THE CONDENSATION OF OLEFINS AND
ACETALS WITH OLEFIN OXIDES

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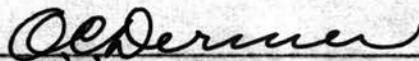
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INTRODUCTION

During the past century ethylene oxide has been subjected to reaction with a large number of compounds. This study was designed to expand the field of ethylene oxide chemistry by subjecting this oxide to reactions not studied or reported as being studied in the literature. The research was limited to the acid-catalyzed addition of ethylene oxide to mono-olefins and to acetals.

HISTORICAL

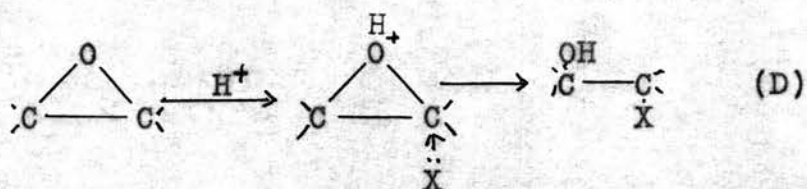## KNOWN REACTIONS OF ETHYLENE OXIDE

Ethylene oxide is a colorless, highly volatile liquid which
boils at $10.7°$. On account of its volatility and reactivity it
is not used as a solvent, but rather as a raw material in numerous
organic syntheses.

Ethylene oxide, and olefin oxides generally, react with many
organic substances containing easily replaceable hydrogens. In
these additive reactions of ethylene oxide the course is always
the same; the ring opens and the hydrogen joins the oxygen, while
the remainder of the addend goes to the carbon. The ethylene
oxide ring may be opened with a large variety of reagents, so
that olefin oxides lead simply to many classes of compounds. The
mechanism and stereochemistry implied in the opening of the oxide
ring in reactions concerned with mobile hydrogen represent a
nucleophilic displacement on the carbon (1), the displaced group
being the oxygen atom. The displacements differ with respect to
the form of the reactive oxide. This may be the oxide itself or
it may be the conjugate acid of the oxide. Thus
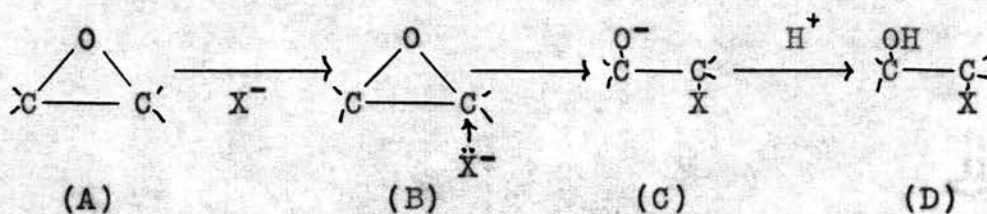
The oxide itself is symbolized by (A). If the displacement is on
the oxide itself (B) there is produced the intermediate (C) which,
by acquiring a proton, gives the acyclic product (D). However,
the conjugate acid of the oxide is much more reactive than the
oxide itself, acid catalysis being very common.

$$
\text{:C} \overset{\displaystyle O}{\underset{\displaystyle}{\triangle}} \text{C:} \xrightarrow{\ H^+\ } \text{:C} \overset{\displaystyle \overset{H}{\overset{+}{O}}}{\underset{\displaystyle}{\triangle}} \text{C} \xrightarrow{\ } \overset{\displaystyle OH}{\text{:C}} \text{---} \overset{\displaystyle C:}{\underset{\displaystyle X}{}} \qquad (D)
$$

Kinetic data by Brønsted and co-workers (2), who investigated the reaction of several oxides with water and several anions, show that, at substantial acid concentrations, reaction by way of the conjugate acid of the oxide (D) is much faster than by attack on the oxide itself.

Often there is a possibility of variation in the form of the attacking nucleophilic species in the opening of an oxide. Thus if the nucleophilic agent is symbolized by YH, the addition of base B^- may convert YH, at least partly, to a superior nucleophilic agent Y^-:

$$YH + B^- \rightleftharpoons BH + Y^-$$

Consequently basic catalysis can be observed in a number of oxide ring openings.

This research is not primarily concerned with the additive reactions of ethylene oxide which involve active hydrogen. However, for elucidation and as an aid in differentiating reactions involving active hydrogen and those not doing so, a summary of the reactions of ethylene oxide requiring the presence of active hydrogen follows. In each case there are numerous variations in the methods of producing reaction; only the more common procedures are mentioned but references that describe other means of preparation are supplied. A complete review of reactions of ethylene oxide with other than active hydrogen compounds is then given.

Reactions with Compounds Containing Active Hydrogen

Water. Wurtz (3) discovered that ethylene glycol is procuced by hydrolyzing ethylene oxide:

$$(CH_2)_2O + H_2O \longrightarrow HOCH_2CH_2OH$$

This reaction may be carried out in the liquid phase, either under the influence of traces of acid catalysts at 50-100° (4,5) or at approximately 200° under pressure with or without a catalyst (3), and catalytically in the vapor phase (6). In any case, consecutive reactions occur to some extent, with the formation of diethylene glycol, $O(CH_2CH_2OH)_2$, triethylene glycol, $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$, and higher polyethylene glycols. In order to minimize the formation of polyglycols, the hydration of ethylene oxide is carried out with a large excess of water. The acid catalysts used in the liquid-phase production of glycols include sulfuric (7-15), oxalic (16,17), and hydrochloric acids (18). In the catalytic vapor-phase process, such catalysts are used as the oxides of aluminum, titanium, zirconium, thorium, tungsten, molybdenum, and vanadium (19,20), and compounds of iron (21). The Distillers Co. Ltd. (22,23) reported that basic catalysts also can produce glycols in the hydration of ethylene oxide. Other experimentalists reporting work on the hydration of ethylene oxide are Nef (24), Reboul (25), Ganze (26), and Twigg (27). The products in any case are isolated by deactivation of the catalyst and fractional distillation.

Alcohols and Phenols. The reaction of alcohols and phenols is analogous to that with water, but yields monoethers of ethylene glycol:

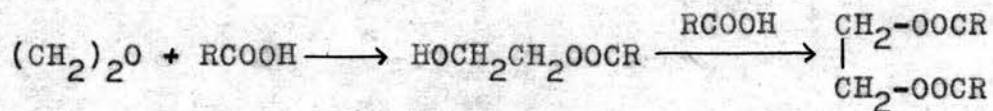$$ROH + (CH_2)_2O \longrightarrow HOCH_2CH_2OR$$

where R may be aliphatic or aromatic.

The reaction of ethylene oxide with simple monohydroxy alcohols is catalyzed by acids, such as boron trifluoride (28,29), aluminum hydrosilicates (30-33), sulfuric acid (34-38), and halides of tin (39), and by basic catalysts such as potassium hydroxide (40,41). The non-catalytic process involves a very slow reaction at temperatures ranging from 200 to 220° and pressures up to 45 atmospheres (42,43). The extension of this reaction to long-chain fatty alcohols was effected by utilizing such catalysts as sulfuric acid (37), dialkyl sulfates (44,45,46) and acidulated hydrosilicates of aluminum (47,48,49). The highly viscous ethers of polyhydric alcohols such as glycerol, sorbitol, pentoses, and ketoses are prepared in the presence of sulfuric acid (50-52). The reaction with polymerized alcohols and carbohydrates such as cellulose and starch proceeds with any one of several basic catalysts, including sodium hydroxide (53-61), liquid ammonia or hydroxylamines (62,63), tertiary amines (64,65) and sodium amalgam (66). Other studies of the reaction of ethylene oxide with alcohols will be listed only as references (67-81).

The reaction of ethylene oxide with phenols is so closely analogous to that of aliphatic alcohols that there is little need to resurvey the field. Those who have published such results are named in the bibliography (82-91).

Carboxylic acids. The reaction of ethylene oxide with organic acids is a common method for the preparation of mono- and di-esters of such acids. Wurtz (92) obtained ethylene glycol mono-acetate by combining ethylene oxide with glacial acetic acid. Reactions of this kind are generally represented as

$$(CH_2)_2O + RCOOH \longrightarrow HOCH_2CH_2OOCR \xrightarrow{RCOOH} \begin{array}{c} CH_2-OOCR \\ | \\ CH_2-OOCR \end{array}$$

This type reaction is catalyzed by small amounts of an acid such as sulfuric acid (93-96) or ferric chloride (97). A high-pressure, high-temperature process for the production of mono-acetates has been developed by the I. G. Farbenindustrie A.-G. (98). Naphthenic acids when heated eith alkylene oxides produce wax-like materials (99). Acidulated hydrosilicates of aluminum have been used to accelerate the reaction of ethylene oxide with acids (100,101). Another catalyst, suggested by Stimlig (102), is sodium benzoate. Dibasic acids react like monocarboxylic acids to yield the bis-(2-hydroxyethyl) esters of the acids (103).

The higher fatty acids such as oleic, stearic, linoleic, abietic, rosin, and tall oil acids yield water-soluble glycol esters which are useful as wetting agents (104-110).

