and melted at 139–140°. The ultraviolet spectrum showed a maximum at λ_{max} 282 mμ, ϵ 15820.

Anal. Calcd. for $C_{60}H_{52}O_{12}$: C, 74.67; H, 5.43. Found: C, 74.47; H, 5.52.

Reaction of XI with chromic acid in acetic acid, as described under IX, yielded IX. A mixed melting point of the two products was not depressed.

2-Hydroxy-4,4'-dibenzyloxy-3,3'-dimethoxydiphenylacetic Acid Lactone (XII).—A similar reaction mixture was diluted with 1000 cc. of water, acidified with sulfur dioxide, and extracted with ether. The ether was dried and distilled to yield 34 g. of viscous yellow tar. The tar was boiled with 75 cc. of benzene, filtered, and the filtrate was diluted with 600 cc. of petroleum ether (b.p. 65–110°). The precipitate was washed several times with petroleum ether by decantation and then warmed with 100 cc. of glacial acetic acid. A heavy precipitate separated from the clear solution upon warming. The mixture was cooled and filtered, and the precipitate was recrystallized from acetic acid to give colorless crystals of XII melting at 229–230°. The ultraviolet spectrum showed the following maxima: λ_{max} 218 mμ, ϵ 45700; λ_{max} 288 mμ, ϵ 15120; $\lambda_{shoulder}$ 324 mμ, ϵ 14700; λ_{max} 330 mμ, ϵ 15710.

Anal. Calcd. for $C_{30}H_{26}O_6$: C, 74.67; H, 5.43. Found: C, 74.48; H, 5.45.

Repeated attempts at oxidation of XII with chromic acid in acetic acid failed to yield IX.

2-Hydroxy-4,4'-diacetoxy-3,3'-dimethoxydiphenylacetic Acid Lactone (XIII).—A slurry of XII in acetic anhydride was treated with a few drops of perchloric acid as above to give a product which was recrystallized twice from methanol to give light yellow crystals of XIII melting at 234–235° with gas evolution. The ultraviolet spectrum showed the following maxima: λ_{max} 280 mμ, ϵ 23950; λ_{max} 317 mμ, ϵ 7600.

Anal. Calcd. for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.20; H, 4.68.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined in 95% ethanol with a Beckman model DU spectrophotometer. All concentrations were approximately 0.02 g. per liter.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Benzothiophene Chemistry. VI. A Peroxide Effect in the Addition of Thiophenols to Benzothiophene 1-Dioxide

BY F. G. BORDWELL, R. D. CHAPMAN AND W. H. MCKELLIN

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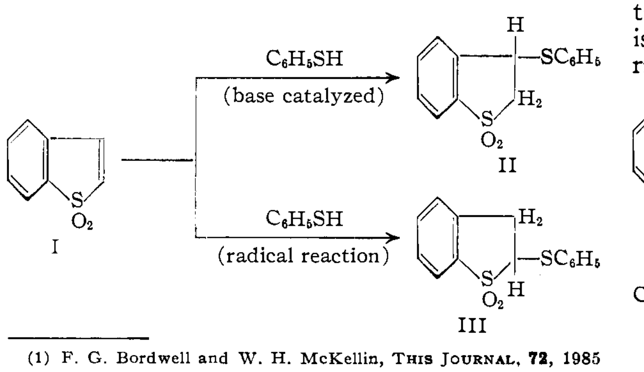
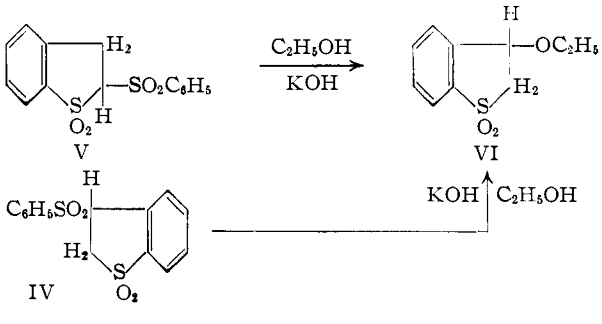
In contrast to base-catalyzed addition of thiophenols to benzothiophene 1-dioxide, which occurred in the 3-position,[1] addition of arylthio radicals (ArS·) took place in the 2-position. Aliphatic thiols, however, gave 3-substituted products under all conditions. Also, thiophenol gave the same product with phenyl vinyl sulfone when the reaction was initiated thermally or by base catalysis.

