Tetrahedron Letters No. 28. pp 2515 - 2518.
0040-4039/78/0708-2515$02.00/0

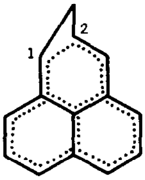
THE CHEMISTRY OF PHENALENIUM SYSTEMS. XXVII.[1) 10,11-HOMOPHENALENE AND ITS IONIC SPECIES

Kazuhiro Nakasuji, Masanori Katada, and Ichiro Murata*

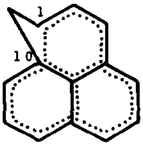
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(Received in Japan 14 April 1978; received in UK for publication 15 May 1978)

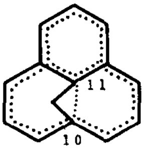
Haddon$^{2)}$ has recently described the chemistry of homoaromatic molecules by the perturbational molecular orbital theory which leads to some interesting predictions regarding three possible homophenalenyl systems (*1*), (*2*), and (*3*). Of these entities, 1,2- (*1*) and 10,11-homoconjugation (*3*) lead to the most unfavorable and favorable energy changes, respectively. While homoconjugation across the 1,2- and 1,10-positions of the phenalenium ion has been experimentally tested by us,$^{3)}$ no indications of the homoaromatic stabilities for *1* and *2* were recognized. In this paper, we wish to report the preparation of 10,11-homophenalene (*4*)$^{4)}$ and the cation and anion derived from *4*. This study completes the experimental test of the series of homophenalenyl systems.



(*1*)

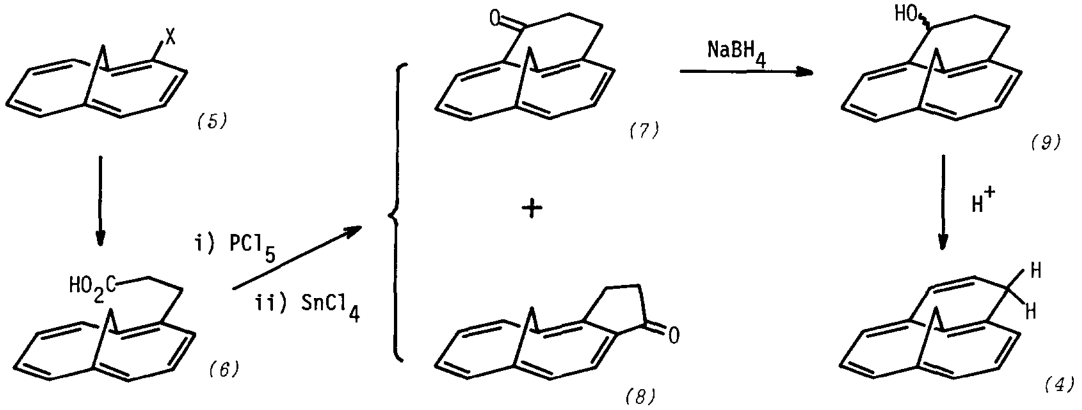


(*2*)



(*3*)

2-Ethoxycarbonyl-1,6-methano[10]annulene (5:X=CO_2Et),$^{5,6)}$ readily available from 1,6-methano-[10]annulene$^{7)}$ in high yield, was converted [$LiAlH_4$/ether, 90% yield] to the corresponding alcohol (*5*:X=CH_2OH), pale yellow needles, m.p. 66°C.$^{6)}$ Chlorination of the alcohol with diethyl malonate [$NaOC_2H_5/C_2H_5OH$, 20°C, 5 h] and hydrolysis with sodium hydroxide followed by decarboxylation afforded the carboxylic acid (*6*),$^{6)}$ as pale yellow needles, m.p. 76-77°C, in 35% yield from the alcohol (5:X=CH_2OH). Cyclization of *6* to the tricyclic ketones (*7*) (yellow needles, m.p. 82-83°C$^{6)}$) and (*8*) (yellow needles, m.p. 111°C$^{6)}$), each in 30% yield, was accomplished by treatment of the corresponding acid chloride [PCl_5/benzene] with $SnCl_4$ in anhydrous benzene. By way of its IR spectrum, the desired six-membered ketone (*7*) [1665 cm^{-1} ($\nu_{C=O}$)] can easily be distinguished from the five-membered ketone (*8*) [1690 cm^{-1} ($\nu_{C=O}$)]. Reduction of *7* [$NaBH_4/C_2H_5OH$] yielded an epimeric mixture of alcohol (*9*).6) Dehydration of *9* with 2-naphthalenesulfonic acid in refluxing benzene for 5 min and chromatographic purification [SiO_2 deactivated with 6% water, hexane] gave 10,11-homophenalene (*4*),6) as a pale yellow oil in 88% yield. The structure of *4* was identified as 10,11-homophenalene on the basis of its analysis,6) MS [m/e 180 (M^+, 39%), 179 (M^+-H, 68%), 165 (M^+-H-CH_2, 100%)], and UV spectrum [λ_{max}=212, 258, 343 nm]. However its structure was most clearly demonstrated by its ^{1}H-NMR spectrum, which showed a sharp AB-quartet at δ=-0.27, 0.35 (J=9.0 Hz), a slightly broadend AB-quartet at δ=3.64, 4.07 (J=26 Hz8)), and a third AB-quartet which is further split into triplets at δ=5.83 (J=9.5, 4.0 Hz), 6.57 (J=9.5, 2.0 Hz) along with a multiplet of aromatic protons at δ=6.5-7.6.