Carboxylic esters containing active methylene groups. Although a study has not been made of the reaction of ethylene oxide with the esters of lower monocarboxylic acids, Pakendorf (111,112, 113) condensed ethylene oxide with diethyl malonate in the presence of several catalysts including piperidine, diethylamine, and tris-(2-hydroxyethyl) amine at room temperature to produce the di-lactone of 1,5-dihydroxypentane-3,3-dicarboxylic acid. The reaction proceeds according to the equation:

$$(CH_2)_2O + CH_2(COOC_2H_5)_2 \longrightarrow \begin{array}{c} H_2CH_2C \\ | \\ O-C \\ \| \\ O \end{array} CHCOOC_2H_5 + C_2H_5OH$$

$$+ (CH_2)_2O \longrightarrow \begin{array}{c} H_2CH_2C \\ | \\ O-C \\ \| \\ O \end{array} C \begin{array}{c} CH_2CH_2 \\ | \\ C-O \\ \| \\ O \end{array} + C_2H_5OH$$

Dakin (114) with the same reagents but a sodium ethoxide catalyst obtained ethyl 2-hydroxyethylmalonate and then, upon further heat-ing, the monolactone. Leland (115) has patented a reaction whereby

ethylene oxide is condensed with palmitic esters in the presence
of metal halides to yield cutting oils. Other condensations of
ethylene oxide with esters and ether-esters are promoted by zinc,
nickel or stannic chlorides (116). The waxy products are used as
surface-active agents.

Very closely resembling the reactions of malonic esters are
those of acetoacetic esters and cyclic beta-keto esters. Paken-
dorf and Machus (117) represented the first condensation by the
equation

$$(CH_2)_2O + CH_3COCH_2COOC_2H_5 \longrightarrow \begin{array}{c} H_2CH_2C \\ | \\ O-C \end{array} \overset{\displaystyle \diagup}{\underset{\displaystyle \diagdown_O}{}} CHCOCH_3 + C_2H_5OH$$

The reaction is catalyzed by water solutions of metal hydroxides
(118). Cyclic beta-keto esters (119) react with ethylene oxide to
yield products very like those obtained from the reaction of aceto-
acetic esters.

Sulfhydryl compounds. Chichibabin and Bestuzhev (120) noted
that equimolar proportions of ethylene oxide and hydrogen sulfide
in aqueous solution at 8-10° over a period of ten days yield thio-
ethylene glycol quantitatively. Doubling the proportions of ethyl-
ene oxide produces 2-mercaptoethoxyethanol.

$$H_2S + (CH_2)_2O \longrightarrow HSCH_2CH_2OH + (CH_2)_2O \longrightarrow HSCH_2CH_2OCH_2CH_2OH$$

Mineral acids, chlorides of aluminum and heavy metals, and glass
beads moistened with the reaction product are reported (121) to
act efficiently as catalysts. The presence of water, lower
alcohols, and catalysts such as porous clay or alumina favors the
production of a sulfonium base, $HOS(CH_2CH_2OH)_3$, besides thio-
glycols (122). Using ferric or aluminum sulfide in the vapor-
phase reaction at 350° produces normal products (123) but over
aluminum oxide at 300-400° significant yields of thiophene and

ethanethiol have been obtained (124). At 200° the same reaction

yields para-oxathiane and para-dithiane (125).

Mercaptans react like lower alcohols to form hydroxyethyl

thioethers (121). Davidson and Olin (126) have patented an alkali-

catalyzed process for the production of long-chain 2-hydroxyethyl

thioethers from aliphatic mercaptans containing from six to twenty-

four carbon atoms. Other patents claim the use of sodium methox-

ide (127,128,129) as catalyst.

Carbothiolic acids react with ethylene oxide to yield 2-hy-

droxyethyl esters (129):

$$(CH_2)_2O + RCOSH \longrightarrow RC(O)SCH_2CH_2OH$$
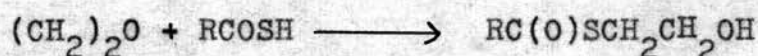
Thiolbenzoic acid, however, on long heating yields small

amounts of 2-mercaptoethyl benzoate by inversion, besides the expec-

ted 2-hydroxyethyl thiolbenzoate.

Alkali acid sulfites combine with ethylene oxide give alkali

isethionates (130). Previous work on this reaction (131-134) had

not definitely established the nature of the product.

Primary and secondary amino compounds. Amines constitute one

of the largest classes of compounds which react with olefin oxides.

Wurtz (135) condensed ethylene oxide with dilute and concentrated

ammonia to produce a mixture of mono-,di-, and triethanolamines.

It has been shown that water must be present in trace amounts to

permit reaction (136).

$$NH_3 + (CH_2)_2O \longrightarrow H_2NCH_2CH_2OH + HN(CH_2CH_2OH)_2 +$$
$$N(CH_2CH_2OH)_3$$
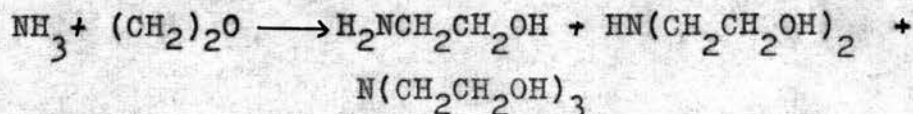
Knorr (137), as well as Germann and Knight (138), showed that the

proportions of the three products depend to a great extent on the

proportions of the reactants, an excess of the olefin oxide favor-

ing the formation of triethanolamine. Numerous references are concerned with methods for production of the ethanolamines (139-158). The presence of excess ethylene oxide tends to produce mono-, bis-, and tris(2-hydroxyethyl) ethers of triethanolamine (159, 160, 161).

Primary and secondary amines, like ammonia, can be condensed with ethylene oxide to yield the corresponding alkyl- and aryl-amino alcohols. With ethylamine, for example, the reaction takes the course:

$$C_2H_5NH_2 + (CH_2)_2O \longrightarrow C_2H_5NHCH_2CH_2OH \xrightarrow{\ 2\ (CH_2)_2O\ }$$

$$C_2H_5N \Big\langle \begin{array}{l} (CH_2CH_2O)_2H \\ CH_2CH_2OH \end{array}$$
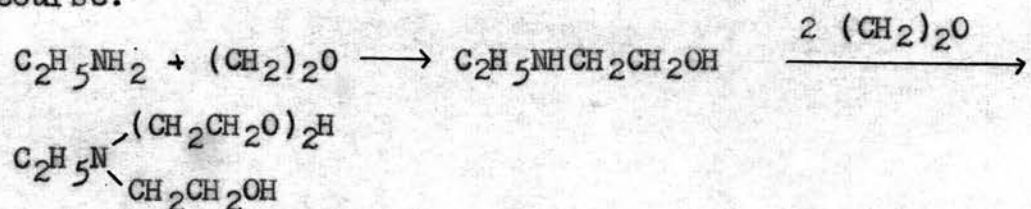
In the absence of water many amines do not react with ethylene oxide, but in some instances, as in the reaction between mono-methylaniline and ethylene oxide to produce the amino alcohol, water does not appear to exert any influence whatsoever on the yield (162). Gabel (163) prepared beta-dibenzylaminoethyl alcohol by heating equimolar portions of dibenzylamine and ethylene oxide at 100°. Ruberg and Shriner (164) condensed a number of aliphatic secondary amines with ethylene oxide to yield mixtures of alcohols of the types $R_2NCH_2CH_2OH$ and $R_2N(CH_2CH_2O)_nH$. In all these and numerous other similar reactions (165-183) the course is exactly the same; the hydrogen of the amine goes to the oxygen and the remainder of the addend unites with the carbon. Thus aliphatic di-amines react with ethylene oxide to produce a material of the constitution $(HOCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2OH)_2$ (184) and meta-phenylene-diamine with ethylene oxide gives meta-(2-hydroxyethylamino)-aniline (185). Bachman and Mayhew (174) and others have performed similar reactions.

Imines also react with ethylene oxide, but the products are used only as intermediates in the production of textile dressings or detergents (186).

Knorr (187) has shown that ethylene oxide reacts with 2-amino-acetaldehyde in the presence of water according to the illustration below:

$$H_2NCH_2CHO + (CH_2)_2O \longrightarrow \begin{array}{c} HN-CH_2CHO \\ | \\ CH_2CH_2OH \end{array}$$
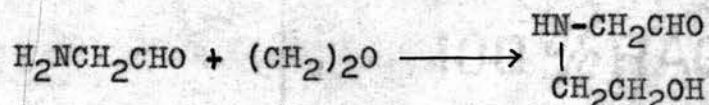
When 2-aminopyridine and ethylene oxide in methyl alcohol are condensed a rearrangement occurs:

(188)
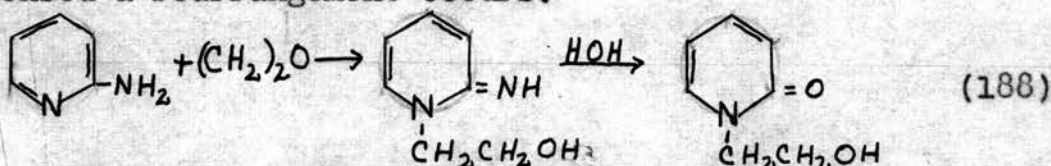
Amino esters when condensed with olefin oxides yield lactones (189-194).

Various polymeric aliphatic amino compounds, such as casein, horn, wool, and glue, react with ethylene oxide in an alkaline medium (195), to form useful hydroxyethylated compounds.

Plisov (196) reported that the condensation of hydrazine with ethylene oxide in the presence of traces of water yields 1,1-bis-(2-hydroxyethyl)hydrazine, while if an excess of water is added only the monosubstituted compound is obtained. Knorr and Brownsdon (197) and others (198-203) have published such work on hydrazine and substituted hydrazines.

