

*p*-Nitrophenylcyclopropane under the same photolysis conditions gave a solid product whose spectra suggested a mixture of at least three compounds. Recrystallization from methanol gave a pure 1:1 adduct of sulfur dioxide and cyclopropane, mp 188.5–190 °C. The infrared spectrum showed bands at 1310 and 1140  $\text{cm}^{-1}$ , suggesting a sulfone **2a** rather than a sultine. The NMR spectrum (described below) was in accord with this structure, as was the fact that it was recovered unreacted from hydrogen peroxide and acetic acid at 78 °C for 4 days, conditions which oxidize sultines to sultones.<sup>2</sup> The crude product of the photolysis showed additional NMR signals at  $\delta$  6.12 (triplet) and 5.75 (doublet of doublets) which resemble the signals due to the benzylic protons in the stereoisomers of **1a**, so apparently both modes of addition occur in the case of *p*-nitrophenylcyclopropane, to give **1c** and **2a**.

*o*-Nitrophenylcyclopropane and sulfur dioxide again gave a sulfone, **2b**, after recrystallization of a crude product. Sultines were not detected.

A number of cyclopropanes were found to give no photochemical reaction with sulfur dioxide. These included phenylcyclopropane, *p*-phenylphenylcyclopropane, *p*-chlorophenylcyclopropane, *p*-bromophenylcyclopropane, *p*-iodophenylcyclopropane, cyanocyclopropane, acetylcyclopropane, cyclopropanecarboxylic acid, and 1-methyl-2-phenylcyclopropane.

A discussion of the mechanism of the photochemical addition of sulfur dioxide to cyclopropanes would not be justified. However, it may be noted that sulfur dioxide absorbs light strongly below 390 nm and is therefore probably the species initially excited in these reactions.

### Experimental Section

**Photolysis of *p*-Cyanophenylcyclopropane in Liquid Sulfur Dioxide.** *p*-Cyanophenylcyclopropane (5.0 g,  $3.5 \times 10^{-2}$  mol) was dissolved in 80–120 mL of liquid sulfur dioxide (–10 °C) under an atmosphere of dry nitrogen. The solution was illuminated through Pyrex with two 275-W GE sunlamps for 25.5 h. The solvent was removed by evaporation, and an NMR spectrum of the residue was taken. The ratio of cyclopropyl absorptions of unreacted *p*-cyanophenylcyclopropane to all other alkyl absorptions was 64:36. A white solid **1a**, mp 87–92 °C, was obtained after recrystallizing the product twice from diethyl ether. An infrared spectrum of this material (KBr pellet) showed absorptions at 2220 (s), 1610 (m), 1507 (m), 1419 (m), 1125 (s), 1110 (s), 900 (m), 845 (s), 710 (s), and 550  $\text{cm}^{-1}$  (s). A 60-MHz NMR spectrum ( $\text{CDCl}_3$ ) showed  $\delta$  7.68 (d, 2 H,  $J = 8$  Hz), 7.36 (d, 2 H,  $J = 8$  Hz), 5.28–4.10 (m, 3 H), 4.33–2.00 (m, 2 H).

Anal. Calcd for  $\text{C}_{10}\text{H}_9\text{NO}_2\text{S}$ : C, 57.95; H, 4.38; N, 6.76; O, 15.44; S, 15.47. Found: C, 58.04; H, 4.53; N, 6.56; S, 15.28.

The white solid (mp 87–90 °C) (0.211 g, 1.02 mmol) was treated with 1.13 g (10 mmol) of 30%  $\text{H}_2\text{O}_2$  in 50 mL of glacial acetic acid at 100 °C for 2 h. The solvent was removed on a Rotavap, and the residue was recrystallized from diethyl ether, giving an almost quantitative yield of white crystals of **3**, mp 118.5–121.5 °C. An infrared spectrum of this material had absorptions at 3110 (w), 3070 (w), 2980 (w), 2235 (s), 1615 (m), 1512 (m), 1345 (s), 1210–1170 (s), 1045 (m), 955 (s), 860 (s), 620 (m), and 570  $\text{cm}^{-1}$  (s). A 60-MHz NMR spectrum (acetone- $d_6$ ) showed  $\delta$  7.81 (perturbed singlet or merging doublets, 4 H), 5.0–4.40 (m, 3 H), 3.28–2.80 (m, 2 H).

Anal. Calcd for  $\text{C}_{10}\text{H}_9\text{NO}_3\text{S}$ : C, 53.80; H, 4.06; N, 6.27; O, 21.50; S, 14.36. Found: C, 53.82; H, 4.08; N, 6.51; S, 14.37.