Hydrocarbon (*4*) is a labile and was converted cleanly into an isomeric mixture (2:1) of *10* and *11* when chromatographed on activated alumina. The mixture could be separated by column chromatography on silica gel impregnated with 10% silver nitrate. On the basis of their NMR spectra with extensive decoupling experiments, these two hydrocarbons must be assigned structures (*10*) [λ_{max}=236, 279 nm]6) and (*11*) [λ_{max}=233, 300 nm].6)

When a CD_2Cl_2 solution of *4* is added to FSO_3H9) in an NMR tube at -75°C a carbonium ion was generated as a dark red solution to which we assign structure (*12*) based on its ^{1}H-NMR spectrum measured at -50°C (see, Fig. 1). The spectrum consisted of the methylene protons of the methano-bridge at δ=2.10 (s, 2H),10) two pairs of doublets at δ=8.60 (J=9.5 Hz, H-4,9), 8.10 (J=8.0 Hz, H-6,7), a doublet of doublets at δ=7.68 (J=9.5 and 8.0 Hz, H-5,8) and an AB_2 multiplet at δ=7.44-7.73. These observations are compatible with the structure (*12*) rather than the *a priori* expected homophenalenium ion (3^+).

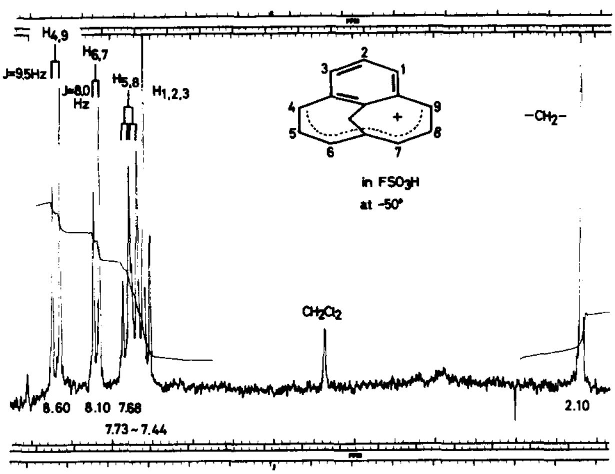


Fig. 1 Nmr Spectrum of *12*

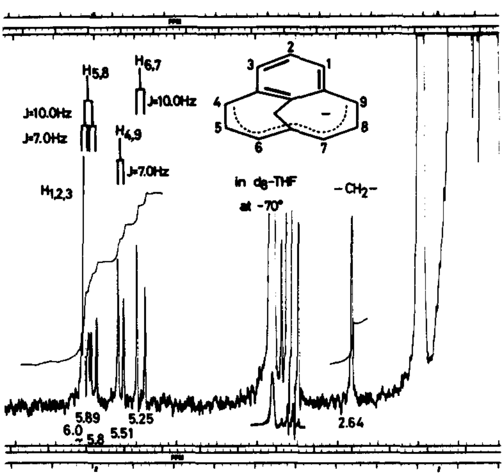
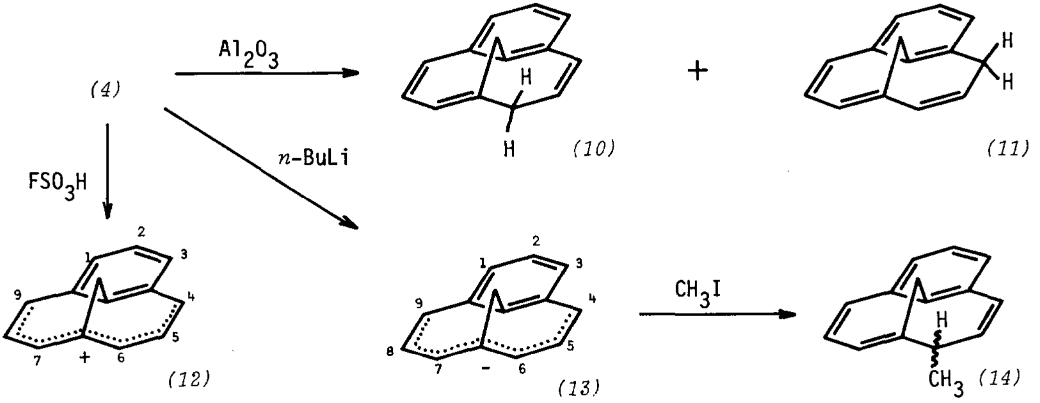


