

PHOTOCHEMISTRY OF LARGE RING CYCLOALKANONES

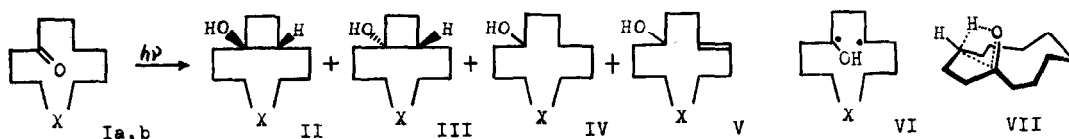
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(Received in Japan 22 January 1970; received in UK for publication 24 February 1970)

Irradiation of cyclodecanone gives 9-hydroxydecalin (1), whereas that of cyclododecanone (Ia) affords cyclobutanol derivatives (2). Our interest in the effect of ring size upon transannular reactivity (3) prompted us to investigate the photoreaction of Ia in further details in comparison with the behaviour of cycloundecanone Ib on which no report has appeared.

The irradiation was effected externally with 200 W high pressure mercury arc upon solutions of Ia and Ib each placed in a Pyrex vessel. Products were analyzed by GLC and TLC, and results are summarized in Table 1 (4).



a: X = CH₂CH₂; b: X = CH₂

TABLE 1. The photolysis of cyclododecanone Ia and cycloundecanone Ib

	Solvent	Irradiation time (hr)	Recovered I (%)	Product yields (%)				
				II	III	IV	V	unidentified
Ia	benzene	25	0	70	6	0	0	1
	cyclohexane	8	0	75	12	trace	0	1
	2-propanol	10	0	67	7	12	0	0
	piperylene	119	0	55	0	0	0	trace
Ib	benzene	48	8	45	13	trace	8	4
	cyclohexane	48	5	34	9	7	5	3
	2-propanol	48	7	19	8	26	trace	3
	piperylene	144	69	0	0	0	0	trace

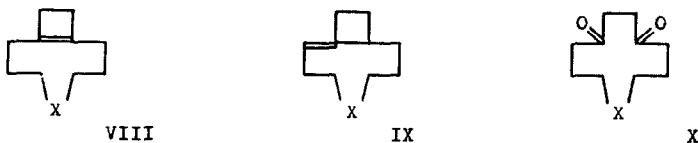
The 11-membered ring ketone Ib was found to form cyclobutanols IIb and IIIb similarly as Ia. No other bicyclic products were isolated. Following differences were observed between the behaviour of Ia and Ib: (a) qualitatively the reaction of Ia proceeds faster;

(b) Ia affords better yields of cyclobutanols and larger values of II/III (cis/trans);
 (c) Ib is more susceptible to photoreduction; (d) only Ib gives unsaturated alcohol Vb (5).
 In short, 11-membered Ib is less accessible to intramolecular cyclization.

In order to ascertain the electronic states of participating species, Ia and Ib were photolyzed in piperylene solution. Under this condition of triplet-quenching, Ia afforded stereoselectively cis-cyclobutanol IIa as a sole product. Even a trace of trans-isomer IIIa was not detected. In contrast, Ib gave none of the products IIB-Vb under the same condition and extremely slow decomposition into tarry products was observed.

The cyclobutanol formation in the photolysis of open chain ketones was demonstrated to occur predominantly via triplet state (triplet/singlet = ca. 10) (6). The stereoselective formation of cis-fused IIa on quenching of Ia(T_1) might possibly be explained by assuming the concerted cyclization (7) of Ia(S_1) through an intermediate such as VII, as this is expected on the basis of Dreiding models. The complete quenching of the photo-reaction of Ib by piperylene indicates that the concerted cyclization of Ib(S_1) is conformationally impossible and Ib(T_1) is the sole active species. Products IIIa, IIB, IIIb, Vb and a part of IIa might arise from the triplet biradical VI. The photoreduction is also proved to proceed via triplet state (8).

Ring cleavage products were not examined due to their further photo-decomposition. The structures of II and III were determined as follows. On dehydration with thionyl chloride, both of the two gave a mixture of VIII and IX. Oxidative cleavage of VIII led to the known 1,4-diketones X (3). cis-Hydration of VIII by means of hydroboration afforded II. Further details will be described in the forthcoming full paper.



REFERENCES AND NOTES

- M. Barnard and N. C. Yang. Proc. Chem. Soc. 302 (1958).
- (a) K. H. Schulte-Elte and G. Ohloff. Chimia, 18, 183 (1964).
 (b) B. Camerino and B. Patelli. Experientia, 20, 260 (1964).
- T. Mori, K. Matsui and H. Nozaki. Bull. Chem. Soc. Japan, 43, 231 (1970).
- Product yields were determined from peak areas of GLC. All new compounds gave correct analyses.
- The structure of Vb (cis,trans mixture) was tentatively assigned on the basis of IR, NMR and catalytic hydrogenation into IVb.
- (a) P. J. Wagner and G. S. Hammond. J. Am. Chem. Soc. 87, 4009 (1965); 88, 1245 (1966).
 (b) D. R. Coulson and N. C. Yang. ibid., 88, 4511 (1966).
- I. Orban, K. Schaffner and O. Jeger. J. Am. Chem. Soc. 85, 3033 (1963).
- R. Simonaitis, G. W. Cowell and J. N. Pitts, Jr. Tetrahedron Letters, 3751 (1967) and refs. cited therein.