On the Alkali Metal Reduction of Phenalene

Robert L. Shannon and Richard H. Cox

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Previous studies have shown that the more acidic hydrocarbons such as cyclopentadiene (pKa = 15)[1] and indene (pKa = 20) yield hydrogen along with the corresponding anion upon alkali metal reduction.[2] However, the less acidic such as fluorene[2] (pKa = 22.8), 4,5-imino and 4,5-methylenephenanthrene[3] (pKa = 22.6), and triphenylmethane[4] (pKa = 31.5) yield either reduced anions or reduced hydrocarbons along with the expected anion. In each of these cases, the reduced products are thought to arise from the initially formed radical anion via a proton transfer mechanism. In contrast to the above systems, the radical anion of phenalene (I) has not been detected by esr and reduction of phenalene is known to produce the phenalenyl radical. It therefore appeared of interest to examine the alkali metal reduction of phenalene to compare it with the previously studied systems. In this report we present nmr and esr evidence for the formation of two diamagnetic species in the alkali metal reduction of phenalene (I): the phenalenyl anion (II) and dihydrophenalene (III). Equilibration experiments relating to the acidity of phenalene or also reported.


I   II   III
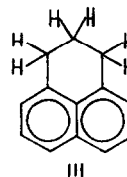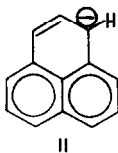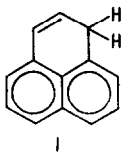
The reaction of phenalene[5] with potassium, in d_8-THF was followed by the nmr in situ technique[3] reported previously. The peak due to the methylene protons in phenalene decreases in intensity with successive reduction until no longer detectable. Concurrently, new signals appear whose intensities increase with further reduction. When the peaks due to phenalene are no longer detectable, the nmr spectrum consists of a pentet at 1.98 ppm, a triplet at 3.03 ppm, a doublet at 5.18 ppm, a triplet at 5.95 ppm and multiplets at ca. 7.12, 7.24, and 7.54 ppm. The relative areas of the doublet at 5.18 ppm and triplet at 5.95 ppm are in a ratio of 2:1 and are thus assigned to the phenalenyl anion (II).[7] The area of the peaks at 1.98, 3.03 ppm and the aromatic proton peaks are in the ratio of 1:2:3 respectively and are assigned to dihydrophenalene[7] (III). The ratio of II:III is 2:1.

The sequence of nmr spectra obtained during the reduction along with esr data allow one to propose a reasonable mechanism for the reduction sequence. Initial contact of the THF solution of phenalene with the potassium mirror yields a nmr spectrum which shows broadened peaks for II along with peaks for III and I. This observation indicates that III is produced in the initial stages of the reduction. The esr spectrum taken at this point is identical to that previously reported for the phenalenyl radical.[8,9] The fact that broadened peaks are observed for II is probably due to an electron exchange between the phenalenyl radical and anion.

Further reduction results in the gradual disappearance of the peaks due to I and an increase in the peaks due to

II and III. At the point when I is no longer detectable, further contact with the potassium mirror results in an

increase in the area of II and a sharpening of the peaks due to II. We attribute this to the reduction of the

phenalenylradical to form II since the esr spectrum of the phenalenyl radical disappears as the area of the peaks

due to II increases. Finally, after the peaks due to II become sharp to the point that the resolution of these

peaks is equal to that of the peaks due to III, further reduction results in the complete disappearance of the

peaks due to III. The esr spectrum at this point is identical to that previously reported for the radical anion of

dihydrophenalene.[10] Further contact with the potassium mirror results in no detectable changes in either the

nmr or esr spectrum.[11]

Similar results are obtained when the reduction is carried out with lithium and sodium. A proton

transfer mechanism outlined below accounts for the observed results. This initial reduction of phenalene

produces the radical anion of phenalene which disproportionates to yield the phenalenyl radical and the anion
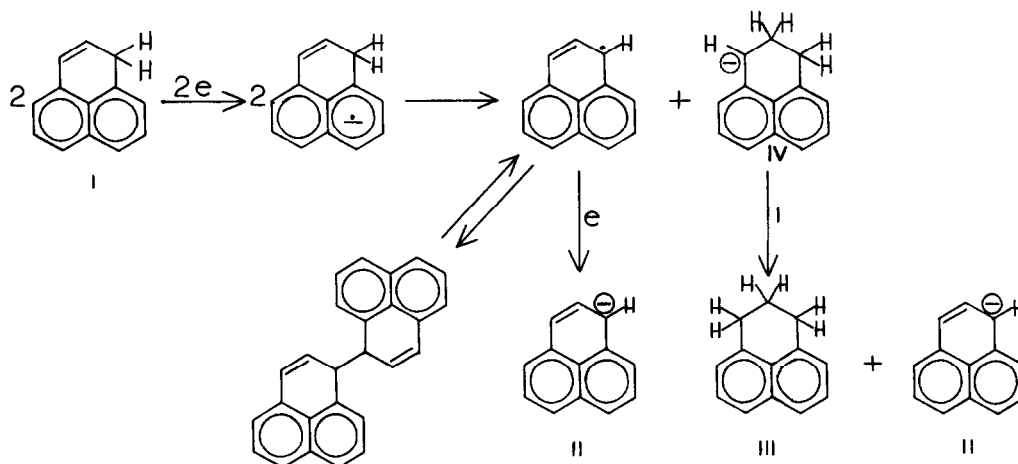
IV. The anion IV reacts with phenalene via proton transfer to give the phenalenyl anion (II) and dihydro-