Jones and Burns (204) reported that hydroxylamine when condensed with ethylene oxide produces N,N-bis(2-hydroxyethyl) hydroxylamine and sometimes tris-(2-hydroxyethyl)amine oxides.

$$H_2NOH + (CH_2)_2O \longrightarrow (HOCH_2CH_2)_2NOH + (CH_2)_2O \longrightarrow$$
$$(HOCH_2CH_2)_3NO$$
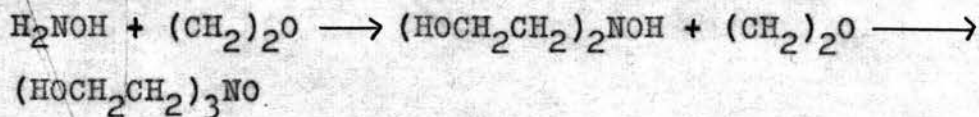
Amides. Amides, according to Gabriel (205), react with ethylene oxide to produce diversified materials later found to be useful intermediates in the production of wetting agents or emulsifiers with fatty acids or similar acids. Piggott (206), deGroote (207), Kaiser and Thurston (208), and several producers of surface-active materials (209,210) have condensed ethylene oxide with amides, both aliphatic and aromatic, to obtain detergents.

Thioureas and guanidines with ethylene oxide produce a variety of hydroxyethylated derivatives. Thioureas react in the iso form, only the hydrogen attached to the sulfur atom participating, to yield S-2-hydroxyethylthioureas (211). Guanidines give wetting agents (208).

Imides, for example phthalimide (212), react with alpha-oxides to yield the N-2-hydroxyethyl derivatives. Hentrich and Kirstahler (213) have condensed imides with numerous olefin oxides to obtain materials which are useful as softening agents. Gabriel (205) has also performed work with imides.

Reactions of ethylene oxide with other compounds having an active hydrogen bonded to nitrogen are noted here only as references (214-221).

Hydrogen halides and other acids. Ethylene oxide combines rapidly with hydrogen chloride in aqueous solution to produce ethylene chlorohydrin (222,223,224). Hydrogen bromide (224,225,226), hydrogen iodide (224), and hydrogen fluoride (227,228) react similarly to produce the respective halohydrins. According to Wurtz (229) ethylene oxide reacts vigorously with hypochlorous acid to produce 2-chloroethanol, but it is difficult to see how this product is possible. Perchloric acid (229,230) and periodic acid (231) react with ethylene oxide to yield the hydroxyethyl perhal-

ogenate which when reduced yields the halohydrin.

Ethylene oxide abstracts the acid from hydrochlorides of amines and amino acids (232) to produce the free amine or amino acid and the halohydrin.

The reactions of metallic chlorides with ethylene oxide constitute another class of compounds which yield halohydrins. Zeise (233,234,235) investigated the reaction of the halides of aluminum, chromium, iron, thorium, and zinc in dilute solution with ethylene oxide. The products were the colloidal metal oxide hydrates and ethylene halohydrins. Wurtz (236) and Walker (237) prior to the work of Zeise had studied the reaction of ethylene oxide with solutions of chlorides of aluminum, magnesium, iron, tin, zinc, manganese, and copper. They illustrated this type reaction as:

$$MnCl_2 + 2\ (CH_2)_2O \xrightarrow{H_2O} 2\ HOCH_2CH_2Cl + Mn(OH)_2$$
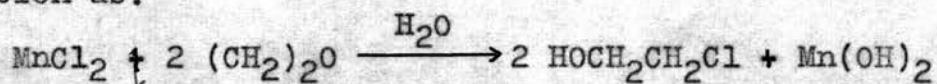
Lenher (238) suggested that manganous chloride be used as a test for the presence of ethylene oxide in water solutions. Roithner (239) reported that calcium chloride also reacts with ethylene oxide to give the hydrated base and the halohydrin.

When ethylene oxide is heated with anhydrous hydrogen cyanide combination occurs with the formation of cyanohydrins (240, 241). For this preparation Jefts and Schmidlin (242) have utilized an aqueous suspension of the oxide, hydroxide or cyanide of magnesium in the presence of hydrogen cyanide. In a vapor-phase reaction ethylene oxide and hydrogen cyanide passed over aluminum oxide at 200° produce acrylonitriles, but over silicon dioxide they produce appreciable amounts of succinonitrile also (243). Thiocyanic acid and ethylene oxide similarly yield 2-thiocyano-

ethanol (244).

Sulfonic acids react with olefin oxides to produce hydroxy-alkyl sulfonates which are useful as wetting agents (245,246,247). The general reaction for this type synthesis is

$$(CH_2)_2O + RSO_3H \longrightarrow RSO_3CH_2CH_2OH$$

Hydrocarbons. While the hydrogen of aromatic compounds can hardly be classed as very active, the condensation of these substances with ethylene oxide under Friedel-Crafts conditions takes the usual form:

$$(CH_2)_2O + ArH \xrightarrow{AlCl_3} ArCH_2CH_2OH$$
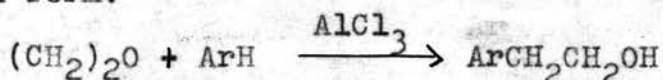
The severity of the conditions often causes consecutive reaction of the product to yield sym-diarylethanes; but since these are far less valuable, their formation is ordinarily repressed by keeping the temperature low (248,249). Hydrogen chloride serves to promote the reaction (250), and inert diluents may be used (251-254). As usual in the Friedel-Crafts reactions, halogenated or nitrated benzenes are largely or wholly resistant to hydroxyethyl-ation (255,256). By these means there have been prepared various beta-arylethanols: phenyl (248-258), the tolyls (255,256), and others (259-263). It is even claimed that aliphatic hydrocarbons are thus convertible to the primary alcohols containing two more carbon atoms (261,262).

Miscellaneous. Phosphine (264) reacts with ethylene oxide as predicted by Knunyantz and Sterden to produce mono-, di-, and tri-ethanolphosphines. However, diphenylarsines (265) yield 1,2-bis-(diphenylarsino) ethane and only minor amounts of 2-(hydroxyethyl)-phenylarsine.

Reaction with Compounds Containing No Active Hydrogen

Though no studies have dealt explicitly with orientation in these reactions, it is evident that they involve an opening of the oxide ring with the oxygen joining the more positive part of the adding molecule while the carbon becomes attached to the more negative part of the molecule.

Halogens and active halides. Several non-metallic halides react with ethylene oxide according to tthe equation

$$MX_n + (CH_2)_2O \longrightarrow XCH_2CH_2MX_{n-1} \longrightarrow (XCH_2CH_2)_nM$$
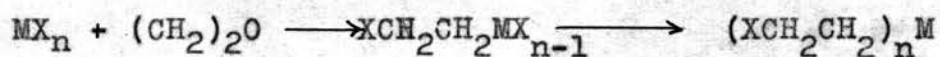
The ratio of ethylene oxide to the halide controls the extent of 2-chloroethylation. This behavior is shown by PCl_5 (266), PCl_3 (267), PBr_3 (268), $POCl_3$ (269,270), S_2Cl_2 (271), $AsCl_3$ (272), $C_6H_5AsCl_2$ (272), $SiCl_4$ (273,274), and various chlorosilanes (275-278). The phosphites so produced are readily isomerized at 130° to phosphonic esters, $XCH_2CH_2PO(OCH_2CH_2X)_2$. With S_2Cl_2 products other than 2-chloroethyl sulfites are produced. Sulfuryl chloride reacts only halfway to yield 2-chloroethyl chlorosulfonate. (271).

A unique study of metal halides by Ribas and Tipia (279,280) demonstrates the only reaction of ethylene oxide with this type of compound under anhydrous conditions. In ether solutions the olefin oxide reacts with magnesium bromide to give a product assigned the formula $CH_2BrCH_2OMgBr.(C_2H_5)_2O$. Subsequent hydrolysis of this complex substance yields ethylene bromohydrin, magnesium bromide and magnesium hydroxide.

Elementary chlorine and bromine react with ethylene oxide to form complexes containing one molecule of halogen per two moles of ethylene oxide. These compounds, studied by Maass and Boomer

(281), are rather unstable; the chlorine complex is dangerously
explosive at 0°, while that with bromine on careful warming can
be made to rearrange to a solid product. In another reaction in-
volving molecular chlorine (282), ethylene oxide, butadiene, and
molecular chlorine interact to produce 3-(2-chloroethoxy)-4-
chlorobutene-1, 1-(2-chloroethoxy)-4-chlorobutene-2, and a mixture
of more complex products in which two moles of chlorine and two
moles of ethylene oxide have added.

Ethylene oxide, acyl halides, and hydrogen halide catalyst
yield 2-haloethyl esters, but even at greatly reduced temperatures
the reaction tends to be explosive (283).

Meerwein and Sonke (284) produced 2-hydroxyethyl trichloro-
acetate by reacting trichloroacetic acid with ethylene oxide in
the presence of diazomethane as a catalyst; Hibbert and Grieg (285)
and Allen and Hibbert (286) however obtained the isomeric cyclic
compound 2-hydroxy-2-dichloromethyl-1,3-dioxolane from dichloro-
acetic acid, and 2-hydroxy-2-trichloromethyl-1,3-dioxolane from
trichloroacetic acid.

In a reaction to be expected of an active halide, chloro-
methyl ether and ethylene oxide in the presence of mercuric chlor-
ide at 100° produce methyl 2-chloroethyl formal (287).

