TABLE II

POLAROGRAPHIC DATA AT DIFFERENT *p*H VALUES FOR *meso*-$\alpha,\alpha'$-DIBROMOSUCCINIC ACID, FUMARIC ACID AND MIXTURES OF BOTH

| | | | | Dibromosuccinic acid or mixture | | | | | | | | Fumaric acid | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Wave I | | | | Wave II | | | | | | | |
| Curve | Dibromosuccinic acid, m*M* | Fumaric acid, m*M* | *p*H | $E_{0.5}$, v. | $i_d/c$, $\mu$a./m*M* | $\frac{i_d}{cm^{2/3}t^{1/6}}$ | $n$[b] | $E_{0.5}$, v. | $i_d/c$, $\mu$a./m*M* | $\frac{i_d}{cm^{2/3}t^{1/6}}$ | $n$[b] | $E_{0.5}$, v. | $i_d/c$ $\mu$a./m*M* | $\frac{i_d}{cm^{2/3}t^{1/6}}$ | $n$[b] |
| 1 | | 0.520 | 0.6 | | | | | | | | | 0.56 | 5.2 | 4.0 | 2.0 |
| 2 | | .520 | 1.1 | | | | | | | | | .62 | 5.2 | 4.0 | 1.8 |
| 3 | | .520 | 2.0 | | | | | | | | | .72 | 5.1 | 3.9 | 1.3 |
| 4 | 0.501 | | 2.0 | 0.06 | 4.7 | 3.6 | 1.1 | 0.72 | 5.3 | 4.1 | 1.1 | | | | |
| 5 | .501 | | 4.0 | .23 | 3.5 | 2.6 | 0.4 | .89 | 3.8 | 2.9 | 1.0 | | | | |
| 6 | .450 | .520 | 4.0 | .22 | 3.5 | 2.6 | | .89 | 3.8[a] | 2.9 | | | | | |
| 7 | | .520 | 5.9 | | | | | | | | | I 1.19 | 1.9 | 1.4 | |
| | | | | | | | | | | | | II 1.46 | 1.9 | 1.4 | |
| 8 | .501 | | 5.9 | .53 | 3.4 | 2.5 | .5 | I 1.19 | 2.1 | 1.6 | 1.5 | | | | |
| | | | | | | | | II 1.47 | 1.8 | 1.4 | 0.8 | | | | |
| 9 | .501 | | 8.1 | .55 | 5.1 | 3.8 | .4 | 1.56 | 4.9 | 3.7 | 1.0 | | | | |
| 10 | .450 | .520 | 8.1 | | | | | 1.56 | 4.8[a] | 3.7 | | | | | |
| 11 | .501 | | 8.7 | .55 | 5.2 | 3.8 | .3 | 1.57 | 4.8 | 3.8 | | | | | |

[a] Concentration of fumaric acid used in calculating $i_d/c$ is 0.970, *i.e.*, the sum of the original concentrations of dibromosuccinic and fumaric acids. [b] Calculated from the equation, $E_{0.75} - E_{0.25} = -0.058/n$.

shows an S-shaped relationship similar to that elsewhere described,[2] with the acid end unexplored because the wave starts to merge with the chloride wave. The $n$ values calculated by means of the equation, $E_{0.75} - E_{0.25} = -0.058/n$, are constant at about 0.4 except that at *p*H 2 it rises to 1.1.

The remote possibility that the first wave observed was due to the reduction of bromofumaric acid formed by the dehydrohalogenation of the dibromosuccinic acid has been investigated. A solution of the dibromosuccinic acid, 10 m*M*, upon standing for 48 hr. showed less than 1% decomposition as shown by tests for the formation of bromide ion. Since the solutions prepared were used within 24 hr. and since in order to account for the $i_d/c$ results obtained there would have to be almost complete conversion to the bromofumaric acid, the possibility that the more positive wave was due to the latter substance is eliminated.