phenalene (III). Further reduction of the phenalenyl radical gives the phenalenyl anion (II) and finally the

radical anion of dihydrophenalene from III. The fact that III is not reduced until all of the radical anion of

phenalene is reduced to the anion (II) indicates that the reduction potential of the radical anion of phenalene

is greater than that of III. Attempts to detect the radical anion of phenalene were unsuccessful. No esr

signals were observed when the reduction of phenalene was carried out with either sodium or potassium at -70°.

Gradual warming of this solution resulted in the appearance of the phenalene radical esr spectrum. This is

consistent with the known dimerization of the phenalene radical at low temperature.[9]

Janzen[12] has suggested that the radical anion of hydrocarbon acids with pKa's equal or greater than 22 should be stable at room temperature if the unpaired electron can be stabilized by delocalization in a naphthalene ring system. Phenalene would fit into this category from the delocalization standpoint. However, there are conflicting reports concerning the acidity of phenalene.[14-16] In an attempt to further define the acidity of phenalene, various equilibration experiments were carried out. The addition of phenalenyl lithium to THF solutions of fluorene, triphenylmethane, and 9,10-dihydroanthracene resulted in nmr spectra in which the phenalene anion was the only detectable anion. A similar experiment with indene resulted in the indenyl anion as the only detectable anion. In experiments with phenalene plus cyclopentadienyl lithium in THF and with phenalene plus sodium methoxide in THF, no phenalene anion (III) could be detected.[13] The above results are in contrast to the previous report[14] of the acidity of phenalene and suggest that the acidity of phenalene lies between indene and fluorene (~21) a value consistent with M.O. predictions[15] and the acidity of a benzo derivative of phenalene.[16]

References

1. pKa's are those given in cyclohexylamine, A. Streitwieser, Jr., and J. H. Hammons, in "Progress in Physical Organic Chemistry," Volume 3, Interscience Publishers, New York, 1965, p. 55.

2. J. J. Eisch and W. C. Kaska, Chem. Ind. (London), 470 (1961); J. Org. Chem., 27, 3745 (1962) and references cited therein.

3. R. H.Cox, E. G. Janzen and J. L. Gerlock, J. Am. Chem. Soc., 90, 5906 (1968).

4. H. O. House and V. Kramar, J. Org. Chem., 27, 4146 (1962).

5. Phenalene was prepared according to the method of Boekelheide and Larrabee.[6] NMR spectra were obtained on a Varian Associates HA-100 spectrometer with a probe temperature of 29°. Esr spectra were obtained on a Varian 4502 spectrometer.

6. V. Boekelheide and C. E. Larrabee, J. Am. Chem. Soc., 72, 1245 (1950).

7. H. Prinzbach, V. Freudenberger and U. Scheidegger, Helv. Chim. Acta., 50, 1087 (1967).

8. P. B. Sogo, M. Nakazaki and M. Calvin, J. Chem. Phys., 26, 1343 (1957).

9. F. Gerson, Helv. Chim. Acta., 49, 1463 (1966).

10. R. F. C. Claridge, B. M. Peake and R. M. Golding, J. Magnetic Res., 6, 29 (1972).

11. No evidence for the formation of the dianion radical of phenalene was obtained.

12. E. G. Janzen and J. L. Gerlock, J. Organometal. Chem., 8, 354 (1967).

13. Although a light yellow-orange color was produced, the concentration of phenalenyl anion was to low to detect by nmr. When oxygen was not excluded, a deep brownish-red color developed with sodium methoxide. This color was shown to be due to the formation of the phenalenyl radical.

14. D. H. Reid, Chem. and Ind. (London), 1504 (1956); Tetrahedron, 3, 339 (1958).

15. A. Streitwieser, Tetrahedron Letts., 23 (1960).

16. A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin and J. I. Brauman, J. Am. Chem. Soc., 89, 59 (1967).