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ALKALI METAL REDUCTION OF WEAKLY ACIDIC HYDROCARBONS 4,5-METHYLENE- AND 4,5-IMINO-PHENANTHRENE

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Summary

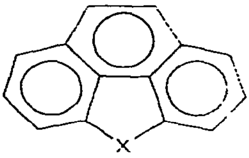
Alkali metal reductions of the title compounds in ether solvents have been followed using NMR spectroscopy to enable diamagnetic intermediates to be detected. With 4,5-methylenephenanthrene, the phenanthrenyl anion and 9, 10-dihydrophenanthrenyl anion are formed in a 1/1 ratio. 9, 10-Dihydro-4,5-methylenephenanthrene was found to be an intermediate in the reduction. Similarly, both the 4,5-imino- and 9,10-dihydro-4,5-imino-phenanthrenyl nitranions are formed in a 1/1 ratio in the reduction of 4,5-iminophenanthrene. A proton transfer mechanism accounts for these results. In the reduction of cyclopentadiene, the cyclopentadienyl anion was the only detectable organic product. However, a significant quantity of indane is formed along with the indenyl anion in the reduction of indene.

Introduction

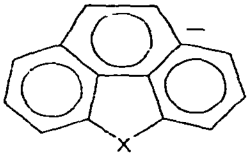
The metalation of weakly acidic hydrocarbons to produce organoalkali intermediates has proven to be a very versatile reaction since these reagents undergo a variety of reactions where the metal atom may be replaced with several different functional groups [1]. In earlier investigations, the major emphasis was on the position of metalation and little attention was given to the mechanism of metalation. Previous ESR investigations have shown that most weakly acidic hydrocarbons react with alkali metals in ether solvents to produce the corresponding radical anion [2,3]. The stability of the radical anion is temperature dependent and usually decomposes to give a diamagnetic species, the carbanion [3]. In certain cases, further reduction of the diamagnetic species yields a dianion radical [3,4]. While ESR studies yield valuable information concerning the radical intermediates of these reductions, the nature of the diamagnetic species remains uncertain in many cases.

Upon alkali metal reduction, the more acidic hydrocarbons such as cyclopentadiene (pK_a 15) and indene (pK_a 21) have been reported to yield hydrogen gas along with the corresponding carbanion [5,6]. However, several examples are known where hydrogen gas is not evolved. For example, Eisch and Kaska [7] have reported that the reduction of fluorene (pK_a 22.8) with lithium metal in THF first produces a short-lived green color due to the radical anion, which at room temperature rapidly changes to the pale yellow color of the fluorenyl carbanion. The hydrogen lost in the formation of the fluorenyl carbanion reduces fluorene to produce small amounts of the tetrahydro- and hexahydro-fluorenes. Similarly, House and Kramer [8] have reported that the reduction of triphenylmethane (pK_a 33) with potassium metal in 1,2-dimethoxyethane does not evolve hydrogen gas but instead, produces various cleavage and reduced products along with (triphenylmethyl)potassium.

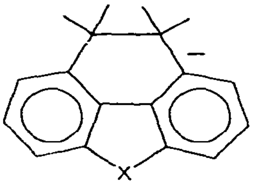
In a preliminary report [9] we have presented evidence for the formation of two anions in the reaction of alkali metals in ether solvents with both 4,5-methylene- and 4,5-imino-phenanthrene (I): the respective phenanthrenyl (II) and 9,10-dihydrophenanthrenyl anions (III). Recent studies of the electrolytic reduction of Ia both in the presence and absence of proton donors have also shown the formation of both IIa and IIIa [10]. At the time of our initial investigation it appeared that the anions II and III were produced in a 2/1 ratio. We have now completed our investigation of this reduction and find that the anions are formed in a 1/1 ratio. A proton transfer mechanism with an equilibrium step accounts for the observed results. We have also investigated the reduction of cyclopentadiene and indene. The cyclopentadienyl anion is the only detectable organic product in the reduction of cyclopentadiene. In the reduction of indene, a significant quantity of indane is formed along with the indenyl anion.



