An Exploratory Study of the Addition Reactions of Ethyleneglycol, 2-Chloroethanol and 1,3-Dichloro-2-Propanol to 1-Dodecene

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Abstract

sec-Dodecyl ethers of ethyleneglycol, 2-chloroethanol, and 1,3-dichloro-2-propanol have been prepared by reacting 1-dodecene with the corresponding substituted alcohol in the presence of BF_3 as a catalyst.

The addition of ethyleneglycol to 1-dodecene proceeds best in the presence of a reaction solvent (e.g., nitromethane), which suppresses side reactions. The resulting ethers consist almost exclusively of the mono-sec-dodecyl derivatives. The maximum yield was about 50 mol% on dodecene intake and 75 %m on converted ethyleneglycol.

The addition of 2-chloroethanol and 1,3-dichloro-2-propanol to dodecene can easily be conducted without a reaction solvent; yields are 77 and 67 mol% respectively on 1-dodecene intake. A reaction scheme for the addition of ethyleneglycol to 1-dodecene is proposed.

Introduction

AMONG THE NUMEROUS OLEFIN REACTIONS known today the addition of alcohols to olefins to form ethers has received relatively little attention. The reaction was carried out for the first time by Semmler (1), who prepared camphene ethyl ether by adding ethanol to camphene under the influence of concentrated sulfuric acid. In 1907 Reychler (2) reported that in the same way trimethylethylene reacts with methanol to form tert-amyl methyl ether. According to Evans and Edlund (3), the preferred starting materials are primary alcohols and lower "tertiary" olefins (e.g., isobutene). Straight-chain olefins display low reactivity; H_2SO_4 is the preferred catalyst, and the reaction reaches an equilibrium depending on the type of olefin used.

This addition reaction was carried out with straight-chain olefins: viz., 1-dodecene and substituted alcohols; viz., ethyleneglycol, 2-chloroethanol, and 1,3-dichloro-2-propanol in combination with a BF_3 catalyst. A survey of the exploratory work is given in this paper.

Experimental Procedure

Analytical procedures are described below. For the hydroxyl value the acetylation method according to Ogg et al. (4) was used. To determine the ethoxy content of glycol ethers, Siggia's method (5) was used.

Chlorine in sec-Dodecyl 2-Chloroethyl Ethers

A sample containing about 1 meq Cl is dissolved in a mixture of 5 ml of n-butanol and 15 ml of absolute ethanol. The solution is heated to reflux, and 1.5 g of metallic sodium is added in small portions via the condenser. After 30 min of refluxing 20 ml of 96% ethanol are added; after cooling down to ambient temperature, 50 ml of 50% aqueous alcohol are added. The product is then acidified with 20% HNO_3 to phenolphthalein, and the number of Cl equivalents is determined by Volhardt's method.

Water in Reaction Mixtures

A weighed sample of the reaction mixture is diluted with a measured amount of a 1:1 methanol/n-butanol mixture of known water content to a standard volume. The water determination is carried out in an aliquot part by the Karl Fischer method.

sec-Dodecyl 2-Hydroxyethyl Ethers and Ethyleneglycol in Reaction Mixtures

A weighed sample taken from a well-stirred reaction mixture and containing about 2.5 meq of hydroxy ethers is shaken with 50 ml of a 1:1 mixture of pentane and diethyl ether and 50 ml of H_2O. After phase separation the resulting bottom layer is extracted three times with 20-ml portions of ether/pentane. The combined ether/pentane fractions are washed three times with a 10 wt% solution of Na_2SO_4 in water,[1] filtered through fluted filter paper, and evaporated in a conical flask. The number of OH equivalents is determined directly in the residue by the acetylation method.

The combined water layers and washings obtained are diluted to a standard volume, and an ethyleneglycol determination is carried out in an aliquot part by oxidation with periodic acid by Pohle's method (6).

