[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Epoxides with Thiourea[1]

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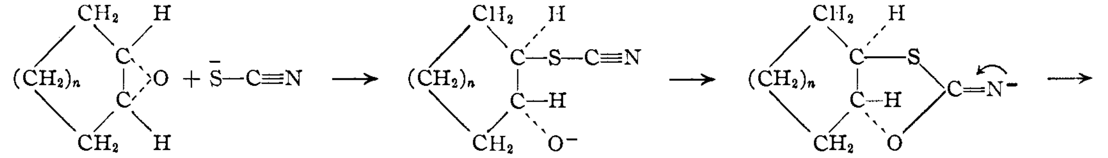
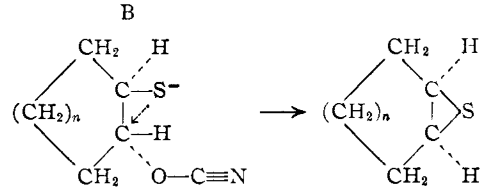
In the preparation of propylene sulfide from propylene oxide and thiourea in aqueous solutions the yield of propylene sulfide is improved by lowering the *p*H of the reaction mixture, which cuts down polymer formation. In the presence of an equivalent amount of an acid the reaction between thiourea and an epoxide yields a β-hydroxythiouronium salt. Generally these salts may be hydrolyzed to yield olefin sulfides or 2-hydroxyalkanethiols depending on the conditions used. The probable course of these reactions is discussed in light of these observations and the failure of S-(*trans*-2-hydroxycyclopentyl)-thiouronium sulfate to yield cyclopentene sulfide.

The transformation of epoxides to episulfides by the action of thiocyanates or thiourea in aqueous solutions at room temperature or below has been known for some time.[2] The mode of replacement of oxygen by sulfur under such mild conditions is sufficiently intriguing that it is perhaps not surprising that further studies of the course and mechanism of these reactions have been reported recently from three separate groups.[3–5] Van Tamelen[3] wrote the series of steps shown for the reaction of cyclic olefin oxides with thiocyanate ion. The evidence for this sequence, other than its inherent logic, was the failure of the reaction in the instance of cyclopentene oxide ($n = 1$) in contrast to the facile formation of cyclohexene sulfide under the same conditions. This is explicable in terms of the mechanism since the required cyclic intermediate B from cyclopentene oxide would contain a highly strained structure whereby two five-membered rings are fused in a *trans* configuration. Furthermore, *trans*-2-hydroxycyclohexyl thiocyanate (protonated A, $n = 2$) gave cyclohexene sulfide on treatment with potassium hydroxide, whereas *trans*-2-hydroxycyclopentyl thiocyanate did not. Finally, cyclopentene sulfide was formed from *trans*-2-chlorocyclopentanethiol and sodium bicarbonate, which suggests that the reaction with cyclopentene oxide would have been successful if C had been formed.



A B



C

Price and Kirk[4] further substantiated this mechanism by observing that D(+)-2,3-butylene oxide with thiocyanate ion gave L(−)-2,3-butylene sulfide indicating that inversion had taken place at each asymmetric carbon. Also, they were able to isolate the N-*p*-nitrobenzoyl derivative of the cyclic intermediate B (protonated form) from a reaction starting with propylene oxide.

Culvenor, Davies and Savige[5] have written comparable mechanisms for the reaction of epoxides with thiourea, substituted thioureas, thioamides and potassium methyl xanthate; they also suggest that intermediates similar to B are important in a number of other reactions involving β-substituted thiols or sulfides.

During the past few years our attention also has been directed toward a study of the course of the reaction of epoxides with thiourea. Most of the work was done with propylene oxide. In our hands yields of propylene sulfide of only about 30% were obtained, together with appreciable amounts of polymer, when propylene oxide was added to aqueous thiourea solutions. Addition of 2.5 mole % of acid to the aqueous solution increased the yields from reactions run under comparable conditions to 50%. Use of an equimolar quantity of acid (hydrochloric, *p*-toluenesulfonic, perchloric, sulfuric, benzoic or acetic) gave the corresponding 2-hydroxy-2-propylthiouronium salt in yields up to 80%.[6] This reaction was also observed with 1-hexene oxide, cyclohexene oxide[6] and cyclopentene oxide. S-(*trans*-2-Hydroxycyclohexyl)-thiuronium sulfate was found to be only slightly soluble in water, and S-(*trans*-2-hydroxycyclopentyl)-thiuronium sulfate was only moderately soluble.

