

DIMETHYLCYCLOBUTENEDIONE

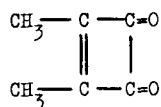
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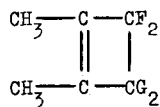
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WE wish to report the synthesis of dimethylcyclobutenedione (dimethylcyclobutadienoquinone) (I), the first simple homolog of cyclobutenedione, several higher analogs of which have been previously reported.¹⁻⁴ All of these have side-chain unsaturation in conjugation with the cyclobutenedione system.



I



II

Methylation of perfluorocyclobutene³ with methyl lithium in ether solution at -45°, an improvement of the general procedure described by Dixon⁵, gave 1,2-dimethyltetrafluorocyclobutene (II) (55%); b.p. 100-104°, $n_D^{27.5}$ 1.3478. Hydrolysis⁶ of compound II with 96-97% sulfuric acid at

¹ E.J. Smutny and J.D. Roberts, J.Amer.Chem.Soc. **77**, 3420 (1955).

² M.P. Cava and D.R. Napier, J.Amer.Chem.Soc. **79**, 3606 (1957).

³ A.T. Blomquist and E.A. LaLancette, J.Amer.Chem.Soc. **83**, 1387 (1961).

⁴ C.M. Sharts and J.D. Roberts, J.Amer.Chem.Soc. **83**, 871 (1961).

⁵ S. Dixon, J. Org.Chem. **21**, 400 (1956).

⁶ J.D. Roberts, G.B. Kline and H.E. Simmons, Jr., J.Amer.Chem.Soc. **75**, 4765 (1953).

65-70° for 70 min gave the diketone I (60%) as a yellow liquid; b.p. 74-76° (2 mm), n_D^{24} 1.4908. (Found: C, 65.41; H, 5.49; mol. wt., 127 (Rast). Calc. for $C_6H_6C_2$: C, 65.44; H, 5.49; mol. wt., 110.) Another reagent, polyphosphoric acid (PPA),⁷ after 1.5 hr at 100-105° also hydrolyzed the fluorocarbon (II) to the diketone I (43%). A similar experiment with 100% orthophosphoric acid afforded only a poor yield of impure I; thus, it was indeed the unique properties of the reagent PPA which were responsible for the clean hydrolysis. These results serve to expand the versatility of PPA, since this is the first recorded case of its ability to hydrolyze gem-dihalo groups⁸. The ditosylhydrazone derivative of I had m.p. 190-191° (dec.). (Found: C, 53.71; H, 5.02; N, 12.60. Calc. for $C_{20}H_{22}O_4N_4S_2$: C, 53.70; H, 4.97; N, 12.55.) The controlled addition of 2,4-dinitrophenylhydrazine reagent⁹ to I gave a mono-2,4-dinitrophenylhydrazone derivative; m.p. 205-208° (dec.). (Found: C, 49.68; H, 3.49; N, 19.45. Calc. for $C_{12}H_{10}N_4O_5$: C, 49.65; H, 3.47; N, 19.30.) The enedione I was soluble in water, ether, chloroform, benzene, dioxane, acetonitrile, and mineral acids. The compound could be stored in the refrigerator indefinitely, or at room temperature for several weeks without visible change.¹⁰

Reaction of compound I with aqueous 30-35% hydrogen peroxide at room

⁷ The reagent was freshly prepared by the addition of 140 g of phosphorus pentoxide in 20 g portions to 90 ml of 85% orthophosphoric acid followed by a period of heating on the steam bath for 3-4 hr. Commercial reagent (Victor Chemical Co.) reacted much too vigorously at 100-105°, and no diketone I was obtained.

^{8a} F.D. Pope and W.E. McEwen, Chem.Rev. **58**, 321 (1958); b R.A. Raphael, E.C. Taylor and H. Wynberg, Advances in Organic Chemistry, Methods and Results Vol. I, pp.35-81. Interscience, New York (1960).

⁹ R.L. Shriner, R.C. Fuson and D.Y. Curtin, The Systematic Identification of Organic Compounds (4th. Ed.) p.219. John Wiley, New York (1956).

¹⁰ In aqueous solution, I underwent a photochemical reaction when exposed to direct sunlight or irradiated with a 275-Watt I.R.-U.V. sunlamp. A yellow, crystalline product with m.p. 222-223° was obtained which analyzed for the molecular formula, $C_{12}H_{12}O_4$. Elucidation of the structure of this dimer is in progress.

temperature readily gave dimethylmaleic anhydride (71%). The infra-red spectrum of I (neat) exhibited absorption characteristic of a strained carbonyl group attached to a four-membered ring at 5.60 and 5.67 μ (unresolved doublet), with shoulders at 5.49 and 5.84 μ ; the first carbonyl overtone absorbed weakly at 2.83 μ . Strong, sharp absorption at 6.21 μ characteristic of an olefinic bond conjugated with a carbonyl group was also present. In the ultra-violet I (ethanol solution) showed the following maxima (ϵ 's in parenthesis) characteristic of α - β unsaturated ketones:¹¹ 216 (18,800), 340 (26), and 355 m μ (shoulder) (23). In contrast to diphenylcyclobutenedione,³ the diketone I showed fair stability in ethanol; the intensity of absorption of the compound in ethanol at 216 m μ decreased in 9 days to 13,500 and in 16 days to 12,080. The diphenyl analog in ethanol deteriorated completely within 12 hr to give a mixture of meso and racemic diethyl α,α' -diphenylsuccinate.

The NMR proton spectrum showed only one unresolved peak at 2.40 p.p.m. to lower field than the resonance of protons in an internal tetramethylsilane standard. In comparison, the NMR spectrum of biacetyl showed a similar single, unresolved peak at 2.25 p.p.m. lower than the standard.

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¹¹

A.E. Gillam and E.S. Stern, An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry (2nd Ed.) pp.103-107. E. Arnold, London (1957).