any excess hydride. The mixture was allowed to warm and the solvent was removed by distillation at reduced pressure. The residue was treated with 100 ml. of water and 150 ml. of 10% sulfuric acid and extracted with 250 ml. of ether. The ether solution was dried over magnesium sulfate and concentrated. The residue was boiled for one hour with 50 ml. of 20% sodium hydroxide solution and the resulting solution extracted twice with ether, treated with Norite, filtered, acidified with concentrated hydrochloric acid, and boiled for one hour. On chilling in an ice-bath the solution deposited 9.62 g. (72%) of slightly yellow crystals of phthalide melting at 58–65°. One recrystallization from water raised the melting point to 71.5–73°, undepressed by admixture of an authentic specimen of phthalide. (Phthalide is reported to melt at 73°.)

Reduction of 2-Methyl 3-Acetoxyphthalate (V).—A solution of 2.38 g. (0.01 mole) of 2-methyl 3-acetoxyphthalate (V), m.p. 175–177°, in 50 ml. of dry tetrahydrofuran was reduced at −60° by the slow addition of 12.5 ml. (0.013 mole) of a 1.04 *M* solution of lithium aluminum hydride in ether. The reaction was exothermic and the mixture had to be cooled and the hydride added slowly (over about 30 minutes). After the addition of 2.5 ml. of ethyl acetate the mixture was allowed to warm to room temperature, concentrated *in vacuo*, treated with 20 ml. of 10% sulfuric acid and 20 ml. of water and extracted twice with 20-ml. portions of ether. The combined ether extracts were dried over sodium sulfate, concentrated, and the residue boiled for 1.5 hour with 20 ml. of 20% hydrochloric acid. On cooling a white solid precipitated which weighed 1.00 g. (68%) and melted at 240–245°. Three recrystallizations from water raised the melting point to 252–254°, undepressed by admixture of an authentic sample[20] of 4-hydroxyphthalide (VII), m.p. 255–256°. The two samples had identical infrared spectra. The acetyl derivative of the 4-hydroxyphthalide formed in the above reduction melted at 96–97° and did not depress the melting point of an authentic specimen.[20]

Reduction of 1-Methyl 3-Acetoxyphthalate (IV).—This was carried out as described for the isomer V, starting with 1.12 g. (0.0047 mole) of IV. Only 50 mg. of solid precipitated from the hydrochloric acid solution; this melted over a range (204–218°). Fractional sublimation at 100° (0.05 mm.) gave two compounds. The more volatile one melted at 119–122° and was probably 7-hydroxyphthalide (VI) since its melting point was not depressed by admixture of an authentic sample of VI[20] melting at 135–136.5° and the infrared spectra of the two samples were very similar. Identification cannot, however, be considered as conclusive. The less volatile component melted above 250° and showed a carbonyl band at 5.82 μ but no hydroxyl band in the infrared. It was not identified.

The aqueous solution from which these compounds had precipitated was extracted twice with 15 ml. portions of ether which after drying and concentration yielded 0.42 g. (49%) of impure 3-hydroxyphthalic acid, converted to the anhydride, m.p. 188–192°, by sublimation. The anhydride was identified by mixture melting point and infrared spectrum. The presence of 3-hydroxyphthalyl alcohol was suspected by analogy with the case of the half-esters of 3-chlorophthalic acid,[5] but the compound was not isolated, perhaps due to its water solubility.

Reaction of the Methyl 3-Acetoxyphthalates with *p*-Toluidine.—A solution of 1.19 g. (0.005 mole) of the ester and 0.85 g. of *p*-toluidine in 1 ml. of pyridine was allowed to stand for one hour. Water (10 ml.) was then added and the precipitated solid collected after chilling.

In the case of the low-melting half-ester IV, an exothermic reaction ensued and there was obtained 0.62 g. (83%) of aceto-*p*-toluide melting at 144–146°, undepressed by admixture of an authentic sample. In contrast, the high-melting half-ester V did not produce an exothermic reaction and led only to the recovery of 0.80 g. (94%) of unchanged *p*-toluidine melting at 42–43°.

