Addition of Alkyl Orthoformates to Olefin Oxides[1]

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Alkyl orthoformates react with olefin oxides in the presence of boron trifluoride to give compounds of the type $HC(A_xOR)(A_yOR)(A_zOR)$, in which A is an olefin oxide unit and x, y, and z are any integers including zero. If the concentration of boron trifluoride exceeds 0.5% or the temperature 10°, the alkyl orthoformate is mostly degraded to the alkyl formate and the dialkyl ether. Concentrated sulfuric acid, anhydrous stannic chloride, hydrated calcium silicate, and boron trifluoride ethereate do not catalyze the reaction. Heating the reagents without catalyst in sealed tubes caused no change at 110–135° and explosion at 145–147°. As might be expected, the 1:1 addition was favored by keeping the orthoformate in excess. The principal differences between this reaction and the addition of acetals to olefin oxides[3] are (a) the tolerance of higher catalyst concentration by the acetals, and (b) the adjacency of olefin oxide units in the acetal adducts, *e.g.*, $CH_3O(CH_2CH_2O)_2CH_2OCH_3$, but predominant nonadjacency in the orthoester adducts, such as $HC(OCH_2CH_2OC_2H_5)_3$.

EXPERIMENTAL

Ethyl orthoformate and ethylene oxide. Boron trifluoride (1.5 g., 0.02 mole) was dissolved in ethyl orthoformate (300 g., 2 moles) at 0° contained in a one-liter, three-neck flask equipped with an ice water-cooled reflux condenser, a power stirrer, and a thermometer. A solution of ethylene oxide (22 g., 0.5 mole) in chilled ethyl orthoformate (150 g., 1 mole) was added to the catalyst solution at such a rate as to maintain the temperature between 3 and 6°. After 5 hr. more at 0–5° the boron trifluoride was destroyed by stirring the mixture for 30 min. with potassium carbonate (25 g.) dissolved in about 30 ml. of water. Anhydrous sodium sulfate (50 g.) was stirred in during 15 min., and the mixture was allowed to warm to room temperature overnight. The solids were filtered off and washed with ethyl ether and the ether washings combined with the filtrate. The mixture was distilled at atmospheric pressure to remove the ethyl ether, degradation products of ethyl orthoformate, and finally the excess ethyl orthoformate. The residue was distilled at reduced pressure through a Todd column to separate the products, which appeared in three principal fractions.

1-Diethoxymethoxy-2-ethoxyethane (I), b.p. 112–117° (35 mm.), n_D^{20} 1.4060, d_{20} 0.9254, yield 45 g. (47%).

Anal. Calcd. for $C_9H_{20}O_4$: C, 56.22; H, 10.49; MR, 50.4. Found: C, 56.40; H, 10.51; MR, 51.0.

I was characterized by hydrolysis in 6*N* hydrochloric acid to (a) ethanol, yielding its 3,5-dinitrobenzoate, m.p. 92°, and (b) 2-ethoxyethanol, also identified as the 3,5-dinitrobenzoate, m.p. 67–69°.[4]

1-Diethoxymethoxy-2-(2-ethoxyethoxy)ethane (II) and ethoxy-bis-(2-ethoxyethoxy)methane (III) were obtained as a mixture boiling at 156–158° (35 mm.) in 17% yield (10 g.). The mixture had n_D^{20} 1.4190 and d_{20} 0.9824.

Anal. Calcd. for $C_{11}H_{24}O_5$: C, 55.90; H, 10.23; MR, 61.5. Found: C, 55.70; H, 10.36; MR, 60.6.

Hydrolysis of the mixture yielded ethanol, 2-ethoxyethanol, and a little liquid boiling at 185–195°, taken to be 2-(2-ethoxyethoxy)ethanol. The kind and quantity of alcohols produced by hydrolysis indicate that III predominated but that some II was present also.

1-Diethoxymethoxy-2-[2-(2-ethoxyethoxy)ethoxy]ethane (IV), 1-[ethoxy-(2-ethoxyethoxy)methoxy]-2-(2-ethoxyethoxy)ethane (V) and tris-(2-ethoxyethoxy)methane (VI) were obtained as a mixture boiling at 184–187° (35 mm.), n_D^{20} 1.4208, d_{20} 0.9887, yield 7 g. (15%).

