Photochemical Alcoholysis of Oxiranes

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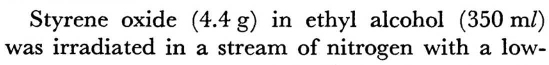
(Received October 15, 1966)

Although the photo-rearrangement of α-epoxyketone has often been investigated, no more than a few reports have been published about the photochemical reactions of other oxiranes.1) However, recent publications on the photolyses of some phenyl-substituted oxiranes2) prompt us to report here the results of our photochemical alcoholysis of oxiranes.

Styrene oxide (4.4 g) in ethyl alcohol (350 m*l*) was irradiated in a stream of nitrogen with a low-pressure mercury lamp (10 W) for four days, by which time the characteristic ultraviolet absorption spectrum of this oxide had completely disappeared. The distillation of the reaction mixture afforded 2-ethoxy-2-phenylethanol (purity higher than 99% by gas chromatographic examination with a column of polypropylene glycol (Ucon oil, LB-550X) at 194°C); bp 86—90°C/1 mmHg (2.9 g, 47% based on the oxide used), identified by elementary analysis (Found: C, 72.04; H, 8.86%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.) and by a comparison of its infrared spectrum with that of an authentic sample.

Similarly, the irradiation of a methyl alcoholic solution (300 m*l*) of styrene oxide (3.7 g) was shown to give 2-methoxy-2-phenylethanol (2.7 g, 60%), identified by means of its infrared spectrum and by gas chromatography under the same conditions as above.



$$C_6H_5\underset{\diagdown O \diagup}{CH{-}{-}CH_2} + ROH \xrightarrow{h\nu} C_6H_5CH(OR)CH_2OH$$

R: C_2H_5, CH_3

On the other hand, it is well known that an alcoholic solution of styrene oxide gives, on being heated with a basic catalyst, a mixture consisting of a larger amount of 2-alkoxy-1-phenylethanol, a so-called "normal product" with respect to the orientation of the cleavage of the oxirane ring, and a smaller amount of 2-alkoxy-2-phenylethanol, a so-called "abnormal product," while, on being heated with an acid, it gives a mixture consisting of a larger amount of the latter and a smaller amount of the former.3) These facts show that the orientation of the ring cleavage of styrene oxide is extremely selective in photochemical alcoholysis, giving the "abnormal product" exclusively, in contrast with catalysed thermal alcoholysis.

The absence of benzyl ethyl ether and benzyl methyl ether in the photo-alcoholysis products eliminates the possibility of the intermediate formation of phenylcarbenes in the photolytic decomposition of styrene oxide in ethyl and methyl alcohol respectively. This contrasts with Kristinsson and Griffin's findings that the irradiation of tetraphenylethylene oxide and *trans*-stilbene oxide in the presence of methyl alcohol afforded benzhydryl methyl ether and benzyl methyl ether *via* diphenylcarbenes and phenylcarbenes respectively.2a,b) The difference in photochemical behaviour between these oxiranes is probably to be ascribed to the structural variation in the oxiranes.

Cyclohexene oxide (1.5 g) in methyl alcohol (300 m*l*), when irradiated for four days with a low-pressure mercury lamp, gave *trans*-2-methoxycyclohexanol (1.0 g, 50%), showing that the configuration of one of the carbon atoms of this oxide is inverted during the photo-alcoholysis. A similar irradiation of this oxide (1.7 g) in ethyl alcohol (300 m*l*) yielded *trans*-2-ethoxycyclohexanol (1.9 g, 76%). These alcohols were identified by a study of their infrared spectra and by gas chromatography on a column of polyethylene glycol (Carbowax 1500) at 168°C. These facts indicate that the photo-alcoholysis of cyclohexene oxide is probably initiated by the photoexcitation of the oxirane group[*1], whereas the photo-alcoholysis of styrene oxide may proceed through the intramolecular transfer of excitation energy from the phenyl to the oxirane group.

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1) R. J. Gritter and E. C. Sabatino, *J. Org. Chem.*, **29**, 1965 (1964).

2) a) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, **77**, 859 (1965). b) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966). c) H. Kristinsson, *Tetrahedron Letters*, **1966**, 2343, d) H. Kristinsson, R. A. Mateer and G. W. Griffin, *Chem. Commun.*, **1966**, 415.

3) W. Reeve and I. Christoffel, *J. Am. Chem. Soc.*, **72**, 1480 (1950); N. B. Chapman, N. S. Isaacs and R. E. Parker, *J. Chem. Soc.*, **1959**, 1925; R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

[*1] The spectrum of cyclohexene oxide in vapour phase and in alcoholic solution exhibits a weak absorption band in the near ultraviolet region (ε: about 5 at 250 mμ in methyl alcohol), the intensity of which increases with decrease in the wavelength. This absorption can be tentatively assigned to the *n*, σ^* transition of the oxirane group.