The studies of fumaric acid at the lower *p*H values (No. 1 to 3) extend earlier work.[6] The existence of two waves at *p*H 5.9 (no. 7) explains the very low value of the diffusion current previously obtained.[6] The $E_{0.5}$ then obtained for fumaric acid was 1.21 which agrees with the value of 1.19 obtained in the present study for the more positive of the two waves due to fumaric acid. Another interesting phenomenon is the gradual increase in $n$ value in the low *p*H region from 1 to 2. It has been established (*cf.* reference 1[6]) that the reduction of fumaric acid is a two-electron process. From the present investigation it is seen that in the reduction of dibromosuccinic acid both waves have similar diffusion current constants. It follows from this and the similarity between the dibromosuccinic acid and the fumaric acid that the reduction of the dibromosuccinic acid to fumaric acid is likewise a two-electron process.

The data obtained indicate that *meso*-$\alpha,\alpha'$-dibromosuccinic acid is reduced in a one-step two-electron process to fumaric acid. The formation of fumaric rather than maleic acid is in line with the evidence found for analogous chemical reactions, in which *trans*-elimination of the bromine atoms takes place.[4,9,10] Typical results are shown by the action of aqueous iodide solution at 90° upon the 2,3-dibromobutanes.[4] The *meso* form gives a butene which is 96% *trans;* the racemic gives a butene which is 91% *cis.* Similar work[10] on *meso*-$\alpha,\alpha'$-dibromosuccinic acid also indicates *trans*-elimination with the formation of fumaric acid.

The conversion attained polarographically is greater than 98% since no maleic acid wave was obtained even at *p*H 8.2 where the $E_{0.5}$ of maleic acid[6] is 0.2 v. lower than the $E_{0.5}$ of fumaric acid and, therefore, easily detectable.

It is unfortunately impossible on the basis of the present work to distinguish between a simultaneous one-electron attack on each of the carbon–halogen bonds and an unsymmetrical two-electron attack on one of the two carbon–halogen bonds with a subsequent rearrangement of the free electron pair and the displacement of the second bromine atom as a bromide ion. However, the chemical evidence[4] seems to favor the latter alternative.

The type of polarographic reduction encountered with the dibromosuccinic acid may be of a general nature and may take place wherever two adjacent halogens occur whose removal will lead to a stable double or triple bond.[5] Further work along these lines is continuing.

**Acknowledgment.**—The authors wish to thank the Atomic Energy Commission for a grant which supported this research project.

[9] W. G. Young, D. Pressman and C. D. Coryell, THIS JOURNAL, **61**, 1640 (1939).

[10] J. Finkelstein, *Ber.*, **43**, 1530 (1910).

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## The Reaction of Propylene Oxide with Thiophenol

BY ROBERT D. SCHUETZ

During the course of an investigation in this Laboratory on the syntheses of tertiary amines containing sulfur, it became necessary to study methods for the preparation of arylthioalkanols which were needed as intermediates. The observations of Kadesch[1] and others[2,3,4,5] have shown that the reaction of aliphatic alcohols with propylene oxide in the presence of an alkaline catalyst yields a secondary alcohol almost exclusively, and in the presence of an acid catalyst a mixture of primary and secondary alcohols. It seemed reasonable that an extension of this work to the reaction of thiophenols with propylene oxide would yield some of the desired arylthioalkanols.

While this work was in progress a paper[6] by Sexton and Britton was published on the reaction of phenol with propylene oxide. These investigators obtained good yields of the secondary aryloxyalkanol with an alkaline catalyst, but only very poor yields of a mixture of the primary and secondary aryloxyalkanols with acid catalysis.

The reaction of thiophenol and propylene oxide using an alkaline catalyst reported here yields a single product, namely, 1-phenylthio-2-propanol, in excellent yield. That only a single product resulted in the above reaction and the proof of its structure was established by careful fractionation of the material obtained through an efficient column capable of separating the two possible isomers and comparison of the product with 1-phenylthio-2-propanol. This compound was also prepared by an extension of the method used by Kirner and Holmes[7] for the synthesis of homologs of 1-phenylthio-2-propanol. The interaction of thiophenol and 1-chloro-2-propanol in aqueous sodium hydroxide resulted in a very good yield of the desired 1-phenylthio-2-propanol. The products obtained by both methods were characterized by comparison with 1-phenylthio-2-propanol prepared by a third different method previously reported.[8] Further characterization of 1-phenylthio-2-propanol was made by preparation of the 3,5-dinitrobenzoate derivative.

