Disulfur Monoxide. Reaction with Dienes

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Disulfur monoxide (S_2O) reacts with 2,3-disubstituted butadienes to form 4,5-disubstituted 3,6-dihydro-1,2-dithiin 1-oxides. The structure of 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (3) was established by independent synthesis. Reaction of *cis*- or *trans*-1,4-dibromo-2,3-diphenyl-2-butene (5 or 4) with sodium polysulfide in dimethylformamide gave a mixture of 4,5-diphenyl-3,6-dihydro-1,2-dithiin (6), 3,4-diphenylthiophene (8), and the cyclic tetrasulfide 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin (7). Oxidation of 6 with hydrogen peroxide–formic acid gave 3. Oxidation of 7 gave a monoxide formulated as 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin 1-oxide (9).

Reactions of sulfur dioxide with conjugated dienes to give five-membered ring sulfones are well known.[1] We have previously reported on the reactions of sulfur monoxide with conjugated dienes.[2] Interest in the reactions of the lower oxides of sulfur has prompted us to examine the reactions of disulfur monoxide (S_2O)[3] with substituted butadienes.

Saito[4] had shown that the sulfur monoxide (SO) generated by pyrolysis (580°, 0.02 mm) of thiirane oxide (1) had been converted almost entirely to S_2O (48%) and SO_2 (40%) on passage through a 30-cm tube. Since the only major contaminant was ethylene, we chose this method for the generation of disulfur monoxide. Evidence for the intermediacy of $(SO)_2$ in the conversion of sulfur monoxide to disulfur monoxide is provided by the mass spectrum[5] of thiirane oxide (1) [$(SO)_2$ m/e calcd 95.93396; found 95.9333; 0.048% of M^+ (m/e 76), the base peak].

Results

Disulfur monoxide generated by pyrolysis of thiirane oxide (1) reacted with 2,3-diphenylbutadiene

(2) to give 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (3) (Scheme I). The structure of 3 was assigned from

SCHEME I

2, R = C_6H_5
10, R = 2-$C_{10}H_7$

3, R = C_6H_5
11, R = 2-$C_{10}H_7$
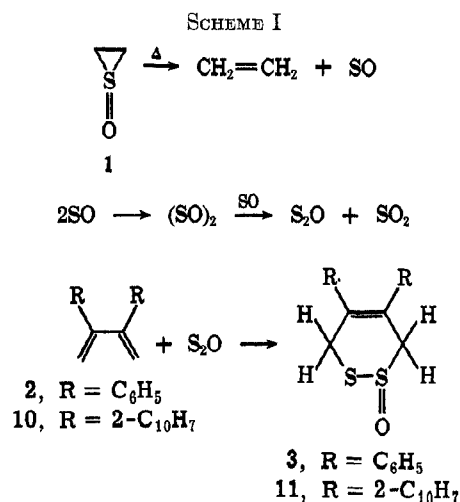
its analysis, from the presence of a very strong absorption band at 1064 cm⁻¹ in its ir spectrum ($CHCl_3$), corresponding to an SO vibration frequency,[6] and from the presence of two overlapping AB quartets in its nmr spectrum. The structure of compound 3 was established by the independent synthesis outlined in Scheme II.

The addition of 1 mol of bromine to 2,3-diphenylbutadiene (2) yielded *cis*- (5) and *trans*-1,4-dibromo-2,3-diphenyl-2-butene (4).[7] Reaction of the *cis*- (5) as well as the *trans*-1,4-dibromo-2,3-diphenyl-2-butene (4) with sodium disulfide in dimethylformamide gave

(1) (a) For a review of the early literature, see S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, pp 13–45. (b) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966). (c) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(2) (a) R. M. Dodson and R. F. Sauers, *Chem. Commun.*, 1189 (1967); (b) R. M. Dodson and J. P. Nelson, *ibid.*, 1159 (1969).

(3) (a) For reviews of the synthesis of sulfur monoxide and disulfur monoxide, see P. W. Schenk and R. Steudel, "Inorganic Sulfur Chemistry," G. Nickless, Ed., Elsevier, London, 1968, p 366; P. W. Schenk and R. Steudel, *Angew. Chem., Int. Ed. Engl.*, **4**, 402 (1965). (b) For a more recent method for the generation of sulfur monoxide, see Y. L. Chow, J. N. S. Tam, and J. E. Blier, *J. Chem. Soc. D*, 1604 (1970).

(4) (a) S. Saito, *Tetrahedron Lett.*, 4961 (1968). (b) For alternate paths for the thermal decomposition of thiirane oxides, see J. E. Baldwin and G. Hofte, *J. Amer. Chem. Soc.*, **93**, 2810 (1971).

(5) J. P. Nelson, Ph.D. Thesis, University of Minnesota, Dec 1969; G. Liuti, S. Dondes, and P. Harteck, Abstract of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 40 T.

(6) S. Ghersetti and G. Modena [*Spectrochim. Acta*, **19**, 1809 (1963)] have reported a strong absorption band at 1075 cm⁻¹ for $CH_3SS(O)CH_3$ in chloroform.

(7) C. F. H. Allen, C. G. Eliot, and H. Bell, *Can. J. Res.*, **17B**, 75 (1939).
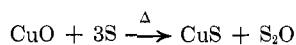
TABLE I

| 1,4-Dibromo-1,4-diphenyl-2-butene | Composition of polysulfide | Temp, °C | Ratio of products | | | | Total yield, % |
			Di-sulfide	Tetra-sulfide	3,4-Diphenyl-thiophene	2,3-Diphenyl-butadiene	
cis-5	Na$_2$S$_2$	70[a]	1.0	Trace	2.4	Trace	70-80
trans-4	Na$_2$S$_2$	70[a]	1.0	Trace	1.7	0.19	70-80
trans-4	Na$_2$S$_2$	Room[b]	1.0	0.13	0.33	0.26	70-80
cis-5	Na$_2$S$_4$	70[c]	1.0	0.77	2.3		70-80
trans-4	Na$_2$S$_4$	70[a]	1.0	0.63	2.2		70-80
trans-4	Na$_2$S$_4$	50[b]	1.0	0.74	0.61		70-80
trans-4	Na$_2$S$_4$	Room[b]	1.0	0.67	0.73		5-10[d]
trans-4	Na$_2$S$_6$	50[b]	1.0	1.6	1.0		70-80
trans-4	Na$_2$S$_8$	50[b]	1.0	0.80	0.52		70-80

[a] These reactions were run using 16.4 mmol of the dibromide (4 or 5) and 19.7 mmol of the sodium polysulfide in 350 ml of dimethylformamide for 24 hr. [b] These reactions were run using 8.2 mmol of the dibromide (4 or 5) and 9.8 mmol of the sodium polysulfide in 175 ml of dimethylformamide for 24 hr. [c] This reaction was run using 5.5 mmol of the dibromide (5) and 6.6 mmol of the sodium polysulfide in 118 ml of dimethylformamide for 24 hr. [d] Polymeric materials were the predominant products.

