ide is obtained can be accounted for by the formation of the piperazinedione.

## Experimental

**Decarboxylation.**—A typical experimental procedure is described. The ratio of reactants is that previously employed in the synthesis of acetamidoketones from amino acids.[5a] Three grams (0.013 mole) α-(benzenesulfonamido)-propionic acid, m.p. 126°, 5.3 ml. (0.065 mole) of pyridine and 7.4 ml. (0.078 mole) of acetic anhydride were mixed in a 25-ml. distilling flask equipped with a cold finger and a side arm arranged to collect the evolved gases under water saturated with carbon dioxide. The reaction mixture was heated immediately after mixing for 40 minutes under gentle reflux, during which time the evolution of gas practically ceased. The volume of gas, corrected for a small blank, was 170 ml. at S.T.P. or 58% of the theoretical amount of carbon dioxide expected if the acid was completely decarboxylated. This gas gave a precipitate with barium hydroxide and was completely soluble in sodium hydroxide.

The reaction mixture was acidified with an excess of hydrochloric acid and ice and extracted with ether. The combined extracts were washed with dilute acid, water, and then with saturated sodium bicarbonate solution until the latter had removed all acid present. The extracts were then dried and the ether removed under vacuum. The residue was extracted with hot 60° petroleum ether, leaving behind a non-crystalline, resinous material. The extracts were evaporated to a small volume and decanted from a small amount of oily substance. Evaporation of the petroleum ether yielded 0.6 g. (39%) of crude diphenyl disulfide melting above 55°. After recrystallization from ethanol-water, the disulfide melted at 60–61°. The diphenyl disulfide was identified by bromination to 4,4′-dibromodiphenyl disulfide, m.p. 93–94°; reported 93.5°.[15]

When benzenesulfonamide was substituted for the α-(benzenesulfonamido)-propionic acid, no reaction was observed and the starting material was recovered; similarly α-(benzenesulfonamido)-propionic acid, when heated with pyridine alone, gave no carbon dioxide and the starting material was recovered. However, if the α-(benzenesulfonamido)-propionic acid was heated under reflux with acetic anhydride, about 30% of the theoretical amount of carbon dioxide was evolved and a dark tar, which could not be crystallized, remained after evaporation of the solvent. No diphenyl disulfide could be detected even after boiling with pyridine. One reaction which was swept out with carbon dioxide and allowed to stand 30 minutes gave only a 33% yield of carbon dioxide and 20% diphenyl disulfide. The gas evolved was completely soluble in sodium hydroxide.

One reaction mixture was worked up by direct distillation of the reaction mixture. From this was isolated a 42% yield of diphenyl disulfide and a hard, dark, resinous material was left in the reaction flask. No benzenesulfonic acid could be isolated as its *p*-toluidine salt from either acid or alkaline extracts obtained from this residue. This residue gave positive qualitative tests for nitrogen and sulfur.

**1,4-Dibenzenesulfonyl-3,6-dimethylpiperazinedione-2,5.**—In one experiment, the acetic anhydride was added in small portions over a period of 30 minutes. There was obtained a 57% yield of carbon dioxide, which includes air introduced along with the acetic anhydride, a 38% yield of diphenyl disulfide and 0.2 g. of 1,4-dibenzenesulfonyl-3,6-dimethylpiperazinedione-2,5 (7%) m.p. 233–235° (uncor.) after recrystallization from ethanol. This compound gave positive qualitative tests for sulfur and nitrogen. It was insoluble in cold, dilute acid or base, but dissolved readily on boiling with 5% sodium hydroxide.

*Anal.* Calcd. for $C_{18}H_{16}N_2S_2$: N, 6.66. Found: N, 6.83.

LOUISVILLE 8, KY. RECEIVED FEBRUARY 19, 1951

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[15] Bourgeois and Abraham, *Rec. trav. chim.*, **30**, 421 (1911).

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[CONTRIBUTION FROM THE NAUGATUCK CHEMICAL DIVISION OF THE U. S. RUBBER CO.]

# Some Thiazolylthio Hydroquinones

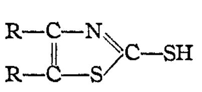
BY THOMAS H. NEWBY AND ELIZABETH C. HOWLETT

2-Mercaptobenzothiazole, 4,5-dimethyl-2-mercaptothiazole and 4-methyl-2-mercaptothiazole were treated with *p*-benzoquinone to give the corresponding thiazolylthio hydroquinones as shown by ultraviolet spectroscopic curves. The dibenzoates of the new compounds were prepared.