The hydroxy ether yield is calculated as follows:

$$\begin{array}{l}\text{Hydroxy ether} \\ \text{yield, mol\% on} \\ \text{dodecene intake}\end{array} = \frac{\text{Hydroxy ether conc., meq/g reaction mixture}}{\text{initial dodecene conc., mmole/g reaction mixture}} \times 100$$

$$\begin{array}{l}\text{Hydroxy ether} \\ \text{yield, mol\% on} \\ \text{converted glycol}\end{array} = \frac{\text{Hydroxy ether conc., meq/g reaction mixture}}{\begin{array}{l}\text{initial glycol conc.} \\ \text{mmole/g reaction} \\ \text{mixture}\end{array} - \begin{array}{l}\text{glycol conc.} \\ \text{mmole/g reaction} \\ \text{mixture}\end{array}} \times 100$$

sec-Dodecyl 2-Chloroethyl Ethers in Reaction Mixtures

A weighed sample taken from a well-stirred reaction mixture and containing about 1.0 meq of chloroethers is shaken with 50 ml of pentane and 50 ml of 50% aqueous ethanol. The resulting lower layer is extracted twice with 10-ml portions of pentane. The combined pentane fractions are washed three times with 10-ml portions of 20% aqueous ethanol and filtered through fluted filter paper into a conical flask; the pentane is evaporated. The number of Cl equivalents is directly determined in the residue by the sodium method. The chloroether yield on 1-dodecene intake can be calculated by the method mentioned above.

Preparation and Identification of sec-Dodecyl 2-Hydroxyethyl Ether

A stream of BF_3 is passed into a mixture of 1116 g dioxane and 372 g of ethyleneglycol containing about

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[1] When nitromethane was used, a 2N NaOH washing of the ether/pentane extracts was included.

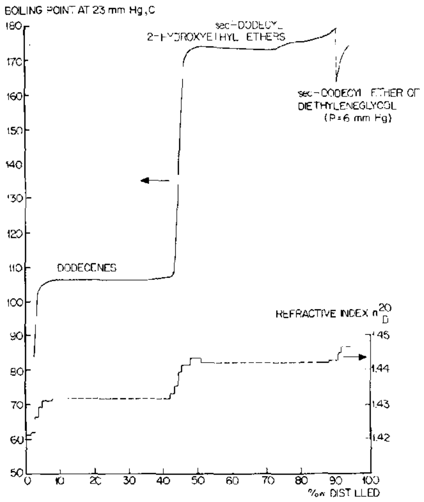


FIG. 1. Distillation of crude hydroxyether, from addition reaction of ethyleneglycol to 1-dodecene.

0.5 wt% H_2O; the temperature is kept below 20C by cooling in ice. When 272 g have been absorbed, the BF_3 stream is stopped and 168 g 1-dodecene are added. This mixture is heated to 95C with vigorous stirring.

After three hours under these conditions the product is rapidly cooled to room temperature and poured out on ice. The resulting upper layer is taken up in a 1:1 (v/v) mixture of diethyl ether and pentane while small amounts of organic material are recovered from the aqueous phase by extraction with an ether/pentane mixture. After washing the combined ether/pentane phases with H_2O and letting the solvent evaporate, the resulting residue is rectified in vacuo (Figure 1).

The analytical data of the main fractions obtained have been collected in Table I.

Preparation and Identification of sec-Dodecyl 2-Chloroethyl Ether

A stream of BF_3 is passed at room temperature into 487 g of 2-chloroethanol containing 0.7% H_2O. When 34 g have been absorbed, the BF_3 addition is discontinued and 168 g 1-dodecene are added. The resulting mixture is heated to 95C with vigorous stirring. After five hours under these conditions the reaction product is cooled to room temperature and extracted five times with 100-ml portions of pentane. The combined pentane extracts are washed with 20% aqueous alcohol and, after the pentane has been flashed off, rectified in vacuo (Figure 2). Analytical data of the main fractions obtained are presented in Table II.

