[Contribution from the Noyes Chemical Laboratory, University of Illinois]

THE REARRANGEMENT OF 2-CHLOROISOPROPYL PHENYL SULFIDE

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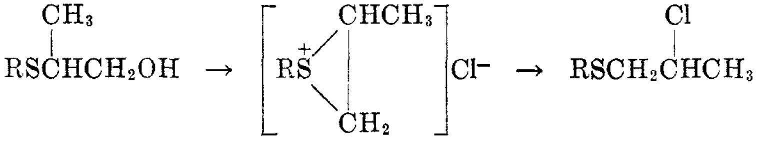
It has been shown that treatment of 2-hydroxyethyl 2-hydroxyisopropyl sulfide and ethyl 2-hydroxyisopropyl sulfide with hydrochloric acid or thionyl chloride yields 2-chloroethyl 2-chloro-*n*-propyl sulfide and ethyl 2-chloro-*n*-propyl sulfide, respectively, instead of the expected isopropyl sulfides (I).[2] It was postulated that the rearrangement proceeds through a cyclic sulfonium intermediate (I).



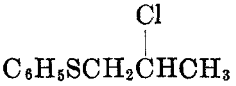
I

Conversely, rearrangement of an *n*-propyl structure to an isopropyl structure is involved in the ring contraction of 6-hydroxy-1,4-dithiacycloheptane to 2-chloromethyl-1,4-dithian (2). Similar rearrangements, presumably involving the intermediate formation of ethylenimonium compounds, have been observed with a number of β-chloro amines (3).

Several observations recorded in the literature indicate that the isomerization of the isopropyl structure to the *n*-propyl structure, encountered in open-chain *alkyl* β-chloro sulfides, may not occur if an *aryl* group is attached to the sulfur atom. The 2,3-*bis*-(phenylmercapto)-1-halopropanes, the preparation of which has been reported (4), contain such an aryl grouping and would be expected to rearrange to 1,3-*bis*-(phenylmercapto)-2-halopropanes if the rearrangement is general. Also the intermediate sulfonium salt may not form since it has been found that certain aryl ω-haloalkyl sulfides form cyclic sulfonium salts less readily than do the corresponding alkyl ω-haloalkyl sulfides (5). In order to determine whether the presence of an aryl group does prevent rearrangement, a study was undertaken of 2-hydroxyisopropyl phenyl sulfide (II), the hydroxy sulfide which would give the simplest aryl β-chloro sulfide with the requisite structure for isomerization. We have found that treatment of this hydroxy sulfide with thionyl chloride does give the rearranged product, 2-chloro-*n*-propyl phenyl sulfide (III), instead of 2-chloroisopropyl phenyl sulfide (IV).

$C_6H_5S\overset{CH_3}{\overset{|}{C}}HCH_2OH$

II



$C_6H_5SCH_2\overset{Cl}{\overset{|}{C}}HCH_3$

III

$C_6H_5S\overset{CH_3}{\overset{|}{C}}HCH_2Cl$

IV

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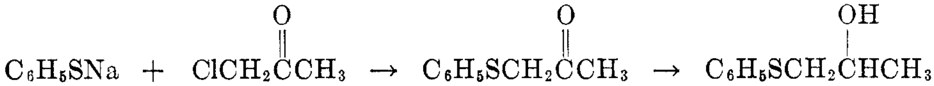
[2] Woodward and co-workers, *J. Chem. Soc.*, 38, 47 (1948) prepared the chlorosulfide from 2-hydroxyethyl 2-hydroxyisopropyl sulfide but did not observe the rearrangement.

2-Hydroxyisopropyl phenyl sulfide (II) was prepared by condensing thiophenol with allyl alcohol in the presence of sulfur. The addition of mercapto compounds to olefins is known to proceed according to Markovnikov's rule in the presence of sulfur (6). Moreover, our product proved to be different from 3-hydroxy-*n*-propyl phenyl sulfide (7), the other possible addition product.

