[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Rearrangements of α-Halogenated Ethers. II.[1] The Preparation and Some Reactions of 2,3-Diphenyl-*p*-dioxene

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2,3-Diphenyl-*p*-dioxene (I) has been prepared. Reaction of ethylene glycol with benzoin in the presence of an acid catalyst leads to the ketal 2-phenyl-2-(α-hydroxybenzyl)-1,3-dioxolane (IIa), the structure of which has been proved. Heating IIa in solvent in the presence of acid at a higher temperature than is required for its formation causes a rearrangement, with elimination of water, to give the dioxene I. Catalytic reduction of I gives a 95% yield of the isomer of 2,3-diphenyl-*p*-dioxane melting at 136°; reduction of I with sodium and 2-pentanol gives both the 48 and the 136° compounds. Therefore the 136° isomer must be *cis* (not *trans* as has been reported elsewhere), and the 48° isomer is *trans*. Reaction of the 2,3-diphenyl-*p*-dioxanes with halogen gives good yields of benzil; reaction with chlorine in the cold gives the same 2,3-dichloro-2,3-diphenyl-*p*-dioxane (V) as is obtained upon addition of chlorine to I. Pyrolysis of V gives essentially quantitative yields of benzil and ethylene chloride. The structure of V is discussed, and a mechanism for the reaction of halogen with the diphenyl-*p*-dioxanes and with I is proposed.

The reaction of phenylmagnesium bromide with *trans*-2,3-dichloro-*p*-dioxane,[3] first reported some twenty-five years ago,[4] leads to an isomer of 2,3-diphenyl-*p*-dioxane melting at 48°. As this isomer is prepared *via* a Grignard reaction and is isolated in high yield (up to 85%),[5] it could be assumed *a priori* to have the *trans* structure; a study of molecular models indicates that the *trans* isomer is preferred, sterically, to the *cis*.

About five years ago Stumpf repeated[6] the preparation of 2,3-diphenyl-*p*-dioxane and isolated an isomeric compound by multiple fractional crystallization from the mother liquors. This isomer, melting at 136°, was obtained in approximately 1% yield, and was shown to be a 2,3-diphenyl-*p*-dioxane by its hydrogenolysis to dibenzyl and glycol.

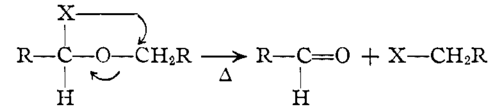
Melting point evidence led Stumpf to assign the *trans* configuration to the 136° isomer and the *cis* configuration to the 48° isomer.[6,7] In addition, Stumpf prepared the lactone, 2,3-diphenyl-*p*-dioxane-5-one, m.p. 113°, from chloroacetic ester and the calcium salt of *meso*-hydrobenzoin. This imparts a *cis* relationship to the phenyl groups of the lactone, since the stereochemistry about the central carbon atoms of the hydrobenzoin is not affected in this reaction. Since, according to Stumpf, lactones and esters always melt higher than the corresponding ethers, the 113° lactone (*cis*) must correspond to the 48° (and not the 136°) isomer of 2,3-diphenyl-*p*-dioxane.

An assignment of configuration in the 2,3-disubstituted-*p*-dioxane series based solely on comparative melting points is not reliable; of six pairs of isomers for which the configuration is known with certainty, the *trans* isomer melts higher in only three cases.[3,8] Furthermore, Stern has recently compiled data[9] which show that, contrary to Stumpf's assumption, when a compound can exist in *dl* or *meso* forms by virtue of two identically substituted adjacent asymmetric carbon atoms, the *meso* (*i.e.*, *cis*) form will have, with few exceptions, the higher melting point.

In order to determine with certainty the configurational assignments of the isomeric 2,3-diphenyl-*p*-dioxanes, it was desired to prepare 2,3-diphenyl-*p*-dioxene (I) from which the dioxanes might be obtained by stereospecific reductions. Catalytic reduction of I should give the *cis* isomer,[10] whereas chemical reduction would be expected to give a mixture of the *cis* and *trans* isomers.

In considering means for the preparation of diphenyl-*p*-dioxene, the preparation of dioxene itself by the removal of chlorine from 2,3-dichloro-*p*-dioxane through the agency of magnesium iodide was recalled.[11] It was felt that if the available (48°) isomer of diphenyl-*p*-dioxane was brominated under free-radical conditions (light), 2,3-dibromo-2,3-diphenyl-*p*-dioxane would result.[12,13] Removal of bromine would then lead to the desired dioxene I. *However, when the bromination was actually attempted, there was obtained a 74% yield not of the desired dibromodiphenyl-p-dioxane, but of benzil.*

The possibility that the formation of benzil had resulted from hydrolysis of the intermediate dibromo compound was excluded by the use of rigorously dry conditions and by other evidence which will be discussed later. Its formation can be explained if one assumes that the desired 2,3-dibromo-2,3-diphenyl-*p*-dioxane had been formed, but underwent a *thermal rearrangement* in which the halogen, in a 1,3-shift, migrated across the ether bond.[14]



$$\mathrm{R{-}\overset{X}{\underset{H}{C}}{-}O{-}CH_2R} \xrightarrow[\Delta]{} \mathrm{R{-}\underset{H}{C}{=}O + X{-}CH_2R}$$

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[1] Paper I in this series: R. K. Summerbell and Daniel R. Berger, THIS JOURNAL, **79**, 6504 (1957).

[2] Northwestern University Fellow, 1955–1956; Allied Chemical and Dye Corp. Fellow, 1956–1957; du Pont Fellow, Summer, 1957.

[3] See R. K. Summerbell and H. E. Lunk, THIS JOURNAL, **79**, 4802 (1957), for the structures of *cis*- and *trans*-2,3-dichloro-*p*-dioxane.

[4] R. Christ and R. K. Summerbell, *ibid.*, **55**, 4547 (1933).

[5] Unpublished results, these laboratories.

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

[7] W. Stumpf, "Chemie und Anwendungen des 1,4-Dioxanes," Verlag Chemie, G.m.b.H., Weinheim/Bergstr., 1956, p. 66.

[8] R. K. Summerbell and G. J. Lestina, THIS JOURNAL, **79**, 3878 (1957).

[9] R. Stern, J. English, Jr., and H. G. Cassidy, *ibid.*, **79**, 5797 (1957); R. Stern, Abstracts of Papers, 131st Meeting of the American Chemical Society, Division of Organic Chemistry, April 8, 1957, Miami, Fla., p. 5-O.

[10] R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

[11] R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, **61**, 3016, 3020 (1939).

[12] M. S. Kharasch and H. C. Brown, *ibid.*, **61**, 2142 (1939).

[13] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, section 8.3c.

[14] See reference 1 for descriptions of the similar rearrangements of (a) 2,2,3,3-tetrachloro-*p*-dioxane to give (2-chloroethoxy)-dichloroacetyl chloride and (b) the latter compound to give ethylene chloride and oxalyl chloride. Additional references to related work are given.