SCHEME II
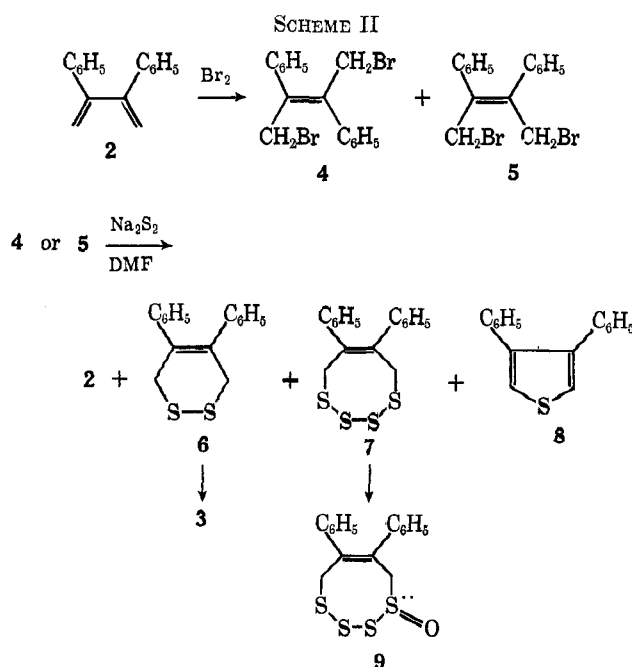
4,5-diphenyl-3,6-dihydro-1,2-dithiin (6) as one of the products (*vide infra*). The nmr spectrum of 6 showed a four-proton singlet at δ 3.33 for the methylene groups. This eliminated 3,4-diphenyl-1-sulfo-2,5-dihydrothiophene as a possible structure for 6. Oxidation of 6 in chloroform solution with a hydrogen peroxide–formic acid mixture yielded 3 identical with 3 prepared above.

Disulfur monoxide (S$_2$O), generated by the pyrolysis of thiirane oxide (1), was also added to 2,3-di-2-naphthyl-1,3-butadiene (10) (Scheme I) to yield 4,5-di-2-naphthyl-3,6-dihydro-1,2-dithiin 1-oxide (11) which had spectral properties similar to those of 3. Compound 11 could also be synthesized by the addition to 10 of disulfur monoxide generated by the reaction of cupric oxide and sulfur[8] at 300–350° at atmospheric pressure in a stream of helium. Attempts to add di-

$$CuO + 3S \xrightarrow{\Delta} CuS + S_2O$$

sulfur monoxide generated by this latter method to 2 gave detectable (nmr spectrum) but very low yields of 3. Attempts to add disulfur monoxide generated from thiirane oxide to 1,3-pentadiene, 1,4-dichloro-1,3-butadiene, *trans,trans*-1,4-dimethyl-2,3-diphenyl-

(8) S. R. Satyanarayana and A. R. Vasudeva Murthy, *Proc. Indian Acad. Sci.*, **A59**, 263 (1964).

butadiene, 1,3-di-*tert*-butylbutadiene, and 1,3-cyclopentadiene gave no detectable 3,6-dihydro-1,2-dithiin 1-oxides.

The 3,6-dihydro-1,2-dithiin 1-oxides (3 and 11) are unstable compounds. They decompose to diene on chromatography on silica gel or alumina, on drying *in vacuo* at 80°, and on being shaken in organic solvents with water. The compounds 3 and 11 are cyclic analogs of Allicin,[9] a bacteriostatic and fungistatic agent isolated from garlic. Compound 3 shows similar bacteriostatic and fungistatic properties.

The reaction of *cis*- (5) and *trans*-1,4-dibromo-2,3-diphenyl-2-butene (4)[10] with sodium polysulfide proved to be of considerable complexity. In addition to the 4,5-diphenyl-3,6-dihydro-1,2-dithiin (6) mentioned above, the following products were also obtained: 2,3-diphenylbutadiene (2), 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin[11] (7), and 3,4-diphenylthiophene (8). The yield and composition of the product mixture, determined by analysis of the nmr spectrum of the crude product, depended on the temperature of the reaction and the ratio of sodium sulfide to sulfur used (Table I). The yield of the tetrasulfide 7 was maximized by polysulfide of the composition Na$_2$S$_6$ and a temperature of 50°. It should be noted that both *cis*- and *trans*-1,4-dibromo-2,3-diphenyl-2-butene (5 or 4, respectively) gave essentially the same mixture of 2, 6, 7, and 8 when allowed to react under similar conditions. More 3,4-diphenylthiophene (8) was obtained from reactions run at 70° than from those run at lower temperature. Our failure to demonstrate the presence of any cyclic trisulfide is also of interest.

The structure of the 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin (7) followed from its nmr spectrum, which showed a sharp singlet (δ 3.99) for the four methylene

(9) C. J. Cavellito and J. H. Bailey, *J. Amer. Chem. Soc.*, **66**, 1950 (1944).

(10) Assignment of the stereochemistry of 5 and 4 is based on the direct comparison of the nmr spectra of 5 and 4 with the nmr spectra of the *cis*- and *trans*-α,α'-dimethylstilbene of established stereochemistry: Y. Nagai, O. Sumamura, and L. Ehara, *Bull. Chem. Soc. Jap.*, **35**, 244 (1962); O. Sumamura and H. Suzuki, *ibid.*, **27**, 231 (1954). *cis*-α,α'-Dimethylstilbene had mp 65.5–67.5° (lit. mp. 67°); nmr (CHCl$_3$-d) δ 7.00 (s, $W_{1/2}$ = 2 Hz, 10.0, C$_6$H$_5$), 2.16 (s, 6.0, CH$_3$). *trans*-α,α'-Dimethylstilbene had mp 106–107° (lit. mp 107°); nmr (CHCl$_3$-d) δ 7.26 (s, $W_{1/2}$ = 1.5 Hz, 10.0, C$_6$H$_5$), 1.88 (s, 6.0, CH$_3$). In both series, the aliphatic protons of the cis isomer are deshielded and the aromatic protons of the cis isomer are shielded with respect to those of the trans isomer.

