these crystals at 70° caused a change to prisms, m.p. 102.5–103.5°. The analytical sample, prepared by further recrystallizations from the same solvent pair, had m.p. 86–87°, which changed to 101–102.5° after storage of the product for one month at room temperature.

Anal. Calcd. for $C_7H_7N_2OBr$: N, 13.03. Found: N, 12.96.

No cyclization products were obtained from reactions in which the substance was treated with potassium amide in liquid ammonia, with sodium ethoxide in ethanol at 150–160°, with sodium hydride in refluxing xylene or with sodium amide in refluxing cumene.

4-Benzylaminopyridine. A mixture of 3 g. of 4-aminopyridine, 4.5 g. of benzaldehyde and 10 ml. of cumene was refluxed for 2 hr., during which period water was removed periodically by co-distillation with cumene. The mixture was cooled, then after addition of 6 ml. of 98% formic acid it was refluxed again for 17 hr. Fifty ml. of water was added to the two-phase system after cooling and the aqueous layer was separated, washed with three 25-ml. portions of ether, then made alkaline with saturated aqueous sodium carbonate. The precipitated white solid weighed 4.19 g. and melted at 107.5–109.5°. Recrystallizations from ether-petroleum ether afforded 3.99 g. (69%) of white prisms, m.p. 110.5–111°. The picrate was formed in methanol and recrystallized from the same solvent, m.p. 138.5–139.5°.[24]

Absorption spectra. The ultraviolet spectra of the 5-azaindole samples were determined from $10^{-4}M$ solutions in 95% ethanol. Measurements were carried out with either a Beckman model DU spectrophotometer or a Beckman model DK-1 instrument.

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[24] T. Kahto and M. Ohta, *J. Pharm. Soc. Japan*, **71**, 217 (1951) report m.p. 108–109.5° for the amine and m.p. 140–142° for the picrate.

Reaction of Styrene Oxide with 2-Naphthalenethiol

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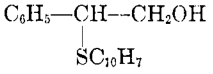
Styrene oxide has been shown by Gilman and Fullhart[2] to react with potassium methyl mercaptide and form the secondary alcohol, $C_6H_5CHOHCH_2SCH_3$. More recently Rondestvedt[3] reported that the reaction of styrene oxide with potassium benzyl mercaptide in dioxane gave the corresponding secondary alcohol. This direction of ring opening was considered normal by these investigators.

Since styrene oxide had been found to react with sodium 2-naphthoxide in water predominantly by nuclear attack, forming 2-(2-hydroxy-1-naphthyl)-2-phenylethanol,[4] and since the analogous compound that would result from a comparable reaction between styrene oxide and 2-naphthalenethiol was now sought, the latter compounds were subjected to appropriate reaction conditions. This was undertaken in spite of the known lack of nucleophilic reactivity of the ring in such thiophenols.[5] The substance that was isolated, in 80% yield, was shown to have structure I. The reaction in aqueous medium with excess sodium hydroxide present was relatively rapid at 0–5°. Little, if any, of the secondary alcohol could have been formed. Both of the possible isomeric alcohols were synthesized by reliable methods for structure proof as reported in the experimental portion.



$$\underset{\textstyle SC_{10}H_7}{C_6H_5—\overset{|}{C}H—CH_2OH}$$

I

The direction of ring opening of styrene oxide in aqueous alkali is thus the same with 2-naphthol and 2-naphthalenethiol. For these two compounds differences in the rate of reaction and structure of products seem to result, in part, from the nature of the nucleophilic species.[5,6] It is our conjecture that solvent effects are partially responsible for the difference in the direction of ring opening of styrene oxide observed by us and the aforementioned investigators.[7] In an experiment not reported here the reaction of styrene oxide with the sodium salt of 2-naphthalenethiol in dioxane evidently formed the secondary alcohol predominantly.

