Free-Radical Chemistry of Cyclic Ethers. VII. Ultraviolet Photolysis of Epoxides and Propylene Sulfide in the Liquid Phase[1]

Roy J. Gritter[2] and Edward C. Sabatino

Department of Chemistry, University of Connecticut, Storrs, Connecticut, and the IBM Research Laboratory, San Jose 14, California

Ultraviolet light has been found to cause carbon–oxygen bond cleavage in epoxides and carbon–sulfur bond cleavage in a thioepoxide. Studies with unsymmetrical epoxides indicated that both carbon–oxygen bonds cleave and that the intermediate diradicals are converted, by subsequent radical reactions which involve no re-arrangements, into alcohols and aldehydes or ketones. For example, the irradiation of propylene oxide gave acetone, isopropyl alcohol, propionaldehyde, and propyl alcohol, though not in equal amounts. A reaction sequence is suggested which is applicable to the irradiation of epoxides and the thioepoxide.

Results from the peroxide-initiated free-radical reactions of epoxides and thioepoxides[1] prompted a study of the effects of ultraviolet light on these classes of compounds in solution. It was thought that ultraviolet light would cleave the carbon–oxygen and carbon–sulfur bonds of the three-membered ring, thus stimulating interest in the type of bond scission reactions and the products arising from these scissions.

It is known from the pioneering work of Gomer and Noyes[3] that photolysis of ethylene oxide gives free radicals, but the products obtained indicate several different types of bond cleavage. Cvetanovic[4] has subsequently restudied the reaction and concurred as to the findings.

Further work by Cvetanovic and Doyle[5] on the gas phase photolysis of 2,3-butylene oxide led them to postulate a diradical intermediate for its breakdown. One interesting product which they identified was iso-butyraldehyde which apparently formed by a free-radical rearrangement reaction. It was hoped that the rearrangement might also occur in the present study when the photolysis was done in solution. The carbon–oxygen bond scission as postulated by Cvetanovic[5] is well supported by the data of Gray and Williams[6] who reported that the bond energies for the carbon–oxygen bonds to be about 30 kcal./mole less than those for carbon–carbon bonds.

The ready availability of both symmetrical and unsymmetrical epoxides permitted a study which could determine the effect of substituents on bond cleavage. The paucity of sulfur compounds of this nature dictated the use of only one representative epoxide for comparison studies.

Results

The products identified from the ultraviolet light-initiated free-radical reactions of epoxides carried out to only a few per cent of reaction to eliminate secondary reactions have indicated that both carbon–oxygen bonds in an unsymmetrical epoxide undergo homolytic cleavage. The intermediate diradicals formed from the initial cleavages are converted, by subsequent radical reactions, into alcohols and ketones. Some of the intermediate radicals have been found to dimerize

and have also been found to add to 1-octene. The modes of the initial epoxide cleavages are seen from the products identified from the photolysis of propylene oxide in the presence and absence of 1-octene, as contained in Table I.

Table I

PRODUCTS IDENTIFIED FROM THE ULTRAVIOLET LIGHT IRRADIATION OF PROPYLENE OXIDE

Propylene oxide, moles	1-Octene, moles	Products identified	Origin
Neat		Acetone	C-1–O cleavage
		Isopropyl alcohol	C-1–O cleavage
		Propionaldehyde	C-2–O cleavage
		Propyl alcohol	C-2–O cleavage
1.5	1.5	Acetone	C-1–O cleavage
		Isopropyl alcohol	C-1–O cleavage
		Propionaldehyde	C-2–O cleavage
		Propyl alcohol	C-2–O cleavage
		2-Hendecanone	C-1–O cleavage with addition to 1-octene
		2-Hendecanol	C-1–O cleavage with addition to 1-octene
		2,5-Hexanedione	C-1–O cleavage with dimerization
		2,5-Hexanediol	C-1–O cleavage with dimerization

Cyclohexene oxide and styrene oxide were photolyzed and found to undergo the same type of cleavage reactions as propylene oxide. Subsequent radical reactions to form alcohols and ketones also occurred. The quantitative data are presented in Table II.

