of amines and higher yields of ammonia are usually obtained, and in that an appreciable amount of nitrogen is liberated during the reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation and Properties of 2,4-Dimethoxyphenyl Alkyl Sulfides[1]

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Since *p*-hydroxyphenyl alkyl sulfides have been found to be active germicides[2] it became of interest to study some analogous dihydroxy compounds. Although the present attempts to prepare 2,4-dihydroxyphenyl alkyl sulfides were unsuccessful the results obtained are of some interest.

Compounds of the type under consideration may obviously be made by alkylation of 2,4-dihydroxythiophenol or of a related derivative which contains groups convertible into hydroxyls. Three possible synthetic methods have been investigated. The action of cold chlorosulfonic acid upon dicarbethoxyresorcinol did not give appreciable amounts of a monosulfonyl chloride which is in contrast to the behavior of carbethoxyphenol[3] with this reagent. A sulfonyl chloride of this type could presumably be reduced to the thiol, alkylated, and the carbethoxy groups removed by hydrolysis. Since thiocyanates can be readily reduced to thiols, direct thiocyanation of resorcinol was attempted according to the method of Kaufmann.[4] No thiocyanoresorcinol could be isolated from the reaction mixture. A non-phenolic compound of unknown structure and a red tar were the only products. The third method of preparation studied involved the demethylation of 2,4-dimethoxyphenyl alkyl sulfides which were prepared by the following series of reactions.

$$(CH_3O)_2C_6H_4 \longrightarrow (CH_3O)_2C_6H_3SO_3K \longrightarrow (CH_3O)_2C_6H_3SO_2Cl \longrightarrow$$
$$(CH_3O)_2C_6H_3{-}SH \longrightarrow (CH_3O)_2C_6H_3{-}S{-}R$$

That the sulfonation product of resorcinol dimethyl ether has the structure indicated was shown by chlorinating it in aqueous solution to the 4,6-dichlororesorcinol dimethyl ether whose structure is known,[5] replacement of the sulfo group by chlorine occurring readily. The 2,4-dimethoxythiophenol has been previously[6] obtained in small amounts as a by-product in the reduction of resorcinol dimethyl ether disulfonyl chloride.

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(1) A portion of a paper presented before the Medicinal Division of the American Chemical Society at the Denver Meeting, August, 1932.

(2) Suter and Hansen, THIS JOURNAL, **54**, 4100 (1932).

(3) Gebauer-Fuelnegg and Schlesinger, *Ber.*, **61**, 781 (1928).

(4) Kaufmann, *ibid.*, **62**, 390 (1929).

(5) Jacobs, Heidelberger and Rolf, THIS JOURNAL, **41**, 463 (1919).

(6) Pollak and Wienerberger, *Monatsh.*, **35**, 1489 (1914).

It has been shown elsewhere[2] that the presence of a methoxyl group in the benzene ring para to a sulfide linkage results in an exaltation of the molecular refraction. The influence of two methoxyl groups upon this property is shown in the last column of Table I.

TABLE I

Compound	d_4^{25}	n_D^{25}	MR Found	MR Calcd.	EM_D
2,4-Dimethoxythiophenol	1.1864	1.5820	47.88	45.52	2.36
2,4-Dimethoxyphenyl ethyl sulfide	1.1204	1.5660	57.71	54.64	3.07
2,4-Dimethoxyphenyl *n*-propyl sulfide	1.0867	1.5580	62.97	59.06	3.91
2,4-Dimethoxyphenyl *n*-butyl sulfide	1.0742	1.5502	67.11	63.48	3.63

Demethylation of the dimethoxyphenyl alkyl sulfides did not give the expected dihydroxy compounds. Small yields of oily products which apparently contained only one hydroxyl group were isolated. Since the structure and purity of these compounds are still somewhat uncertain their discussion is deferred.

Experimental

2,4-Dimethoxybenzenesulfonic Acid.—To 25 g. (0.18 mole) of resorcinol dimethyl ether was added gradually with stirring 27 g. (0.36 mole) of concentrated sulfuric acid. The temperature of the reaction mixture rose to 85°. After standing for one hour the viscous mixture was poured into a saturated potassium carbonate solution. The white crystalline precipitate which contained some carbonate and sulfate was dried in the oven at 110°. The yield of crude product, which is satisfactory for the preparation of the sulfonyl chloride, was 49 g. The theoretical yield is 46.5 g. Since the potassium salt was not easily obtained in a completely pure state the *p*-toluidine salt was prepared for identification and analytical purposes. This compound separated slowly from a dilute hydrochloric acid solution of *p*-toluidine and the potassium salt. After two recrystallizations from a mixture of ethyl alcohol and chloroform it melted at 191–192° (corr.).