Aldehydes and Ketones. Bogert and Roblin (288) prepared a
series of cyclic acetals (1,3-dioxolanes) in 25 to 35% yields by
reacting ethylene oxide with aldehydes and ketones in the presence
of anhydrous stannic chloride or other Lewis acids:

$$(CH_2)_2O + H_3CCHO \longrightarrow \begin{array}{c} CH_2-O \\ | \\ CH_2-O \end{array} \rangle H-C-CH_3$$
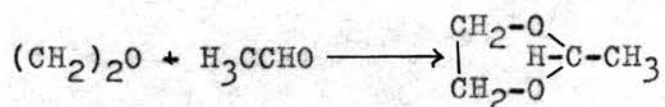
Petrov (289) confined most of his work to ketones and utilized

another catalyst, boron trifluoride. He noted that when an inert solvent was used aldehydes gave 1,3-dioxolanes, whereas without the solvent polymerization occurred.
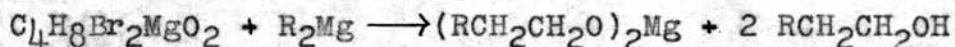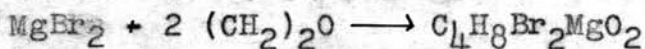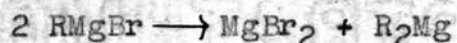
Acid anhydrides. The reaction of acid anhydrides with ethylene oxide is a general reaction but one not studied extensively. Wurtz (290) found that acetic anhydride with ethylene oxide yields the diacetate of ethylene glycol; Staudinger (291) received the diacetate of ethylene glycol and unesterified polyethylene glycol. These reactions are catalyzed by ferric chloride (292) or small amounts of sulfuric acid. Phthalic anhydride (293) was condensed with ethylene oxide to produce water-soluble derivatives; in these reactions an inert solvent and a catalyst, sodium phthalate, were used. von Peski and Coltof (294) condensed succinic anhydride with ethylene oxide in the presence of organic bases to develop quite useful capillary agents.

Organometallic compounds. Ethylene oxide has been shown to combine with Grignard reagents to form the corresponding hydroxy-ethyl derivatives (295,296,297,298).

$$RMgX + (CH_2)_2O + H_2O \longrightarrow RCH_2CH_2OH + Mg(OH)X$$
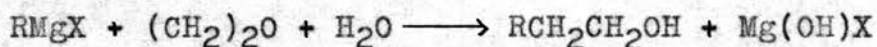
R may be an alkyl or aryl radical and X is halogen.

Huston and Agett (299) have reviewed the field of ethylene oxide-Grignard reactions and have developed the following mechanism:

$$2\ RMgBr \longrightarrow MgBr_2 + R_2Mg$$

$$MgBr_2 + 2\ (CH_2)_2O \longrightarrow C_4H_8Br_2MgO_2$$

$$C_4H_8Br_2MgO_2 + R_2Mg \longrightarrow (RCH_2CH_2O)_2Mg + 2\ RCH_2CH_2OH$$

Faucounau (300), as well as others (301,302), reacted Grignard reagents of monoalkylacetylenes with ethylene oxide. Dorrer and Hopff (303) condensed ethylene oxide with phenylsodium and para-tolylsodium to obtain phenethyl alcohol and beta-para-tolylethyl

alcohol. Gilman and Towle (304) found alpha-picolyllithium, alpha-picolylmagnesium bromide and alpha-picolylmagnesium iodide to be suitable for the preparation of hydroxyethyl-substituted derivatives. Numerous other references are found which overlap previously stated reactions and will therefore be included only as references (305-319).

Miscellaneous compounds. Ethylene oxide does not react with phenyl isocyanate in a closed container for 18 hours, only the polymer, triphenyl isocyanurate, being produced (320).

Arsenous oxide reacts with ethylene oxide to yield 2-hydroxy-ethanearsonic acid (321). Nitrogen dioxide (322) reacts with ethylene oxide to form the 2:1 ethylene oxide complex, presumably 2-nitroethyl nitrate. Nitrites (323) are claimed to react with ethylene oxide to produce 2-nitroethanol; for example, barium nitrite from 0 to 40° reacts with this oxide to yield 2-nitro-ethanol. Sulfur dioxide, according to Albertson and Fernelius (324), yields a 1:1 compound whose structure is not known because of its low stability at normal temperatures.

Roithner (325) treated ethylene oxide with calcium iodide and believed he produced iodoform; but this work is old and of doubtful validity.

Tertiary amines react with ethylene oxide in the presence of traces of water to produce trialkyl-2-hydroxyethylammonium hydroxides.(326,327,168-170).

Trialkylamine oxides with ethylene oxide in the presence of small amounts of water produce water-soluble basic compounds use-ful as wetting agents (328,329).

Hentrich and Gundel (247) have synthesized useful wetting agents by condensing ethylene oxide with high-molecular-weight alkylsulfinyl chlorides in an autoclave at high temperatures.

Cyanides of alkali or alkaline earth metals produce alkylene cyanohydrins (330-333) while alkali thiocyanates yield besides the cyanohydrin appreciable amounts of ethylene sulfides (334,335).

Polymerization. In practically every catalytic reaction of ethylene oxide the products contain some polymerized ethylene oxide. Strictly speaking this is not a typical additive reaction of ethylene oxide; hence only a partial history of this process will be presented. Ethylene oxide provides an excellent example of polymerizable compounds not involving a double bond. Treating ethylene oxide with various agents such as strong bases of inorganic halides produces a profound and highly exothermic condensation. The products range from low-molecular-weight liquids to very high-molecular-weight solids. It is generally agreed that these polymerized compounds contain a long chain of $-(CH_2CH_2O)-$ residues linked together. Hibbert and Perry (336) obtained experimental evidence that the polymerization of ethylene oxide involves first activation by the catalyst followed by ring fission, the addition of water to yield the glycol, and addition of another molecule of the open-chain form of ethylene oxide to yield the polymer. The reaction is often carried out in the vapor phase using basic catalysts such as sodium or potassium hydroxide, trimethylamine, triethylphosphine, and potassium carbonate. The vapor-phase polymerization of ethylene oxide in the presence of alumina, activated fuller's earth, zinc chloride and stannic chloride is also well known. Acid catalysts (sulfuric acid, phosphoric acid, boron trifluoride or hydrochloric acid) usually yield mainly p-dioxane and highly polymerized polyethylene glycols.

EXPERIMENTAL : Part A

Interaction between ethylene oxide and olefins

This project was inspired by the acid-catalyzed Prins addition of formaldehyde into the double bond of olefins (337), which yields 1,3-glycols, formals, esters, and unsaturated primary alcohols. There seems to be considerable similarity between formaldehyde (methylene oxide) and ethylene oxide in chemical behavior; both react additively with a wide variety of reagents in the presence of either acidic or basic catalysts, the more electronegative part of the addend becoming attached to the carbon of the formaldehyde or ethylene oxide. Hence an analog of the Prins reaction seemed reasonable:

$$\text{C} = \text{C}_H + (CH_2)_2O \xrightarrow{\text{acid}} \text{C} = \text{C}_{CH_2CH_2OH}$$

(cyclize)

(polymerize)
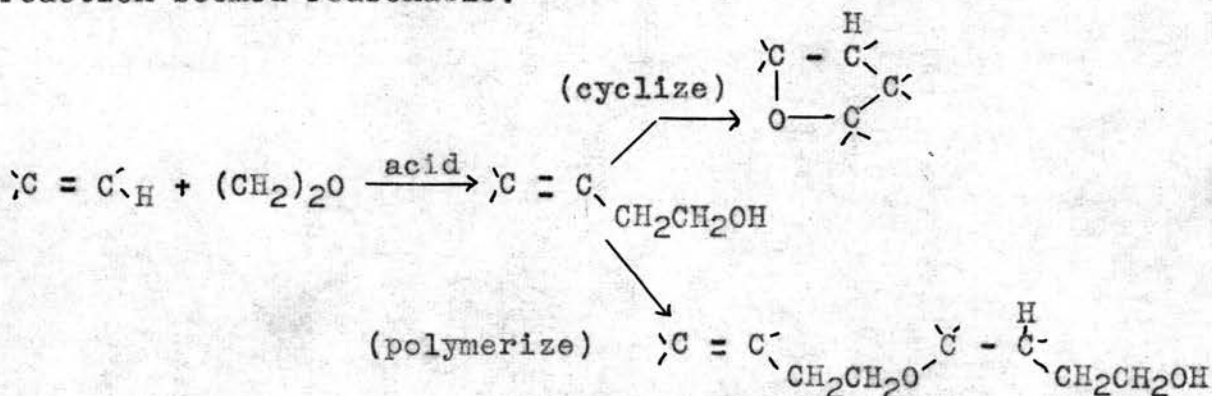
Acid catalysts were chosen because it is known that ethylene oxide is thereby converted to p-dioxane and polyethylene glycol, and styrene and isobutylene to polymers. It was hoped that simultaneous activation of the two would cause interaction.

No work has been reported in the literature on the production of 1:1 addition compounds from olefins and olefin oxides. However, Seger and Sachanen (338) have quite recently published that a mono-olefinic hydrocarbon containing at least three carbon atoms can be condensed with an olefinic oxide or sulfide in a 4:1 molar ratio at 500 to 700° F. For example 280 g. of 1-decene was con-

densed with 22 g. of ethylene oxide to yield 83 g. of residue and 191 g. of 1-decene. It was not definitely established whether this residue, claimed to be useful as an additive for lubricating oils, was a mixture of the two polymers or a true co-polymer. Schulze (339) using dehydrogenation catalysts such as calcined bauxite and aluminum chloride was able to condense ethylene oxide with ethylene in an autoclave at 300° F. and 500 lbs./sq.in. to produce butadiene. Whaley (340) extended the work of Schulze to the use of bauxite impregnated with barium hydroxide, but he utilized comparatively high temperatures (1100 to 1300° F.); again the only product reported was butadiene.

