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THE CHEMISTRY OF FULVALENEDIONE SYSTEM I
HALOGEN DERIVATIVES OF DIPHENYLHEPTATRIAFULVALENE-3,4-DIONE

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It has recently been reported that cyclobutadienoquinone$^{1)}$ and sesquifulvalene-1,4-quinone$^{2)}$ are quite stable while their parent cyclo-olefines are too unstable to be isolated. We have planned the study on heptatriafulvalene-3,4-dione (II) to know how the introduction of a quinoid structure influences on the stability of its parent heptatriafulvalene (I) which has been predicted$^{3)}$ to be poly olefinic rather than aromatic, expecting that II may fall in the same category of the above stable quinones. The present paper deals with our preliminary results on the synthesis and properties of several derivatives (VII) of II.

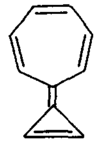
It is well known that the direct alkylation of tropolones is not easy$^{4)}$. The cyclopropenylation of tropolones, however, was accomplished with ease with cyclopropenium cation (VI)$^{5)}$ in such a way that VI [1 m mol] was added to a stirred solution of halotropolone (V) [1 m mol] and triethylamine [1 m mol] in 3 ml of acetonitrile at room temperature, giving VIIa: mp 280°C (Found: C, 56.15; H, 2.68%), VIIb: mp 260°C (Found: C, 46.84; H, 2.04%), VIIc: mp 188°C (Found: C, 67.53; H, 3.55%) and VIId: mp 191°C (Found: C, 60.30; H, 3.15%) as deep orange needles. These compounds are stable on exposure to light at room temperature and on heating at around 150°C in solid states, sparingly soluble in polar solvents such as acetonitrile or acetone, but gradually destroyed in less polar solvents such as methylene chloride, chloroform, benzene or dioxane and rapidly destroyed in hydroxylic solvents. These properties are surely correspond to those of quinocyclopropenone (IV: R=Br)$^{6)}$, suggesting a significant contribution of dipolar structure (VII-B) for the stability of these compounds.

The electronic spectra of VIIa~d exhibit absorption maxima (1st band) at

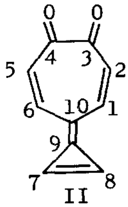
Table 1. Spectroscopic Evidence of VII and VIII

DIONE-FORM (VII)			SALT-FORM (VIII)			
	λ nm (log ε) in CH_3CN	IR in KBr cm^{-1}		NMR 100 MHz in CF_3COOH δ	λ nm (log ε) in CH_3CN ($HClO_4$)	IR in KBr cm^{-1}
VIIa	256(4.49) 280(4.57) 378(4.22) 432(4.66) 452(4.86)	1829 m 1622 s 1573 vs 1431 vs 1352 vs 1177 s	VIIIa	9.32(s) H_1,H_6 8.52 o-H of Ph 8.05 p,m-H of Ph	286(4.69) 297(4.72) 390(4.33) 415(4.40)	1609 vs 1596 vs 1405 vs 1359 m 1325 vs
VIIb	258(4.29) 283(4.42) 387(4.09) 432(4.38) 456(4.60)	1824 m 1616 s 1571 s 1431 vs 1353 vs 1175 m	VIIIb	9.58(s) H_1,H_6 8.50 o-H of Ph 8.05 p,m-H of Ph	244(4.01) 286(4.34) 325(4.33) 400(3.99) 422(4.04)	1596 vs 1410 vs 1357 m 1315 vs
VIIc	253(4.38) 279(4.45) 364(4.09) 426(4.43) 449(4.82)	1828 m 1608 s 1593 vs 1427 s 1361 vs 1332 s 1178 m	VIIIc	9.42(d) H_1 8.83(d,d) H_6 7.93(d) H_5 $J_{H_1-H_6}$=1.9 Hz $J_{H_6-H_5}$=11.6 Hz 8.49 o-H of Ph 8.02 p,m-H of Ph	284(4.72) 316(4.43) 395(4.39) 411(4.43)	1620 vs 1596 vs 1410 vs 1367 vs 1345 vs 1310 vs
VIId	255(4.41) 280(4.47) 368(4.15) 451(4.81)	1828 m 1603 s 1596 vs 1428 s 1364 vs 1339 s 1180 m	VIIId	9.73(d) H_1 8.79(d,d) H_6 7.88(d) H_5 $J_{H_1-H_6}$=1.9 Hz $J_{H_6-H_5}$=11.6 Hz 8.49 o-H of Ph 8.02 p,m-H of Ph	288(4.58) 320(4.52) 400(4.36) 420(4.37)	1610 vs 1595 vs 1411 vs 1364 vs 1310 vs
VIIe	255(4.45) 280(4.51) 370(4.19) 452(4.82)	1825 m 1594 s 1436 s 1375 vs 1335 s 1178 m	VIIIe	9.32(d) H_1 8.90(d) H_6 $J_{H_1-H_6}$=2.4 Hz 8.51 o-H of Ph 8.02 p,m-H of Ph 1.55(d) isopropyl	288(4.73) 412(4.52)	1604 s 1593 vs 1410 vs 1321 vs