The nature of the products obtained on alkaline hydrolysis of the various salts was found to depend on the procedure used. If excess *aqueous alkali was added to* the acidic solutions of the salts the major product was the alkene sulfide, except in the instance of S-(*trans*-2-hydroxycyclopentyl)-thiuronium sulfate, which failed to yield any cyclopentene sulfide. If the *acidic salt solutions were added to*

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[1] This investigation was carried out as a part of American Petroleum Institute Project 48B.

[2] K. Dachlauer and L. Jackel, French Patent 797,621; *C. A.*, **30**, 7122 (1936).

[3] E. E. van Tamelen, THIS JOURNAL, **73**, 3444 (1951).

[4] C. C. Price and P. F. Kirk, *ibid.*, **75**, 2396 (1953).

[5] C. C. Culvenor, W. Davies and W. E. Savige, *J. Chem. Soc.* 4480 (1952).

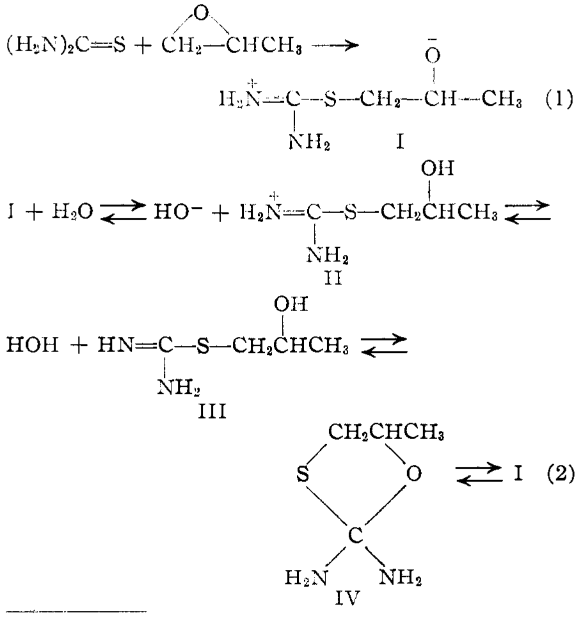
[6] The reaction of thiourea with a number of reactive ethers in the presence of acids has been observed previously, see L. C. King, R. M. Dodson and L. A. Subluskey, THIS JOURNAL, **70**, 1176 (1948), and L. A. Subluskey and L. C. King, *ibid.*, **73**, 2647 (1951). The reaction of cyclohexene oxide with *p*-toluenesulfonic acid and thiourea has been described by F. N. Hayes, Doctoral Dissertation, Northwestern University, June, 1949.

an excess of aqueous alkali the major product was the 2-hydroxyalkanethiol in every instance.

Propylene sulfide was formed also by heating a dioxane solution of 2-hydroxy-1-propylthiuronium acetate, or by heating an aqueous solution of the acetate (albeit in poor yield), or by pyrolysis of the dry benzoate. Aqueous solutions of the chloride or sulfate did not yield propylene sulfide on heating. Thus, propylene sulfide can be generated in weakly acidic solutions (*p*H 6), but not in solutions of *p*H of 1–2. In the reaction of propylene oxide with thiourea in aqueous solutions (neutral at the start), the solution becomes basic (*p*H 10) almost immediately. Under these conditions the propylene sulfide partially polymerizes; as mentioned previously, use of 2.5 mole % of acid reduced the quantity of polymer and improved the yield. In reactions where aqueous solutions of bases were added to the thiuronium salts better yields were obtained using sodium carbonate than with sodium hydroxide (some polymer formed) or potassium bicarbonate. In the sodium carbonate neutralization the solution became buffered and the *p*H did not rise much above 8. When the sodium carbonate solution was added in increments, propylene sulfide formation was observed to occur at the point where the *p*H rose above 7.0.

Our interpretation of these results is essentially that of previous workers,[3–5] but some additional points are elucidated. The probable reaction sequences are illustrated with the reaction of propylene oxide and thiourea in aqueous solution.

