by the reduction of carbanions[8] we have reduced fluorenylpotassium with potassium and obtained the dianion radical.

Results and discussion

The reaction of fluorene with potassium at room temperature rapidly forms the yellow-colored solution of the carbanion without evidence of hydrogen evolution. The visible absorption spectrum (Fig. 1) is similar to that reported for fluorenylsodium in THF[9]. Dilution of a concentrated solution does not alter the positions or relative intensities of the peaks significantly. No electron spin resonance (ESR) signal is obtained at this point. Further reduction with potassium produces a strong ESR

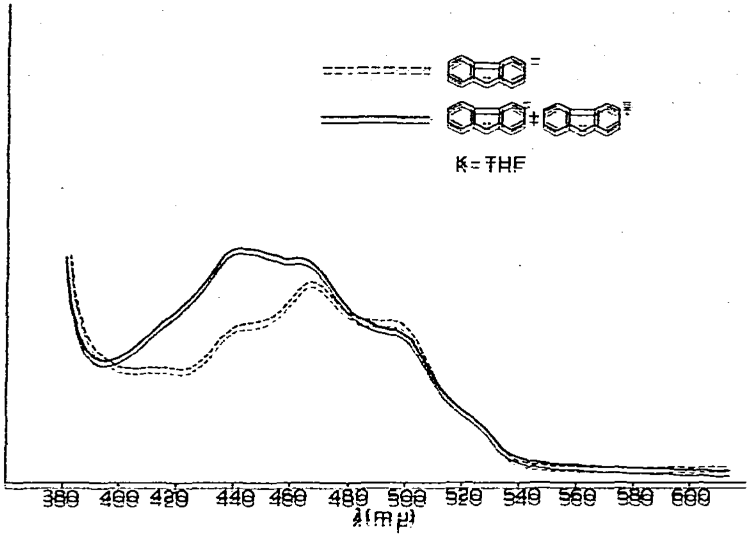


Fig. 1. Absorption spectrum of fluorenylpotassium and fluorenyldipotassium dianion radical in THF.

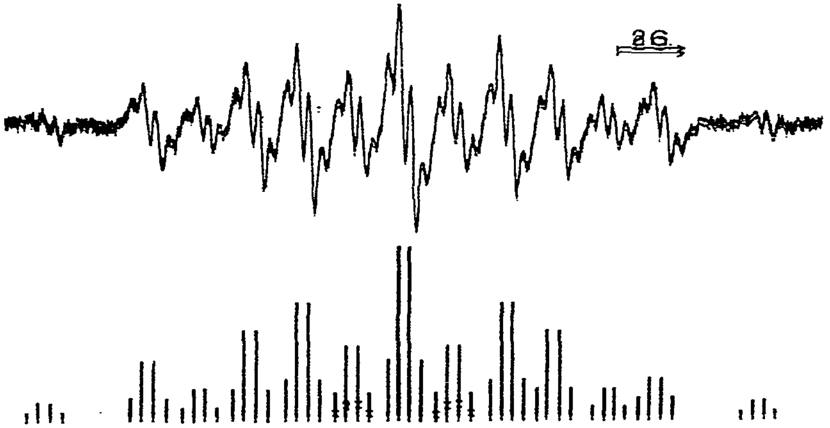
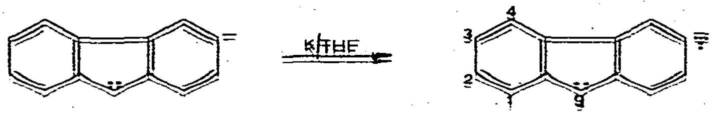


Fig. 2. Electron spin resonance spectrum of fluorene dianion radical produced from potassium reduction of fluorenylpotassium in THF. The "stick" diagram was constructed from proton coupling constants given in text. No potassium splitting is observed.

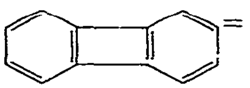
signal. The color of the solution remains essentially the same although the visible absorption spectrum indicates the presence of a new band in the 430–440 mμ region (Fig. 1).

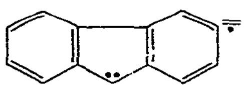
The well-resolved ESR spectrum of the new radical can be fitted to the following coupling constants: 4.53 gauss (G) (2 equivalent protons), 3.05 G (4 approximately equivalent protons) and 0.35 G (3 approximately equivalent protons). These values are in good agreement with coupling constants predicted from calculated spin densities using HMO theory[10] for the dianion radical:

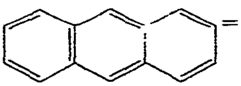


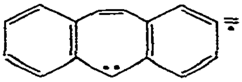
From these calculations and from spectra obtained from 1- and 9-methylfluorene dianion radicals the following assignments have been made: $A_1 = A_2 = 3.05$ G; $A_3 = A_9 = 0.35$ G; $A_4 = 4.53$ G. The preparation of 9-phenylfluorene dianion radical already has been described[8,10]. For this radical $A_1 = 2.76$ G; $A_2 = A_4 = 3.98$ G; $A_3 = 0.59$ G. Very little spin density resides in the phenyl ring and no hyperfine splitting from phenyl protons is resolved. The dianion radical of carbazole also has been obtained. The ESR spectrum is essentially the same as observed for 9-phenylfluorene. This substantiates our assignment of structure and coupling constants. Since calculations show no spin density on the acidic carbon or nitrogen in the dianion radical no coupling from phenyl hydrogens in 9-phenylfluorene or nitrogen from carbazole is expected.

