ethanol gave 2.6 g. of yellow crystalline material; recrystallized from ethanol, pale yellow needles, m.p. 308–310°.

Anal. Calcd. for $C_9H_4O_4NSBr$: C, 35.78; H, 1.34. Found: C, 36.03; H, 1.35.

This same bromonitro acid resulted on treatment of an aqueous solution of sodium 5-nitrobenzothiophene-2-carboxylate with a molar proportion of bromine in aqueous solution. In all probability it is 7-bromo-5-nitrobenzothiophene-2-carboxylic acid.

4-Cyanomethyl-1,2-naphthoquinone from 4-Cyanocarbethoxymethyl-1,2-naphthoquinone by the Action of Triton B.—4-Cyanocarbethoxymethyl-1,2-naphthoquinone (500 mg.) was dissolved in 80 ml. of Triton B solution. A deep purple color developed immediately. On standing the solution turned a deep red. After 25 minutes the solution was acidified with 6*N* hydrochloric acid, and a bright yellow solid was deposited, 350 mg., m.p. 172–178°. It was recrystallized from dilute acetone, 290 mg. (79%) of fine yellow needles, m.p. 208–211°. The material gave no mixed m.p. depression with a sample of authentic 4-cyanomethyl-1,2-naphthoquinone prepared by the method of Gates, *et al.*[24] Its previously unreported phenazine was prepared by boiling equivalent proportions of the quinone and *o*-phenylenediamine in acetic acid for five minutes and diluting the solution with water. The product was recrystallized from benzene–hexane and then from alcohol, pale yellow needles, m.p. 200–202°.

Anal. Calcd. for $C_{18}H_{11}N_3$: C, 80.28; H, 4.12. Found: C, 80.00; H, 4.35.

The phenazine gives a blood-red coloration with concentrated sulfuric acid. It was identical with the phenazine formed from an authentic sample of 4-cyanomethyl-1,2-naphthoquinone.

2-Bromo-7-(cyanomethyl)-benzothiophene-4,5-quinone.—2-Bromo-7-(cyanocarbethoxymethyl)-benzothiophene-4,5-quinone (400 mg.) was dissolved in 7 ml. of Triton B. The initially green solution went dark and finally a dull red-purple color. After standing for 45 minutes the solution was diluted with about three times its volume of distilled water and filtered. The filtrate was carefully acidified with 6 *N* hydrochloric acid, and on scratching small reddish crystals were deposited. As the compound decomposed on attempts at crystallization, it was converted into its phenazine, which is stable, by boiling equivalent amounts of the crude quinone and *o*-phenylenediamine in acetic acid for 5 minutes and diluting the solution with water. The product was crystallized from dilute acetic acid, deep yellow microscopic needles, m.p. 253–254° with decomposition.

Anal. Calcd. for $C_{16}H_8N_3SBr$: C, 54.26; H, 2.28. Found: C, 54.27; H, 2.39.

With concentrated sulfuric acid the phenazine gives an olive-green color.

ROCHESTER 20, N. Y.

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA]

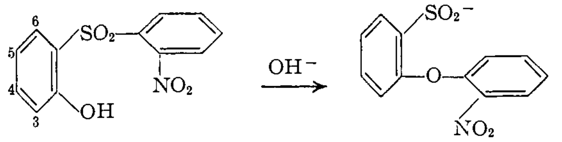
The Synthesis and Smiles Rearrangement of 2-Hydroxy-5-methyl-2'-nitrodiphenyl Sulfone and Several of its Methyl and Halogen Derivatives[1,2]

BY TOSHIHIKO OKAMOTO[3] AND J. F. BUNNETT

RECEIVED MAY 14, 1956

The synthesis of several sulfones of types IV and V is reported. Proof of their structures is presented, and several products and by-products of their alkali-promoted (Smiles) rearrangement are described.

McClement and Smiles[4] reported that the alkali-induced rearrangement of 2-hydroxy-2'-nitrodiphenyl sulfones to 2-(*o*-nitrophenoxy)-benzenesulfinic acids is accelerated by methyl groups in the 6-position. Bunnett and Zahler[5] showed that the acceleration could be rationally interpreted on steric grounds. However, it seemed desirable to prove by experiment whether or not the acceleration was actually due to the *bulk* of the 6-methyl groups, and to gather good kinetics data on the rearrangement. This paper describes the preparation of several compounds required for the kinetics work, proof of their structures, and careful description of the products and by-products of several typical rearrangements. Our rate measurements are presented and discussed in the following paper.[6]



Our thinking was this: if the acceleration is really due to the bulk of the 6-methyl groups, rather than to their electron-releasing effect as was originally proposed by McClement and Smiles, large 6-substituents of opposite electronic effect ought also to accelerate the reaction. We found that they do.[6] It was necessary, though, to be able to recognize what part of the change in rate caused by the introduction of a 6-substituent might be due to its electronic effect, and for this purpose we chose to compare the rates of rearrangement of isomers of types IV and V. The electronic effect of a 4-substituent (in IV) ought to be similar to that of the same substituent in the 6-position (as in V). The 5-methyl group is a constant factor in all the sulfones prepared in this work; it serves to block the position *para* to the hydroxy group and thereby simplifies problems of synthesis.

The parent sulfone IVa, its rearrangement to sulfinic acid VIa and evidence for the structure of the latter were described by Levy, Rains and Smiles.[7] We have repeated and confirmed much of their work, including particularly the isolation of VIa from the rearrangement, oxidation of VIa to the corresponding sulfonic acid XI and desulfonation of the latter to the ether Xa. Alternatively, we have mercuridesulfinated[8] VIa to form (presumably) VIII (R = H) which in turn was demercu-

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[1] Research supported by the Office of Ordnance Research, U. S. Army.