Azlactone Tests.[6]—These tests were performed as described for aspirin.[6] The 1-methyl 3-acetoxyphthalate (IV) gave an intense blue color whereas the 2-methyl isomer V gave only a faint blue color, even on prolonged standing.

NOTRE DAME, INDIANA

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[20] E. L. Eliel, D. E. Rivard and A. W. Burgstahler, *J. Org. Chem.*, **18**, 1679 (1953).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

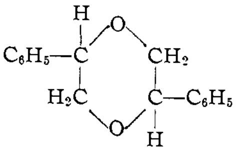
The Structure of Styrene Oxide Dimers.[1] II. Chemical Evidence

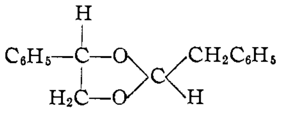
BY R. K. SUMMERBELL AND M. J. KLAND-ENGLISH

RECEIVED MAY 5, 1955

Polymerization of styrene oxide with acid catalysts results in a mixture, the dimer fraction of which yields three compounds: *cis*- and *trans*-2,5-diphenyl-1,4-dioxane (1), previously prepared by the reaction of 2,5-dichloro-1,4-dioxane with phenylmagnesium bromide, and the cyclic acetal, 2-benzyl-4-phenyl-1,3-dioxolane (II).

In the previous paper,[2] the reaction of 2,5-dichloro-1,4-dioxane with phenylmagnesium bromide to give two isomeric 2,5-diphenyl-1,4-dioxanes (I) was described. However, the proof of structure of the products was not entirely satisfactory, since ether cleavage experiments gave phenylethylene glycol in yields too low to exclude the possibility of an acetal II or ketal III structure. Also, hydrogenation experiments of Baker[3] and co-workers on the isomers I failed to give the anticipated high yields of 2-phenylethanol, and three moles of hydrogen rather than two were absorbed. If the reaction were halted when only two moles of hydrogen had been absorbed, one-third of the unchanged starting material was recovered. This behavior is anomalous if the compounds in question do have the assumed dioxane structures. Recently, Stumpf[4] has briefly described similar hydrogenation experiments in which high yields of the expected alcohol were obtained, but no details are given as to hydrogen uptake.


I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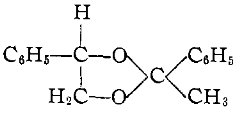
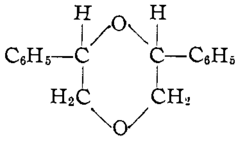

III


IV

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[1] Abstracted from the Ph.D. thesis of Mathilde J. Kland-English, Northwestern University, 1948.

[2] L. A. Bryan, W. M. Smedley and R. K. Summerbell, THIS JOURNAL, **72**, 2206 (1950).

[3] R. H. Baker, K. Cornell and M. Cron, *ibid.*, **70**, 1490 (1948).

[4] W. Stumpf, *Z. Elektrochem.*, **57**, 690 (1953).

Emerson[5] has reported dimers of styrene oxide obtained as by-product when alcohols are condensed with that epoxide using acid catalysts. He suggested that they were "probably 2,6-diphenyldioxane contaminated with some of the 2,5-isomer." The present research was initiated to establish more definitely the structure of the isomers of I, and to determine their relationship to the styrene oxide dimers.

We have polymerized styrene oxide with several acid catalysts and isolated three dimers from the reaction products. Two of these dimers were identical with the two isomers of I obtained by treating phenylmagnesium bromide with 2,5-dichloro-*p*-dioxane. The third dimer was shown to be 2-benzyl-4-phenyl-1,3-dioxolane.

Acid-catalyzed Reactions of Styrene Oxide.—When styrene oxide is added to a benzene solution of anhydrous stannic chloride at 0–40°, a mixture of dimeric products results, in addition to some higher styrene oxide polymers. Substitution of acetophenone[6] for benzene as the solvent does not change the results appreciably, and in either case fractionation of the dimeric mixture yields 2-benzyl-4-phenyl-1,3-dioxolane (II) as the chief product, along with about 5% of the *cis* and *trans* isomers of 2,5-diphenyldioxane (I).

