

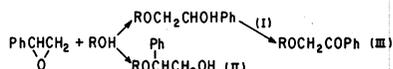
The Alkali-Catalyzed Reaction of Styrene Oxide with Saturated Fatty Alcohols

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The alkali-catalyzed reaction of styrene oxide with 12-, 14-, 16-, and 18-C long-chain alcohols gave $\text{ROCH}_2\text{CHOHC}_6\text{H}_5$ as the main product. Structure was confirmed by CrO_3 oxidation to the phenacyl ether, $\text{ROCH}_2\text{COC}_6\text{H}_5$.

THE REACTION of styrene oxide with short chain primary alcohols such as methyl (2) or allyl (1) alcohol under alkaline catalysis apparently takes place to yield a mixture of two isomers (I, II), in which the secondary alcohol predominates.



The present paper is a continuation of an investigation of the alkali-catalyzed reaction of long chain alcohols (dodecanol, tetradecanol, hexadecanol, octadecanol) with epoxides (ethylene oxide, propylene oxide, 1,2-butylene oxide) (4, 5, 6). In the present investigation, oxidation to the phenacyl ether (III) agrees with other evidence (4) to show that for each of the three unsymmetrical oxides the ring opens in the same way, under alkaline catalysis, to give a secondary alcohol as the main product.

Gas liquid chromatography of the distilled ether alcohol fraction showed two peaks, a minor forerun and a major component representing about 85% of the fraction. The minor component was formed in too small an amount to be isolated in a pure state. Low temperature crystallization from acetone removed the minor component in the filtrate

and gave the pure ether alcohol (I) listed in Table I.

The two components are apparently the isomers I and II since a fraction obtained from the acetone filtrate, or as a forerun on redistillation, rich in the lesser component (II), has the same molecular weight, refractive index, and per cent hydroxyl as the isolated ether alcohol (I). The infrared spectra are the same except for subtle differences in the 1600-, 1350-, and 1100- cm^{-1} regions.

Chromic acid oxidation of I gave the phenacyl ether (III) listed in Table I, identified by elemental analysis and infrared spectra, proving I to be a secondary alcohol.

EXPERIMENTAL

Materials. Normal primary alcohols purified from good commercial grades by redistillation and low temperature crystallization from acetone had the following constants: dodecanol, n_D^{25} 1.4409; tetradecanol, n_D^{40} 1.4383, m.p. 37.4–38.4°; hexadecanol, n_D^{60} 1.4361, m.p. 49.3–49.6°; octadecanol, n_D^{60} 1.4380, m.p. 57.9–58.4°. Purity by GLC, 97–99%.

Styrene oxide was redistilled, from a good laboratory grade, through a 13-inch column packed with Berl saddles, collecting the fraction $b_{7.5}$ 67–67.5°.

Analysis for terminal epoxide (3): theory, 13.32%; found: 13.20%.

Table I. Properties of Ether Alcohols and Phenacyl Ethers

R	Ether Alcohol, ROCH ₂ CHOHPh				Phenacyl Ether, ROCH ₂ COPh		
	Yield of distilled product (corrected for purity), %	Melting point, °C.	n_D^{60}	Purity ^a (GLC), %	Melting point, °C.	n_D^{60}	Purity ^a (GLC), %
C ₁₂ H ₂₅	29	20 ^b	1.4727	98	36.7-37.1	1.4769	98
C ₁₄ H ₂₉	33	31.3-31.8	1.4710	99 ⁺	45.7-46.3	1.4755	99 ⁺
C ₁₆ H ₃₃	30	39.8-40.5	1.4700	99 ⁺	52.1-52.6	1.4739	99
C ₁₈ H ₃₇	29	46.6-47.0	1.4688	99	58.1-59.0	1.4728	99 ⁺

^a Found and theoretical values for OH, C, and H agreed within 0.2, 0.2, and 0.1%, respectively. ^b Freezing point.

Preparation of Ether Alcohols. The reaction of styrene oxide with fatty alcohols is illustrated in the case of tetradecanol. Tetradecanol (214 grams, 1 mole) and 1.07 grams (0.5%) potassium hydroxide were heated to 130°, and 180 grams (1.50 moles) of styrene oxide was added dropwise with stirring over a period of 3 hours. The stirred mixture was kept at 130° to 140° C. for another 3 hours, cooled, neutralized, washed, and distilled through a 13-inch Vigreux column at 0.05 mm. of pressure. After removing 85 grams of tetradecanol, the ether alcohol fraction distilled at 160-68.5° C. (111 grams, yield 33%). The product was redistilled and crystallized from 5 volumes of acetone at -25° to give 1-phenyl-2-tetradecyloxyethanol, m.p. 31.3-31.8° C. corrected, which showed only one component in the vapor phase chromatogram.

Chromic Acid Oxidation. A solution of 0.55 gram (0.0055 mole) of chromium trioxide in 50 ml. of glacial acetic acid was stirred into a solution of 1.125 grams (0.00336 mole) of the pure ether alcohol from tetradecanol at room temperature. After the color changed to green, water and ethyl ether were added. The ether extract was washed with water, aqueous sodium carbonate, and again with water until the washings were neutral. Evaporation of the ether extract

gave the keto ether, yield 88%, recrystallized from acetone to give tetradecyl phenacyl ether, m.p. 45.7-46.3°, purity greater than 99% by GLC. The infrared spectrum showed a strong CO peak, characteristic ether absorption, and the absence of hydroxyl or carboxylic acid groups.

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RECEIVED for review November 27, 1967. Accepted May 31, 1968. Presented at the 3rd Middle Atlantic Regional Meeting, ACS, Philadelphia, Pa., February 1-2, 1966. The Eastern Regional Research Laboratory is a Laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S., Department of Agriculture.