Photorearrangement of a γ-Butyrolactone: Generation of Intermediates in Photochemical Reactions

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Summary The photolysis of 6,7,8,9-tetrahydro-9-hydroxy-7-oxo-5,8-methano-5*H*-benzocycloheptene-10-carboxylic acid lactone yields, in addition to CO_2, naphthalene, keten, 3,4-benzotricyclo[3,3,0,$0^{2,8}$]octan-7-one, and benzobicyclo[2,2,2]octadienone, the same products obtained from the sensitized photolysis of benzobicyclo[2,2,2] octadienone.

WHILE γ-butyrolactones have been shown to yield products from the photochemically-induced loss of carbon dioxide,[1] the efficiency of this process has usually not been high. We report that a quantitative loss of CO_2 can be effected from the γ-butyrolactone (I) with a high efficiency (ϕ_{dis} *ca.* 0·5). Photolysis of (I) with or without a sensitizer yields, in addition to CO_2, benzobicyclo[2,2,2]octadienone (II), napthalene (III), keten (IV), and 3,4-benzotricyclo[3,3,0,$0^{2,8}$]-octan-7-one (V).

The relative yields of the four products vary with the extent of conversion as indicated in the Table. The structures of the four products were established either by comparison with authentic samples or by degradation to known compounds.†

A reasonable mechanism for this transformation would be the photochemical elimination of CO_2 followed by the rearrangement of the remaining diradical intermediate (VI) to the products through a series of di-π-methane rearrangements[2] as shown in the Scheme. Two control experiments were conducted to determine the extent of interconversion of the products. Irradiation of (V) in acetone with 2537 Å light led to no detectable products, thus demonstrating its

† All new compounds gave satisfactory elemental analyses.

stability under the rearrangement conditions. However, when benzobicyclo[2,2,2]octadienone (II) was irradiated in acetone under conditions identical to those employed with the lactone, naphthalene and 3,4-benzotricyclo[3,3,0,0,^{2,8}]-octan-7-one (V) were obtained in good yield[3]. Keten was trapped in a separate experiment as ethyl acetate. The Table shows the relative conversions of (II) into (III) and (V) under these conditions.

TABLE

The Photorearrangement of (I) *and* (II)

Ketone[a]	Sensitizer	Lamps	Time (hr.)	Conversion (%)	Products (in mmoles)			
					(I)	(II)	(III)	(V)
(I)	Acetone[b]	2537 Å	2	56	0·32	0·077	0·069	0·240
(I)	Acetone[b]	2537 Å	5	72	0·20	0·103	0·160	0·300
(I)	None	3000 Å	4	85	0·094	0·014	0·255	0·251
(I)	Acetophenone	3500 Å	3	23	0·537	0·025	0·012	0·106
(II)	None	3000 Å	4	100	—	0·0	0·77	0·0
(II)	Acetone[b]	2537 Å	2·25	53	—	0·41	0·227	0·112
(II)	Acetophenone	3500 Å	5	63	—	0·29	0·147	0·276

[a] All runs were carried out using 0·71 mmole of the ketone dissolved in 15 ml. of benzene, degassed with nitrogen and irradiated in quartz tubes in a merry-go-round apparatus using the lamps indicated above. [b] Acetone was the solvent in this run.

While it is apparent that the formation of the tricyclic ketone (V) from the lactone cannot occur exclusively *via* the benzobicyclo[2,2,2]octadienone, in the sensitized reaction in the high conversion runs a fraction of (V) may be formed by this alternative route.

Two possible mechanisms can be written for this interconversion both employing the di-π-methane route as shown in the Scheme.[4] In order to differentiate between these two mechanisms, labelled benzobicyclo[2,2,2]octadienone (II; L = D) was prepared.‡ After irradiation and work-up, the position of the label in the products was determined by n.m.r. Analysis of the spectrum showed that >95% of the label appeared at positions 1 and 8 in the tricyclic ketone (Vb; L = D) and at the adjacent β-positions in naphthalene (III; L = D). The recovered ketone (II) showed no scrambling of the deuterium label.

Thus, mechanism *a* which includes the diradical intermediate (VI) suggested in the lactone rearrangement correctly accounts for the distribution of the label. It should be noted that the mechanism suggested for the decomposition of the intermediate (VI) in the lactone photolysis also accounts for the distribution of label in the naphthalene product (III; L = D) and in the recovered ketone (II). The inefficiency of the ketone rearrangement (ϕ_{dis} = 0·22) relative to the lactone photolysis (ϕ_{dis} = 0·5) may be due to the conversion of the diradical intermediate into ketone (II) [ϕ = 0·11 for the appearance of (II) from the lactone].

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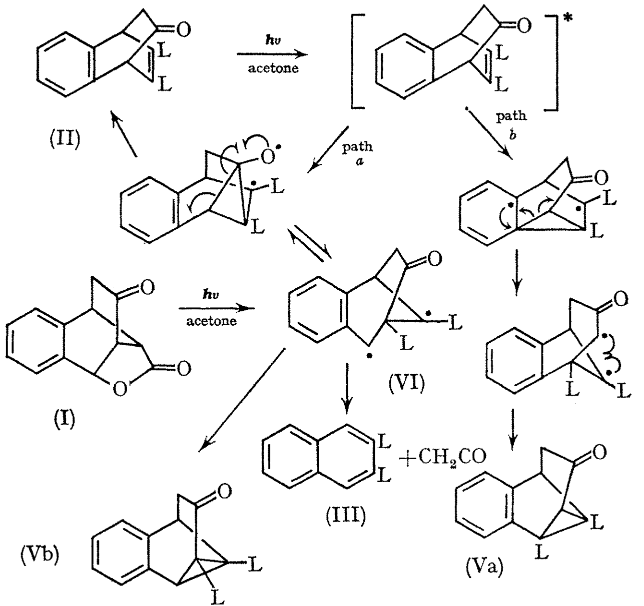

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‡ The ketal of ketone (II) was deuteriated by the method used earlier on benzobicyclo[2,2,2]octatrienes (ref. 2).

[1] (a) R. Simonaitis and J. N. Pitts, *J. Amer. Chem. Soc.*, 1968, **90**, 1389, *ibid.*, 1969, **91**, 108.
(b) I. S. Krull and D. R. Arnold, *Tetrahedron Letters*, 1969, **1247**.

[2] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, 1968, **90**, 6096, and subsequent papers.

[3] During the mechanistic studies on the photolysis of ketone (II), a preliminary report by J. Ipaktschi, *Tetrahedron Letters*, 1969, 215 appeared showing that (II) yielded naphthalene and tricyclic ketone (V) upon irradiation in acetone. Our results agree with those reported in that communication.

[4] A similar study has been carried out on a methylated analogue in which the bridgehead positions were unlabelled (H. Hart and R. K. Murray, jun., *Tetrahedron Letters*, 1969, 379. These two labelling studies gave the same results, *i.e.*, positions 1 and 4 in benzobicyclo-[2,2,2]octadienone remain benzylic throughout the transformation.