Reaction 1 can give rise to the product whose structure may be written in one of the forms I–IV. In acidic solutions this reaction is catalyzed (propylene oxide reacting in the protonated form) and the product can be isolated as a salt II. The structure of this salt was established by alkaline hydrolysis and ethylation with ethyl iodide to yield 1-ethylthio-2-propanol (identified through its α-naphthylurethan[7]). This does not establish the position of attack of thiourea on propylene oxide since 2-ethylthio-1-propanol rearranges readily to 1-ethylthio-2-propanol in acidic solutions,[7] and a 1-hydroxy-2-propylthiuronium cation, if formed, would be expected by analogy to rearrange giving II.



$$(H_2N)_2C{=}S + \overset{O}{CH_2{-}CHCH_3} \longrightarrow H_2\overset{+}{N}{=}\underset{NH_2}{C}{-}S{-}CH_2{-}\overset{O^-}{CH}{-}CH_3 \quad (1)$$

I

$$I + H_2O \rightleftharpoons HO^- + H_2\overset{+}{N}{=}\underset{NH_2}{C}{-}S{-}CH_2\overset{OH}{C}HCH_3 \rightleftharpoons$$

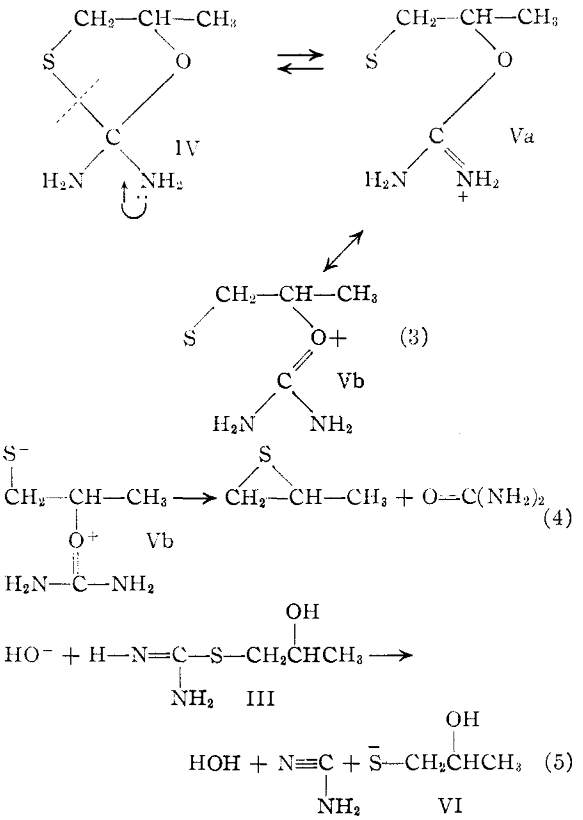
II

$$HOH + HN{=}\underset{NH_2}{C}{-}S{-}CH_2\overset{OH}{C}HCH_3 \rightleftharpoons$$

III

$$\rightleftharpoons I \quad (2)$$

IV



IV Va Vb (3)

$$\overset{S^-}{CH_2}{-}\underset{O^+{=}C(NH_2)_2}{CH}{-}CH_3 \longrightarrow \overset{S}{CH_2{-}CH}{-}CH_3 + O{=}C(NH_2)_2 \quad (4)$$

Vb

$$HO^- + H{-}N{=}\underset{NH_2}{C}{-}S{-}CH_2\overset{OH}{C}HCH_3 \longrightarrow$$

III

$$HOH + N{\equiv}\underset{NH_2}{C} + \bar{S}{-}CH_2\overset{OH}{C}HCH_3 \quad (5)$$

VI

The fact that during the course of reaction 1 the *p*H rises rapidly from 7 to 10 and remains there strongly suggests that the equilibrium expressed in 2 favors form II. The high basicity of such compounds (compare O-alkylureas and amidines) is generally ascribed to the high degree of resonance possible in the protonated form[8] (II in this case). A cyclic structure for III (not shown) is less likely since a comparable degree of resonance would not be possible.

The importance of the intermediate structure IV is indicated by the failure of cyclopentene oxide to yield cyclopentene sulfide, despite the formation of a cation corresponding to II (sulfate salt isolated). S-(*trans*-2-Hydroxycyclopentyl)-thiuronium sulfate would not be expected to yield a cyclic structure comparable to IV on neutralization due to the strain in the *trans*-5,5-fused ring. A structure comparable to III can be formed, however, which accounts for the formation of *trans*-2-hydroxycyclopentanethiol when excess base was used.