The bromination of diphenyl-*p*-dioxane to give benzil gave added interest to the proposed preparation of 2,3-diphenyl-*p*-dioxene (I). In addition to its reduction, we hoped to study the addition of halogen across the double bond in the hope of isolating the 2,3-dihalo-2,3-diphenyl-*p*-dioxane. The availability of this compound, a possible intermediate in the bromination of 2,3-diphenyl-*p*-dioxane, would be helpful in a mechanistic study of the halogenation reaction.

Preparation of 2,3-Diphenyl-*p*-dioxene.—The reaction of benzoin with ethylene glycol in the presence of acid has been reported[15] to yield over 90% of benzoin ethylene ketal [2-phenyl-2-(α-hydroxybenzyl)-1,3-dioxolane], (IIa). This compound was prepared as one of a series of aromatic ketals, and its structure was assumed rather than proved. In fact, the authors state that several reaction products are possible, and that the reason for assigning a ketal structure to the product would be discussed in a later paper. As of 1956, some eight years later, this discussion had not been reviewed in "Chemical Abstracts" or "Chemisches Zentralblatt."

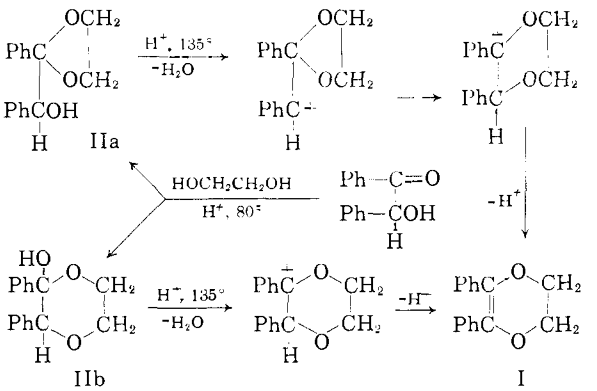
We have repeated the reaction of benzoin with glycol, in the hope that the alcohol moiety of benzoin would react first, followed by cyclization to give 2-hydroxy-2,3-diphenyl-*p*-dioxane (IIb) or its dehydration product, the dioxene I, rather than the ketal IIa. The compound II (*a* or *b*) was obtained in good yield when the reactants were heated under reflux in benzene, in the presence of *p*-toluene-sulfonic acid.[16] When the intermediate II was heated with acid in xylene solution, water was eliminated and the desired dioxene was obtained in over 30% yield from benzoin (54% yield from II). The structure of the dioxene was indicated by its infrared spectrum and proved by its reduction to the known 2,3-diphenyl-*p*-dioxanes (see below). Also, it will be shown that the compounds obtained upon pyrolysis of the halogen addition products of I are those that would be expected on the basis of a dioxene structure for I.

The formation of I from II led to a reconsideration of the structure of II. If the structure was that of the hydroxydioxane IIb, a straightforward elimination of water would lead to I. However, if the structure was that of the ketal IIa, as has been stated in the literature, it was necessary to postulate a rearrangement leading to the formation of I (Chart I). Because it seemed interesting to determine whether a rearrangement actually was occurring, the structure of II has been investigated. On the basis of the following evidence, the structure is that of the ketal IIa.

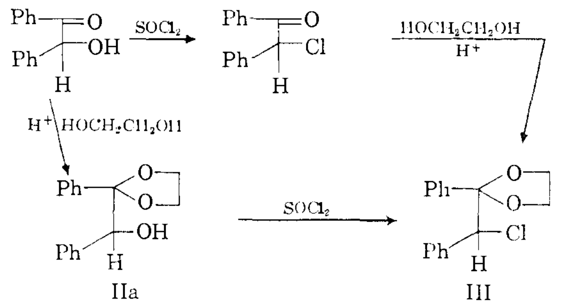
1. If the structure were that of IIb, it is not easy to understand why the compound is isolable under the conditions used for its synthesis. It should lose water as fast as formed and yield I directly.

2. *Mild* hydrolysis of II gave benzoin. Benzil ethers (such as IIb) are hydrolyzed easily, but not easily enough to have been cleaved by our extremely mild conditions.[17]

CHART I



3. Reaction of II with thionyl chloride gave a corresponding chloro compound, III. The dioxolane structure of the latter was indicated by the fact that it did not react with hot 95% ethanol. It seems improbable that the rather inert chlorine in III is on a carbon attached to both an ether oxygen and a benzene ring.[18] The dioxolane structure of III was also strongly indicated by its formation from desyl chloride and ethylene glycol. The formation of III from II therefore indicates, but does not prove, the structure of II.[19]



4. The acetate IV obtained from treatment of the alcohol II with acetic anhydride underwent basic hydrolysis to regenerate II. Treatment of III with silver acetate also yielded IV. Baring unlikely rearrangements during basic hydrolysis[20] and during the silver acetate reaction,[21] IV and II are indicated to have the same dioxolane ring structure as III.

5. A final piece of evidence, which is conclusive, lies in the oxidation of II with alkaline permanganate. Under basic conditions, acetals and ketals are not hydrolyzed.[22] If the alcohol IIb were subjected to oxidation with alkaline permangnate, no reaction would be anticipated. If, however, IIa were oxidized under these conditions, the alcohol should be converted to a ketone. Hydrolysis of

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(15) E. J. Salmi, U. Tamminen and P. Lourenkuru, *Suomen Kemistilehti*, **20B**, 1 (1947); *C. A.*, **42**, 537 (1948).

(16) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

(17) R. L. Burwell, Jr., *Chem. Revs.*, **54**, 615 (1951).

(18) Halogen atoms adjacent to an ether oxygen are quite reactive to alcoholysis; see L. Summers, *ibid.*, **55**, 301 (1955). Also, see below the rapid ethanolysis of 2,3-dichloro-2,3-diphenyl-*p*-dioxane.

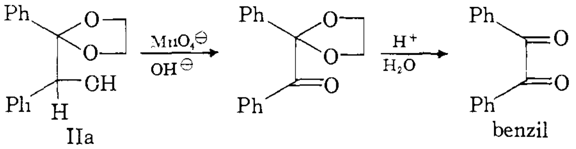
(19) See J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, pp. 114–115, for a discussion of the reaction of thionyl chloride with alcohols.

(20) J. Hine, *ibid.*, pp. 266ff.

(21) If a stable carbonium ion is assumed in the silver acetate reaction, ring enlargement might occur. However some of the resulting rearranged ions would almost certainly eliminate a proton to form 2,3-diphenyl-*p*-dioxene (I); it was looked for but not found.