2-Hydroxy-*n*-propyl phenyl sulfide (VI), an oil, was made by an unequivocal method; acetonyl phenyl sulfide (V), prepared from sodium phenyl mercaptide and chloroacetone, was reduced with aluminum isopropoxide under mild conditions.



$$C_6H_5SNa + ClCH_2\overset{\overset{O}{\|}}{C}CH_3 \rightarrow \underset{V}{C_6H_5SCH_2\overset{\overset{O}{\|}}{C}CH_3} \rightarrow \underset{VI}{C_6H_5SCH_2\overset{\overset{OH}{|}}{C}HCH_3}$$

V VI

The conversion of 2-hydroxyisopropyl phenyl sulfide (II) to a chlorosulfide was effected in 83% yield by use of thionyl chloride. That rearrangement occurred, giving 2-chloro-*n*-propyl phenyl sulfide (III) instead of 2-chloroisopropyl phenyl sulfide (IV), was shown by several reactions. The chloro sulfide was oxidized to a chloro sulfone by the usual method in 75% yield. Formation of the sulfone served to prevent any further rearrangement since this grouping no longer can form a sulfonium salt. That the chloro sulfone was 2-chloro-*n*-propyl phenyl sulfone (VII), was shown by hydrolysis with sodium carbonate solution and conversion of the unisolated hydrolysis product to the 3,5-dinitro ester (IXb), m.p. 184.5–185.5°. The ester was obtained in only 15% yield based on the chloro sulfone, but no other product was isolated. It was found to be identical with the 3,5-dinitrobenzoate (IXa) prepared from 2-hydroxy-*n*-propyl phenyl sulfone (VIII). Nitration of the chloro sulfone produced a 77% yield of a solid nitro derivative, presumed to be 2-chloro-*n*-nitrophenyl sulfone (X) since phenyl sulfones are known to yield the *m*-nitro derivatives almost exclusively (9).

Reactions used to characterize the chloro sulfide were also found to yield derivatives of 2-hydroxy-*n*-propyl phenyl sulfide (VI). Condensation of the chloro sulfide with sodium *p*-nitrobenzoate or partial hydrolysis followed by treatment with *p*-nitrobenzoyl chloride gave products which were found to be identical with the *p*-nitrobenzoate of 2-hydroxy-*n*-propyl phenyl sulfide.

EXPERIMENTAL

All melting points are uncorrected.

2-Hydroxyisopropyl phenyl sulfide (II). This compound was prepared by a modification of the method used for the synthesis of 2-hydroxyethyl 2-hydroxyisopropyl sulfide (1). A solution of 55.1 g. (0.5 mole) of thiophenol, 34.8 g. (0.6 mole) of allyl alcohol, and 0.5 g. of sulfur was heated under reflux for twenty-four hours. An ether solution of the crude product was washed with 5% sodium hydroxide solution and with water, and then dried over magnesium sulfate. Removal of the ether and distillation of the residue from a Claisen flask yielded 44.0 g. (52%) of the hydroxy sulfide; b.p. 100–114° (0.5–0.7 mm.). Fractionation of a sample through a 10-cm., vacuum-jacketed, Vigreux column gave an almost colorless oil with a pleasant sulfide odor; b.p. 98–100° (0.5 mm.); n_D^{20} 1.5710; d_{20}^{20} 1.103; MR_D 50.14. Calc'd for $C_9H_{12}OS$: MR_D 49.66.

Anal. Calc'd for $C_9H_{12}OS$: C, 64.24; H, 7.19; S, 19.05.
Found: C, 64.28; H, 7.29; S, 18.92.

The *sulfide p-nitrobenzoate* (XI) was made from 1.7 g. of the hydroxy sulfide (II) by the general procedure for preparing esters using an acid chloride and pyridine (10). Less than one gram of the white crystalline product remained after three recrystallizations from dilute ethyl alcohol; m.p. 47–48°.

Anal. Calc'd for $C_{16}H_{15}NO_4S$: C, 60.55; H, 4.76; N, 4.41; S, 10.10.
Found: C, 60.69; H, 4.73; N, 4.11; S, 10.28.