The interaction of thiophenol and propylene oxide catalyzed by acids resulted in a very poor yield of a product which is very probably a mixture of the two possible isomers, namely, 1-phenylthio-2-propanol and 2-phenylthio-1-propanol. That a mixture of the two isomers resulted under acid catalysis was indicated by a comparison of the 3,5-dinitrobenzoates of the product with the 3,5-dinitrobenzoates of 1-phenylthio-2-propanol and 2-phenylthio-1-propanol. The latter derivative, a new compound, was prepared from 2-phenylthio-1-propanol synthesized by the method of Fuson and Koehneke.[8]

The formation of a single compound when propylene oxide interacts with thiophenol in the presence of sodium thiophenolate, an alkaline catalyst, is in good general agreement with previous work on the reactions of unsymmetrical epoxy compounds with aliphatic alcohols, phenols[6] and aliphatic mercaptans.[9,10]

## Experimental

**Preparation of 1-Phenylthio-2-propanol. First Method.**—Two-tenths of a mole (22 g.) of thiophenol was added to 80 ml. of 10% sodium hydroxide. The mixture was stirred until the solution of thiophenol was complete. A 10% excess of 1-chloro-2-propanol (21 g., 0.22 mole) was then added over a quarter-hour period. The reaction mixture was refluxed at 100° with vigorous stirring for a half-hour longer to ensure complete reaction. The top oily layer was removed and the water layer extracted with 50 ml. of ether. The ether extract and oil were combined, dried over magnesium sulfate and the ether removed. The product on distillation through a 20-cm. Vigreux column gave 29.0 g. of 1-phenylthio-2-propanol boiling at 108–110° (1.5 mm.), corresponding to a 86.5% yield based on the thiophenol; $d^{25}$ 1.1014, $n^{20}$ 1.5715, *p*-nitrobenzoate, m.p. 64.0–65.0°.[8,11] The 3,5-dinitrobenzoate, m.p. 112–113°,[11] has not previously been reported.

*Anal.* Calcd. for $C_{16}H_{14}O_6N_2S$: S, 8.85. Found: S, 8.93.

**Second Method.**—To two-tenths of a mole (22 g.) of thiophenol was added 50 mg. of metallic sodium which reacted vigorously to form the sodium thiophenolate which was insoluble in the excess thiophenol. A 10% excess (12.8 g., 0.22 mole) of propylene oxide was added over a quarter-hour period with vigorous stirring. There was initially a considerable evolution of heat causing a rise in temperature sufficient to cause vigorous refluxing of the propylene oxide and it was necessary to cool the reaction in a water-bath. After the addition of the propylene oxide was complete, the reaction was heated on a water-bath brought gradually to a temperature of 100° for an additional half-hour.

The product on distillation through a 20-cm. Vigreux column gave 30 g. of product boiling at 110–112° (2 mm.) corresponding to an 89% yield of 1-phenylthio-2-propanol based on the thiophenol. This reaction was run a second time and similar results were obtained. The products from both reactions were combined and 50 g. was fractionated, using a 13 mm., 100 cm. Podbielniak column with a minimum of 100 plates. Nine fractions and a residue, all approximately equal in weight, were obtained. The 3,5-dinitrobenzoates prepared from the first fraction and from the residue melted at 112.5–113.5° and each on admixture with an authentic sample of the 3,5-dinitrobenzoate of 1-phenylthio-2-propanol showed no depression in melting point. In a third reaction to prepare this compound 22 g. (0.2 mole) of thiophenol and 12.8 g. (0.22 mole) of propylene oxide were heated together at a temperature high enough to cause rapid refluxing of the propylene oxide and with vigorous stirring for three hours. Distillation of the reaction mixture gave the reactants back unchanged.

**Preparation of 2-Phenylthio-1-propanol.**—This compound was prepared by the addition of thiophenol to allyl alcohol in the presence of sulfur according to the method of Fuson and Koehneke.[8] The 3,5-dinitrobenzoate,[11] m.p. 84.5–85.5°, has not previously been reported.

