

Experimental Section<sup>8</sup>

**Nature of Catalysts.**—Catalyst A<sup>9</sup> (Houdry HA-100s) is a  $\gamma$ -alumina catalyst which has been described as essentially non-acidic, and has been utilized as a dehydration catalyst in a large number of published examples<sup>10</sup> by several different workers. Catalyst A has a sodium content of 0.1–0.2% and was utilized in the form of 0.125-in. pellets.

Catalyst B<sup>11</sup> (Kaiser Chemicals, KA-101) is a quasicrystalline alumina, as determined by X-ray diffraction,<sup>12</sup> which can be referred to as  $\chi, \rho$ -alumina. The X-ray pattern is diffuse and intermediate between amorphous  $\rho$  and the more crystalline  $\chi$ , but distinct from each. A minor phase (ca. 20–30%) which coexists with the above dominant phase resembles  $\gamma$ -alumina, but is more diffuse. The catalyst is supplied as pellets, 8–14 mesh, with a surface area of 360 m<sup>2</sup>/g. Sodium content is 0.40%, expressed as Na<sub>2</sub>O.

Catalyst C<sup>13</sup> is catalytic zirconium oxide, containing 98% ZrO<sub>2</sub> and 2% alumina with a surface area of 50 m<sup>2</sup>/g and a pore volume of 0.21 cc/g, supplied as 0.125-in. pellets.

Catalyst D<sup>13</sup> is catalytic tungsten oxide, containing approximately 95% WO<sub>3</sub> with a surface area of 17 m<sup>2</sup>/g and a pore volume of 0.19 cc/g.

Catalysts were prepared by heating at the dehydration temperature for a period of 1 hr under reduced pressure (20–25 mm) in a nitrogen atmosphere. Fresh samples of catalyst were used in each run. After this pretreatment they were used directly as described below.

**Dehydration of *trans*-1,5-Heptadien-4-ol (1).**—*trans*-1,5-Heptadien-4-ol<sup>14</sup> (10 g, 0.09 mol) was added dropwise at a rate of 0.25 ml/min through a 22-mm Pyrex tube packed to a depth of either 15 or 25 cm with catalyst and externally heated with a Lindberg Hevi-Duty split-tube furnace. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice-acetone bath, and subsequently warmed to room temperature, washed with water, filtered through anhydrous magnesium sulfate, and analyzed immediately by glpc (see Table I for product analyses). No attempt was made to maximize the yields.

The dehydration products were identified by collecting each peak emanating from the chromatograph in glass V tubes immersed in cooling baths: (a) in isooctane for uv analysis, and (b) in CDCl<sub>3</sub> for nmr analysis. In each case, the product was identified by comparison of the uv, nmr, and glpc retention times to those of authentic samples in our laboratories.

**Registry No.**—1, 24581-03-1; 8, 1002-27-3; 1,3,5-heptatriene, 2196-23-8; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; ZrO<sub>2</sub>, 1314-23-4; WO<sub>3</sub>, 1314-35-8.

(8) Gas-liquid partition chromatography was performed with an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370-A electronic integrator for peak area measurement; dual 15-ft 15% TCEP on 60/80 mesh Chromosorb W columns were utilized for analysis. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202, nmr spectra with a Varian A60-A using TMS as an internal standard (CDCl<sub>3</sub> solvent). All compounds were identified by both uv and nmr spectra and glpc retention times and comparison to authentic samples.

(9) Houdry Process and Chemical Co.

(10) See, for example, L. Klemm, J. Shabtai, and D. Taylor, *J. Org. Chem.*, **33**, 1480 (1968), and references cited therein.

(11) Kaiser Chemicals, Division of Kaiser Aluminum and Chemical Corp.

(12) Private communication, Dr. Robert B. Emerson, Staff Research Associate, Chemical Aluminas, Kaiser Chemicals, Box 1031, Baton Rouge, La.

(13) Strem Chemicals, Inc.

(14) C. Spangler and G. F. Woods, *J. Org. Chem.*, **30**, 2218 (1965).

## Photochemical Deoxygenation of Aryl Sulfoxides

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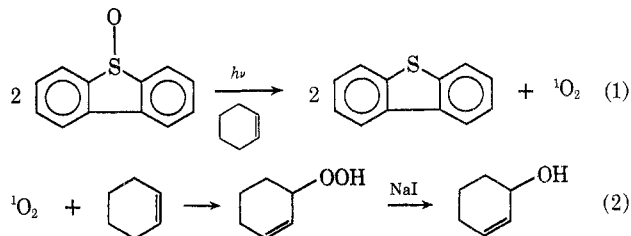
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Several selective and mild chemical methods have recently been reported for reduction of sulfoxides to the

corresponding sulfides.<sup>2</sup> To supplement these reports, we wish to communicate the photodeoxygenation of some aryl sulfoxides in good yields.