Procedures and Results

Styrene + Ethylene Oxide. Styrene was first chosen for attempted reaction with ethylene oxide because of its high reactivity. Since it was impossible to predict the degree of activation by concentrated sulfuric acid of styrene and ethylene oxide individually, all three orders of combination of these components were used; (1) the acid catalyst was added to equal volumes of styrene and ethylene oxide; (2) monomeric styrene was added to a homogeneous mixture of ethylene oxide and the acid catalyst; (3) ethylene oxide was added to styrene and ethyl ether in the presence of the catalyst.

Experiment 1. Twenty ml. of sulfuric acid (36 $\underline{N}$) was added slowly with mechanical stirring to a homogeneous mixture of 30 ml. of freshly distilled styrene and 30 ml. of ethylene oxide (liquid) contained in a 500-ml. three-necked flask kept at 0°. The reaction mixture was allowed to warm to room temperature. As the reaction mixture was treated with the catalyst it acquired a deep purple color.

It was found necessary to neutralize the sulfuric acid before separation of the products. This neutralization consisted of the addition of the reaction mixture to a concentrated solution of potassium carbonate exactly equivalent to the original amount of acid. Neutralization caused the purple color of the reaction mixture to change to yellow, and two layers formed. The water layer (designated as Layer 1) was washed three times with ethyl ether, the washings being added to the water-insoluble layer (designated as Layer 2.).

Layer 1. Fractional distillation through a 12-ball Snyder column gave Cut A, b.p. 85-90°; Cut B, b.p. 98-101°; and a residue.

Cut A. Refractionation of the liquid yielded a mixture essentially constant-boiling, 86-90°, which was tested for water by use of anhydrous cupric sulfate; the test was positive. To a second portion was added bromine; an orange precipitate formed which melted at 64° after recrystallization from alcohol. This established the organic component as p-dioxane, which forms an azeotrope with water boiling at 87.8° and an addition compound with bromine melting at 65-6° (341).

Cut B. This portion was assumed to be water.

Layer 2. Removal of the ether left a very viscous liquid. Upon further heating a product (Cut C) distilled at 100-104°, after which decomposition of the residue began even at reduced pressure.

Cut C. Further purification did not sharpen the boiling point, but the material with bromine water gave a crystalline precipitate, m.p. 65° (from alcohol). This established the compound as p-dioxane, b.p. 101.3°.

Residue. The odor of the residue strongly suggested styrene polymer; hence a portion was removed and distilled with a little sulfur at reduced pressure. This gave a liquid distilling at 130°, the remainder being decomposed. Qualitative tests (344) with bromine showed unsaturation of the liquid, a precipitate being formed which was recrystallized from ethyl alcohol. The melting point of the product was 72° whereas styrene dibromide melts at 73° (341); this established the residue as mainly polymerized styrene.

Experiment 2. Twenty-five ml. of sulfuric acid (36 $\underline{N}$) was added slowly to a solution of 30 ml. of styrene and 30 ml. of ethyl ether. A white viscous layer appeared on top, and when ethylene oxide was added at 0°, no noticeable change occurred.

Separation and analysis of the products were performed as in Experiment 1 and led to identical results.

Experiment 3. The addition of styrene to acidulated ethylene oxide yields only the oxonium salt of p-dioxane which melts at 101°.

At this point it was decided that a somewhat less reactive olefin might prove more satisfactory, inasmuch as its polymerization would be less rapid. The olefin chosen for this work was isobutylene.

Isobutylene + Ethylene Oxide. In the first experiments use was made of an Adams low-pressure hydrogenation apparatus. Thirty-five ml. of sulfuric acid (36 $\underline{N}$) was added to the pressure bottle and saturated with ethylene oxide gas. Isobutylene then was forced in at 20 lbs./sq.in. at room temperature until no more was absorbed. After twelve hours under pressure, two layers of liquid had formed; these were removed from the apparatus, separated and analyzed. (The upper layer was designated as Layer 1, the lower as Layer 2.)

Layer 1. Fractional distillation yielded portions distilling at $100\text{-}106^\circ$ and $170\text{-}180^\circ$, and a small decomposed residue. The lower-boiling fraction gave a negative test for the presence of oxygen by the Ferrox test (342). The unsaturation test with bromine was positive but slow, as can be expected for petroleum fractions except in acidic solutions. The refractive index at 20° was 1.4100. It was concluded that this fraction was diisobutylene, a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. The higher-boiling fraction was similarly tested and revealed to be a mixture of triisobutylenes.

Layer 2. This fraction was neutralized as usual with potassium carbonate. The color of the solution thereupon changed from a deep wine tint to a yellow tint. Fractional distillation produced a cut distilling at 86-90° and another at 97-102°. The lower-boiling fraction was proven to be the same impure water-dioxane azeotrope obtained in the styrene work. The higher-boiling fraction was again assumed to be water.

In similar runs, sulfuric acid was tried as catalyst at other concentrations: 12 $\underline{N}$, 6 $\underline{N}$, 2 $\underline{N}$, 0.5 $\underline{N}$, and 0.1 $\underline{N}$. The pressures were slightly increased, from 20 to 25 lbs./sq.in. for ethylene oxide and from 25 to 35 lbs./sq.in. for isobutylene. These experiments were performed to establish the effect of more dilute catalyst on decreasing the degree of polymerization of isobutylene. It was concluded that the only effect of diluting the catalyst with water was to decrease the conversion to polyisobutylene and p-dioxane.

The reaction was next studied with liquefied ethylene oxide and isobutylene. Twenty-five ml. of concentrated sulfuric acid was added slowly with stirring to a homogeneous mixture of 75 ml. of ethylene oxide and 75 ml. of isobutylene. The reaction flask and gas trap were held at -15° throughout the course of the reaction. As the sulfuric acid was added to the reactants, a deep purple color appeared. The stirring was continued for six hours after all the acid had been added. The system was then allowed to warm slowly to room temperature and the contents of the gas trap were allowed to distill and identified by boiling point. They proved to be unreacted ethylene oxide (b.p. 10.7°) and isobutylene (b.p. -6.6°).

The crude products were neutralized with a potassium carbonate-water slush, and the lower layer (designated as Layer 1), which was mostly water, was washed three times with ethyl ether. The washings were added to the water-insoluble layer (designated as Layer 2).

Layer 1. This portion was steam-distilled for thirty minutes and the distillate fractionally distilled through a three-ball Snyder column to yield the following Cuts: Cut A, b.p. 86-91°, and Cut B, b.p. 96-100°. Cut A was dried with anhydrous potassium carbonate; it then boiled (micro) at 101-102°. In addition another portion treated with a concentrated solution of mercuric chloride formed a precipitate which was stable to sublimation (341) which is representative of p-dioxane. Cut B, boiling at 99°, was assumed to be water.

Layer 2 was fractionally distilled with a twelve-ball Snyder column, yielding Cut A, b.p. 30-40° (ether); Cut B, b.p. 102-106°; and Cut C, b.p. 170-179°. Cuts B and C proved to be mixtures of di- and triisobutylenes which were identified by unsaturation tests with bromine and boiling points. At this point experimentation with sulfuric acid as a catalyst was discontinued.

The next catalyst chosen for study was boron trifluoride. In order to test its efficacy in a liquid-phase reaction of ethylene oxide with isobutylene at room temperature it was necessary to select a solvent and coordinating agent for the gaseous boron trifluoride. The catalytic solutions were prepared by holding 100 ml. each of ethyl ether, p-dioxane, sulfuric acid (36 $\underline{N}$), and phosphoric acid (which had been rendered anhydrous with phosphorus pentoxide) at -15°, and passing in boron trifluoride until 30 g. had been added. The color in each case changed to a deep brown.

The prepared catalyst solution was placed in the Adams pressure bottle and saturated with ethylene oxide at 20 lbs/sq.in., then with isobutylene at 35 lbs./sq.in., These additions were alternated until no more gas was absorbed upon standing for 12 hours. The two-phase reaction mixture was then removed and the upper stratum, Layer 1, was separated from the lower layer, Layer 2.

The catalyst was removed from Layer 1 by addition of a saturated solution of potassium carbonate, and the two-phase mixture was separated into a water-insoluble portion, Layer 1-A, and a water-soluble portion, Layer 1-B.

Layer 1-A was subjected to distillation at reduced pressure until extensive decomposition began. The distillate was then fractionated in a Todd column into Cut A, b.p. $100-102^{\circ}$, and Cut B, b.p. $170-178^{\circ}$. These were identified as p-dioxane and triisobutylene by qualitative tests previously described. The residue from Layer 1-A was a semisolid waxy mass which decomposed upon elevation of temperature. Inspection of the semisolid material under a microscope revealed no crystalline character. This wax was then subjected to solubility tests based on the study of polyethylene glycols (343) and general information on the solubility of polyisobutylenes (344). The wax was found to be soluble or dispersible in water, methyl alcohol, ethyl alcohol, and aromatic hydrocarbons but only slightly soluble in carbon tetrachloride, ethyl ether, and the alkanes. These are properties of the polyethylene glycols, rather than those to be expected for a copolymer of the pattern $(OC_6H_{12})_n$. The alkanes and the carbon tetrachloride solutions upon evaporation did leave a white residue,

insoluble in water, methanol and ethanol. Unsaturation tests with bromine gave positive results. The following conclusions were drawn: the semisolid wax from the reaction of ethylene oxide with isobutylene in the presence of boron trifluoride etherate, boron trifluoride-sulfuric acid, boron trifluoride-phosphoric acid, or boron trifluoride-p-dioxane is a mixture of isobutylene polymers and polyethylene glycols, and there is no copolymerization of these compounds. The water solubility of the mixed polymers is due to the ability of the polyethylene glycols to act as surface-active agents, thus solubilizing and masking the polyisobutylenes. Since the proportion of polyisobutylenes in the mixed polymers was only 25 to 30% by weight it is believed that such apparent water solubility could be exhibited.

