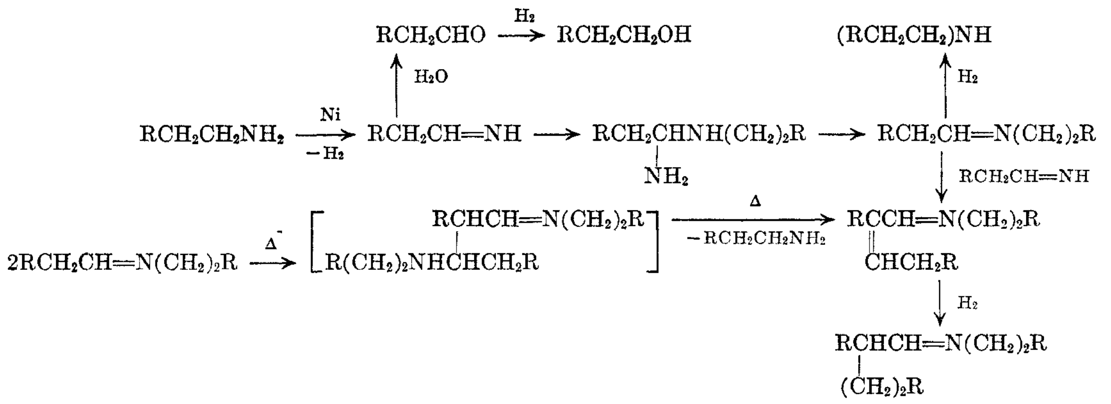
(3)

sure (100 p.s.i.g.) was slowly released, the contents were filtered and distilled. *n*-Octanal (10.1 g.), *n*-octylamine (136 g.), 1-octanol (16.5 g.), and di-*n*-octylamine (28.5 g.), which distilled at 145–155° (3 mm.), were obtained in the initial distillates. A fraction (13.0 g.) distilling at 195–197° (2 mm.), n_D^{25} 1.4652, was also obtained. A very strong infrared band at 6.1–6.18 μ was attributed to superposition of the substituted imine and olefinic absorptions.

Anal. Calcd. for $C_{24}H_{47}N$: C, 82.49; H, 13.50; N, 4.01. Found: C, 82.44, 83.24; H, 12.75, 13.59; N, 3.90, 3.94.

The ultraviolet absorption spectrum of the compound exhibited a characteristic imine maximum at 231 mμ.

The imine (12.0 g.) was hydrolyzed in refluxing 20% hydrochloric acid (100 ml.). The mixture was cooled and extracted with ether. The ether extracts were dried over magnesium sulfate, the ether evaporated, and the residue refluxed with ethanolic 2,4-dinitrophenylhydrazine reagent. 2-*n*-Hexyl-2-decenal 2,4-dinitrophenylhydrazone, melting at 103.5–104.5°, precipitated on cooling.

Anal. Calcd. for $C_{22}H_{34}N_4O_4$: C, 63.28; H, 8.14. Found: C, 63.11; H, 8.83.

An attempted preparation of an oxime from this aldehyde failed.

The aqueous solution from the acid hydrolysis yielded a white, waxy solid, m.p. 192–196°. This was identified as *n*-octylamine hydrochloride (lit.[12] m.p. 198°).

The imine can now be formulated as *N*-(2-*n*-hexyl-2-decenylidene)-*n*-octylamine.

A trace (1.3 g.) of a primary amine (infrared analysis) which sublimed during the distillation was recrystallized from methanol, m.p. 108–109°.

Anal. Calcd. for $C_{24}H_{51}N$: N, 3.97. Found: N, 3.97.

This amine was diazotized and coupled with β-naphthol to give a red solid, melting point 174–176°. The identity of the amino compound is not known.

The Guerbet condensation of cyclohexylamine yielded cyclohexene, cyclohexanone, cyclohexanol, and *N*-cyclohexylidenecylohexylamine, boiling point 93–95° (2 mm.), n_D^{25} 1.4904. Migonac[7] gives a boiling point of 117–118° (9 mm.), n_D^{21} 1.4972, for this compound. The imine was refluxed with an ethanolic solution of 2,4-dinitrophenylhydrazine reagent. Cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 158–160°, was isolated.

A higher boiling fraction from the cyclohexylamine reactions distilled at 180–195° (4 mm.) with decomposition. Infrared analysis showed the presence of a primary amine, but the product was not otherwise identified.