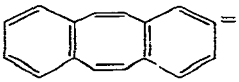
The formation of a stable dianion of fluorene would not appear to be unreasonable since biphenylene[11], anthracene[11], and dibenzocyclooctatetraene[12] dianions are well known:











Fluorene dianion radical is clearly one of the two missing members in a homologous series of stable dianions. Dibenzocycloheptatrienyl dianion radical has not been made but is expected to be stable since the synthesis of cycloheptatrienyl dianion radical itself has been reported[13].

On the basis of these results it would appear that the dipotassium salt of fluorene obtained by Brown[3,5] is in fact the dianion radical. Alkylation of fluorenylidenedipotassium gave mainly 9,9-dimethylfluorene[5]. This product probably arises from alkylation of fluorene dianion radical to produce initially 9-methylfluorene radical anion. Subsequent reactions *via* 9-methylfluorene carbanion[14] would lead to 9,9-dimethylfluorene.

We have also investigated the reaction of potassium and sodium with benzofluorenes. In certain cases, depending on the pK_a of the hydrocarbon, the initially formed radical anion is stable at room temperature.

The reaction of 1,2-benzofluorene (1,2-BF), 2,3-benzofluorene (2,3-BF), 3,4-benzofluorene (3,4-BF) and 4,5-methylenephenanthrene (4,5-BF) with potassium in THF at room temperature produces the carbanion directly. Upon further reduction the dianion radical is formed*. The reaction with sodium also gives the carbanion from 1,2-BF and 3,4-BF but the dianion radical is not produced by further reduction. With 4,5-BF a fairly stable solution of the radical anion is obtained**. 2,3-BF gives

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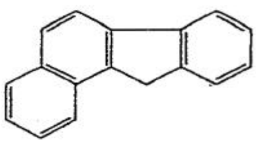
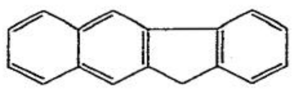
* Detailed presentation of the ESR and visible spectra of these species will be published elsewhere in the near future[15].

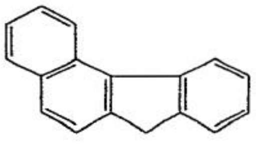
** This radical anion also has been obtained by electrolytic reduction of 4,5-methylenephenanthrene[17].



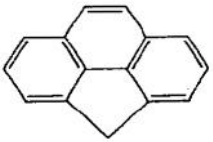
1,2-BF
pK_a[**] = 20.0



2,3-BF
23.2



3,4-BF
19.4



4,5-BF
22.6

mixtures of radicals attributed to the mono- and dianion. The radical anion of 4,5-BF is most stable when the bulk of the remaining material is in the form of the carbanion whereas it is least stable when mostly unreacted 4,5-BF is present in solution. This data is consistent with a previously proposed metalation mechanism[2] which involves proton transfer from unreacted hydrocarbon to the radical anion which functions as a strong base. It does not however rule out an alternate mechanism involving hydrogen atom transfer from the radical anion to unreacted hydrocarbon.

It seems reasonable that the metalation of weakly acidic aromatic hydrocarbons should proceed *via* initial one electron reduction of the aromatic system. The initially formed radical anion may decompose to the carbanion. The more acidic compounds (indene[18], $pK_a = 18.2$, cyclopentadiene[19], $pK_a = 15$) evolve hydrogen in the process. The radical anions of less acidic compounds disproportionate with reduction of the aromatic rings while those of very weak carbon acids, *e.g.* 9-methylanthracene ($pK_a = 27.7$)[18] are stable indefinitely[20]. Radical anions of weak carbon acids stable at room temperature would appear to be derived from those hydrocarbons with pK_a's equal or greater than 22 if the unpaired electron can be stabilized by delocalization in a naphthalene or phenanthrene ring system. For compounds with less delocalization stability *e.g.* fluorene, the radical anions are not as stable although the pK_a of the parent hydrocarbon is similar. A number of factors obviously play a significant role in determining the stability of the radical anion of a weak carbon acid. Further work in the elucidation of the mechanism of metalation of weak carbon acids is in progress.

Experimental

Chemicals used for this study are commercially available. High vacuum techniques were used to obtain samples of solvents and alkali metals free from impurities. Approximately $5\text{–}10 \times 10^{-4}$ *M* solutions of fluorene or benzofluorenes were used. Lower concentrations of hydrocarbon gave only carbanion in some cases but not dianion radical. Reactions were carried out on high surface alkali metal mirrors and were performed as rapidly as possible (approximately $\frac{1}{2}$–4 h). On standing

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[*] pK_a values are taken from ref. 16.

for extended periods of time other radicals were detected by ESR possibly derived from cleavage products[21] or slow reactions with solvent.

ESR experiments were performed on a Varian 4502 EPR spectrometer. Visible absorption spectra were obtained with a Cary Model 14 spectrophotometer.

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