EXPERIMENTAL[8]

Reaction of styrene oxide with 2-naphthalenethiol in aqueous sodium hydroxide. A mixture of 2-naphthalenethiol (11.0 g., 0.069 mole, Eastman product recrystallized to m.p. 80–82°) in sodium hydroxide (5.0 g., 0.125 mole) and water (75 ml.) was stirred under nitrogen with warming to aid dissolution of the thiol. This was then cooled in an ice bath to below 5° prior to the addition of styrene oxide (4.0 g., 0.033 mole, b.p. 45° (2 mm.), n_D^{20} 1.5345) in portions in 5 min. A reaction occurred almost immediately as evidenced by the appearance of a fine precipitate. After 2 hr. the mixture was allowed to warm to room temperature, filtered, washed by

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[1] Taken in part from the M.S. thesis of Herbert S. Wilgus III, December 1955.

[2] H. Gilman and L. Fullhart, *J. Am. Chem. Soc.*, **71**, 1478 (1949).

[3] C. S. Rondestvedt, Jr., *J. Org. Chem.*, **21**, 911 (1956).

[4] C. O. Guss and L. H. Jules, *J. Am. Chem. Soc.*, **72**, 3878 (1950).

[5] *Eg.*, D. S. Tarbell, and A. H. Herz, *J. Am. Chem. Soc.*, **75**, 1668 (1953) and references mentioned there.

[6] O. R. Quale and E. E. Royals, *J. Am. Chem. Soc.*, **64**, 226 (1942); J. F. Bunnett and G. T. Davis, *J. Am. Chem. Soc.*, **76**, 3011 (1954).

[7] C. O. Guss and H. R. Williams, *J. Org. Chem.*, **16**, 1809 (1951).

[8] Temperature measurements are uncorrected.

dispersion in water until the filtrate was no longer turbid when acidified, and dried to obtain 9.0 g. (96.8%), m.p. 87–98°. Acidification of the first filtrate gave 5.7 g. of recovered thiol, m.p. 75–82°.

Two recrystallizations from heptane[9] gave 7.4 g. (80%), m.p. 100–103°. The pure 2-(2-naphthylmercapto)-2-phenylethanol (I) melted at 102–103°, from dilute ethanol.

Anal. Calcd. for $C_{18}H_{16}OS$: C, 77.11; H, 5.75. Found: C, 77.29; H, 6.04.

p-Nitrobenzoate was prepared as cream colored leaves from dilute ethanol, m.p. 106–108°.

Anal. Calcd. for $C_{25}H_{19}NO_4S$: C, 69.90; H, 4.46. Found: C, 70.17; H, 4.60.

Synthesis of α-(2-naphthylmercapto)phenylacetic acid. From 2-naphthalenethiol and mandelic acid. A mixture of 2-naphthalenethiol (8.0 g., 0.05 mole) and mandelic acid (6.1 g., 0.04 mole) was heated in a large test tube under nitrogen at an oil bath temperature of 190–195° for one hour.[10] The warm, amber colored reaction mixture, still liquid, was transferred by means of ethanol (100 ml.) to a beaker, and the resulting slurry warmed with 8 g. sodium bicarbonate in 250 ml. water to form the sodium salt. Some insoluble dinaphthyl disulfide was filtered off. Air was then bubbled through the aqueous filtrate at about 40° for 4 hr. to oxidize unreacted thiol to disulfide, finally giving 2.4 g. of the recrystallized disulfide, m.p. 137–139°, reported[11] m.p. 139°. Acidification of the aqueous mixture with concentrated hydrochloric acid produced 7.35 g. solid which, after three recrystallizations from dilute acetic acid (carbon black), gave 5.4 g. (45.9%), m.p. 169–171°. The analytical sample, from dilute ethanol, melted at 171–172°.

Anal. Calcd. for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79. Found: C, 73.52; H, 4.97.

Anilide was prepared by heating the acid with aniline at 150–170° under nitrogen for 2 hr. and found to melt at 173.5–174.5°, fine white needles from dilute ethanol.

Anal. Calcd. for $C_{24}H_{19}NOS$: C, 78.03; H, 5.18. Found: C, 78.09; H, 5.52.

p-Bromoanilide, similarly prepared, was a better derivative since its melting point was 188–189°, white needles from dilute ethanol.

Anal. Calcd. for $C_{24}H_{18}BrNOS$: C, 64.28; H, 4.05. Found: C, 64.43; H, 4.32.

