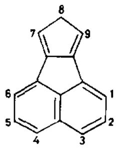
Tetrahedron Letters No. 34, pp 3009 - 3012, 1975. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND ACIDITY OF 8H-CYCLOPENT[*a*]ACENAPHTHYLENE. A NEW ACIDIC HYDROCARBON

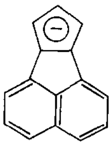
Kagetoshi Yamamoto, Masataka Morioka, and Ichiro Murata*
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

(Received in Japan 21 June 1975; received in UK for publication 14 July 1975)

The acidity of hydrocarbon is an intriguing field in organic chemistry.[1)] In 1960, Streitwieser, Jr. reported that the acidity of hydrocarbon can be assumed from the change in the π-bond energy resulting from the difference in conjugation between the hydrocarbon and the corresponding conjugate base.[2)] The correlation predicts the p*K*a of unknown hydrocarbon, 8*H*-cyclopent[*a*]acenaphthylene (*1*), to be 17.[2)] This prediction led us to examine the synthesis of *1* and its anion (*2*) as well as the acidity measurement of *1*.



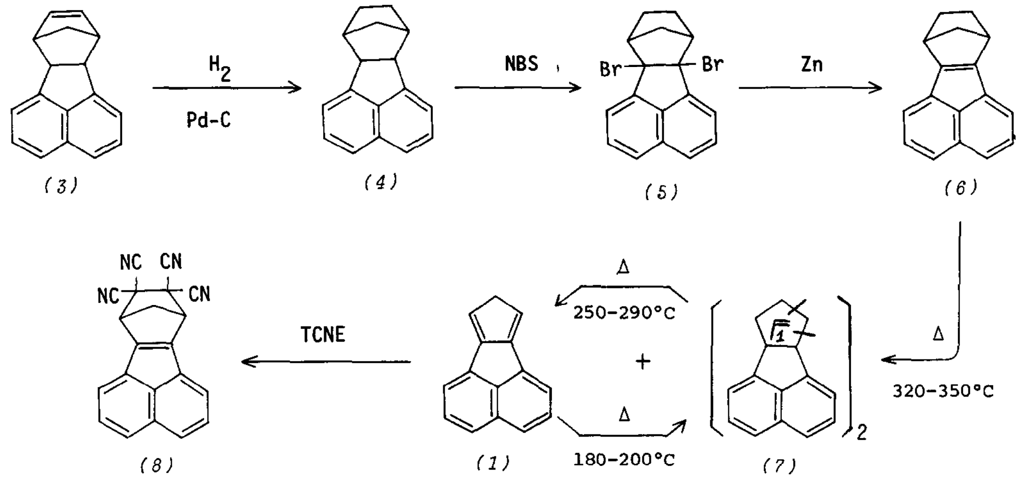
(*1*)



(*2*)

Catalytic reduction (10% Pd-C, ethanol) of a mixture of *exo*- and *endo*-6b,7,10,10a-tetrahydro-7,10-methanofluoranthene (*3*),[3)] prepared from the Diels-Alder reaction of cyclopentadiene and acenaphthylene, yields 86% of the norbornane derivative (*4*),[4)] colorless crystals, mp 62-67°C, m/e 220 (M^+, 100%), 179 (41%), 165 (22%), 153 (50%), 152 (97%) and 151 (80%). The hydrocarbon (*4*) was converted in 47% yield by N-bromosuccinimide in carbon tetrachloride to the dibromide (*5*),[4)] which gave the air-sensitive norbornene derivative (*6*),[4)] orange needles, mp 85-86°C, in 93% yield, upon debromination with zinc-powder in refluxing ethanol. The structure of *6* was established through its spectroscopic properties. Its uv spectrum, λ_{max} (cyclohexane) 232 nm (log ε 4.64), 292 (3.79), 328 (4.02), discloses the presence of an acenaphthylene chromophore.[5)]

Mass spectrum of *6* shows the prominent peaks at m/e 218 (M^+, 25%), 190 ($M^+-C_2H_4$, 100%), 189 (40%) which is suggestive of an ease of the fragmentation of ethylene by thermolysis of *6*.