Nitrile reactions. A 300-ml. rocking autoclave was charged with 160.0 g. (1.44 moles) of *n*-heptanenitrile, 21.0 g. (0.1 mole) of tripotassium phosphate, and 8.0 g. of a 1:1 mixture of copper chromite–nickel catalyst. The reaction was pressured with 600 p.s.i.g. of hydrogen and heated to 210° for 20 hr. The hydrogen pressure fell to 200 p.s.i.g. The mixture was cooled and filtered. The filtrate was distilled at 179–181° to yield 124.0 g. of *n*-heptanenitrile. The residue contained *n*-heptamide (20.0 g.), which was recrystallized from methanol, m.p. 95.5–97°.

Anal. Calcd. for $C_7H_{15}NO$: C, 65.21; H, 11.63. Found: C, 65.24; H, 12.15.

Benzamide (m.p. 124–126° was obtained from similar treatment of benzonitrile.

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(7) G. Migonac, *Ann. chim.*, [11], 2, 225 (1934).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

The Reaction of Glycidaldehyde and Mesityl Oxide Epoxide with Hydrogen Sulfide

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Received March 25, 1960

Glycidaldehyde and the epoxide of mesityl oxide react with hydrogen sulfide to form, respectively, 3-hydroxy-2-mercaptopropionaldehyde, isolated as a dimer, and 4-hydroxy-3-mercapto-4-methyl-2-pentanone. A mechanism involving the initial addition of hydrogen sulfide to the carbonyl group is postulated to account for the formation of these products.

The direction of addition of reagents to an unsymmetrical epoxide can usually be predicted from the nature of the groups attached to the oxirane ring.[1] As one generalization it may be said that if one of the substituents on the oxirane ring is an electron-withdrawing group the effect, almost invariably, is to inhibit reaction at the attached oxirane carbon in favor of the oxirane carbon further

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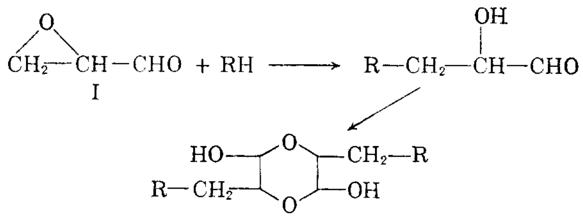
(1) See R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 59, 737–799 (1959) for a recent review of this subject.

removed. Among the few exceptions which are reported to result in the alternate displacement are the addition of hydrogen sulfide to ethyl β,β-dimethylglycidate[1,2] and the addition of ammonia and amines to certain β-aryl-substituted glycidic acid derivatives.[1] The irregular behavior of these epoxides has not been adequately explained.

The addition of hydrogen sulfide to epoxides having a carbonyl (aldehyde or ketone) group attached to the oxirane ring also appears to occur in a manner contrary to the general rules of orientation. The present investigation has shown that the base-catalyzed reaction of hydrogen sulfide and glycidaldehyde (2,3-epoxypropionaldehyde)(I) results in 3-hydroxy-2-mercaptopropionaldehyde (II), isolated as a crystalline dimer (III) in 90% and higher yield. Similarly, treatment of the epoxide of mesityl oxide, 3,4-epoxy-4-methyl-2-pentanone (IX), with hydrogen sulfide in the presence of a basic catalyst yields 4-hydroxy-3-mercapto-4-methyl-2-pentanone (X) as the principal product.

These results were surprising, as the electron-withdrawing character of the carbonyl group and, in the case of glycidaldehyde, the absence of substituents other than hydrogen on the terminal carbon, should strongly favor displacement on the β-oxirane oxygen. Indeed, it has been shown[3] that the acid-catalyzed addition of active hydrogen compounds to glycidaldehyde results in β-substituted lactaldehydes as the predominant products; these were isolated as dimeric compounds:

