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4-DIPHENYLMETHYLENE-1,2-DIPHENYLBUTATRIAFULVALENE-3,5-DIONE

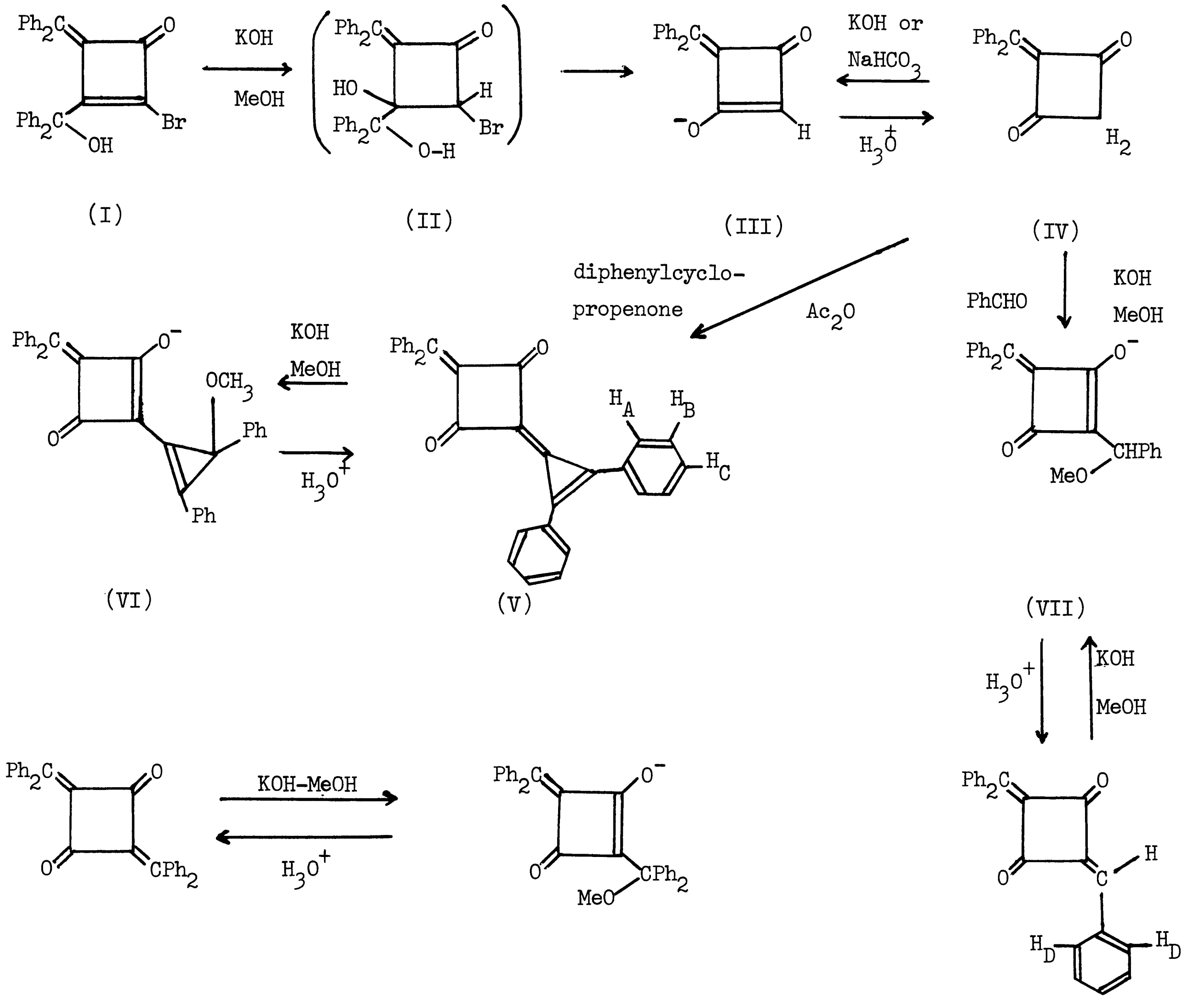
Fumio TODA

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama

The title butatriafulvalenedione (V) was prepared by the condensation of diphenylmethylenecyclobutane-1,3-dione (IV) with diphenylcyclopropenone. The spectral data of V were discussed. V was dissolved in methanolic potassium hydroxide in the form of the enolate anion (VI), and the acidification of the solution recovered V.

Derivatives of penta-¹⁾ and hepta-triafulvalenedione²⁾ have been reported. However, no butatriafulvalenedione system has yet been known. This communication deals with the preparation of the title butatriafulvalenedione (V), and its physical and chemical properties. The preparation of a new methylenecyclobutane-1,3-dione (IV), from which V was prepared, was also described.

