Fulvalmixene. I. Synthesis and Reaction of Fulvalmixene-1, 4-quinone

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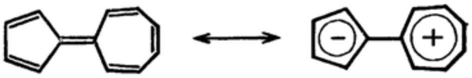
Fulvalmixene[1] (I), one of the non-benzenoid aromatic compounds, is an interesting compound because of the possible contribution of ionic structures like Ia and for examination of its aromaticity. Its stability has been predicted to a certain extent from theoretical considerations[2].



The synthesis of I has so far not been attained; only the tetrabenzo derivative[3] is known. The syntheses of 2, 3-benzofulvalmixene-1, 4-quinone and its parent compound, fulvalmixene-1, 4-quinone are described herein.

Reaction of indane-1, 3-dione (II) and 2 mol. equivalents of tropylium bromide (III) in aqueous solution afforded 2, 2-ditropylindane-1, 3-dione (IV), m. p. 167.5~168°C in 95%

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[1] The authors wish to use fulvalmixene as the name for cycloheptatrienylidene cyclopentadiene although mixed fulvalene[3] or sesquifulvalene* has been used. *W. von E. Doering, "Theoretical Organic Chemistry" (Kékule Symposium), Butterworth (1959), p. 35.

[2] R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950); J. F. Tinker, *J. Chem. Phys.*, **19**, 981 (1951); B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique", Masson et Cie., Paris (1952).

[3] B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, E. Fisher, Y. Hirshberg, D. Lavie and M. Mayot, *Bull. soc. chim. France*, **19**, 73 (1952).

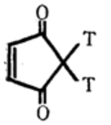
[4] Heating of ditropylmalononitrile at 170~190°C results in formation of 8, 8-dicyanoheptafulvene (T. Nozoe, T. Mukai and K. Osaka, This Bulletin, in press).

[5] C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959).

yeild (Found: C, 84.29; H, 5.41. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 227 (4.69), 252 (4.31), IR $\nu_{\mathrm{C=O}}$ 1728, 1699 cm^{-1}) Heating of IV at 175~180°C for 30 min. under reduced pressure[4] left a red residue with liberation of cycloheptatriene. Recrystallization of this residue from benzene gave 2, 3-benzofulvalmixene-1, 4-quinone (V) as red needles, m. p. 244~245°C (Found: C, 81.71; H, 4.13. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 247 (4.43), 257 (4.40), 452 (4.57). IR $\nu_{\mathrm{C=O}}$ 1645 cm^{-1}).

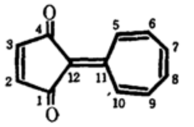
Reaction of cyclopentene-3, 5-dione[5] (VI) and 2 mol. equivalents of III in aqueous solution and adjustment of the reaction mixture to pH 6~7 with sodium hydrogen carbonate afforded in 93.5% yield, 4, 4-ditropylcyclopentene-3, 5-dione (VII) as yellow prisms, m. p. 121~122°C (Found: C, 82.45; H, 5.84. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%. IR $\nu_{\mathrm{C=O}}$ 1735, 1696 cm^{-1}). Pyrolysis of VII did not give VIII.

Reaction of VI and 1 mol. equivalent of III in the presence of 1 mol. equivalent of hydrobromic acid and dehydrogenation of the resulting yellow oily product with chloranil in xylene gave fulvalmixene-1, 4-quinone (VIII) as red plates, m. p. 179~180°C (Found: C, 78.41; H, 4.26. Calcd. for $C_{12}H_8O_2$: C, 78.25; H, 4.38%. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 222 (4.35), 253 (4.16), 420 (4.37). IR $\nu_{\mathrm{C=O}}$ 1643 cm^{-1}).



T = Tropyl

VII



VIII

The double bond at 2, 3 position in VIII is active and undergoes addition to give the following adducts:

Dibromide (IX).—Yellow scales, m. p. 148°C (decomp.) (Found: C, 42.51; H, 2.42. Calcd. for $C_{12}H_8O_2Br_2$: C, 41.89; H, 2.34%. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (4.30), 267 (4.21), 452 (4.43). IR $\nu_{\mathrm{C=O}}$ 1627 cm^{-1}). V does not undergo the addition of bromine.

Cyclopentadiene Adduct (X).—Red prisms, m. p. 188~189°C (Found: C, 81.51; H, 5.25. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 235 (3.82), 289 (3.83), 450 (4.43). IR $\nu_{\mathrm{C=O}}$ 1620 cm^{-1}).

Diazomethane Adduct (XI).—Orange needles, m. p. above 280°C (Found: C, 68.67; H, 4.33; N, 12.08. Calcd. for $C_{13}H_{10}O_2N_2$: C, 69.01; H, 4.46; N, 12.38%. UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (4.33), 266 (4.23), 451 (4.42). IR $\nu_{\mathrm{C=O}}$ 1618 cm^{-1}).

These 2, 3-adducts showed a red shift of ca. 30 mμ in the first absorption band in their ultraviolet spectra, compared to that of VIII, and the C=O stretching vibration in their infrared spectra also showed a shift of ca. 20 cm^{-1} to lower frequencies[6]. These phenomena might be explained by assuming that conjugation within the O=C–C=C–C=O group hinders conjugation between the carbonyl group and the seven-membered ring.

Absence of hydroxyl band in the infrared spectra of adducts shows that they do not exist in the enol forms, 1, 4-dihydroxyfulvalmixenes.

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[6] The C=O stretching vibration in the dibromide IX is in smaller wave number region than in X and XI because it is an α-bromoketone (cf. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen Co., Ltd., London (1958), p. 139.