Layers 1-B and 2 were combined and completely neutralized with potassium carbonate. Steam distillation yielded only p-dioxane and a residue containing the salts of boron trifluoride, sulfuric acid, or phosphoric acid.

Since the range of temperatures, volumes and pressures that can be handled in the Adams apparatus is rather limited, other methods were devised to produce reaction between ethylene oxide and isobutylene.

(a) A homogeneous mixture of 75 ml. of ethylene oxide and 150 ml. of isobutylene maintained at -15° was treated dropwise with catalyst (boron trifluoride etherate, boron trifluoride-sulfuric acid, boron trifluoride-phosphoric acid, boron trifluoride-p-dioxane, or anhydrous stannic chloride) until 50 ml. had been added. The reaction mixture was kept for 12 hours at -15° and then warmed to room temperature. The mixture was neutralized with potassium carbonate and separated into two layers. The dried water-insoluble layer when vacuum-distilled yielded a liquid

boiling at 101-103°, identified as p-dioxane. The pot residue was a mass of wax which proved to be the same type mixture of polyethylene oxides and polyisobutylenes as previously found. The only organic product found in the water layer was again p-dioxane. The contents of the gas trap proved to be unreacted isobutylene and ethylene oxide.

(b) Seventy-five ml. of ethylene oxide was saturated with boron trifluoride through a diffusion tube. Isobutylene was bubbled into this complexed oxide until the volume had doubled. The mixture was kept for 12 hours at -15° after which a controlled temperature elevation to about 30° was effected. The crude reaction mixture was then treated as usual. The results were identical with those in (a).

(c) A specially constructed reaction vessel consisting of a steel tube with removable, self-sealing caps on each end, lined with a Carius tube and fitted with a safety valve, was used. Ethylene oxide was liquefied at -18° and a portion of it was saturated with boron trifluoride, mixed with the rest, and treated with isobutylene. The following five ratios were used.

Volume of oxide saturated, ml.	Additional volume of oxide used, ml.	Volume of iso-butylene, ml.
75	25	100
50	50	100
25	75	100
10	40	100
25	25	100

The special tube was cooled to -20° and the reaction mixture placed in it. The tube was sealed off and allowed to stand for 10 hours at room temperatures. In the treatment of the reaction

mixture, the gases remaining after reaction were proved to be unreacted isobutylene and ethylene oxide in the ration of 2:1 respectively. The neutralized reaction mixture contained only potassium fluoborates, p-dioxane, and the same waxy non-copolymeric product previously obtained.

Experiments with other catalysts ($ZnCl_2$, $HgCl_2$, $AlCl_3$, HPF_6, H_2PO_3F, HPO_2F_2) consisted in adding the catalyst to equal volumes of ethylene oxide and isobutylene and then sealing the mixture in a magnesium citrate bottle. Examination of the products was done in exactly the same manner as in previous trials. The results of these experiments with diversified catalysts were essentially the same as previously obtained.

Discussion

The desired interaction of alpha-oxides with mono-olefins in the presence of acid catalysts does not occur under the given reaction conditions. Acid catalysis is not suitable in the production of intermolecular additions in the liquid phase at ordinary temperatures and slightly increased pressures.

It is possible, though highly doubtful, that some specific acid catalyst not tried might give the desired results. The vapor-phase reaction at increased temperatures and greatly increased pressures was not attempted because of the difficulties and hazards involved in such experiments. The vapor-phase condensation at increased temperatures and one atmosphere pressure over acidulated clays also remains untested and might be successful. Seger and Sachanen (338) have already eliminated the non-catalytic high-pressure, high-temperature method as unsatisfactory in producing 1:1 addition compounds.

EXPERIMENTAL : Part B

ADDITION OF ACETALS TO OLEFIN OXIDES

Introduction

Acetals are compounds bearing the general formula $(R_3CO)_2CHR'$, where R and R' may be hydrogen or alkyl radicals (alike or unlike). Both Dancer (345) and Alsberg (346) as early as 1864 reported that under the influence of dry hydrogen chloride, a typical aldehyde reacts readily with a molecule of an aliphatic alcohol to form a moderately stable addition product called a hemiacetal, $HOCHR'-(OCR_3)$, which readily combines with a second molecule of the alcohol to yield the acetal. Adkins (347,348,349) critically studied this reaction, and especially its catalysis.

Only one reference is found which is directly related to this reaction. Gresham (350) reported that ethylene oxide reacts with 1,3-dioxolane at greatly increased pressure and temperature to produce a copolymer which is useful as an additive to lubricants. No proof of structure was given, and no reference to acid catalysis.

Procedures and Results

The initial experiments were designed to find the most efficacious means of effecting reaction between alpha-oxides and acetals. Hawkins (351) in his work with acetals and olefins found that boron trifluoride when complexed with an acetal was a very effective catalyst.

The catalyst was prepared by passing anhydrous boron trifluoride through a gas-dispersion tube into a known volume of the acetal at -15°. The weight of the catalyst added was recorded.

Pilot run 1. One hundred ml. of methylal (distilled over sodium) was used to absorb 7 g. of boron trifluoride at -15°. The solution was treated with ethylene oxide at 20 lbs./sq.in. in the Adams low-pressure hydrogenation apparatus for 12 hours. Thereafter it was added slowly to a flask containing a slush of potassium carbonate and fitted with a water-cooled condenser. After removal of a little carbonaceous material by filtration through glass wool, the two strata were separated and the lower one was steam-distilled to remove any volatile product. However, no such product was received. The upper layer was rapidly distilled up to 200°. The dried distillate was fractionated in the Todd column, yielding cuts shown on page

Pilot run 2. One hundred ml. of pure methylal containing 7 g. of boron trifluoride was stirred and treated with 25 ml. of liquid ethylene oxide dropwise at -12°. Each drop of the oxide reacted visibly and the reaction mixture changed from a light tan to deep wine color. When all the ethylene oxide had been added the stirring was continued for three hours. Thereafter the crude reaction mass was treated as in Pilot run 1.

Pilot run 3. One hundred ml. of pure methylal containing 11 g. of boron trifluoride was held at -12° while 75 ml. of ethylene oxide was added dropwise. The flask was swirled to facilitate mixing of the reactants. The reaction mixture was set aside for 6 hours and then treated as in Pilot run 1.

Estimation of boiling points: The boiling point to be expected for $CH_3OCH_2CH_2OCH_2OCH_3$, the 1:1 addition compound of ethylene oxide and methylal, was predicted as follows:

$C_2H_5OCH_2OC_2H_5$, ethylal:	b.p.	87°
$C_2H_5OC_2H_5$, ethyl ether:	b.p.	<u>35°</u>
-OCH_2-, methyleneoxy group:	(difference)	52°
$CH_3OCH_2CH_2OCH_3$, 1,2-dimethoxyethane:	b.p.	84°
-OCH_2-, (as above)		<u>52°</u>
$CH_3OCH_2OCH_2CH_2OCH_3$, 1-(methoxymethoxy)- 2-methoxyethane	est. b.p.	136°

TABLE I

Plateau boiling points and volumes

Pilot run	40-50° cut, ml.	126-146° cut, ml.	175-195° cut°, ml.	Residue, ml.
1	50	15	20	10
2	40	30	10	10
3	45	20	15	8

The 40-50° cut was of course recovered methylal. Since the second pilot run was convenient and produced the highest yield of product in the desired range, 126-146°, it was chosen as the standard method for the preparation of new products.

Ethylene oxide with methylal

Five hundred grams of methylal was treated with 12 g. of boron trifluoride and thereafter with 200 g. of ethylene oxide.

The experiment was conducted at 0° in a three-necked flask fitted with a mercury-sealed mechanical Herschberg stirrer, a gas trap, and an ice-water-cooled Friedrichs condenser. The ethylene oxide was contained in a weighed vessel which was arranged so that the liquid could be distilled into the condenser, liquefied, and dropped into the activated methylal. Each drop of ethylene oxide added caused vigorous reaction at first but less later on. The mixture was gradually added to a slush of excess potassium carbonate contained in a round-bottomed flask fitted with a water-cooled condenser. This mixture was then transferred to a separatory funnel and allowed to stand for 12 hours to facilitate partition. The lower layer of water and water-soluble material was removed and steam-distilled briefly. The first 20 ml. of distillate when saturated with anhydrous potassium carbonate yielded a non-aqueous layer weighing 6 g.. This was identified as p-dioxane by its boiling point (101°), and its precipitation with mercuric chloride (344). The upper main layer was rapidly distilled up to 140° where noticeable decomposition began, and the distillate was fractionally distilled through a three-ball Snyder column. Three cuts were taken: Cut I, b.p. 40-55°; Cut II, b.p. 60-104°; and Cut III, b.p. 105-140°. The residue from this distillation was combined with the residue from rapid distillation and rapidly distilled at reduced pressure yielding Cut IV, b.p. 90-180°, (145 mm.), and Cut V, b.p. 82-240° (10 mm.). The residue weighed 11 grams.

Cut I, assumed to be methylal, weighed 150 grams.

Cut II was refractionated in the Todd column to yield 2 g. of methylal, boiling at 44°, 3 g. of p-dioxane, boiling at 101° and 12 g. of product distilling sharply at 130-131.5°.

Cut III in the Todd column yielded 85 g. of the product boiling at 130-131.5° (750 mm.) which for convenience is called Compound A.

