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THE CHEMISTRY OF PHENALENIUM SYSTEM XXII.[1]
ON THE QUESTION OF 1,2- AND 1,10-HOMOCONJUGATION IN THE PHENALENIUM ION.

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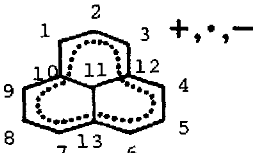
Haddon[2] has recently reported the first and second order energy change for the insertion of a homoconjugate linkage into the phenalenyl system (*1*) by the use of the perturbational molecular orbital (PMO) theory. He has pointed out that 1,2- and 1,10-homoconjugation lead to the first order (dominant) energy change $[E^1(\times 1/\delta\beta)]$ of -1.3407β and -1.1039β, respectively.[2] Thus far only an experimental work aimed to prepare 1,2-homophenalenium ion is protonation of 2,3-homophenalenone (*2*)[3] which leads to the protonated species (*3*) rather than (*4*). We now report the protonation of the epimeric mixture of alcohols (*5*)[3] and pleiadiene (*13*)[4] to show no evidence for the formation of 1,2- and 1,10-homophenalenium ions, respectively.



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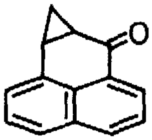

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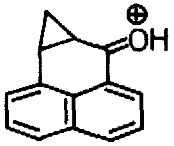

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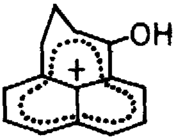
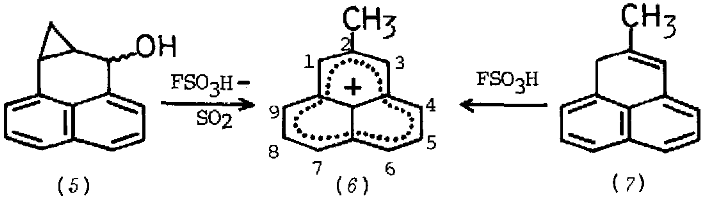
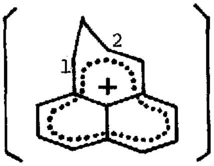


(*4*)

The alcohol (*5*) was prepared as described previously[3] by acid catalyzed isomerization of naphtho[1,8]tricyclo[4.1.0.0^{2,7}]heptene.[4b,c] The nmr spectrum of (*5*) in FSO_3H-SO_2 exhibits complex signals, which could not be analizable, in the temperature range of -70° to -20°C. The spectrum of the above solution at 30°C, however, discloses formation of the 2-methylphenalenium ion (*6*) along with minute quantities of decomposition products. Thus the symmetrical nmr feature, δ=2.86 (s, CH_3), 9.12 (s, H-1,3), 9.20 (d, J=8.0 Hz, H-4,6,7,9), 8.32 (t, J=8.0

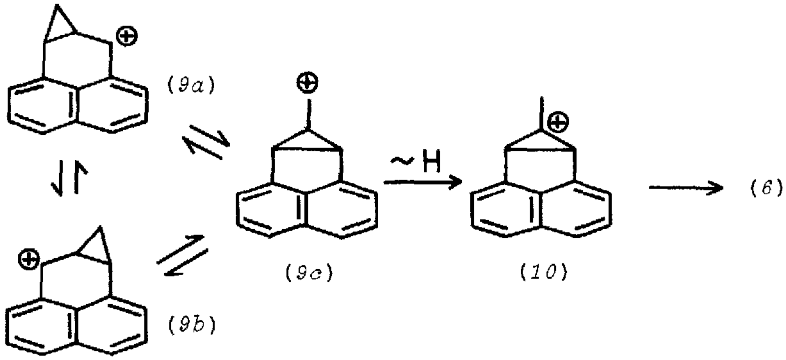


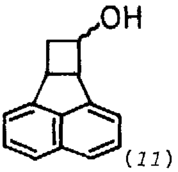
(5) (6) (7)



(8)

Hz, H-5,8), strongly supports the formation of (*6*) which was further confirmed by an alternative synthesis from 2-methylphenalene (*7*)[5] using Pagni's method.[6] The formation of (*6*) may be rationalized by the interconversion of methylene groups of the primarily formed cyclopropylcarbinyl cation (*9a*, *9b*, and *9c*) followed by intramolecular 1,2-hydride shift as shown in the following scheme.