From 2-naphthalenethiol and ethyl α-bromophenylacetate. Ethyl α-bromophenylacetate (6.1 g., 0.025 mole, n_D^{20} 1.5385) was added slowly to a stirred mixture of 2-naphthalenethiol (4.0 g., 0.025 mole) in sodium hydroxide (2.0 g., 0.05 mole) dissolved in water (50 ml.) under nitrogen. A precipitate began to appear after 20 min. at room temperature. At the end of 2 hr. the reaction mixture was transferred to a boiling flask containing 10 g. sodium hydroxide in water. The total volume was finally 200 ml. This was refluxed 2 hr. to produce a clear solution. The warm solution was treated with carbon black, being careful to keep the solution warm enough to prevent the crystallization of the sodium salt. Acidification of the filtrate with concentrated hydrochloric acid and recrystallization of the resulting solid from dilute acetic acid gave 6.6 g. (90.4%) fine, white needles, m.p. 169–172°. A mixed melting point of this acid and that prepared by the alternate method showed no depression.

Reduction of α-(2-naphthylmercapto)phenylacetic acid to I. Tetrahydrofuran was preferred to ether as the solvent because the acid was insoluble in ether. The α-(2-naphthylmercapto)phenylacetic acid (4.4 g., 0.015 mole, m.p. 169–117°) in tetrahydrofuran (30 ml.) was added to lithium aluminum hydride (1.0 g., 0.026 mole) in tetrahydrofuran (25 ml.) over a 15-min. period. After an additional 30 min. the mixture was treated with 10 ml. concentrated hydrochloric acid in 40 ml. water. The organic layer was taken up in ether and washed with 4% aqueous sodium hydroxide to remove some acid that was not reduced. After the ether solution was dried over anhydrous potassium carbonate and the solvent removed, the product was recrystallized from heptane[9] (carbon black) to yield 3.1 g. (73.8%), m.p. 100–103°. A mixture melting point with pure 2-(2-naphthylmercapto)-2-phenylethanol (I) from the reaction of styrene oxide with 2-naphthalenethiol was 101–103°.

Synthesis of 2-(2-naphthylmercapto)-1-phenylethanol. The preparation of α-(2-naphthylmercapto)acetophenone from phenacyl chloride and 2-naphthalenethiol followed the procedure of Long.[12] A nearly theoretical yield was obtained, m.p. 97–98°, white needles from ethanol.

Anal. Calcd. for $C_{18}H_{14}OS$: C, 77.66; H, 5.07. Found: C, 77.41; H, 5.41.

The *2,4-dinitrophenylhydrazone* melted at 209–210°, reddish orange needles from ethyl acetate–benzene.

Anal. Calcd. for $C_{24}H_{18}N_4O_4S$: C, 62.87; H, 3.96. Found: C, 63.03; H, 4.21.

Reduction of this ketone with excess lithium aluminum hydride by the conventional procedure provided an oil that soon solidified to a solid, m.p. 57–60° in quantitative yield. Recrystallization from a mixture of heptane[9] and benzene gave fine, white needles, m.p. 59–60°.

Anal. Calcd. for $C_{18}H_{16}OS$: C, 77.11; H, 5.75. Found: C, 77.16; H, 6.11.

The *p-nitrobenzoate* of this alcohol melted at 114–115°, yellow, from dilute ethanol.

Anal. Calcd. for $C_{25}H_{19}NO_4S$: C, 69.90; H, 4.46. Found: C, 69.80; H, 4.81.

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Reaction of Phenols with Phosphorus Pentachloride[1]

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Although the reaction of alcohols with phosphorus pentachloride is a standard method for the preparation of alkyl chlorides, little is known concerning the mechanism.[2] Gerrard and Phillips have postulated the formation of $ROPCl_4$ as an intermediate in this reaction.[3] This intermediate can be used to explain the formation of the alkyl chloride and phosphorus-containing by-products which are also obtained.[3] Although such alkoxyphosphorus tetrachlorides have never been isolated to our

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[1] Presented at the Southwest Regional Meeting of the American Chemical Society, San Antonio, Tex., Dec. 4–6, 1958.

[2] For a comprehensive review of earlier work and further work on the mechanism, see W. Gerrard, *J. Chem. Soc.*, 741 (1946).

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