Cut IV was then fractionated at 98 mm. and yielded 47 g. of product boiling at 139-140.5°. This proved stable to redistillation at atmospheric pressure, where it boiled at 185° (748 mm.). It is temporarily called Compound B.

Cut IV residue and Cut V were fractionated at 1 mm. but no distinct plateaus were obtained. In the range of 90-200°, 28 separate portions were received, none over 12 grams. Percentage yields for the several cuts were calculated and will be recorded as part of a general summary of numerical data.

TABLE II

Properties of Compound A

	Experimental	Theoretical for $C_5H_{12}O_3$
Molecular weight (vapor density method)(351)	119, 121	120
C, %, avg. of 2 values (353)	49.56	50.00%
H, %, avg. of 2 values	9.87	10.00%
Refractive Index, $n_D^{25°}$	1.3913	
Density @ 25°, g./ml.	0.9465	
Molar Refraction (354)	30.12	30.07

Proof of structure. Compound A was tested with sodium metal for hydroxyl groups; this test was negative. Since acetals on hydrolysis yield aldehydes and alcohols, a small portion of Compound A was refluxed with 5% hydrochloric acid for twenty minutes. Distillation of the mixture gave 4 ml. of distillate at 64°, 3 ml. at 86-100°, and 5 ml. at 123°. The 64° cut, dried over calcium oxide and treated with 3,5-dinitrobenzoyl chloride in dry ligroin,

gave a precipitate which was recrystallized from alcohol. The yellow-brown crystals melted at 107°. This identified this portion as methyl alcohol, with known boiling point 64°, and 3,5-dinitrobenzoyl derivative melting at 108° (345). The 86-100° cut warmed with 2,4-dinitrophenylhydrazine reagent (345) gave a yellow precipitate, melting at 165° (from alcohol). The literature value for the melting point of formaldehyde 2,4-dinitrophenylhydrazone is 167° (345). The cut boiling at 123° formed a precipitate when treated with p-nitrobenzoyl chloride in pyridine; this after recrystallization from acetone melted at 49°. The literature value for the melting point of the p-nitrobenzoate of ethylene glycol monomethyl ether is 51° (344). Thus Compound A hydrolyzes to methanol, formaldehyde, and 2-methoxyethanol. These data identified Compound A as 1-methoxymethoxy-2-methoxyethane.

TABLE III

Properties of Compound B

	Experimental	Theoretical for $C_7H_{16}O_4$
Molecular weight (vapor density method)(352)	166, 167	164
C, %, avg. of 2 values (353)	51.20	51.22
H, %, avg. of 2 values	9.74	9.75
Refractive index, $n_D^{27°}$	1.4089	
Density @ 27°, g./ml.	0.9896	
Molar refraction (354)	41.16	41.10

Proof of structure. Two possible structures were formulated for this product (Compound B) depending on whether the two ethylene oxide units add into the methylal molecule adjacent to each other or not:

(1) $CH_3OCH_2OCH_2CH_2OCH_2CH_2OCH_3$ (adjacent oxide units)

(2) $CH_3OCH_2CH_2OCH_2OCH_2CH_2OCH_3$ (non-adjacent oxide units)

Differentiation between these two was accomplished by hydrolysis and identification of the alcohols produced. Structure 1 would produce CH_3OH and $HOCH_2CH_2OCH_2CH_2OCH_3$ while structure 2 would produce two moles of ethylene glycol monomethyl ether, $HOCH_2CH_2O-CH_3$. Hydrolysis of Compound B patterned after that of Compound A yielded methanol, formaldehyde, and a liquid boiling at 190-193°. Since the monomethyl ether of diethylene glycol boils at 194°, structure 1 is proved correct. These data identified Cut IV as 1-(2-methoxyethoxy)-2-methoxymethoxyethane.

No efforts were made to identify the higher-boiling products because (1) they were probably not obtained pure, and (2) they are undoubtedly of the type $CH_3OCH_2(OCH_2CH_2)_nOCH_3$, and thus not directly related to the goal of this work.

A second run, in which the molar ratio of ethylene oxide to acetal was increased to 3:1, was made in order to test the effect of this variable on yield. The results are found in the summary of numerical data.

Propylene oxide with methylal

Owing to the smallness of the supply of propylene oxide only one run was made. Nine hundred twelve grams of methylal, 17 g. of boron trifluoride, and 232 g. of propylene oxide were caused to react essentially as for ethylene oxide (p. 33). Treatment of the reaction mixture as before gave the following rough fractions:

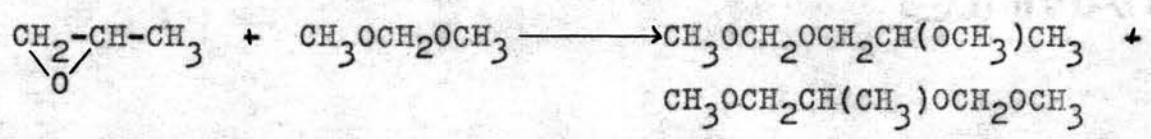| Fraction	Boiling Point, °C.	Weight, g.
1	40-55	587
2	77-89	15
3	90-134	8
4	135-149	340
5	150-220	90
Residue		40

On redistillation Fraction 1 proved to be excess methylal.
Fractions 2 and 3 were negligibly small but probably contained
some dimethyldioxane. Fraction 4 when refractionated in the Todd
column at 744 mm. yielded these cuts:

Cut I   - 130 to 133°, 2 grams

Cut II - 133 to 135°, 0.5 grams

Cut III - 135 to 143°, 330 grams

The residue from Fraction 4 was combined with Fraction 5 and
fractionation continued in the Todd column:

Cut IV   - 144 to 175°, 10 g.

Cut V   - 175 to 195°, 8 g.

Residue - 195° plus, 195 g.

In this reaction there exists the possibility or even the probability that two isomeric forms are produced. This may be shown by
the equation:

$$CH_2\text{-}CH\text{-}CH_3 + CH_3OCH_2OCH_3 \longrightarrow CH_3OCH_2OCH_2CH(OCH_3)CH_3 +$$
$$CH_3OCH_2CH(CH_3)OCH_2OCH_3$$

This was considered the reason for the width of distilling range
of Cut III; hence without further attempts to separate the
isomers structural identification was undertaken.

TABLE IV

Properties of Cut III

	Experimental	Theoretical for $C_6H_{14}O_3$
Molecular weight (vapor density method)(352)	131, 132	134
C, %, avg. of 2 values (353)	53.73	53.70
H, %, avg. of 2 values	10.45	10.41
Refractive Index, $n_D^{32°}$	1.3902	
Density @ 32°, g./ml.	0.9182	
Molar Refraction (354)	34.64	34.84

No other fractions were identified. Yield data will be found in the summary of numerical data.

Ethylene oxide with ethylal:

The object at this time was to extend the reaction by varying the acetal involved instead of the oxide. Without changing the aldehyde base, ethylal was selected for the next trial. The desired reaction was:

$$(CH_2)_2O + (C_2H_5O)_2CH_2 \xrightarrow{BF_3} C_2H_5OCH_2CH_2OCH_2OC_2H_5$$
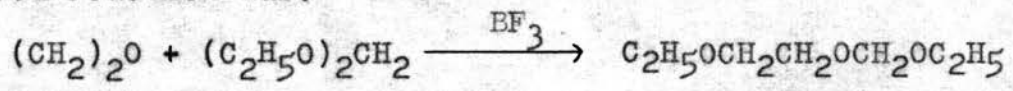
A run was made essentially as with methylal, with 1560 g. of ethylal, 15 g. of boron trifluoride, and 220 g. of ethylene oxide. The reaction mass was neutralized, dried and the layers separated. The lower layer was steam-distilled, yielding 8 g. of p-dioxane. The first rapid distillation of products through a three-ball Snyder column yielded three portions:

Portion A, b.p. 70-105°   1000 g.

Portion B, b.p. 105-175°   610 g.

Portion C, b.p. 175° plus   80 g. (residue)

Portion A on fractionation through a twelve-ball Snyder column yielded 865 grams of ethylal, and 16 grams of p-dioxane;

the rest was slop cuts or still bottoms.

Portion B was fractionated in the Oldershaw column into the following cuts:

Cut	L	M	N	O	P	Q	Residue
B.p., °C.	101-10	111-30	131-50	151-60	161-70	171-95	
Wt., g.	3	8	12	10	430	8	90

Cut P was refractionated at 746 mm. in the Todd column, yielding:

Cut	P-1	P-2	P-3	P-4	P-5	P-6	Residue
B.p., °C.	160-1	161-2	162-3	163-4	164-5	165-70	
Wt., g.	4	5	7	364	12	7	8

TABLE V

Properties of Cut P-4

	Experimental	Theoretical for $C_7H_{16}O_3$
Molecular weight (vapor density method)(352)	149, 150	148
C, %, (353)	56.80	56.77
H, %	10.78	10.81
Refractive Index, $n_D^{32°}$	1.3940	
Density @ 32°, g./ml.	0.8974	
Molar Refraction (354)	39.37	39.46

In addition the compound was found to be inactive to metallic sodium, and did not give the Schiff test for aldehydes (342) in the pure state. However when it was refluxed with 6 $\underline{N}$ hydrochloric acid for ten minutes the test was positive. These physical and chemical tests, along with the principles of homology, proved the compound to be 1-(ethoxymethoxy)-2-ethoxyethane.