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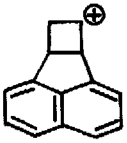
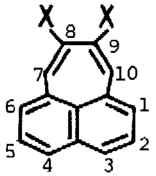


(*12*)

Since the nmr spectrum of the cyclobutanol (*11*), obtained through the hydroboration of naphtho[1,8]bicyclo[3.2.0]hept-6-ene,[7] in FSO_3H-SO_2 shows complex multiplets and no signals attributable to (*6*), the possibility of the rearrangement *via* the cyclobutyl cation (*12*) could be ruled out. In accordance with the prediction by PMO theory that a 1,2-homoconjugate linkage leads to the most unfavorable energy change for the phenalenyl system (*1*)[2] no evidence support for the existence of *a priori* expected 1,2-homophenalenium ion (*8*) can be obtained.

On the other hand, protonation of pleiadiene (*13*: X=H) would be a reasonable route leading to 1,10-homophenalenium ion (*14*).[2] Addition of a CD_2Cl_2 solution of (*13*: X=H) to FSO_3H at -78°C in an nmr tube proceeds to give a dark reddish purple solution. The carbon skeleton of pleiadiene remains unchanged is manifested by the fact that quenching of the FSO_3H solution with water at -78°C affords 70% recovery of (*13*: X=H). The nmr spectrum of the solution at -50°C is in complete accord with the formation of the benzotropylium ions (*15*: X=H) and (*16*: X=H). Although the ratio of the resulting cations, (*15*) and (*16*), is dependent on the time elapsed, the formation of (*15*) is always favored over (*16*) [(*15*)/(*16*)=1.5 ~ 2.0]. This trend accords well with the Hückel charge densities of (*13*) [q_1=1.07330, q_2=1.06333].[8) Thus, for (*15*: X=H), the methylene protons at C-1 appear at δ=4.83 (bd), the vinyl protons at C-2 and C-3 appear as an AB-quartet at δ=6.69 and 7.15 ($J_{2,3}$=9.5 Hz) with the upper half tripled due to coupling with H-1,1′ ($J_{1,2}$=4.5 Hz), the seven-membered ring proton at C-7 appears at δ=9.04 (d, $J_{7,8}$=11 Hz) and the remaining aromatic protons appear as a complex set of signals in the range δ=8.0-8.6; and (*16*: X=H) exhibits broad doublet of methylene protons of C-3 at δ=4.71, AB-quartet of H-1 and H-2 at δ=7.24 ($J_{1,2}$=9.5 Hz) and 7.52 ($J_{1,2}$=9.5 Hz, $J_{2,3}$=4.5 Hz), H-7 doublet at δ=8.91 ($J_{7,8}$=11 Hz) together with a multiplets of H-4,5,6,8,9,10 at δ=8.0-8.6 region. On warming to -20°C (two hours), new signals were appeared at δ=5.13 (bs, H-10,10'), δ=9.42 (d, $J_{7,8}$=10 Hz) and δ=8.0-8.8 (8H, m) assignable to new cationic species (*17*: X=H) in addition to (*15*: X=H) and (*16*: X=H) in a 3:1:3 ratio.