TABLE I

Addition of Ethyleneglycol to 1-Dodecene. Analysis of Fractions Obtained by Analytical Rectification of Reaction Product

Boiling point C	Weight g	Product	Analysis: Hydroxyl value meq/g	Analysis: Ethoxy content mmole/g
106–107 (23 mm)	62	Dodecene (1-dodecene content: 4%)	......	......
171–179 (23 mm)	79	sec-Dodecyl 2-hydroxyethyl ether	4.38 [4.35][a]	4.32 [4.35]
164–174 (6 mm)	6	sec-Dodecyl ether of diethyleneglycol	3.73 [3.66]	6.15 [7.32]

[a] Values between brackets: theoretical.

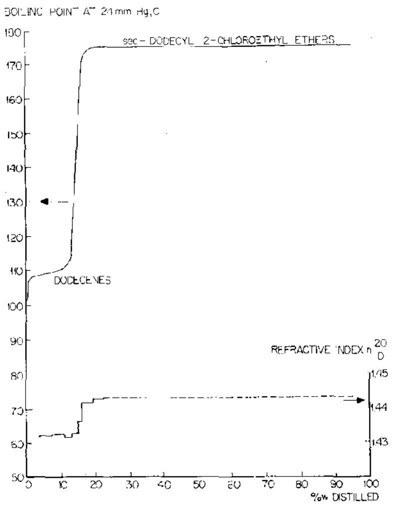


FIG. 2. Distillation of crude chloroethers from addition of 2-chloroethanol to 1-dodecene.

TABLE II

Addition of 2-Chloroethanol to 1-Dodecene. Analysis of Fractions Obtained by Analytical Rectification of Reaction Product[a]

Boiling point C	Weight g	Product	Analysis
108–111 (25 mm)	24	Dodecene	1-dodecene content: 2%
174–175 (25 mm)	169	sec-Dodecyl 2-chloroethyl ether	Cl content 4.02 meq/g [theor. 4.02]

[a] After the chloroether had been converted into the corresponding hydroxyether by refluxing with a solution of sodium acetate in acetic acid to form the acetate (7), followed by saponification, the following analytical results were obtained:

Hydroxyl value: 4.26 meq/g
Ethoxy content: 4.32 mmole/g
} [theor. 4.35]

NMR and IR measurements: primary OH groups; 2 CH_3 groups/mole

Preparation and Identification of sec-Dodecyl 1,3-Dichloro-2-Propyl Ether

A stream of BF_3 is passed at room temperature into 876 g 1,3-dichloro-2-propanol. When 6.8 g have been absorbed, BF_3 addition is stopped and 168 g 1-dodecene are added. The mixture is then heated to 95C with vigorous stirring. After 10 min of reaction time the reaction product is cooled down to room temperature. The chloroethers are isolated by extracting the crude reaction product five times with 200-ml portions of pentane. After washing the combined pentane extracts with 20% aqueous ethanol and after evaporation of the pentane, the resulting residues are rectified in vacuo. Yield: 198 g sec-dodecyl 1,3-dichloro-2-propyl ethers.

Collected in Table III are the analytical data of the chloroethers and of the corresponding dihydroxy ethers formed by reaction of the chloroether with sodium acetate (7) in refluxing acetic acid and by saponification of the resulting acetates.

TABLE III

Addition of 1,3-Dichloro-2-Propanol to 1-Dodecene. Analysis of sec-Dodecyl 1,3-Dichloro-2-Propyl Ether Obtained by Analytical Rectification of Reaction Product

Properties	sec-Dodecyl 1,3-dichloro-2-propyl ether	sec-Dodecyl 1,3-dihydroxy-2-propyl ether
Boiling range	172–173 (9 mm)	....
O_2 Content, mat/g	3.50 [theor. 3.361]	11.7 [theor. 11.5]
Cl Content, meq/g	6.78 [theor. 6.72]	....
OH Value "	....	7.38 [theor. 7.69]
Test for vicinal OH groups with HIO_4	.. ....	negative
IR/NMR analysis	....	primary OH groups