Treatment of styrene oxide with 48% hydrobromic acid gives the isomers I and the cyclic acetal II in similar proportions, as well as some bromohydrin, m.p. 39°.

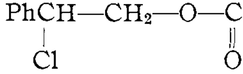
With dilute hydrochloric acid as the catalyst, only the cyclic acetal was isolated pure, but the presence of a small amount of the ketal, 2-methyl-2,4-diphenyl-1,3-dioxolane (III), in the acetal fraction of the distillate was also indicated by the presence of small amounts of acetophenone among the hydrolysis products.

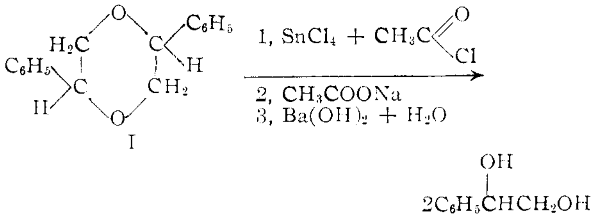
Structure of the Dioxolanes II and III.—Four possible structures for the products isolated from both the styrene oxide dimerizations and the Grignard reaction need to be considered. They are: 2,5-diphenyl-1,4-dioxane (I), 2-benzyl-4-phenyl-1,3-dioxolane (II), 2-methyl-2,4-diphenyl-1,3-dioxolane (III) and 2,6-diphenyl-1,4-dioxane (IV). All four may exist in both *cis* and *trans* modifications.

The structure of the dioxolane II was established by acid hydrolysis to phenylacetaldehyde, identified as the 2,4-dinitrophenylhydrazone (m.p. 121°), and to phenylethylene glycol (m.p. 65–66°).

Compound II was also prepared by refluxing phenylethylene glycol with dilute sulfuric acid according to the method of Zincke,[7] who had obtained it in an impure state and erroneously attributed the dioxane structure I to it.

No pure compound having the proper characteristics for the ketal III could be isolated even when acetophenone was used as a solvent. However, hydrolysis in the presence of 2,4-dinitrophenylhydrazine reagent of the acetal fraction from the styrene oxide dimerization gave a small quantity of the acetophenone derivative (m.p. 235–240°). From this it was inferred that some ketal was formed in the acid-catalyzed dimerizations of styrene oxide, but that it was only a minor reaction product.

Structure of the Isomers I.—The isomeric *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes (m.p. 121–122° and 175°, resp.) from the styrene oxide dimerization were shown by mixed melting points and spectra[8] to be identical with the isomers I obtained by the Grignard reaction on 2,5-dichloro-1,4-dioxane. Since the structural proof of I was not conclusive, additional evidence was sought. At this time, the work of Smorgonskii[9] on the cleavage of aliphatic ethers with acid halides in the presence of anhydrous acid catalysts came to our attention. Cleavage of the isomers I with benzoyl chloride and anhydrous stannic chloride gave the chlorobenzoate V,  $\underset{\displaystyle Cl}{PhCH}—CH_2—O—\underset{\displaystyle \overset{\|}{O}}{C}—Ph$, in over 50% yields. The chloroacetate was prepared similarly in much better yields, but could not be obtained free of the diacetate. Both chloroesters are liquids with very pleasant odors, and decompose on heating at atmospheric pressure, the chlorobenzoate liberating benzoic acid. The crude chloroacetate was refluxed with potassium acetate and acetic anhydride to convert it to the diacetate, which was then hydrolyzed with aqueous barium hydroxide to phenylethylene glycol, isolated in better than 50% yield calculated on the basis of the original amounts of I employed.



The fact that more than one mole of the pure glycol resulted from the cleavage of a mole of either of the isomers I proved that these compounds do indeed have a dioxane structure. Both the acetal II and the ketal III structures were eliminated by these experiments, since each of them could yield only one mole of the glycol per mole of starting material. The isolation and characterization of the cyclic acetal II further supports this conclusion.

