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THE CHEMISTRY OF PHENALENIUM SYSTEM. IV.[1)]

1H-CYCLOHEXA[4,5,6-de]METHANO[10]ANNULEN-1-ONE. A BRIDGED ANALOG OF PHENALENONE.

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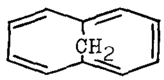
Excellent studies of bridged[10]annulenes by Vogel and coworkers have been stimulated by interest in the aromatic character exhibited by these compounds.[2)] The characteristics of the nmr spectrum of 1,6-methano[10]annulene 1, i.e. the absorption of the peripheral protons at very low field combined with the considerable shielding of the bridged methylene protons, clearly indicate the presence of an induced diamagnetic ring current in this molecule.[3)] On the other hand, phenalenone 2 [4)] is an abnormally highly polarized ketone, similar to tropone and cyclopropenones in many of its properties. This polarization is shown by the high dipole moment (3.89 D),[5)] low carbonyl streching frequency (1637 cm^{-1})[6)] and the basicity ($pK_b = 0.4$).[7)]

In the course of our studies on the phenalenium systems[1)] we interested in a new ketone, 1H-cyclohexa[4,5,6-de]methano[10]annulen-1-one 3, which involve a 1,6-methano[10]annulene skeleton instead of naphthalene moiety in 2. We now describe the preparation and properties of 3.



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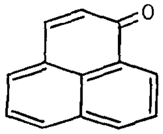

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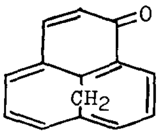

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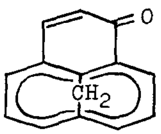
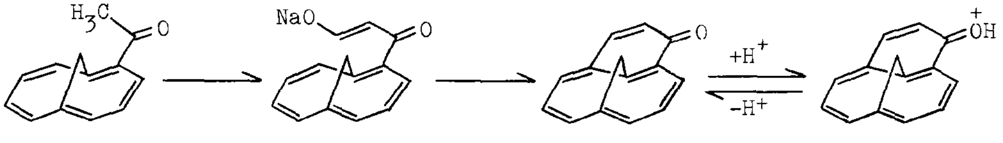


3a

Substance 3 was obtained simply by the reaction of 2-acetyl-1,6-methano[10]-annulene 4[8)] with ethylformate in the presence of sodium hydride and by the subsequent dehydration with sulfuric acid. Isolation with chloroform and chromatography on alumina and recrystallization from ether gave 3 as reddish orange prisms of mp. 86-87.5° in 58% yield. Anal. Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found : C, 86.29; H, 5.22 %. MS, m/e 194 (M^+, 51 %), 166 (M-CO, 21 %), 165 (M-CO-H, 100 %). Although the molecular model shows the three carbon units on the 1,6-methano[10]-annulene system to be more strained than the parent annulene 1 the 1H-cyclohexa-[4,5,6-de]methano[10]annulene 3 is a very stable compound. The retention of the annulene skeleton$^{9)}$ in 3 is clearly indicated by physical data shown below.



4 5 3 6

Good evidence for strong polarization of 3 is its dipole moment. We find 4.36 D in benzene at 25°.$^{10)}$ Comparison of this value with the 3.89 D of phenalenone and the 4.3 D of tropone$^{11)}$ indicate that 3 is strongly polarized ketone. These polarization is also reflected in the carbonyl streching frequency of 1605 cm^{-1} and in the high basicity (pK_b = -2.6)$^{12)}$; the ketone dissolves reversibly in trifluoroacetic acid with formation of a dark red cation 6. The electronic spectra show marked solvent dependent: $\lambda\lambda_{max}$(cyclohexane) 212 nm (log ε, 4.40), 256 (4.23), 292 (4.26) and 392 (3.95); $\lambda\lambda_{max}$(methanol) 207 (4.39), 218 (4.37, sh.), 257 (4.20), 295 (4.27), 407 (4.00) and 465 (3.37, sh.); $\lambda\lambda_{max}$(conc. sulfuric acid) 263 (4.16), 288 (3.92, sh.), 410 (4.04, sh.), 450 (4.21) and 530 -560 (3.24 at 550 nm).