[2] Described in part in a preliminary communication: T. Okamoto and J. F. Bunnett, *J. Org. Chem.*, **21**, 487 (1956).

[3] On leave from the Pharmaceutical Institute, University of Tokyo, 1954–1956; grateful recipient of a Fulbright travel grant.

[4] C. S. McClement and S. Smiles, *J Chem Soc.*, 1016 (1937).

[5] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 369 (1951).

[6] J. F. Bunnett and T. Okamoto, THIS JOURNAL, **78**, 5363 (1956).

[7] A. A. Levy, H. C. Rains and S. Smiles, *J. Chem. Soc.*, 3264 (1931).

[8] J. F. Bunnett, *Chem. Eng. News*, **32**, 4019 (1954); *J. Chem. Soc.*, 4717 (1954).

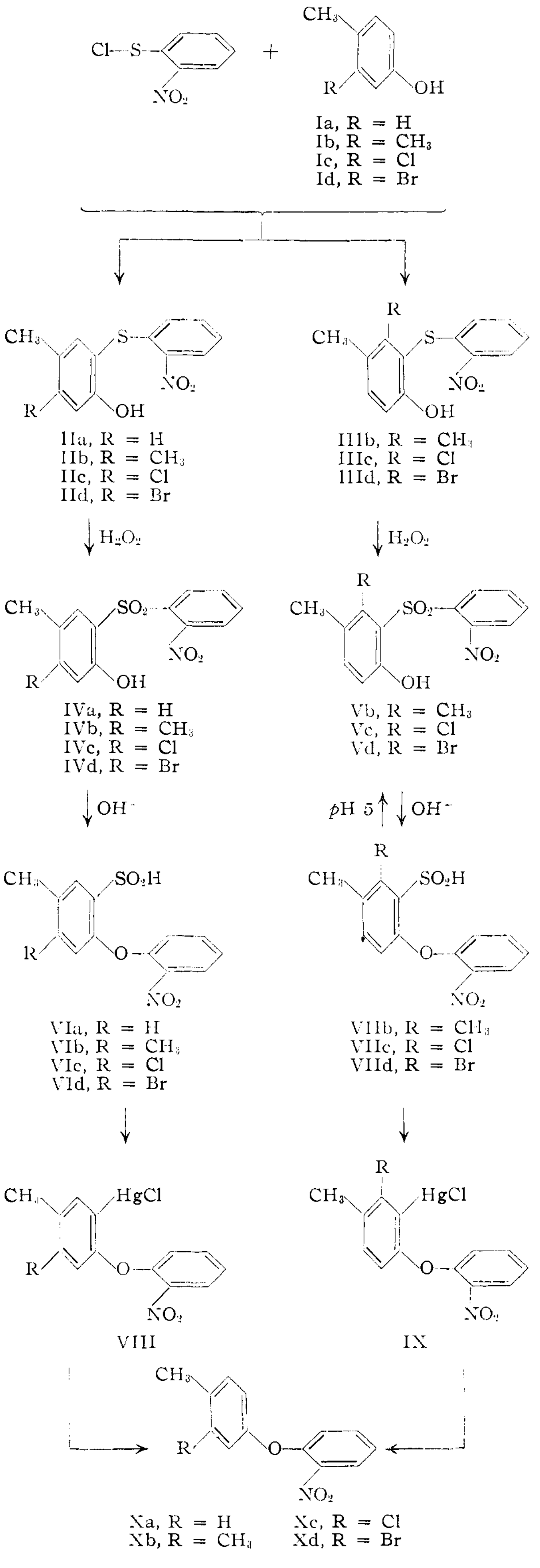
rated to the same ether Xa. The latter procedure for removal of the sulfino group, due to McClement and Smiles,[4] is considerably more efficient and convenient.

The general procedure for preparation of the 4- and 6-substituted derivatives of IVa was as follows: A 3-substituted-4-methylphenol (Ib, Ic or Id) was condensed with *o*-nitrobenzenesulfenyl chloride to form a mixture of isomeric sulfides of types II and III. The isomers were separated by chromatography on alumina, a process which in this application was exceedingly tedious. The isomer formed in lesser amount was assigned structure III, and the predominant product structure II. These assignments were later confirmed, as described below. The separated sulfides were then oxidized to the sulfones of types IV and V, which were the materials desired for the kinetics study.

At one time in an attempt to avoid the tedious separation of IIb and IIIb, we oxidized a mixture of the two to a mixture of the sulfones IVb and Vb and then tried to separate the sulfones by chromatography on alumina. IVb was eluted straightforwardly by chloroform, but Vb could not be recovered from the column. Presumably Vb was rearranged with catalysis by the basic alumina of the column, and the VIIb so formed underwent further transformations. This was the first indication that the difference in rates of rearrangement of isomeric sulfones of types IV and V is as tremendous as we now know it to be. Our kinetics study[6] has since shown that the 6-substituted isomers (V) rearrange about 500,000 times as fast as the 4-substituted isomers (IV). The difference is much greater than indicated by the rough measurements of McClement and Smiles.