Anal. Calcd. for $C_{13}H_{28}O_6$: C, 55.69; H, 10.06; MR, 72.5. Found: C, 55.84; H, 10.36; MR, 71.8.

Hydrolysis of the mixture yielded ethanol, 2-ethoxyethanol, a liquid boiling at 194–197° (n_D^{20} 1.4237), evidently 2-(2-ethoxyethoxy)ethanol, and some still higher-boiling material. Since only a very little liquid boiling above 197° was obtained, no direct identification was made. However, its mode of formation and its high boiling point indicate that it was 2-[2-(2-ethoxyethoxy)ethoxy]ethanol. The kind and quantity of alcohols formed by hydrolysis products indicate that VI predominated in the mixture.

Methyl orthoformate and ethylene oxide. Methyl orthoformate (318 g., 3 moles), ethylene oxide (50 ml., 1 mole) and boron trifluoride (1.5 g., 0.02 mole) were caused to react as before. After the ethyl ether, methyl orthoformate degradation products, and excess methyl orthoformate were removed, 30 g. (20%) of 1-dimethoxymethoxy-2-methoxyethane (VII) was obtained, b.p. 172–174° (743 mm.), n_D^{20} 1.4012, d_2 1.001.

Anal. Calcd. for $C_6H_{14}O_4$: C, 47.99; H, 9.39; MR, 36.4. Found: C, 48.09; H, 9.41; MR, 36.5.[5]

VII was characterized by hydrolysis in 6*N* hydrochloric acid to (a) methanol, yielding the α-naphthylurethan, m.p. 118.5–119.5°, and (b) 2-methoxyethanol, also characterized as the α-naphthylurethan, m.p. 112–113°.[4]

The residue from VII distilled with decomposition even at reduced pressure.

Ethyl orthoformate and propylene oxide. Ethyl orthoformate (450 g., 3 moles), propylene oxide (30 g., 0.5 mole) and boron trifluoride (1.5 g., 0.02 mole) were caused to react as before. After the preliminary fractions had been removed, further distillation at reduced pressure through a Todd column gave three principal portions.

Fraction 1, consisting of the isomeric 1:1 adducts of propylene oxide and ethyl orthoformate, boiled at 113–119° (36 mm.) n_D^{20} 1.4040, d_2 0.9123, yield 39 g. (37%). No attempt was made to separate or characterize the individual isomers.

Anal. Calcd. for $C_{10}H_{22}O_4$: C, 58.22; H, 10.75; MR, 55.0. Found: C, 57.99; H, 11.12; MR, 55.3.

Fraction 2, consisting of the isomeric 2 propylene oxide: 1 ethyl orthoformate adducts, had b.p. 151–153° (36 mm.) n_D^{20} 1.4169, d_{20} 0.9411, yield 26 g. (20%). Again no attempt was made to separate or characterize isomers.

Anal. Calcd. for $C_{13}H_{28}O_5$: C, 59.05; H, 10.67; MR, 70.7. Found: C, 58.40; H, 10.71; MR, 70.6.

Fraction 3, consisting of the isomeric 3 propylene oxide: 1 ethyl orthoformate adducts, boiled at 172–174° (36 mm.), n_D^{20} 1.4211, d_{20} 0.9572, yield 18 g. (11%).

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(1) Abstracted from a thesis submitted by Frank Bier Slezak in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Oklahoma Agricultural and Mechanical College, 1955.

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(3) O. C. Dermer and A. M. Durr, *J. Am. Chem. Soc.*, **76**, 912 (1954).

(4) N. D. Cheronis and J. B. Entrikin, *Semimicro Qualitative Organic Analysis*, Thomas Y. Crowell Company, New York, N. Y., 1947.

(5) Analyses by Geller Laboratories, New York, N. Y.

Anal. Calcd. for $C_{16}H_{34}O_6$: C, 59.59; H, 10.62; MR, 86.4. Found: C, 59.71; H, 10.94; MR, 85.4.

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The Addition of Hydrogen Bromide to Allyl Chloride[1]

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The ionic addition of hydrogen bromide to allyl chloride would appear to be a rather simple reaction, which should follow Markownikoff's rule. However, conflicting reports have appeared in the literature. Shostakovskii[2] reported an unusual dependence of orientation on temperature; the addition reaction yielded 1-chloro-2-bromopropane exclusively at 18°, 1-chloro-3-bromopropane at −19°, and equal amounts of the two isomers at 0°. That same year Antsus,[3] referring to Shostakovskii's work, claimed that the orientation is independent of temperature (−19° to 18°) and that in all cases he obtained only 1-chloro-2-bromopropane. Although the earlier paper has been quoted in a recent review,[4] Antsus' work appears to have been overlooked.