The nmr spectrum of 3 $^{13)}$ confirms the structure. The spectrum in carbon tetrachloride is very complex and could not be analyzed except AB-quartet at δ 0.05 and 0.75 (J=9.5 Hz) of bridged methylene protons, 1H doublet at δ 6.12 (J=10.0 Hz) of H-2 proton and X-part of the ABX-system at δ 7.91 ($|J_{AX} + J_{BX}|$= 9.8 Hz). The chemical shift of H-2 proton in 3 (δ 6.12) is relatively high field than that of phenalenone (δ 6.66)$^{14)}$ and is comparable to those of cyclohexenone (δ 5.93)$^{15)}$ and cyclopentenone (δ 6.10).$^{15)}$ From these findings the ground state of the molecule is best represented by the slightly perturbed 1,6-methano[10]annulene with the enone bridge at 1,10-positions such as 3a. The spectrum in trifluoroacetic acid (Fig.) is rather informative. The AB-quartet at δ 1.27 and 1.77 is assigned to the bridged methylene protons (J=10.0 Hz), 1H doublet at δ 7.01 to the H-2 proton ($J_{2,3}$=9.0 Hz), 1H doublet at δ 7.91 to the H-3 proton ($J_{3,2}$=9.0 Hz), 1H doublet of doublets at δ 7.72 to the H-8 proton ($J_{8,9}$=10.0, $J_{8,7}$=8.0 Hz), 1H doublet at δ 8.78 to the H-9 proton ($J_{9,8}$=10.0 Hz), X-part of the ABX-system (H-4,5,6) at δ 8.14 to the H-6 proton ($|J_{4,6} + J_{5,6}|$=9.6 Hz) and 3H multiplet around δ 7.5 to the H-4,5 and 7 protons, respectively. These assignments are confirmed by double irradiation experiments.

As expected, ring protons of the protonated ketone exhibited the anticipated downfield nmr chemical shifts relative to their corresponding parent ketone. However, the magnitude of this charge-induced deshielding is much smaller as compared to the case of phenalenone.14) The bridged methylene protons (centered at δ 1.53) are found more than 1 ppm downfield16) from those of the unprotonated ketone (centered at δ 0.38) and are similar to those of 2,5-dihydro-1,6-methano-[10]annulene (centered at δ 1.7)17) and anti-1,6:8,13-bismethano[14]annulene (centered at δ 2.18).18)

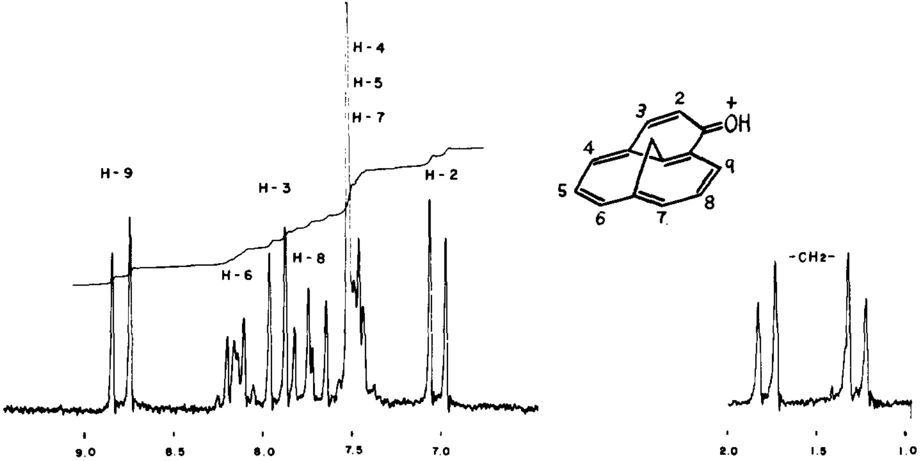


Fig. Nmr spectrum of 3 in CF_3COOH (100 MHz, TMS)

The exact explanation of this phenomenon is not clear but this may be attributed to the steric strain of this skeleton which may contribute to weakening the delocalization of positive charge over the peripheral framework. Consequently induced diamagnetic ring current developed in the [10]annulene moiety is substantially reduced in the protonated ketone 6.

Currently, studies are being extended to the formation of the parent hydrocarbon cation and anion of this new ring system.

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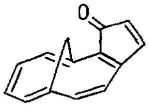

(i)

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