Fig. 2 Nmr Spectrum of *13*

The corresponding anion of *4* was produced immediately as a deep green solution by treatment of a THF-d_8 solution of *4* with *n*-butyllithium in a NMR tube under vaccum at -78°C. The ^{1}H-NMR spectrum measured at -70°C of this anion in THF-d_8 (see, Fig. 2) displayed signals at δ=2.64 (s, 2H, $-CH_2-$), 5.25 (d, 2H, J=10.0 Hz, H-6,7), 5.51 (d, 2H, J=7.0 Hz, H-4,9), 5.89 (dd, 2H, J=10.0 and 7.0 Hz, H-5,8) and an overlapping multiplet at δ=5.8-6.0 (AB_2, aromatic).[11] This is clearly not the ^{1}H-NMR spectrum of the delocalized 10,11-homophenalenide ion (3^-) since the low-field resonance of the bridge protons located above the ring[12] indicates the absence of a ring current. This finding suggests that the anion is a heptatrienide ion formulated as *13*. Quenching of the anion gave the methylated product (*14*)[6] quantitatively. The site of the methyl group[15] in *14* was suggested by its almost identical UV spectrum [λ_{max}=235, 280 nm] with that of *10* combined with the ^{1}H-NMR spectrum of *14*. This is exactly the result expected from the quenching of *13*.



Although the PMO theory predicts that the lowest first order energy change arises from 10,11-homoconjugation in *3*,2) available experimental evidence suggests that both cation (*12*) and anion (*13*) are not pronouncedly homoaromatic. These results strongly suggest that the stabilization energy provided by the benzenoid conjugation in *12* and *13* overcomes the stabilizing effect due to introduction of 10,11-homoconjugation into the phenalenyl system such as in *3*.

References and Notes

1) Part XXVI of this series, see K. Nakasuji, E. Todo, and I. Murata, *Angew. Chem.*, 89, 821 (1977); *Angew. Chem. internat. Edit.*, 16, 784 (1977).

2) R. C. Haddon, *J. Am. Chem. Soc.*, 97, 3608 (1975).

3) K. Nakasuji and I. Murata, *Tetrahedron Letters*, 2155 (1976).

4) The corresponding keto derivative of *4*, 4,10*b*-methano-8*H*-benzo[*ab*]cyclodecen-8-one, has already been synthesized. I. Murata, T. Nakazawa, and T. Tatsuoka, *Tetrahedron Letters*, 1789 (1971). For crystal and molecular structure of this ketone, see R. Yahashi, H. Shimanouchi, and Y. Sasada, *Bull. Chem. Soc. Jpn.*, 46, 1441 (1973).

5) E. Vogel and W. A. Böll, *Angew. Chem.*, 76, 784 (1964).

6) All new compounds gave correct elemental analyses and ^{1}H-NMR spectral characteristics that were in accord with their structures.

7) E. Vogel and H. D. Roth, *Angew. Chem.*, 76, 145 (1964).

8) To best of our knowledge, this J-value is the largest geminal coupling constant yet reported.

9) J. W. Larsen, P. A. Bouis, C. R. Watson, Jr., and R. M. Pagni, *J. Am. Chem. Soc.*, 96, 2284 (1974); R. M. Pagni, P. A. Bouis, and P. Easley, *Tetrahedron Letters*, 2671 (1975).

10) This chemical shift is comparable to that of protonated 1,6-methano[10]annulene: P. Warner and S. Winstein, *J. Am. Chem. Soc.*, 91, 7785 (1969). δ-Values were determined relative to the $CDHCl_2$ signal assumed to lie at δ=5.28 ppm from TMS.

11) δ-Values were determined relative to the low-field THF signal assumed to lie at δ=3.63 ppm from TMS.

12) The strong shielding of the methylene protons [δ=-0.45 and -0.9513), -0.7 and -1.214)] located above the negatively charged 10π ring was observed in 1,5-methanocyclononatetraenyl anion.

13) P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, 88, 3461 (1966).

14) W. Grimme, M. Kaufhold, U. Dettmeier, and E. Vogel, *Angew. Chem.*, 78, 643 (1966); *Angew. Chem. internat. Edit.*, 5, 604 (1966).

15) The stereochemistry of the methyl group has not been investigated.