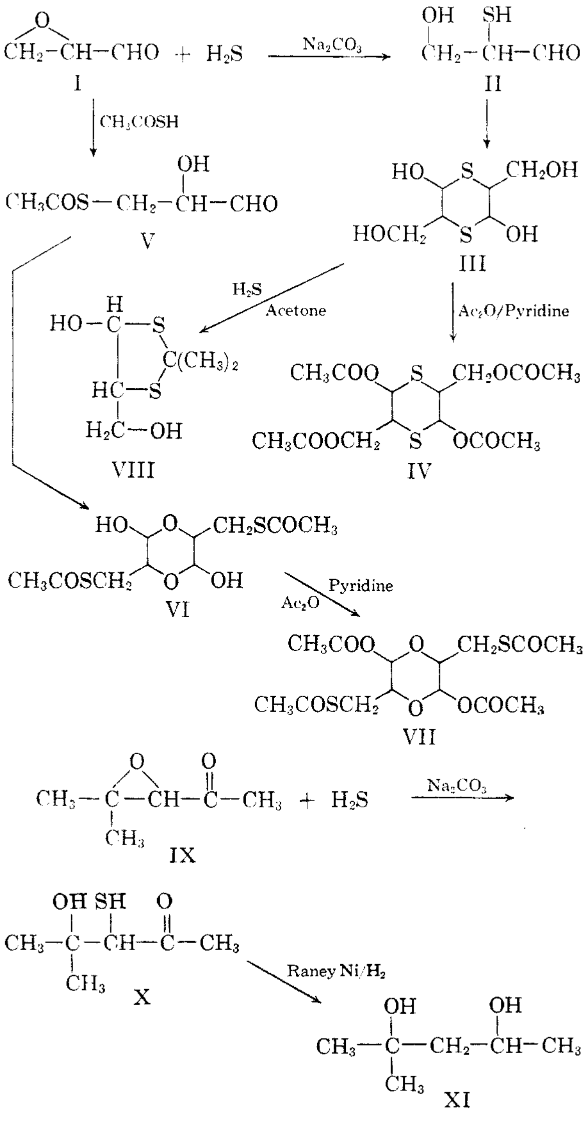


(RH = hydrochloric acid and acetic acid; when RH was methanol, the dimethyl acetal of β-methoxylactaldehyde was the chief product.) The oxirane addition reactions of 3,4-epoxy-4-methyl-2-pentanone have not been reported.

Product III, from the reaction of glycidaldehyde and hydrogen sulfide, was identified as 3,6-dihydroxy-2,5-bis(hydroxymethyl)-*p*-dithiane on the basis of its elemental composition and infrared spectrum. Its spectrum was consistent with structure III and unambiguously eliminated an alternate possible structure, that of 3,6-dihydroxy-2,5-bis(mercaptomethyl)-*p*-dioxane, which might have resulted had the hydrogen sulfide added at the terminal oxirane carbon of glycidaldehyde so as to form 2-hydroxy-3-mercaptopropionaldehyde. Confirming this distinction was the nonidentity of the tetraacetate (IV) of III and the diacetate (VII) of the dimer (VI) of 2-hydroxy-3-thioacetoxypropionaldehyde (V). The latter resulted from the addition of thiolacetic acid to glycidaldehyde; the structure of the dimer (VI) was indicated by its elemental composition, molecular weight, and its infrared spectrum.

The structure of product X from the reaction of the epoxide of mesityl oxide and hydrogen sulfide was assigned on the basis of its elemental composition and infrared spectrum, and its conversion with Raney nickel and hydrogen to 2-methylpentane-2,4-diol (XI). Formation of this diol firmly established the location of the mercapto group in the parent compound.

The base-catalyzed reaction of III with hydrogen sulfide in aqueous acetone afforded a substance whose composition corresponds to that of 2,2-dimethyl-4-hydroxy-5-hydroxymethyl-1,3-dithiolane (VIII). This structure was supported by infrared analysis, and by the fact that acetone was formed on treatment of the substance with mer-



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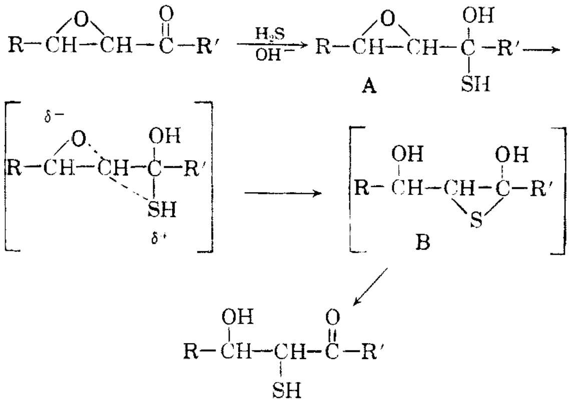
(2) V. F. Martynov and N. A. Rozepina, *Zhur. Obshcheĭ Khim.*, **22**, 1577 (1952); *Chem. Abstr.*, **47**, 8016 (1953).