Table II

QUANTITATIVE IRRADIATION OF EPOXIDES

Reactant	Product	Yield,[a] % conversion
Propylene oxide	Acetone	0.28
	Isopropyl alcohol	0.21
	Propionaldehyde	0.01
	Propyl alcohol	0.01
	2,5-Hexanedione	0.22
Cyclohexene oxide	Cyclohexanone	0.23
	Cyclohexanol	0.14
Styrene oxide	Acetophenone	0.03
	2-Phenylethanol	0.14
	1-Phenylethanol	0.13

[a] Based on the original charge of epoxide.

(1) Part VI: *Nature*, **198**, 284 (1963); previous paper to this study is V: *J. Org. Chem.*, **28**, 3437 (1963).
(2) To whom inquiries should be addressed at IBM.
(3) R. Gomer and W. A. Noyes, *J. Am. Chem. Soc.*, **72**, 101 (1950).
(4) R. J. Cvetanovic, *Can. J. Chem.*, **33**, 1684 (1955).
(5) R. J. Cvetanovic and J. C. Doyle, *ibid.*, **35**, 605 (1957).
(6) P. Gray and A. Williams, *Trans. Faraday Soc.*, **55**, 760 (1959).

The ultraviolet photolysis of propylene sulfide resulted mainly in the formation of a high-boiling clear resinified material. No compound boiling lower than allyl disulfide was obtained, and the only product that could be identified was allyl disulfide. Table III summarizes the photolytic reactions of propylene sulfide.
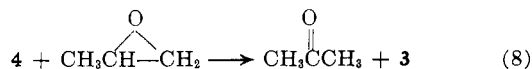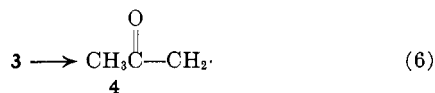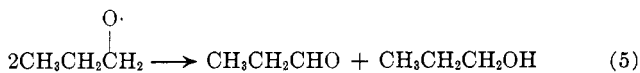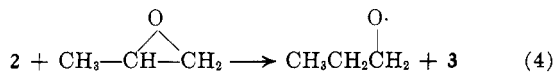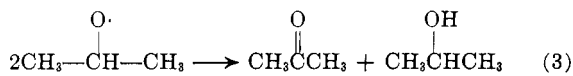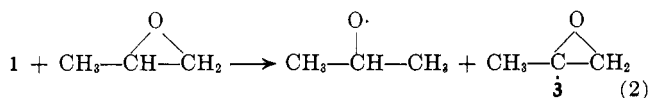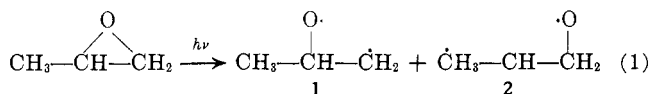
TABLE III
REACTIONS OF PROPYLENE SULFIDE

Reactants (moles, g.)	Reaction conditions	Products identified	Yield,[a] % conversion	Residue, g.
Propylene sulfide (0.10, 7.41)	Ultraviolet, 15°, 72 hr.	Allyl disulfide	0.05	5.95
Propylene sulfide (0.10, 7.41)	Ultraviolet, 15°, 24 hr.	Allyl disulfide	<0.01	6.00

[a] Based on the total amount of propylene sulfide used.

Discussion

The ultraviolet photolysis of the symmetrical epoxide, cyclohexene oxide, resulted in the homolytic cleavage of a carbon–oxygen bond with subsequent formation of cyclohexanol and cyclohexanone. In the unsymmetrical epoxides, propylene oxide and styrene oxide, both carbon–oxygen bonds were found to undergo scission. The following sequence would describe the photochemical decomposition of propylene oxide and is applicable to the breakdown of the other epoxides.