Anal. Calcd. for $C_{15}H_{19}O_5NS$: N, 4.31. Found: N, 4.33, 4.34.

Chlorination of Potassium 2,4-Dimethoxybenzenesulfonate.—Chlorine was passed into a solution of 1.8 g. of the potassium salt dissolved in 50 cc. of water until no more precipitate formed. The yellowish solid was recrystallized from 85% ethyl alcohol. The yield of fine white needles of the dichloro compound was 0.7 g. or 48% of the theoretical amount. The melting point was 116.5–117.5°, which is in good agreement with the values given in the literature[5,7] for the 4,6-dichlororesorcinol dimethyl ether.

2,4-Dimethoxybenzenesulfonyl Chloride.—In a small round-bottomed flask were placed 64 g. (0.25 mole) of dry finely powdered potassium 2,4-dimethoxybenzene sulfonate and 64 g. (0.42 mole) of phosphorus oxychloride. The reactants were thoroughly mixed and heated on the steam-bath for an hour. After cooling to room temperature the reaction mixture was poured with vigorous stirring onto chipped ice. The white solid which separated was dissolved in ether, the ether dried with calcium chloride and evaporated at room temperature. There remained 40 g. of the sulfonyl chloride melting at 67–69°, which is 68% of the theoretical amount. At ordinary temperature this changes to a purple mass which is insoluble in ether, so must be preserved in a refrigerator. The crude product was used for the preparation of the thiol. It may be recrystallized from a mixture of benzene and petroleum ether (60–90°) from which it is deposited as fine white needles which soften at 69° and melt at 70.5°.

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(7) Auwers and Pohl, *Ann.*, **405**, 279 (1914).

Anal. Calcd. for $C_8H_9O_2ClS$: S, 13.55. Found: S, 13.57.

By treatment of the sulfonyl chloride with a mixture of ethyl alcohol and concentrated ammonia solution the amide was formed. After two crystallizations from hot alcohol this melted at 166–167°.

Anal. Calcd. for $C_8H_{11}O_4NS$: N, 6.45. Found: N, 6.44, 6.47.

2,4-Dimethoxythiophenol.—The sulfonyl chloride was reduced by the method described in "Organic Syntheses"[8] for preparing thiophenol. From 140 g. (0.6 mole) of the crude sulfonyl chloride there was obtained 50 to 55 g. (49–54% of the theoretical amount) of a colorless oil boiling at 115–117° under 5 mm. pressure. The bright yellow lead salt was analyzed.

Anal. Calcd. for $C_{16}H_{18}O_4S_2Pb$: Pb, 37.98. Found: Pb, 37.83.

2,4-Dimethoxyphenyl Alkyl Sulfides.—These were prepared in the same manner as the *p*-methoxyphenyl alkyl sulfides previously described.[9] The results are tabulated in Table II.

TABLE II

Compound	Yield, %	B. p., °C.	Pressure, mm.	Sulfur, % Calcd.	Sulfur, % Found
$(CH_3O)_2C_6H_3SCH_3$[10]	82	115–118 m. p. 38–39	4	17.40	17.51
$(CH_3O)_2C_6H_3SC_2H_5$	90	140–142	7	16.17	16.11
$(CH_3O)_2C_6H_3SC_3H_7$-*n*	83	157–160	8	15.10	14.87
$(CH_3O)_2C_6H_3SC_4H_9$-*n*	92	148–151	6	14.17	14.21

Summary

Monosulfonation of resorcinol dimethyl ether gave the 4-sulfonic acid. Several derivatives of this have been prepared.

A series of four 2,4-dimethoxyphenyl alkyl sulfides has been prepared. The molecular refraction of these compounds shows considerable exaltation.

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[8] "Organic Syntheses," John Wiley and Sons, N. Y., 1921, Vol. I, p. 71.

[9] Suter and Hansen, THIS JOURNAL, **54**, 4103 (1932).

[10] The melting point given by Pollak and Wienerberger, Ref. 6, for this compound is 33–37°.