(3) G. B. Payne, W. J. Sullivan, P. R. Van Ess, and P. H. Williams, *J. Am. Chem. Soc.*, **82**, 4883(1960).

curic chloride in dilute hydrochloric acid. VIII was also formed in minor yield in the reaction of glycidaldehyde with hydrogen sulfide in acetone solution.

Examples of the addition of hydrogen sulfide to epoxides having a carbonyl group adjacent to the oxirane ring have not been found in the literature. The aforementioned reaction of ethyl β,β-dimethylglycidate with sulfhydryl anion,[2] which resulted in a 20% yield of ethyl 3-hydroxy-2-mercapto-3-methylbutyrate, may be similar in nature, however. The products of the present study from hydrogen sulfide and the two α,β-epoxycarbonyl compounds may be accounted for by the mechanism outlined below (in which for simplicity, and because of the several possible variations, ionic species have not been indicated.) In the initial step, hydrogen sulfide (or the sulfhydryl anion) adds to the carbonyl group to give a hemithiohydrate (A); intramolecular displacement by sulfur on the adjacent oxirane carbon then leads to a dihydroxy episulfide (B), which rapidly rearranges to product, in the present instance the β-hydroxy-α-mercaptocarbonyl derivatives II and X. A mechanism of this sort is consistent with the known tendency of hydrogen sulfide (and mercaptans) to add to the carbonyl group; the nucleophilic displacement may be analogous to that occurring in the formation of epoxy ethers from α-haloaldehydes[4] and α-haloketones,[5] and to other displacement reactions with various α-substituted carbonyl compounds.[6]



EXPERIMENTAL

3-Hydroxy-2-mercaptopropionaldehyde dimer. A solution of 216 g. (3.0 moles) of glycidaldehyde[7] in 2 l. of acetone was stirred with 2.0 g. of sodium carbonate and treated continuously with hydrogen sulfide. A temperature of 5–10° was maintained with an ice water bath. After 4 hr. addition of hydrogen sulfide was discontinued, but stirring was continued for an additional 16 hr. The reaction product separated as a white solid which was collected by filtration; it weighed 259 g., m.p. 101–104°. The acetone filtrate was again saturated with hydrogen sulfide and allowed to stand at room temperature for 24 hr.; an additional 47 g. of solid, m.p. 128–130°, was obtained. The combined product was slurried with 300 ml. of cold water, filtered, and the filter cake washed with acetone. After air-drying, it was treated with 500 ml. of boiling acetone, filtered, and dried to give 293 g. (92% yield), m.p. 130–132°.

Anal. Calcd. for $C_6H_{12}O_4S_2$: C, 34.0; H, 5.7; S, 30.2. Found: C, 34.0; H, 5.7; S, 29.6.

The infrared spectrum of the product (Nujol mull) had maxima at 3.02 μ (hydroxyl) and 14.7 μ (thioether); there was no absorption indicative of sulfhydryl, carbonyl or ether groups.

Concentration of the mother liquor and acetone washings gave 19.2 g. of oily material which crystallized from ether-acetone to give 6.1 g., m.p. 112–113°. (This product was subsequently identified as 2,2-dimethyl-4-hydroxy-5-hydroxymethyldithiolane—see preparation below.)

Tetraacetate of 3-hydroxy-2-mercaptopropionaldehyde dimer. To 5.3 g. (0.025 mole) of the dimer of 3-hydroxy-2-mercaptopropionaldehyde was added 10 ml. of pyridine and 25 ml. of acetic anhydride. The mixture was allowed to stand at room temperature overnight and was then poured over 200 g. of crushed ice to which had been added 15 ml. of concd. hydrochloric acid. The resultant mixture was extracted with ether and the extract was dried over magnesium sulfate. On concentrating the ether extract to about 20 ml. and cooling, 7.2 g. of crystalline product was obtained; recrystallization from benzene-hexane gave 5 g., m.p. 161–162°.

Anal. Calcd. for $C_{14}H_{20}O_8S_2$: C, 44.2; H, 5.3; S, 16.8; mol. wt. 380. Found: C, 44.9; H, 5.5; S, 16.2; mol. wt. (ebullioscopic in benzene), 385.

The infrared spectrum of the product had a strong maximum at 5.72 μ (carboxylic ester), but there was no absorption at 5.9–6.0 μ (thiol carboxylic ester).