The 2,6-diphenyl-1,4-dioxane structure IV is unlikely, in view of the non-selective cleavage of the isomers I by hydrogenolysis.[3,4] Here one would expect preferential hydrogenation of the dibenzyl ether linkage in IV, leading to the β,β'-diphenyldiethyl ether, $Ph—CH_2CH_2—O—CH_2CH_2Ph$, as a principal product. However, none of this compound was found in the hydrogenolysis experiments referred to.

The steric relationship of phenyl substituents in the isomers I was inferred from melting point data according to certain well-known empirical rules.[10]

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[5] W. S. Emerson, THIS JOURNAL, **67**, 516 (1945).

[6] It was originally hoped that condensation of acetophenone and styrene oxide to the cyclic ketal III would occur.

[7] E. C. T. Zincke, *Ann.*, **216**, 286 (1883).

[8] M. J. Kland, R. K. Summerbell and I. M. Klotz, THIS JOURNAL, **75**, 3709 (1953).

[9] L. M. Smorgonskii, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 416 (1947) (in Russian); *C. A.*, **42**, 858 (1948).

[10] H. Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. IV, pp. 449ff.

It has recently been shown by Summerbell and Stephens[11] that although these rules are not applicable to 2,6-disubstituted dioxanes, they do apply to a number of 2,5-disubstituted dioxanes of proven configuration. Further evidence for these configurations was obtained from ultraviolet spectra of the compounds in question, and has been presented in a separate paper.[8]

Experimental

2,5-Diphenyl-1,4-dioxane.—The *cis* and *trans* isomers of this compound were synthesized and isolated substantially as described by Bryan, Smedley and Summerbell,[4] from 2,5-dichloro-1,4-dioxane and phenylmagnesium bromide.

Catalytic Dimerizations of Styrene Oxide. (a) Acetophenone as Solvent.—Acetophenone (24 g., 0.2 mole)[12] was cooled in an ice-bath until it solidified. Then 2.6 g. (0.01 mole) of anhydrous stannic chloride was added rapidly, and the temperature rose to 20°. The mixture was allowed to warm until it softened slightly, after which styrene oxide (30.0 g., 0.25 mole) was added dropwise with vigorous shaking until the white solid which first formed disappeared (over 1 hour). The reaction mixture was allowed to come to room temperature (about 28°) and diluted with an equal volume of ether. This solution was washed three times with a 10% aqueous sodium hydroxide solution. The washings were extracted with ether and the combined ether extracts washed thrice with water and dried over anhyd. sodium sulfate. The ether solution was decanted from the drying agent and stored overnight at −10°. Since this did not induce crystallization, the solvent was evaporated and the orange residue distilled *in vacuo*, yielding the following fractions: (I) b.p. 89–95° (19–20 mm.) (22 g. chiefly unchanged acetophenone); (II) 85–170° (15–11 mm.) (6 g. chiefly unchanged styrene oxide); (III) 180–185° (10 mm.) (12 g. major part of distillate, 184–185°). Crystals from III were filtered under suction after the fraction had been stored overnight at −10°. The precipitate was washed with alcohol, and about 0.7 g. of fluffy white crystals with a wide range of m.p. was obtained. Fractional crystallization from ether yielded a white solid, m.p. 165–166°. Mixed m.p. with our "high-melting isomer" from the Grignard synthesis of 2,5-diphenyldioxane, 167–169°. The mother liquor yielded needles which melted over a range in the vicinity of 112°. They were dissolved in acetone, and allowed to crystallize slowly at room temperature as the solvent evaporated. Prisms identical with our "low-melting isomer" were deposited from solution. The mother liquor yielded a small amount of material which had a constant m.p. of 113.5–114°, after repeated recrystallization from 95% ethanol.