(22) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 628.

the ketone with acid, would then give benzil. When the oxidation was carried out in an aqueous medium at 100°, there was obtained an 80% yield of a compound which gives an analysis consistent with that of, and has an infrared absorption spectrum consistent with, the *mono*-ethylene ketal of benzil (2-phenyl-2-benzoyl-1,3-dioxolane). Hydrolysis of this ketal, m.p. 67°, gave a 67% yield of benzil. On the basis of this evidence, then, the structure of the alcohol II is that of the dioxolane, benzoin ethylene ketal, IIa.



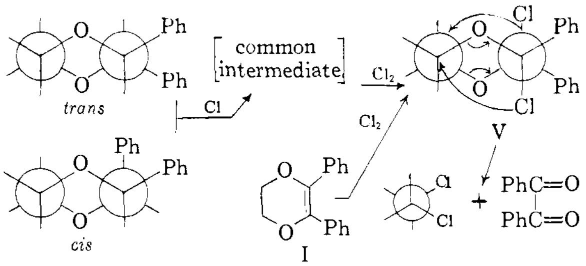
It has thus been shown that, in the preparation of 2,3-diphenyl-*p*-dioxene, an intermediate five-member ring compound is formed which undergoes ring expansion, with elimination of water, to give the product.[23]

Reaction of the 2,3-Diphenyl-*p*-dioxanes and 2,3-Diphenyl-*p*-dioxene with Halogen.—The original observation that bromination of 2,3-diphenyl-*p*-dioxane (m.p. 48°) gave rise to benzil was made upon bromination of the dioxane in refluxing carbon tetrachloride solution under the illumination of a bright white light. Evaporation of solvent gave benzil. Chlorination of diphenyldioxane under similar conditions did not give rise to benzil as readily; evaporation of the solvent after chlorination afforded an oil, the distillation of which gave a yellow, viscous liquid, which was shown to contain benzil by the preparation of some typical carbonyl derivatives (*p*-nitro- and 2,4-dinitrophenylhydrazones). Bromination of the 136° isomer of 2,3-diphenyl-*p*-dioxane gave results corresponding to bromination of the 48° isomer: benzil was obtained in 49% yield. Addition of bromine to 2,3-diphenyl-*p*-dioxene gave benzil in 54% yield.

The lesser reactivity of chlorine than bromine toward this rearrangement[24] led to its use in investigating the course of the reaction. Now that 2,3-diphenyl-*p*-dioxene was available it could be used to prepare the supposed intermediate in the halogenation reactions, 2,3-dihalo-2,3-diphenyl-*p*-dioxane. Indeed, when chlorine was added to the dioxene in cold methylene chloride solution, a 72% yield of 2,3-dichloro-2,3-diphenyl-*p*-dioxane (V) was obtained. The halogens of V are extremely reactive, giving with absolute ethanol a compound which gives an analysis consistent with that of the corresponding bisethoxy compound. Treatment of V with phenylmagnesium bromide gives not the expected 2,2,3,3-tetraphenyl-*p*-dioxane, but the original dioxene I. This result is parallel to that of the reaction of 2,3-dichloro-*p*-dioxane with aliphatic Grignard reagents, which results in the formation of *p*-dioxene.[29] A contributing factor favoring elimination in the reaction of V with phenyl Grignard reagent is undoubtedly the formation of the resulting conjugated system.

Chlorination of *either* the 136° or the 48° isomer of 2,3-diphenyl-*p*-dioxane in cold carbon tetrachloride solution and in the presence of ultraviolet radiation gave high yields, as indicated by the infrared absorption spectra, of the *same* dichlorodiphenyl-*p*-dioxane as was obtained upon addition of chlorine to I. Heating the carbon tetrachloride solution at reflux for one week led to very little change in the infrared spectrum, indicating some thermal stability for V. However, when V was held as a melt at 190° for one-half hour, there was obtained a 90% yield of benzil and a 70% yield of ethylene chloride. Because of the small quantity of material (5 g.) involved in the pyrolysis, and because of the losses involved in isolating ethylene chloride by distillation and benzil by recrystallization, these yields may be considered as essentially quantitative. These results[14] are interpreted in the following manner: in the halogenation of the 2,3-diphenyl-*p*-dioxanes, halogenation occurs at the benzylic positions, as expected,[12,13] to give the *same* intermediate 2,3-dihalo-2,3-diphenyl-*p*-dioxane from either diphenyl-*p*-dioxane; this intermediate then undergoes a rearrangement involving migration of the halogen atom across the ether linkage (Chart II). The spatial arrangement of a compound such as V, assuming the large phenyl groups to be equatorial, would be such that a transannular migration across the ether bond could easily be effected.

CHART II



This mechanism assumes a *trans* addition of chlorine across the double bond of I to give V. The chloride V is a compound of rather poor melting point (105–118°), and hence could be a mixture of the *cis* and *trans* isomers, or the poor melting point could be a manifestation of the reactivity of the

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[23] Similar acid-catalyzed dehydrations leading to ring expansion are known. For instance, see B. Witkop, THIS JOURNAL, **72**, 614 (1950), for the rearrangement of spiro-(cyclopentane-1,2′-dihydroindoxyl) to tetrahydrocarbazole.

[24] The order of reactivity toward the rearrangement of α-halo ethers is iodine > bromine > chlorine, as shown by the data: chloromethyl methyl and bromomethyl methyl ethers are both stable compounds,[25] whereas iodomethyl methyl ether decomposes at room temperature to give iodomethane and polymeric formaldehyde.[26] α,β-Dibromo-α,β-dichloroethyl ethyl ether rearranges on heating to give a bromine migration, the products being bromochloroacetyl chloride and ethyl bromide.[27] Similarly, α,β,β-tribromo-α,β-dichloroethyl ethyl ether gives, on heating to 60°, ethyl bromide and a quantitative yield of dibromochloroacetyl chloride.[28] Experiments in the present work also have shown bromine to be more labile toward the rearrangement than chlorine.

[25] A. Karvonen, *Acad. Sci. Fennicae*, **3A**, 1; *Chem. Zentr.* **83**, 11, 1266 (1912).

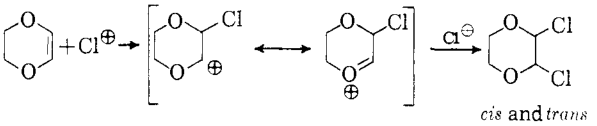
[26] L. Henry, *Bull. acad. roy. Belg.*, [3] **25**, 439 (1893); *Ber.*, **26R**, 933 (1893).

[27] H. Crompton and P. M. Triffitt, *J. Chem. Soc.*, **119**, 1874 (1921).

[28] I. A. Smith, *ibid.*, 1099 (1927).

[29] R. K. Summerbell and L. N. Bauer, THIS JOURNAL, **57**, 2346 (1935); **58**, 759 (1936).