Quite late in this work it was discovered that the sulfones IVb and Vb easily could be separated from each other by taking advantage of the difference in rates of rearrangement and of the facile *reverse* Smiles rearrangement[9] of sulfinic acid VIIb to sulfone Vb. A mixture of IVb and Vb was dissolved in aqueous sodium hydroxide and *within one minute* carbon dioxide was added to precipitate unrearranged IVb. During this time, Vb had rearranged entirely to VIIb which remained soluble in the aqueous bicarbonate solution. The mixture was extracted with benzene, and evaporation of the benzene extracts furnished nearly pure IVb. Acidification of the aqueous layer precipitated VIIb which was collected and heated in a buffered solution at *p*H 5 for 30 minutes on the steam-bath. These are conditions for the reverse rearrangement (VIIb → Vb), and Vb separated as it was formed. It was collected and crystallized once, and its melting point was three degrees higher than had ever been observed before. By this technique substantial amounts of IVb and Vb could be prepared in a condition of high purity in an afternoon's work; previously, weeks had been required to prepare smaller amounts which were less pure. This technique was also applied with advantage to the separation of the chlorosulfones IVc and Vc.

The sulfoxide corresponding to sulfone Vb was isolated from an uncompleted oxidation of sulfide



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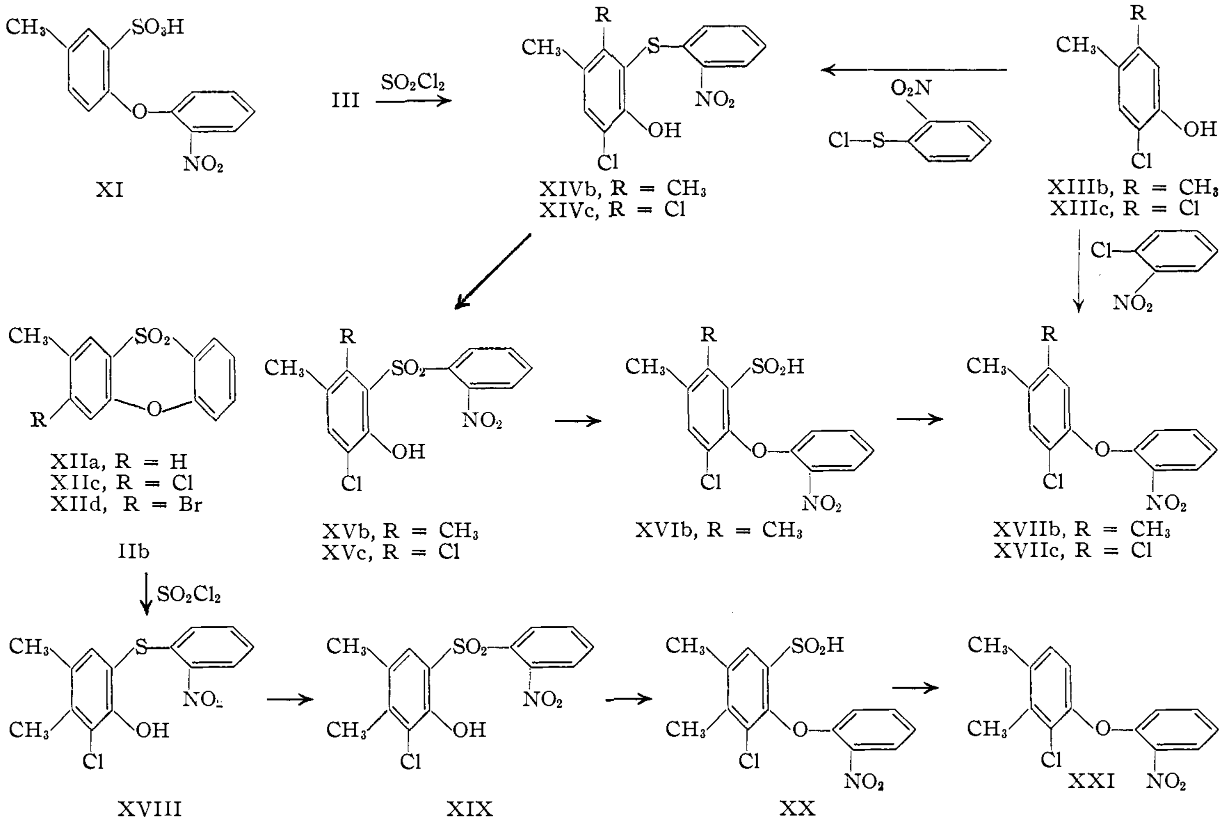
(9) R. R. Coats and D. T. Gibson, *J. Chem. Soc.*, 142 (1940).



IIIb. An interesting property of this sulfoxide is that it shows no infrared absorption in the region (around 3300–3600 cm.$^{-1}$) expected for a phenol; the same characteristic has been reported for the parent *o*-hydroxydiphenyl sulfoxide itself.[10]

All the sulfones of types IV and V were allowed to rearrange in the presence of excess sodium hydroxide to form sulfinic acids of types VI and VII, respectively. Evidence that the rearrangements had gone as represented was obtained by submitting all the sulfinic acids to mercuridesulfination, presumably to form mercury compounds of types VIII and IX, and finally removing the mercury function by the action of hydrochloric acid to form ethers of type X. Each pair of isomeric sulfones gave rise to the same ether. Ethers Xa, Xc and Xd were also independently synthesized from the appropriate 3-substituted-4-methylphenol (Ia, Ic or Id) and *o*-chloronitrobenzene.

