lar precipitate was removed by filtration after stirring for 2 hr. Distillation of the filtrate gave 24 g. of product distilling at 92–97° (0.4 mm.) which solidified. The product was further purified by redistillation at 100° (1 mm.) to give 19 g. (25%) of product which melted at 38–40°.

Anal. Calcd. for $C_{12}H_6O_3$: C, 66.01; H, 12.00. Found: C, 66.18; H, 12.07.

Bis(2-hydroxy-2-methylpropyl) ether. This was prepared similarly to the bis(2-hydroxy-2-ethylbutyl) ether and distilled at 78° (0.2 mm.). The product was purified by recrystallization from Skellysolve B and melted at 65–66°[13] (22% yield).

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 59.19; H, 11.31.

Bis(2-hydroxy-2-butylhexyl) ether. This was prepared similarly to the bis(2-hydroxy-2-ethylbutyl)ether but on distillation of the reaction solvent the product was purified by recrystallization from Skellysolve B instead of by distillation. The product melted at 85–85.5° (23% yield).

Anal. Calcd. for $C_{20}H_{12}O_3$: C, 72.67; H, 12.81. Found: C, 72.77; H, 13.08.

MORRIS PLAINS, N. J.

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[13] M. Godchot, *Compt. rend.*, **184**, 820 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Preparation of Substituted 1,4-Dioxanes

MELVIN J. ASTLE AND BIRGIT EKMAN JACOBSON[1]

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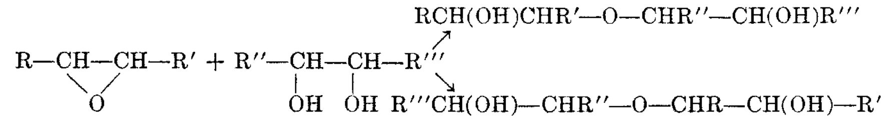
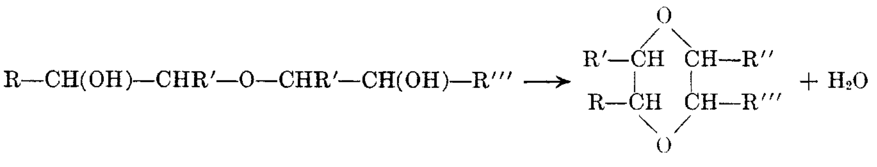
Olefin oxides and glycols react at low temperatures to give dihydroxyethers which on heating lose water to form substituted dioxanes. This seems to be a general method for making substituted dioxanes and a wide variety of such compounds can be made by proper selection of the olefin oxide and the glycol. The method is particularly useful in preparing unsymmetrical dioxanes.

It has been reported in the literature[2,3] that olefin oxides react with glycols to form dihydroxyethers. The reaction may be represented as follows:





It may be expected also that ring closure might occur to form 1,4-dioxanes, but this reaction has not been reported.

The present work describes the preparation of a number of 1,4-dioxanes from certain olefin oxides and glycols by addition and ring closure.

Reactions were carried out with three olefin oxides and five 1,2-glycols. The olefin oxides used were propylene oxide, 2,3-butylene oxide, and styrene oxide; the glycols were ethylene glycol, 1,2-propanediol, 2,3-butanediol, phenyl-1,2-ethanediol, and catechol. Eight substituted *p*-dioxanes were obtained, including methyldioxanes, phenyldioxanes, and phenylmethyldioxanes. In most of the reactions, concentrated sulfuric acid was used as a catalyst and in all but two reactions an excess of glycol was used.

EXPERIMENTAL

The reaction of propylene oxide and ethylene glycol is illustrative of the experimental procedures used.

Ethylene glycol (186 g., 3 mol.) was placed in a 3-neck flask in an ice bath and 10 g. of concentrated sulfuric acid was added gradually. Propylene oxide (116 g., 2 mol.) was then added dropwise during a 30-min. period with constant stirring of the mixture at temperatures below 30°. After addition of the oxide was complete, the mixture was gradually heated to reflux temperature and was then stirred under reflux at 120° for 2 hr. and allowed to cool to room temperature. The first distillation gave a distillate boiling at 75–97° at atmospheric pressure leaving a black tarry residue. The distillate separated into two layers on cooling. Each layer was separately extracted with ether and the combined ether extracts were dried over anhydrous sodium sulfate. The ether was evaporated and the residue redistilled.

Two low boiling fractions were obtained: the fraction boiling from 39–78° consisted largely of propionaldehyde and the one boiling from 80–100° was principally dioxane and water. Monomethyl-1,4-dioxane (b.p. 106–109° at 741 mm. n_D^{20} 1.4187) was then obtained. The yield was 54 g. or 27%. The infrared absorption spectra, which indicated clearly

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[1] From the M.S. thesis of Birgit Ekman Jacobson.

[2] P. A. Levene and A. Walti, *J. Biol. Chem.*, **75**, 325 (1927).

[3] M. S. Kharasch and W. Nudenberg, *J. Org. Chem.*, **8**, 189 (1943).