In a previous paper in this series[1] it was demonstrated that the sulfonyl group in benzothiophene 1-dioxide (I) activated the α,β-double bond to addition of electron-donating reagents [amines, alcohols (basic catalyst), thiophenol (basic catalyst), etc.] in a manner comparable to the sulfonyl, carbonyl, cyano, etc., groups in similar open-chain molecules. It has now been found that the mode of addition of thiophenols to I is reversed in radical-type additions.

Thiophenol fails to add to I in alcohol solution in the absence of a basic catalyst, but when I was refluxed in thiophenol (b.p. 168°) solution for 30 minutes a high yield of addition product III isomeric with that II from the base-catalyzed reaction[1] was obtained. Oxidation of II to 3-phenylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide (IV) was accomplished with 30% hydrogen peroxide in acetic acid. The structure of the disulfone, IV, follows from its preparation from 3-bromo-2,3-dihydrobenzothiophene 1-dioxide[1] and sodium benzenesulfinate in alcohol solution. The latter reaction is a direct displacement of bromide rather than elimination and addition, since sodium benzenesulfinate does not add to I under these conditions. Oxidation of III gave 2-phenylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide (V). The isomeric pairs, II and III, and their oxidation products, IV and V, differed markedly in melting points, infrared spectra and other physical properties as did also comparable pairs prepared from I and *p*-thiocresol. Both IV and V reacted readily with alcoholic potassium hydroxide to give 3-ethoxy-2,3-dihydrobenzothiophene 1-dioxide (elimination of benzenesulfinic acid and addition of alcohol to I); IV appeared to react more readily than did V. These elimination reactions show that the phenylsulfonyl group is in each instance attached to the heterocyclic ring and completes the structure proof of V. The





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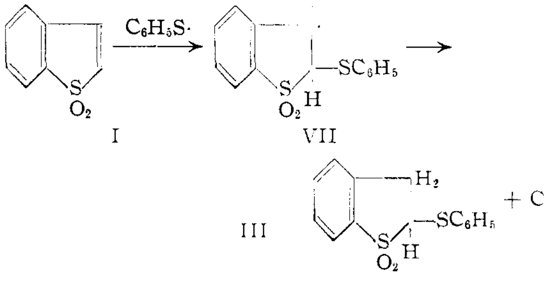
[1] F. G. Bordwell and W. H. McKellin, THIS JOURNAL, 72, 1985 (1950).

isolation of VI from the reaction of V with base in alcoholic solution suggests, at first sight, a preference for elimination of benzenesulfinate ion rather than ring-opening (to give *o*-(2-phenylsulfonylethenyl)-benzenesulfinate ion). This may not be the case, however, since the ring opening might well be reversible, whereas the elimination of benzenesulfinate is not (note the failure of benzenesulfinate ion to add to I mentioned earlier).

Evidence that the reaction of thiophenol with I to give III is of a radical rather than an ionic type was provided by the fact that in carbon tetrachloride solution the formation of III was shown to be catalyzed by benzoyl peroxide and by ultraviolet light. Also, catalysis by peroxide was observed in *p*-dichlorobenzene solution at 175°. Phenyl disulfide failed to catalyze the reaction and hydroquinone failed to inhibit it.

The addition of thiophenoxide ion ($C_6H_5S^-$) to the 3-position and the phenylthio radical ($C_6H_5S\cdot$) to the 2-position in I is consistent with the evidence that the sulfonyl group conjugates with electron pairs[2] but does not conjugate with single electrons.[3] Reaction of $C_6H_5S\cdot$ at the 2-position gives the relatively stable intermediate VII (conjugation with the benzene ring). Radicals appear to be able to initiate reaction only at the α-position of α,β-unsaturated systems, such as that present in I; other examples are



the addition of phenyl radicals to cinnamic acid,[4] and the addition of alkylthio radicals to acrylates.[5]

In contrast to the behavior of thiophenols the aliphatic thiols benzyl mercaptan and 1-hexanethiol gave only 3-substituted products under all conditions tried. With benzyl mercaptan, benzoyl peroxide failed to exert a catalytic effect. It seems probable that the reactions with the aliphatic thiols are ionic in type. Aliphatic thiols are, of course, more basic than thiophenols, and all thiols are well-known to be excellent electron-pair donors. Also, RS· are probably more difficult to generate than are ArS· radicals.

