

[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH DEPARTMENT, THE DOW CHEMICAL COMPANY, FREEPORT, TEX.]

Reaction of Epoxides with Ferric Chloride¹

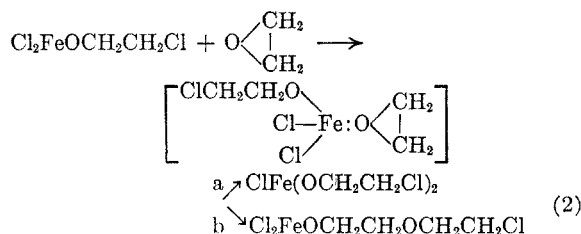
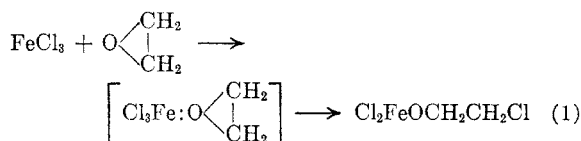
ALEXEJ B. BOŘKOVEC

Received December 2, 1957

The reactions of ferric chloride with ethylene oxide and propylene oxide are described. The structure of the reaction products indicates that "internal polymerization" takes place before all of the three chlorine atoms are displaced by the epoxide. The effect of solvents upon the reaction and the formation of by-products is discussed.

The epoxy group is, in general, quite reactive towards reagents of the Lewis-acid type, especially certain halides of metallic and semi-metallic elements, in which, under suitable conditions, all of the halogen can be ultimately replaced by an alkoxy group derived from the corresponding epoxide.

In this work the reaction between ethylene and propylene oxides and anhydrous ferric chloride was investigated. The two epoxides react quite violently with chlorides of Al,² Ti,³ Sb,⁴ Bi,⁴ Si⁵ and B⁶ and if the molar ratio of the reactants is sufficient, completely substituted metal chloroalkoxy compounds result. Ferric chloride,² on the other hand, when allowed to react with three or more moles of ethylene oxide, yields an oily product which contains approximately one-third of the total chlorine in ionic (*i.e.*, hydrolyzable) form, presumably as unreacted Fe-Cl groups. The reaction may be imagined to proceed in several steps *via* iron compound-epoxide intermediates.⁷ The first step is analogous



(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 1957.

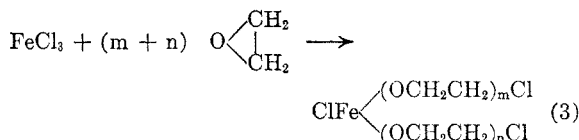
(2) F. Schmidt, U. S. Patent 2,700,048 (1955).

(3) M. S. Malinovskii, *J. Gen. Chem. (U.S.S.R.)*, 10, 1918 (1940); *Chem. Abstr.*, 35, 4736 (1941); J. B. Rust and L. Spialter, U. S. Patent 2,709,174 (1955).

(4) M. S. Malinovskii and M. K. Romantsevich, *Sbornik Statei Obshchei Khim.*, 2, 1366-1369 (1953); J. B. Rust and L. Spialter, U. S. Patent 2,511,013 (1950); D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, 79, 897 (1957).

(5) W. I. Patnode and R. O. Sauer, U. S. Patent 2,381,137 (1945).

(6) J. D. Edwards, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1470 (1955); 348 (1957); D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, 79, 900 (1957).



to the reaction of other metal halides^{3,4} with an epoxide but in the second step ferric chloride is distinct from all the elements hitherto investigated in that it forms (2b) a compound containing a dimerized OCH₂CH₂ unit. There seems to be a competition between the functional groups (—OCH₂CH₂Cl and —Cl) for the epoxide depending upon the number of undisplaced Cl atoms. As shown in equation (3), which summarizes the reaction in general terms, even if (m+n) > 3 the last chlorine atom remains undisplaced and the alkoxy side-chains increase in length. This process may be called "internal polymerization" in order to distinguish it from a different polymerization process which, especially at higher temperatures, takes place in the presence of Lewis acids.⁸⁻¹⁰ The latter reaction can be quite effectively minimized by keeping the temperature below 5° but the extent of the "internal polymerization" is also dependent upon the temperature and the maximum chain length will not under such conditions exceed five units. As the equation (3) indicates the reaction product is a mixture of isomeric and homologous compounds and because all attempts for separation of the components by crystallization, distillation, extraction, etc. failed, the most valuable information was obtained by hydrolyzing the mixture and identi-

(7) No such intermediate was ever isolated in several attempts; the epoxy ring seems to be too reactive to permit stability. Analogous compounds derived from tetrahydrofuran and BCl₃ have been isolated (see reference 6).

(8) See for example K. H. Meyer, *High Polymers*, Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1942, pp. 195-196 and the references mentioned there. The mechanism of this polymerization is still far from being fully understood but it can be assumed that since catalysts such as metal oxides or carbonates are also active it must be different from the "internal polymerization" suggested above.

(9) Petrochemicals Ltd., Belgian Patents 550,445 and 551,608 (1956); F. N. Hill, F. E. Bailey, and J. T. Fitzpatrick, Abstracts of Papers, 1T, 132nd Meeting of the American Chemical Society (1957).