Since a kinetics study was contemplated, it was desirable to know to what extent the rearrangements resulted in products other than the sulfinic acids. The by-products suspected were phenoxathiin 10-dioxides of type XII, which might be formed by ring closure of the sulfinic acids in alkaline solution with the elimination of nitro groups,[11] and *o*-nitrophenol which would be produced by cleavage of the sulfones by excess hydroxide ion present in the medium. Careful examination of the products of rearrangement of sulfones IIa, IIc and IId under the conditions chosen for the rate studies showed that phenoxathiin dioxides were indeed formed to a small extent (<5%), but neither *o*-nitrophenol nor any other organic by-product could be found.[12] The reactions were thus attractive for rate studies.

Proof of Structures.—The orignal assignment of structure II to the major and III to the minor products of condensations of *o*-nitrobenzenesulfenyl chloride with phenols of type I was made on the basis of two assumptions: that substitution would occur only at the 2- and 6-positions, *ortho* to the hydroxy group, and that the 3-substituent would disfavor substitution in the 2-position. The first assumption is verified by the fact that the sulfones of types IV and V all rearrange readily. The second was confirmed by chlorinating sulfides IIIb and IIIc to form chlorosulfides XIVb and XIVc, respectively. XIVb was also obtained by condensation of *o*-nitrobenzenesulfenyl chloride with chlorophenol XIIIb. Moreover, the corresponding sulfones XVb and XVc gave, *via* a sequence of rearrangement, mercuridesulfination and demercuration, ethers of type XVII which were also formed by reaction of phenols XIIIb and XIIIc with *o*-chloronitrobenzene and alkali.

Besides serving to confirm structural assignments, these reactions furnished compounds of interest for the kinetics study, especially sulfone XVb and the corresponding sulfinic acid XVIb. An isomeric series was prepared by chlorinating sulfide IIb to chlorosulfide XVIII, oxidation to chlorosul-

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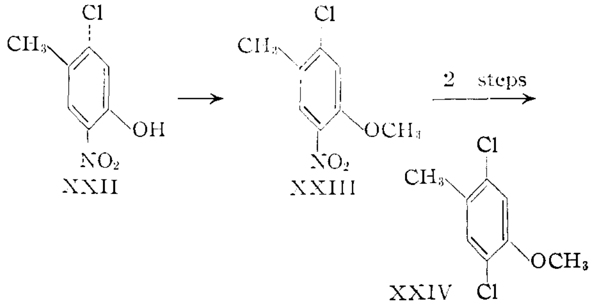
[10] E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, This Journal, **73**, 1220 (1951).

[11] B. A. Kent and S. Smiles, *J. Chem. Soc.*, 422 (1934).

[12] To minimize hydrolytic cleavage of the sulfones, hydroxide ion in aqueous dioxane was chosen as the basic reagent to promote the rearrangement. The nucleophilic reactivity of hydroxide ion in aqueous dioxane is relatively low; *cf.* J. F. Bunnett and G. T. Davis, This Journal, **76**, 3011 (1954).

fone XIX, rearrangement to sulfinic acid XX, and two-step desulfination to ether XXI.

The above structural assignments depend on the authenticity of the chlorophenols of type XIII. Evidence for the structure of 6-chloro-3,4-dimethylphenol has been given by Hinkel, Collins and Ayling.[13] 2,5-Dichloro-4-methylphenol (XIIIc) is a new compound. It was prepared by chlorination of 3-chloro-4-methylphenol (Ic) with sulfuryl chloride, but this does not prove its structure. Its structure is indicated by the fact that its methyl ether XXIV has also been prepared from the known 5-chloro-2-nitro-4-methylphenol (XXII) *via* its methyl ether XXIII. The identity of samples of XXIV from the two different sources was established by the identity of their melting points and infrared spectra, and by the fact that a mixed melting point was not depressed.



XXII

XXIII

XXIV

Experimental[14]

***o*-Nitrobenzenesulfenyl chloride** was generously furnished by the Monsanto Chemical Co. **3-Chloro-4-methylphenol** (Ic)[15] and **3-bromo-4-methylphenol** (Id)[16] were prepared by standard methods.

Sulfides IIb and IIIb.—*o*-Nitrobenzenesulfenyl chloride (18.9 g.) and Eastman Kodak Co. 3,4-dimethylphenol (13.6 g.) were combined with 30 cc. of chloroform and the solution was heated at 100–110° for three hours. The solvent was removed by vacuum evaporation, and the residue was treated with dilute sodium hydroxide solution. The undissolved fraction was removed and discarded, and the desired sulfides were precipitated by acidification of the alkaline solution. When dry, the mixture of IIb and IIIb weighed 20.7 g. (75%). The mixture was separated by crystallization from chloroform into three fractions, and each fraction was further fractionated by chromatography on alumina with benzene and then chloroform and then acetone being used as solvents. The first fraction from the crystallization proved to be richest in IIb, and eventually 4.23 g. of pure IIb was isolated. The third fraction was richest in IIIb, and eventually 1.09 g. of pure IIIb was obtained.

4,5-Dimethyl-2-hydroxy-2′-nitrodiphenyl sulfide (IIb) melts at 163–165°[17] and is obtained as yellow prisms from chloroform.

Anal. Calcd. for $C_{14}H_{13}NO_3S$: C, 61.06; H, 4.75. Found: C, 60.93; H, 4.81.

5,6-Dimethyl-2-hydroxy-2′-nitrodiphenyl sulfide (IIIb) melts at 175–177° and is obtained as yellow prisms from chloroform or acetic acid.

Anal. Calcd. for $C_{14}H_{13}NO_3S$: C, 61.06; H, 4.75. Found: C, 61.17; H, 4.75.