*Anal.* Calcd. for $C_{16}H_{14}O_6N_2S$: S, 8.85. Found: S, 8.89.

**Reaction of Thiophenol and Propylene Oxide with Acids.**—To 22 g. (0.20 mole) of thiophenol was added 0.5 g. of concd. sulfuric acid. To this well stirred solution was added 12.8 g. (0.22 mole) of propylene oxide over a quarter hour period. There was a slight rise in temperature of approximately 5°. The reaction mixture was heated on a water-bath at a temperature sufficient to cause vigorous refluxing of the propylene oxide for an hour and then fractionated, first at atmospheric and then under reduced pressure. Practically all the propylene oxide and thiophenol were recovered unreacted. The reaction was repeated using benzenesulfonic acid, and reflux was maintained by means of an oil-bath. The temperature was slowly raised from 75 to 130° over a 24-hour period at which time reflux had stopped. After cooling the reaction mixture was washed first with water and then with 5% sodium hydroxide.

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(1) Kadesch, This Journal, **68**, 41 (1946).

(2) Chitwood and Freure, *ibid.*, **68**, 680 (1946).

(3) Bartlett and Ross, *ibid.*, **70**, 926 (1948).

(4) Swern, Billen and Knight, *ibid.*, **71**, 1152 (1949).

(5) Hayes and Gutberlet, *ibid.*, **72**, 3321 (1950).

(6) Sexton and Britton, *ibid.*, **70**, 3606 (1948).

(7) Kirner and Holmes, *ibid.*, **51**, 3409 (1929).

(8) Fuson and Koehneke, *J. Org. Chem.*, **14**, 706 (1949).

(9) Todsen, Pollard and Rietz, This Journal, **72**, 4000 (1950).

(10) Scott Searles, *ibid.*, **73**, 124 (1951).

(11) Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 137, 138.

Vacuum distillation using a 20-cm. Vigreux column gave 15 g. of thiophenol, 3 g. of product, b.p. 120–125° (3 mm.) and 5 g. of high boiling residue. The 3,5-dinitrobenzoate of the product had a m.p. 92–100°, indicating a mixture of the phenylthiopropanols. The reaction was repeated a third time using 85% phosphoric acid. Distillation gave 15 g. of thiophenol, 4 g. of product, b.p. 110–125° (1–2 mm.) and 5 g. of residue. The 3,5-dinitrobenzoate of the product had a m.p. 90–98°, again indicating a mixture of the phenylthiopropanols.

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## Carbon-alkylation Reactions of Nitroalkanes. The Reaction of *p*-Nitrobenzyltrimethylammonium Iodide and Sodium 2-Propanenitronate

BY HAROLD SHECHTER AND RALPH B. KAPLAN

*p*-Nitrobenzyl halides react with sodium salts of nitro compounds to yield carbon-alkylated derivatives, whereas benzyl halides substituted in the para position with other groups, either electronegative or electropositive, give oxygen-alkylated products.[1] Recently Hamlin[2] reported that reaction of aqueous benzyldimethylphenylammonium chloride with the sodium salt of 1- or 2-nitropropane yields benzaldehyde and dimethylaniline. It has now been found that *p*-nitrobenzyltrimethylammonium iodide reacts rapidly with sodium 2-propanenitronate, in refluxing ethanol, to yield 2-methyl-2-nitro-*p*-nitrophenylpropane, trimethylamine and sodium iodide (Equation 1), whereas reaction of benzyltrimethylammonium iodide and sodium 2-propanenitronate occurs slowly in diethylene glycol at 150° to give benzaldehyde in low yields. It appears, therefore, that alkylation reactions of salts of nitroalkanes with benzyl halides or quaternary benzylammonium compounds follow similar courses and that alkylation of nitroparaffins by amines does not always proceed through an elimination–addition mechanism.[3]

$$p\text{-}NO_2C_6H_4CH_2N(CH_3)_3I + (CH_3)_2CNO_2Na \longrightarrow p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 + (CH_3)_3N + NaI \quad (1)$$