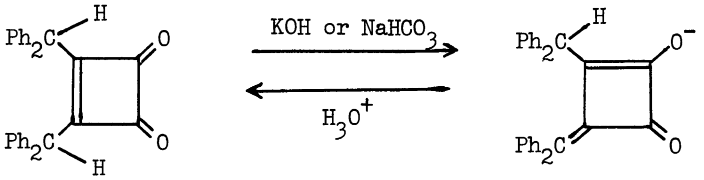
A mixture of I³⁾ (0.5 g), MeOH (20 ml) and KOH (0.4 g) was heated under reflux for 10 min. The reaction mixture was decomposed with water and extracted with ether. From the ether solution, benzophenone (0.18 g, quantitative yield) was obtained. Acidification of the water solution afforded IV (0.22 g, 88% yield) as orange yellow needles, mp 162-164°C. IR,⁴⁾ 1800 (w), 1760 (w) and 1710 (vs) (C=O), 1545 (vs) (C=C), 1370 (m) (CH_2) and 1120 cm^{-1} (s) (unassignable); UV, 312 (9000) and 374 nm (ε, 13400); NMR, 2.51 (s, Ph, 10H) and 6.26 τ (s, CH_2, 2H). The recrystallization of IV from AcOEt-MeOD afforded IV-d_2 quantitatively, which showed neither CH_2 signal (6.26 τ) in the NMR spectrum nor δCH_2 (1370 cm^{-1}) in the IR spectrum. IV dissolved in KOH-MeOH and even in aqueous $NaHCO_3$, from both the solutions IV was recovered quantitatively by the acidification. The UV spectrum of IV in 5% KOH-MeOH, 248 (13200) and 305 nm (ε, 13400) is cpmparable to that of IX, 256 (16200) and 324 nm (ε, 24500),⁵⁾ and that of XI, 240 (13600) and 330 nm (ε, 21700)⁶⁾ both in 5% KOH-MeOH. To the enolized forms of IX and XI, the enolate anion structures X⁵⁾ and XII⁶⁾ have been assigned respectively.



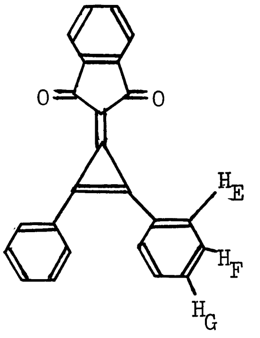
(I) (II) (III) (IV)

(VI) (V) (VII)

(IX) (X) (VIII)



(XI) (XII)



(XIII)

A mixture of IV (0.3 g, 1.2 mmoles), diphenylcyclopropenone7) (0.6 g, 3 mmoles) and acetic anhydride (10 ml) was heated under reflux for 30 min. The crude crystals separated out were recrystallized from ethyl acetate to afford V (0.15 g, 29%) as yellow prisms, mp 269-271°C (dec). Found: C, 88.28; H, 4.54%; Mol wt (M^+), 436.1453. Calcd for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62%; Mol wt, 436.1463. IR, 1840 (m) (triafulvene), 1655 (vs) (C=O) and 1510 (vs) and 1475 cm^{-1} (vs) (C=C); UV, 340 (12300), 412 (57100), and 430 sh nm (ε, 51000); NMR, 1.40-1.53 (m, H_A, 4H), 2.25-2.35 (m, H_B and H_C, 6H), and 2.45-2.65 τ (m, $=CPh_2$, 10H). The benzylidene analog VIII was prepared by the KOH-catalyzed condensation of IV with benzaldehyde in MeOH in a 63% yield, reddish brown needles, mp 217°C. Found: C, 85.47; H, 4.73%; Mol wt (M^+), 336.1169. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%; Mol wt, 336.1150. IR, 1680 (vs) (C=O) and 1620 (m), 1580 (s), and 1550 cm^{-1} (vs) (C=C); UV, 329 (10500), 400 sh (24000), 428 sh (44000), and 454 nm (ε, 68000); NMR, 1.67-1.79 (m, H_D, 2H), 2.35-2.63 (m, Ph, 13H), and 2.67 τ (s, =CH, 1H).

The strong deshielding of H_A of V (1.40-1.53 τ) is mainly due to the diamagnetic anisotropy of the carbonyl, since H_D of VIII (1.67-1.79 τ) is also deshielded, and since it has been reported that the main cause for the strong deshielding of H_E of XIII (1.20-1.35 τ) is the diamagnetic anisotropy of the carbonyl. The UV spectrum of V was little affected by the polarity of the solvent used for the measurement. The similar behaviors of XIII1) and 3,4,5,6-tetrachloro-1,2-diphenyltriapentafulvalene8) have been reported. On the basis of the NMR and the UV spectral studies, one can conclude that the contribution of cyclopropenyl cation structure to the ground state of V is small, if any. However, polarizability of the carbonyl of V (νC=O, 1655 cm^{-1}) is much greater than those of VIII (1680 cm^{-1}), IV (1710 cm^{-1}), and IX (1692 cm^{-1} in KBr)5), but is comparable to that of XIII (1660 cm^{-1} in CH_2Cl_2)1).

The butatriafulvalenedione (V) dissolved in KOH-MeOH probably in the form of an enolate anion, and the acidification of the solution recovered V quantitatively. A possible enolate anion structure is VI, since the UV spectral bands of V in 5%-KOH-MeOH, 262 (11900), 280 sh (9900), and 417 nm (ε, 15200), were at the wavelength region longer than those of VIII in the same solvent, 254 (19400) and 322 nm (ε, 27000).

The enolate anion structure VII is probable, since the structure X has been postulated for the enolate anion produced by dissolving IX in KOH-MeOH.5) The assumption was confirmed to be correct by the isolation of potassium salt of VII as colorless fine needles in a 75% yield, in the reaction of VIII with 15% KOH-MeOH at room temperature, mp> 265°C. Found: C, 73.51; H, 4.54%. Calcd for $C_{24}H_{19}O_3K$: C, 73.10; H, 4.82%. IR, 1580-1540 (vs) ($=C-O^-$) and 1075 cm^{-1} (s) ($-O-CH_3$); IR (hexachlorobutadiene), 2830 (m), 1450 (m) and 1380 cm^{-1} (w) (CH_3). The strong band at 1580-1540 cm^{-1} is corresponding to that of salt of carboxylic acid at 1610-1550 cm^{-1}. However, all attempts of the isolation of potassium salt of VI failed.

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