$$CH_3-\overset{O}{\overset{\triangle}{CH-CH_2}} \xrightarrow{h\nu} CH_3-\overset{O\cdot}{CH}-\overset{}{\dot{C}H_2} + \dot{C}H_3-CH-\overset{\cdot O}{CH_2} \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad \mathbf{1} \qquad\qquad \mathbf{2}$$

$$\mathbf{1} + CH_3-\overset{O}{\overset{\triangle}{CH-CH_2}} \longrightarrow CH_3-\overset{O\cdot}{CH}-CH_3 + CH_3-\overset{O}{\overset{\triangle}{C-CH_2}} \quad (2)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{3}$$

$$2CH_3-\overset{O\cdot}{CH}-CH_3 \longrightarrow CH_3\overset{O}{\overset{\parallel}{C}}CH_3 + CH_3\overset{OH}{\overset{|}{CH}}CH_3 \quad (3)$$

$$\mathbf{2} + CH_3-\overset{O}{\overset{\triangle}{CH-CH_2}} \longrightarrow CH_3CH_2\overset{O\cdot}{CH_2} + \mathbf{3} \quad (4)$$

$$2CH_3CH_2\overset{O\cdot}{CH_2} \longrightarrow CH_3CH_2CHO + CH_3CH_2CH_2OH \quad (5)$$

$$\mathbf{3} \longrightarrow CH_3\overset{O}{\overset{\parallel}{C}}-CH_2\cdot \quad (6)$$
$$\qquad\qquad \mathbf{4}$$

$$\mathbf{4} + \mathbf{4} \longrightarrow CH_3COCH_2CH_2COCH_3 \quad (7)$$

$$\mathbf{4} + CH_3\overset{O}{\overset{\triangle}{CH-CH_2}} \longrightarrow CH_3\overset{O}{\overset{\parallel}{C}}CH_3 + \mathbf{3} \quad (8)$$

Although the reactions in the above sequence rationalize the formation and amounts of the observed products, they are not intended to constitute the only possible mechanism for these reactions, for one can also include other mixed dimerization reactions of the acetonyl radical.
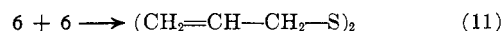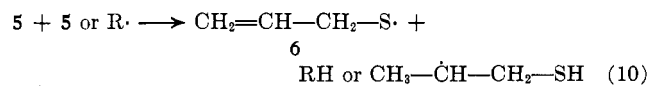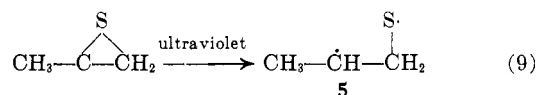
An important reaction and one of major concern to this study is the initial homolytic cleavage of both carbon–oxygen bonds to form diradicals **1** and **2**. The subsequent rearrangements of **1** directly to acetone and **2** to acetaldehyde were neglected since hydrogen atom

shifts are very rare.[7a] The hydrogen atom abstraction reactions 2 and 4 involved carbon–hydrogen bond formation and *not* oxygen–hydrogen bond formation, not only because it permits a reasonable mechanism to be written, but also because the polar effects in the two possible transition states predict carbon–hydrogen bond formation to be favored.[7b] The formation of the acetonyl radical, **3**, in the same reactions may require that a short-chain reaction be operating; the slight excess of acetone over isopropyl alcohol suggests that this is the case. Most of the acetonyl radicals apparently disappear by reaction 7, as evidenced. Finally, it can be noted that the products are similar to those obtained in vapor phase photolyses of epoxides and those formed from the diradical which results when an oxygen atom adds to an olefin.[8]

The proposed C–O bond scissions receive added support when other initial cleavages are considered. If C-1–H scission is considered with propylene oxide, the formation of propyl alcohol cannot be explained. If C-2–H scission (that found in the peroxide initiated reaction[1]) is occurring, the isopropyl alcohol found cannot be explained. An finally, if C–C bond cleavages are considered, the three carbons skeleton cannot arise from this path and many more products should be formed.[5]

The quantitative data indicate that the C-1–O to C-2–O cleavage ratio is about 25:1 with propylene oxide and about 1:1 with styrene oxide. The differences in the two ratios is not ready explained; more study is necessary to clarify these ratios. The cyclohexene oxide study only gives an indication of the importance of the various chain and termination steps.

