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## Solvolysis of 1,2-Epoxydodecane<sup>1</sup>

S. WAWZONEK<sup>2</sup> AND H. J. BLUHM<sup>2,3</sup>

*Abstract.* The solvolysis of 1,2-epoxydodecane in formic acid followed by saponification gave mainly 1,2-dodecanediol and a small amount of the isomeric 2,2'-dihydroxydidodecyl ethers. No products from a coil effect were isolated. The structure of the ether was demonstrated by oxidation and synthesis. Assignment of configuration to the isomeric ethers was made on the basis of the infrared spectra.

In the acid-catalyzed hydrolysis of cyclooctene (4) substantial amounts of 1,4-cyclooctanediol have been isolated in addition to 1,2-cyclooctanediol. The formation of the 1,4-diol is attributed to the transfer of a hydride ion across the ring (transannular effect).

Investigation of acyclic compounds for the presence of a similar phenomenon has not been reported. Since a carbon chain can assume a spiral configuration it is conceivable that certain atoms along the chain, if long enough, could come into close enough proximity to a reactive center to facilitate the transfer of a hydride ion (coil effect). To test this concept the products formed in the solvolysis of 1,2-epoxy-dodecane (1) have been investigated. Hydride transfer in this example would give rise to structural isomers of dodecanediol.

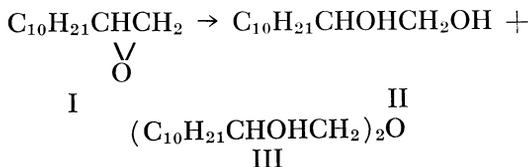
Solvolysis of 1,2-epoxydodecane (I) in formic acid followed by saponification of the resulting formates gave a mixture of products. The majority of the 1,2-dodecanediol (II) (89.7%) was separated from the mixture as the isopropylidene ketal by chromatography on alumina. Conversion of pure 1,2-dodecanediol (II) to the isopropylidene derivative was 95 per cent efficient. The remainder of the product consisted of a mixture of isomeric 2,2'-dihydroxydidodecyl ethers (III) (3.5%) and unchanged 1,2-dodecanediol (2.6%). Tailings of intermediate fractions amounted to 1.5%. No isomeric dodecanediols were found.

The isomeric 2,2'-dihydroxydidodecyl ethers (III) could be separated mechanically after crystallization into pure compounds. Their structures were demonstrated by oxidation and synthesis.

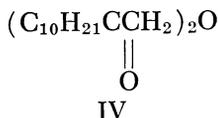
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<sup>3</sup> Abstracted in part from the Ph.D. thesis, February, 1963, of H. J. Bluhm.



Oxidation with sodium dichromate gave 1,1'-oxydi-2-dodecanone (IV)



together with cleavage products which gave 1-undecanol and 1,2-dodecanediol on reduction with lithium aluminum hydride. Reduction of the diketone (IV) with lithium aluminum hydride regenerated a mixture of the isomeric 2,2'-dihydroxydodecyl ethers (III). This reaction definitely establishes that diastereoisomers are involved rather than structural isomers. This result is contrary to the observation that acidic hydrolysis of epoxides gives in general a mixture of structural ethers (3,8).

Two possible explanations exist for this discrepancy. The structural isomer involving an ether linkage through the secondary alcohol may have been formed but may be lower melting and hence present in the small amounts of oils formed. The second possibility suggests that the size of the decyl group may make the reaction unilateral.

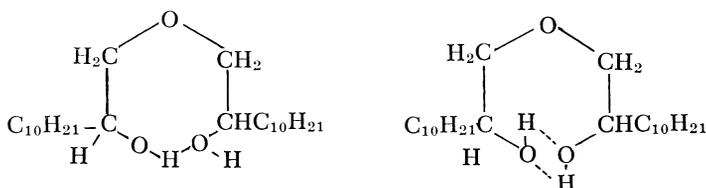
The same mixture of isomers (III) was formed by the reaction of 1,2-epoxydodecane (I) with the sodium salt of 1,2-dodecanediol (II) in refluxing diglyme. Other products isolated were a trimer, impure tetramer and polymeric materials. No structural isomers of III were isolated.