The white solid (mp 118.5–121.5 °C) ( $7.98 \times 10^{-2}$  g,  $3.58 \times 10^{-4}$  mol) was dissolved in 5.0 mL of dimethyl sulfoxide. Sodium bicarbonate (0.252 g, 3.00 mmol) was added to the solution, and the mixture was heated at 125–130 °C for 24 h. The dimethyl sulfoxide was distilled at reduced pressure. The remaining brown residue was acidified and partitioned between ether and water. The ether layer was dried over anhydrous magnesium sulfate. The ether was removed on a Rotavap, leaving 30.4 mg of a yellow-brown residue whose infrared spectrum showed absorptions at 3400–2500 (w), 3050 (w), 2940 (w), 2210 (s), 1690 (s), 1605 (m), 1407 (m), 1258 (s), 1100–1020 (broad s), and 800  $\text{cm}^{-1}$  (broad s).

**Photolysis of *p*-Nitrophenylcyclopropane in Liquid Sulfur Dioxide.** *p*-Nitrophenylcyclopropane (0.25 g, 1.5 mmol) was placed in a 100-mL Pyrex round-bottom flask which was fitted with a gas

inlet and a cold-finger condenser. The system was flushed for 5 min with nitrogen which had been passed through Drierite. A mixture of acetone and dry ice was placed in the cold finger and 30 mL of anhydrous sulfur dioxide was condensed into the flask. The flask and its contents were illuminated at –10 °C with a 275-W GE sun lamp for 10 h. The sulfur dioxide was removed by evaporation, and a 100-MHz NMR spectrum of the residue was taken (dimethyl sulfoxide- $d_6$ ). No signals for *p*-nitrophenylcyclopropane starting material were observed. The most notable signals in the spectrum were a series of nine peaks from  $\delta$  6.2 to 5.6. A triplet ( $J = 6$  Hz) appeared at  $\delta$  6.12; a triplet appeared at  $\delta$  5.90; and a doublet of doublets pattern was centered at  $\delta$  5.72. Integration ratios of the two triplets and doublet of doublets were 27.3, 54.5, and 18.2, respectively.

The solid material obtained from the photolysis of *p*-nitrophenylcyclopropane in liquid sulfur dioxide was recrystallized from absolute methanol to give white solid **2a** with a mp of 188.5–190 °C. An infrared spectrum of the material (KBr pellet) showed bands at 3100 (w), 3080 (w), 3030 (w), 2968 (w), 1608 (m), 1598 (m), 1515 (s), 1445 (m), 1345 (s), 1310 (s), 1190 (m), 1140 (s), 850 (m), 785 (m), 730 (m), and 525  $\text{cm}^{-1}$  (m). A 60-MHz NMR spectrum (dimethyl sulfoxide- $d_6$ ) showed  $\delta$  8.32 (d, 2 H,  $J = 9$  Hz), 7.77 (d, 2 H,  $J = 9$  Hz), 5.93 (t, 1 H,  $J = 9.5$  Hz), 4.5–4.1 (m, 2 H), 2.8–2.3 (m, 2 H).

Anal. Calcd for  $\text{C}_9\text{H}_9\text{NO}_4\text{S}$ : C, 47.57; H, 3.99; N, 6.16; O, 28.16; S, 14.11. Found: C, 47.59; H, 3.98; N, 6.23; S, 13.95.

The white solid (mp 188.5–190 °C) (0.38 g, 1.67 mmol) was heated at 78 °C in 50 mL of glacial acetic acid with 1.13 g (10 mmol) of 30%  $\text{H}_2\text{O}_2$  for 4 days. After 4 days the solvent and water were removed on a Rotavap. The remaining white solid was recrystallized from absolute methanol to give 0.34 g (90%) of unreacted starting material, mp 188.5–190 °C.