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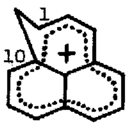

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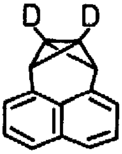

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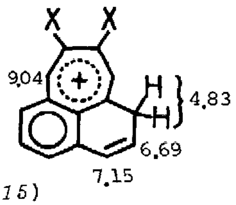

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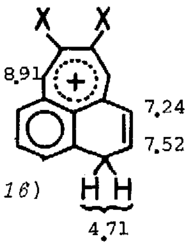

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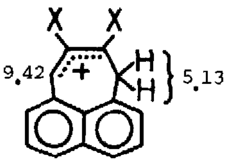
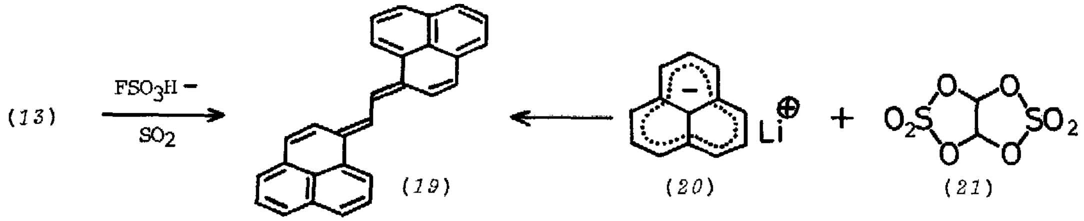


(*17*)

The assignment of the H-7 in these cations was made possible through the use of pleiadiene-8,9-d_2 (*13*: X=D) which was prepared from naphtho[1,8]tricyclo[4.1.-0.$0^{2,7}$]heptene-1,3-d_2 (*18*)[9) using the silver ion catalyzed isomerization.[4b) The simplified spectrum of (*13*: X=D) in FSO_3H exhibits absorption at δ=9.04 (*15*: X=D), 8.91 (*16*: X=D) and 9.42 (*17*: X=D), all absorptions being broad singlets.

We have not found it possible to establish that these cations undergo conversion to the anticipated ion (*14*) at the more elevated temperatures.

When (*13*: X=H) was allowed to dissolve in FSO_3H-SO_2 at -78°C, a dark green solution was obtained whose nmr spectrum shows paramagnetic line broadning. Brief warming of the solution to room temperature resulted in color change to reddish purple from which 10,10'-biphenafulvenyl (*19*)10) was obtained (<1% yield) after water quenching as a sole isolable product. The structure of (*19*) was confirmed by an independent synthesis through reaction of lithium phenalenide (*20*) with glyoxal sulfate (*21*).11)



(*19*) (*20*) (*21*)

Evidences described in this paper suggest that the gain in resonance energy accompanying homoconjugation across the 1,2- and 1,10-positions of the phenalenium ion (*1*) may be too small to detect the cations (*8*) and (*14*).

1) For Part XXI, I. Murata, K. Yamamoto, M. Morioka, M. Tamura, and T. Hirotsu, *Tetrahedron Lett.*, 2287(1975).

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

3) I. Murata and K. Nakasuji, *Tetrahedron Lett.*, 1591(1973).

4) a) V. Boekelheide and G. K. Vick, *J. Amer. Chem. Soc.*, 78, 653(1956); b) I. Murata and K. Nakasuji, *Tetrahedron Lett.*, 47(1973); c) R. M. Pagni and C. R. Watson, *ibid.*, 59(1973).

5) V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.*, 72, 1240(1950).

6) a) J. W. Larsen, P. A. Bouis, C. R. Watson, Jr., and R. M. Pagni, *J. Amer. Chem. Soc.*, 96, 2284(1974); b) R. M. Pagni, P. A. Bouis, and P. Easley, *Tetrahedron Lett.*, 2671(1975).

7) J. E. Shields, D. Gavrilovic, J. Kopecky, W. Hartmann, and H.-G. Heine, *J. Org. Chem.* 39, 515(1974).

8) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations", W. H. Freeman and Co., San Fransisco (1965), p. 170.

9) H. Kume, Master Thesis, Osaka University (1973).

10) I. Murata, K. Nakasuji, and H. Kume, *Tetrahedron Lett.*, 3405(1973).

11) Cf. H. Sauter and H. Prinzbach, *Angew. Chem.*, 84, 297(1972); *Angew. Chem. internat. Edit.*, 11, 296(1972), We thank Mr. H. Kume for this experiment.