### Experimental

**2-Methyl-2-nitro-*p*-nitrophenylpropane.**—*p*-Nitrobenzyltrimethylammonium iodide (30 g., 0.093 mole), m.p. 195°, lit. 198°,[4] was added to a mixture of sodium (2.2 g., 0.096 mole) and 2-nitropropane (65 g., 0.75 mole) in absolute ethanol (400 ml.) and the solution was then refluxed for 30 hours. As the solution was heated, the odor of trimethylamine became apparent, and trimethylamine was evolved continuously throughout the reaction. The brown mixture was then distilled until much of the alcohol had been removed. The residue, upon being cooled slowly, crystallized first to yield *p*-nitrobenzyltrimethylammonium iodide (5.3 g., 0.0165 mole, 17.7%), m.p. 194–195°, and then a crude mixture of the quaternary ammonium salt and 2-methyl-2-nitro-*p*-nitrophenylpropane. Decolorization and fractional recrystallization of the crude product from mixtures of ethanol and water yielded pure 2-methyl-2-nitro-*p*-nitrophenylpropane (12.4 g., 0.585 mole) in 63% yield; m.p. 64–65°, lit.[1c] 65°. The melting point of the product was not depressed by an authentic sample which was prepared from *p*-nitrobenzyl chloride and sodium 2-propanenitronate.[1c]

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[1] (a) T. Posner, *Ber.*, **31**, 657 (1898); (b) L. Weisler and R. W. Helmkamp, THIS JOURNAL, **67**, 1167 (1945); (c) H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767 (1949); (d) H. B. Hass, E. J. Berry and M. L. Bender, *ibid.*, **71**, 2290 (1949); (e) H. B. Hass and M. L. Bender, *ibid.*, **71**, 3482 (1949).

[2] W. E. Hamlin, Abstract, Ph.D. Thesis, University of Illinois, 1949.

[3] H. R. Snyder and W. E. Hamlin, THIS JOURNAL, **72**, 5082 (1950).

[4] E. Stedman, *J. Chem. Soc.*, 1902 (1927).

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## The Clemmensen Reduction of Butyroin

BY WALTER T. SMITH, JR.

It was surprising to find that reduction of butyroin with amalgamated zinc and hydrochloric acid gave not octanol-4, as might be expected, but instead gave a ketone, octanone-4. This is unusual in two respects; first, in that a ketone is formed under conditions which usually result in the reduction of ketones to hydrocarbons and, second, in that it appears to involve the reduction of a hydroxyl group while leaving a carbonyl group untouched.

Under the conditions used for the reduction, the octanone as well as the butyroin are essentially insoluble in the reaction mixture. It seemed likely that if the reaction mixture was homogeneous the octanone might be more easily reduced to octane. However, when runs were made in which the water was replaced by sufficient ethyl alcohol or acetic acid to make a completely homogeneous reaction mixture, the main product was still octanone-4.

Although the yield of octanone-4 is 36% when the reduction is carried out for only two hours, the amount of octanone formed is not decreased by its reduction to octane when the time of the reaction is extended. Thus, in runs of four, ten and twenty-seven hours the yield of ketone is 50–60%.

The amount of octane formed in any of the reactions, even those running for as long as twenty-seven hours, must be very small. The boiling point of the small foreruns rose steadily to that of octanone-4, with no leveling off near the boiling point of octane. In order to exclude the possibility that any octane which might be formed was escaping through the condenser, a twenty-hour run was made in which any vapors which escaped through the condenser were collected in a trap cooled in Dry Ice and isopropyl alcohol. Only a trace of liquid was collected in the trap and its refractive index was not that of octane. It appears that octanone-4 is resistant to reduction under the conditions employed here. When a sample of octanone-4 was refluxed with amalgamated zinc and hydrochloric acid for five days the forerun was not appreciably larger than in other runs on butyroin, although the recovered octanone-4 had a wider boiling range than originally.

The possibility that 4,5-octanediol might be an intermediate in the reaction was suggested by the fact that this glycol has been reported to yield octanone-4 when heated with dilute sulfuric acid in a sealed tube.[1] To test this possibility *meso*-4,5-octanediol was refluxed with hydrochloric acid of the same concentration used in the reductions. Although some ketone is formed in this way, the amount is so small that the glycol cannot be considered as an intermediate. The presence of amal-

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