**Photolysis of *o*-Nitrophenylcyclopropane in Liquid Sulfur Dioxide.** Under a dry nitrogen atmosphere, a solution of 5.0 g (31 mmol) of *o*-nitrophenylcyclopropane in 80 mL of anhydrous liquid sulfur dioxide at –10 °C was irradiated through Pyrex with two 275-W GE sun lamps for 5 h. The sulfur dioxide was removed by evaporation. The addition of carbon tetrachloride to the residue caused the precipitation of a brown solid. An NMR spectrum of the  $\text{CCl}_4$  solution showed absorptions only for *o*-nitrophenylcyclopropane starting material. Recrystallization of the brown solid was attempted from methanol with some success. Much of the solid remained as tar. White to pale yellow crystals of **2b** were obtained (mp 137–140 °C). An infrared spectrum of the material (KBr pellet) showed bands at 3100 (w), 3040 (w), 3000 (w), 2970 (w), 1607 (m), 1520 (s), 1450 (m), 1405 (m), 1350 (s), 1310 (s), 1255 (m), 1185 (s), 1145 (s), 842 (m), 805 (s), 791 (m), 755 (m), 721 (m), 602 (m), and 527  $\text{cm}^{-1}$  (m). An NMR spectrum of the solid (dimethyl sulfoxide- $d_6$ ) showed  $\delta$  8.35–7.55 (m, 4 H), 6.11 (t, 1 H), 4.45–4.10 (m, 2 H), 2.85–2.35 (m, 2 H). A small impurity giving a triplet at  $\delta$  5.93 was observed, probably from a small amount of para impurity in the *o*-nitrophenylcyclopropane starting material. A methanol impurity gave a singlet at  $\delta$  3.35, so the material was placed under high vacuum for a second 24 h before elemental analysis.

Anal. Calcd for  $\text{C}_9\text{H}_9\text{NO}_4\text{S}$ : C, 47.57; H, 3.99; N, 6.16; O, 28.16; S, 14.11. Found: C, 47.72; H, 4.04; N, 6.24; S, 13.93.

**Registry No.**—**1a**, 61332-74-9; **2a**, 61332-75-0; **2b**, 61332-76-1; **3**, 61332-77-2; **5**, 61332-78-3; *p*-cyanophenylcyclopropane, 1126-27-8; sulfur dioxide, 7446-09-5; dimethyl sulfoxide, 67-68-5; *p*-nitrophenylcyclopropane, 6921-44-4; *o*-nitrophenylcyclopropane, 10292-65-6.

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### Photochemistry of Epoxides. 3. Direct Irradiation of Propylene Oxide in the Gas Phase<sup>1a</sup>

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The photochemistry of a number of systems containing the epoxide chromophore has been studied during the past

**Table I. Pressure Dependence of Rate of Product Formation**

Propylene oxide pressure, mm	Inert gas pressure, mm	Slope, <sup>a</sup> min <sup>-1</sup>
0.52	0	$3.88 (\pm 0.06) \times 10^{-3}$
0.88	0	$2.79 (\pm 0.03) \times 10^{-3}$
2.65	0	$2.35 (\pm 0.06) \times 10^{-3}$
0.52	35 (He)	$1.21 (\pm 0.04) \times 10^{-3}$
0.52	177 (He)	$1.03 (\pm 0.03) \times 10^{-3}$
0.52	35 (N <sub>2</sub> )	$0.88 (\pm 0.06) \times 10^{-3}$

<sup>a</sup> Least-squares slope through 100 min of irradiation obtained from plots of absorbance at  $\sim 1740 \text{ cm}^{-1}$  vs. time. Data averaged from three separate runs.

**Table II. Pressure Dependence of Product Ratios**

Propylene oxide pressure, mm	Inert gas pressure, mm	Acetone <sup>a</sup>	Propanal <sup>a</sup>
0.52	0	1.0	18.2
0.52	35 (He)	1.0	2.0
0.52	177 (He)	1.2	1.0
0.52	35 (N <sub>2</sub> )	1.0	1.9

<sup>a</sup> Relative product ratios compared to the amount of acetone formed at 0.52 mm of propylene oxide pressure.

decade. These include aryl substituted epoxides,<sup>2</sup>  $\alpha,\beta$ -epoxy ketones,<sup>3</sup>  $\beta,\gamma$ -epoxy ketones,<sup>4</sup> and 3,4-epoxyalkenes.<sup>5</sup>

Very few systems have been studied in which the epoxide moiety is the absorbing chromophore. The first reported photolysis of a simple epoxide was carried out by Noyes<sup>6</sup> in which ethylene oxide was irradiated at 200 nm; however, the important question concerning the nature of the primary process was not answered.

The mercury sensitized photolysis of ethylene oxide has been reported<sup>7</sup> and reinvestigated by Cvetanović<sup>8</sup> as well as extended to other epoxides. Finally, various alcohols and carbonyl products were obtained by direct irradiation of neat propylene oxide at 254 nm.<sup>9</sup> A free-radical chain process was postulated.