The hydrolysis reaction written for step 3 appears most reasonable in view of the presence of the electron-donating oxygen and nitrogen atoms. Two of the four important resonance forms Va and Vb of the product of this hydrolysis are shown. It is possible to visualize a base-catalyzed ring opening of IV (attack on one of the hydrogens of nitrogen

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(7) R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, **11**, 476 (1946).

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 213.

and cleavage of the C–S bond), but this does not appear to be the case since in the presence of high concentrations of hydroxide ion reaction 5 involving III, an open-chain form of IV, completely overshadows reaction 3. This indicates that the rate of reaction 5 depends on the hydroxide ion concentration, whereas that of reaction 3 does not.[9]

Support for reaction 4 was obtained by isolation of urea in several experiments utilizing dioxane as the solvent. Urea also has been isolated by Culvenor, Davies and Heath.[10]

In attempts to obtain optimum preparative conditions a number of observations were made with regard to reaction variables. In the presence of acid reaction 1 to form the thiuronium salt is rapid at 0–5° even with epoxides that are only slightly soluble in water (cyclopentene or cyclohexene oxides). Use of excess thiourea did not improve the yield, and when hydrochloric acid was used the yields were lower at 25 and 50° than at 0° (probably because of chlorohydrin formation). The yields were determined by addition of the salts to excess aqueous sodium hydroxide and alkylation with methyl sulfate, the product being isolated as 1-methylthio-2-propanol. In several experiments the formation of a compound $C_7H_{16}OS_2$ at the expense of 1-methylthio-2-propanol was observed. The structure of this compound has not been established.

Yields of thiuronium salts in reaction 1 were based on the amount of 1-methylthio-2-propanol obtained on alkaline hydrolysis and methylation rather than the yield of 2-hydroxy-1-propanethiol, since the latter was obtained in relatively poor yield (35 *vs.* 75%). The lower yield of 2-hydroxy-1-propanethiol is due to a side reaction with some species in solution (probably HS^-) since the isolation procedure was shown to be satisfactory, and the yields of hydroxy thiols in instances where pure salts were used (cyclopentyl and cyclohexyl) were good.

Experimental[11]

Formation of Thiuronium Salts from Epoxides and Thiourea in the Presence of Acids.—In a typical run 40 g. (0.5 mole) of thiourea was added to a solution of 15 ml. (0.5 equiv.) of sulfuric acid in 175 ml. of water, and the mixture was cooled to 0–5°. Only part of the thiourea is soluble under these conditions, but it dissolves as the reaction proceeds. Twenty-nine grams (0.5 mole) of propylene oxide was then added over the course of 1.5–2 hr. to the stirred solution, the temperature being maintained at 0–5°. After completing the addition the stirring and cooling were continued for about 10 min. and then the ice-bath was removed and the mixture allowed to warm to room temperature in the course of about 2 hr. Runs using other acids or epoxides were made in the same manner. The reactions are exothermic and are probably substantially complete after the addition of the epoxide is finished. Allowing as long as 22 hr. at 3° followed by 6 hr. at room temperature did not improve the yields of products obtained on alkaline hydrolysis.

In otherwise identical experiments the yield of 1-methylthio-2-propanol (from alkaline hydrolysis and methylation, see below) were shown to be the same (73%) using either 1.0 or 2.6 moles of thiourea per mole of propylene oxide and one equivalent of sulfuric acid.

The total yield of products (propylene sulfide + polymer; 1-methylthio-2-propanol + $C_7H_{16}OS_2$, or thiuronium salt) were comparable in runs using acetic, perchloric, hydrochloric, sulfuric or benzoic acids (the nature of the product was determined by the method of work-up, see below).

S-(*trans*-2-Hydroxycyclohexyl)-thiuronium Sulfate.—From 49 g. (0.5 mole) of cyclohexene oxide in the above procedure there was obtained by cooling the mixture to 0° and collecting the solid on a filter 86.1 g. (77%) of the salt, m.p. 300–310°. Recrystallization from 50% alcohol gave material melting at 310–315°.

Anal. Calcd. for $C_{14}H_{30}O_6N_4S_3$: C, 37.65; H, 6.77. Found: C, 38.00; H, 6.51.