(11) H. Poisel and V. Schmidt [*Chem. Ber.*, **104**, 1714 (1971)] also obtained a cyclic tetrasulfide by the reaction of 3,6-dibromo-1,4-dimethylpiperazine-2,5-dione with sodium disulfide. For additional references to the formation of cyclic tetrasulfides see R. Rahman, S. Safe, and A. Taylor, *Quart. Rev., Chem. Soc.*, **24**, 208 (1970).

protons. Any branching in the sulfur portion of this cyclic compound should have resulted in two AB quartets for these protons in the nmr spectrum of **7**. When the nmr spectrum of **7** was taken at lower temperatures the singlet for methylene protons began to broaden and became quite broad ($W_{1/2} = 5.2$ Hz) at $-60°$. This suggested a slow interconversion between different conformers of **7** at low temperatures, which became quite rapid at room temperature. Oxidation of **7** in methylene chloride solution with 1 molar equiv of *m*-chloroperbenzoic acid at $-30°$ gave a monoxide (**9**), which showed two widely separated AB quartets in its nmr spectrum. This has been formulated as 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin 1-oxide (**9**) in analogy with the oxidations of 1,5-dihydro-2,3,4-benzotrithiepin.[12] Attempted oxidation of **7** with 2 molar equiv of *m*-chloroperbenzoic acid gave sulfur, 3,4-diphenylthiophene (**8**), and another compound, which, because of its instability, has eluded characterization.

Discussion

Disulfur monoxide has been shown to have the following structural parameters.[13] From the dipole moment

$$\mu_{SSO} = 1.47 \text{ D}$$
$$\mu_{SO} = 1.58 \text{ D}$$
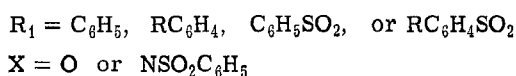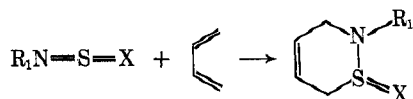$$\mu_{SS} = 0.30 \text{ D}$$

data it can be concluded that the bond order of the S–S bond would be close to 2.0.

Sulfur dioxide reacts with dienes to give five-membered ring sulfones in a concerted reaction.[1] Sulfur monoxide reacts with dienes to give five-membered ring sulfoxides. The latter reaction probably proceeds through a diradical intermediate.[2b,14] Phosphorus dihalides, phosphorus trihalides, and trialkyl phosphites also react with 1,3-dienes to give five-membered ring phosphorus containing heterocyclic compounds,[15] presumably *via* polar intermediates.[16]

In contrast, *N*-sulfinyl compounds react with 1,3-dienes to give six-membered ring compounds, 2-substituted 3,6-dihydro-1,2-thiazine 1-oxides, or 1-imines[17] (Scheme III). In the present work it has been shown that disulfur monoxide reacts similarly with 1,3-dienes to give six-membered ring products.

Scheme III

$$R_1 = C_6H_5, \quad RC_6H_4, \quad C_6H_5SO_2, \quad \text{or} \quad RC_6H_4SO_2$$

$$X = O \quad \text{or} \quad NSO_2C_6H_5$$

The reason for this difference in behavior of disulfur monoxide and *N*-sulfinyl compounds from sulfur dioxide and sulfur monoxide apparently lies in the availability, in the former compounds, of a double bond with a very low dipole moment (S=S or S=N) connected to an electron-withdrawing substituent. Orbitals on both atoms of this double bond are of such size and energy that overlap with orbitals on the diene is favorable. Hence, the S=S or S=N double bond is involved in the cycloaddition giving a six-membered ring. In sulfur dioxide and sulfur monoxide the high dipole moment of the S–O bond make it a poor dienophile. The orbitals on oxygen are small and of low (large negative) energy. This favors participation of nonbonding of antibonding electrons on sulfur in the cycloaddition and thus leads to five-membered rings.

Examination of a Dreiding model of compound **3** shows that the molecule prefers the boat conformation. In this conformation the double bond is predicted to have no effect on the coupling constants of the adjacent geminal protons, since the dihedral angle formed by one C–H bond and the plane of the double bond is about 120°, while the other C–H bond lies in the plane of the double bond.[18] The large observed geminal coupling constant ($J_{AB} = J_{A'B'} = 13.2$ Hz) is consistent with predominance of that conformation possessing an axial sulfoxide[19] [13.7 Hz in 3,3,5,5-tetradeuteriothiane (ax) 1-oxide].[19] The geminal coupling constant adjacent to an equatorial sulfoxide has been found to be smaller [11.7 Hz in 3,3,5,5-tetradeuteriothiane (eq) 1-oxide].[19] The large separation of the chemical shifts of the geminal protons ($\delta \nu_A 4.21$, $\nu_B 3.68$; $\nu_{A'} 4.44$, $\nu_{B'} 3.68$) also indicates the predominance of one conformer.[19b] However, with the information available, any direct assignment of the chemical shifts to the geminal protons would be speculative.

3

The distance between the axial protons in the boat conformation of **3** was estimated, from the Dreiding model, to be 2.6 Å. Since this is greater than twice the van der Waals radius of the hydrogen atom (2×1.2 Å), the steric interaction between these hydrogen atoms should not destabilize the boat conformation.

Experimental Section[20]

2,3-Diphenyl-2,3-butanediol.—Pinacolic reduction of acetophenone (95.50 g, 0.795 mol) in absolute ethanol (390 ml)–

(12) B. Milligan and J. M. Swan, *J. Chem. Soc.*, 2901 (1965).

(13) D. J. Meschi and R. J. Meyers, *J. Mol. Spectrosc.*, **3**, 409 (1959).

(14) R. A. Sikstrom, Ph.D. Thesis, University of Minnesota, Feb 1971.
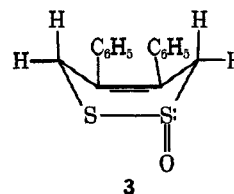
(15) For a recent review of cycloaddition of trivalent phosphorus compounds see L. D. Quin in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 47.