It was of interest to attempt to extend these reactions to open-chain α,β-unsaturated sulfones. Styrenyl *p*-tolyl sulfone ($C_6H_5CH{=}CHSO_2C_7H_7$) reacted with *p*-thiocresol at the reflux point to give a very small yield of 2-phenyl-2-*p*-tolylthioethyl *p*-tolyl sulfone [$C_6H_5CH(SC_7H_7)CH_2SO_2C_7H_7$], the same product as that obtained in the base-catalyzed reaction. Thiophenol reacted at the reflux point with phenyl vinyl sulfone to give a good yield of 2-phenylthioethyl phenyl sulfone($C_6H_5SCH_2CH_2SO_2C_6H_5$), which was obtained also in the base-catalyzed reaction.

Experimental[6]

2-Phenylthio-2,3-dihydrobenzothiophene 1-Dioxide (III).—A solution of 1.0 g. (0.006 mole) of benzothiophene 1-dioxide in 5 ml. (0.05 mole) of thiophenol was refluxed for 30 minutes and the resulting solution cooled and treated with 50 ml. of 10% aqueous potassium hydroxide. After 30 min. the solid formed was collected on a filter. Recrystallization from alcohol gave 1.2 g. (72%) of material melting at 119–120°. The infrared spectrum of III taken in chloroform solution differed from that of 3-phenylthio-2,3-dihydrobenzothiophene 1-dioxide (II).

Anal. Calcd. for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38. Found: C, 61.04; H, 4.56.

Oxidation of 1.33 g. of III dissolved in 20 ml. of glacial acetic acid with 5 ml. of 30% hydrogen peroxide was accomplished by refluxing the solution for 15 min. and diluting with 50 ml. of water. Recrystallization of the crude product from alcohol gave 1.0 g. (70%) of **2-phenylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide** (V), m.p. 116–117°.

Anal. Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.53; H, 3.92. Found: C, 54.57; H, 3.89.

The oxidation experiment was repeated several times with similar results. Later on one trial, material of m.p. 148–150° was obtained. Seeding a solution of the low melting form with this material gave the form m.p. 148–150°. Subsequent oxidations gave only the higher melting form. Infrared spectra of these dimorphic forms in chloroform solution were identical and differed from that of 3-phenylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide (IV).

Anal. Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.53; H, 3.92. Found: C, 54.61; H, 3.75.

2-*p*-Tolylthio-2,3-dihydrobenzothiophene 1-Dioxide.—A mixture of 1.0 g. (0.006 mole) of I and 6 ml. of *p*-thiocresol was refluxed for 30 min. and the excess *p*-thiocresol removed by extraction with 50 ml. of 10% potassium hydroxide. The yield was 1.5 g. (85%) of material, m.p. 118–120°. Recrystallization from alcohol gave material melting at 118–119°.

Anal. Calcd. for $C_{15}H_{14}O_2S_2$: C, 62.04; H, 4.86. Found: C, 61.89; H, 4.82.

Oxidation as described for V above gave **2-*p*-tolylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide**, m.p. 185–186°.

Anal. Calcd. for $C_{15}H_{14}O_4S_2$: C, 55.88; H, 4.37. Found: C, 55.96; H, 4.37.

3-Phenylsulfonyl-2,3-dihydrobenzothiophene 1-Dioxide (IV).—A solution containing 1.0 g. (0.004 mole) of 3-bromo-2,3-dihydrobenzothiophene 1-dioxide and 0.89 g. (0.0044 mole) of sodium benzenesulfinate dissolved in 80 ml. of alcohol was stirred for 3 hr. The alcohol was partially evaporated and water added to crystallize 0.9 g. (72%) of product melting at 175–176°. Recrystallization from alcohol gave material melting at 176–177°, which did not depress the m.p. of a sample prepared by the oxidation of 3-phenylthio-2,3-dihydrobenzothiophene 1-dioxide.[1] The m.p. of a mixture of 2- and 3-phenylsulfonyl-2,3-dihydrobenzothiophene 1-dioxides was 100–150°, and their infrared spectra were different.

The reaction of 1.0 g. (0.006 mole) of benzothiophene 1-dioxide with 1.3 g. (0.0065 mole) of sodium benzenesulfinate in 50 ml. of alcohol at reflux for 12 hr. gave on dilution with water a practically quantitative yield of 3-ethoxy-2,3-dihydrobenzothiophene 1-dioxide, m.p. 107–108°.[1]

3-*p*-Tolylthio-2,3-dihydrobenzothiophene 1-Dioxide.—This compound was prepared by essentially the same procedure used for 3-phenylthio-2,3-dihydrobenzothiophene 1-dioxide.[1] Recrystallization from alcohol gave material, m.p. 115–116°, in high yield. A second recrystallization gave material melting at 115.5–116°.