(I)



(II)



(III)

(a: X = CH_2; b: X = NH)

Experimental

4,5-Methylenephenanthrene and 4,5-iminophenanthrene were of commercial origin (K and K and Aldrich) and were used without further purification. Indene (Eastman) was freshly distilled immediately prior to use. Cyclopentadiene was prepared by standard procedures from the dimer. Solvents were distilled from either sodium metal or lithium aluminum hydride and were stored under vacuum over sodium benzophenone ketyl until needed. Samples were prepared to a concentration of 0.3 *M* in starting hydrocarbon under high vacuum in usual 5 mm NMR tubes which had been fitted on top with an "onion-dome" bulb to accommodate the alkali metal mirror. Sodium and potassium mirrors were prepared by distilling the respective metals into the bulb under vacuum from an attached side-arm. The rubidium and cesium mirrors were prepared in the same manner by fusing rubidium chloride and cesium chloride with calcium under vacuum to obtain the respective metal. Freshly cut lithium metal, in a glove bag with an argon atmosphere, was placed into the bulb and the tube immediately placed under vacuum. In this manner, a "reactive" metal surface was available for the reduction. Finally, the appropriate solvent was distilled into the NMR tube, tetramethylsilane (TMS) added, and the tube sealed under vacuum.

Proton NMR spectra were obtained using a Varian Associates HA-100 spectrometer operating in the field-sweep mode with a probe temperature of 29° C. Calibration of the spectra was accomplished utilizing the frequency difference network. A Hitachi R-20 spectrometer was also used for some experiments.

In a typical run, a spectrum was taken before any reaction had taken place. The NMR tube was then inverted for a few seconds which allowed the solution to come in contact with the metal mirror and reduction to occur. The NMR tube was then placed upright such that the solution returned to the bottom of the NMR tube and another spectrum was taken at that point. This process was repeated until no further changes in the spectrum occurred. In this manner, the sequence of events occurring during the reduction of the hydrocarbons could be followed easily by NMR.

Results and discussion

The alkali metal reduction of 4,5-methylenephenanthrene in THF at low temperatures has been shown by ESR studies to first produce the radical anion, the stability of which depends upon the alkali metal used and the temperature [3]. Either raising the temperature to room temperature or further reduction of the radical anion produces a red/orange color with loss of the ESR signal, indicating the formation of diamagnetic species. Still further reduction results in the appearance of new ESR signals attributed to the dianion radical. In following this reduction by NMR to observe the diamagnetic products formed, the peak due to the methylene protons of 4,5-methylenephenanthrene was used to monitor the disappearance of the starting material.

Partial reduction of Ia in THF-d_8 with potassium produces a NMR spectrum which consists of four singlets at 3.115, 5.593, 6.051 and 7.719 ppm and two complete three-spin patterns (Fig. 1). Since Ia possesses an axis of symmetry, observation of two three-spin patterns presents at least three possibilities: (a) the anion is nonplanar, (b) bonds are broken in the reduction, or (c) two (or more) diamagnetic species are formed during the reduction. Integration of the signals at this point shows the three-spin patterns to be present in unequal amounts. Furthermore, the singlets at 5.593 and 6.051 ppm are close to the singlet observed at 5.89 ppm for H-9 of fluorenyllithium [11]. The chemical shift and integration data eliminate possibilities a and b and are only consistent with two species which are assigned structures IIa and IIIa.

Further reaction with the metal mirror at this stage results in a gradual increase in the NMR signals due to IIIa relative to those of IIa. The intensity of the signals assigned to IIIa increase with subsequent reaction until they are ca. equal to those of IIa. Finally, the intensities of the signals due to IIa and IIIa become equal (Fig. 1) and further reduction results in the complete disappearances of the signals due to IIa and a broadening of the signals due to IIIa. The disappea-

