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THE CHEMISTRY OF FULVALENEDIONE SYSTEM. II.1)
THE PREPARATION AND PROPERTIES OF DIPHENYLHEPTATRIAFULVALENE-3,4-DIONE.

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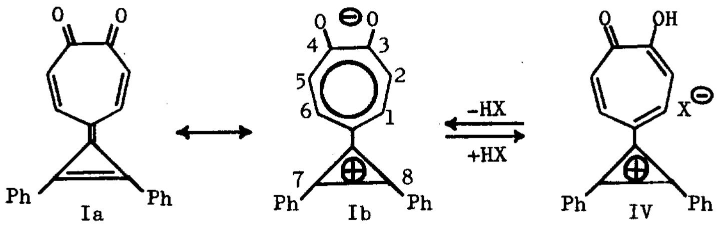
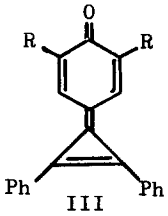
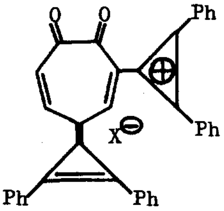
In a recent publication1) we have discussed some stable halogen derivatives of heptatriafulvalenedione (I). The present communication deals with the parent compound (I), which is not only a seven-membered vinylog of diphenylcyclopropenone (II)2) but also a quinone derivative of heptatriafulvalene. Tropolone was treated with an equimolar amount of 1,2-diphenyl-3-ethoxycyclopropenium ion3) in an acetonitrile solution in the presence of triethylamine to afford IV (6.0% yield; X=ClO_4: yellow needles; mp 190°C; $C_{22}H_{15}O_6Cl$ (Found: C, 64.52; H, 4.06%); $\lambda_{max}^{CH_3CN}$ nm (log ε): 276 (4.64), 320 sh (4.31), 394 (4.45), 408 (4.46); ν_{max}^{KBr}: 1619, 1594, 1500, 1412, 1387, 1355, 1266 cm^{-1}) and V (1.0% yield; X=BF_4: orange needles; mp 263°C; $C_{37}H_{23}O_2BF_4$ (Found: C, 75.50; H, 4.23%)). IV and V were proved to be 5- and 3,5-dicyclopropenylation products of tropolone respectively on the basis of the nmr data; IV: (Table 1), V: $\delta_{CF_3CO_2H}^{TMS}$ 9.62 (1H, d, JH_1-H_6=1.3 Hz, H_1), 9.12 (1H, dd, JH_5-H_6=11.4 Hz, H_6), 8.48 (8H, m, ortho-H of Ph), 7.83 (13H, m, H_5 and metha- , para-H of Ph)4). V exhibits infrared spectral bands (KBr) characteristic of the cyclopropene double bond at 1828 cm^{-1} and of the cyclopropenium ion5) at both 1400 (s) and 1321 (vs) cm^{-1}. V ($\lambda_{max}^{CH_3CN}$ nm (log ε): 250 (4.20), 283 (4.36), 406 (4.23), 440 (4.21), 460 (4.23)) is similar to I and its halogen derivatives in electronic spectra, suggesting that V is represented by a heptatriafulvalene-3,4-dione structure rather than the alternative 1,2-dione structure (VI). The addition of triethylamine to IV in an acetonitrile solution effected its immediate and complete conversion to the corresponding dione (I); deep orange needles,