Anal. Calcd. for $C_{15}H_{14}O_2S_2$: C, 62.04; H, 4.86. Found: C, 62.11; H, 4.95.

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[2] F. G. Bordwell and Glenn D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

[3] C. C. Price and J. Zomlefer, *ibid.*, **72**, 14 (1950); C. G. Overberger, D. E. Baldwin and H. P. Gregor, *ibid.*, **72**, 4864 (1950). The failure of sulfones to react in the α-position with bromine radicals (see ref. 1) also supports this viewpoint.

[4] C. F. Koelsch and V. Boekelheide, THIS JOURNAL, **66**, 412 (1944).

[5] M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **13**, 97 (1948).

[6] Melting points are uncorrected. Microanalyses were by Miss P. Craig and Miss J. Sorenson.

A mixed m.p. of 2- and 3-*p*-tolylthio-2,3-dihydrobenzothiophene 1-dioxides was 85–105°.

Oxidation as described above for V gave **3-*p*-tolylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide**, m.p. 187–188°.

Anal. Calcd. for $C_{15}H_{14}O_4S_2$: C, 55.88; H, 4.37. Found: C, 56.06; H, 4.25.

A mixed m.p. of 2- and 3-*p*-tolylsulfonyl-2,3-dihydrobenzothiophene 1-dioxides was 150–170°.

Reaction of IV and V with Alcoholic Potassium Hydroxide.—A solution of 1.0 g. of 3-phenylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide (IV) in 29 ml. of 2% alcoholic potassium hydroxide was refluxed for 15 minutes, the solution chilled and the crystals collected. The yield of 3-ethoxy-2,3-dihydrobenzothiophene 1-dioxide,[1] m.p. and mixed m.p., 105–108°, was 0.38 g. (58%). Processing the mother liquors brought the total yield to 73%.

Under comparable conditions V gave a mixture, m.p. 78–93°. Extending the reflux time to one hour gave a first crop of crystalline 3-ethoxy-2,3-dihydrobenzothiophene 1-dioxide melting at 105–106° of 0.26 g. (35%). A second crop of less pure material, m.p. 96–98°, raised the yield to 52%.

Peroxide and Light-catalyzed Additions in Carbon Tetrachloride and *p*-Dichlorobenzene Solutions.—Benzothiophene 1-dioxide (I) is only slightly soluble in carbon tetrachloride at 0°, and its recovery from solution was used as a criterion for extent of reaction. A mixture of 1.0 g. (0.006 mole) of I, 1.3 g. of thiophenol (distilled under nitrogen) and 25 ml. of carbon tetrachloride was swept with nitrogen for 15 min. and then refluxed for one hour. The recovery of I, m.p. 136–140°, obtained on cooling to 0° was 0.79 g. (79%) (recovery on blank runs was 90–95%). A 50% yield of material, m.p. 111–114° (known m.p. 119–120°), was obtained from the mother liquors. In an identical run with about 5 mole per cent. of benzoyl peroxide added the recovery of material on cooling was only 12% (m.p. 90–110°). From this run 31% of product, m.p. 110–114°, was obtained. Judging from the recovery of I (69%) addition of phenyl disulfide (5 mole %) had no appreciable catalytic effect and hydroquinone (10 mole %) had no retarding effect.

Comparable experiments were carried out under nitrogen with a 30 min. reflux time in a Vycor flask in the dark, and with irradiation from an ultraviolet lamp. Recovery of I in the light-catalyzed reaction was 50%, as compared to 91% in the blank, and a 31% yield of product, m.p. 113–117°, was obtained. The m.p. of the latter was not depressed when mixed with an authentic sample of 2-phenylthio-2,3-dihydrobenzothiophene 1-dioxide, m.p. 123–124°.

Experiments were also run with 1.0 g. of I and 1.2 ml. of thiophenol in 10 g. of *p*-dichlorobenzene for 10 minutes at 175°. Recovery of I was effected by pouring the mixture into 15 ml. of carbon tetrachloride and cooling to 0°. Recovery in a blank run was 83%, with thiophenol added it was 52%, and in the presence of 5 mole % of benzoyl peroxide it was 4%. With 15 mole % of phenyl disulfide added recovery was 48% (no effect) and with 5 mole % of hydroquinone present it was 59% (no effect).