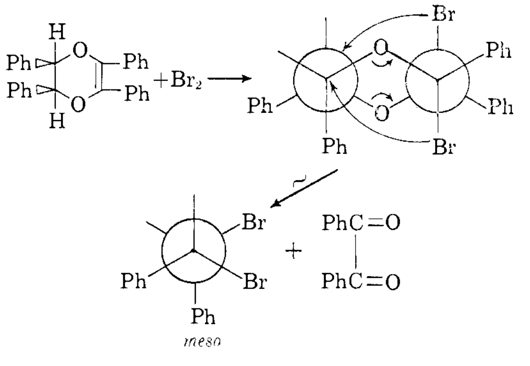
chlorine atoms in this molecule. The latter is probably correct; if addition of chlorine to I gave a mixture of isomers, in a supposedly ionic reaction,[30] one would not expect to get essentially the *same* mixture of isomers in the free-radical chlorination of both the *cis* and *trans* isomers of 2,3-diphenyl-*p*-dioxane. Summerbell and Lunk have shown that addition of chlorine to *p*-dioxene itself leads to mixtures of the *cis* and *trans* isomers of 2,3-dichloro-*p*-dioxane, with the *cis* compound actually predominating in solvents such as carbon tetrachloride and methylene chloride.[3] This is interpreted in terms of resonance stabilization of an intermediate carbonium ion, which may then react further to give either the *cis* or the *trans* product.



This mechanism may also be considered in the chlorination of the substituted dioxene I. However, steric considerations become of much greater importance now than in the case of the chlorination of *p*-dioxene. In the latter case, the asymmetric carbons of the product are attached to carbon, halogen, oxygen and small hydrogen atoms. In the former case, they are bonded to carbon, halogen, oxygen and *large* phenyl groups. These large groups should have a powerful influence in determining the configuration of the product; the tendency will be for the large groups to assume equatorial positions, leading to axial addition of chlorine. A model in which the two aromatic rings are equatorial and the halogen axial is much less strained or hindered, sterically, than one in which one phenyl and one halide are axial, and one of each is equatorial. This latter arrangement would correspond to *cis* addition of halogen to the double bond.

If one were to use a dioxane substituted on both sides of the ring, it might be anticipated that the halogen migration would be stereospecific, giving rise to either the *dl*- or *meso*-ethylene halide derivatives, depending on the configuration of the dioxane used. Madelung and Oberwegner prepared[31] *cis*-tetraphenyl-*p*-dioxene by catalytic reduction of tetraphenyl-*p*-dioxadiene. *trans*-Bromination, followed by the type of rearrangement that we are suggesting, should give rise to the *meso* form of stilbene dibromide; in practice, the *meso* compound was actually obtained. However, this is not conclusive, since the *meso* form is known[32] to be the more stable isomer of stilbene dibromide, and could conceivably have resulted from epimerization of the *dl*-isomer during the reaction.

Additional evidence concerning the mechanism of the rearrangement is furnished by the kinetic data. It has been shown that the rearrangement of 2,2,3,3-tetrachloro-*p*-dioxane to (2-chloroethoxy)-dichloroacetyl chloride follows first-order kinetics,[1] and Frankel and his co-workers have shown that the rearrangement of tetrachloroethylene oxide to give trichloroacetyl chloride, which probably proceeds by a similar mechanism, is of the first order.[33] The kinetic data may be taken, therefore, along with the evidence previously presented, as indicating a first-order intramolecular rearrangement of the α-halo ethers studied.



Reduction of 2,3-Diphenyl-*p*-dioxene.—The original purpose of this work was to prepare the two isomers of 2,3-diphenyl-*p*-dioxane by methods suitable for assigning configurations. The availability of 2,3-diphenyl-*p*-dioxene now made this possible. However, samples of the two isomers first had to be prepared in order to have a basis on which to compare the reduction products of the dioxene. The 48° isomer has long been known,[4] and the 136° isomer was prepared by subjecting the mother liquors from a preparation of the 48° isomer to a chromatographic separation over alumina; in this manner, the high melting isomer was obtained in approximately 1% yield. In another preparation of the 48° isomer, the 136° isomer was obtained in small yield (0.5 g. compared to 45 g. of the major isomer) directly as a third crop of crystals from the ether solution.

Catalytic reduction of 2,3-diphenyl-*p*-dioxene over platinum oxide in glacial acetic acid afforded a 95% yield of the isomer melting at 136°. This compound had an infrared spectrum identical with that of the 136° compound isolated by chromatography as described above, and is therefore probably identical with the compound of melting point 136° previously described by Stumpf.[6,7] Chemical reduction of 2,3-diphenyl-*p*-dioxene by means of sodium and 2-pentanol gave an 18% yield of the 48° isomer and a 34% yield of the 136° isomer. Since catalytic hydrogenation is known to give predominantly the *cis* isomer,[10] the *cis* configuration in the 2,3-diphenyl-*p*-dioxane series must be assigned to the isomer melting at 136°, and *not* to the 48° isomer as previously suggested.[6,7] The 48° isomer must correspondingly be *trans*.

The chromatographic separation of the two isomers furnishes additional evidence that the 48° isomer has the *trans* configuration. It would be anticipated that the more symmetrical, less polar molecule (*trans*, in the specific case of the 2,3-diphenyl-*p*-dioxanes) would be the first to be eluted from the column; in practice, the 48° isomer is the first to appear.

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(30) E. E. Royals, ref. 22, pp. 342ff.

(31) W. Madelung and M. E. Oberwegner, *Ann.*, **526**, 195 (1936).

(32) R. E. Buckles, W. E. Steinmetz and N. G. Wheeler, This Journal, **72**, 2496 (1950).

(33) D. M. Frankel, C. E. Johnson and H. M. Pitt, *J. Org. Chem.*, **22**, 1119 (1957).

One-step Preparation of 2,3-Diphenyl-*p*-dioxene.—The preparation of 2,3-diphenyl-*p*-dioxene described above involved two steps: (a) formation of a ketal (IIa) by reaction of benzoin in the presence of acid with ethylene glycol in refluxing benzene, and (b) treatment of the ketal with acid in boiling xylene. Removal of both moles of water in a single step by using xylene as the original azeotropic agent was tried, but the desired product was contaminated with tetraphenylfuran,[34] an impurity which was not easily removed. A distinct improvement was achieved by using an excess of ethylene glycol as the solvent and *p*-toluenesulfonic acid as a catalyst. Under these conditions, a 31% yield of 2,3-diphenyl-*p*-dioxene of high purity was obtained. This yield is comparable to that of the two step synthesis, and the method is simpler.

Acknowledgment.—We wish to thank Drs. E. S. Graham and H. E. Lunk for invaluable discussions during the course of this work.

