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Reaction of Epoxides with Ferric Chloride¹

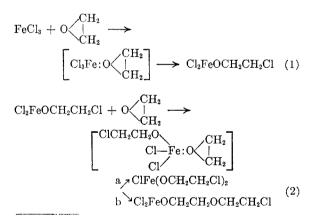
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The reactions of ferric chloride with ethylene oxide and propylene oxide are described. The structure of the reaction products indicates that "internal polymerization" takes place before all of the three chlorine atoms are displaced by the epoxide. 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 compoundepoxide 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).

(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).

$$\begin{array}{ccc} FeCl_{3}+(m+n) & O \swarrow \begin{array}{c} CH_{2} \\ CH_{2} \\ CIFe \swarrow \begin{array}{c} (OCH_{2}CH_{2})_{m}Cl \\ (OCH_{2}CH_{2})_{n}Cl \end{array} (3) \end{array}$$

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 (-O-CH₂CH₂Cl 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 sidechains 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-

(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).

⁽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. Pathode and R. O. Sauer, U. S. Patent 2,381,137 (1945).

⁽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 tetrahydro-furan and BCl_{s} 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.

fying the resulting chlorohydrins. Table I shows typical results of the hydrolysis of $FeCl_3$ -ethylene and propylene oxide reaction products.

TABLE I PRODUCTS OF HYDROLYSIS OF ADDUCTS

	% of $Cl(C_2H_4O)_nH$ or $Cl(C_3H_6O)_nH$ Produced					
Ratio of Reagents	n = 1	n = 2	n == 3	n = 4	n > 4	
$\begin{array}{l} \text{FeCl}_{3} + 4 \text{ E.O.} \\ \text{FeCl}_{3} + 4 \text{ P.O.} \end{array}$	23 34	$\frac{31}{32}$	$\begin{array}{c} 27 \\ 15 \end{array}$	12 10	7	

Recently Worsfold and Eastham⁴ suggested a rather different explanation for the formation of compounds derived from tin tetrachloride. The basic idea which was well supported by kinetic data represented the growing side chain as an ion which increased in length by reacting with additional molecules of ethylene oxide. Unfortunately, the termination step where the chloroalkoxy compound was supposed to be formed was only schematically presented without much regard for the distances between the carbonium ion and the chlorine-tin group; it is difficult to imagine how these two centers could come sufficiently close together to accomplish the suggested reaction.

Propylene oxide reacts very much like ethylene oxide; only the analysis of the products of hydrolysis is much more difficult owing to the presence of isomeric chlorohydrins (when n = 4, 16 isomers are possible). The reactivity of propylene oxide is much lower than that of ethylene oxide, as is evident in the by-product formation. 1,4-Dioxane is the chief by-product of the ethylene oxide reaction¹¹ but the corresponding dimethyldioxane is not formed in the propylene oxide reaction.

Solvents can have a very pronounced effect upon the nature of the reaction products. Ethers (and alcohols) take part in the reaction in a rather complicated fashion as a consequence of an extensive alkoxyl interchange. The hydrolysis of the

$$>$$
Fe $-$ OR + R₂'O \longrightarrow $>$ Fe $<$ OR $OR_{2'}$ \longrightarrow $>$ Fe $-$ OR' + ROR'

reaction products then yields a mixture of chloro and hydroxy ethers instead of chlorohydrins. According to Meerwein and co-workers¹² a highly reactive oxonium compound is formed first; it apparently reacts further with the excess of the epoxide in a way similar to that indicated in Equation 3. Aromatic solvents are to some extent alkylated by the epoxide¹³ and 2-phenylethanol was actually identified among the products of the FeCl₃-ethylene oxide reaction when benzene was used as a solvent. Halogenated hydrocarbons seem to be most suitable as reaction media in spite of the fact that ferric chloride is insoluble in them and vigorous stirring is required to keep it in suspension.