(16) Y. Ogata and M. Yamashita, *J. Org. Chem.*, **36**, 2584 (1971).

(17) (a) For a recent review of the cycloaddition reactions of *N*-sulfinyl compounds see G. Kresge in, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 453. (b) "Thionitrosobenzene" and phenylphosphinothioylidene also react with dienes to form six-membered ring compounds: P. Tavs, *Angew. Chem.*, **78**, 1057 (1966); S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *J. Chem. Soc. D*, 1186 (1971). Mechanistically, the reactions of "thionitrosobenzene" resemble those of sulfur monoxide and apparently proceed *via* radical intermediates: R. M. Dodson and W. S. Li, unpublished results.

(18) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1899 (1963).

(19) (a) B. J. Hutchinson, K. K. Anderson, and A. R. Katritzy, *ibid.*, **91**, 3839 (1969); (b) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966); (c) A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 1086 (1968); (d) see also R. M. Dodson, P. D. Hammen, and R. A. Davis, *J. Org. Chem.*, **36**, 2693 (1971); D. N. Harpp and J. G. Gleason, *ibid.*, **36**, 1314 (1971).

(20) All melting points were determined in capillary tubes on a calibrated Mel-temp melting point apparatus. Infrared spectra were determined on a Perkin-Elmer Model 257 spectrometer. Nuclear magnetic resonance spectra were taken on Varian Associates A-60 or T-60 spectrometers. All mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6D spectrometer by Mr. Adrian S. Swanson and his assistants. Anhydrous sodium sulfide was prepared by heating crystalline Na$_2$S·9H$_2$O (Mallinkrodt Analytical Reagent) at 0.1 mm and 100° for 24 hr.

benzene (390 ml) solution with aluminum foil (Reynolds Wrap) (24.00 g, 0.890 g-atom) in the presence of a small amount of mercuric chloride (1.50 g, 5.5 mmol), according to the procedure of Newman,[21] gave a thick oil. This crude product was triturated with petroleum ether (bp 30–60°, 100 ml). The resulting white solid was collected on a Buchner funnel and washed with petroleum ether (25 ml), giving 2,3-diphenyl-2,3-butanediol isomers as a white solid (84.60 g, 88%), mp 74–85° (lit.[21] mp 100–123°, 54–59%, material obtained by distillation of crude product); ir (Nujol) 3300–3500 cm^{-1} (b s, OH); nmr (CCl$_4$) δ 7.15, 7.10 (9.9, 2-, 3-C$_6$H$_5$), 2.85 (b s, $W_{1/2}$ = 2 Hz), and 2.37 (b s, $W_{1/2}$ = 2 Hz) (2.0, 2-, 3-OH), 1.42, 1.37 (s, 6.1, 1-, 4-CH$_3$). The nmr spectrum indicates a 1:1 ratio of meso and dl isomers.

2,3-Diphenyl-1,3-butadiene (2).—2,3-Diphenylbutadiene has been prepared by Allen, Eliot, and Bell,[7] in 30% yield, by dehydration of 2,3-diphenyl-2,3-butanediol with acetyl bromide. Alder and Haydn[22] have prepared 2,3-diphenylbutadiene, in 80% yield, by dehydration of 2,3-diphenyl-2,3-butanediol with anhydrous potassium bisulfate at 150–170° (13 mm). We have found the latter method to be quite convenient for the preparation of 2,3-diphenylbutadiene, although, in our hands, the yield was only 35%.

2,3-Diphenyl-2,3-butanediol (50.00 g, 0.202 mol) was mixed with powdered, freshly fused potassium bisulfate (1.25 g, 9.2 mmol). The mixture was distilled at 13 mm by gradual heating with an oil bath to a final bath temperature of 210°. Heating had to be controlled very carefully between 160 and 180°. The product distilled between 145 and 170° (13 mm) and had a tendency to solidify in the condenser. The distillation took 2.5 hr. The distillate was cooled in a freezer (−15°). It was then slowly warmed to room temperature and filtered, giving 2,3-diphenylbutadiene (2) as a white, crystalline solid (10.40 g, 25%): mp 41–46°; nmr (CHCl$_3$-d) δ 7.03–7.47 (2-, 3-C$_6$H$_5$), ν_A 5.25, ν_B 5.47 (AB quartet, J_{AB} = 2 Hz, 1-, 4-CH$_2$).

The filtrate was dried (Drierite) in chloroform (80 ml) solution and then treated with bromine (11.10 g, 69.5 mmol) in chloroform (15 ml) at 0°. Removal of the solvent and trituration of the residue with acetone gave an off-white solid (10.4 g). Further trituration and crystallization of the residue from acetone gave *trans*-1,4-dibromo-2,3-diphenyl-2-butene (4) as a white, crystalline solid (8.80 g, 12%), mp 151.5–153° (lit.[7] mp 144–147°). The dibromide was converted to 2,3-diphenylbutadiene, mp 46–47° (lit.[7] mp 46–47°), with zinc in 90% yield according to the procedure of Allen, Eliot, and Bell.[7]

cis- and *trans*-1,4-Dibromo-2,3-diphenyl-2-butene (5 and 4).—2,3-Diphenylbutadiene (13.00 g, 63.0 mmol) was dissolved in carbon tetrachloride (130 ml) and the solution was dried (Drierite). The solution was cooled in an ice bath and bromine (10.10 g, 63.2 mmol) in carbon tetrachloride (15 ml) was added drop by drop until the red color persisted (17.8 ml of bromine solution was needed). After 15 min the solvent was removed. The crude product was crystallized from acetone (ca. 130 ml) to give two crops of *trans*-1,4-dibromo-2,3-diphenyl-2-butene as white crystals (16.33 g, 71%): mp 151.5–153° (lit.[7] mp 144–147°); nmr (CHCl$_3$-d) δ 7.48 (s, 10.3, 2-, 3-C$_6$H$_5$), 4.05 (s, 3.7, 1-, 4-CH$_2$). The mother liquor was evaporated and the resulting greenish-white solid was dissolved in hot hexane. The solution was filtered from some greenish-black tarry material. When cooled, the solution deposited *cis*-1,4-dibromo-2,3-diphenyl-2-butene as a white, crystalline solid (2.75 g, 12%): mp 100.8–101.8°; nmr (CHCl$_3$-d) δ 7.13 (s, 10.1, 2-, 3-C$_6$H$_5$), 4.52 (s, 3.9, 1-, 4-CH$_2$).