Experimental[35]

2-Phenyl-2-(α-hydroxybenzyl)-1,3-dioxolane (IIa) was prepared essentially as described by Salmi, *et al.*[15] Benzoin (53 g., 0.25 mole), ethylene glycol (15.5 g., 0.25 mole), *p*-toluenesulfonic acid (1.0 g.) and 250 ml. of dry benzene were heated under reflux for 24 hours, using a trap to collect water as it distilled from the reaction vessel[16]; 6 ml. of water was collected. Benzene (170 ml.) was then distilled from the reaction vessel, and, upon cooling, the residue gave 37 g. of white crystals, m.p. 133–138°. After one recrystallization from chloroform, the m.p. was raised to 144.1–144.5° (reported[15] 144°). The highest melting point obtained for a sample of this material was 146.0–146.8°. The yield of IIa was 58%. Infrared absorption bands are (s = strong; m = medium; w = weak; reported as microns as a potassium bromide press): 2.85s, 3.28w, 3.35w, 3.39w, 3.43m, 6.69m, 6.80m, 6.88s, 7.19w, 7.42w, 8.10s, 8.29s, 8.45s, 8.62s, 8.90s, 9.17m, 9.23m, 9.40s, 9.59s, 9.71s, 10.02s, 10.39s, 10.57s, 10.91w, 11.86m, 12.66w, 12.95s, 13.24m, 14.3s (broad), 15.1w.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.97; H, 6.29. Found: C, 75.36; H, 6.27.

Hydrolysis of IIa.—In an attempt to trap the hydrolysis product of the compound which was later proved to be IIa as its semicarbazone, 1.00 g. (0.0039 mole) of the dioxolane and 0.44 g. (0.0039 mole) of semicarbazide hydrochloride were dissolved in 75 ml. of 65% aqueous dioxane. After the solution had stood overnight at room temperature, the solvent was removed by heating on the steam-bath, and the residue was recrystallized from ethanol to give 0.50 g. of benzoin (60% yield), m.p. 134–137°. The product was identical in the infrared with an authentic sample of benzoin.

Preparation of 2-Phenyl-2-(α-hydroxybenzyl)-1,3-dioxolane Acetate (IV).—Compound IIa (2.0 g.), potassium acetate (0.5 g.) and acetic anhydride (15 ml.) were heated on the steam-bath for 1.5 hours. The solution was then poured onto ice and allowed to stand for one hour. The resulting solid was filtered and air-dried to give a white compound, m.p. 102–103°; recrystallization from aqueous ethanol raised the m.p. to 103.0–103.5°. The yield of the acetate was 2.0 g., or 86%. Infrared absorption bands are (potassium bromide press): 3.40w, 3.50w, 5.77s, 6.68m, 6.90m, 7.16m, 8.05s, 8.15 (shoulder), 8.26 (shoulder), 8.51m, 9.23m, 9.50s, 9.69s, 9.83m, 10.20w, 10.53m, 10.96m, 11.82w, 12.40w, 12.95m, 14.05s, 14.40m, 15.10w.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.08. Found: C, 72.67; H, 5.93.

Hydrolysis of IV.—A solution of 1.00 g. of the acetate IV and 1.00 g. of sodium hydroxide in 100 ml. of 50% aqueous dioxane was heated under reflux for 24 hours. On cooling, crystals separated; these were filtered and washed with cold ethanol. The yield was 0.52 g. (62%) of material melting at 145.5–146.1°, identical in the infrared with the dioxolane IIa, m.p. 144.1–144.5°.

2-Phenyl-2-(α-chlorobenzyl)-1,3-dioxolane (III) was prepared by heating a solution of the dioxolane IIa (10.25 g., 0.040 mole), thionyl chloride (11.90 g., 0.100 mole) and 100 ml. of dry carbon tetrachloride under reflux overnight. The major portion of the solvent was then removed by distillation, and the oily residue was diluted with ethanol. After treatment with Norite, there was obtained 6.6 g. of crystals, m.p. 72–75°; after one recrystallization from aqueous ethanol, the m.p. was raised to 75.2–75.7°. The yield of the colorless product was 60%. Infrared absorption bands are (potassium bromide press): 3.30w, 3.40m, 3.46m, 6.70m, 6.80w, 6.89s, 7.96m, 8.19s, 8.38m, 8.60s, 8.84m, 9.25m, 9.51s, 9.69s, 9.92s, 10.01s, 10.31s, 10.52s, 10.90w, 11.81s, 12.55s, 12.77w, 13.21m, 13.44s, 14.3s (broad), 14.63s, 15.60s.

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.94; H, 5.50. Found: C, 69.88; H, 5.20.

Reaction of III with Silver Acetate.—A mixture of compound III (10.0 g., 0.00364 mole), silver acetate (6.0 g., 0.00355 mole), acetic acid (200 ml.) and acetic anhydride (25 ml.) was stirred overnight at 100° with protection from atmospheric moisture. The brown color of silver acetate was slowly replaced by the purple color of silver chloride. After cooling, the solid was filtered to give 4.95 g. (97.4%) of silver chloride. Most of the solvent (190 ml.) was removed by distillation at reduced pressure, and to the residue was added 50 ml. of a saturated aqueous solution of sodium bicarbonate. The neutralized solution was extracted with ether, the ether dried over magnesium sulfate and partially evaporated. Cooling to Dry Ice–acetone temperature gave a first crop of crystals amounting to 0.35 g., m.p. 100–102°, which were identical in the infrared with the acetate IV previously prepared from 2-phenyl-2-(α-hydroxybenzyl)-1,3-dioxolane, m.p. 103.0–103.5°. The ether was removed by distillation and evacuation at 0.5 mm. for one hour at room temperature, and the oil was seeded with a crystal from the first crop. After standing at 5° for three days, the mass became semi-solid and was triturated in ethanol to give an additional 0.45 g. of the same product. The residue weighed 5 g., and could not be crystallized, but its infrared spectrum was essentially the same as that of the crystalline products. The yield of crystalline acetate was 8%.

Reaction of Desyl Chloride with Ethylene Glycol.—A solution of desyl chloride (4.00 g., 0.0174 mole), ethylene glycol (10.00 g., 0.161 mole), *p*-toluenesulfonic acid (0.1 g.) and 100 ml. of xylene was heated under reflux for 24 hours, without the use of an azeotrope trap. Most of the solvent was then removed by distillation, and the residue was placed in an open dish overnight. The resulting oily crystals were recrystallized from ethanol, to give 0.93 g. of material, m.p. 74.0–75.2°, identical in the infrared with 2-phenyl-2-(α-chlorobenzyl)-1,3-dioxolane, m.p. 75.2–75.7°, prepared by the action of thionyl chloride on the corresponding alcohol. The yield was 20%.

