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PYROLYTIC GENERATION OF CARBONYLCYCLOPROPANE‡ (DIMETHYLENE KETENE) AND ITS DIMERIZATION TO DISPIRO-[2,1,2,1]-OCTANE-4,8-DIONE

Gary J. Baxter[A], Roger F. C. Brown[A*], Frank W. Eastwood[A], and Kevin J Harrington[B]
[A]Department of Chemistry, Monash University, Clayton 3168, Australia
[B]Division of Chemical Technology, CSIRO, South Melbourne 3205, Australia

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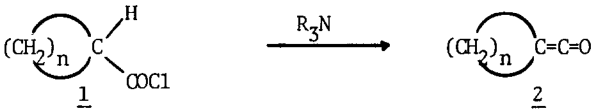
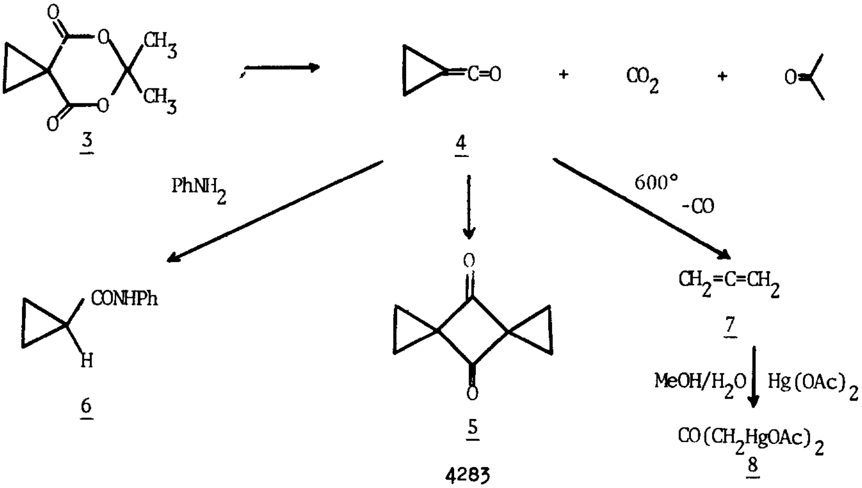
Cyclic ketenes (2) can be generated in solution by treatment of the appropriate acid chloride (1) with a tertiary amine[1], but the reaction fails in the case of the cyclopropane system (1, n = 2) This failure has been rationalized in terms of increasing I-strain[1] in going from the cyclopropyl to the cyclopropylidene structure. Previous attempts to generate ketene 4, either by decomposition of a mixed anhydride[2] or of the trimethylsilyl ester[10] of cyclopropane-1,1-dicarboxylic acid, or by thermolysis of a cyclobutanone[3] failed, though we now show that the temperature employed (700 - 1000°) in the latter method was too high to permit the survival of the ketene 4.



We have previously shown[4] that thermolysis of 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's acid, isopropylidene malonate) and its derivatives provides a practical route to ketene and substituted ketenes. We now report that pyrolysis of 2,2-dimethyl-1,3-dioxan-4,6-dione-5-spirocyclopropane[5] (3) at 500°/0.05 mm through a packed silica tube readily affords



carbonylcyclopropane (4) (infrared spectrum measured at about -196°, ν_{max} 2145, 2125 cm^{-1}), which on warming to room temperature gives the ketene dimer, *dispiro*-[2,1,2,1]-*octane*-4,8-*dione* (5). Introduction of aniline vapour into the pyrolysate stream yielded the anilide 6 (m.p. 110-111°, 16%) (lit.[6] m p. 110-111°). Pyrolysis of ester 3 (1 g) gave the pure *dione* 5, (180 mg, 45%), m.p. 190° (EtOH), (Found. C, 70.6, H, 5.9. $C_8H_8O_2$ requires C, 70.7, H, 5.9%) ν_{max} (Nujol) 3080 (cyclopropane C-H), 1725 (C=O) cm^{-1}. Mass spectrum *m/e* 136 (M^+, 84%), 121 (14), 108 (13), 80 (22), 79 (46), 68 (59), 40 (100). P.m r. spectrum ($CDCl_3$) δ 2 93, s. ^{13}C [^1H] spectrum ($CDCl_3$) δ 209.69 (C=O), 50.65 (spiro C), 21.85 (CH_2)

In the infrared spectrum of the ketene measured at -196°, an absorption at 1940 cm^{-1} is attributed to allene. When the pyrolysis was carried out at 600° no ketene was detected. The pyrolysate gas obtained on warming the cold trap, when bubbled through aqueous-methanolic mercuric acetate gave the oxymercurial compound 8, m.p 175° (lit.[7] m.p. 176 6 - 177.5°) The allene is presumed to arise from decarbonylation of the ketene 4.

Reaction of cyclobutane-1,1-dicarboxylic acid with acetic anhydride, acetone and sulphuric acid gave 2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione*-5-*spirocyclobutane*, m.p. 81° (EtOH/pentane), (Found: C, 58.5; H, 6.5 $C_9H_{12}O_4$ requires C, 58 7, H, 6.6). ν_{max} (Nujol) 1730 cm^{-1}. Mass spectrum· *m/e* 169 (M-15, 25%), 82 (100%). P.m.r. spectrum ($CDCl_3$) δ 1.65, s, 6H (CMe_2), 2 0-3.1, m, 6H (CH_2). The ester gave on pyrolysis at 430°/0 003 mm a product which on warming to room temperature yielded dispiro[3,1,3,1]-decane-5,10-dione, m.p. 85° (lit.[8] m p. 85°), in quantitative yield. The anilide, m.p 111° (lit [9] m p. 111°), was formed in the manner described above confirming the presence of carbonylcyclobutane.

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‡ Chemical Abstracts nomenclature cyclopropylidenemethenone