# PROTONATION OF ACENAPHTHYLENE MONO- AND DINEGATIVE IONS

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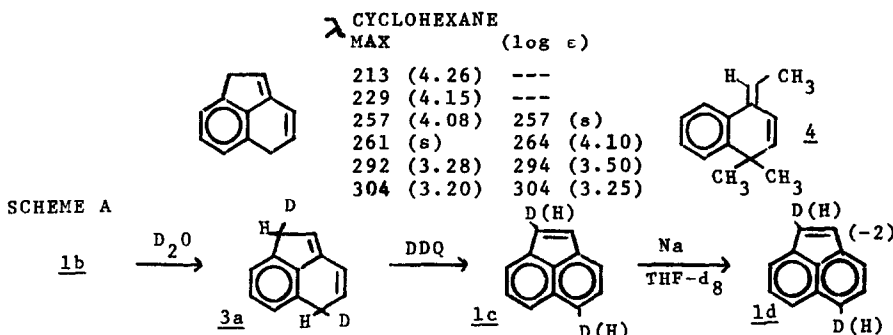
The synthetic utility of alkali metal reductions of aromatic hydrocarbons in the presence of proton donors has been recognized for some time (2,3).   In principle, under conditions of kinetic control the reduction may involve either the radical anion or the dianion or both in the product determining step (2,3).   The application of HMO charge densities in predicting the positions of protonation in these reductions has been remarkably successful (4,5).   With alternant hydrocarbons the position of highest electron density is identical in both the radical anion and the dianion.   With non-alternant systems, however, the possibility arises that the position of highest electron density in the radical anion may not correspond with the position of highest electron density in the dianion, thus presenting the interesting possibility of two distinct dihydro products in the reduction of non-alternant hydrocarbons.   Acenaphthylene (1) is a non-alternant hydrocarbon for which the mode of reduction, based on HMO charge densities, does depend on whether
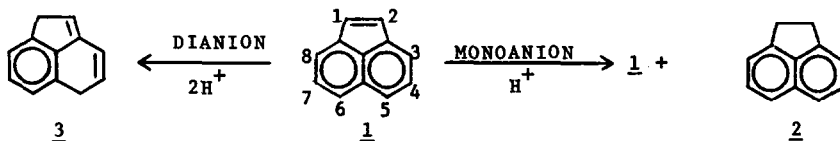
the radical anion (1a) or the dianion (1b) is the precursor.   Thus, the monoanion should give acenaphthene (2) while the dianion is predicted (4) to yield 1,5-dihydroacenaphthylene (3).

We have reported previously (6) the nmr spectrum of 1b. We now wish to report

that the reaction of 1b with water gives quantitatively 3 whereas the corresponding

reaction of 1a gives equimolar amounts of 1 and 2. Both the dianion and the

radical anion were prepared by reaction of 1 with sodium in tetrahydrofuran.

Samples of the anions were quenched by injection under nitrogen into a large volume

of degassed water. Use of undegassed water or inverse addition of water to the

anion solution gave substantial quantities of 2 when 1b was quenched.

1,5-Dihydroacenaphthylene is an apparently highly acidic

(predicted pK 20-23 (9)) compound. It is thermally stable (benzene, sealed tube

95°, 24 hrs.) in the absence of air but isomerizes to 2 when treated with refluxing

alcoholic KOH (1$\underline{M}$) for 1 hr. The structure of 3 was proven* by comparison of its

UV spectrum with the published (10)spectrum of 4 and by the reaction Scheme A.

λ CYCLOHEXANE MAX   (log ϵ)

213 (4.26)	---
229 (4.15)	---
257 (4.08)	257 (s)
261 (s)	264 (4.10)
292 (3.28)	294 (3.50)
304 (3.20)	304 (3.25)

SCHEME A

The reaction of 1b with D$_2$O gave 3a which was dehydrogenated with 2,3-dichloro-

5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene to give the dideuterated

acenaphthylene 1c which was then converted to the dianion. The nmr spectrum of the

dianion 1d (Figure 1) shows clearly by both integrated intensities and spin-spin

splitting patterns that deuterium is incorporated in the 1 and 5 positions (6).

Comparison of the integrated areas of the peaks from the deuterated and undeuterated

positions makes it appear that the dehydrogenation proceeds with a primary deuterium

isotope effect of approximately 7.

* After the results reported here had been obtained (7) a report appeared (8) that

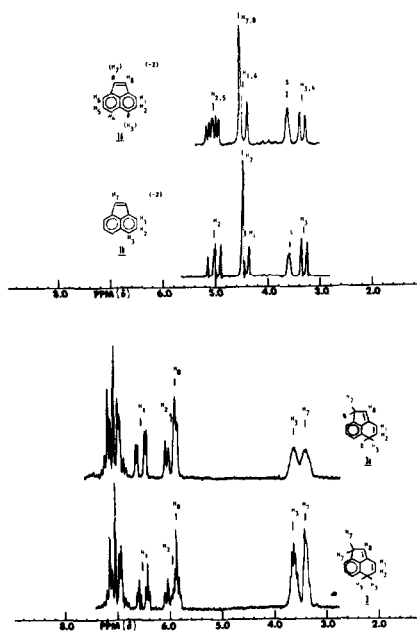3 may be isolated by adding a proton source to solutions of doubly metalated 2.

FIGURE 1.   NMR Spectra of 1,5-dihydroacenaphthylene (lower), the dinegative
ion of acenaphthylene (upper) derived from it via Scheme A and their
dideuterated derivatives.   NMR assignments are as shown.   Peaks marked S are
due to partially protonated solvent present in the THF-d_8 used to prepare the
dinegative ion.

Finally, it should be noted that in favorable instances such as the present one, charge induced chemical shifts offer a convenient method of simplifying the nmr spectra of compounds which are easily reduced to diamagnetic anions. This appears to be particularly useful for aromatic hydrocarbons, for which no paramagnetic shift reagents are at present available.

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