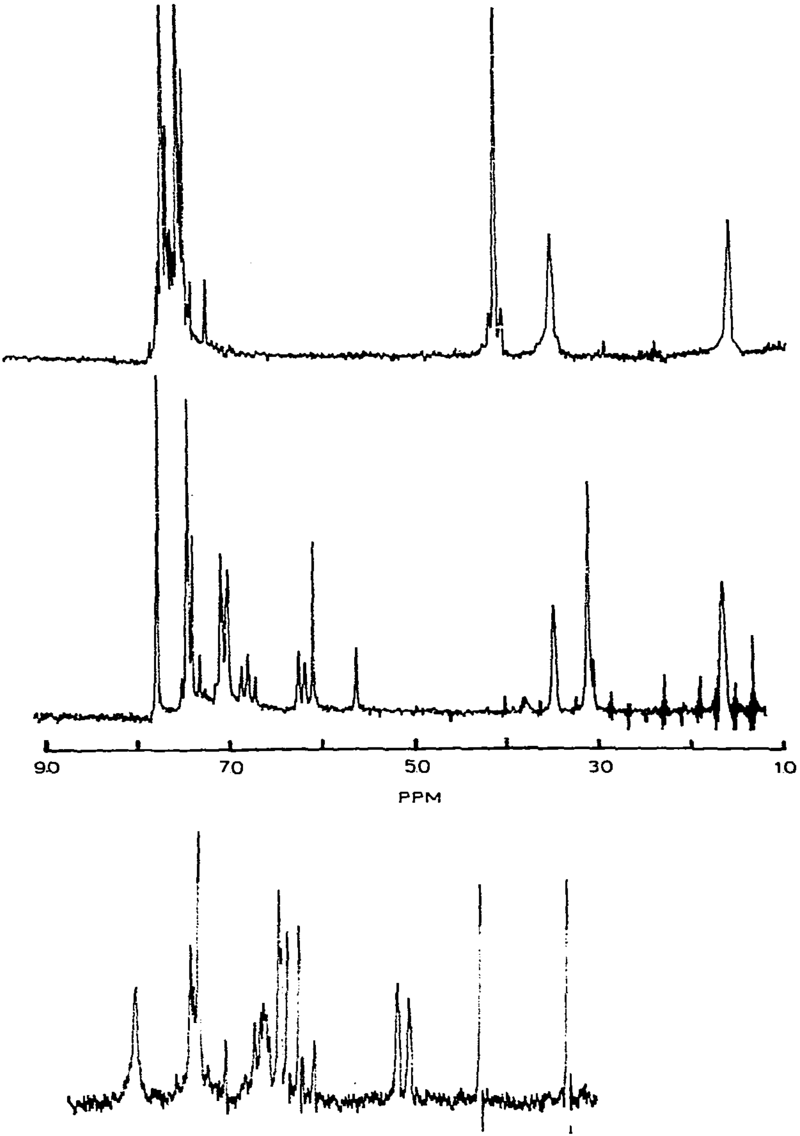


Fig. 1. Top: The 100 MHz spectrum of 4,5-methylenephenanthrene in THF-d_8. Middle: The spectrum obtained from intermediate reduction of 4,5-methylenephenanthrene with potassium metal. Bottom: An expansion of the low field portion of the spectrum at the point when the intensities of the peaks due to IIa and IIIa become equal. The peaks at 1.6 and 3.4 ppm are due to residual THF.

rance of the signals due to IIa is consistent with the formation of the dianion radical of 4,5-methylenephenanthrene. Chemical shift and coupling constant data for II and III are given in Table 1*.

The sequence of visible spectra obtained during reduction is also consistent with the above data. During the reduction of 4,5-methylenephenanthrene with

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*Chemical shifts and coupling constants obtained from LAOCN3 [12].

TABLE 1

NMR PARAMETERS OF THE ANIONS

	$\nu_{1,8}$[a]	$\nu_{2,7}$	$\nu_{3,6}$	$\nu_{10,11}$	ν_9	$J_{1,2}$[b]	$J_{1,3}$	$J_{2,3}$
IIa	7.003	7.351	7.405	7.534	6.051	7.34	0.32	7.81
IIIa	6.181	6.752	6.996	3.115	5.593	6.71	0.47	7.97
IIb	7.362	7.664	7.759	7.851		7.50	0.32	7.64
IIIb	6.601	7.105	7.340	3.228		7.01	0.37	8.05