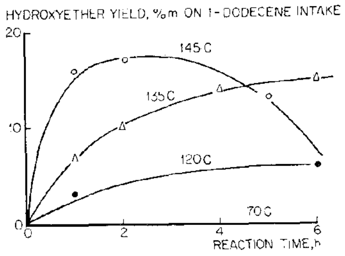
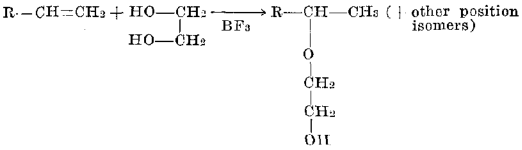


FIG. 3. Addition of ethyleneglycol to 1-dodecene; influence of reaction temperature. Reaction conditions: ethyleneglycol/dodecene molar ratio = 3; and BF_3 concentration in ethyleneglycol = 15.5%w.

Results and Discussion

Addition of Ethyleneglycol to 1-Dodecene

The addition of ethyleneglycol to 1-dodecene to yield sec-dodecyl 2-hydroxyethyl ether proceeds according to:



$$R-CH=CH_2 + \underset{HO-CH_2}{HO-CH_2} \xrightarrow[BF_3]{} R-\underset{\underset{\underset{\underset{OH}{|}}{CH_2}}{\underset{|}{CH_2}}}{\underset{|}{\underset{O}{|}}}{CH}-CH_3 \text{ (+ other position isomers)}$$

In Figures 3–5 the ether yields determined in small samples which were taken from the reaction mixture under various conditions have been plotted as a function of reaction time. The maximum attainable yield on dodecene intake is rather low, viz., about 25 mol%. The ether formation is favored mainly by a large excess of ethyleneglycol. The influence of reaction temperature and BF_3 concentration on the ultimate ether yield is small; their main effect is on the reaction rate.

The amounts of water and ethyleneglycol found in the samples (Figure 6) strongly suggest that the main side-reaction is the formation of polyglycols and water, thus rendering the selectivity of the conversion of ethyleneglycol into sec-dodecyl 2-hydroxyethyl ether very low, viz., about 5%.

The yield could be raised to about 50 mol% on 1-dodecene intake with dioxane and nitromethane as reaction solvents (Figures 7 and 8).

The figures also show that, in the presence of these solvents, the reaction can be carried out at a temperature some 40C lower, viz., at 95C instead of 135C. Under these conditions, side reactions of the ethyleneglycol are strongly suppressed, as indicated in the reduction of water formation and the increase in yield on converted glycol from 5 to about 50 mol%.

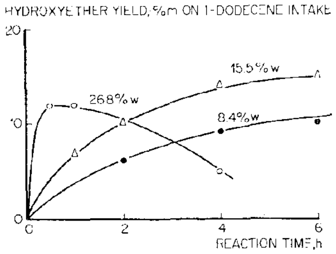


FIG. 4. Addition of ethyleneglycol to 1-dodecene; influence of BF_3 concentration in ethyleneglycol. Reaction conditions: ethyleneglycol/dodecene molar ratio = 3; and temperature = 135C.

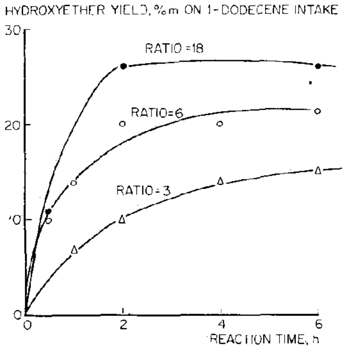
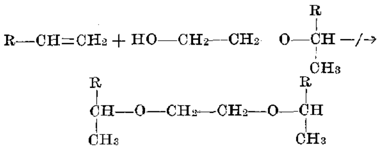


FIG. 5. Addition of ethyleneglycol to 1-dodecene; influence of ethyleneglycol/dodecene molar ratio. Reaction conditions: temperature = 135C; and BF_3 concentration in ethyleneglycol = 15.5 wt%.

From a comparison of Figures 7 and 8 it can be concluded that the BF_3 catalyst is more active in the presence of nitromethane than with dioxane. With nitromethane the optimum yield is attained in half the time at about half the BF_3 concentration.