Because an actual temperature dependence such as was claimed[2] would be theoretically significant, we have reexamined the ionic addition of hydrogen bromide to allyl chloride with particular attention to olefin purification,[5] exclusion of air and light,[5] and possibilities of product isomerization. The procedures previously described[2,3] were followed closely. Products were identified by comparison of physical and spectral properties with those of authentic samples independently synthesized.

Contrary to both previous reports,[2,3] mixtures of isomers were obtained in all experiments. Except in those experiments in which we failed to exclude air completely, the product distribution was virtually invariable with Markownikoff orientation predominating (90 ± 2%). The orientation was independent of temperature (−18° to 18°), of the use of acetic acid solvent, and of reaction time. When air was admitted, the peroxide-effect[5] led to greatly altered product distributions. No isomerization could be detected when either of the two isomeric products (1-chloro-2-bromopropane and 1-chloro-3-bromopropane) was treated with hydrogen bromide under the same conditions used in the addition reactions. This observation precludes the possibility that either chlorobromopropane is an intermediate in the formation of the other. That is, they are formed independently in the reaction mixture, probably from two different intermediates or transition states.

Based on the report[6] that some migration of chlorine occurs in the addition of hypochlorous acid to Cl^{36}-labeled allyl chloride, an attempt was made to detect 1-bromo-2-chloropropane in the product mixture. Infrared spectral analysis[7] did indeed suggest the presence of very small amounts of this isomer mixed with the 1-chloro-2-bromopropane fraction, but conclusive evidence was not obtained.

EXPERIMENTAL[8]

Independent synthesis of the chlorobromopropanes. 1-Chloro-2-bromopropane and 1-chloro-3-bromopropane were prepared from phosphorus tribromide (0.27 mole) and the appropriate chloropropanol (0.53 mole). After the initial addition of phosphorus tribromide at 0°, the mixture was allowed to warm to room temperature and was stirred for 10 hr. longer. The 1-chloro-2-bromopropane[9] was obtained in 77% yield; b.p. 118–120°, n_D^{20} 1.4776, d_4^{20} 1.537. The 1-chloro-3-bromopropane[9] was obtained in 75% yield; b.p. 140–142°, n_D^{20} 1.4866, d_4^{20} 1.592. The infrared spectra of the two isomers were similar but were readily distinguished by the following non-common bands (s and m refer to strong- and medium-intensity absorption, respectively; numbers refer to wavelength in microns): for 1-chloro-2-bromopropane, 7.25 (s), 8.90 (m), 9.00 (m), 9.95 (s), 11.05 (s); for 1-chloro-3-bromopropane, 7.56 (s), 10.50 (s), 11.65 (s), 11.90 (s).

A small amount of 1-bromo-2-chloropropane[9b] was prepared in poor yield from thionyl chloride and 1-bromo-2-propanol (b.p. 67–70°/40 mm., n_D^{20} 1.4760, d_4^{20} 1.542; obtained in 62% yield by the reaction of 48% hydrobromic acid with propylene oxide[10]). In the one preparation attempted, the amount of 1-bromo-2-chloropropane obtained

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[1] From the M. S. thesis of J. S. Conte, Louisiana State University, August, 1956.

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[5] To preclude free radical addition. M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933). F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

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[7] When one product mixture was distilled, several fractions boiling in a 1° range were collected. The infrared spectra of those boiling between 115° and 117° (very small amounts of material) showed medium-intensity absorption at 9.05 μ. This band gradually disappeared in the spectra of the fractions boiling between 118° and 122°. The independently prepared 1-bromo-2-chloropropane, alone of the three isomers, showed absorption at 9.05 μ.

[8] All infrared spectra were obtained with a Perkin-Elmer Model 21 double-beam recording infrared spectrophotometer (0.05 mm. cells, NaCl windows)

[9] (a) I. Heilbron, "Dictionary of Organic Compounds," p. 479, Oxford University Press, London, 1953 (b) A. Dewael, *Bull. soc. chim. Belges.*, **39**, 87 (1930).

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