TABLE I

REACTIONS BETWEEN OLEFIN OXIDES AND 1,2-GLYCOLS IN THE PRESENCE OF SULFURIC ACID

Oxide	Glycol	Reaction Time, Hr.	Reaction Temp.	Product	B.P.	Yield,
Propylene oxide	Ethylene glycol	2	120	Methyl-1,4-dioxane	102–108	27.0
	1,2-Propanediol	5	120	2,5-Dimethyl-1,4-dioxane	115–117	44.5
	2,3-Butanediol	7.5	120	2,3,6-Trimethyl-1,4-dioxane	128–135	44.3
	2,3-Butanediol	4.0	118	2,3,6-Trimethyl-1,4-dioxane	128–135	17.3
2,3-Butylene oxide	Ethylene glycol	6.0	119	2,3-Dimethyl-1,4-dioxane	124–128	11.0
	1,2-Propanediol	5.0	115	2,3,6-Trimethyl-1,4-dioxane	128–135	12.1
	2,3-Butanediol	5.0	126	2,3,5,6-Tetramethyl-1,4-dioxane	135–149	28.4
Styrene oxide	Ethylene glycol	3.0	25	Phenyl-1,4-dioxane	80–81/5 mm.	27.6
	Ethylene glycol	1.0	132	Phenyl-1,4-dioxane	80–81/5 mm.	41.0
	Ethylene glycol	1.0	132(1)	Phenyl-1,4-dioxane	80–81/5 mm.	36.3
	Ethylene glycol	1.0	132(2)	Phenyl-1,4-dioxane	80–81/5 mm.	29.3
	1,2-Propanediol	5.0	130	Methylphenyl-1,4-dioxane	103–106/8 mm.	47.8
	2,3-Butanediol	10.0	140	Phenyl-2,3-dimethyl-1,4-dioxane	93–95/3 mm.	25.0

(1) BF_3/ether catalyst
(2) Toluene sulfonic acid catalyst

the presence of a methyl substituent, were otherwise identical with the spectra of pure 1,4-dioxane.

DISCUSSION OF RESULTS

The results obtained for the reactions of olefin oxides with glycols are summarized in Table I.

More work was done with styrene oxide than with any of the other olefin oxides. The reaction with any of the glycols was exothermic and the addition of styrene oxide was carried out below room temperature. The reaction of styrene oxide with glycols gave homogeneous solutions which separated into two phases on heating to about 120°. In all cases where styrene oxide (1 mol.) and ethylene glycol (3 mol.) were reacted in the presence of concentrated sulfuric acid without external heating, the reaction mixture remained homogeneous, even after vigorous stirring at room temperature for 5 days. When the homogeneous mixture was distilled, the distillate separated into layers. One layer was ether soluble and the second ether insoluble, but water soluble. These layers were separately extracted with ether, the combined ether solutions dried over anhydrous sodium sulfate, and redistilled under reduced pressure. The yields of phenyl-1,4-dioxane thus obtained were 20–27%. A considerably better yield (41%) of this product was obtained when a similar reaction mixture was stirred under reflux (about 130°) for 1 hr. The mixture separated into a brown, oily, ether insoluble material consisting of water, dioxane, unreacted ethylene glycol and some unidentified material and an ether soluble material consisting of phenyldioxane and some phenylacetaldehyde. *p*-Toluenesulfonic acid and boron trifluoride were found to be effective catalysts for the preparation of substituted dioxanes.

Infrared absorption spectra indicated that the products were phenyl substituted cyclic ethers. Boiling points and indices of refraction agreed with known compounds.

These facts are consistent with the idea that the reaction proceeds in two steps in which $C_6H_5CH(OH)CH_2OCH_2CH_2OH$ or $C_6H_5CH(CH_2OH)—O—CH_2CH_2OH$ is first formed. Either of these compounds would be expected to be soluble in the excess glycol and water used. Cyclization gives the phenyldioxane which is much less soluble in the glycol and water and so separation into two phases occurs.

In every case 2,5-diphenyl-1,4-dioxane was obtained as a by-product. This product probably was obtained by the cyclic dehydration of 1-phenyl-1,2-ethanediol from the reaction of water with styrene oxide.

A number of reactions between styrene oxide and catechol were attempted and all failed to give an Indication of hydroxy ether or dioxane formation. Only black tars were obtained.

The formation of methyl substituted dioxanes appears to be a much slower reaction and again hydroxy ethers are first formed which lose water at higher temperatures with the formation of dioxanes. The reaction mixtures remain homogeneous even after several hours at reflux temperatures because of the greater solubilities of the alkyl substituted dioxanes in the reaction mixture. Separation into two phases does not occur until after distillation.