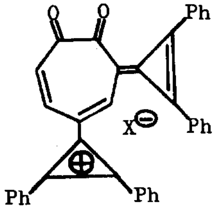
Ia Ib IV



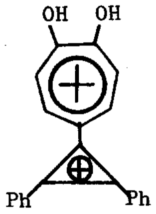
III



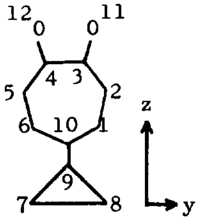
V



VI



VII



VIII

blackening at 180~190°C without melting, $C_{22}H_{14}O_2$ (Found C, 84.88; H, 4.31%); $\lambda_{max}^{CH_3CN}$ nm (log ε): 251 (4.33), 278 (4.40), 352 (4.03), 422 sh (4.65), 444 (4.76): ν_{max}^{KBr}: 1820, 1600, 1488, 1460, 1444, 1396, 1320 cm⁻¹. It quantitatively regenerates the original cation (IV) by means of acid. I is stable to air, light and heat (up to 150°C) in solid state, while diphenylquinocyclopropenenone, lacking substituents <u>ortho</u> to the quinoid carbonyl group (III: R=H)$^{6)}$, is too unstable to be isolated. In contrast to the case of III (R=t-Bu)$^{7)}$, I shows a small hypthochromic shift in its electronic spectrum on going from polar to non-polar solvents (λ_{max} (longest wavelength) 444 nm (log ε 4.76) in acetonitrile, 441 (4.72) in acetone, 447 (4.55) in dichloromethane, 432 (4.49) in benzene, 429 in dioxane), presumably because the excited state is more stabilized than the ground state by a polar solvent. The chemical shifts of the phenyl-ring protons of I (Table 1) are intermediate between those of IV and II. The difference in chemical shift between the ortho and meta-para protons of phenyl groups for I (0.51 ppm) does not differ significantly from that for the IV cation (0.58 ppm). These facts suggest that there is a considerable contribution of a polar structure (Ib) for I. The low carbonyl stretching of 1600 cm⁻¹ also suggests the contribution of Ib. In contrast to the small shift in phenyl protons a remarkably high-field shift

Table 1

Comparison of the NMR Spectral Data of II, I, IV, and VII. (ppm*, 100MHz at 25°).

Compounds	Solvents	H_1, H_6	H_2, H_5	(JH_1-H_2)	o-H of Ph	m,p-H of Ph
II	CH_3CN				7.79	7.47
I	CH_3CN	7.66	6.40	12.0 Hz	8.09	7.58
IV	CH_3CN	8.41	7.43	11.6 Hz	8.41	7.83
	CF_3CO_2H	9.06	8.21	11.6 Hz	8.57	8.02
	conc. H_2SO_4 (VII)	9.30	8.64	11.6 Hz	8.52	7.99

* CH_2Cl_2 was used as the internal standard, 5.30 ppm

Table 2

Calculated Electronic Structure and Spectrum of Heptatriafulvalenedione (VIII).10)

Bond	Bond length(Å)	Atom	Charge density	Free valence	Transition energy ΔE(ev)	f(cgs)	(Observed)* ΔE(ev)
1-2	1.362	1	0.952	0.484	3.12	1.080(z)	2.79(2.89**)
1-10	1.446	2	1.028	0.494	3.55	0.041(y)	3.52
2-3	1.448	3	0.726	0.265	3.64	0.068(y)	
3-4	1.469	7	0.857	0.481	4.37	0.016(y)	4.46
7-8	1.327	9	0.887	0.231	4.91	0.311(z)	4.94
7-9	1.413	10	1.152	0.223	5.62	0.385(z)	<6.20
9-10	1.375	11	1.417				
3-11	1.235						

* The spectrum of the 7,8-diphenyl derivative (I) in CH_3CN.

** The longest wavelength-absorption maximum of I in dioxane.

was observed in seven-membered ring protons, especially in H_2 and H_5, on going from IV to I, showing a large negative charge at the C_2 and C_5 positions in I. I has a large vicinal coupling constant, 12.0 Hz, indicating the same degree of bond alternation as those of tropone or 2-chlorotropone8). These experimental observations of nmr, together with the electronic spectrum of I, are in adequate agreement with the calculated charge densities or transition energies obtained by the application of the semiempirical variable bond-length SCF·LCAO-π-MO·CI-method9) to VIII (Table 2). The calculated dipole moment of the ground state of VIII, 13.13 D, is comparable with the value of 13.16 D for III11).

The nmr of H_2 and H_5 of IV (7.43 ppm in CH_3CN) showed a low-field shift of

1.21 ppm in conc. sulfuric acid and one of only 0.78 ppm in trifluoroacetic acid (Table 1). The electronic spectral absorption of IV in the long-wavelength region ($\lambda_{max}^{CH_3CN}$: 408 nm) showed a hypthochromic shift of 28 nm in conc. sulfuric acid and one of only 16 nm in trifluoroacetic acid(12). These facts indicate that a further protonation of IV takes place to form a divalent cation, VII ($\lambda_{max}^{conc.\ H_2SO_4}$ nm (log ε): 230 (4.49), 257 (4.61), 321 (4.63), 380 (4.35)) in conc. sulfuric acid, but not in trifluoroacetic acid(13).

Acknowledgements

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11) A. S. Kende, Advances in Chem. Physics, Bd 8, 133 (1965).
12) Tropolone shows a low-field shift of ring protons in nmr (1.1~1.2 ppm) and a hypthochromic shift of the electronic spectral absorption (about 30 nm) in both trifluoroacetic acid and conc. sulfuric acid because of the formation of the dihydroxytropylium cation.
13) We have observed the same phenomenon with the tropolonyl-5-tropylium cation. The details will be reported in the near future.