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FLASH THERMOLYSIS OF BICYCLO [2.2.1] -2-HEPTEN-2,3-DICARBOXYLIC ANHYDRIDE : THE GENERATION OF FULVEN-6-ONE.

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Fulven-6-one 4 has been postulated as an intermediate in the thermolysis of a variety of ortho-substituted aromatic compounds (¹). In this note is reported the generation of 4 by a totally different pathway and its characterisation by trapping experiments and low temperature infrared spectroscopy.

Flash thermolysis (²) of bicyclo [2.2.1]-2-hepten-2,3-dicarboxylic anhydride 1 (³) at 550° ($P = 5.10^{-3}$ torr) gave a crude product consisting essentially of ethylene and a highly reactive compound, stable in the gas phase, but giving a red polymer at very low temperature in the condensed phase. This reactive intermediate was proved to be fulven-6-one 4 by the following experiments.

Thermolysis of 1 with the simultaneous introduction of methanol led to methyl cyclopentadiene-1-carboxylate 6 (80-85% yield) which was obtained nearly pure after vacuum evaporation of the methanol in excess (⁴) : ^{1}H-N.M.R. (CCl_4) : $\delta = 7.34$ (br.t., 1H), 6.63 (m, 2H), 3.72 (s, 3H), 3.26 (m, 2H) ; I.R. (film) : $\nu_{C=O} = 1725$, $\nu_{C=C} = 1595$ cm^{-1} ; U.V. (ethanol) : $\lambda_{max} = 275$ nm ($\varepsilon = 5900$). After 48h at room temperature, 6 gave rise to a mixture of two dimers (⁵).

Further evidence of the formation of 4 was obtained by condensing the thermolysate in a cryostat on a sodium chloride plate and recording the infrared spectrum at −196° (⁶). Sharp bands at 2119 and 2123 cm^{-1} were observed (⁷). These bands vanished by the time the temperature −160° was attained and broad bands appeared between 1550 and 1750 cm^{-1}, due to the formation of a red polymer film on the plate.

A rational mechanism for the clean rearrangement 1 ⟶ 4 is depicted in the scheme. The anhydride 2, not isolated even at 450° (temperature at which the conversion of 1 was only 10%), gives rise to the anhydride 3 by two successive [1.5] hydrogen shifts (⁸). Then this latter, after CO_2 extrusion and rearrangement , leads to the ketene 4 easily trapped with methanol.

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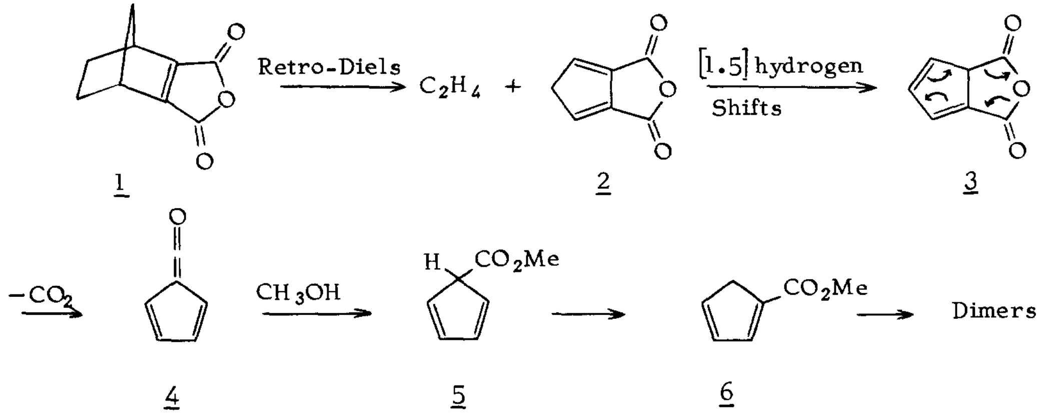

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References and Footnotes

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8) Such [1.5] hydrogen shifts have already been observed in disubstituted cyclopentadiene chemistry : see for example S. Mc Lean and P. Haynes, Tetrahedron, 21, 2329 (1965).