Addition of Benzyl Mercaptan to Benzothiophene 1-Dioxide (I).—One gram of I was dissolved in 6 ml. of benzyl mercaptan and the solution refluxed for one hour in the presence of a small amount of benzoyl peroxide. The solution was then cooled, shaken with 50 ml. of 10% potassium hydroxide and extracted with ether. The ether was evaporated and the resulting oil oxidized with 5 ml. of 30% hydrogen peroxide in 20 ml. of acetic acid by refluxing for 30 min. The product was precipitated by dilution and recrystallized from alcohol; the yield was 0.89 g. (51%), m.p. 185–188°. After several further crystallizations from alcohol an analytical sample of **3-benzylsulfonyl-2,3-dihydrobenzothiophene 1-dioxide**, m.p. 195–195.5°, was obtained.

Anal. Calcd. for $C_{15}H_{14}O_4S_2$: C, 55.88; H, 4.38. Found: C, 55.84; H, 4.38.

An identical product, m.p. 194–196°, was obtained in 89% yield from the reaction of benzyl mercaptan with I in benzene solution in the presence of a small amount of sodium, followed by oxidation.

In experiments carried out between I and benzyl mercaptan at 175° in *p*-dichlorobenzene solution for 30 min. in the presence and absence of benzoyl peroxide, comparable quantities of I were recovered (43 and 42%, respectively).

Addition of 1-Hexanethiol to Benzothiophene 1-Dioxide (I).—Using a procedure comparable to that described for benzyl mercaptan (benzoyl peroxide present), one gram of I and 6 ml. of 1-hexanethiol yielded after oxidation 0.64 g. (34%) of crystals melting at 75–77°. Recrystallizations from alcohol gave **3-(1-hexylsulfonyl)-2,3-dihydrobenzothiophene 1-dioxide**, m.p. 80–81°.

Anal. Calcd. for $C_{14}H_{20}O_4S_2$: C, 53.14; H, 6.37. Found: C, 53.08; H, 6.30.

A 38% yield of product, m.p. 77–79°, the m.p. of which was not depressed by admixture with the above compound, was prepared by the reaction of 1-hexanethiol with I in benzene (small amount of sodium added), followed by oxidation.

Addition of *p*-Thiocresol to Styrenyl *p*-Tolyl Sulfone.—A mixture of 2.26 g. (0.01 mole) of styrenyl *p*-tolyl sulfone and 6.1 g. (0.05 mole) of *p*-thiocresol was refluxed for 1 hour. Upon cooling crystals separated, which on recrystallization from methanol–acetone yielded a few mg. of material, m.p. 173–173.5°, which did not depress the m.p. of a sample of the addition product obtained in good yield using the sodium salt of *p*-thiocresol.[7]

Addition of Thiophenol to Vinyl Phenyl Sulfone.—A solution containing 1.0 g. (0.006 mole) of vinyl phenyl sulfone, 0.72 g. (0.007 mole) of thiophenol, 0.05 g. (0.002 mole) of sodium and 20 ml. of absolute alcohol was refluxed for 2 hr. Evaporation of the alcohol in a current of air, and treatment of the residue with 20 ml. of water gave 1.6 g. (94%) of material melting at 69–70°. Recrystallization gave **2-phenylthioethyl phenyl sulfone**, m.p. 71–71.5°.

Anal. Calcd. for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.04; H, 4.80.

A mixture of 2.0 g. (0.012 mole) of vinyl phenyl sulfone and 10.7 g. (0.12 mole) of thiophenol was refluxed for 2 hr., cooled, 100 ml. of water added and the excess of thiophenol steam distilled from the product. On cooling 3.1 g. (94%) of material melting at 65–68° crystallized. This m.p. was not depressed by admixture of the substance with a sample of 2-phenylthioethyl phenyl sulfone described above.

One gram (0.004 mole) of 2-phenylthioethyl phenyl sulfone was heated with 5 ml. of 30% hydrogen peroxide and 5 ml. of acetic acid at the reflux point for 10 min. and the solution diluted with 10 ml. of water. On cooling 1.1 g. of product, m.p. 182–184°, was obtained. Recrystallization gave 1,2-bis-phenylsulfonylethane, m.p. 183–184°.

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[7] E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1316 (1935).