The photolytic stability of propylene sulfide is very low, for almost complete resin formation resulted where most of the epoxides were recovered unchanged. Interestingly, no thioacetone trimer was found, only allyl disulfide. The nature of the initial cleavage is undoubtedly the cleavage of a S–C bond to give a biradical which readily polymerizes. The product probably forms by the following reaction sequence.

$$CH_3-\overset{S}{\overset{\triangle}{C-CH_2}} \xrightarrow{ultraviolet} CH_3-\overset{S\cdot}{\overset{|}{CH}}-\dot{C}H_2 \quad (9)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{5}$$

$$\mathbf{5} + \mathbf{5} \text{ or } R\cdot \longrightarrow CH_2=CH-CH_2-S\cdot + \quad$$
$$\qquad\qquad\qquad\qquad \mathbf{6}$$
$$\qquad\qquad RH \text{ or } CH_3-\dot{C}H-CH_2-SH \quad (10)$$

$$\mathbf{6} + \mathbf{6} \longrightarrow (CH_2=CH-CH_2-S)_2 \quad (11)$$

Experimental

(7) (a) C. Walling, "Molecular Rearrangements," Vol. 1, P. D. Mayo, Ed., New York, N. Y., 1963, p. 416; (b) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(8) R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958).

(9) F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 4959 (1953).

not change on standing either in the bottle or the reaction vessels.

The authentic compounds used for comparative gas chromatographic and infrared identifications were either purified commercially available compounds or ones prepared in these laboratories by known methods.[1] The ultraviolet-initiated free-radical reactions were carried out with end absorption from a spiral internal light source which emitted 95% of light of 2537 Å. (Hg resonance lamp) to a limited extent to eliminate secondary reactions. For the quantitative determination of products the reactions were maintained at approximately 15°. The following illustrative reaction mixtures were photolyzed for 72 hr., except in the case of propylene sulfide. For gas chromatography, column A was 10 ft., Ucon polar; column B was 10 ft., 3% Carbowax; column C was 10 ft., di-n-decyl phthalate; and column D was 10 ft., silicone.

Irradiation of Propylene Oxide with 1-Octene.—Propylene oxide (1.5 moles, 87.12 g.) and 1.5 moles of 1-octene (168.32 g.) were photolyzed and the reaction mixture was distilled to remove the unchanged epoxide and 1-octene. Continued distillation through the 12-in. nichrome-wire-spiral column separated the distillable materials (1.91 g.) from the high boiling residue (0.40 g.). The infrared spectra of the distillate fractions possessed the following two important bands: 3475 (hydroxyl function) and 1710 cm.$^{-1}$ (carbonyl function). Identification of products was made by comparitive gas chromatography: acetone, column A, 46°, 5 lb. of He, 11.5 min., and column A, 70°, 5 lb., 5.7 min.; isopropyl alcohol, A, 70°, 5 lb., 11.2, and A, 85°, 5 lb, 7.5 min.; propionaldehyde, A, 45°, 10 lb., 6.0 min., and A, 55°, 10 lb. 4.6 min.; propyl alcohol, A, 70°, 5 lb., 22.2 min., and A, 85°, 5 lb., 14.5 min.; 2-hendecanone, column B, 157°, 10 lb., 6.0 min.; 2-hendecanol, column B, 157°, 10 lb., 8.8 min.; 2,5-hexanedione, B, 157°, 5.4 min.; and 2,5-hexanediol, 156°, 10 lb., 19.0 min.

Irradiation of Propylene Oxide.—Propylene oxide (3.1 moles, 180 g.) was photolyzed as described above. The reaction mixture was distilled through an 18-in. tantalum-wire-spiral column to give (1) a fraction containing mainly unchanged propylene oxide (approximately 160 g.), (2) a fraction whose infrared spectrum showed the presence of bands ascribable to the hydroxyl and carbonyl functions (ca. 5 g.), and (3) a polymeric residue (approximately 1 g.). Identification of products was made by gas chromatography on column A: acetone, 50°, 5 lb. of He, 8.9 min.; propionaldehyde, 50°, 5 lb., 7.4 min.; isopropyl alcohol, 89°, 10 lb., 7.8 min.; and propyl alcohol, 89°, 10 lb., 15.4 min.