S-(*trans*-2-Hydroxycyclopentyl)-thiuronium Sulfate.—In a similar manner 32 g. (0.38 mole) of cyclopentene oxide gave 30.0 g. of salt. Concentration of the filtrate on the steam-bath to about half its volume and filtering brought the total yield to 45 g. (57%) of product melting at 195–197° dec. The material in the mother liquor was not recovered. Recrystallization from 85% alcohol raised the m.p. to 205–206°.

Anal. Calcd. for $C_{12}H_{26}N_4O_6S_3$: C, 34.43; H, 6.26. Found: C, 34.39; H, 6.76.

S-(2-Hydroxypropyl)-thiuronium Benzoate.—Twenty-nine grams (0.5 mole) of propylene oxide was added during one hour to a stirred mixture of 38 g. (0.5 mole) of thiourea and 61 g. (0.5 mole) of benzoic acid in 300 ml. of acetone at 15–20°. The mixture was stirred for an additional 5 hr. at 20–25°. The voluminous crystalline precipitate formed was collected on a filter and dried; the yield of colorless salt melting at 111–113° was 103 g. (81%). Recrystallization from 70% acetone raised the m.p. to 112–114°.

Anal. Calcd. for $C_{11}H_{16}O_3N_2S$: C, 51.54; H, 6.29; N, 10.93. Found: C, 51.56; H, 6.20; N, 11.10.

Propylene Sulfide.—To a reaction mixture prepared on a 0.5 mole scale from propylene oxide, thiourea and sulfuric acid, as described above, there was added a solution of 53 g. (0.5 mole) of sodium carbonate in 250 ml. of water. The addition was carried out at 20–25° and required 0.5 hr. The resulting oil was separated and the aqueous phase washed with petroleum pentane, the pentane extract being combined with the oil. After one hour more oil had separated from the aqueous phase and the extraction was repeated. The combined extracts were dried over anhydrous sodium sulfate and distilled from a 3-plate Vigreux column; the yield of propylene sulfide, b.p. 72–75°, was 23.3 g. (63%).

***p*H Changes in the Formation of Propylene Sulfide.**—In a run identical with that described above the *p*H of the mixture was measured with a glass electrode as increments of 2 *M* aqueous sodium carbonate solution were added. The reaction mixture remained clear as the *p*H increased from 1.6 to 7.0. At *p*H 7 propylene sulfide began to separate. Additional increments of sodium carbonate solution brought the *p*H to 8, at which point the propylene sulfide was extracted with pentane. The aqueous solution was allowed to stand for 40 min. during which time the *p*H gradually dropped to 7.0 and more propylene sulfide was formed. After another pentane extraction the *p*H remained constant at 7.0 for 30 min. and very little propylene sulfide was formed. An additional increment of sodium carbonate increased the *p*H to 8.4 and more propylene sulfide was formed. On standing for 30 min. the *p*H dropped again (to 7.6); after extraction of the propylene sulfide the *p*H was 7.1, and little propylene sulfide formation was observed for the next 20 min. Another increment of sodium carbonate resulted in a further quantity of propylene sulfide. Distillation of the combined extracts yielded 24 g. (65%) of propylene sulfide, b.p. 72–75°.

In an experiment where propylene oxide was gradually added to a stirred aqueous solution of thiourea at 20–25° the *p*H rose within 5 min. to 10.1 and remained essentially constant during the 30 min. required to add the oxide. Propylene sulfide began to separate from the solution after about 20 min. During an additional 2.5 hr. of standing the *p*H of the solution gradually dropped to 9.4. In experi-

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[9] The possibility that reaction of V, or its tautomer, $HSCH_2CH(CH_3)—O—C(NH_2)=NH$, with hydroxide ion to yield VI takes precedence over reaction 5 appears remote since O-alkyl ureas are stable in alkaline solution; see R. H. McKee, *Am. Chem. J.*, **26**, 209 (1901). Also, this route is precluded in the cyclopentane series.

[10] C. Culvenor, W. Davies and N. Heath, *J. Chem. Soc.*, 278 (1949).

[11] Microanalyses were by Miss Joyce Sorenson. Melting points are uncorrected.

ments comparable to this the yield of propylene sulfide was about 30% and polymer was formed. Use of 2.5 mole % of hydrochloric acid under similar conditions also gave propylene sulfide directly, and the yield was increased to 51% (the reaction mixture in each instance stood overnight prior to isolation of the propylene sulfide).