The present study was initiated in order to study the photochemistry of simple acyclic epoxides and to elucidate their primary photochemical processes. Irradiation of propylene oxide in the gas phase (0.5 mm) at 185 nm results in the formation of propanal and acetone as well as smaller amounts of ethanol, 1-propanol, and ketene. The progress of the reaction was monitored by following the appearance of the carbonyl absorption bands in the infrared. The  $1740\text{-cm}^{-1}$  band of propanal and the  $1720\text{-cm}^{-1}$  band of acetone could not be effectively separated. Plots of carbonyl absorbance vs. time remained linear throughout at least the first 100 min of irradiation. The slopes of these plots are then proportional to the rates of formation of the carbonyl products. Representative values are given in Table I. Added inert gas or increased epoxide pressure both have a profound effect upon the rate of carbonyl product formation (Table I) as well as the nature of the carbonyl products (Table II).

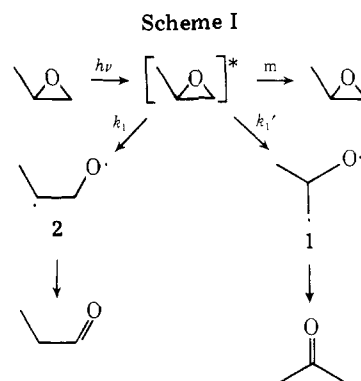
At 0.5 mm pressure, in the absence of inert gas, the product mixture consists of 95% propanal, 5% acetone, and traces of ethanol and propanol. In the presence of added helium, at the same epoxide pressure, the rate of carbonyl product formation is reduced. In the case of 177 mm helium pressure, the products were 45% acetone and 38% propanal along with varying amounts of ethanol, propanol, ketene, and several unidentified compounds. The results were essentially the same when nitrogen was used as the inert gas. GLC analysis of many runs showed that the absolute yields of acetone, ethanol, and pro-

**Table III. Relative Yields of Propanal and Acetone from Oxygen Atom/Olefin Reaction and Propylene Oxide Photolysis**

Reaction	Acetone	Propanal	Phase
$\text{O}(^3\text{P}) / \text{CH}_2\text{=CH-CH}_2\text{O}$	1	9	Gas <sup>10</sup>
$\text{O}(^3\text{P}) / \text{CH}_2\text{=CH-CH}_2\text{O}$	1	46	Liquid <sup>11</sup>
$\text{O}(^3\text{P}) / \text{CH}_2\text{=CH-CH}_2\text{O}$	1	6.3 (14)	Solid <sup>12,13</sup>
$\text{CH}_2\text{=CH-CH}_2\text{O} / h\nu$	1	> 18	Gas (this work)

panol were essentially independent of the pressure of inert gas (Table II).

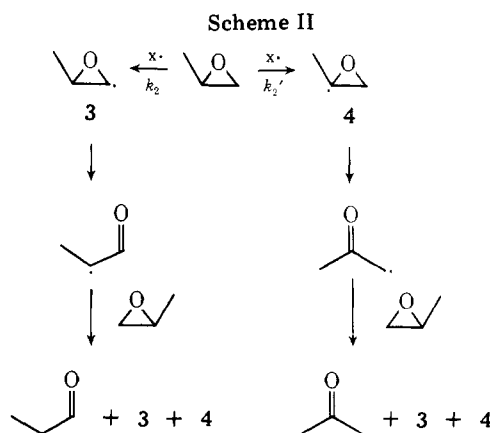
These results are consistent with the mechanism shown in Scheme I for the low-pressure runs. The photolysis produces



an excited state epoxide which opens predominantly to di-radical 2 followed by a 1,2-hydrogen atom shift to give propanal. One would expect a large value for  $k_1/k_1'$  due to the differences in stability of the primary (1) and secondary (2) radicals. These same radical intermediates are formed in the reaction of oxygen atoms,  $\text{O}(^3\text{P})$ , with propylene.<sup>10-13</sup> The relative yields of propanal and acetone from the propylene/oxygen atom studies are similar to those obtained in the present study (Table III).

When the pressure is increased, either by an increase in propylene oxide pressure or by added inert gas, the excited propylene oxide is quenched, thus reducing the amount of propanal formed. The exact nature of this pressure-quenchable excited state is not known, although an initial  $n\text{-}\sigma^*$  excitation probably occurs.