Oxidation of IIa.—A mixture of IIa (10.0 g., 0.039 mole), potassium permanganate (4.2 g., 0.027 mole), sodium hydroxide (1.6 g., 0.040 mole) and 200 ml. of water was stirred on the steam-bath until the permanganate color was no longer present (2.5 hours). The precipitated manganese dioxide was filtered and washed with ether; the green aqueous layer was also extracted with ether. (An ether-insoluble solid compound was encountered at this point, and was identified as starting material: 0.60 g., m.p. 144–145°.) The ether washing and extracts were combined, dried over magnesium sulfate, and the ether removed and replaced by hexane. Crystallization from ether–hexane gave 7.4 g., m.p. 64–66°. Recrystallization gave a m.p. of 65.0–65.8°. This sample still contained some starting material, as shown by hydroxyl absorption in the infrared; several recrystallizations from hexane and from ethanol were necessary to remove it. The final m.p. was 66.6–67.5°; the yield was 75%. Infrared absorption bands of the product, 2-phenyl-2-benzoyl-1,3-dioxolane, are (potassium bromide press): 3.38w, 3.43w, 5.92s, 6.22m, 6.30w, 6.70w, 6.78w, 6.89s, 7.60w, 7.90s, 8.09s, 8.25m, 8.49m, 9.00s, 9.21m, 9.59s, 9.72s, 9.90m, 10.22w, 10.55s, 10.75w, 11.15s, 11.35 (shoulder), 13.03s, 13.39s, 14.31s, 14.67s, 14.92m, 15.66w.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.34; H, 5.54.

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(34) N. Zinin, *Chem. Zentr.*, **38**, 373 (1867); *J. prakt. Chem.*, [1] **101**, 160 (1867); *Jahresber. Fortsch. Chem.*. **20**, 417 (1867).

(35) Microanalyses were by Miss Hilda Beck. Melting points were taken on a Fisher–Johns block and are uncorrected.

Hydrolysis of 2-Phenyl-2-benzoyl-1,3-dioxolane.—A solution of 2-phenyl-2-benzoyl-1,3-dioxolane (1.00 g.) in 30 ml. of 2 *N* hydrochloric acid and 30 ml. of dioxane was heated under reflux for 1.5 hours. After standing for several hours at room temperature, the solution was seeded with benzil; chilling on ice and filtering gave 0.40 g. of yellow crystals, m.p. 95.5–96.0°. The filtrate was heated for another 2.5 hours, water (30 ml.) was added, and the solution was again seeded, to give an additional 0.15 g., m.p. 95.2–95.8°. The total yield of benzil was 0.55 g., or 67% of theory. Positive identification was made by a comparison of the infrared spectrum with that of an authentic sample of benzil.

Preparation of 2,3-Diphenyl-*p*-dioxene (I). (a) **From 2-Phenyl-2-(α-hydroxybenzyl)-1,3-dioxolane** (IIa).—Compound IIa (70 g., 0.272 mole) was heated under reflux with 1.0 g. of *p*-toluenesulfonic acid in 500 ml. of dry xylene. The system was arranged for the removal of water as formed by use of a trap.[16] After 15 hours, most of the xylene was removed by distillation, and the residue was poured into an open dish and set aside. Slow evaporation of the solvent left oily crystals which were recrystallized from ethanol to give 35 g. of light yellow needles, m.p. 94–95°. The highest m.p. obtained for a sample of this material was 95.3–95.8°, for a pure white product. The yield of 2,3-diphenyl-*p*-dioxene was 54%. Infrared absorption bands are (2–10 μ, carbon tetrachloride solution; 10–16 μ, carbon disulfide solution): 3.28w, 3.38w, 3.41w, 3.48w, 6.06s, 6.21m, 6.66m, 6.90m, 7.80s, 7.92s, 8.79s, 9.00s, 9.23m, 9.64w, 10.29s, 10.98s, 11.29m, 11.34m, 13.15s, 14.4s, 14.94s.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.96; H, 5.76.

(b) **From Benzoin in Ethylene Glycol Solution.**—Benzoin (10.6 g., 0.05 mole) and 0.1 g. of *p*-toluenesulfonic acid were heated under reflux in 125 ml. of ethylene glycol for 13 hours; no trap was used. The solution was diluted with 200 ml. of water, cooled, and extracted with ether. After evaporation of the ether, the residue was taken up in ethanol, treated with Norite, and cooled to give crystals, which, after one recrystallization, gave 3.7 g., m.p. 95.0–95.8°, identical in the infrared with the previously prepared 2,3-diphenyl-*p*-dioxene. The yield was 31%.

Addition of Bromine to 2,3-Diphenyl-*p*-dioxene (I).—Compound I (6.00 g., 0.0252 mole) was dissolved in 100 ml. of anhydrous carbon tetrachloride. To this solution, protected from atmospheric moisture with a calcium chloride tube, was added a solution of bromine (4.0 g., 0.025 mole) in 50 ml. of dry carbon tetrachloride. The dropwise addition took one-half hour. The reaction was cooled on an ice-bath during the addition. After stirring the reaction solution at 0° for one hour, the absence of benzil was shown by an examination of the infrared spectrum. The mixture was heated under reflux for two hours, and the solvent was then removed by distillation from the steam-bath, care being taken that the solution did not become wet. The residue was heated on the steam-bath for another hour and the infrared spectrum was taken. The spectrum showed the presence of a large percentage of benzil. The residue was taken up in hot ethanol, and cooling gave 2.85 g. (54%) of yellow needles, m.p. 95.2–96.0°. The mixed m.p. with authentic benzil was not depressed, and the infrared spectrum was identical with that of benzil.

Bromination of *trans*-2,3-Diphenyl-*p*-dioxane.—A solution of 1.20 g. (0.005 mole) of the *trans* (m.p. 48°) isomer of 2,3-diphenyl-*p*-dioxane dissolved in 75 ml. of dry carbon tetrachloride was heated to reflux with illumination from a bright white light. To this solution was added, dropwise, a solution of bromine (1.60 g., 0.010 mole) in 30 ml. of carbon tetrachloride. The addition took 1.5 hours and the solution was boiled gently for an additional two hours; a gas which fumed on exposure to air, presumably hydrogen bromide, was evolved during the entire period. The bromine color remained as the bromine was added, and the solution was deep red at the end of the addition, but it became orange during the refluxing period. After standing overnight, the solvent was removed by distillation. The residual oil was crystallized from anhydrous ether to give 0.75 g. of yellow needles, m.p. 90–95°. Recrystallization from ether raised the m.p. to 94–95°, and the compound had an infrared spectrum identical with that of authentic benzil, m.p. 95°. The mixed m.p. with benzil showed no depression. The yield was 73%.

Bromination of *cis*-2,3-Diphenyl-*p*-dioxane.—The *cis* (m.p. 136°) isomer of 2,3-diphenyl-*p*-dioxane was brominated in exactly the manner described above for the bromination of the *trans* isomer, with the exception that the residual oil from evaporation of carbon tetrachloride was recrystallized from ethanol rather than from ether. The yield of benzil was 49%.