IIc and IIIc.—*o*-Nitrobenzenesulfenyl chloride (23.0 g.), 17.0 g. of Ic and 30 cc. of chloroform were combined and heated for three hours at 100–110°. After the solvent had been removed by vacuum evaporation, the mixture was treated with dilute sodium hydroxide solution. The resulting solution was filtered, and to the filtrate hydrochloric acid was added. The precipitated mixture of IIc and IIIc was crystallized from chloroform. The first crop of crystals (9.9 g.) was nearly pure IIc. The second crop (5.9 g.) was further fractionated by chromatography on alumina with chloroform being used as solvent. Eventually 2.31 g. of nearly pure IIc and 0.76 g. of nearly pure IIIc were so obtained.

4-Chloro-2-hydroxy-5-methyl-2′-nitrodiphenyl sulfide (IIc), m.p. 191–193°, was obtained as yellow needles by crystallization from benzene.

Anal. Calcd. for $C_{13}H_{10}ClNO_3S$: C, 52.79; H, 3.41. Found: C, 53.10; H, 3.58.

6-Chloro-2-hydroxy-5-methyl-2′-nitrodiphenyl sulfide (IIIc), m.p. 175–177°, was obtained as yellow needles by crystallization from benzene.

Anal. Calcd. for $C_{13}H_{10}ClNO_3S$: C, 52.79; H, 3.41. Found: C, 52.77; H, 3.58.

Sulfides IId and IIId.—*o*-Nitrobenzenesulfenyl chloride (18.9 g.), 18.6 g. of Id and 30 cc. of chloroform were heated at 100–110° for three hours. By procedures similar to those described above, 7.95 g. of nearly pure IId and 0.64 g. of nearly pure IIId were isolated.

4-Bromo-2-hydroxy-5-methyl-2′-nitrodiphenyl sulfide (IId), m.p. 198–200°, was obtained as yellow needles by crystallization from benzene.

Anal. Calcd. for $C_{13}H_{10}BrNO_3S$: C, 45.89; H, 2.96. Found: C, 45.88; H, 2.96.

6-Bromo-2-hydroxy-5-methyl-2′-nitrodiphenyl sulfide (IIId), m.p. 174–176°, was obtained as yellow needles by crystallization from benzene.

Anal. Calcd. for $C_{13}H_{10}BrNO_3S$: C, 45.89; H, 2.96. Found: C, 46.15; H, 3.26.

3-Chloro-4,5-dimethyl-2-hydroxy-2′-nitrodiphenyl Sulfide (XVIII).—A solution of IIb and sulfuryl chloride in chloroform was allowed to stand for ten hours at room temperature. The product was isolated by standard procedures and finally was purified by chromatography on alumina. XVIII was obtained as yellow needles, m.p. 164–166°, by crystallization from benzene.[17]

Anal. Calcd. for $C_{14}H_{12}ClNO_3S$: C, 54.28; H, 3.91. Found: C, 55.35; H, 4.09.

3-Chloro-5,6-dimethyl-2-hydroxy-2′-nitrodiphenyl Sulfide (XIVb).—A solution of IIIb (0.5 g.) and sulfuryl chloride (0.6 g.) in 20 cc. of chloroform was allowed to stand for ten hours at room temperature. The product was isolated by standard procedures and finally was purified by chromatography on alumina. XIVb was obtained by crystallization from chloroform as yellow prisms of m.p. 183–185°.

XIVb was also obtained by heating 4.0 g. of 6-chloro-3,4-dimethylphenol[4,13] (XIIIb), m.p. 70–71°, with 4.5 g. of *o*-nitrobenzenesulfenyl chloride for three hours at 100–110°. After isolation of the product by standard procedures and purification by chromatography on alumina, XIVb was obtained as yellow prisms of m.p. 187–189° (lit.[4] 189°). The identity of the two samples was proved by the identity of their infrared spectra and the fact that a mixed melting point was not depressed.

Anal. Calcd. for $C_{14}H_{12}ClNO_3S$: C, 54.28; H, 3.91. Found: C, 54.31; H, 3.99.

3,6-Dichloro-2-hydroxy-5-methyl-2′-nitrodiphenyl Sulfide (XIVc).—IIIc was chlorinated as described above for IIIb, and the product was finally purified by chromatography on alumina. XIVc was obtained as yellow needles from benzene, m.p. 200–202°.

Anal. Calcd. for $C_{13}H_9Cl_2NO_3S$: C, 47.28; H, 2.75. Found: C, 47.80; H, 2.83.

Preparation of XIVc by condensation of *o*-nitrobenzenesulfenyl chloride with 3,6-dichloro-4-methylphenol (XIIIc) was not attempted. It was believed that two chlorine atoms would deactivate the phenol so strongly as to prevent condensation.

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(13) L. E. Hinkel, W. T. Collins and E. E. Ayling, *J. Chem Soc.*, **123**, 2968 (1923); see also E. Diepolder, *Ber.*, **42**, 2916 (1909).

(14) Analyses for carbon and hydrogen by Micro-Tech Laboratories, Skokie, Ill.

(15) F. Ullmann and C. Wagner, *Ann.*, **355**, 367 (1907).

(16) A. Higginbottom, P. Hill and W. F. Short, *J. Chem. Soc.*, 263 (1937); H. J. Lucas and N. F. Scudder, This Journal, **50**, 244 (1928).