[a] In ppm downfield from TMS. [b] In hertz.

potassium in THF, a broad absorption develops with a maximum at 500-510 nm in addition to a sharp peak at 365 nm. Similar spectra have been reported during the reduction of I in an investigation of the ion-pairing of II [13]. Only one adsorption of 505 nm is reported for 4,5-methylenephenanthrenyl-lithium and -cesium anions in cyclohexylamine [14]. One would expect the visible spectrum of III to be similar to that reported for the fluorenyl anion which has an intense peak at 365 nm and a broad three-peak absorption between 440 and 500 nm with the maximum of 470 nm [3]. The visible spectrum obtained during reduction of I can be well accounted for by overlapping the spectra of 4,5-methylenephenanthrenyl and fluorenyl anions.

The reduction of Ia with sodium in THF-d_8 follows a slightly different course in that an additional intermediate in the reduction is detectable (Fig. 2). Initially, the reaction with sodium first produces the 4,5-methylenephenanthrenide radical anion. On further reduction the radical anion decomposes and yields a NMR spectrum in which the absorption due to Ia has disappeared with the appearance of two new peaks at 2.97 and 3.68 ppm (Fig. 2) plus some new aromatic peaks. If this solution is allowed to stand for ca. 10 minutes, it gives a spectrum indicating that Ia is present with a new peak at 3.17 ppm. After repeating the above process several times, the peaks due to Ia disappear completely (Fig. 2). Furthermore, the peaks at 2.97 and 3.68 ppm have decreased in intensity along with an increase in the peak at 3.17 ppm and the peaks in the aromatic region which are assigned to IIIa. Subsequent reduction produces a spectrum similar to that obtained with potassium in that IIa and IIIa are produced in a 1/1 ratio. The peaks at 2.97 and 3.68 ppm in the above spectra are assigned to the 9,10 and methylene protons, respectively, of 9.10-dihydro-4,5-methylenephenanthrene (IV). Apparently IV is more acidic than 4,5-methylenephenanthrene and equilibrium is reached within a period of minutes (Scheme 1)*. That the rate of proton transfer is cation-dependent is consistent with other proton transfer studies [15,16]. Ion-pairing may, however, affect the relative rates of proton transfer observed for various anions [16].

Several combinations of metal and solvent were used for the reduction of Ia including K/dioxane, K/ether, K/Me—THF, K/THF, K/DME, K/diglyme, Na/THF, Li/THF, Rb/THF, and Cs/THF. In all cases a 1/1 ratio of II/III was obtained before formation of the dianion radical from IIa. Furthermore, with potassium, a constant amount of IIa was formed before IIIa began to appear in the spectrum. The only difference in the reductions was in the time required to form the 1/1 ratio of IIa and IIIa. In diglyme, the reaction was very fast and

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*IV should be similar to fluorene in acidity. In cyclohexylamine, fluorine is reported [14] to be slightly less acidic than 4,5-methylenephenanthrene (22.8 vs. 22.6). Our studies were carried out in THF which could account for the reversal in acidities.