2-Hydroxy-3-thioacetoxypropionaldehyde dimer. To 57.0 g. (0.75 mole) of thiolacetic acid was added dropwise 54.0 g. (0.75 mole) of glycidaldehyde, while maintaining the temperature of the stirred reaction mixture at 35–40° with an ice water bath. Stirring was continued an additional 2 hr. after combination of the reagents. At this time, titration for epoxide[8] indicated that less than 2% of the glycidaldehyde remained. After standing 3 days at room temperature, the entire reaction mixture had solidified; it was then washed with ether and dried to give 109.5 g. (98.6%), m.p. 122–123°. Recrystallization of a portion of this product from dioxane-dichloroethane did not improve the melting point.

Anal. Calcd. for $C_{10}H_{16}O_6S_2$: C, 40.5; H, 5.4; S, 21.6; mol. wt., 296. Found: C, 40.5; H, 5.4; S, 21.4; mol. wt. (ebullioscopic in ethylene dichloride), 265.

The infrared spectrum of the compound showed absorption maxima at 3.04 μ (hydroxyl) and 5.95 μ (thiocarboxylic ester).

2,5-Diacetoxy-3,6-di(thioacetoxymethyl)-p-dioxane. To 1.5 g. (0.005 mole) of the dimer of 2-hydroxy-3-thioacetoxypropionaldehyde was added 5 ml. of acetic anhydride and 7 ml. of pyridine and the solution allowed to stand at room temperature for 16 hr. The reaction mixture was then poured into 25 ml. of ice water containing 5 ml. of concd. hydrochloric acid. The mixture was extracted with ether and the extract dried over magnesium sulfate. After removal of most of the ether on the steam bath, crystallization of the solid from ethanol-ether gave 1.4 g. (74%), m.p. 166.5–167°.

Anal. Calcd. for $C_{14}H_{20}O_8S_2$: C, 44.2; H, 5.3; S, 16.8;

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(4) C. L. Stevens, E. Farkas, and B. Gillis, *J. Am. Chem. Soc.*, **76**, 2695 (1954).

(5) C. L. Stevens, and A. J. Weinheimer, *J. Am. Chem. Soc.*, **80**, 4072 (1958).

(6) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958).

(7) G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959).

(8) By hydrogen chloride in aqueous magnesium chloride. (See J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, New York, 1953, p. 134.

mol. wt. 380. Found: C, 44.5; H, 5.4; S, 16.1; mol. wt. (ebullioscopic in benzene), 390.

The infrared absorption spectrum had maxima at 5.70 μ (carboxylic ester) and 5.90 μ (thiocarboxylic ester).

A mixed melting point of this product and the isomeric substance, the tetraacetate of 3-hydroxy-2-mercaptopropionaldehyde dimer (m.p. 162–163°) was 139–145°.

Reaction of glycidaldehyde with hydrogen sulfide in water-acetone. A solution of 14.7 g. (0.205 mole) of glycidaldehyde in 185 ml. of water and 1000 ml. of acetone containing 0.5 g. of sodium carbonate was continuously treated with hydrogen sulfide for 4 hr. at ambient temperature. After further stirring for 16 hr., titration showed less than 0.002 mole of glycidaldehyde remaining. After standing an additional 3 days, no solid had precipitated. The solvent was then removed under reduced pressure, and the residue was dried in a vacuum desiccator to give 21 g. of crude solid. The solid was treated with hot acetone, leaving 4.6 g. (21.2% yield) of acetone-insoluble material, m.p. 131–132°. (A mixed melting point showed this to be the 3-hydroxy-2-mercaptopropionaldehyde dimer.) Concentration of the acetone extract gave 14.6 g. (39.5% yield), m.p. 98–102°; recrystallization from ether raised the m.p. to 112–113°. Analysis of this product was in agreement with *2,2-dimethyl-5-hydroxy-4-hydroxymethyl-1,3-dithiolane.*

Anal. Calcd. for $C_6H_{12}O_2S_2$: C, 40.0; H, 6.7; S, 35.5; mol. wt., 180. Found: C, 40.0; H, 6.7; S, 35.3; mol. wt. (ebullioscopic in ethylene dichloride), 181.

The infrared spectrum of the product had absorption maxima at 2.9 μ (hydroxyl), 7.2 μ (methyl), and 8.4 μ (probably *gem*-dimethyl).