Anal. Calcd for C$_{16}$H$_{14}$Br$_2$ (366.10): C, 52.49; H, 3.86. Found: C, 52.42; H, 3.80.

4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-Oxide (3).—A gas-phase pyrolysis apparatus was constructed which allowed passage of a gas through 30 cm of coiled Pyrex tubing (6 mm i.d.) which was itself heated in an Abderhalden-type chamber by refluxing solvent. With helium gas flowing through the chamber at the rate of 6 l./hr and heat being supplied by refluxing diphenyl ether (bp 259°), the gas exiting the chamber had a temperature of 250–259°. The residence time of the gas in the heated chamber under these conditions was estimated to be 2–3 sec. By the time the gas had traveled from the exit of the heated chamber to the reaction vessel itself (30 cm), it had cooled to slightly above room temperature.

Generation of Disulfur Monoxide from Thiirane Oxide.—Thiirane oxide (1) (1.00 g, 13.1 mmol) was placed in the vaporiza-

tion chamber (a 125 ml, three-necked, round-bottom flask) and heated to 70° with an oil bath. Helium gas (6 l./hr) was passed over the surface of the thiirane 1-oxide and through the pyrolysis chamber, which was heated by refluxing diphenyl ether (bp 259°). The pyrolysis gases were passed through 30 cm of Pyrex tubing to the bottom of the reaction vessel (125 ml, three-necked, round-bottom flask, equipped with a water cooled condenser, a Drierite drying tube and a magnetic stirrer) into a stirred solution of 2,3-diphenyl-1,3-butadiene (2) (2.00 g, 9.7 mmol) in toluene (50 ml). This process was continued for 6 hr; during this time 0.30 g of thiirane oxide (1) had been evaporated. The toluene was then evaporated under reduced pressure at room temperature. Crystallization of the residue from carbon tetrachloride yielded 0.20 g (53% based on thiirane oxide consumed) of 3: mp 126–127°; ir (KBr) 1490 (m, aromatic), 1440 (m), 1052 (vs, SO); ir (CHCl$_3$) 1064 cm^{-1} (SO); ir (CS$_2$) 1084 cm^{-1} (SO); nmr (CHCl$_3$-d) δ 7.18 (s, 10.3, 4-, 5-C$_6$H$_5$); two overlapping AB quartets: ν_A 4.21, ν_B 3.68 (J_{AB} = 13.2 Hz), $\nu_{A'}$ 4.44, $\nu_{B'}$ 3.68 ($J_{A'B'}$ = 13.2 Hz) (3-, 6-CH$_2$); mass spectrum molecular ion 286 (0.0023% of B), 284 (0.014% of B, M − 2), 270 (0.077% of B, M − O), 236 (0.001% of B, M − H$_2$SO, 3,4-diphenylthiophene), 206 (base peak, M − S$_2$O), 80 (94.6% of B, S$_2$O), 64 (27.0% of B, S$_2$), 48 (32.4% of B, SO).

Anal. Calcd for C$_{16}$H$_{14}$OS$_2$ (286.42): C, 67.10; H, 4.93; S, 22.39. Found: C, 66.63, 66.57; H, 4.87, 4.65; S, 21.88, 22.15.

Generation of Disulfur Monoxide from Cupric Oxide and Sulfur.—Cupric oxide (8.00 g, 0.10 mol) and sulfur (9.60 g, 0.30 g-atom) were powdered well, mixed with glass helices (8.00 g), and packed into a column (48 × 2.5 cm o.d.). This column was covered with asbestos sheet, wound with Nichrome wire (6.7 m, 22 ohms), and then fitted with a glass jacket (35.5 × 3.5 cm o.d.) placed 7.5 cm from the bottom of the column. The top of the column was connected through tygon tubing to a gas inlet tube leading to the bottom of a 100-ml, three-necked, round-bottomed flask fitted with a water condenser and a stopper. A solution of 2,3-diphenylbutadiene (1.00 g, 4.8 mmol) in toluene (50 ml) was placed in the flask. Pure and dry helium (dried with a Drierite tower) was passed at the rate of 200 ml/min through the system from the bottom of the packed column. The solution was stirred with a magnetic stirrer. The glass column was heated gradually by the heating coil starting with 30 V on the variac and increasing the voltage by 5 V every 30 min to a final voltage of 59 V. In a blank experiment 59 V was found to give a temperature of about 325° inside the column with the same helium flow. The gases from the top of the column were swept through the diene solution held at room temperature for 9 hr. The heating was stopped, and after the column had cooled to room temperature, the gas flow was stopped. The toluene solution was filtered to remove the small amount of suspended solids (sulfur?) and the filtrate was evaporated under vacuum at room temperature. The nmr spectrum (CHCl$_3$-d) of the residual pale yellowish-white solid (1.06 g) showed lines at 209, 222.5, 246, 259.75, and 273.5 Hz (downfield from tetramethylsilane) which corresponded to those of the adduct, 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (3). From the nmr spectrum the amount of the adduct was estimated to be about 3–4% of the residue. The rest was the unconverted diene 2.

4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-Oxide (3) from 4,5-Diphenyl-3,6-dihydro-1,2-dithiin (6).—4,5-Diphenyl-3,6-dihydro-1,2-dithiin (0.100 g, 0.36 mmol) was dissolved in chloroform (5.0 ml) and the solution was cooled in an ice bath. Formic acid (0.4 ml) was added and the mixture was stirred to form an emulsion. Five drops of 30% hydrogen peroxide was added over a period of 5 min. The suspension was stirred for an additional 0.5 hr in an ice bath and then allowed to warm to room temperature over a period of 15 min. The reaction mixture was added to saturated sodium chloride solution (20 ml). The chloroform layer was separated. The aqueous layer was extracted twice with chloroform (15 ml). The combined chloroform layers were dried with Drierite for 1 hr. Removal of the solvent on a rotary evaporator left a pale yellowish-white solid (0.094 g). An nmr spectrum of this crude product showed the presence of the expected monosulfoxide, the starting disulfide, and a trace of 2,3-diphenylbutadiene. One crystallization from chloroform-petroleum ether (bp 60–70°) gave a pale yellowish-white solid, 3 (0.048 g, 45%), mp 126–127°, mmp 126–127° with the sample of 3 prepared by gas-phase pyrolysis of thiirane oxide. The ir and nmr spectra of the two samples were superimposable.