Rectification in vacuo of the reaction products (Figure 1) provides little evidence of the formation of appreciable amounts of di-sec-dodecyl glycol ether by reaction of another molecule of dodecene with sec-dodecyl 2-hydroxyethyl ether:

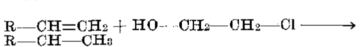


$$R-CH=CH_2 + HO-CH_2-CH_2-O-\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{CH}} \not\rightarrow \overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{CH}}-O-CH_2-CH_2-O-\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{CH}}$$

The initial water content of the ethyleneglycol-solvent-BF_3 mixture proved to have a great influence on the rate of ether formation and on reaction selectivity of the ethyleneglycol conversion. Table IV shows that an increase in water content from 0.5 to 1.3 wt% doubles the time required to reach maximum ether formation but that it leads to a rise in ether yield on converted ethyleneglycol from 49 to 76 mol%.

Addition of 2-Chloroethanol to 1-Dodecene

This reaction, yielding sec-dodecyl 2-chloroethyl ether, proceeds as follows:



$$R-CH=CH_2 + HO-CH_2-CH_2-Cl \longrightarrow R-\underset{\underset{O-CH_2-CH_2-Cl}{|}}{CH}-CH_3 \text{ (+ other position isomers)}$$

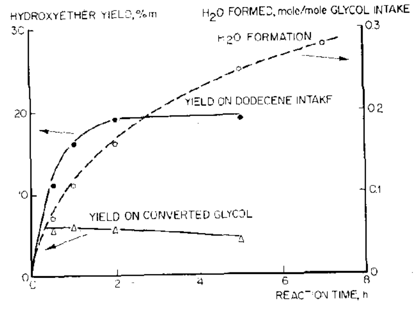


FIG. 6. Addition of ethyleneglycol to 1-dodecene; glycol consumption and H_2O formation during reaction. Reaction conditions: ethyleneglycol/dodecene molar ratio = 9; BF_3 concentration in ethyleneglycol = 15.5 wt%; reaction temperature = 135C; and initial water content of glycol/BF_3 phase = 0.6 wt%.

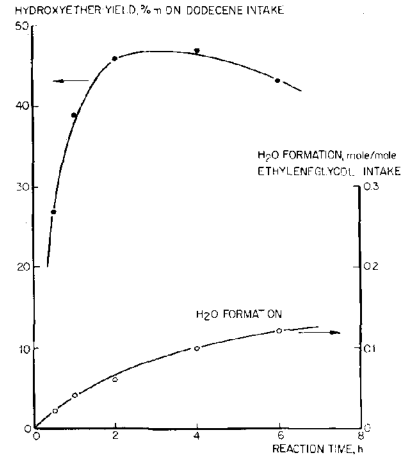


FIG. 7. Addition of ethyleneglycol to 1-dodecene, using dioxane as reaction solvent. Reaction conditions: ethyleneglycol/dodecene molar ratio = 6; dioxane/ethyleneglycol weight ratio = 3; BF_3 concentration in ethyleneglycol-dioxane = 15.5 wt%; temperature = 95C; and initial H_2O concentration in glycol-dioxane-BF_3 = 0.3 wt%.

TABLE IV

Addition of Ethyleneglycol to 1-Dodecene. Influence of H_2O on Reaction Rate and on Yield of sec-Dodecyl 2-Hydroxyethyl Ether on Converted Ethyleneglycol[a]

H_2O Content of glycol/ BF_3/ nitromethane mixture %w	Time required to attain optimum hydroxyether yield h	Hydroxyether yield	
		on 1-dodecene intake %m	on converted ethyleneglycol %m
0.5	1	51[b]	49[b]
1.3	2	49	76

[a] Reaction conditions: 1-dodecene/glycol/BF_3 molar ratio = 1/6/2; nitromethane/glycol weight ratio = 3; temperature = 95C.

[b] Values taken from Figure 8.

