

PHOTOLYSIS OF 1,2-DIOXOLANES ¹

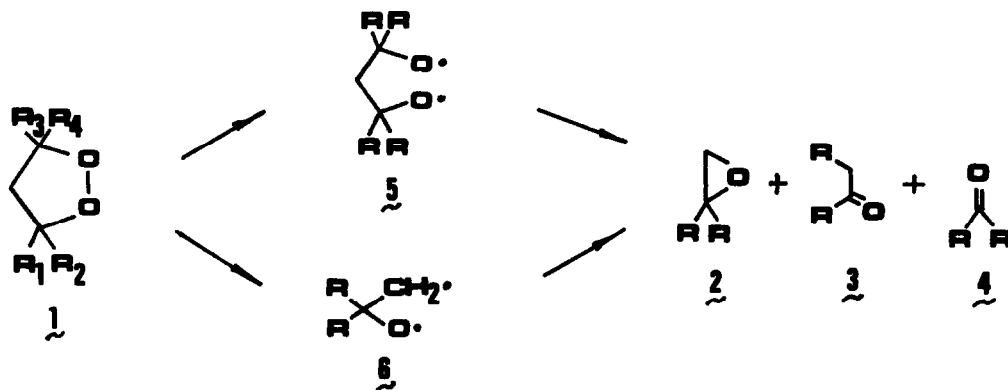
Waldemar Adam* and Nelson Duran

Department of Chemistry, University
of Puerto Rico, Rio Piedras, P.R. 00931

(Received in USA 22 February 1972; received in UK for publication 28 February 1972)

Concerning the photolysis of 5-membered ring cyclic peroxides, so far only the oxonides² and β -peroxylactones³ have been examined. Since the latter photo-decarboxylation afforded epoxides as major products,³ analogously photo-deketonization of 1,2-dioxolanes (1) would constitute a novel route to epoxides. We now wish to report our preliminary results on the photolysis of derivatives of (1).

On irradiation of 1.0 M solutions of the 1,2-dioxolanes in benzene at 350 nm for 72 hrs, the major photo-products (see Scheme) were epoxides (2), and ketones (3) and (4), all identified by glpc retention times and infrared spectra. Control experiments showed that all the products, except the aromatic epoxides, were stable to the photolysis conditions. The quantitative glpc results are summarized in the Table. Although over 90% product balance was established in each case, large amounts of involatile residue was formed.



The photolysis results of (1) indicate that in every case epoxide is the major product. The trend of decreasing epoxide yield (see Table) with degree of phenylation for (1a), (1c), and (1e) is probably due to the photo-lability of the aromatic epoxides, rather than reflecting ease of cyclization of the diradical precursor. The increased amount of involatile residue with decreasing epoxide yield speaks in favor of this interpretation.

	R ₁	R ₂	R ₃	R ₄	% (2)	% (3)	% (4)	Residue
(1a)	Me	Me	Me	Me	70	13	7	4
(1b)	Me	Me	Me	Ph	64	14	1	15
(1c)	Me	Ph	Me	Ph	40	24	10	18
(1d)	Me	Ph	Ph	Ph	23	21	8	23
(1e)	Ph	Ph	Ph	Ph	15	9	13	34

The preliminary data on hand is insufficient to decide whether diradical (5) or (6) is the precursor to the photo-products (see Scheme). However, it is evident that the 1,2-dioxolanes are analogous in their photolytic behavior to the β -peroxylactones,³ in that both afford epoxides as the major product. We are examining the stereochemistry of this reaction and the spin states of the diradicals.

Financial support by the National Science Foundation, the Petroleum Research Fund, and the A.P. Sloan Foundation is gratefully acknowledged.

REFERENCES

1. Paper XV. in the Cyclic Peroxide series. Presented at the Cyclic Peroxide Symposium, Metrochem 71, ACS Regional Meeting, San Juan, P.R., April 30, 1971.
2. P.R. Story, W.H. Morrison, T.K. Hall, J.P. Farine, and C.E. Bishop, Tetrahedron Lett., 3291 (1968); P.R. Story, W.H. Morrison, and J.M. Butler, J. Am. Chem. Soc., 91, 2398 (1969).
3. W. Adam and G. Santiago, J. Am. Chem. Soc., 93, 4300 (1971).