The combined mid-fractions (29.15 g.) from three runs were redistilled and four cuts taken between 100–160° (3 mm.). Due to difficulties encountered during the distillation, specific temperatures were not recorded, but the following fractions were collected: (I) 8.0 g., $n^{26.0}\mathrm{D}$ 1.5135; (II) 0.5 g., $n^{26.3}\mathrm{D}$ 1.5573; (III) 4.0 g., $n^{26.3}\mathrm{D}$ 1.5613; (IV) 10.0 g., $n^{26.5}\mathrm{D}$ 1.5623. On prolonged storage at −10°, fraction IV deposited about 0.8 g. of a white solid which was very difficult to purify by recrystallization because of its low m.p. (41–42°). The mother liquor yielded crystals, m.p. 38–39°. A sample weighing 0.0213 g. (m.p. 36–38°) was dissolved in alcohol with 0.0296 g. of 2,4-dinitrophenylhydrazine, and several drops of concentrated hydrochloric acid were added. The solution was boiled for a minute, then cooled and scratched to induce crystallization of the phenylacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 119–120°. The precipitate weighed 0.0128 g. (Much impure derivative remained in solution.) Recrystallized from alcohol, it melted at 120–121° and gave no m.p. depression with a known sample of phenylacetaldehyde 2,4-dinitrophenylhydrazone. This same derivative was obtained in high yield from the mother liquor as well, indicating that this fraction was composed largely of acetals.

(b) Using Benzene as Solvent.—Styrene oxide was polymerized using the procedure described under (a) above, except that benzene was substituted for acetophenone as solvent. The following fractions were obtained on vacuum distillation: (I) b.p. 85° (15 mm.), 6 g.; (II) b.p. 178–185° (10–11 mm.), 8.5 g. Fraction II contained a white solid which was filtered, washed with 95% ethanol, and recrystallized from ether and chloroform. The purified plates obtained (m.p. 175°) showed no depression in m.p. when mixed with a sample of our high melting isomer which had been similarly purified until it had a m.p. of 174–175°. The viscous filtrate, after prolonged storage at low temperature yielded needles which melted at 122° after recrystallization from ethanol (mixed m.p. with our "low-melting isomer," 122–123°).

(c) Reaction of Styrene Oxide with 48% Hydrobromic Acid.—Fifty g. (0.3 mole) of 48% hydrobromic acid was added dropwise with shaking to 30 g. (0.25 mole) of styrene oxide. The emulsion which formed broke gradually, separating into an organic top layer containing a small quantity of gummy precipitate, and an aqueous layer. The mixture remained at room temperature for two days, after which the water layer was pipetted off and the remainder dissolved in ether. The ether solution was washed with 10% aqueous sodium carbonate, then with water, and dried over anhydrous sodium sulfate. The gummy precipitate was only difficultly soluble in ether, but overnight storage of the ether solution did not induce crystallization. The solvent was therefore evaporated and the residue fractionally distilled *in vacuo:* (I) up to 101° (23 mm.) (dark yellow-green "oil"), $n^{27.0}\mathrm{D}$ 1.5803; (II) 101–108° (chiefly 101–102°; light yellow-green "oil"), 3.7 g., $n^{27.4}\mathrm{D}$ 1.5841; (III) 108–148° (light green, blue fluorescence), $n^{27.5}\mathrm{D}$ 1.5684; (IV) 145–152° (yellow oil, bright green fluorescence), 10.2 g., $n^{27.6}\mathrm{D}$ 1.5629; (V) residue, solidified on cooling. This was dissolved in ether and cooled in an ice-bath. A white solid was obtained which, on recrystallization from ether, melted at 165.5–166.5°. This gave no depression with our high-melting isomer. The combined ether filtrates were evaporated and stored at low temperature, as were the first four fractions. Fraction II yielded crystals which could not be recrystallized from ether, alcohol or chloroform because of their low melting point and reactivity. The clean crystals were therefore picked out mechanically and others dried on a porous plate. Crystals thus separated from the liquid melted at 36–39° and had a vesicant action. Styrene bromohydrin would be expected as a possible product from the reaction of hydrogen bromide with styrene oxide, and the analytical results were consistent with this assignment of structure. It has not previously been reported as a solid.[13]

Anal. Calcd. for C_8H_9OBr: C, 47.79; H, 4.51. Found: C, 48.21; H, 4.5.