(17) McClement and Smiles[4] reported that condensation of *o*-nitrobenzenesulfenyl chloride with 3,4-dimethylphenol formed IIb of m.p. 157°, and made no mention of the formation of IIIb. We think they had IIb in impure form. Their melting points for substances derived from IIb were all lower than observed by us. Thus they reported m.p. 152° for XVIII, m.p. 155° for XIX and m.p. 115° for XXI.

General Procedure for Oxidation of Sulfides to Sulfones.—The sulfide, of type II, III, XIV or XVIII, was suspended in about ten times its weight of glacial acetic acid and four to five molecular proportions of hydrogen peroxide were added in the form of a 30% solution. The mixture was heated three to four hours on the steam-bath. It was diluted with water, and the precipitated sulfone was recrystallized from a benzene–petroleum ether mixture or from dilute acetic acid. Properties and analytical data for the sulfones so prepared are listed in Table I. All these compounds showed strong infrared absorption in the region 1120 to 1160 cm.$^{-1}$ characteristic of sulfones.[18]

When sulfide IIIb was heated with three molecular proportions of hydrogen peroxide in acetic acid for one hour, a mixture of Vb and the corresponding sulfoxide was produced. The sulfoxide was isolated by crystallizing the mixture from a benzene–chloroform mixture in which the sulfone is more soluble. 5,6-Dimethyl-2-hydroxy-2′-nitrodiphenyl sulfoxide was obtained as pale yellow needles of m.p. 200–202°.

Anal. Calcd. for $C_{14}H_{13}NO_4S$: C, 57.72; H, 4.50. Found: C, 57.63; H, 4.52.

The structure of this compound is further confirmed by the facts that it could be oxidized to sulfone Vb and that its infrared spectrum has a well-defined band at 1000–1020 cm.$^{-1}$ characteristic of sulfoxides.[18] As mentioned above, the characteristic phenolic hydroxyl band was missing from the infrared spectrum.

The first attempt to oxidize IId to IVd furnished a compound of m.p. 190–192° (pale yellow prisms from benzene), which was probably the corresponding sulfoxide. It was further oxidized by hydrogen peroxide in acetic acid to form IVd. A similar compound, m.p. 175–178°, was formed during the incomplete oxidation of IIId to Vd. It also appeared as pale yellow prisms from benzene, and was probably a sulfoxide because it could be further oxidized to Vd. Another apparent sulfoxide, m.p. 175–178° (pale yellow needles from benzene), was obtained from an incomplete oxidation of XIVb to XVb. It showed characteristic sulfoxide but not sulfone absorption in the infrared.

TABLE I

SULFONES

Sulfone	M.p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
IVa	140–142[a]	$C_{13}H_{11}NO_5S$	53.23	3.78	53.22	3.86
IVb	178–181	$C_{14}H_{13}NO_5S$	54.71	4.26	54.40	4.23
IVc	128–130	$C_{13}H_{10}ClNO_5S$	47.64	3.08	47.34	3.24
IVd	152–154	$C_{13}H_{10}BrNO_5S$	41.95	2.71	41.61	2.90
Vb	146–148	$C_{14}H_{13}NO_5S$	54.71	4.26	54.51	4.26
Vc	169–171	$C_{13}H_{10}ClNO_5S$	47.64	3.08	47.71	3.26
Vd	154–156	$C_{13}H_{10}BrNO_5S$	41.95	2.71	42.32	2.85
XVb	178–180[b]	$C_{14}H_{12}ClNO_5S$	49.20	3.54	49.00	3.72
XVc	135–137	$C_{13}H_9Cl_2NO_5S$	43.11	2.51	43.54	3.06
XIX	179–181[c]	$C_{14}H_{12}ClNO_5S$	49.20	3.54	49.55	3.68

[a] Levy, Rains and Smiles[7] reported m.p. 140–141° for IVa. [b] McClement and Smiles[4] reported m.p. 177° for XVb. [c] See footnote 17.

General Procedure for the Preparation of Sulfinic Acids.—A sulfone (Table I) was dissolved in 0.5% aqueous sodium hydroxide containing 1.5 moles of sodium hydroxide per mole of sulfone. The solution was allowed to stand a few minutes or was heated several hours on the steam-bath, depending on whether or not there was a 6-substituent in the sulfone. The solution was saturated with carbon dioxide and was then extracted with benzene to remove unrearranged sulfone and phenoxathiin dioxide that may have formed. The water layer was acidified with hydrochloric acid, and the precipitated crystalline mass was collected on a suction filter, washed several times with distilled water and finally dried at room temperature in a vacuum over phosphorus pentoxide. Recrystallization was avoided because of the instability of sulfinic acids to heat. Properties and analyses for the sulfinic acids so obtained are listed in Table II. It will be noted that the agreement between calculated and found percentages for carbon and hydrogen is poor according to the usual standards. The hydrogen analysis is high for all the sulfinic acids and the carbon analysis is low except for VIa and the 6-substituted sulfinic acids (VIIb, VIIc and XVIb). It is possible that traces of water remaining in the analytical samples caused the effects noted. All the 6-substituted sulfinic acids analyzed high for carbon. It is not obvious why the 6-substituents should cause such an effect.