Although the reaction was catalyzed by concentrated sulfuric acid, BF_3 gave better results in regard to yield and by-product formation. The reaction conditions should be about the same as for the addition of ethyleneglycol so the olefin is stirred with an excess of the chloroalcohol at 95C in the presence of BF_3. In Figure 9 the ether yield and amount of water formed have been plotted against reaction time. As the small amounts of water indicated that there was no appreciable formation of di(2-chloroethyl) ether, no experiments were carried out with solvents.

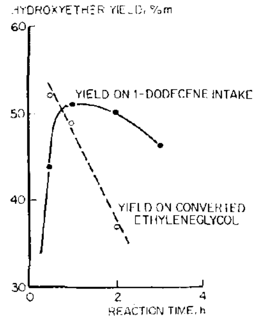


FIG. 8. Addition of ethyleneglycol to 1-dodecene, using nitromethane as reaction solvent. Reaction conditions: ethyleneglycol/dodecene molar ratio = 6; nitromethane/ethyleneglycol weight ratio = 3; BF_3 concentration in ethyleneglycol-nitromethane = 8.4 wt%; temperature = 95C; and initial H_2O concentration in glycol-nitromethane = 0.5 wt%.

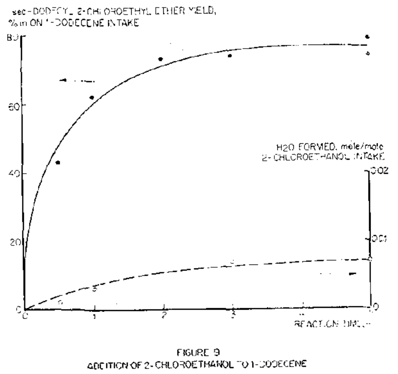
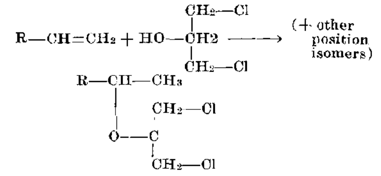


FIG. 9. Addition of 2-chloroethanol to 1-dodecene. Reaction conditions: temperature = 95C; 2-chloroethanol/dodecene molar ratio = 6; BF_3 concentration in chloroethanol = 6.5 wt%; and initial water content of 2-chloroethanol/BF_3 mixture = 0.7 wt%.

A comparison of Figure 9 with Figure 8 shows that, under about equal conditions in regard to temperature, alcohol/olefin molar ratio, and BF_3 and water concentrations, the maximum ether yield is higher than in the case of ethyleneglycol, viz., 77 mol% as against 52 mol% on 1-dodecene intake.

Addition of 1,3-Dichloro-2-Propanol to 1-Dodecene

From this work it was concluded that the addition of alcohols to straight-chain 1-alkenes is stimulated by the presence of a chloride or a hydroxy group at the carbon atom adjacent to the one carrying the OH group to be etherified. Hence it was assumed that 1,3-dichloro-2-propanol would react relatively easily with 1-dodecene to form a sec-dodecyl 1,3-dichloro-2-propyl ether according to:



$$R—CH{=}CH_2 + HO—\overset{\displaystyle CH_2—Cl}{\underset{\displaystyle CH_2—Cl}{\overset{|}{\underset{|}{CH2}}}} \longrightarrow \begin{array}{l} R—CH—CH_3 \\ \quad\;\; | \quad\;\; CH_2—Cl \\ \quad\;\; | \qquad | \\ \quad\;\; O—C \\ \qquad\quad\; | \\ \qquad\quad\; CH_2—Cl \end{array} \text{(+ other position isomers)}$$

This assumption proved correct; the ether yield on dodecene intake was 67 mol% under the following reaction conditions:

1,3-dichloro-2-propanol/1-dodecene molar ratio = 6.8
BF_3 concentration in the propanol = 0.8 wt%
Initial H_2O concentration in BF_3/1,3-dichloro-2-propanol mixture = 0.1 wt%
Reaction time = 10 min
Temperature = 95C

The reaction rate was much higher than in the addition of ethyleneglycol and chloroethanol even though the catalyst concentration was much lower. A water determination in the reaction product gave little evidence of the formation of di(1,3-dichloropropyl) ether.