Kharasch and Khodair<sup>3</sup> found that diphenyl sulfoxide on direct photolysis in benzene gave biphenyl (53%), diphenyl sulfide (7%), and a small amount of diphenyl disulfide and that dibenzothiophene and dibenzothiophene dioxide were inert under these conditions. We find that in nonaromatic solvents direct photolysis of the aryl sulfoxides in Table I gives good to excellent yields of the corresponding sulfides. Diphenyl and *p*-tolyl phenyl sulfides, however, are photolabile, giving several products,<sup>3,4</sup> so that the yields of sulfide are diminished. Nevertheless, sensitized photolysis of diphenyl and *p*-tolyl phenyl sulfoxides with triplet sensitizer benzophenone or acridine<sup>5</sup> gives only the corresponding sulfides as products<sup>6</sup> and indicates that the photoreduction probably proceeds *via* the triplet excited state.<sup>5</sup> In further support of this conclusion, it was found that piperylene<sup>7</sup> could effectively prevent the deoxygenation of diphenyl sulfoxide, for example.

To determine the fate of the oxygen lost, dibenzothiophene oxide was photolyzed in the presence of cyclohexene as a trap for singlet oxygen.<sup>8</sup> From the amount of 2-cyclohexen-1-ol obtained (glc yield), we find a minimum of 41% of the available oxygen in the sulfoxide reacting as <sup>1</sup>O<sub>2</sub> (eq 1, 2).<sup>9</sup>



Photolysis of *dialkyl* sulfoxides<sup>10</sup> has been found to give mixtures of products, notably aldehydes and disulfides, but not dialkyl sulfides. Pyrolysis of dialkyl sulfoxides with available  $\beta$  hydrogens is known to give largely olefinic products and sulfenic acids.<sup>11</sup> If only  $\alpha$  hydrogens are available a rearrangement of the sulfide and formation of aldehyde and sulfhydryl prod-

(1) NSF Predoctoral Fellow, 1970–1972.

(2) J. P. A. Castellón and H. H. Szmant, *J. Org. Chem.*, **30**, 1338 (1965); I. Granth, A. Kalir, and Z. Pelak, *J. Chem. Soc. C*, 2424 (1969); D. W. Chasar, *J. Org. Chem.*, **36**, 613 (1971); T.-L. Ho and C. M. Wong, *Syn. Commun.*, **3**, 37 (1973); H. C. Brown and M. Ravindran, *Synthesis*, 42 (1973).

(3) N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967).

(4) W. Carruthers, *Nature (London)*, **209**, 908 (1966).

(5) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, pp 131, 132.

(6) Sulfide products can be easily purified from sensitizers and sulfoxides by tlc or column chromatography with silica gel.

(7) N. C. Yang, *J. Amer. Chem. Soc.*, **90**, 504 (1968); G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, **83**, 2396 (1961).

(8) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(9) A referee has pointed out that formation of oxygen atoms seems more likely than direct formation of singlet molecular oxygen, and that sensitization by dibenzothiophene of <sup>3</sup>O<sub>2</sub> formed in the reaction to singlet oxygen may account for the peroxide detected. Although our data do not permit unambiguous distinction between direct and indirect formation of singlet oxygen, the relatively good yield of peroxide formed and the absence of any products expected from cyclohexene and atomic oxygen [*e.g.*, epoxy-cyclohexane and cyclohexanone: T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2747 (1969)] give some support to direct formation of singlet oxygen.

(10) R. G. Petrova and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.* (10), 1857 (1966); T. Sato, Y. Goto, T. Tohyama, S. Hayashi, and K. Kata, *Bull. Chem. Soc. Jap.*, **40**, 2975 (1967).

(11) C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, **82**, 1810 (1960).

