

model. We made an attempt to determine the eutectic point by two simple sublimations starting with 1.2 g of sample which was 71% mole fraction *d*. Our results, shown in Table VI, fall short of the reported value. The first 9.4 mg of material from the second sublimation was 83% mole fraction *d*.

Conclusions

Fractionation can occur during the sublimation of optically active compounds and such fractionation may be predictable on the basis of melting point vs. composition curves. In the absence of such curves, when dealing with racemic compounds (as opposed to racemic mixtures and racemic solid solutions), it has been shown previously that it is possible to determine the relative position of the starting composition with respect to the eutectic point.⁸ For the enhancement of optical activity, fractional sublimation provides an alternative to fractional crystallization for suitable compounds. This may be especially useful when working with material of very low optical purity. There are advantages and disadvantages inherent in a choice between fractional crystallization and fractional sublimation. This choice must be made on the basis of the properties of the individual compounds under investigation and has been discussed elsewhere.¹

One of the authors (D.L.G.) would appreciate receiving correspondence from other researchers who may have experienced similar results.

Experimental Section

Rotations of **1** were taken using a Rudolph Model 80 polarimeter. All other rotations were taken on a Perkin-Elmer Model 141 automatic recording polarimeter. All rotations have an accuracy of 1% or better.

The preparation of optically active **1** has been reported.⁹ All other compounds were purchased and sublimed prior to use: D(-)-mandelic acid and DL-camphoric acid (Sigma Chemical Co.), *d*-camphoric acid (Eastman), and L(+)-mandelic acid (Aldrich). The solid samples were carefully ground and mixed in a ball mill apparatus. Heating bath and oven temperatures were kept at least 10 °C below the melting point of the most volatile modification. Sublimations in the temperature gradient oven (condition 1) were allowed to proceed for 1–4 days; those in a standard sublimation apparatus (condition 2) typically were interrupted after 2–4 h to obtain fractions. Optical rotations were determined on ca. 1–2% solutions in 95% ethanol.¹⁰ Enantiomeric purity is based upon the rotations obtained for pure isomers.

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Registry No.—Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxylic acid, 61117-21-3; DL-mandelic acid, 611-72-3; L-mandelic acid, 17199-29-0; D-mandelic acid, 611-71-2; *dl*-camphoric acid, 560-05-4; *d*-camphoric acid, 124-83-4.

References and Notes

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Photochemical Addition of Sulfur Dioxide to Certain Arylcyclopropanes

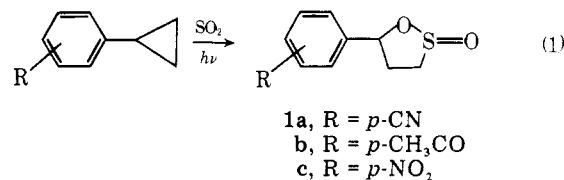
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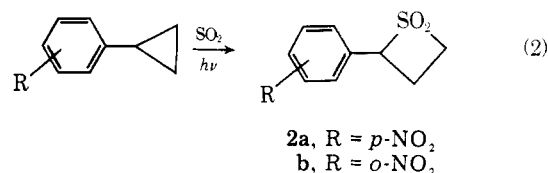
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During some studies of the photochemical addition of halogens to arylcyclopropanes,¹ it was observed that if the solvent was sulfur dioxide, some of the cyclopropanes added sulfur dioxide in preference to halogen, and that the same reactions occurred in the absence of halogen. Although the phenomenon has not been investigated in detail, we report here a brief survey of its scope.

Sulfur dioxide has been found to add to cyclopropanes in two ways. The first, reaction 1, is to form sultone **1** as a mixture of geometric isomers.

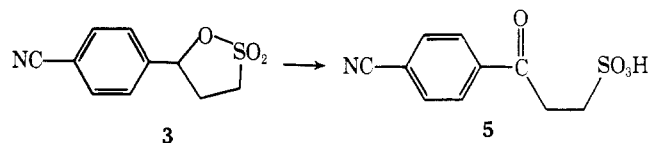


The second, reaction 2, is to form sulfone **2**.

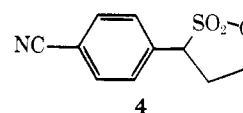


Our best characterized example of reaction 1 is the formation of **1a** from *p*-cyanophenylcyclopropane. When *p*-cyanophenylcyclopropane was irradiated in sulfur dioxide solution with sun lamps for 25.5 h, there was a 36% conversion to **1a**, a white solid with mp 87–92 °C. The infrared spectrum showed a single strong band in the S=O region at 1120 cm⁻¹ and the NMR spectrum showed two complex multiplets in the aliphatic region at 2.00–4.33 (2 H) and 4.10–5.28 ppm (3 H). These data suggested a mixture of the two geometric isomers of **1a**. To test this hypothesis, a peroxide oxidation to the sultone **3** was carried out. Compound **3** was a solid with mp 118.5–121.5 °C. It gave a correct analysis for addition of one oxygen atom and appropriate change in the infrared spectrum, the band at 1120 cm⁻¹ having been replaced with a strong pair at 1345 and 1210–1170 cm⁻¹.

Sultone **3** was further oxidized with dimethyl sulfoxide to distinguish it from the isomer **4**, which would have formed if the original sultone **1a** had had the corresponding orientation of the sulfur–oxygen bond. Oxidation gave a product with a strong ketone carbonyl at 1690 cm⁻¹, as expected for **5**, and



no bands at 2500–2900 or 1725 cm⁻¹, which would have been expected from the aldehydic product from **4**.



p-Acetylphenylcyclopropane in sulfur dioxide was irradiated to give a viscous oil whose infrared and NMR spectra closely resembled those of **1a**, indicating that the isomeric mixture of sultines **1b** had formed.

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 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.² The crude product of the photolysis showed additional NMR signals at δ 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, 3.5×10^{-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 cm^{-1} (s). A 60-MHz NMR spectrum (CDCl_3) showed δ 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% H_2O_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 cm^{-1} (s). A 60-MHz NMR spectrum (acetone- d_6) showed δ 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) (7.98×10^{-2} g, 3.58×10^{-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 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 δ 6.2 to 5.6. A triplet ($J = 6$ Hz) appeared at δ 6.12; a triplet appeared at δ 5.90; and a doublet of doublets pattern was centered at δ 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 cm^{-1} (m). A 60-MHz NMR spectrum (dimethyl sulfoxide- d_6) showed δ 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% H_2O_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 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 cm^{-1} (m). An NMR spectrum of the solid (dimethyl sulfoxide- d_6) showed δ 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 δ 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 δ 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.

References and Notes

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Photochemistry of Epoxides. 3. Direct Irradiation of Propylene Oxide in the Gas Phase^{1a}

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