Fraction IV yielded more solid which melted over a wide range, and consisted of a mixture of *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes. These were separated by fractional crystallization from acetone and identified by means of mixed m.p. and ultraviolet spectra with the isomers previously isolated from the reaction of 2,5-dichloro-1,4-dioxanes with phenylmagnesium bromide. After standing over a period of months at low temperature, the filtrate from fraction IV deposited another solid, m.p. 39–42°, identical with the acetal II obtained from the mid-fraction of the styrene oxide polymerization with anhydrous stannic chloride (mixed m.p. 39–42°). Hydrolysis in the presence of 2,4-dinitrophenylhydrazine also yielded phenylacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 120–121°.

2-Benzyl-4-phenyl-1,3-dioxolane (II).—The catalytic dimerization of styrene oxide yielded this compound as a major product (see under (a), preceding section). It was also synthesized for comparison purposes from phenylethylene glycol according to the method of Zincke.[7] From 7.2 g. of the glycol, 2.0 g. of the purified acetal was obtained (b.p. 150–152° (1 mm.)). A fuchsin aldehyde test on the product was negative. When Zincke's compound was stored at −10° for a week or more and the solid allowed to melt partially, then filtered rapidly, a small quantity of

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(11) R. K. Summerbell and J. R. Stephens, THIS JOURNAL, **76**, 731, 6401 (1954).

(12) M. T. Bogert and R. O. Roblin, Jr., *ibid.*, **55**, 3741 (1933). This experiment was planned in the hope of preparing the unknown ketal III. The acetophenone evidently functions only as a solvent, as no ketal formation has been observed.

(13) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **207**, 918 (1938); J. Read and W. G. Reid, *J. Chem. Soc.*, 1488 (1928); H. Lund, *Ber.*, **70B**, 1520 (1937); S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949); A. Kirrmann and P. Chancel, *Bull. soc. chim.*, (France), 227 (1951).

white solid was isolated, m.p. 37–40°. The melt remained cloudy, owing to the presence of some higher melting impurity,[14] clearing between 54 and 64°. A mixture of the solid with that from the mid-fractions of styrene oxide dimerizations melted at 36–40°, also producing a cloudy melt.

Zincke's compound (0.16 g.) was dissolved in 10 cc. of 95% ethanol and 0.15 g. of 2,4-dinitrophenylhydrazine and 10 drops of concd. hydrochloric acid added. The mixture was boiled for a minute, and rapidly formed a derivative on cooling, weight of 0.0695 g. Much impure derivative remained in solution in the alcohol. The recrystallized derivative melted at 120–121° (lit. 121°). Cleavage of the solid acetal fraction from the styrene oxide dimerizations by acetyl chloride in the presence of zinc chloride, treatment with sodium acetate, hydrolysis, and the isolation of phenylethylene glycol by the method described below established the glycol half of the acetal structure II.

Catalytic Cleavage of Isomers I and Conversion to Phenylethylene Glycol. (a) Cleavage with Acid Chlorides.—The technique employed was an adaptation of the method of Smorgonskii[9] for cleaving aliphatic ethers. Since the compounds cleaved were the more reactive and higher boiling benzyl ethers, it was unnecessary to run the reactions in sealed tubes, as was done by Smorgonskii.