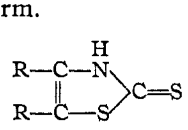
The addition of alkyl and aryl mercaptans to *p*-benzoquinone to give alkylthio and arylthio hydroquinones is well described in the literature[1]; however, no references to the reaction of thiazole mercaptans with quinone could be found. Inasmuch as alkylthio and arylthio hydroquinones had been found in this Laboratory to be of value as antioxidants, some thiazolylthio hydroquinones were prepared. 2-Mercaptobenzothiazole, 4,5-dimethyl-2-mercaptothiazole and 4-methyl-2-mercaptothiazole were used as starting materials because of cost and availability.

The reaction of mercaptans with *p*-benzoquinone to give dihydroxyphenyl monothioethers is complicated in many cases by the formation of di- and polythioethers; the initially formed dihydroxyphenyl thioether may or may not be oxidized by *p*-benzoquinone or air to the quinone thioether. If this oxidation occurs, a second molecule of mercaptan may add and the entire cycle be repeated.[1a]

The reaction of a thiazole mercaptan with *p*-benzoquinone is further complicated by the fact that thiazole mercaptans may exist in either the thiol (I) or the thione (II) form.



I



II

It is possible, then, for the product to be either a thioether or an aminohydroquinone derivative. Thiourea adds to *p*-benzoquinone to give a thioether.[2]

The additions of the thiazole mercaptans to *p*-benzoquinone were accomplished smoothly to give the desired 1:1 reaction products in good yield.

The compound obtained by treating 2-mercaptobenzothiazole with *p*-benzoquinone was subjected to ultraviolet spectrosopic analysis to determine its structure.[3] The curve obtained in this manner was compared to the curves obtained for authentic samples of 1-methyl-2-thio-1,2-dihydrobenzothiaz-

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[1] (a) J. Troeger and A. Eggert. *J. prakt. Chem.*, **53**, 482 (1896); (b) T. Posner, *Ann.*, **336**, 85 (1904); (c) J. Snell and A. Weissberger. THIS JOURNAL, **61**, 450 (1939); (d) O. Dimroth, L. Kraft and K. Aichinger, *Ann.*, **545**, 124 (1940).

[2] M. Schubert. THIS JOURNAL, **69**, 712 (1947).

[3] Ultraviolet spectroscopic analysis through the courtesy of Mr. J. E. Newell of the U. S. Rubber Company General Laboratories.

ole and 2-methylthiobenzothiazole[4] and found to correspond very closely to the latter curve. Figure 1 shows the curve obtained for 2-(benzothiazolylthio)-hydroquinone and Table I gives a comparison of the maxima and inflection points for this compound with those of 1-methyl-2-thio-1,2-dihydrobenzothiazole and 2-methylthiobenzothiazole. These data show the thioether structure of 2-(benzothiazolylthio)-hydroquinone and by analogy of the other products.

TABLE I

| 2-Methylthiobenzothiazole | | 2-Thio-1-methyl-1,2-dihydrobenzothiazole | | 2-(Benzothiazolylthio)-hydroquinone | |
|---|---|---|---|---|---|
| $\lambda_{max.}$ | log $E_{max.}$ | $\lambda_{max.}$ | log $E_{max.}$ | $\lambda_{max.}$ | log $E_{max.}$ |
| 300.5 | 3.92 | 324.5 | 4.41 | 300.5 | 4.03 |
| ~290[a] | 4.01 | ~282 | 3.43 | ~287 | 4.08 |
| 280 | 4.09 | ~255 | 3.87 | 280 | 4.10 |
| ~244 | 3.92 | 241 | 4.14 | 224.5 | 4.45 |
| 224 | 4.36 | 231 | 4.13 | | |

[a] Indicates an inflection point.

The hydroquinone structure for these compounds was established by the preparation of their dibenzoates. The attempted extension of these reactions to $\alpha$-naphthoquinone yielded only tars from which no pure compounds could be isolated.