The chloroalkoxyferric chlorides are extremely sensitive towards moisture and, when partially hydrolyzed, form amorphous solids possessing an extremely large surface area. Both unhydrolyzed and partially hydrolyzed compounds have been found to have surprising capacity for catalyzing the polymerization of alkylene oxides.¹⁴

EXPERIMENTAL

Reaction of ferric chloride with ethylene oxide. A suspension of 32.4 g. (0.2 mole) of anhydrous (sublimed) ferric chloride in 500 ml. of carbon tetrachloride which was previously dried over phosphorous pentoxide was placed in a dry 1000-ml. flask furnished with a stirrer, reflux condenser, and a gas dispersion tube. The system was cooled to -10° and a mixture (approx. 1:1) of nitrogen and ethylene oxide was introduced through the tube while the contents of the flask were vigorously stirred. Efficient stirring had to be maintained as long as there was any solid present to prevent the formation of a sticky cake. While the temperature was maintained between -10° and 0° , 36 g. (0.8 mole) of ethylene oxide was introduced within 6 hr. The mixture was then stirred 1 hr. at room temperature and filtered under nitrogen. The filtrate was distilled under reduced pressure to remove the solvent and about 1 ml. of 1,4dioxane. The remaining dark brown (in thin layers bright yellow), viscous liquid (66 g.) was kept at 100° (0.1 mm.) for 10 min. and then in vacuo for 24 hr.

Hydrolysis of the ferric chloride-ethylene oxide reaction product. A solution of 170 g. (0.5 mole) of the reaction product in 500 ml. of carbon tetrachloride was mixed with 50 ml. of water and refluxed for 2 hr. on a steam bath. The brown precipitate was isolated by filtration (filtrate A). mixed with 100 ml. of water, heated on a steam bath for 24 hr., and again collected (filtrate B). Filtrate B was saturated with potassium carbonate (kept cool) and extracted twice with 50 ml. of ether. The ethereal extracts were combined with filtrate A, dried over potassium carbonate, and distilled. After the solvents were removed, the liquid (about 100 ml.) was transferred to a smaller flask and distilled at reduced pressure using 120-cm., helices-packed column operated at reflux ratio of 100:1. The individual fractions (see Table I) were analyzed (infrared spectra, refractive index, % of OH and Cl, mol. wt.) and compared with actual samples of the chlorohydrins. The total amount of recovered chlorohydrins was 155 g. (92%). The last fraction (n > 4 in Table I) was the distillation residue and consisted of a mixture of several extended chlorohydrins.

Reaction of ferric chloride with propylene oxide. The apparatus was the same as used for ethylene oxide. Propylene oxide (in 10% excess of the theoretical) mixed with an equal volume of carbon tetrachloride was added dropwise,

⁽¹¹⁾ A. Favorsky, J. Russ. Phys.-Chem. Soc., 38, 741 (1905); Chem. Zentr., I, 15 (1907).

⁽¹²⁾ H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, J. prakt. Chem., 154, 84 (1939).

⁽¹³⁾ J. Colonge and P. Rochas, Compt. rend., 223, 403 (1945).

⁽¹⁴⁾ M. E. Pruitt and J. M. Baggett, U. S. Patents 2,706,181 (1955); 2,706,182 (1955); 2,706,186 (1955).

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 chloridepropylene 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_3H_6O Units in the Chlorohydrin					
	1	2	3	4		
B.b., °C.	46-50	97-103	85-94	Residue		
p, mm.	25	20	2			
$n_{\rm D}^{25}$	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 caled.	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

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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 3hydroxypropionylphosphonate (I) and tetraethyl 1,3-dihydroxypropylidenediphosphonate (II).

$$\begin{array}{c} \mathrm{HOCH_{2}CH_{2}C(O)P(O)(OC_{2}H_{5})_{2}}\\ \mathrm{I}\\ \mathrm{HOCH_{2}CH_{2}C(OH)[P(O)(OC_{2}H_{5})_{2}]_{2}}\\ \mathrm{II}\end{array}$$

In an attempt to stabilize these products by acetylation, the crude diethyl hydrogen phosphite $-\beta$ -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:

$$(C_{2}H_{5}O)_{2}P(O)H + CH_{2} = C = O \xrightarrow{BF_{3}} \left[CH_{2} = C \xrightarrow{OH}_{P(O)(OC_{2}H_{5})_{2}}\right] \xrightarrow{CH_{2} = C = O}_{IV}$$

$$IV$$

$$CH_{2} = C(OCOCH_{3})P(O)(OC_{2}H_{5})_{2}$$

$$III$$

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-

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

⁽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).