2,3-Di-2-naphthyl-2,3-butanediol.—β-Acetonaphthone (87.0 g, 0.515 mol) was dissolved in dry benzene (250 ml) and absolute

(21) M. S. Newman, *J. Org. Chem.*, **26**, 582 (1961).
(22) K. Alder and J. Haydn, *Justus Liebigs Ann. Chem.*, **570**, 201 (1950).

ethanol (250 ml). The resulting solution was heated to boiling, and aluminum foil (20.0 g, 0.740 g-atom) cut in small pieces (1 in.²) was added to it at a rate that kept the mixture gently refluxing (*ca.* 1.5 hr). The reaction mixture was then heated under reflux for an additional 4 hr. It was cooled to 10°, and the complex was decomposed with cold, dilute hydrochloric acid. The suspension was extracted with benzene. The combined benzene extracts were washed with 5% hydrochloric acid, water, and 5% aqueous sodium bicarbonate and dried (MgSO₄). Evaporation of the solvent and trituration of the residue with petroleum ether afforded a white solid (70.0 g, 80%). Crystallization from benzene–petroleum ether gave 2,3-di-2-naphthyl-2,3-butanediol (65.0 g, 74%):[23] mp 179–182° (lit. mp 158–171°,[23a] 184°,[23b] 165–171°[23c]); ir (KBr) 3520 (ms), 3450 (bw, OH), 3035 (w, aromatic), 2960 (ms), 2925 (w, CH₃), 1620 (w), 1599 (ms), 1500 (ms, aromatic), 1370 (s), 1350 (ms), 1320 (ms, CH₃), 1150 (ms), 1110 (s), 1095 (vs, C–O), 895 (ms), 850 (s), 820 (s), 750 (vs, aromatic); nmr (CHCl₃-*d*) δ 8.00–7.20 (14.4, C₁₀H₇), 2.76, 2.36 (s, 2.0, 2, 3-OH), 1.64, 1.68 (s, 5.6, 1,4-CH₃). The two isomers are present in the ratio 1:2.3.

Anal. Calcd for C₂₄H₂₂O₂ (342.44): C, 84.18; H, 6.48. Found: C, 83.95; H, 6.26.

1,4-Dibromo-2,3-di-2-naphthyl-2-butene.—2,3-Di-2-naphthyl-2,3-butanediol (17.1 g, 0.05 mol) was mixed with β-naphthylamine (0.2 g), and acetyl chloride (freshly distilled and purified) (40 ml) was added. The reaction was vigorously exothermic, and the mixture started refluxing without further heating. When the vigor of the reaction had subsided, the mixture was heated under reflux for another 4 hr and then was cooled and added to ice-water. The aqueous suspension was extracted with benzene. The combined benzene layers were washed with water and 5% NaHCO₃ and dried (MgSO₄). The solvent was removed in a rotary evaporator, and the residue was dissolved in carbon tetrachloride (200 ml). Bromine (7.2 g, 0.045 mol) in dry carbon tetrachloride (90 ml) was added dropwise to the above solution, cooled in an ice-water bath. The solvent was removed under reduced pressure. Crystallization of the residue from acetone gave 11.5 g (49%) of 1,4-dibromo-2,3-di-2-naphthyl-2-butene: mp 205.5–206.5° dec; ir (KBr) 3030 (w), 3020 (w, aromatic), 2950 (w, CH₂), 1596 (ms), 1500 (ms, aromatic), 1426 (s), 1358 (s), 1200 (s), 1185 (s, CH₂), 1122 (ms), 1060 (w), 868 (s), 820 (s), 768 (ms), 748 (s), 740 (s), 730 (ms, aromatic); nmr (CHCl₃-*d*) δ 8.08–7.47 (14.0, C₁₀H₇), 4.28 (very small singlet), 4.20 (s, 4.0, 1,4-CH₂).

Anal. Calcd for C₂₄H₁₈Br₂ (466.22): C, 61.83; H, 3.89; Br, 34.28. Found: C, 16.90; H, 3.62; Br, 34.54.

2,3-Di-2-naphthyl-1,3-butadiene (10).—1,4-Dibromo-2,3-di-2-naphthyl-2-butene (9.3 g, 0.02 mol) was dissolved in acetone (250 ml) with stirring, and the resulting solution was heated to boiling. Zinc dust (3.8 g, 0.58 g-atom) was added at such a rate that gentle reflux was maintained. After the addition was completed (*ca.* 0.5 hr) the mixture was heated under reflux with stirring for another 2 hr and then was filtered while still hot. The filtrate was concentrated under reduced pressure and cooled. The resulting precipitate was collected on a Buchner funnel and dried under vacuum. Recrystallization from petroleum ether (bp 40–60°) gave 4.8 g (79%) of 2,3-di-2-naphthyl-1,3-butadiene: mp 143–144°; ir (KBr) 3025 (w), 1597 (ms), 1580 (s), 1500 (ms, aromatic), 1120 (ms), 905 (s), 893 (vs, = CH₂), 857 (s), 820 (vs), 765 (ms), 740 (vs, aromatic); nmr (CHCl₃-*d*) δ 7.93–7.23 (cm, 14.4, C₁₀H₇), 5.73, 5.45 (AB quartet, J_{AB} = 2 Hz, 4.0, 1,4-CH₂).

Anal. Calcd for C₂₄H₁₈ (306.41): C, 94.08; H, 5.92. Found: C, 93.82; H, 5.75.

4,5-Di-2-naphthyl-3,6-dihydro-1,2-dithiin 1-Oxide (11). A.—Disulfur monoxide, generated from cupric oxide and sulfur as described above, was passed in a stream of helium through a solution of 2,3-di-2-naphthylbutadiene (1.00 g, 3.3 mmol) in dry toluene (50 ml) in a 100-ml three-necked flask for 7 hr. The gas flow was stopped after the column cooled. The toluene solution was filtered on a Hirsch funnel to remove some suspended sulfur. The filtrate was evaporated in a rotary evaporator under reduced pressure without applying heat. The nmr spectrum of the residue showed the presence of unreacted diene and *ca.* 60% conversion of the diene to the desired adduct 11. The residue was dissolved in benzene, and petroleum ether (bp 30–60°) was added until the solution became cloudy. When cooled in the refrigera-

tor, the solution deposited white, crystalline 4,5-di-2-naphthyl-3,6-dihydro-1,2-dithiin 1-oxide (11) (0.60 g, 48%): mp 138–139°; ir (KBr) 1595, 1500 (m, aromatic), 1060 (vs, S=O), 890 (m), 855 (s), 815 (s), 740 cm⁻¹ (s, aromatic); nmr (CHCl₃-*d*) δ 8.00–7.10 (m, 14.15, C₁₀H₇), two overlapping AB quartets, ν_A 4.61, ν_B 3.79, J_{AB} = 13.4 Hz, $\nu_{A'}$ 4.37, ν_B 3.79, $J_{A'B'}$ = 13.4 Hz, 3,6-CH₂.