## Experimental[5]

**(2-Benzothiazolylthio)-hydroquinone.**—*p*-Benzoquinone (22 g., 0.2 mole) was dissolved in 150 ml. of boiling methanol and the solution cooled rapidly to 0–5° in an ice-bath, whereupon the *p*-benzoquinone crystallized in fine needles.[1d] A slurry of 2-mercaptobenzothiazole (33.5 g., 0.2 mole) in 100 ml. of ice-cold methanol was then added and the mixture was stirred for two hours at 0–5°. Most of the material went into solution. The product was isolated by filtering off a small amount of methanol-insoluble material and then quenching the filtrate in 500 ml. of hot water. The aqueous mixture was boiled and the lumps broken up until the solid was no longer sticky. After filtration and drying at 100°, 42 g. (76%) of crude product was obtained melting at 204.5–208°. After recrystallization from ethyl acetoacetate the melting point was 218–219°. The pure compound is soluble in methanol only to the amount of 3% even at elevated temperature. The solubility peculiarity evident from the above also exists when acetic acid is used as a solvent.

*Anal.* Calcd. for $C_{13}H_9O_2NS_2$: C, 56.73; H, 3.27; N, 5.09; S, 23.27. Found: C, 56.01; H, 3.29; N, 5.05; S, 23.42.

The dibenzoate[6] melted at 150–151°.

*Anal.* Calcd. for $C_{27}H_{17}O_4NS_2$: N, 2.89; S, 13.20. Found: N, 2.88; S, 13.16.

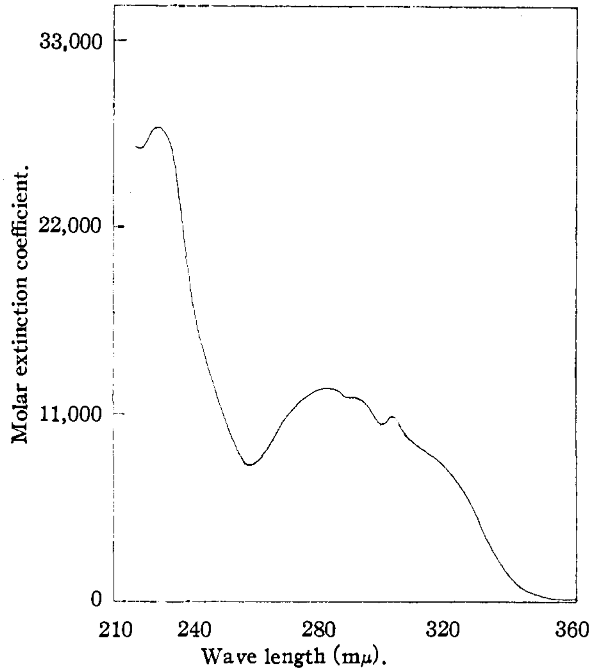

Fig. 1.

**(4,5-Dimethyl-2-thiazolylthio)-hydroquinone.**—*p*-Benzoquinone (11 g., 0.1 mole) and 4,5-dimethyl-2-mercaptothiazole (15 g., 0.1 mole) reacted as was described above. The product was worked up by removing most of the methanol under vacuum and then pouring the residue into 300 ml. of hot water. After boiling the slurry and filtering and drying the precipitate, a yield of 23 g. (90%) was obtained. Treatment of this solid with hot methanol removed a small amount of methanol-soluble material leaving 20 g. (77%) melting at 169–171°.

*Anal.* Calcd. for $C_{11}H_{11}O_2NS_2$: N, 5.54; S, 25.30. Found: N, 5.37; S, 25.57.

The dibenzoate[6] melted at 153–154°.

*Anal.* Calcd. for $C_{25}H_{19}O_4NS_2$: N, 3.07; S, 14.00. Found: N, 3.00; S, 13.91.

**(4-Methyl-2-thiazolylthio)-hydroquinone.**—*p*-Benzoquinone (22 g., 0.2 mole) and 4-methyl-2-mercaptothiazole (26 g., 0.2 mole) reacted as was described above. The product was worked up by filtering off the methanol-insoluble material (11 g.) and then quenching the filtrate in hot water. After boiling the slurry for a short time the precipitate was collected. The dried product weighed 32 g. (67%) and melted at 158–161° after washing with hot benzene.

*Anal.* Calcd. for $C_{10}H_9O_2NS_2$: N, 5.88; S, 26.89. Found: N, 5.89; S, 27.04.

The dibenzoate[6] melted at 113–114°.

*Anal.* Calcd. for $C_{24}H_{17}O_4NS_2$: N, 3.13; S, 14.32. Found: N, 3.05; S, 14.28.

NAUGATUCK, CONN.

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[4] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1321 (1939).

[5] All melting points are uncorrected.

[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 137, Procedure 5.