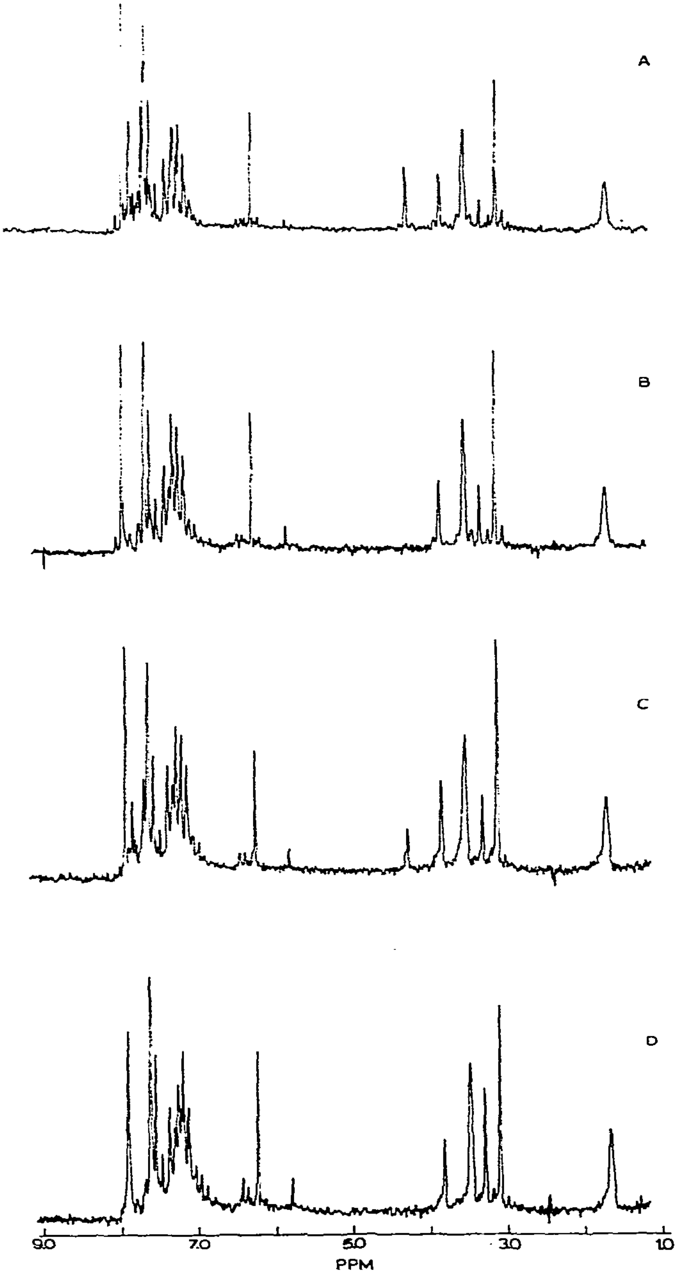
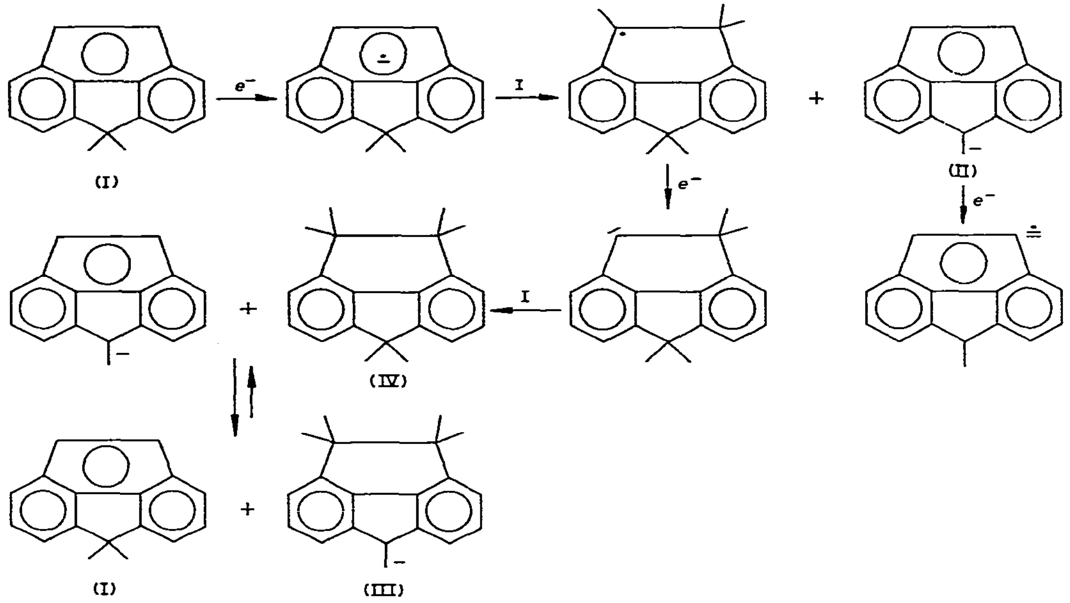


Fig. 2. A sequence of 100 MHz spectra obtained during the reduction of 4,5-methylenephenanthrene with sodium in THF-d_8: (A) the spectrum obtained after initial reduction; (B) the spectrum obtained after allowing the solution giving rise to A to stand for ca. 15 min; (C) the inital spectrum obtained after further reduction of B; and (D) the spectrum obtained after allowing the solution giving rise to C to stand for ca. 15 min. The peaks at 1.6 and 3.4 ppm are due to residual THF.