TABLE II

SULFINIC ACIDS

Sulfinic acid	M.p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
VIa	134–136	$C_{13}H_{11}NO_5S$	53.22	3.78	53.63	3.85
VIb	130–132	$C_{14}H_{13}NO_5S$	54.71	4.26	53.89	4.[illegible]2
VIc	140–142	$C_{13}H_{10}ClNO_5S$	47.64	3.08	46.83	3.43
VId	135–137	$C_{13}H_{10}BrNO_5S$	41.95	2.71	41.10	3.28
VIIb	122–124	$C_{14}H_{13}NO_5S$	54.71	4.26	55.13	4.56
VIIc	128–130	$C_{13}H_{10}ClNO_5S$	47.64	3.08	47.71	3.51
XVIb	136–138	$C_{14}H_{12}ClNO_5S$	49.20	3.54	50.86	4.05
XX	137–139	$C_{14}H_{12}ClNO_5S$	49.20	3.54	48.26	3.87

General Procedure for Desulfination of Sulfinic Acids.—A sulfone (100 mg.) (Table I) was dissolved in 4 cc. of 0.25 *M* sodium hydroxide and heated on the steam-bath a few minutes if there was a 6-substituent or several hours if there was not. The solution was acidified with acetic acid, 0.15 g. of mercuric chloride was added and the solution was heated on the steam-bath for 30 minutes. The precipitate, presumably a mercury compound, was collected and suspended in a mixture of 5 cc. of concentrated hydrochloric acid and 5 cc. of ethanol. The mixture was refluxed one hour on the steam-bath, diluted with water and extracted with benzene. The benzene extract was concentrated to furnish the crude ether which was purified by chromatography on alumina. All ethers but Xb were finally obtained as colorless prisms by crystallization from petroleum ether. Properties, yields and analyses of the diphenyl ethers so obtained are recorded in Table III.

Substituted Diphenyl Ethers from *o*-Chloronitrobenzene and Phenols.—*o*-Chloronitrobenzene was mixed with a phenol of type I or XIII (2.0 molecular proportions) and potassium hydroxide (1.2 molecular proportions) and the mixture was heated in an oil-bath at 120–130° for two or three hours. The cooled mass was treated with 5% aqueous sodium hydroxide and the resulting suspension was extracted with benzene. The ether remaining after evaporation of the benzene was purified by chromatography on alumina. All the ethers in Table III except Xb and XXI were prepared in this fashion, and identity of the ethers prepared in the two different ways was established in each case by the identity of infrared spectra and the failure of mixed melting points to be depressed.

Thorough Examination of Rearrangement Products.—The rearrangements of three sulfones under the conditions chosen for the kinetics study were studied with particular care as follows: the sulfone (about 0.003 to 0.004 mole) was combined with sodium hydroxide (1.2 molecular proportions) in 250 cc. of 50% dioxane and maintained at 46° for 5 hours in the case of IVa and 54 hours in the cases of IVc and IVd. The solution was then concentrated to about 100 cc. under reduced pressure and was extracted with benzene (phenoxathiin dioxide fraction). The aqueous layer was saturated with carbon dioxide and again was extracted with benzene (sulfone fraction). The water layer was then acidified with acetic acid and mercuric chloride (1.5 moles per mole of sulfone) and 20 cc. of ethanol were added. The solution was heated on the steam-bath for 30 minutes and the precipitated product was collected and boiled for one hour with 30 cc. of concentrated hydrochloric acid and 30 cc. of ethanol. It was strongly diluted with water and extracted with benzene (ether fraction). Each fraction of benzene extract was concentrated and the residue chromatographed on alumina.

From 1.173 g. of IVa, 688 mg. (75%) of Xa and 1.6 g. of XIIa (1.6%) were obtained. No *o*-nitrophenol could be found. 2-Methylphenoxathiin 10-dioxide (XIIa) was obtained as colorless needles, m.p. 135–137° (lit.[19] 134–135°), by crystallization from a benzene–petroleum ether mixture.

Anal. Calcd. for $C_{13}H_{10}O_3S$: C, 63.38; H, 4.09. Found: C, 63.72; H, 4.24.

From 1.117 g. of IVc, 685 mg. (76%) of Xc and 47 mg. (4.9%) of XIIc were obtained, and 61 mg. (5.5%) of unre-

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[18] K. C. Schreiber, *Anal. Chem.*, **21**, 1168 (1949); D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

[19] C. M. Suter and F. O. Green, THIS JOURNAL, **59**, 2578 (1937).

TABLE III

SUBSTITUTED DIPHENYL ETHERS OBTAINED BY DESULFINATION OF SULFINIC ACIDS

Starting sulfone	Product ether	Yield, %	M.p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
IVa	Xa	60	47–49	$C_{13}H_{11}NO_3$	68.11	4.84	68.36	4.73
IVb	Xb[a]	71						
Vb	Xb[a]	99						
IVc	Xc	57	59–61	$C_{13}H_{10}ClNO_3$	59.21	3.82	59.22	3.85
Vc	Xc	31						
IVd	Xd	55	62–64	$C_{13}H_{10}BrNO_3$	50.67	3.27	51.06	3.51
Vd	Xd	29						
XVb	XVIIb[b]	70	78–80	$C_{14}H_{12}ClNO_3$	60.55	4.36	60.65	4.35
XVc	XVIIc	29	76–78	$C_{13}H_9Cl_2NO_3$	52.37	3.04	52.35	3.04
XIX	XXI[c]	57	121–123	$C_{14}H_{12}ClNO_3$	60.55	4.36	61.01	4.32

[a] Melting points and analyses were not determined for Xb, but the samples obtained from IVb and Vb were found to have identical infrared spectra. [b] McClement and Smiles[4] reported m.p. 71° for XVIIb. [c] See footnote 17.

acted IVc was recovered. No *o*-nitrophenol was found. 3-Chloro-2-methylphenoxathiin 10-dioxide (XIIc) was obtained as colorless needles, m.p. 178–180°, by crystallization from a benzene–petroleum ether mixture.