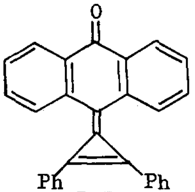
near 450 nm (Table 1) which are strikingly similar in both the band shape and the intensity to that of quinocyclopropenone (IV: R=t-Bu)7) except for a bathochromic shift of about 50 nm. The solvent effect on the spectra, however, is



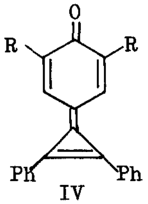
I



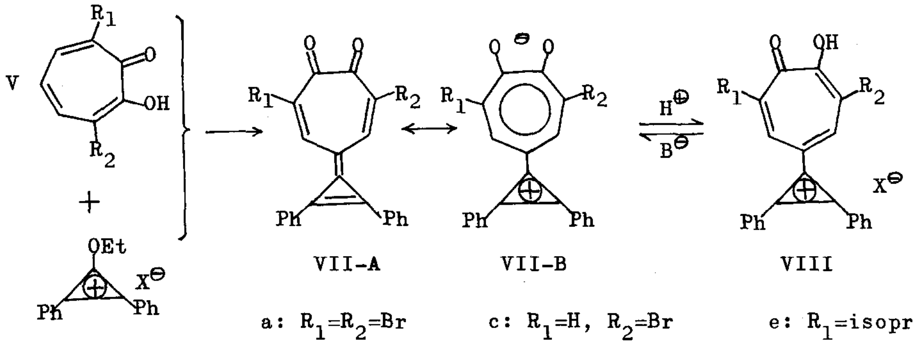
II



III



IV



V
VI
VII-A
VII-B
VIII

a: $R_1=R_2=Br$
b: $R_1=R_2=I$
c: $R_1=H$, $R_2=Br$
d: $R_1=H$, $R_2=I$
e: R_1=isopropyl, $R_2=Br$

analogous to that observed in III[7] rather than IV (R=t-Bu) as refered in Table 2. A bathochromic shift which increases with solvent polarity may be due to the transition to a more polar excited state[8]. VII shows an n→π* absorption band which appears as a tail of the first band at long-wave reagion in non-polar solvent but not in polar solvent[8]. The infrared spectra of VII show a cyclopropene C=C stretching band at around 1828 cm⁻¹ for VIIa~d, and a strong carbonyl band at 1616~1622 cm⁻¹ for VIIa,b and at 1603~1608 cm⁻¹ for VIIc,d[9]. VIIa~d failed to

Table 2. Effect of the Solvent Polarity on the Long-Wavelength Transition of Heptatriafulvalenediones: nm (log ε)

	CH_3CN	Acetone	CH_2Cl_2	Benzene	Dioxane
VIIa	452(4.86)	450(4.75)	458(4.39)	448(4.53)	†
VIIb	456(4.60)	454(4.68)	462(4.56)	452(4.39)	448(4.49)
VIIc	449(4.82)	447(4.80)	454(4.66)	443(4.64)	439(†)
VIId	451(4.81)	449(4.75)	455(4.55)	444(4.43)	439(4.58)
VIIe	452(4.82)	447(4.77)	454(4.78)	444(4.45)	442(4.19)
III	447(4.41)		448(4.42)	440(4.42)	426(4.41)
IV: R=tBu	402(4.87)		406(4.84)	410(4.74)	410(†)

give satisfactory nmr spectra in neutral solvent because of their poor solubilities, but VIIe: orange needles, mp 172°C (Found: C, 69.38; H, 4.41%), shows the nmr in 60MHz: $\delta^{TMS}_{CDCl_3}$: 8.43 (1H, d, J=1.8 Hz, H_1), 7.63 (1H, d, J=1.8 Hz, H_6), 8.13 (4H, m, o-H of Ph), 7.71 (6H, m, p,m-H of Ph).

The quantitative protonation of VIIa~e was effected with strong acids such as CF_3COOH or $HClO_4$ to give stable yellow salts VIIIa ($X=ClO_4$): mp 219°C (Found: C, 46.67; H, 2.65%), VIIIb ($X=ClO_4$); mp 198°C (Found: C, 39.91; H, 2.40%), VIIIc ($X=ClO_4$): mp 218°C (Found: C, 53.80; H, 3.16%), VIIId ($X=ClO_4$): mp 214°C (Found: C, 48.97; H, 2.96%), VIIIe ($X=ClO_4$): mp 186°C (Found: C, 56.53; H, 4.09%), which regenerated the original VIIa~e with base. The salts (Table 1) show nmr signals of seven-membered ring protons at quite low field and very strong infrared bands of cyclopropenium group at 1400~1410 cm^{-1}.10) The salts have no intense infrared absorption in the reagion 1570~1430 cm^{-1}, unlike general troponoids possessing an intense absorption of conjugated C=C bonds11) in this reagion. Acetic acid protonates VIIc,d but does not VIIa,b showing that the successive introduction of α-halogen atom decreases the basicity of VII. VIIa,b seem to be less basic than IV (R=Br, pka 3.86)). More detailed information on the basicity of VII, however, must wait for further study.

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† Exact values were not obtained due to a poor solubility.