SCHEME 1



difficult to control whereas in ether the reaction was much slower. As for metals, the reaction is fastest with cesium and slowest with lithium. These results are also consistent with other studies where it has been shown that the rate of proton transfer is cation dependent [16, 17].

The reduction of 4,5-iminophenanthrene (IIb) with potassium in THF similarly produces two three-spin patterns and singlets at 3.228 and 7.851 ppm (Fig. 3). These results are consistent with the formation of both the normal and reduced nitranions, IIb and IIIb, analogious to the reduction of Ia. The absence of singlets near 5.593 and 6.051 in the spectrum of these nitranions confirms their assignment to the C-9 protons in the spectrum of IIa and IIIa. Like the reduction of Ia, the nitranions IIb and IIIb are formed in a ratio of 1/1 prior to the reduction of IIb to the dianion radical. Furthermore, various combinations of metal and solvent also give IIb and IIIb in the 1/1 ratio [12].

The above results are consistent with a proton transfer mechanism given in Scheme 1. In the initial reduction Ia is converted into the radical anion [3]. The radical anion then reacts with 4,5-methylenephenanthrene in a proton transfer step to give IIa and the benzyl type radical. Further reduction of the benzyl type radical produces the anion which reacts with another molecule of 4,5-methylenephenanthrene in a proton transfer step to give IV and IIa. The rate of establishing the equilibrium between IIa and IV to give Ia and IIIa is cation dependent as it occurs within ca. 15 minutes with lithium and sodium but rapidly with potassium and rubidium. This could be related to the ion pairing as IIa forms loose ion pairs with sodium and lithium and tight ion pairs with potassium and rubidium [13, 18]. The starting material produced in this equilibrium is recycled thus accounting for the 1/1 ratio of carbanion products. Apparently, this reduction is similar to the