Anal. Calcd. for $C_{13}H_9ClO_3S$: C, 55.62; H, 3.23. Found: C, 55.42; H, 3.28.

From 1.489 g. of IVd, 674 mg. (54%) of Xd and 46 mg. (3.5%) of XIId were obtained, and 40 mg. (3%) of unreacted IVd was recovered. No *o*-nitrophenol was found. 3-Bromo-2-methylphenoxathiin 10-dioxide (XIId) was obtained as colorless needles, m.p. 189–191°, by crystallization from a benzene–petroleum ether mixture.

Anal. Calcd. for $C_{13}H_9BrO_3S$: C, 48.01; H, 2.79. Found: C, 47.80; H, 3.03.

The Sequence VIa → XI → Xa.—An aqueous solution of VIa, sodium hydroxide and potassium permanganate was heated 30 minutes on the steam-bath. The mixture was filtered, sulfuric acid was added to the filtrate, and the acidified filtrate was concentrated almost to dryness *in vacuo*. The residue was crystallized from chloroform as colorless plates, m.p. 105–107°. The analysis indicates that these were the dihydrate of 2-(*o*-nitrophenoxy)-5-methylbenzenesulfonic acid (XI).

Anal. Calcd. for $C_{13}H_{11}NO_6S{\cdot}2H_2O$: C, 45.21; H, 4.38. Found: C, 45.30; H, 4.33.

One hundred milligrams of XI was boiled for three hours with 10 cc. of 60% sulfuric acid. The mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with a sodium carbonate solution and then was evaporated to a small volume and chromatographed on alumina. The product, after crystallization from petroleum ether, had m.p. 45–47° and the melting point was not depressed on admixture with authentic Xa.

2,5-Dichloro-4-methylphenol (XIIIc).—A solution of 5.68 g. of Ic and 6.0 g. of sulfuryl chloride in 50 cc. of chloroform was allowed to stand overnight at room temperature. The solution was concentrated *in vacuo*, the residue was steam distilled, and the distillate was extracted with benzene. After evaporation of the benzene, 6.1 g. of raw product remained. By chromatography on alumina, the greatest part of this was obtained as impure XIIIc of m.p. 60–62°.

In another run, the crude XIIIc was converted to its acetate ester which was purified by chromatography and finally hydrolyzed, but the purity of the XIIIc obtained was no greater.

Finally, pure XIIIc was obtained by refluxing its purified methyl ether XXIV (below) with hydroiodic acid (sp. gr. 1.5) for three hours, isolating the product by standard procedures and finally crystallizing it from petroleum ether. Colorless needles, m.p. 64–66°, were obtained. This purified XIIIc was used to prepare a sample of XVIIc which was identical with XVIIc derived from XIVc.

5-Chloro-2-nitro-4-methylphenol (XXII).—This compound was prepared in two ways. First, the known[20] 5-chloro-2-nitro-4-methylaniline, m.p. 165–167°, was diazotized and the diazonium solution was decomposed in a boiling aqueous solution of sodium sulfate, copper sulfate and sulfuric acid. The yield of crude XXII was about 40%; the crude product was purified by chromatography on alumina and finally crystallization from petroleum ether, whence it was obtained as long yellow needles, m.p. 70–72° (Davies[20] reported m.p. 71°). Second, Ic was nitrated by nitric acid in glacial acetic acid (two hours at room temperature) with care to use an equimolar amount of nitric acid. The product was purified by chromatography on alumina, and its m.p. was again 70–72°. The identity of the two samples was shown by the identity of infrared spectra and the failure of a mixed melting point to be depressed.

5-Chloro-2-nitro-4-methylanisole (XXIII).—A solution of 2.0 g. of XXII and excess diazomethane in ether was allowed to stand two hours at room temperature. The ether was removed and the residual yellow oil was purified by chromatography on alumina with benzene being used as solvent. The first fractions were recrystallized from petroleum ether; 1.2 g. of colorless prisms of m.p. 93–95° (lit.[21] 94°) was obtained.

Anal. Calcd. for $C_8H_8ClNO_3$: C, 47.66; H, 4.00. Found: C, 47.90; H, 4.00.

2,5-Dichloro-4-methylanisole (XXIV).—This compound was also prepared in two ways. The first, which shows its structure, involved reduction of XXIII with tin and hydrochloric acid to the corresponding amino compound which was then converted to XXIV by a Sandmeyer reaction.[21] The XXIV so obtained had, after purification by chromatography on alumina, m.p. 30–32°. The second method, which was preparatively useful, involved treating XIIIc with excess diazomethane in ether solution for two hours at room temperature, removing the solvent and purifying the residue by chromatography on alumina with a petroleum ether–benzene mixture being used as solvent. The white solid so obtained had m.p. 30–32°. A mixed melting point of the two samples was not depressed, and their infrared spectra were identical.

Anal. Calcd. for $C_8H_8Cl_2O$: C, 50.29; H, 4.22. Found: C, 50.60; H, 4.33.

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[20] J. J. Blanksma, *Rec. trav. chim.*, **29**, 414 (1910); W. Davies, *J. Chem. Soc.*, **119**, 853 (1921).

[21] O. De Vries, *Rec. trav. chim.*, **28**, 395 (1909), prepared XXIII by another method, and thence XXIV of m.p. 29° (or 44°). His structural assignments are supported by work of L. Limpach, *Ber.*, **22**, 789 (1889), and of F. Kaufler and F. Wenzel, *ibid.*, **34**, 2238 (1901).