(1) **Benzoyl Chloride.**—With benzoyl chloride the reaction was carried out as follows: a sample of the dioxane weighing from 0.5 to 1.0 g. was dissolved in 10% in excess of an equimolar amount of benzoyl chloride and heated to effect solution of the solid dioxanes. The mixture was then allowed to cool (but not crystallize), and while it was still fluid, a drop of anhydrous stannic chloride was added by means of a capillary pipet. The reaction was instantaneous, liberating heat, and the solution darkened, becoming a viscous mass. This was cooled, dissolved in ether, and extracted twice with small portions of 10% aqueous potassium hydroxide to remove the stannic chloride and excess benzoyl chloride. The ether solution was then dried over anhydrous sodium sulfate, filtered and evaporated to near dryness. The residue was transferred to a 10-ml. distilling flask and distilled *in vacuo*, the first few drops being discarded. Even with rapid distillation, decomposition of the chlorobenzoate occurred, so that the yield was 56.5% of theory when a mixture of 2,5-diphenyldioxanes from the Grignard synthesis was cleaved by the above method and the styrene chlorobenzoate isolated.

Anal.[15] Calcd. for $C_{15}H_{13}O_2Cl$: Cl, 13.60. Found: Cl, 13.79.

(2) **Acetyl Chloride.**—When acetyl chloride was used instead of benzoyl chloride in the cleavage of our dioxanes I, an excess of the acid chloride served as the solvent. The addition of anhydrous stannic chloride to the solution resulted in a spontaneous reaction similar to the one described previously. The excess reagent was then evaporated on a steam-bath, ice-water added, and the mixture extracted thrice with ether. The combined ethereal extracts were then washed with 10% aqueous alkali, dried over anhydrous sodium sulfate, filtered and evaporated. The crude chloroacetate was distilled *in vacuo* from a 10-ml. distilling flask, and the fraction boiling between 105 and 110° at 3–4 mm. was collected. When 72% of the theoretical yield of the chloroester had been collected, the distillation was stopped owing to decomposition of the residue in the flask on further heating. The product was a pleasant smelling liquid which lost hydrogen chloride on standing.

Anal. (On a sample from the cleavage of a mixture of the isomers I.[16]) Calcd. for $C_{10}H_{11}O_2Cl$: C, 60.46; H, 5.58. Found: C, 62.46, 62.22; H, 5.79, 5.83.

(b) **Isolation of Phenylethylene Glycol from the Cleavage Products.**—Subsequent work on the chloroacetates revealed that chlorine analyses varied with the length of exposure of the chloroester to acetyl chloride in the presence of the catalyst. The chloroester from 1 g. of I was therefore converted to the diacetate by heating the crude reaction mixture after removal of acetyl chloride with a mixture of potassium acetate (3 g.) and acetic anhydride. After refluxing one hour, the solution was cooled, diluted with ice-water (5 cc.), and 12 g. of barium oxide added. Refluxing was resumed for another hour, after which the solution was cooled and extracted repeatedly with ether, the combined extracts dried over anhydrous sodium sulfate, filtered and evaporated. Weight of the crude glycol from the cleavage of a mixture of isomers was 1.1 g., or 95% of theory. After two recrystallizations from ether–petroleum ether, 0.65 g. of very pure crystalline glycol was obtained, melting at 65–66°. The melting point was not lowered when mixed with authentic glycol; yield 56%.

Cleavage experiments and conversion to the glycol were repeated with 0.5-g. samples of purified *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes with quantitative results similar to those described for the isomeric mixtures.

A blank experiment following a similar procedure and starting with phenylethylene glycol, gave a similar yield of the purified glycol, the remainder apparently having been decomposed during the refluxing with barium oxide or lost during the extraction. Since similar losses must have occurred in all of these hydrolysis experiments, the yields of 57% are sufficient to prove that dioxane structures are correct for both isomers (I).

Acknowledgment.—This research was supported in part by two grants: a Northwestern University Fellowship (1944–1945), and an Allied Chemical and Dye Fellowship (1945–1946).

EVANSTON, ILLINOIS

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[14] Possibly the ketal III. When styrene oxide is dimerized with dilute HCl and the purified acetal fraction treated with 2,4-dinitrophenylhydrazine reagent, a small quantity of acetophenone 2,4-dinitrophenylhydrazone is obtained along with the phenylacetaldehyde derivative; m.p. 235–240°; known, 243–245°; mixed m.p. 240–242°.

[15] Analyst, J. Gibbs.

[16] Analyst, M. Hines.