CHEMISTRY LETTERS, pp. 217-218, 1978. Published by the Chemical Society of Japan

SYNTHESIS AND PYROLYTIC DECARBONYLATION OF 4-CYCLOPENTENE-1,2,3-TRIONE

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4-Cyclopentene-1,2,3-trione 1 is synthesized by either dehydration of 2,2-dihydroxy-4-cyclopentene-1,3-dione 4 or pyrolysis of 2-chloro-2-formyloxy-4-cyclopentene-1,3-dione 5. Pyrolysis of 1 gives the bis-ketene 6 by decarbonylation, which is confirmed by ring closure to cyclobutenedione 2 as well as by trapping with methanol or hydrogen chloride.

Although a number of 4-cyclopentene-1,2,3-triones have been synthesized, the parent compound 1 has remained unknown.[1] An interesting point on the chemical property of 1 would be whether or not it gives cyclobutenedione 2 by pyrolytic decarbonylation. Indanetrione has been reported to give benzocyclobutenedione on pyrolysis.[2] We wish here to describe the synthesis and pyrolysis of 1.

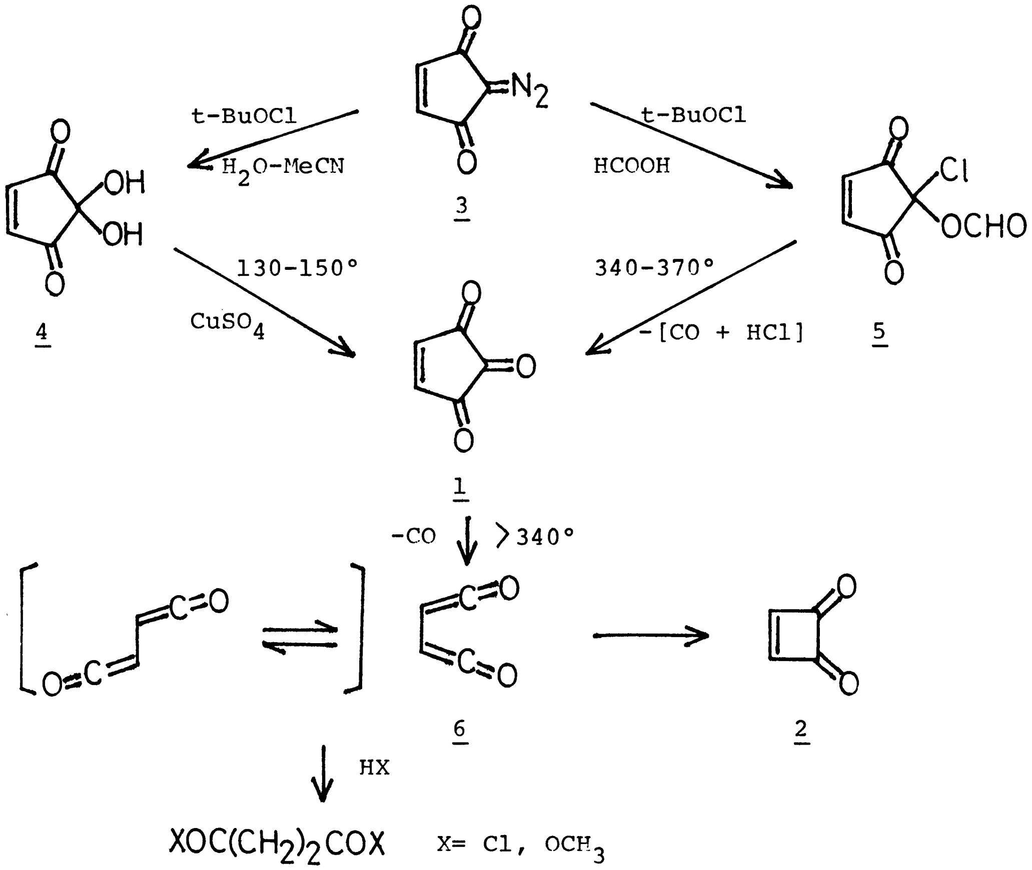
As potential precursors for 1, 2,2-dihydroxy-4-cyclopentene-1,3-dione 4 and 2-chloro-2-formyloxy-4-cyclopentene-1,3-dione 5 were prepared as follows. Treatment of 2-diazo-4-cyclopentene-1,3-dione 3[3] with one equiv. of tert-butyl hypochlorite in 10% aqueous acetonitrile at 0°C gave 4 in 62% yield [yellow crystals; m.p. 84-87°C; ν_{max}(KBr) 3400, 1730, 1720, 1630, 1040, 878 cm^{-1}; λ_{max}(CH$_3$CN) 217 (ε 12800), 341 (190), 407 nm (280)· δ ((CD$_3$)$_2$CO) 6.2 (br. OH), 7.50 (s)]. Similar treatment of 3 with the reagent in formic acid gave 5 quantitatively [yellow crystals; m.p. 71-72°C; ν_{max}(KBr) 1725, 1565 cm^{-1}; δ (CDCl$_3$) 7.41 (2H, s), 8.00 (1H, s)].

Heating of an admixture of 4 with excess anhydrous copper(II) sulfate in a sublimator at 130-150°C *in vacuo* successfully provided 1 as red crystals in 71% yield[4] [m.p. 175-177°C; ν_{max}(Nujol) 1790, 1754, 1725 cm^{-1}; λ_{max}(anhydrous CH$_3$CN) 218 (13000), 254 (sh, 1780), 340 (sh, 12), 455 (13), 541 nm (11); δ ((CD$_3$)$_2$CO) 8.13 (s)]. The trione 1 was also obtained by flash pyrolysis of 5 at 340-370°C in 3-5% yield[5] along with a trace amount of cyclobutenedione 2[6] (PMR) and an appreciable amount of succinoyl chloride (50-80% based on hydrogen chloride to be liberated). This result and the mass spectrum of 1 (m/e 110 (M$^+$, 4%), 82 (M-CO, 61%), 54 (M-2CO, 82%), 26 (M-3CO, 100%)) are suggestive of fairly ready pyrolytic decarbonylation of 1. The trione 1 readily adds water, particularly in moist solutions, reverting to 4.

On flash pyrolysis at 430°C *in vacuo* and leading the pyrolysate into methylene chloride cooled at -78°C, 1 gave 2 in a 9% yield besides polymeric materials [2: δ (CDCl$_3$) 9.70 (lit. 9.73[6]); Diels-Alder adduct with diphenylisobenzofuran:

light orange needles; m.p. 207-209°C decomp.; ν_{max}(KBr) 1795, 1765 cm^{-1}; δ ($CDCl_3$) 4.26 (2H, s), 7.0-8.0 (14H, m)]. When the pyrolysate was led into methanol, dimethyl succinate was obtained in good yield.

These results indicate the intermediary formation of the bis-ketene (1,4-dioxo-1,3-butadiene) 6 by decarbonylation of the central carbonyl group. Thermal cyclization of such a bis-ketene to a cyclobutenedione has been observed in the photo-reaction of diphenylcyclobutenedione.[7]



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4) In the absence of $CuSO_4$, the trione 1 was not obtained purely due to co-sublimation and an appreciable degree of decomposition of the diol 4.

5) In this pyrolysis, 1 crystallized out in the column just out of the heating part and was obtained by scratching out.

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(Received December 6, 1977)