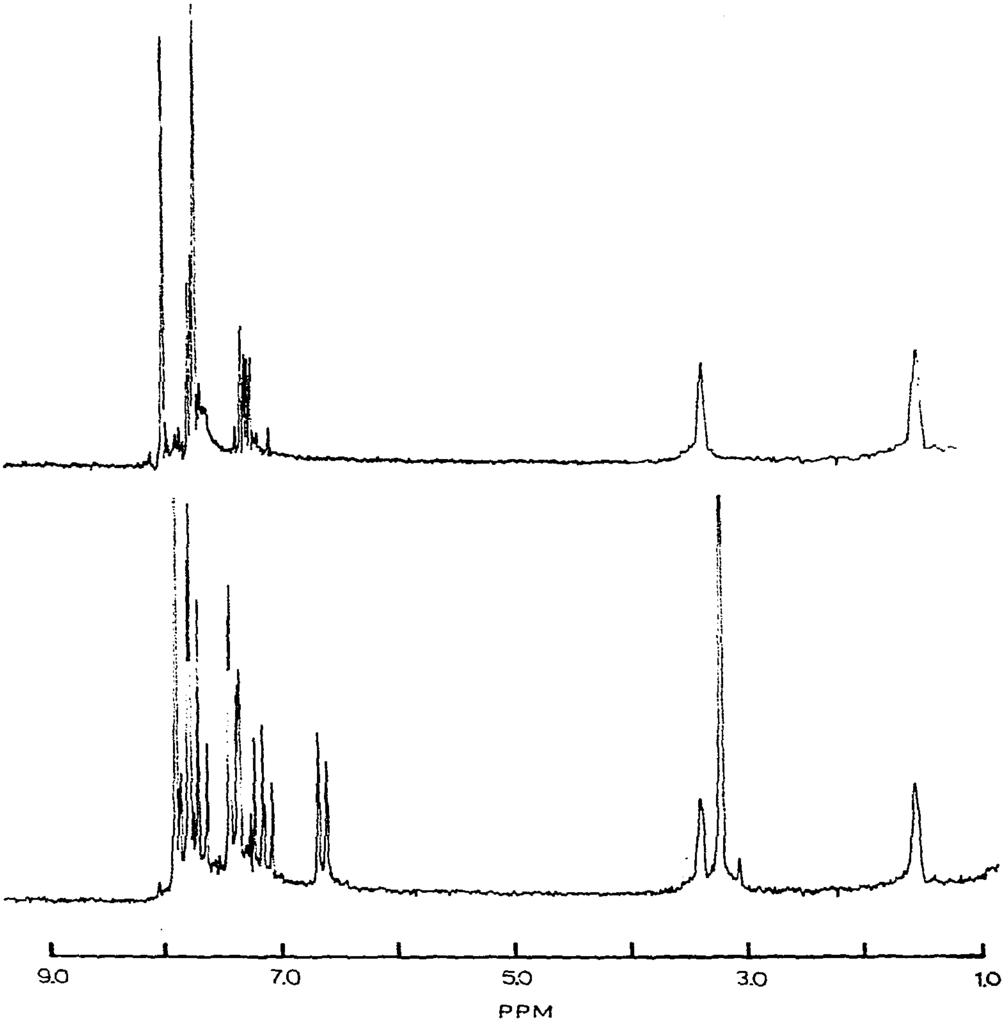


Fig. 3. Upper trace, the 100 MHz NMR spectrum of 4,5-iminophenanthrene in THF-d_8; lower trace, the 100 MHz NMR spectrum of the nitranions IIb and IIIb with sodium in THF-d_8. The peaks at 1.6 and 3.4 ppm are due to residual THF.

well studied Birch reduction [19] with the exception that the starting material is also acting as the proton donor *.

The reduction of fluorene and carbazole with either sodium or potassium in THF-d_8 give spectra attributable to the corresponding carbanion and nitranion only. No evidence was found for a dihydro reduced product similar to that found for 4,5-methylenephenanthrene. In these compounds the initially reduced materials are probably reduced further more readily than are the starting materials, giving eventually tetra- and hexa-hydrofluorene and carbazole anions at concentrations too low to detect by NMR [7].

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* Normal Birch reduction of phenanthrene produces 9,10-dihydrophenanthrene [20].