In an experiment using 29 g. (0.5 mole) of propylene oxide, 57 g. (0.75 mole) of thiourea and 30 ml. (0.5 mole) of glacial acetic acid in 300 ml. of water the *p*H was observed to increase from about 2 to 6 during addition of the oxide and subsequent standing at room temperature. On heating the solution on the steam-bath for 10 min. propylene sulfide was formed and isolated as before (b.p. 70–75°, 8% yield; longer periods of heating gave more propylene sulfide but this was not isolated). In comparable runs using hydrochloric or sulfuric acids the final *p*H was 1–2 and heating these solutions did not produce propylene sulfide.

Formation of Propylene Sulfide in Dioxane Solution.—Forty-four grams (0.75 mole) of propylene oxide and 38 g. (0.5 mole) of thiourea were added to 100 ml. of dioxane containing 0.27 ml. (0.005 mole, 1 mole %) of sulfuric acid. This mixture was heated on the steam-bath for 50 min. with occasional shaking. It was then distilled at atmospheric pressure until the head temperature was 99° (3-plate Vigreux) and about 70 ml. of distillate had been collected. The distillate was diluted with 3 volumes of water, the oil separated, and the aqueous phase washed twice with pentane, the washings being combined with the oil. These combined extracts were washed 4 times with water, dried over anhydrous calcium sulfate and distilled to yield 21.1 g. (57%) of propylene sulfide boiling at 72–75°.

In a similar run the mixture was cooled rather than distilled after the reaction period. Urea crystallized and was collected on a filter. After recrystallization from ethanol-acetone the yield of urea was 75%, m.p. 128–130°. Further recrystallization gave material melting at 130–132°. A qualitative test for sulfur was negative, the mixed m.p. with authentic urea was 130–132° and urea nitrate prepared from the two samples melted at 156–157° dec. (mixed m.p., gave no depression).

Twenty-nine grams (0.5 mole) of propylene oxide was added during 0.5 hr. to a stirred mixture of 38 g. (0.5 mole) of thiourea and 30 ml. (0.5 mole) of glacial acetic acid in 100 ml. of dioxane. The initial temperature was 3°, but was allowed to rise spontaneously during the addition of the oxide and thereafter until the mixture refluxed. Crystals of urea appeared as the solution cooled, and after standing overnight these were collected. After drying in a vacuum desiccator 22 g. (73%) of urea, m.p. 130–132°, was obtained. A 41% yield of propylene sulfide was obtained by diluting the filtrate with water and extracting as described above.

Cyclohexene Sulfide, Failure of Cyclopentene Sulfide Formation.—Forty grams (0.18 mole) of S-(*trans*-2-hydroxycyclohexyl)-thiuronium sulfate was slurried in 700 ml. of water. To this mixture at 25° was added with stirring 19.1 g. (0.18 mole) of sodium carbonate in 100 ml. of water (requiring 0.5 hr.). The mixture was stirred 20 min. longer at 25°, warmed to 50° for 15 min., cooled, the resulting oil separated, and the aqueous phase extracted with pentane. The oil and extracts were combined, washed with water, dried over anhydrous sodium sulfate and distilled to yield 14.1 g. (69%) of cyclohexene sulfide boiling at 77–79° at 35 mm.

A similar experiment was carried out with 20.9 g. (0.1 mole) of S-(*trans*-2-hydroxycyclopentyl)-thiuronium sulfate. After all the sodium carbonate had been added at 20–25° the reaction mixture remained clear for a few minutes and then a solid began to precipitate. This material (9.8 g.) melted at 100–102° dec. and was basic (its aqueous solution had a *p*H of about 8). No suitable solvent for crystallization was found and no further work was carried out on this material. It might be S-(*trans*-2-hydroxycyclopentyl)-thiourea.

1-Methylthio-2-propanol.—The reaction mixture resulting from the preparation of 2-hydroxypropylthiuronium sulfate on a 0.5 mole scale (see above), was added to a solution of 85 g. (2 moles, 100% excess) of sodium hydroxide in 125 ml. of water at 20° during 0.5 hr. To the resulting clear solution 63 g. (0.5 mole) of methyl sulfate was added with good stirring during the course of 1 hr. at 20–40°. The mixture was extracted with ether for 18–20 hr. in a continuous apparatus. Distillation of the extract yielded 38.5 g. (72.6%) of product boiling at 55–58° at 10 mm.

