Matrix Preparation of Cyclobutadiene

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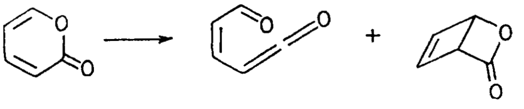
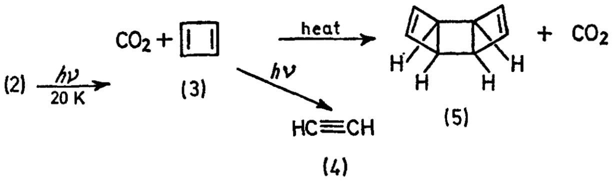
Summary Photolysis of 2-oxabicyclo[2,2,0]hex-5-en-3-one in solid argon or nitrogen gives carbon dioxide and cyclobutadiene.

As part of a programme to determine the effects of gas matrices on the photochemistry of organic molecules, the behaviour of α-pyrone (1)[1] at 20·4K was studied. Short-term irradiation (2 min) of (1) in argon (1 : 800) with light from a medium-pressure mercury lamp, filtered through nickel sulphate, gave product which exhibited strong absorption at 2137, 2148, and 2158 (=C=O str) and 1685 cm^{-1} (HC=O str) characteristic of aldoketens.[2] On further irradiation, new bands appeared at 1850 and 1826 cm^{-1} which are very similar in position to the bands previously assigned to the lactone (2) formed photochemically from (1) in solution.[1] Comparison of the spectrum of the photolysate with that of independently synthesized (2) shows that the former contains all the bands of (2) in the expected ratios.†



(1) + Conformers (2)



Long-term irradiation (3·2 h) of (1) led to the efficient formation of carbon dioxide[3] after the bands due to starting material had disappeared. We have independently photolysed (2) in argon or nitrogen matrices (M/R *ca.* 500) at

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† Photoirradiation of a nitrogen matrix containing (1) produced aldoketens more selectively. In a typical experiment irradiation of 90 mm of α-pyrone in nitrogen (1:500) for 25 min resulted in *ca.* 60% reaction of (1) with new bands at 2148vs, 1678s, 1599m, 1558w, and 1222m cm^{-1} attributable to aldoketen formation. The ratio of the intensity of the aldoketen band at 2148 cm^{-1} to the most intense band in the spectrum of (2) at 1868 cm^{-1} was *ca.* 100:1.

temperatures between 10 and 20·4K and have shown that (2) produces carbon dioxide[3] (bands at 2350 and 662 cm^{-1}) as a major photoproduct with only small amounts of aldoketen. In a typical experiment irradiation of (2) in argon (M/R = 550) for 3·6 h at 20·4K resulted in the complete destruction of starting material, the formation of carbon dioxide[3] (2350 and 662 cm^{-1}) and aldoketen (2137 and 2148 cm^{-1}),‡ and the appearance of major bands at 1236 (ν_{C-C}, ring), 653 (in plane ring deform.), and 573 cm^{-1} (out of plane ring deform.) which we tentatively attribute to cyclobutadiene (3). Absorption centred at 747 cm^{-1} initially grows at a similar rate as those bands attributed to (3) but then increases more rapidly and is due at least in part to the formation of acetylene (4).§ The richest portion of the spectrum of photolysed (2) is shown in the Figure.

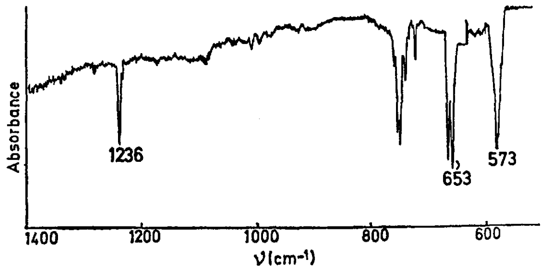

FIGURE. *I.r. spectrum of richest portion of photolysed* (2) *after* 3·75 h *of irradiation of a* 70 mm *sample* (M/R = 550).

External trapping of the photolysate and re-deposition in the cryostat of a sample of the trapped material prepared at room temperature gave i.r. bands due to the *syn*-dimer[4,5] (5) of cyclobutadiene (3) and carbon dioxide.

These results suggest that (2) decomposes to carbon dioxide and cyclobutadiene (3). The latter can undergo further photodecomposition to acetylene (4) or, dimerize upon warming of the matrix (or during the trapping and redeposition procedure), to the *syn*-dimer (5).¶

Irradiation of (2) in an argon matrix (M/R ~ 1/200) for 2 h at 20K gave rise to a weak broad band of λ_{max} = 405 nm, a value consistent with calculations[7] of the u.v. spectrum of (3), and previous claims by Maier.[8]

Acknowledgement is made to the Research Foundation of the State University of New York for a summer fellowship and to the Research Corporation for a Frederick Gardner Cottrell Grant.

(*Received*, 12*th July* 1972; *Com.* 1204.)

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‡ No other absorption due to the aldoketen could be detected as only a very small quantity of this substance was formed.

§ Acetylene was identified by comparison of bands in the i.r. spectrum of photolysed (2) with those of an authentic sample of (4) in argon. The dimer (5) was identified by comparison of its published i.r. spectrum[5] with that of the redeposited photolysate.

¶ Bimolecular reactions between reactants and/or products in this system are extremely unlikely in solid argon and nitrogen between 10 and 20·4K because of the low rates of diffusion under these conditions.[6]

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[2] For comparable values of keten carbonyl stretching frequencies see O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, 1968, **90**, 2449; L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, 1968, **90**, 5993; 1969, **91**, 531.
[3] C. L. McIntosh and O. L. Chapman, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April, 1972, ORGN, No. 27, reported the formation of carbon dioxide from the photolysis of (2).
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[6] See B. Meyer, "Low Temperature Spectroscopy", American Elsevier, New York, 1971, Ch. 6.
[7] N. L. Allinger, C. Gilardeau, and L. W. Chow, *Tetrahedron*, 1968, **24**, 2401.
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