The optical isomers possible for the dimer III are the *dl* and *meso* forms. Based upon the melting point the higher melting compound is probably the *meso* form. This configuration is further substantiated by a comparison of the dimers with respect to the intramolecular hydrogen bonding possible. Such bonding is common and generally occurs in 5, 6, or 7 membered rings (7). The infrared spectra of compounds with internal hydrogen bonds usually exhibit a sharp band due to free hydroxyl and a broad band at lower frequency due to hydrogen bonded hydroxyl. The amount of separation of these two bands is a sensitive measure of the strength of the hydrogen bond (1).

Studies on a number of diols (5) have indicated that 1,4-butanediol showed stronger hydrogen bonding than 1,2-propanediol and that 1,6-hexanediol had no hydrogen bonding. The lat-

ter compound would require a nine membered ring for hydrogen bonding whereas the 1,4-diol utilizes a seven atom ring for its bonding. No data are given for 1,5-pentanediol.

Hydrogen bonding in dimer II must occur by forming an eight membered ring. It is also conceivable that double hydrogen bonding could be present to some degree.



An examination of molecular models indicates that hydrogen bonding could take place in both *dl* and *meso* forms. However, the *dl* modification should give stronger bonding because the decyl groups are further removed from each other than they are in the *meso* form. The pronounced steric interactions between the decyl groups in the *meso* form should give rise to a more intense free hydroxyl band in the infrared. Inspection of the spectra in Nujol indicates a stronger free hydroxyl band in the dimer with a melting point of 92-94°. This isomer must be the *meso* form and the 82-84° melting compound must be the *dl* modification. It should be noted that this difference was apparent only in the crystalline form. The spectra of the dimers in chloroform solution were essentially identical.

NMR spectra in deuterated chloroform were essentially identical except for the peaks for the methylene groups adjacent to the ether oxygen. The *dl*-isomer gave a single peak at 3.5 ppm and the *meso*-isomer gave a doublet at 3.5 and 3.57 ppm. These peaks were not affected by an increase in temperature. The explanation for this difference is not apparent at the present time.

The results of the solvolysis of 1,2-epoxydodecane (I) indicate that the coil effect is practically nonexistent in this reaction. One apparent reason may be the rapid coiling and uncoiling of the hydrocarbon chain at the temperatures used to carry out the reaction.

The possibility that the polar intermediate formed may actually repel the mobile hydrocarbon chain from its vicinity seems unlikely in view of the intramolecular interaction reported for branched-chain fatty acids (2).

#### EXPERIMENTAL<sup>4</sup>

##### 2,2-Dimethyl-4-decyl-1,3-dioxolane. 1,2-Dodecanediol (9) (II)

<sup>4</sup> Melting points and boiling points are not corrected. The petroleum ether used boiled at 30-60°.

(1.46 g.) in dry acetone (100 ml.) was treated with a small amount of anhydrous magnesium sulfate and a trace of *p*-toluenesulfonic acid monohydrate and the reaction mixture was allowed to stand for 24 hours at room temperature. Neutralization with 5 per cent sodium hydroxide was followed by three extractions with ether. Removal of the ether was followed by placing the residual oil under a high vacuum to remove condensation products of acetone. The crude isopropylidene derivative (1.65 g.) (95%) could be purified by chromatography on alumina or by distillation. 2,2-Dimethyl-4-decyl-1,3-dioxolane was a colorless liquid; b.p. 78-79° (0.2 mm); m.p. 1-3°;  $n_D^{25}$ , 1.430;  $d_4^{25}$ , 0.8665.

*Anal.* Calcd. for  $C_{15}H_{13}O_2$ : C, 74.32; H, 12.48. Found: C, 74.57; H, 12.95.

This compound was also prepared directly from the epoxide (I). A stirred solution of dry carbon tetrachloride (50 ml.) containing several drops of anhydrous stannic chloride was treated slowly at room temperature with a solution of 1,2-epoxydodecane (I) (5.0 g.) and acetone (9.5 g.) in carbon tetrachloride (75 ml.). A slight exothermic effect was noted during this addition. The resulting solution was treated with excess 5 per cent sodium hydroxide and the carbon tetrachloride after washing with water was removed by distillation. The residual yellow oil gave on distillation 5.1 g. of the cyclic acetal. The pot residue contained a small amount of 1,2-dodecanediol (II).