The quenching experiments clearly indicate that most of the acetone is not formed from the same intermediate as the propanal. The bulk of the acetone is thought to be produced by the mechanism shown in Scheme II. A free-radical initiator



abstracts a hydrogen atom from propylene oxide to give a mixture of oxiranyl radicals 3 and 4. One would predict a large

Table IV

Time, min	Absorbance at 1740 cm <sup>-1</sup>	
	1	2
0	0	0
19	0.031	0.027
34	0.053	0.048
49	0.084	0.079
65	0.107	0.106
80	0.132	0.131
107	0.178	0.180
123	0.204	0.205

Table V

Time, min	Absorbance at 1740 cm <sup>-1</sup>	
	3	4
0	0	0
19	0.017	0.010
34	0.024	0.017
50	0.032	0.022
72	0.045	0.031
94	0.058	0.044
110	0.061	0.051
124		0.055
132		0.061
149		0.066

value for  $k_2'/k_2$  based upon the expected radical stabilities. Radical 4 is produced exclusively in both the di-*tert*-butyl peroxide catalyzed addition of propylene oxide to 1-octene<sup>14</sup> and the photochlorination of propylene oxide.<sup>15</sup> Radicals 3 and 4 have been prepared by photolysis of di-*tert*-butyl peroxide in propylene oxide at -40 °C.<sup>16</sup> From the reported ESR spectrum, one can estimate a 4/3 ratio of ~2.6. At 70 °C or higher,<sup>14,15</sup> 4 is essentially the only radical formed. Radicals 3 and 4 would be expected to open to  $\alpha$ -carbonyl radicals. This has been observed for 4.<sup>14,16</sup> The free-radical chain process is completed by the  $\alpha$ -carbonyl radicals abstracting a hydrogen atom from propylene oxide.

As the pressure is increased, the primary photoprocess, shown in Scheme I, is quenched thus decreasing propanal formation. Furthermore, the free-radical chain route becomes more significant as the pressure is increased; however, the absolute amount of free-radical chain route does not change significantly under the conditions studied. We propose that the majority of the propanal is formed via Scheme I, while the majority of the acetone is formed via Scheme II.

### Experimental Section

**General.** The propylene oxide was purified by two distillations through a fractionating column and its purity checked by gas chromatography. The irradiations were carried out using a low-pressure mercury arc constructed of Suprasil quartz to allow use of the 1849-Å line. The lamp was mounted inside a 66-l. cell which also serves as the housing for a long path infrared optical system. A 66-l. reference cell was also used so that crossed-beam analysis could be carried out. The system was entirely mercury free (oil diffusion pumps, electronic pressure gauges, etc.) to ensure that mercury photosensitization could not be occurring. A Perkin-Elmer Model 21 spectrophotometer was used to obtain all spectra. The system was monitored as to the rate of formation of carbonyl products by following the increase in absorbance of the carbonyl band at ~1740 cm<sup>-1</sup>. After irradiation the entire sample was trapped at -196 °C and then subjected to GLC analysis. Each product was collected on a Perkin-Elmer Model 154-L vapor fractometer and identified by direct comparison with authentic material.

**Irradiation of Propylene Oxide.** The photolysis cell was charged with 0.5 mm of propylene oxide and monitored by following the in-

crease in carbonyl absorbance. The results of two representative runs at 0.52 mm are shown in Table IV.

**Irradiation of Propylene Oxide with Inert Gas.** The photolysis cell was charged with 0.52 mm of propylene oxide and various pressures of helium and nitrogen. The photolysis was monitored by following the increase in carbonyl absorbance. Ketene was formed in the presence of inert gas as indicated by its absorption spectrum. Two representative runs, with 35 mm added helium (3) and 177 mm added helium (4), are shown in Table V.

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**Registry No.**—Propylene oxide, 75-56-9.

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### Configurational Stability of the Unsubstituted Cyclopropyl Radical in the Hunsdiecker Reaction

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The stereochemistry of the cyclopropyl radical has been studied in a wide variety of situations, including the Hunsdiecker reaction of cyclopropanecarboxylic acids,<sup>1</sup> the reduction of cyclopropyl halides with organotin hydrides<sup>2</sup> or sodium borohydride,<sup>3</sup> and the photolysis or thermolysis of cyclopropanecarboxylic acid peroxy esters.<sup>4</sup> The various configurational results that have been observed include retention, partial retention, partial inversion, and complete thermodynamic equilibration. All cyclopropyl radicals examined hitherto, however, possess one or more  $\beta$  substituents (1) to monitor the configuration, and most also have an  $\alpha$  substituent (2). Substitution can alter the final configurational