Irradiation of Propylene Oxide. Quantitative Run.—Propylene oxide (0.20 mole, 11.62 g.) was photolyzed at 15° as described. A very slow distillation of the reaction mixture through an 18-in. tantalum-wire-spiral column removed only propylene oxide. The remaining material was quantitatively analyzed by gas chromatography and the following conversions were calculated: acetone, 0.28%; isopropyl alcohol, 0.21%; propionaldehyde, 0.01%; propyl alcohol, 0.01%; 2,5-hexanedione, 0.22%; all based on the original charge of epoxide.

Irradiation of Cyclohexene Oxide in the Presence of 1-Octene.—Cyclohexene oxide (0.20 mole, 19.63 g.) and 0.02 mole of 1-octene (2.24 g.) were photolyzed as described above. The infrared spectrum of the irradiated reaction mixture showed bands at 3475 and 1710 cm.$^{-1}$. These bands were not present in the spectrum of the nonirradiated cyclohexene oxide. Identification of products from the distilled reaction mixture was made by gas chromatography: cyclohexanone, column B, 106°, 10 lb., 6.5 min., and column A, 95°, 10 lb., 13.3 min.; and cyclohexanol, B, 106°, 10 lb., 10.5 min., and A, 95°, 10 lb., 16.7 min. Identification of the products arising from the intermediate radicals adding to 1-octene was not made.

Irradiation of Cyclohexene Oxide. Quantitative Run.—Cyclohexene oxide (0.10 mole, 9.81 g.) was photolyzed at 15° as described above. The infrared spectrum of the reaction mixture showed hydroxyl and carbonyl bands. The quantitative determinations were made by gas chromatography without distillation of the reaction mixture. The following conversions were obtained: cyclohexanone, 0.23%, and cyclohexanol, 0.14%.

Irradiation of Styrene Oxide. Quantitative Run.—Styrene oxide (0.10 mole, 12.01 g.) was photolyzed at 15° as described above. The infrared spectrum of the irradiated styrene oxide contained bands at 3475 and 1710 cm.$^{-1}$. These bands were not contained in the spectrum of the nonirradiated styrene oxide. Identification of products was made by gas chromatography: acetophenone, column C, 165°, 10 lb. of He, 23.2 min., 0.03%; 2-phenylethanol, B, 153°, 15 lb., 14.2 min., 0.14%; and 1-phenylethanol, 153°, 15 lb., 9.4 min., 0.13%.

Irradiation of Propylene Sulfide.—Propylene sulfide (0.10 mole, 7.41 g.) was photolyzed for 72 hr. as previously described. The viscous reaction mixture was distilled and only 0.15 g. of material was obtained (Kugelrohr tube distillation,[10] over 150°, 0.15 mm.) Identification of allyl disulfide was made by gas chromatography (column D, 104°, 5 lb. of He, 7.7 min., and 133°, 10 lb., 7.6 min.). Thioacetone or its trimer could not be identified in the reaction mixture (the gas chromatographic conditions caused the trimer to go to the monomer).

Irradiation of Propylene Sulfide.—Propylene sulfide (0.10 mole, 7.41 g.) was photolyzed for 24 hr. at 15° as previously described. The reaction mixture was again very polymeric and only 2.0 g. of material could be distilled by a Kugelrohr tube distillation[10] (over 150°, 0.01 mm.). Identification of allyl disulfide was made by gas chromatography (column A, 145°, 15 lb. of He, 3.6 min.). Thioacetone or its trimer could not be identified in the reaction mixture. Gas chromatography (column A, 15 lb. of He) showed that the propylene sulfide used did not contain allyl mercaptan.

(10) E. Spaeth and F. Dengel, *Ber.*, **71B**, 114 (1938).