The *sulfone p-nitrobenzoate* (XIIa) was produced when a mixture of 0.3 g. of the sulfide ester (XI), 1.0 g. of 30% hydrogen peroxide solution, and 3 ml. of acetone was heated under reflux for eight hours. After distillation of the acetone the crude solid was recrystallized twice from dilute ethyl alcohol and once from 95% ethyl alcohol. The white crystalline sulfone melted at 112–113°.

Anal. Calc'd for $C_{16}H_{15}NO_6S$: C, 55.01; H, 4.33; N, 4.01; S, 9.18.
Found: C, 55.06; H, 4.37; N, 3.99; S, 8.98.

The *hydroxy sulfone* (XIII) was prepared by slowly adding, with cooling and stirring, 17.0 g. of 30% hydrogen peroxide solution to 8.4 g. of the hydroxy sulfide (II) dissolved in 100 ml. of glacial acetic acid. After the initial heat of reaction had dissipated, the solution was heated overnight at 60–70°. Distillation of the solvents under diminished pressure gave the theoretical amount of residue, which failed to crystallize and boiled at 164–170° (1.2 mm.). 2-Hydroxyisopropyl phenyl sulfone is reported to melt at 46° (11).[3]

The *sulfone benzoate* (XIV) was obtained from 1.0 g. of the undistilled hydroxy sulfone (XIII) by the method of Otto (11). Less than one gram of white crystals remained after three recrystallizations from dilute ethyl alcohol; m.p. 80.5–81.5°. Otto reports the melting point as 71–72°.

Anal. Calc'd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; S, 10.53.
Found: C, 63.28; H, 5.57; S, 10.35.

The *sulfone p-nitrobenzoate* (XIIb) obtained previously by oxidation of the sulfide *p*-nitrobenzoate (XI) also was synthesized from 1.0 g. of the undistilled hydroxy sulfone (XIII) by the general procedure involving the use of pyridine (10). Four recrystallizations of the crude product from ethyl alcohol gave about two-tenths gram of white crystals; m.p. 112–113°. A mixture of this ester with the sulfone *p*-nitrobenzoate (XIIa), prepared from the sulfide ester, melted at 112–113°.

The *sulfone 3,5-dinitrobenzoate* (XV) was prepared from 2.0 g. of the undistilled hydroxy sulfone (XIII) by use of 3,5-dinitrobenzoyl chloride and pyridine (10). About two grams of white crystals remained after two recrystallizations from ethyl alcohol; m.p. 121.5–122.5°.

Anal. Calc'd for $C_{16}H_{14}N_2O_8S$: C, 48.73; H, 3.59; N, 7.11; S, 8.13.
Found: C, 49.23; H, 3.72; N, 7.28; S, 8.31.

2-Hydroxy-n-propyl phenyl sulfide (VI). Acetonyl phenyl sulfide (V) was prepared in 86% yield from 1.0 molar quantities of sodium phenyl mercaptide and chloroacetone by the procedure of Autenrieth (12); b.p. 83–87° (0.3–0.5 mm.); m.p. 32–35°. Fractionation of a sample through a 10-cm., vacuum-jacketed, Vigreux column gave an almost colorless product; b.p. 87° (0.4 mm.); m.p. 35–36°. *Acetonyl phenyl sulfide* has been reported to melt at 34–35° (13) and 36° (12).

The *keto sulfone* (XVI) was prepared from 1.7 g. of the keto sulfide (V) by oxidation with hydrogen peroxide in glacial acetic acid in the usual manner. Recrystallization from water gave a white crystalline product; m.p. 55.5–56.5°. *Acetonyl phenyl sulfone* is reported to melt at 56–57° (13, 14).