Addition of Chlorine to 2,3-Diphenyl-*p*-dioxene (I).—To a solution of 10.0 g. (0.042 mole) of I in 100 ml. of dry methylene chloride was added chlorine gas at the rate of 0.001 mole per minute for 60 minutes. During the addition the solution was cooled and stirred on the ice-bath. The solvent was removed and the residue recrystallized from ether at Dry Ice temperature to give 9.4 g. of product of indefinite m.p. (105–118°). Recrystallization did not raise the m.p., but the sample gave a satisfactory analysis for 2,3-dichloro-2,3-diphenyl-*p*-dioxane (V). The yield of the white compound was 72%. The compound is extremely unstable, even in a desiccator, and must be used immediately when prepared. Infrared absorption bands are as follows (carbon disulfide solution): 3.24w, 3.36w, 3.40w, 7.58w, 7.84m, 8.14s, 8.41w, 8.82s, 8.97s, 9.20w, 9.61w, 9.77w, 10.35s, 10.43s, 10.88m, 11.32w, 11.67w, 12.89s, 14.0s, 14.3s, 14.6 (shoulder), 15.15m.

Anal. Calcd. for $C_{16}H_{14}O_2Cl_2$: C, 62.17; H, 4.57. Found: C, 62.37; H, 4.56.

Chlorination of *trans*-2,3-Diphenyl-*p*-dioxane. (a) **High Temperature.**—2,3-Diphenyl-*p*-dioxane (*trans*, m.p. 48°. 4.80 g., 0.020 mole) was dissolved in 80 ml. of dry carbon tetrachloride and heated to reflux under the illumination of a bright white light. Chlorine gas was passed through the solution for 30 minutes at the rate of 0.0013 mole per minute and the solution was heated under reflux for an additional 10 minutes. The infrared absorption spectrum of the solution showed no absorption due to benzil or ethylene chloride; the spectrum consisted of weak bands attributable to the starting material and of strong bands of 2,3-dichloro-2,3-diphenyl-*p*-dioxane (V). The solvent was removed by distillation at atmospheric pressure, and the residue was distilled *in vacuo*. Three grams of a yellow oil, b.p. 165–176° (3.0 mm.), was obtained [reported for benzil: b.p. 188° (12 mm.)]. The oil was dissolved in 95% ethanol and the 2,4-dinitro- and *p*-nitro-phenylhydrazones were prepared in the usual way.[36] The former melted at 188–189° (reported for benzil[37] 189°), the latter at 276–279° (reported[38] 290°).

(b) **Low Temperature.**—Six grams (0.025 mole) of the *trans* isomer of 2,3-diphenyl-*p*-dioxane was dissolved in 50 ml. of dry carbon tetrachloride and cooled on the ice-bath. The solution was illuminated with ultraviolet radiation. Chlorine was passed into the stirred solution at the rate of 0.0025 mole per minute for 20 minutes, and the solution was then stirred until the chlorine color disappeared (0.5 hour). Nitrogen was passed through until no more hydrogen chloride was evolved, and the infrared spectrum of the solution was taken. The spectrum was almost identical with that of V prepared from 2,3-diphenyl-*p*-dioxene (above). Small differences in the spectra could be accounted for by a minor impurity of starting material.

Chlorination of *cis*-2,3-Diphenyl-*p*-dioxane.—The *cis* (m.p. 136°) isomer of 2,3-diphenyl-*p*-dioxane was chlorinated at 0° in the same manner as described for the low temperature chlorination of the *trans* isomer. In this case, however, the compound was practically insoluble in the cold solvent, but, as the chlorination proceeded, solution occurred. After nitrogen was passed through the solution, it was still pale yellow in color; however, the infrared absorption spectrum showed no sign of benzil, nor could the odor of chlorine be detected. The spectrum of the solution was identical with that of V, and there was no detectable absorption due to starting material.

Pyrolysis of 2,3-Dichloro-2,3-diphenyl-*p*-dioxane (V).—In a small round-bottom flask was placed 5.0 g. (0.0162 mole) of 2,3-dichloro-2,3-diphenyl-*p*-dioxane, and the compound was heated to reflux for 0.5 hour on a sand-bath at 190°. At the end of this time, the condenser was replaced by a small distillation head, and 1.1 g. (69%) of ethylene chloride, b.p. 80–2°, $n^{25}\text{D}$ 1.4424, was obtained. The residue was recrystallized from ethanol to give 3.1 g. (91%) of

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[36] R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," third edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[37] R. L. Shriner and R. C. Fuson, *ibid.*, p. 264.

[38] F. Wild, "Characterisation of Organic Compounds," University Press, Cambridge, 1948, p. 140.

benzil, yellow needles, m.p. 95.5–96.0°. The infrared spectra of both compounds were identical with the spectra obtained from authentic samples.

Ethanolysis of 2,3-Dichloro-2,3-diphenyl-*p*-dioxane (V).—When compound V, either as the isolated crystalline compound or as a crude chlorine addition product of I in methylene chloride, was mixed with anhydrous ethanol, an immediate and exothermic reaction took place, to give an essentially quantitative precipitate of 2,3-bisethoxy-2,3-diphenyl-*p*-dioxane, m.p. 172.5–174.0°. Infrared absorption bands are (carbon disulfide solution): 3.28w, 3.38m, 3.41w, 3.46w, 7.19w, 7.81m, 8.01m, 8.54s, 8.95 (shoulder), 9.09s, 9.37s, 9.55s, 9.77m, 10.29s, 10.87m, 13.16s, 14.12s.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.42; H, 7.41.

Reaction of 2,3-Dichloro-2,3-diphenyl-*p*-dioxane (V) with Phenylmagnesium Bromide.—A solution of phenylmagnesium bromide (0.03 mole) was prepared from 0.73 g. of magnesium and 4.7 g. of bromobenzene in dry ether. To this solution was added, dropwise, 3.1 g. (0.01 mole) of V in 15 ml. of ether at such a rate that a gentle reflux was maintained. After heating under reflux for an additional 0.5 hour, the mixture was hydrolyzed by pouring over ice containing ammonium chloride. The ether layer was separated and dried over sodium sulfate, and the ether was then removed by heating on the steam-bath. The resulting paste was recrystallized from ethanol, after treatment with Norite, to give 1.7 g. of a compound, m.p. 94–95°, which was identical in the infrared with 2,3-diphenyl-*p*-dioxene (I). The yield, including a second crop of 0.2 g., was 79%.

Attempted Addition of Hydrogen Chloride to 2,3-Diphenyl-*p*-dioxene (I).—Compound I (5.0 g., 0.021 mole) was dissolved in 50 ml. of dry carbon tetrachloride. Into the boiling solution was passed hydrogen chloride gas at the rate of 0.0035 mole per minute for 20 minutes. Nitrogen was then passed through the solution for 30 minutes, and an infrared absorption spectrum of the solution was taken. There was no change from the starting dioxene.

The above was repeated, but this time at 10°. After passing in hydrogen chloride for 20 minutes at 0.002 mole per minute and bubbling nitrogen through the cold solution until no more hydrogen chloride was evolved, the infrared spectrum showed only the presence of I.