Anal. Calcd for C₂₄H₁₈OS₂ (386.54): C, 74.58; H, 4.69; S, 16.59. Found: C, 73.90, 73.94, 73.27, 73.62; H, 4.70, 4.68, 4.76, 4.78; S, 16.57.

B.—Disulfur monoxide was generated by the pyrolysis of thiirane oxide as described above. 2,3-Di-2-naphthylbutadiene (1.0 g, 3.26 mmol) was dissolved in toluene (50 ml) and the mixture of gases from the pyrolysis of thiirane oxide vapors was passed through this solution for 7 hr. The solvent was removed under reduced pressure at room temperature. The residue was dissolved in chloroform, and petroleum ether (bp 30–60°) was added until the solution became cloudy. On being cooled overnight, the solution deposited crystals of 11 (0.70 g, 56%), mp 138–139°. This material (11) was identical in all respects (mixture melting point and ir spectrum) with the sample described in A above.

Reaction of *trans*-1,4-Dibromo-2,3-diphenyl-2-butene with Sodium Tetrasulfide. 3,4-Diphenylthiophene (8), 4,5-Diphenyl-3,6-dihydro-1,2-dithiin (6), and 6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin (7). A solution of *trans*-1,4-dibromo-2,3-diphenyl-2-butene (6.00 g, 16.4 mmol) in dimethylformamide (100 ml) was added slowly to the deep purple solution of anhydrous sodium sulfide (1.53 g, 19.7 mmol) and sulfur (1.89 g, 0.059 g-atom) in dimethylformamide (250 ml). The resulting mixture was stirred at 70° for 24 hr and then poured into water (700 ml) and ice (200 g). The aqueous suspension was saturated with sodium chloride and extracted with ether (3 × 200 ml, 2 × 150 ml). The combined ether extracts were washed with water (150 ml) and saturated sodium chloride solution (150 ml) and dried overnight (Drierite). Evaporation of the ether extracts under aspirator pressure left a red semisolid (4.5 g). Trituration of this residue with ether (2 × 20 ml) left a pale yellow solid residue (0.84 g). Trituration of this yellow residue with chloroform left a bright yellow solid (0.40 g), mp 119–120°, which was shown to be sulfur (mixture melting point). Evaporation of the chloroform triturates gave a very pale yellow solid (0.44 g, 1.32 mmol), mp 142–147°. A part of this solid was sublimed (100°, 0.1 mm). Crystallization of the white sublimate from chloroform–hexane gave 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin (7) as white crystals: mp 151–152°; ir (KBr) 3040 (w), 3000 (w, aromatic), 2970 (w), 2900 (w, CH₂), 1597 (ms), 1570 (w), 1485 (s, aromatic), 1430 (vs, CH₂), 1220, 1205 (ms), 1073, 1023 (ms, aromatic), 930 (ms), 845 (ms), 775 (vs), 755 (vs), 740 (s), 700 (vs), 690 (vs, aromatic), 660 (ms); nmr (CHCl₃-*d*) δ 7.13 (s, 10.3, 6,7-C₆H₅), 4.09 (s, 3.7, 5,8-CH₂); nmr (CS₂) δ 7.07 (s), 3.99 (s). When the chloroform solution was cooled, the absorption band of the aromatic protons remained sharp while the absorption band of the methylenic protons broadened as shown (0°, $W_{1/2}$ = 0.70 Hz; −30°, $W_{1/2}$ = 1.3 Hz; −60°, $W_{1/2}$ = 5.2 Hz).

Anal. Calcd for C₁₆H₁₄S₄ (334.54): C, 57.45; H, 4.22; S, 38.34. Found: C, 57.52; H, 4.22; S, 38.72.

The ether triturate on evaporation gave a reddish yellow solid (3.41 g). This was chromatographed on silica gel. Elution with petroleum ether (bp 60–70°)–benzene (9:1) gave after some initial fractions containing sulfur, a pale yellow crystalline solid (1.71 g), mp 111–113°. Crystallization from ethanol–water gave 3,4-diphenylthiophene (8) as shiny white flakes (1.55 g, 6.56 mmol), mp 113–114° (lit.[24] mp 114°); nmr (CHCl₃-*d*) δ 7.32 (s) overlapping 7.24 (s).

Anal. Calcd for C₁₆H₁₂S (236.34): C, 81.31; H, 5.12; S, 13.57. Found: C, 81.06; H, 5.13; S, 13.40.

Further elution with petroleum ether (bp 60–70°)–benzene (4:1) removed a pale yellow solid (0.99 g), which appeared to be a mixture of two compounds. Repeated extraction of this solid with hexane gave a white solid (0.20 g, 0.6 mmol; total 0.64 g, 1.91 mmol), mp 140–143°, which was shown to be identical with the 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin isolated above (nmr spectrum).

The hexane extracts on evaporation gave 4,5-diphenyl-3,6-dihydro-1,2-dithiin (6), mp 89–93° (0.75 g, 2.77 mmol). Sublimation and crystallization of the sublimate from hexane gave analytically pure 4,5-diphenyl-3,6-dihydro-1,2-dithiin (6): mp

(23) (a) See ref 21; Newman reports a yield of 18%; (b) M. P. Balfe, J. Kenyon, and C. E. Searle, *J. Chem. Soc.*, 380 (1951); (c) R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc. C*, 2203 (1969).

(24) O. Hinsberg, *Chem. Ber.*, **48**, 1611 (1915).