The reduction of acetonyl phenyl sulfide (V) was carried out by the procedure employed with acetonyl ethyl sulfide (1). The keto sulfide, 83.0 g. (0.5 mole), and 300 ml. of a 1 *M*

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[3] It is possible that the compound reported by Otto (11) as 2-hydroxyisopropyl phenyl sulfone may be the 2-hydroxy-*n*-propyl phenyl sulfone, a compound also prepared in this investigation and found to melt at 46–47°.

solution of aluminum isopropoxide (15) were used, and the reaction was allowed to continue for forty-eight hours. Distillation of the crude product from a Claisen flask yielded 38.5 g. (46%) of *2-hydroxy-n-propyl phenyl sulfide*, b.p. 87–97° (0.4 mm.). Fractionation of a sample through a 10-cm., vacuum-jacketed, Vigreux column gave a colorless oil with a pleasant odor, b.p. 85.5–86.5° (0.3–0.4 mm.); n_D^{20} 1.5705; d_{20}^{20} 1.103; MR_D 50.21; Calc'd for $C_9H_{12}OS$: 49.66.

Anal. Calc'd for $C_9H_{12}OS$: C, 64.24; H, 7.19.
Found: C, 64.03; H, 7.05.

A number of derivatives of 2-hydroxy-*n*-propyl phenyl sulfide (VI) were obtained by the procedures used for the preparation of the corresponding derivatives of 2-hydroxyisopropyl phenyl sulfide (II).

The *sulfide p-nitrobenzoate* (XVIIa), approximately one-half gram, was obtained from 1.7 g. of the hydroxy sulfide (VI). The white crystalline solid melted at 64.5–65.5° after three recrystallizations from ethyl alcohol.

Anal. Calc'd for $C_{16}H_{15}NO_4S$: C, 60.55; H, 4.76; N, 4.41; S, 10.10.
Found: C, 60.71; H, 4.95; N, 4.44; S, 10.17.

The *sulfone p-nitrobenzoate* (XVIIIa) obtained by oxidation of 0.5 g. of the sulfide ester (XVIIa), melted at 163.5–164.5° after three recrystallizations from ethyl alcohol.

The crude *hydroxy sulfone* (VIII), prepared from 12.6 g. of the hydroxy sulfide (VI) was dissolved in ether, and the ether solution was washed with 5% sodium bicarbonate solution and with water. Distillation of the ether left 14.0 g. (93%) of residue. Two recrystallizations of a small sample of the product from a large volume of petroleum ether (b.p. 30–60°) gave white crystals; m.p. 46–47°.

Anal. Calc'd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04.
Found: C, 54.26; H, 6.26.

The *sulfone benzoate* (XIX), about one-half gram, was prepared from 2.0 g. of the hydroxy sulfone (VIII). The white crystalline product melted at 55–56° after two recrystallizations from 95% ethyl alcohol followed by two recrystallizations from dilute ethyl alcohol.

Anal. Calc'd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; S, 10.53.
Found: C, 63.25; H, 5.47; S, 10.35.

The *sulfone p-nitrobenzoate* (XVIIIb) was prepared from 2.0 g. of the hydroxy sulfone (VIII). Two recrystallizations from 95% ethyl alcohol gave approximately one gram of white crystals; m.p. 163.5–164.5°. A mixture of this compound with the sulfone ester (XVIIIa) obtained from the sulfide ester melted at 163.5–164.5°.

Anal. Calc'd for $C_{16}H_{15}NO_6S$: C, 55.01; H, 4.33; N, 4.01; S, 9.18.
Found: C, 55.15; H, 4.58; N, 3.88; S, 9.21.

The *sulfone 3,5-dinitrobenzoate* (IXa), about one and one-half grams, was obtained from 1.0 g. of the hydroxy sulfone (VIII). The white crystalline product melted at 184.5–185° after two recrystallizations from 95% ethyl alcohol.

Anal. Calc'd for $C_{16}H_{14}N_2O_8S$: C, 48.73; H, 3.59; N, 7.11; S, 8.13.
Found: C, 48.81; H, 3.39; N, 7.04; S, 8.22.

Nitration of the hydroxy sulfone (VIII) by a modification of the procedure of Ipatieff, Pines, and Friedman (9b) for the nitration of alkyl phenyl sulfones gave a compound believed to be *2-hydroxy-n-propyl m-nitrophenyl sulfone nitrate* (XX). One gram of the hydroxy sulfone, dissolved in 4 ml. of concentrated sulfuric acid, was treated with 3 ml. of concentrated nitric acid, added dropwise with swirling over a 15-minute period. After the reaction mixture had cooled to room temperature it was poured on cracked ice and triturated until a solid was obtained. One recrystallization from 50% ethyl alcohol solution gave 1.2 g. of a white crystalline solid, m.p. 90–91°, which corresponds to an 83% yield of the expected product.

