Communications TO THE EDITOR

Dibenzo[*a,e*]tropylium and 5-Phenyldibenzo[*a,e*]tropylium Cations

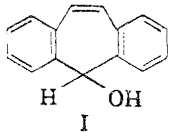
Sir:

In order to get further information on the properties of compounds presenting the tropylium structure, dibenzo[*a,e*]cycloheptatrien-5-ol (I, m.p. 120°. *Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.29; H, 5.80) was prepared by sodium borohydride reduction of dibenzo[*a,e*]cycloheptatrienone. (The product, m.p. 98°, previously reported[1] as I, was found to be a mixture of I with a large amount of 5-ethoxydibenzo[*a,e*]cycloheptatriene, m.p. 100°. *Anal.* Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.27; H, 6.85.) Both I and its 5-phenyl derivative[1] II gave deep red colors when treated with sulfuric, perchloric, or formic acid. The solutions in sulfuric acid had rather similar absorption spectra (see Table I), which can be assumed to be due to the ions III and IV.

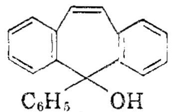
TABLE I

ABSORPTION MAXIMA IN 98% SULFURIC ACID

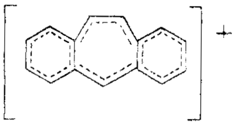
Ion	λ	Log ε	λ	Log ε	λ	Log ε	λ	Log ε	λ	Log ε	λ	Log ε	λ	Log ε
III	236	4.16	270	3.84	306	5.09	380	4.02	398	3.95	508	3.52	540	3.51
IV	240	4.26	268	4.10	312	5.01	384	3.76	414	3.70	528	3.65	564	3.69



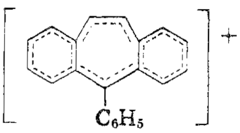
I



II



III



IV

Compound I was transformed by thionyl chloride into a covalent chloride (m.p. 123–125°. *Anal.* Calcd. for $C_{15}H_{11}Cl$: C, 79.45; H, 4.89; Cl, 15.66. Found: C, 79.00; H, 5.20; Cl, 15.63), which with silver perchlorate gave a dark red salt, dec. p. 135°. *Anal.* Calcd. for $C_{15}H_{11}^+ \, ClO_4^-$: ClO_4, 34.2. Found: ClO_4, 34.5.

As a measure for the stability of the ions the values of pK_{R^+} were determined in aqueous sulfuric acid by the method of Deno, Jaruzelski and Schriesheim[2]: found for III, −3.7; for IV, −5.7. These data, when compared with those for the tropylium (pK_{R^+}, 4.75)[3] and the benzotropylium (pK_{R^+}, 1.6)[4] ions,[5] show that the fusion of a second benzene ring to the tropylium cation further strongly decreases its stability, probably because of the many high-energy non-Kekulè structures involved in the resonance of the ions of the benzohomologs. On the other hand, the comparison of the value of pK_{R^+} of III with those of the diphenylcarbonium ion (pK_{R^+}, −13.3) and the fluorenylium ion (pK_{R^+}, −14.0)[2] clearly shows that the former ion is much more stable. This should be due to a partial persistence of the peculiar stability of the tropylium system, even when it is fused to two aromatic rings, although another factor may be quite important: the passage from the tetragonal configuration of the carbinol to the trigonal one of the ion diminishes the strain in the seven-membered ring of ion III, but increases it in the five-membered one of the fluorenylium ion.

The decrease in stability of IV compared to III is quite interesting, as it is in net contrast with the large increase produced by the introduction of a third phenyl group into the diphenylcarbonium ion. This could be explained by assuming that the phenyl group in IV is very far from achieving coplanarity with the conjugated system and therefore cannot have much influence on the resonance stabilization of the ion, while the electron-attracting properties of the aromatic group play a major role in diminishing the strength of the secondary base II. This gives a further proof of the intrinsic electronegativity of the phenyl group, for which evidence is so far rather scarce.[6,7]

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[1] W. Treibs and H.-J. Klinkhammer, *Ber.*, **84**, 671 (1951).

[2] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3047 (1955).

[3] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 76, 3203 (1954).

[4] H. H. Rennhard, E. Heilbronner, and E. Eschenmoser, *Chemistry & Industry*, 415 (1955).

[5] These data may not be exactly comparable, as they were obtained by different methods, but certainly hold for a qualitative differentiation.

[6] G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1955, p. 365.

[7] N. N. Lichtin and H. Glazer, *J. Am. Chem. Soc.*, **73**, 5537 (1951).