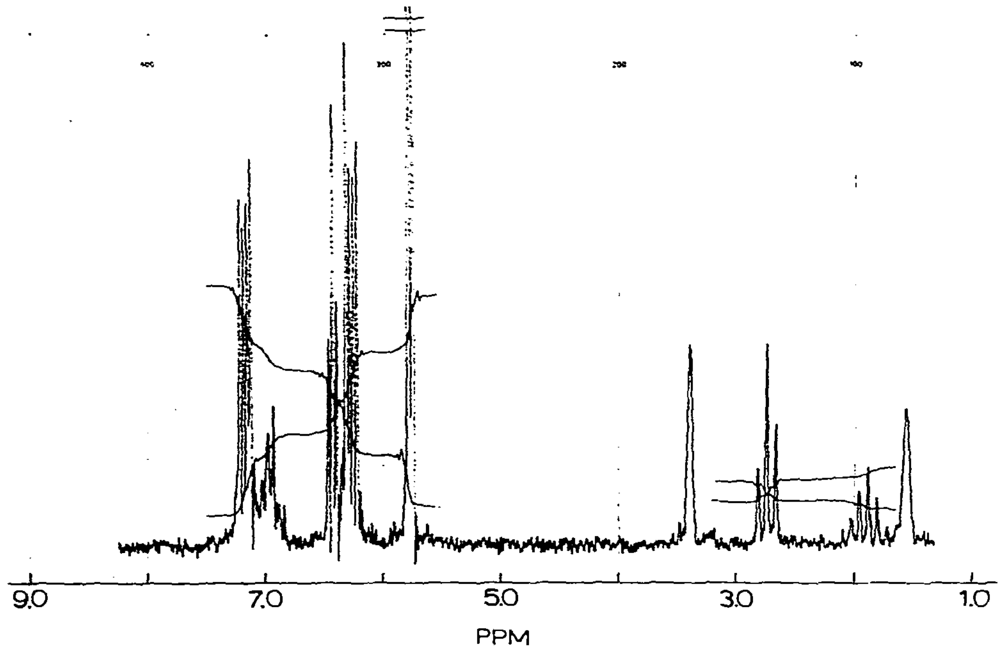

Fig. 4. The 60 MHz NMR spectrum of the reduction products of indene in THF-d_8 at the point in which the methylene protons of indene are no longer detectable. The peaks at 1.6 and 3.4 ppm are due to residual THF.

In view of the above findings with 4,5-methylenephenanthrene, we have carried out similar experiments with cyclopentadiene and indene. The reduction of cyclopentadiene with sodium in THF-d_8 yields a NMR spectrum in which the cyclopentadienyl anion is the only detectable organic product[*]. Furthermore, no precipitate is observed suggesting that sodium hydride is not formed during the reduction[**]. Hydrogen gas is the only other detectable product.

In contrast to these results, evidence was obtained for a reduced product in the reduction of indene. The reduction of indene with sodium in THF-d_8 yields the NMR spectrum shown in Fig. 4. In addition to the peaks expected for the indenyl carbanion, the spectrum also shows a quintet at 2.0 ppm, a triplet at 2.84 ppm and an AA'BB' pattern centered at 7.08 ppm. Integration of the areas of the quintet and triplet yields a ratio of 1/2. These three sets of peaks are assigned to indane on the basis of their chemical shifts [23] and considering the most likely reduced product expected from reduction. Integration shows that the indenyl carbanion and indane are produced in a 6/1 ratio. Hydrogen gas accounts for the remainder of the protons. These observations are similar to those reported previously [6a]. Two competing processes have been postulated to account for these products: (1) an acid-base type reaction to account for the hydrogen gas and (2) a reduction involving the radical anion of indene similar to that outlined

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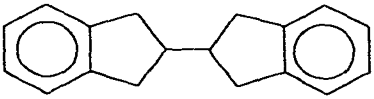
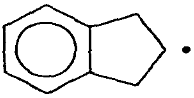
[*] This reduction was carried out with concentrations of cyclopentadiene up to 1.0 *M* in an effort to detect dihydro products. Cyclopentene has been observed in the reduction of cyclopentadiene with sodium and liquid ammonia [21].

[**] Sodium hydride is not soluble in THF solution to any appreciable extent. [22].

in Scheme 1 to account for the indane. A small amount of 2,2-biindanyl (V) was isolated in the previous study [6a] and its formation is feasible from the dimerization of the 2-indanyl free radical (VI), and intermediate suggested in the second process above. The present investigation does not allow additional comments concerning the previously suggested mechanism [6a] for the reduction of indene.



(V)



(VI)

The above results clearly show that in many cases, during the alkali metal reduction of weakly acidic hydrocarbons in aprotic solvents, the starting hydrocarbon can and does act as a proton donor. Although it is not possible from the above results to clearly determine the factors responsible for this behavior, one of the most important would appear to be the stability of the initially formed radical anion. The radical anion of cyclopentadiene has not been detected [6b]. Although the radical anion of indene has not been detected, we feel that the above results suggest that it is an intermediate in the reduction*. With 4,5-methylenephenanthrene, the radical anion is stable at room temperature under certain conditions [3]. Janzen has suggested that weak carbon acids with pK_a's greater than 22 will form stable radical anions if the electron can be delocalized in a naphthalene or phenanthrene ring [3]. A number of other factors such as the thermodynamics of the overall reaction, electron affinity, and the starting hydrocarbon having an easily reducable double bond obviously play a significant role in determining whether a hydrocarbon will give reduced products upon alkali metal reduction. Further work is in progress to elucidate these factors. In any event, investigators using alkali metal reduction of hydrocarbons for the preparation of carbanions should take into account the possibility of reduced products being formed.

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