Anal. Calc'd for $C_9H_{10}N_2O_7S$: C, 37.24; H, 3.47; N, 9.65; S, 11.05.
Found: C, 37.38; H, 3.35; N, 9.54; S, 11.08.

2-Chloro-n-propyl phenyl sulfide (III), the chloro sulfide from 2-hydroxyisopropyl phenyl sulfide (II). A modification of the procedure of Fuson, Price, and Burness (1) for the conversion of hydroxy sulfides to chloro sulfides was employed. The reaction was carried out in the hood because of the possible vesicant properties of the product. A solution of 16.8 g. (0.1 mole) of 2-hydroxyisopropyl phenyl sulfide (II) in 25 ml. of dry chloroform was treated with 9.2 g. (0.11 mole) of colorless thionyl chloride, dissolved in 15 ml. of dry chloroform. After removal of the solvent and excess thionyl chloride the crude product was fractionated through a 10-cm., vacuum-jacketed, Vigreux column; b.p. 83–86° (0.1–0.2 mm.); yield 15.5 g. (83%). The product was a colorless oil with a characteristic odor; n_D^{20} 1.5680.

Anal. Calc'd for $C_9H_{11}ClS$: C, 57.90; H, 5.94; Cl, 18.99; S, 17.17.
Found: C, 57.83; H, 5.90; Cl, 18.94; S, 17.43.

2-Hydroxy-n-propyl phenyl sulfide p-nitrobenzoate (XVIIb) from 2-chloro-n-propyl phenyl sulfide (III). This derivative was prepared by a modification of the general procedure for the formation of esters from alkyl halides and salts of acids (16). A solution of sodium ethoxide was prepared from 0.23 g. of sodium metal and 10 ml. of absolute ethyl alcohol, and 1.84 g. of *p*-nitrobenzoic acid was added. The mixture was swirled for five minutes to complete the formation of the salt, and 1.87 g. of the chloro sulfide (III) was added. The heterogeneous mixture was heated under reflux for one and one-half hours, and the solvent was distilled on a steam-bath. The residue was extracted with ether, the ether extract was washed with 5% sodium bicarbonate solution and with water, and the ether was removed on a steam-bath. Recrystallization of the product three times from 95% ethyl alcohol yielded about one-half gram of white crystals; m.p. 64–65°. A mixture of this product with the 2-hydroxy-*n*-propyl phenyl sulfide *p*-nitrobenzoate (XVIIa) prepared previously melted at 64–65°.

Oxidation of 0.4 g. of this sulfide *p*-nitrobenzoate (XVIIb) to the *sulfone p-nitrobenzoate* (XVIIIc) was carried out as previously indicated (XVIIa → XVIIIa). Two recrystallizations of the crude product from 95% ethyl alcohol left 0.3 g. of white crystals; m.p. 163.5–164.5°. Mixtures of this product with the samples of 2-hydroxy-*n*-propyl phenyl sulfone *p*-nitrobenzoate (XVIIIa and XVIIIb) prepared previously melted at 163.5–164.5°.

Hydrolysis of 2-chloro-n-propyl phenyl sulfide (III) and conversion of the product to 2-hydroxy-n-propyl phenyl sulfide p-nitrobenzoate (XVIIc). The hydrolysis was carried out by a modification of the method used for the hydrolysis of 2-chloroethyl 2,2-dichloroethyl sulfide (17). The undistilled chloro sulfide (III), obtained from 25.2 g. of 2-hydroxyisopropyl sulfide, was stirred for two days with a solution of 12.6 g. of sodium bicarbonate in 2 l. of water. The reaction mixture was extracted with ether, the ether extract was washed with water and dried over magnesium sulfate, and the ether was removed on a steam-bath. Distillation of the crude product produced 18 g. of a colorless oil; b.p. 98–106° (1.0–1.5 mm.). The product must have contained some unchanged chloro sulfide since it gave a positive test for halogen with silver nitrate solution.