101–102°; ir (KBr) 3050 (w), 3035 (w), 3000 (w, aromatic), 2910 (w), 2865 (w, CH₂), 1600 (w), 1575 (w), 1489 (ms, aromatic), 1440 (ms), 1388 (ms, CH₂), 1245 (w), 1213 (w), 1160 (w), 1062 (w), 1027 (w, aromatic), 920 (w), 915 (w), 912 (w), 785 (ms), 780 (ms), 733 (ms), 718 (s), 686 (vs, aromatic); nmr (CHCl₃-*d*) δ 7.00 [s, 10.2, 4,5-(C₆H₅)], 3.33 (s, 3.8, 3,6-CH₂).

Anal. Calcd for C₁₆H₁₄S₂ (270.42): C, 71.07; H, 5.22. Found: C, 71.25; H, 5.29.

Further elution with ether gave an unidentified orange, pungent liquid (0.44 g) which was not identified.

6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin is quite unstable towards heat. On sublimation, in addition to the white solid (**7**) isolated above, a yellow crusty solid was obtained. This was found to be a mixture of the tetrasulfide **7**, the disulfide **6**, 3,4-diphenylthiophene (**8**), and sulfur. Similar decomposition took place when **7** was heated in refluxing xylene.

The nmr spectrum of the initially isolated crude material in the above reaction showed the presence of all the compounds isolated above. Because of the clear separation of signals for methylenic protons in the tetrasulfide **7** from those in the disulfide **6**, calculation of the molar ratio of the three products was possible. The molar ratio tetrasulfide–disulfide–2,3-diphenylthiophene was calculated to be 1:1.6:3.5. This was almost identical with the ratio of the isolated products.

Reactions of *cis*- and *trans*-1,4-dibromo-1,4-diphenyl-2-butene with sodium polysulfide (Table I) were run using the conditions and method of analysis described above.

6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin 1-Oxide (9).— 6,7-Diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin (**7**) (0.91 g, 2.72 mmol) was dissolved in methylene chloride (36 ml) and cooled to −25 to −30°. A solution of *m*-chloroperbenzoic acid (0.55 g,

2.72 mmol) in 21 ml of methylene chloride was also cooled to −25 to −30° and was added drop by drop to the above solution with stirring over a period of 30 min. The resulting mixture was allowed to warm slowly to room temperature (1 hr) and gave a yellow solution. This was washed with 5% sodium bicarbonate solution (2 × 50 ml) and water (1 × 50 ml) and was dried overnight (Drierite). Evaporation of the methylene chloride solution gave a pale yellow solid, which on crystallization from carbon tetrachloride–hexane gave 0.34 g (0.96 mmol, 35%) of 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiocin 1-oxide (**9**): mp 135.3–137.3°; ir (KBr) 1060 cm⁻¹ (S=O); nmr (CHCl₃-*d*) two overlapping AB quartets: ν_A 4.94, ν_B 3.62, J_{AB} = 14.3; $\nu_{A'}$ 5.32, $\nu_{B'}$ 4.49, $J_{A'B'}$ = 12.8; 7.13 (C₆H₅).

Anal. Calcd for C₁₆H₁₄OS₄ (350.54): C, 54.82; H, 4.02. Found: C, 54.80; H, 4.05.

Registry No.—2, 2548-47-2; 3, 34826-14-7; 4, 34804-71-2; **5**, 6363-17-3; **6**, 34804-73-4; **7**, 34804-74-5; **8**, 16939-13-2; **9**, 34804-76-7; **10**, 34804-77-8; **11**, 34792-39-7; disulfur monoxide, 20901-21-7; *meso*-2,3-diphenyl-2,3-butanediol, 4217-65-6; *dl*-2,3-diphenyl-2,3-butanediol, 22985-90-6; *meso*-2,3-di-2-naphthyl-2,3-butanediol, 24227-54-1; *dl*-2,3-di-2-naphthyl-2,3-butanediol, 24227-55-2; 1,4-dibromo-2,3-di-2-naphthyl-2-butene, 34804-80-3.

Benzofurazan Oxide. Reaction with Sulfur Enolate Anions

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This paper reports a new synthesis of 2-substituted 1-hydroxy-3-oxobenzimidazoles, in fair yields, from the reaction of benzofurazan oxide and β-carbonyl sulfones. 2-Phenylthioacetophenone, however, gave the corresponding quinoxaline 1,4-dioxide.

The condensation of benzofurazan oxide (**1**) with enamines[3] and other enolate anions[4,5] to give substituted quinoxaline 1,4-dioxides has been reported and a mechanism for the reaction has been suggested. The condensation of benzofurazan oxide with primary and secondary aliphatic nitro compounds[6] in basic media to yield 1-hydroxy-3-oxobenzimidazole and 1,3-dioxobenzimidazole derivatives, respectively, has also been reported. In this paper we report a new synthetic route to 1-hydroxy-3-oxobenzimidazole (**4R₁**) and its 2-substituted derivatives from the reaction of β-keto sulfones **2** and α-sulfonyl carboxamides **3** with benzofurazan oxide in an alkaline medium (Scheme I). On the other hand, 2-phenylthioacetophenone reacted with benzofurazan oxide to give a compound similar to those described by Haddadin, *et al.*,[4] which was assigned the quinoxaline 1,4-dioxide structure (Scheme II). (The

compounds obtained by the reaction of benzofurazan oxide with substituted 2-phenylthioacetophenone will be the subject of a subsequent paper.)

Synthesis.—β-Keto sulfones **2** and α-sulfonyl carboxamides **3** were synthesized by the direct reaction of sodium benzenesulfinate dihydrate with the corresponding α-halo ketones and α-halo amides, respectively.[7] 2-Phenylthioacetophenone (**7**) was prepared from 2-bromoacetophenone and sodium thiophenate in a Williamson type synthesis. The structures of all the starting materials were confirmed by ir and nmr spectroscopy.

The reaction of 2-benzenesulfonylacetophenone (**2R₁**) with benzofurazan oxide in 4% methanolic potassium hydroxide solution afforded 1-hydroxy-3-oxobenzimidazole (**4R₁**) in 90% yield. 2-Nitrobenzenesulfonanilide (**5**) and benzoic acid (**6**) were the major byproducts that were isolated. The structure of **4R₁** was established by its controlled reduction with carbon disulfide to 1-hydroxybenzimidazole (**11**), which is in tautomeric equilibrium with the 3-oxobenzimidazole **12**.[8] The melting point, ir, and nmr of **11** were identical with those of an authentic sample prepared by the reduction of *o*-nitroformanilide with ammonium sulfide.[9]

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(2) Submitted in partial fulfillment toward the masters degree requirements.

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