Desired hydrocarbon (*1*) was prepared pyrolytically from *6* as follows. Pyrolysis of *6* was performed by passing a benzene solution of *6* with a nitrogen stream through a quartz tube packed with quartz chips at 320-350°C. Chromatography of the pyrolysate resulted, along with a mixture of *6* and *1*, in a 28% yield of yellow needles, mp 175-178°C, which was shown to be an intermolecular Diels-Alder dimer (*7*)$^{4)}$ of *1* by its uv and mass spectral data [λ_{max} (cyclohexane) 227 nm (log ε 4.57), 288 (3.71), 326 (3.92); m/e 380 (M^+, 4%), 190 ($M^+/2$, 100%), 189 (27%)]. Since the separation of *1* and *6* was so difficult due to the thermal and air instability of *1*, the mixture was heated in a benzene solution at 180-200°C (in a sealed tube) to convert *1* to the dimer (*7*). The combined yield of *7* is 35%. Successive pyrolysis of *7* at 250-290°C resulted in the formation of 8*H*-cyclopent[*a*]acenaphthylene (*1*)$^{4)}$ in 7.7% yield as orange needles, mp 88-90°C. The identity of *1* is established by its mass, m/e 190 (M^+, 100%), 189 (M^+-H, 85%); uv, λ_{max} (THF), 232 nm (log ε 4.55), 238 (4.56), 332 (3.92), 349 (4.07), 368 (4.01); and nmr spectrum [see Fig-1], δ ($CDCl_3$) 3.73 (2H, t, J=1.5 Hz), 6.59 (2H, t, J=1.5 Hz) and 7.48-7.80 (6H, m). The structure of *1* was further proved by its reaction with tetracyanoethylene to give the adduct (*8*),$^{4)}$ yellow needles, mp 192°C (decomp.), in quantitative yield, identified by its spectral properties.[6] Although *1* is sensitive to oxygen, it can be stored under nitrogen at -20°C for a week.

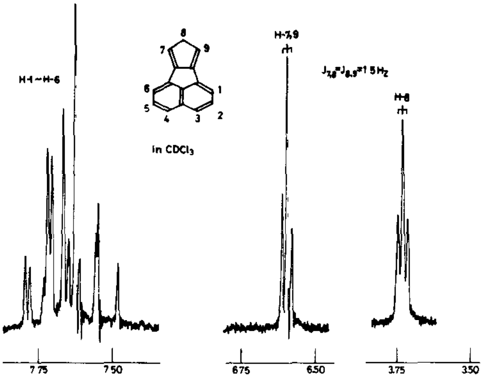


Fig-1. 100 MHz nmr spectrum of *1*.

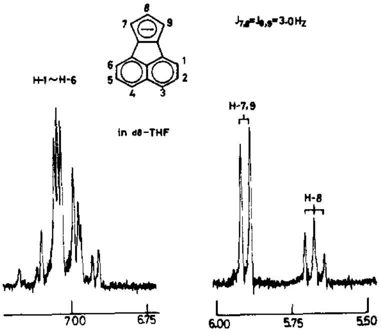


Fig-2. 100 MHz nmr spectrum of *2*.

Treatment of *1* in d_8-THF with a hexane solution of *n*-butyllithium *in vacuo* leads instantaneously to the generation of a dark-red solution of the anion (*2*). The nmr spectrum[7] [Fig-2] shows, besides the aromatic protons multiplet at δ 6.90-7.12, an A_2X-system at δ 5.90 and 5.68 for H-7,9 and 8 with the coupling constant, $J_{7,8}=J_{8,9}=3.0$ Hz. This spectral pattern is fully consistent with the symmetrical anion (*2*). It should be noted that the chemical shift of the aromatic protons, H-1~6, was moved upfield by about 0.6 ppm on passing from the hydrocarbon (*1*) to the corresponding anion (*2*). Therefore, we presume that the negative charge resides not only on the cyclopentadienide moiety but also on the naphthalene skeleton in some extent.[7] When the anion (*2*) was quenched with deuterium oxide a selective deuteriation occured only at C-8. The cite of deuteriation is in accord with the calculated π-electron density of *2*.[8]