*Solvolysis of 1,2-Epoxydodecane (I).* Ninety per cent formic acid (30 ml.) was treated with stirring with 1,2-epoxydodecane (I) (6.2 g.) over a period of 30 minutes. After an additional stirring of 30 minutes the reaction mixture was heated at 100° for 90 minutes. Removal of the excess formic acid was followed by the addition of 10 percent sodium hydroxide (50 ml.) and stirring at room temperature for two hours. Extraction with ether gave 6.67 g. of a white fluffy product which was treated with acetone for twenty days and the resulting product was isolated by the method described previously. The resulting material (7.73 g.) was chromatographed on alumina (70 g.) using petroleum ether, ethyl ether and absolute methanol as eluting solvents. The first of these eluted the cyclic ketal (6.93 g.); a 15:1 ethyl ether-methanol mixture eluted with dimer (II) (0.27g.) with a melting point of 75-92°; elution with methanol gave 0.20 g. of impure 1,2-dodecanediol; m.p. 53-60°. Intermediate fractions using varying ratios of solvents amounted to 0.12 g.

Analysis of the dimer (II) gave the following results.

*Anal* Calcd. for  $C_{24}H_{50}O_3$ : C, 74.56; H, 13.03. Found: C, 74.72; H, 12.83.

Separation by crystallization or chromatography failed. Crystallization from petroleum ether containing a few drops of methanol followed by mechanical separation gave amorphous crystals melting at 82-84° and flat needless melting at 92-94°.

*Anal.* Calcd. for  $C_{24}H_{50}O_3$ : C, 74.56; H, 13.03; mol. wt., 386.6. Found (m.p. 82-84°): C, 74.79; H, 12.79; mol. wt., 406.0. Found (m.p. 92-94°): C, 74.71; H, 13.03; mol. wt., 401.5 (Mechrolab osmometer; solvent,  $HCCl_3$ .)

The molecular weights are slightly high because of intermolecular hydrogen bonding. 1,2-Dodecanediol (II) under similar conditions gave a value of 211.4 (Calcd. 202.3).

Infrared spectra of the dimers were identical in chloroform. Bands appeared at 2580, 2480 (broad) and 1115 (broad)  $cm^{-1}$ . Spectra in Nujol mulls were likewise similar except for the more pronounced splitting of the hydroxyl band for the 92-94° melting isomer at 3260 and 3510  $cm^{-1}$ . The hydroxyl band for the 82-84° melting isomer was at 3320  $cm^{-1}$ .

*Reaction of 1,2-Epoxydodecane (I) with the Sodium Salt of 1,2-Dodecanediol (II).* A stirred solution of 1,2-dodecanediol (II) (5.0 g.) in diglyme (150 ml.) was treated with 50 per cent sodium hydride dispersion (1.2 g.) in mineral oil over the course of one hour and the resulting mixture was stirred and heated for another hour. To this mixture at reflux 1,2-epoxydodecane (4.6 g.) in diglyme (50 ml.) was added over a 2 hour period and the resulting suspension was stirred at reflux for 8 hours. Treatment with water was followed by extraction with ether and repeated washings with water of the ether layer. Removal of the ether gave 8.95 g. of a yellowish-brown solid. Successive recrystallizations from acetone and from a petroleum ether-methanol mixture gave 0.88 g. of the dimer melting at 82-91°. A second crop (0.57 g.) obtained by concentrating the mother liquor melted at 80-90°. These products were identical with that obtained from the solvolysis of 1,2-epoxydodecane.

The acetone filtrate gave, upon removal of the solvent, a reddish brown oil which was chromatographed on alumina (50 g.). Elution with petroleum ether and ethyl ether gave a small amount of polymeric oil. Further elution with 50:1 ether-methanol mixture gave 0.31 g. of an impure tetramer which was recrystallized from petroleum ether; m.p. 43-44°.

*Anal.* Calcd. for  $C_{48}H_{98}O_5$ : C, 77.85; H, 13.00; mol. wt., 754. Found: C, 76.32; H, 12.99; mol. wt., 722 ( $HCCl_3$ , Mechrolab osmometer).