TABLE I  
 PHOTOLYSIS OF ARYL SULFOXIDES

Registry no.	Sulfoxide	Solvent	Time, hr	Filter <sup>a</sup>	% conversion <sup>b</sup>	Yield of sulfide, % <sup>b</sup>
1013-23-6	Dibenzothiophene oxide	C <sub>6</sub> H <sub>6</sub>	23	R	~100	>95
		50% aq AcOH	10	C	~80	>90
		50% aq AcOH <sup>c</sup>	4.25	U	50	90-95
945-51-7	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO	C <sub>6</sub> H <sub>12</sub>	21	R	100	40
		50% aq AcOH	7	N	40-50	~70
948-56-1	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S(O)C <sub>6</sub> H <sub>5</sub>	50% aq AcOH	10	N	~30	~85
		C <sub>6</sub> H <sub>6</sub> <sup>d</sup>	6	P	40-50	90-95
1193-82-4	C <sub>6</sub> H <sub>5</sub> S(O)CH <sub>3</sub>	C <sub>6</sub> H <sub>12</sub>	7	N	~80	~95
		50% aq AcOH	7	N	0	

<sup>a</sup> R = Rayonet reactor with low-pressure Hg arc lamps; others using Hanovia H-450W medium-pressure immersion lamp with N, no filters; C, Corex filter; P, Pyrex filter; and U, uranium glass filter (cut off about 320 nm). <sup>b</sup> Yields and conversions were determined by tlc, vpc, and nmr analysis. Identifications were confirmed by mass spectrometry. <sup>c</sup> With acridine or chrysene as triplet sensitizer; under the same conditions with no sensitizer, about 10% conversion to sulfide was observed. <sup>d</sup> With acridine or benzophenone as triplet sensitizers; under the same conditions with no sensitizer there was no reaction.

ucts may occur.<sup>12</sup> With this in mind, we attempted the pyrolysis<sup>13</sup> of aryl sulfoxides. While diphenyl sulfoxide was stable to heat (250°), dibenzothiophene oxide readily (250°, several minutes) lost oxygen by an undetermined mechanism to give near-quantitative yields of dibenzothiophene as determined by tlc and nmr. Methyl phenyl sulfoxide under the same conditions gave thioanisole (80-90% conversion, 60-70% yield by nmr) plus other products. Aryl sulfides were found to be thermally stable.

#### Experimental Section

*p*-Tolyl phenyl sulfide was made from commercially available thiophenol and *p*-iodotoluene by the method of Fournier, *et al.*<sup>14</sup> Sulfoxides were either obtained commercially (Aldrich or Eastman) or prepared from the corresponding available sulfides by *m*-chloroperbenzoic acid oxidation according to the method of Johnson and McCants.<sup>15</sup> Solvents and sensitizers were commercially available and purified before use. Thin layer chromatography was done on commercial silica gel plates (Eastman) with no activation, and vapor phase chromatography was performed on a Varian Aerograph Model 1200 with SE-30 columns.

**General Procedure for Photolysis.**—Substrates, sensitizers,

(12) W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind. (London)*, 342 (1966).

(13) Pyrolyses were done neat, condensed phase, in stoppered nmr tubes. Atmosphere had no effect.

(14) E. Fournier, L. Petit, J. Pichon, and M. Dursin, *Bull. Soc. Chim. Fr.* (5), 1754 (1966).

(15) C. R. Johnson and D. M. McCants, *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

and solvents were added to dry quartz test tubes and degassing was effected by freeze-pump-thaw cycles or nitrogen purging. Solutions were irradiated while suspended vertically around a Hanovia immersion lamp or in a Srinivasan-Griffin photochemical reactor and analyzed. Acid solutions were made alkaline and extracted with methylene chloride before analysis.

Thus, 45 mg (0.22 mmol) of dibenzothiophene oxide was dissolved in 10 ml of benzene in a quartz test tube and degassed by three freeze-pump-thaw cycles. The stoppered solution was irradiated (Rayonet reactor) for 23 hr at 40-50°. The reaction mixture was filtered through a short column of silica gel and the solvent was removed under vacuum, giving 39 mg (96%) of chromatographically pure dibenzothiophene (tlc, nmr).

**Trapping of Singlet Oxygen.**<sup>16</sup>—To a quartz test tube were added 30 mg (0.15 mmol) of dibenzothiophene oxide, 10 ml of cyclohexene, and 1 ml of acetic acid. The solution was purged with nitrogen and photolyzed (Hanovia lamp with Pyrex filter) until tlc showed that no sulfoxide remained. The reaction mixture gave positive spot tests<sup>17</sup> for peroxide and was treated with sodium iodide for 4 hr, after which the spot tests were negative. Work-up was by the method of Nickon and Bagli<sup>16</sup> and analysis of the final solution by vapor phase chromatography showed approximately 4 mg (±1 mg, 0.031-0.051 mmol) of 2-cyclohexen-1-ol (comparison with known sample). This corresponds to a lower limit yield of 41% overall from the available oxygen (0.075 mmol of O<sub>2</sub>) in dibenzothiophene oxide.

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(16) A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, **83**, 1498 (1961).

(17) F. Feigl, "Spot Tests in Organic Analysis," 6th ed, Elsevier, Amsterdam, 1960, pp 534, 535.