Isolation of Reaction Products

The sec-dodecyl chloro- and hydroxy ethers can be recovered by pouring out the reaction mixtures on ice, collecting the water-insoluble material, and distilling in vacuo.

It has been found however that the ethers can also

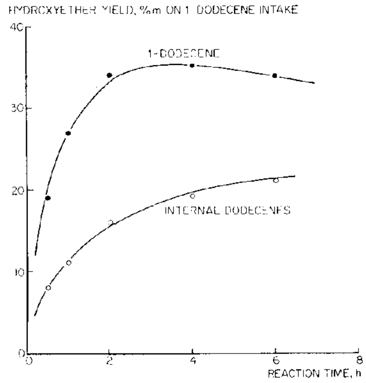


FIG. 10. Addition of ethyleneglycol to 1-dodecene; reactivities of 1-dodecene and internal dodecenes. Reaction conditions: temperature = 95C; ethyleneglycol/dodecene molar ratio = 3; dioxane/ethyleneglycol weight ratio = 3; and BF_3 concentration in ethyleneglycol-dioxane mixture = 16.7 wt%.

be isolated by extracting the reaction mixtures with pentane at ambient temperature. The pentane extracts, which contain a mixture of olefins, the secondary alkyl ethers, and some higher-boiling material, can be separated by distillation in vacuo (Figure 2). The bottom layer contains the excess of the starting alcohol and the BF_3 catalyst. In the case of ethyleneglycol the isolation proceeds best with nitromethane as the reaction solvent on account of its poor miscibility with pentane.

Course of Addition of Ethyleneglycol to 1-Dodecene

According to IR analysis, the dodecene recovered from the reaction products of 1-dodecene and ethyleneglycol which represent the maximum of the yield-time curve contained 96% of internal dodecenes (Table I). Figure 10 shows that these olefins are less reactive in the etherification reaction than 1-dodecene. From Figure 11 it is seen that sec-dodecyl 2-hydroxyethyl ether decomposes rapidly in a simulated reaction mixture in which dodecene has been replaced by n-dodecane.

These findings suggest that the addition reaction proceeds according to the following reaction scheme:

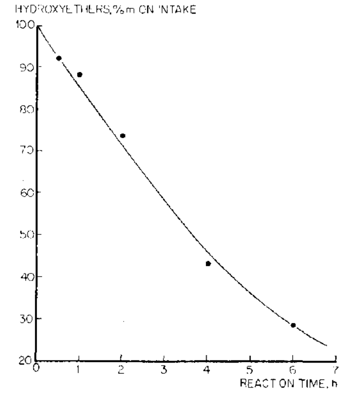


FIG. 11. Addition of ethyleneglycol to 1-dodecene; rate of decomposition of sec-dodecyl 2-hydroxyethyl ethers in a simulated reaction mixture. Reaction conditions: temperature = 95C. Composition: sec-dodecyl 2-hydroxyethyl ether 7.3 wt%, n-dodecane 10.4 wt%, ethyleneglycol 13.3 wt%, H_2O 0.5 wt%, BF_3 14.1 wt%, dioxane 52.5 wt%, and diethyleneglycol 1.9 wt%.

$$\begin{array}{ll} \text{1-dodecene} + \text{ethyleneglycol} & \rightarrow \text{sec-dodecyl} \\ & \quad \text{2-hydroxy-} \\ \text{internal dodecenes} + \text{ethyleneglycol} & \rightleftarrows \text{ethyl ethers} \end{array}$$

The fact that the yield-time curves pass through a maximum can be explained as follows. Initially the reacting olefin is mainly of the 1-alkene type. Decomposition of the reaction product leads to the more slowly reacting internal olefins, and ultimately decomposition predominates over the formation reaction. It is not known whether a direct isomerization of the 1-dodecene to its internal isomers takes place at the same time.

Probably a similar reaction scheme applies to the addition of 2-chloroethanol and 1,3-dichloro-2-propanol to 1-dodecene.

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