2-Hydroxy-n-propyl phenyl sulfide p-nitrobenzoate (XVIIc), about three-tenths gram, was obtained from 5 g. of the hydrolysis product and *p*-nitrobenzoyl chloride. After four recrystallizations from 95% ethyl alcohol it melted at 64.5–65.5°. A mixture of this product with the *p*-nitrobenzoate (XVIIb) prepared from 2-hydroxy-*n*-propyl phenyl sulfide (VI) melted at 64.5–65.5°.

The *sulfone p-nitrobenzoate* (XVIIId) was obtained from 0.3 g. of the above sulfide ester (XVIIc) in the usual manner. It melted at 163.5–164.5° after two recrystallizations from 95% ethyl alcohol. Mixtures of this product with other samples (XVIIIa, XVIIIb, and XVIIIc) of 2-hydroxy-*n*-propyl phenyl sulfone *p*-nitrobenzoate melted at 163.5–164.5°.

2-Chloro-n-propyl phenyl sulfone (VII). Oxidation of 15.5 g. of the chloro sulfide (III) was carried out by treatment with 28.3 g. of 30% hydrogen peroxide solution in 60 ml. of glacial acetic acid. After removal of the solvents the crude product was distilled through a 10-cm., vacuum-jacketed, Vigreux column. The colorless oil boiled between 130° and 138° at 0.2–0.4 mm. The yield was 13.5 g. (75%).

Anal. Calc'd for $C_9H_{11}ClO_2S$, C, 49.42; H, 5.07; Cl, 16.21; S, 14.66.
Found: C, 49.41; H, 4.96; Cl, 16.16; S, 14.76.

Nitration of the chlorosulfone (VII) by the procedure employed for the preparation of

2-hydroxy-*n*-propyl *m*-nitrophenyl sulfone nitrate (XX) produced a compound thought to be *2-chloro-n-propyl m-nitrophenyl sulfone* (X). From 0.8 g. of the chloro sulfone 0.75 g. (77%) of white crystals was obtained after two recrystallizations from 50% ethyl alcohol solution, m.p. 72.5–73.5°.

Anal. Calc'd for $C_9H_{10}ClNO_4S$: C, 40.99; H, 3.82; N, 5.31; Cl, 13.45; S, 12.16.
Found: C, 41.15; H, 3.81; N, 5.44; Cl, 13.48; S, 12.41.

Hydrolysis of 2-chloro-n-propyl phenyl sulfone (VII) and conversion of the product to 2-hydroxy-n-propyl phenyl sulfone 3,5-dinitrobenzoate (IXb). A mixture of 2.2 g. of the chloro sulfone (VII), 200 ml. of 0.1 *N* sodium carbonate solution, and 0.2 g. of potassium iodide was heated under reflux for two and one-half hours. The resulting homogeneous solution was extracted with ether. The ether solution was washed with water and dried over sodium sulfate. The residue obtained by removal of the ether was treated with 3,5-dinitrobenzoyl chloride in the usual manner. After four recrystallizations from ethyl alcohol 0.6 g. (15%) of the white crystalline ester was obtained; m.p. 184.5–185°. A mixture of this product with the 2-hydroxy-*n*-propyl phenyl sulfone 3,5-dinitrobenzoate (IXa) prepared previously melted at 184.5–185°.

SUMMARY

2-Hydroxyisopropyl phenyl sulfide undergoes rearrangement to give 2-chloro-*n*-propyl phenyl sulfide when treated with thionyl chloride.

The structure of the product was shown by oxidation of the chloro sulfide to the chloro sulfone, hydrolysis of the chloro sulfone to the hydroxy sulfone, and treatment of the hydroxy sulfone with 3,5-dinitrobenzoyl chloride. The 3,5-dinitrobenzoate was found to be identical with that of 2-hydroxy-*n*-propyl phenyl sulfone.

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