That the expected reaction and ring closure in fact had taken place was most evident in the three cases where the reaction product was identified as methyl-1,4-dioxane, 2,3-dimethyl-1,4-dioxane, and phenyl-1,4-dioxane. Each of these compounds could not have been formed except by a reaction of the olefin oxide with the appropriate glycol. In the reactions of propylene oxide with propylene glycol, of 2,3-butylene oxide with 2,3-butylene glycol, and of styrene oxide with phenyl-1,2-ethanediol, the substitued dioxanes could be expected to be formed either by dimerization of the glycol or by reaction between the olefin oxide and the glycol. However, when the oxide was added to the glycol, an exothermic reaction occurred at temperatures much lower than those required for condensation of the glycol directly to the dioxane. Some of the glycol was undoubtedly converted to the corresponding dioxane by self-condensation at higher temperatures.

Neutralization of the acidic reaction mixture with sodium bicarbonate before distillation decreased the yields of the substituted dioxanes by preventing the acid catalyzed cyclization which would have occurred during distillation. For example, only a 4% yield of trimethyl dioxane and a 9% yield of phenyl dioxane was obtained compared with 12% and 20–27% yields from identical reaction mixtures distilled without neutralization. This indicates that part of the ring closure which would have taken place in acidic media during the distillation did not occur after neutralization. Instead over 60% of the weight of the reaction mixture consisted of high boiling distillation residues and unreacted glycol.

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[CONTRIBUTION FROM MELLON INSTITUTE]

Reaction of 4-Phenyl-1,3-dioxane with Acetic Anhydride

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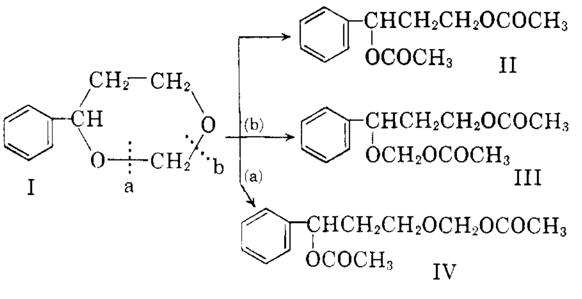
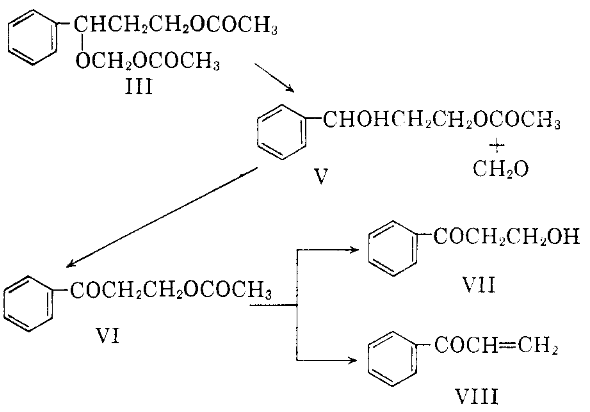
The acetylation of 4-phenyl-1,3-dioxane yields 1,5-diacetoxy-3-phenyl-2-oxapentane—not 1,3-diacetoxy-1-phenylpropane as has been elsewhere reported.

Shorygina[1] reports, without evidence, that the reaction between 4-phenyl-1,3-dioxane (I) and acetic anhydride results in the formation of 1,3-diacetoxy-1-phenylpropane (II). On the contrary, we find under the experimental conditions described by Shorygina, that the product is 1,5-diacetoxy-3-phenyl-2-oxapentane (III) obtained by cleavage at position *b*. No evidence was found for the presence of isomeric 1,5-diacetoxy-5-phenyl-2-oxapentane (IV) which would result from ring opening at position *a*.



Our results are in agreement with those of Senkus[2] who reports that the acetylation of several 4- and 5-substituted 1,3-dioxanes gives diacetylated products which retain the methylene group, and of Ness, Hann, and Hudson[3] who describe the acetylation of cyclic formals to yield products in which the acetoxy group is attached to the primary carbon atom and the acetoxymethoxy to the secondary carbon atom.

The reaction of 4-phenyl-1,3-dioxane (I) with acetic anhydride yielded a diacetate product from which was obtained, after crystallization followed by distillation, an 80% yield (based on I consumed) of 99.0–99.5 mole % pure diacetate (III). Preferential hydrolysis of the purified diacetate yielded formaldehyde plus 3-acetoxy-1-phenyl-1-propanol (V). The latter was oxidized to β-acetoxypropiophenone (VI).



Acidic hydrolysis of VI yielded β-hydroxypropiophenone (VII) whose identity was established by conversion to its known semicarbazone, α-naphthylurethane and pyrazoline derivatives.

Alkaline hydrolysis of VI with sodium hydroxide resulted in a hydrolytic product containing benzoylethylene (VIII), identified by the preparation of its dibromo derivative. The formation of benzoylethylene from VI is an example of a base-catalyzed olefin-forming elimination reaction.[4]

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[1] N. V. Shorygina, *J. Gen. Chem.* (*U.S.S.R.*), **26**, 1643 (1956).

[2] M. Senkus, *J. Am. Chem. Soc.*, **68**, 734 (1946).

[3] A. T. Ness, R. M. Hann, and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 2215 (1943).

[4] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, Chap. VIII.