A 9.0-g. (0.05 mole) sample of the material was stirred and heated in a flask with 27 g. (0.1 mole) of mercuric chloride and 30 ml. of 0.1*N* hydrochloric acid. As part of the mercuric chloride became black, a portion of the reaction mixture was distilled through a Claisen distillation head. The first 3 ml. collected (b.p. 41–99°) was treated with 2,4-dinitrophenylhydrazine reagent, giving 1.1 g. of orange-yellow solid. This solid melted at 124–125° after recrystallization from 90% ethanol; a mixed melting point taken with an authentic sample of the same derivative of acetone showed no depression.

Reaction of 3-hydroxy-2-mercaptopropionaldehyde dimer with acetone and hydrogen sulfide. In 200 ml. of hot water was dissolved 21.2 g. (0.1 mole) of 3-hydroxy-2-mercaptopropionaldehyde dimer, m.p. 131–132°. After cooling the solution to about 20°, 1 l. of acetone was added and the stirred solution was then treated continuously with hydrogen sulfide for 8 hr. The hydrogen sulfide-saturated mixture was allowed to stand for 4 days at room temperature. After removal of water and acetone under reduced pressure, the residue was treated with hot acetone to give 5.9 g. of acetone-insoluble material, m.p. 128–131°. The acetone extract was stripped under vacuum to give 25.9 g. (71.9%) of crude solid residue which, on recrystallization from acetone-ether, melted at 112–113°.

The infrared spectrum of this material was identical with that of the product obtained from aqueous glycidaldehyde, acetone, and hydrogen sulfide and tentatively identified as 2,2-dimethyl-4-hydroxy-5-hydroxymethyl-1,3-dithiolane; a mixed melting point taken with the latter product showed no depression.

Reaction of 3,4-epoxy-4-methyl-2-pentanone with hydrogen sulfide. A stirred mixture of 114 g. (1.0 mole) of 3,4-epoxy-4-methyl-2-pentanone (prepared by epoxidation of mesityl oxide with alkaline hydrogen peroxide[9]), 500 ml. of acetone and 1 g. of sodium carbonate was continuously treated with hydrogen sulfide for 8 hr. at 15°. The reaction mixture was allowed to stand at room temperature for 2 days, during which no solid product separated. The acetone was removed at reduced pressure and the residue was then pumped at 50° (1 mm.) to a constant weight of 139.2 g. (94%). Analyses of this residual material corresponded approximately to *4-hydroxy-3-mercapto-4-methyl-2-pentanone.*

Anal. Calcd. for $C_6H_{12}O_2S$: C, 50.0; H, 7.8; S, 19.4. Found: C, 48.6; H, 8.16; S, 21.6.

The infrared spectrum of the product showed maxima at 2.95 μ (hydroxyl), 3.92 μ (sulfhydryl), 5.78 μ (carbonyl), and 7.2 μ (methyl).

Attempted distillation of a portion of the product led to extensive decomposition.

Desulfurization and hydrogenation of the product of 3,4-epoxy-4-methyl-2-pentanone and hydrogen sulfide. A solution of 29.6 g. (0.2 mole) of the product described above in 150 ml. of ethanol was treated with about 30 g. of Raney nickel and hydrogen at an initial pressure of 800 p.s.i.g. and temperature of 40°. After 16 hr., the mixture was filtered, fresh catalyst was added, and the treatment repeated. This procedure was repeated twice more, and on the final treatment the temperature was raised to 94° for 3 hr. After this time, hydrogen was no longer absorbed; a total of 0.41 mole of hydrogen had reacted.

The catalyst was filtered from the product and the colorless filtrate was distilled. In addition to 145 ml. of ethanol, there was obtained 16.2 g. (68.6%) of colorless liquid, b.p. 47° (0.5 mm.), n_D^{20} 1.4272; there was 0.8 g. of distillation residue. The composition of the product fraction corresponded to 2-methylpentane-2,4-diol (redistilled commercial material has b.p. 198° (760 mm.), and n_D^{20} 1.4274).

Anal. Calcd. for $C_6H_{14}O_2$: C, 61.0; H, 11.9; hydroxyl value, 1.69 equiv./100 g.; α-glycol, 0.0 mole/100 g. Found: C, 60.9; H, 11.9; hydroxyl value, 1.72 equiv./100 g.; α-glycol (by periodate oxidation method), 0.006 mole/100 g.

The infrared spectrum of this product was identical with that of an authentic sample of 2-methylpentane-2,4-diol.

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(9) R. S. Wilder and A. A. Dolnick, The Publiker Commercial Alcohol Co., U. S. Patent **2,431,718** (1947).