Elution with 25:1 ether-methanol gave 0.67 g. of a trimer; m.p. 34-5°.

*Anal.* Calcd. for  $C_{36}H_{74}O_4$ : C, 75.79; H, 12.98; mol. wt., 570. Found: C, 75.27; H, 13.09; mol. wt., 583 (HCCl<sub>3</sub> Mechrolab osmometer).

The infrared spectrum in Nujol was very similar to that of the dimer.

Further elution with 9:1 and 4:1 ether-methanol gave 0.184 g. of the dimer. The remaining fractions using methanol as the eluant consisted of 1,2-dodecanediol (II).

*Oxidation of 2,2'-Dioxydodecyl Ether (III).* A solution of the dimer (III) (0.55 g.) in glacial acetic acid (40 ml.) was treated with sodium dichromate dihydrate (0.50 g.) and the reaction mixture was allowed to stand at room temperature for 4 hours. After this period an additional 0.25 g. of dichromate was added and the solution was heated to 60° and then allowed to stand at room temperature for an additional two hours. Addition of water was followed by five extractions with petroleum ether. The combined extracts were washed with water and then with 5 percent sodium hydroxide. Acidification of the latter followed by extraction with ether gave 0.18 g. of a slightly yellow oil which gave an infrared spectrum characteristic of a carboxylic acid. This material was reduced with lithium aluminum hydride (0.25 g.) in ether (100 ml.) and gave an oil (0.16 g.) which was chromatographed on alumina (5 g.) Elution with ether gave 1-undecanol (0.10 g.); m.p. 10.5-12°;  $n_D^{20}$ , 1.4402; mol. wt. 178.1. The literature (6) reports  $n_D^{20}$ , 1.4410.

Further elution of the reduction product with methanol gave impure 1,2-dodecanediol (II).

The petroleum ether extracts containing the non-acidic products gave an oily solid which was recrystallized from petroleum ether; yield, 0.18 g.; m.p. 65.5-67°. The yellow filtrate was chromatographed on silicic acid (12 g.). A 1:1 petroleum ether-ethyl ether mixture eluted 0.16 g. of a slightly yellow oil whose infrared spectrum exhibited a strong carbonyl band with a negligible hydroxyl band. This was closely followed by 0.09 g. of a solid with a melting point of 64-65.5°. This solid was combined with the material isolated by crystallization and recrystallized twice from 95 percent ethanol. The 1,1'-oxy-di-2-dodecanone (IV) (0.21 g.) obtained melted at 66-67°.

*Anal.* Calcd. for  $C_{24}H_{46}O_3$ : C, 75.33; H, 12.12; mol. wt., 382.6. Found: C, 75.12; H, 11.88; mol. wt., 378.8. (HCCl<sub>3</sub>, Mechrolab osmometer).

The infrared spectrum gave bands at 1740 and 1125  $cm^{-1}$  for a solution in carbon tetrachloride.

The 2,4-dinitrophenylhydrazone after three crystallizations

from 95 percent ethanol-ethylacetate gave yellow needles; m.p. 121-122°.

*Anal.* Calcd. for  $C_{36}H_{54}O_9N_8$ : C, 58.20; H, 7.32; N, 15.08. Found: C, 58.26; H, 7.49; N, 15.33.

The 0.16 g. of oil mentioned above was reduced with lithium aluminum hydride in ether. The reduced product (0.14 g.) gave 0.015 g. of 1,2-dodecanediol (II) and a yellow oil which proved to be impure 1-undecanol.

*Reduction of 1,1'-Oxydi-2-dodecanone (IV).* 1,1'-Oxydi-2-dodecanone (0.04 g.) and lithium aluminum hydride (0.08 g.) in ether (25 ml.) were refluxed for 4 hours. The addition of water gave a sticky white mass which was dissolved by the addition of 10 percent sulfuric acid. The ether layer gave a solid which was recrystallized from petroleum ether containing methanol; yield, 0.038 g. The material consisted of amorphous crystals, m.p. 92-94° and flat needles, m.p. 82-84°, identical with the dimer (III). The lower melting isomer appeared to be present in a larger amount.

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