The above was repeated, using dry ether as solvent and working at 10–15°. Hydrogen chloride was passed in at the rate of 0.002 mole per minute for 12 minutes, and the solution was placed in an open dish and allowed to evaporate to dryness at room temperature. The residue weighed 5.0 g., and its infrared absorption spectrum was identical with that of I. The recovery was 100%.

Preparation of *trans*-2,3-Diphenyl-*p*-dioxane.—The 48° isomer of 2,3-diphenyl-*p*-dioxane was first reported by Christ and Summerbell in 1933[4]; however, because of the isolation in the present work of the 136° isomer from this preparation, the reaction will be described in detail.

To a solution of 0.50 mole of phenylmagnesium bromide, prepared from 79 g. of bromobenzene and 12.2 g. of magnesium turnings in 200 ml. of anhydrous ether, was added, slowly and with stirring, 31.4 g. (0.20 mole) of *trans*-2,3-dichloro-*p*-dioxane, at such a rate that the heat of reaction caused gentle refluxing of the ether. Upon completion of the addition, the ether solution was hydrolyzed by pouring onto 400 g. of ice containing 25 ml. of concentrated sulfuric acid. The ether layer was removed and washed thrice with 10% aqueous sodium bicarbonate and thrice with water. After drying over anhydrous sodium sulfate, the ether solution was evaporated to a convenient volume and placed in a cold room at −5°. Crystallization afforded 10 g. of crude product; recrystallization from ethyl acetate gave 3 g. of 2,3-diphenyl-*p*-dioxane, m.p. 43–46°. Infrared absorption bands are (potassium bromide pellet): 3.31m, 3.39m, 3.46m, 3.57s, 6.21w, 6.28w, 6.87s, 7.22w, 7.30w, 7.40w, 7.50w, 7.61w, 7.91s, 8.03w, 8.21w, 8.98s, 9.25m, 9.50m, 9.69w, 10.09s, 10.55s, 11.00m, 11.22m, 11.85w, 13.15s, 13.39s, 14.4s (broad), 15.40m.

The ether solution from which the crystals had grown was concentrated and freed of ether by evacuation. The residual oil was saved for chromatographic separation into its components (see below).

trans-2,3-Diphenyl-*p*-dioxane forms a yellow picrate, m.p. 89.2–89.9° from ethanol.

Anal. Calcd. for $C_{22}H_{19}O_9N_3$: C, 56.29; H, 4.08. Found: C, 56.22; H, 4.05.

The isolation of *cis*-2,3-diphenyl-*p*-dioxane from the preparation of the *trans* isomer was accomplished by chromatography of the residual oil (obtained as described above) over 80–200 mesh alumina, using a column 4 feet by one inch packed in pentane. The eluent was ether–pentane, starting with 20% ether and gradually changing the concentration until pure ether was used. Products were obtained in the following order: biphenyl, m.p. 61–65° [mixed m.p. with authentic biphenyl (m.p. 68–69°) was 65–68°], *trans*-2,3-diphenyl-*p*-dioxane, m.p. 43–6° (10 g.), identified by infrared, and *cis*-2,3-diphenyl-*p*-dioxane, m.p. 134°, 0.3 g.

The 134° solid was rechromatographed to give pure material. The compound gave an analysis consistent with that of a diphenyldioxane, and it was assumed to be identical with the 136° isomer of 2,3-diphenyl-*p*-dioxane to which Stumpf had assigned the *trans* structure.[6,7] It was later shown to be identical with the product obtained upon catalytic hydrogenation of 2,3-diphenyl-*p*-dioxene (below).

In another preparation of 2,3-diphenyl-*p*-dioxane (m.p. 48°), 1.1 moles of phenylmagnesium bromide and 0.50 mole of 2,3-dichloro-*p*-dioxane were used. The first two crops of crystals from ether solution, amounting to 45 g., were the expected isomer; the third crop, obtained from the mother liquor in the normal fashion, melted at 133–134°, and weighed 0.5 g. The infrared spectrum was identical with that of the compound isolated by chromatography as described above. Infrared absorption bands are (potassium bromide pellet): 3.32w, 3.40w, 3.44m, 3.52m, 6.21w, 6.69m, 6.82m, 6.90s, 7.20w, 7.25s, 7.33w, 7.40w, 7.45w, 7.62w, 7.83s, 8.26w, 8.39w, 8.63w, 8.91s, 9.06s, 9.22s, 9.55w, 9.70m, 9.97w, 10.02w, 10.45s, 10.90m, 11.07s, 11.51s, 11.69s, 12.30m, 13.10w, 13.41s, 14.05s, 14.46s, 15.38w.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.01; H, 6.50.

Catalytic Reduction of 2,3-Diphenyl-*p*-dioxene (I).—A solution of 2.38 g. (0.010 mole) of I in 150 ml. of glacial acetic acid containing 10 ml. of acetic anhydride was shaken with hydrogen in a Paar apparatus at 20–30 pounds pressure (absolute) in the presence of 0.1 g. of platinum oxide until the theoretical uptake of hydrogen had occurred. The catalyst was removed by filtration and the solvent removed on the steam-bath *in vacuo* to leave a residue from which crystals deposited on cooling. After recrystallization from ethanol containing a small amount of acetic acid, the product, 2.29 g. (95%), melted at 128–133°. The analytical sample melted at 132.7–133.5°, although samples obtained later melted as high as 136°. The infrared spectrum was identical with that of the 134° compound obtained by chromatography from the preparation of the 48° isomer of 2,3-diphenyl-*p*-dioxane (above).

Chemical Reduction of 2,3-Diphenyl-*p*-dioxene (I).—Compound I (5.0 g., 0.021 mole) was dissolved in a mixture of 100 ml. of dry benzene and 150 ml. of dry 2-pentanol. With stirring, 3 g. of sodium was added in small pieces. After the sodium had reacted (2–4 hours), approximately 100 ml. of solvent was removed *in vacuo*, 150 ml. of water was added, and the mixture was extracted in ether. The ether layer was washed (water, dilute hydrochloric acid, water) and dried (magnesium sulfate). The ether and most of the pentanol was then removed by distillation at atmospheric pressure and a crop of crystals (1.4 g.) was obtained. They melted at 131–133° and were identical in the infrared with the 136° isomer of 2,3-diphenyl-*p*-dioxane previously obtained. The last traces of pentanol were removed from the solvent by thrice adding carbon tetrachloride and evaporating the solution *in vacuo* at 100°. After pumping the residual oil dry, it was chromatographed over 80–200 mesh alumina, packed in pentane, using ether-pentane as the eluent, to give, in the following order, 0.2 g. of I, 0.9 g. of the 48° compound (18% yield), and 0.3 g. of the 136° compound. The total yield of the 136° isomer (1.7 g.) was 34%.

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