The p*K*a value of the hydrocarbon (*1*) examined was based on that of cyclopentadiene,[9] by using the following equation:[10]

$$pKa_1 - pKa_2 = \log[R_2^-]/[R_2H] - \log[R_1^-]/[R_1H] \quad \text{(equilibrium condition)}$$

where R_1H and R_2H are *1* and cyclopentadiene, respectively, and the concentrations are those in the equilibrium mixture. The concentrations of the each component were determined nmr spectroscopically. Several measurements gave p*K*a=14 ± 0.5

for *1*. Although there is a slight discrepancy between the experimentally observed and theoretically predicted2) p*K*a of *1*, we feel that our present results provide new example of the relatively small group of planar acidic hydrocarbons1) and shed light on the correlation between the acidity of hydrocarbon and ΔM value.2) Presumably a factor affecting the thermodynamic stability of the cyclopentadienide ion in *2* is the annelation of acenaphthylene that allows somewhat charge delocalization. In this context, studies on the cyclohept[*a*]acenaphthylenylium ion11) are particularly noteworthy and will be reported soon.

REFERENCES AND NOTES

1) H. F. Ebel, *"CH-Acidität" in Methoden der Organishen Chemie* (Houben-Weyl), Band XIII/1, ed, by E. Muller, Georg Thieme Verlag, Stuttgart, (1970), p.27; See also, P. Eilbracht and K. Hafner, *Angew. Chem.*, 83, 802 (1971); *Angew. Chem. internat. Edit.*, 10, 751 (1971); B. L. McDowell and H. Rapoport, *J. Org. Chem.*, 37, 3261 (1972); C. Tuchscherer, M. Bruch, and D. Rewicki, *Tetrahedron Letters*, 865 (1973).

2) A. Streitwieser, Jr. *Tetrahedron Letters*, 23 (1960), No.6.

3) R. Baker and T. J. Mason, *J. Chem. Soc., (C)*, 1970, 596.

4) All new compounds gave satisfactory elemental analyses.

5) R. A. Friedel and M. Orchin, *"Ultraviolet Spectra of Aromatic Compounds,"* John Wiley and Sons, New York, 234 (1951).

6) MS, m/e 318 (M^+,<1%), 190 (M^+-TCNE, 100%), 189 (81%), 159 (50%), 131 (29%), 128 (23%); uv, λ_{max} (CH_3OH) 231 nm (log ε 4.59), 267 (3.76), 327 (4.21), 350 (sh, 3.83); nmr δ (d_6-acetone) 2.58-2.90 (2H, m, $-CH_2-$), 5.16 (2H, dd, J=2.0 Hz,$\geq$CH), 7.67 (2H, dd, J=7.0, 7.4 Hz), 7.98 (2H, dd, J=7.4, 0.7 Hz), and 8.08 (2H, dd, J=7.0, 0.7 Hz).

7) The nmr spectrum was taken on a Varian XL-100 spectrometer in d_8-THF at -20°C. δ-Values were determined in d_8-THF relative to the low field THF signal assumed to lie at δ 3.63 ppm from TMS.

8) Variable-β SCF-MO calculation predicts the molecular diagram shown on the right (π-electron densities and π-bond orders) for the anion (*2*).

9) The experimental p*K*a=15 for cyclopentadiene was taken from Dessy et. al; R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, 84, 2899 (1962).

10) cf. D. J. Cram, *"Fundamentals of Carbanion Chemistry,"* Academic Press, New York, p.1 (1965).

11) cf. M. A. Battiste, *J. Amer. Chem. Soc.*, 85, 2175 (1963).