Anal. Calcd. for $C_4H_{10}OS$: C, 45.24; H, 9.49. Found: C, 45.22; H, 9.29.

In a similar experiment using hydrochloric acid and just the stoichiometric quantity of sodium hydroxide at 80° there was isolated after manual extraction and distillation a 25% yield of 1-methylthio-2-propanol, b.p. 48–51° (7 mm.), and 22% of a compound boiling at 128–131° at 7 mm.

Anal. Calcd. for $C_7H_{16}OS_2$: C, 46.62; H, 8.94. Found: C, 46.70; H, 8.73.

It seemed likely that this substance might be 6-methyl-4,7-dithia-2-octanol, $CH_3CH(OH)CH_2SCH_2CH(SCH_3)CH_3$, formed by the reaction of 2-hydroxypropyl mercaptide ion on propylene sulfide, especially since a transient turbidity was sometimes observed during the alkali treatment. A comparable product obtained from the reaction of these two substances did not, however, have an identical infrared spectrum and the structure of these materials remains unsettled.

1-Ethylthio-2-propanol.—Repetition of the above experiment with 2-hydroxypropylthiouronium sulfate, but using ethyl iodide instead of methyl sulfate, gave after two distillations 26.0 g. (43%) of material boiling at 60–61° at 7 mm.; Fuson, Price and Burness[7] report 76° at 15 mm.

The **α-naphthylurethan** prepared from this sample melted at 86–89°; m.p. 85–88° was reported,[7] and the α-naphthylurethan of 2-ethylthio-1-propanol melts[7] at 66–68°.

Anal. Calcd. for $C_{16}H_{19}O_2NS$: C, 66.40; H, 6.62. Found: C, 66.72; H, 6.85.

2-Hydroxyalkanethiols.—2-Hydroxypropanethiol was obtained by adding a solution of 2-hydroxypropyl mercaptide ion, obtained as above, to a solution of 60 ml. (1 mole) of sulfuric acid in 150 ml. of water. The solution was filtered from the precipitated sodium sulfate and the mixture extracted for 20 hr. with ether in a continuous extractor. Distillation gave 5.2 g. of material boiling at 25–35° at 14 mm., and 15.2 g. (35%) of 2-hydroxy-1-propanethiol boiling at 55–57° (14 mm.). The boiling point of the latter has been reported as 51° at 12 mm.[12] and 44–45° at 8 mm.[13]

The low yield was not due to isolation difficulties since the recovery by the extraction procedure gave an 87% return. In this experiment a 160% excess of thiourea was used and it is possible that bisulfide ion present in the mixture from hydrolysis of thiourea may have converted some of the 2-hydroxy-1-propanethiol under the acid conditions to 1,2-propanedithiol (b.p. 152°), accounting for the low boiling forerun.

The preparation of *trans*-2-hydroxycyclohexanethiol and *trans*-2-hydroxycyclopentanethiol was carried out in an analogous manner using the pure thiouronium sulfates. After extracting three times (manual) with ether, drying the ether extract and distilling, a 71% yield of *trans*-2-hydroxycyclohexanethiol, b.p. 97–99° (15 mm.), was obtained; a b.p. of 100° (18 mm.) is reported.[10] The 2,4-dinitrophenyl sulfide was prepared by heating a mixture of 0.66 g. (0.005 mole) with 1.0 g. (0.005 mole) of 2,4-dinitrochlorobenzene dissolved in 10 ml. of pyridine on the steam-bath for 1 hr., and diluting the mixture with ice-water. Recrystallization of the solid obtained from alcohol gave 1.3 g. (87%) of derivative, m.p. 133–135° (135° reported[10]).

In a similar manner a 67% yield of *trans*-2-hydroxycyclopentanethiol, b.p. 112–114° (35 mm.), was obtained. The reported b.p. is 92–94° (15 mm.).[8]

2,4-Dinitrophenyl *trans*-2-hydroxycyclopentyl sulfide was obtained in 77% yield as described above. After recrystallization from aqueous alcohol it melted at 114–116°.

Anal. Calcd. for $C_{11}H_{12}O_5N_2S$: C, 46.47; H, 4.07. Found: C, 46.72; H, 4.22.

EVANSTON, ILLINOIS

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[12] B. Sjoberg, *Ber.*, **75B**, 13 (1942).

[13] H. Williams and F. Woodward, *J. Chem. Soc.*, 38 (1948).