Ethylene oxide with dimethyl acetal

The final extension of the reaction herein studied was to vary the aldehyde base of the acetal. The acetal chosen for this

purpose was dimethyl acetal, derived from acetaldehyde. The desired condensation was:

$$(CH_3O)_2CHCH_3 + (CH_2)_2O \longrightarrow CH_3OCH(CH_3)OCH_2CH_2OCH_3$$

Twenty grams of boron trifluoride was complexed with 900 g. of dimethyl acetal. The addition of the catalyst caused a deep purple color to form which was unlike the normal dark brown color evidenced in other cases. The activated acetal was then caused to react with 88 g. of ethylene oxide in the usual manner. Neutralization, drying and rough distillation gave the following portions:

Cut X, b.p. 105-130°

Cut Y, b.p. 130-155°

Cut Z, b.p. 155-180°

Residue, above 180°

Each cut proved to contain hydroxyl compounds, presumably from hydrolysis, and was therefore treated with metallic sodium. Cuts X and Z were almost wholly hydrolyzed material and were discarded, but Cut Y yielded an appreciable portion which was not reactive to sodium metal. This portion was refractionated, yielding 69 g. of product distilling at 141° (746 mm.).

TABLE VI

Properties of Cut Y

	Experimental	Theoretical for $C_6H_{14}O_3$
Molecular weight (vapor density method)(352)	135, 136	134
C, % (353)	53.70	53.73
H, %	10.41	10.45
Refractive Index, $n_D^{32°}$	1.3930	
Density @ 32°, g./ml.	0.9218	
Molar Refraction (354)	34.75	34.84

These physical data confirm the structure assigned to the compound prepared, $CH_3OCH(CH_3)OCH_2CH_2OCH_3$.

In the extension of this reaction it was considered desirable to investigate the utilization of catalysts other than boron trifluoride. Aluminum chloride, calcium chloride, zinc chloride and mercuric chloride were tried as heterogeneous catalysts in the liquid-phase reaction of ethylene oxide with methylal. However it was found that these catalysts were insoluble in methylal and produced no reaction after five hours. Solvation of the catalyst in an inert solvent was not attempted since the time did not permit.

The non-catalytic reaction of the oxides and acetals, which would enormously simplify isolation of products, was attempted for ethylene oxide and methylal. The reactants in a 5:1 ratio of acetal to oxide were sealed in Carius tubes and heated in a furnace. This treatment at 125° did not produce a significant amount of addition product within 16 hours. At temperatures exceeding 125°, the reaction was uncontrollable and repeatedly resulted in explosion. It was first believed that the explosions were due to the presence of oxygen, but evacuation of air and blanketing with nitrogen or methane did not eliminate detonation.

Discussion

There can be no doubt of the course and general applicability of the acetal-olefin oxide addition. All the compounds produced have been fully characterized as to structure by both physical and chemical means, excepting only the individual isomers derived from propylene oxide, where two orientations are possible. The general formula for the 1:1 products is $R_3COCH_2CHR'OCHR''OCR_3$, where R, R', and R'' are hydrogen or alkyl radicals, like or unlike. Multiple addition of the oxide to yield $R_3C(OCH_2CHR')_nOCHR''OCR_3$ is also possible, especially for ethylene oxide. Indeed, the formation of compounds in which $\underline{n}$ is 2 or more is undoubtedly the chief reason for low yields from formaldehyde acetals at least. Consequently future work can considerably improve yields of the 1:1 product, presumably the most desirable, by operating at higher molar ratios of acetal to oxide - say 5:1 at least. It was conceived more important in the present research to prove generality of the reaction than to discover optimum conditions.

Another desirable study, now that the reaction is known to proceed, would be to test it in the vapor-phase, either over an acid catalyst or purely thermally. It would have much better technological possibilities if it could be made (a) continuous and (b) uncatalyzed, so that the only treatment of reaction products would be simple distillation.

Some speculation on further extension of the reaction may be permissible. The principal untested variations of the alpha-oxide component are a trimethylene oxide or 1,3-oxide type - of no commercial importance - and olefin sulfides, which definitely are worth trying. Instead of acetals, ketals, $R_2C(OR')_2$, and the very

similar ortho-esters, $RC(OR')_3$, will probably add to ethylene oxide to yield $R'OCH_2CH_2OCR_2OR'$ and $R'OCH_2CH_2OCR(OR)_2$, respectivly. Whether cyclic acetals, e.g., 1,3-dioxolanes, add ethylene oxide under acid catalysis remains uncertain; if they do, the products may be polymeric. Finally, alkyl nitrites have the same stability to aqueous base but hydrolyzability in acids analogous to acetals, and may react in like manner with alpha-oxides.
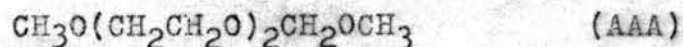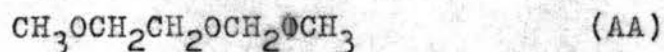
The products of the present research are mixed acetals of an ethylene glycol monoether and some other alcohol. They would therefore be expected to resemble the glycol ethers and acetals in solvent properties and consequent utility. They do in fact dissolve cellulose acetate well, and are miscible with both water and hydrocarbons. As intermediates their use would be limited to that of acetals. They might also find application in the fuel industry as additives to jet fuels since they are comparatively rich in oxygen.
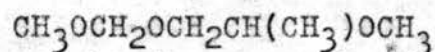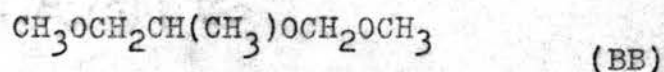
Summary of Numerical Data

(1) Ethylene oxide - methylal :
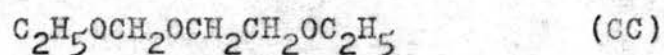
    Compounds isolated: Symbol

        $CH_3OCH_2CH_2OCH_2OCH_3$ (AA)

        $CH_3O(CH_2CH_2O)_2CH_2OCH_3$ (AAA)

(2) Propylene oxide - methylal:

    Compounds isolated: Symbol

        $CH_3OCH_2CH(CH_3)OCH_2OCH_3$

                             (BB)

        $CH_3OCH_2OCH_2CH(CH_3)OCH_3$

(3) Ethylene oxide - ethylal:

    Compound isolated: Symbol

        $C_2H_5OCH_2OCH_2CH_2OC_2H_5$ (CC)

(4) Ethylene oxide - dimethyl acetal

    Compound isolated: Symbol

        $CH_3OCH(CH_3)OCH_2CH_2OCH_3$ (DD)
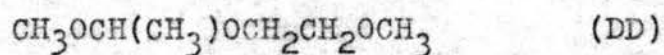
Compound	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	O (by difference) Calcd.	Found
AA	50.00	49.56	10.00	9.88	40.00	40.57
AAA	51.22	51.20	9.75	9.74	39.02	39.06
BB	53.73	53.70	10.45	10.41	35.82	35.89
CC	56.77	56.80	10.81	10.78	32.42	32.42
DD	53.73	53.70	10.45	10.41	35.82	35.89

Compound	Molecular Weight Calcd.	Found	Density in g./ml.	Refractive Index	Molar Refraction Calcd.	Found
AA	120	121	0.9465;25°	1.3913;25°	30.07	30.12
AAA	164	166	0.9896;27°	1.4089;27°	41.10	41.16
BB	134	132	0.9182;32°	1.3902;32°	34.64	34.84
CC	149	148	0.8974;32°	1.3940;32°	39.45	39.37
DD	134	136	0.9218;32°	1.3930;32°	34.84	34.37

Compound	Boiling Point, °C. Press., mm.		Molar Ratio of acetal to oxide	% Yield, based on oxide
AA	131	750	2:1	18
AA	"	"	3:1	53
AAA	185	748	2:1	14
AAA	"	"	3:1	5
BB	135-43	744	3:1	61
CC	163-64	746	3:1	49
DD	141	746	3:1	22

Compound AA is miscible with or dissolves water, lower alcohols,
ethers, aromatic and aliphatic hydrocarbons, esters, and cellulose
acetate.

Compound AAA exhibits the same properties as Compound AA.

Compound BB shows miscibilities and solvent powers similar to those
of Compound AA

Compounds CC and DD display miscibility with water, lower alcohols,
ethers, aromatic and aliphatic hydrocarbons, but less solvent
ability for cellulose acetate.

SUMMARY

The attempted acid-catalyzed condensation of mono-olefins with olefin oxides does not produce 1:1 addition compounds or copolymers under the conditions described.

The hitherto unstudied acid-catalyzed condensation of olefin oxides with acetals produces significant yields of new products, generally formulated as $R_3COCH_2CHR'OCHR"OCR_3$, where R, R' and R" are hydrogen nor alkyl radicals, alike or unlike. All successful reactions were carried out at or near 0° in liquid phase in the presence of boron trifluoride; the attempted non-catalytic sealed-tube reaction at increased temperatures was ineffective at 125°, and above 125° the reaction was uncontrollable. Aluminum chloride, zinc chloride, calcium chloride and mercuric chloride as hetero-geneous catalysts in the attempted liquid-phase reaction produced no 1:1 addition products.

The reaction of ethylene oxide with methylal produces two compounds, namely 1-(methoxymethoxy)-2-methoxyethane and 1-(2-methoxymethoxyethoxy)-2-methoxyethane. Propylene oxide when condensed with methylal yields 1-(methoxymethoxy)-2-methoxypropane, and the isomer 1-methoxy-2-(methoxymethoxy)propane. Ethylal in the presence of ethylene oxide forms 1-(ethoxymethoxy)-2-ethoxy-ethane, and dimethyl acetal when reacted with ethylene oxide yields 1-(1-methoxyethoxy)-2-methoxyethane.

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TYPIST PAGE

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