(10) A quite different case of "internal polymerization" was discovered in the addition of acetals to olefin oxides; see O. C. Dermer and A. M. Durr, Jr., *J. Am. Chem. Soc.*, 76, 912 (1954).

the temperature being kept below 30° and the addition lasting 8 hr. The mixture was then stirred overnight. The solvent was removed in the same manner as above. The reaction product was a black (bright yellow in thin layers), viscous oil.

Anal. Calcd. for $C_{12}H_{24}Cl_3FeO_4$: Cl, 26.9 (ionic chlorine, 9.0); Fe, 14.2; mol. wt., 395. Found: Cl, 27.1 (ionic chlorine, 8.9); Fe, 14.5; mol. wt., 390.

Hydrolysis of the ferric chloride-propylene oxide reaction product. The procedure was the same as in the former case except that the iron-containing residue after being heated with water and filtered out was extracted with two 50-ml. portions of acetone. The acetone extract was then combined with the other filtrates. The amount of the ferric chloride-propylene oxide product was 197 g. (0.5 mole), and 130 g. (85% yield) of the chlorohydrins was isolated. The results of the fractional distillation of the mixture are summarized in Table II.

TABLE II
IRON-FREE COMPONENTS OF THE HYDROLYZED FERRIC CHLORIDE-PROPYLENE OXIDE REACTION PRODUCT

| | No. of C_2H_5O Units in the Chlorohydrin | | | |
|-----------------|--|--------|--------|---------|
| | 1 | 2 | 3 | 4 |
| B. b., °C. | 46-50 | 97-103 | 85-94 | Residue |
| p, mm. | 25 | 20 | 2 | ... |
| n_D^{25} | 1.4370 | 1.4412 | 1.4440 | 1.4501 |
| Mol. wt. calcd. | 94.5 | 152.6 | 210.7 | 258.8 |
| % OH calcd. | 18.0 | 11.1 | 8.1 | 6.3 |
| % Cl calcd. | 37.5 | 23.3 | 16.8 | 13.2 |
| Mol. wt. found | 95 | 163 | 212 | 280 |
| % OH found | 17.5 | 10.7 | 8.2 | 5.9 |
| % Cl found | 37.8 | 22.8 | 17.0 | 13.1 |

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF TENNESSEE EASTMAN COMPANY,
DIVISION OF EASTMAN KODAK CO.]

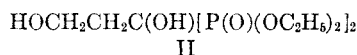
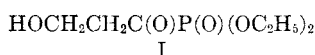
Reaction of Ketene with Dialkyl Hydrogen Phosphites and Acylphosphonates

RICHARD L. McCONNELL AND H. W. COOVER, JR.

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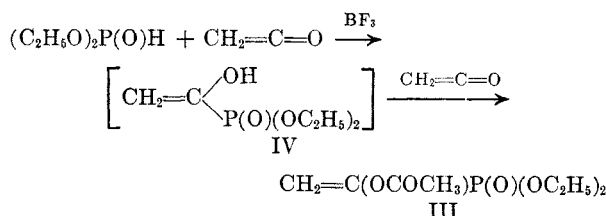
Diethyl 1-acetoxyvinylphosphonate was obtained when a crude β -propiolactone—diethyl hydrogen phosphite reaction mixture containing excess diethyl hydrogen phosphite was treated with ketene. The structure of the diethyl 1-acetoxyvinylphosphonate was proved by reducing this compound to the known diethyl 1-acetoxyethylphosphonate. The enol form of diethyl acetylphosphonate is a probable intermediate in the reaction of diethyl hydrogen phosphite with ketene to form diethyl 1-acetoxyvinylphosphonate. The infrared spectra of the products obtained when diethyl acetylphosphonate is treated with ketene indicate that a lactone, probably the β -lactone of 3-diethylphosphono-3-hydroxybutyric acid, is formed in addition to diethyl 1-acetoxyvinylphosphonate.

In recent papers, the reaction of phosphites with lactones was described.^{1,2} The phosphonates derived from the interaction of trialkyl phosphites with lactones were stable, distillable materials; however, those derived from the interaction of dialkyl hydrogen phosphites with lactones were rather sensitive to distillation, even at low pressures. For example, the reaction products from diethyl hydrogen phosphite and β -propiolactone included diethyl 3-hydroxypropionylphosphonate (I) and tetraethyl 1,3-dihydroxypropylidenediphosphonate (II).



In an attempt to stabilize these products by acetylation, the crude diethyl hydrogen phosphite— β -propiolactone reaction mixture was treated with ketene. Although the product obtained was distillable, it did not prove to be the acetyl derivative of either I or II. Again, the higher boiling fractions were rather unstable to distillation at low pressures.

The distillable material was found to be diethyl 1-acetoxyvinylphosphonate (III). This product apparently was formed by reaction of ketene with excess diethyl hydrogen phosphite present in the reaction mixture, since good yields of III were obtained by reaction of pure diethyl hydrogen phosphite with ketene. This reaction was observed independently by Kennedy and Meaburn.³ The formation of III could be explained by the following equation:



The postulated intermediate, IV, is the enol form of diethyl acetylphosphonate. This is a probable intermediate since carbonyl compounds are known to react readily with dialkyl hydrogen phos-

(1) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4450 (1956).

(2) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4453 (1956).

(3) J. Kennedy and G. M. Meaburn, *Chem. & Ind. (London)*, 930 (1956).