which gave a positive test for carbonyl group with 2,4dinitrophenylhydrazone reagent, but a crystallizable derivative was not obtained.

Reaction of Dipropionyldiimide with Compounds Containing an Active Hydrogen.—A solution of dipropionyldiimide was prepared by the addition over 45 min. of 0.80 g. (0.005mole) of bromine in 10 ml. of bromobenzene to a stirred suspension of 1.72 g. (0.005 mole) of mercury dipropionylhydrazine in 40 ml. of bromobenzene. Only 7 ml. (0.0003mole) of nitrogen was evolved, so it was assumed that the solution contained 0.004 mole of dipropionyldiimide in 50 ml. of bromobenzene (0.08 molar). The red solution was filtered and 5-ml. portions added to each of the 10 liquids listed in Table I. The time required for the disappearance of color is listed in that table.

A 2.2-g. (0.015) sample of distilled dipropionyldiimide was added to 30 ml. of methanol. Nitrogen (142 ml., 42%) was evolved and the mixture retained a faint pink color. Distillation left a residue which after recrystallization melted at 130–133° and weighed 0.6 g. Its melting point was not depressed by authentic 1,2-dipropionylhydrazine.

Anal. Caled. for C₆H₁₂O₂N₂: C, 50.0; H, 8.35; N, 19.4. Found: C, 49.88; H, 8.67; N, 19.2.

The distillate was hydrolyzed with aqueous alkali and volatile products removed. The residue was taken up in

water, acidified, extracted with ether and the ether extract exactly neutralized with 0.0029 mole of alkali. The residue left from evaporation of this solution yielded *p*-methylpropionanilide when heated with *b*-toluidine.

Catalysis of Vinyl Polymerization by Dipropionyldiimide.
Catalysis of Vinyl Polymerization by Dipropionyldiimide.
Solutions containing 0.18 g. (0.0012 mole) of distilled dipropionyldiimide and 5 ml. of styrene, acrylonitrile or methyl methacrylate in 10 ml. of benzene were warmed in a waterbath at 75-80° for 2 hr. together with solutions of the vinyl monomers containing no dipropionyldiimide. The solution containing styrene and dipropionyldiimide was decolorized in 1 hr. The others remained pink throughout the experiment. The mixtures were poured into 30 ml. of methanol and the polymer which separated was filtered and dried. A sample of polyacrylonitrile also was prepared by allowing a solution containing 0.18 g. of dipropionyldiimide, 5 ml. of acrylonitrile, 5 ml. of methanol and 10 ml. of benzene to stand at 20° for 18 hr. The yields of polymer are summarized in Table II.

Both polyacrylonitrile samples absorbed strongly at 5.8 μ indicating the presence of a carbonyl group in the product, while the sample of polystyrene prepared in the presence of dipropionyldimide absorbed strongly at 5.96 μ indicating an amide structure obtained through copolymerization of dipropionyldimide with styrene.

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A New Synthesis of a Dioxadiene

By R. K. Summerbell and Gregory J. Lestina

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An alkyl substituted dioxadiene has been made for the first time. When *trans*-2,5-bis-(iodomethyl)-*p*-dioxane was treated with hot base, the elimination of the elements of hydrogen iodide produced a diolefin, 2,5-bis-(exomethylene)-*p*-dioxane. This substance was isomerized by means of a palladium-on-charcoal catalyst to a stable diolefin, 2,5-dimethyl-*p*-dioxadiene. Treatment of either diolefin with methanol in the presence of a trace of acid produced the dimethoxyacetal of dimethoxyacetone, thus supporting a dioxane structure for that compound.

Introduction

In most respects, a dioxadiene acts as an aliphatic vinyl ether, but certain of its properties are those of a resonance-stabilized system.1-6 Prior to the present work, only two methods of synthesizing dioxadienes have been available. Symmetrical tetraphenyldioxadiene⁵ is prepared readily by condensing benzoin with methanol and heating the adduct in refluxing acetic anhydride. Although this synthesis is convenient, the resulting compounds have all of the dioxadiene hydrogens substituted by aryl groups, thus preventing the study of many important types of reactions. The simple parent compound, dioxadiene, is formed by the action of the magnesium iodide-magnesium-butyl ether system on symmetrical tetrachlorodiox-anes.^{1,4} To prepare homologs of dioxadiene by this method would require unavailable starting materials, since no preparation of the necessary chlorinated substituted dioxanes has been reported, and the isolation of the requisite compounds from chlorination of alkyl dioxanes will

(1) R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, 61, 3020 (1939).

(2) G. R. Lappin and R. K. Summerbell, J. Org. Chem., 13, 671 (1948).

(3) G. R. Lappin and R. K. Summerbell, THIS JOURNAL, 78, 2600 (1948).

(4) L. W. Pickett and E. L. Sheffield, ibid., 68, 216 (1946).

(5) W. Madelung and M. E. Oberwegner, Ann., 490, 201 (1931); 526, 195 (1936).

(6) J. Y. Beach. J. Chem. Phys., 9, 53 (1941).

probably occasion considerable difficulty. In a recent study, the pyrolysis of 2,5-dimethoxy-p-diox-ane⁷ failed to yield the expected dioxadiene.

The structure of 2.5-bis-(iodomethyl)-p-dioxane recently has been proved,⁸ and the compound is prepared readily in quantity. It occurred to us that this compound might serve as a convenient starting material for the synthesis of a dialkyldioxadiene, if the elements of hydrogen halide could be removed to form a diexomethylene dioxane and the latter could be rearranged to form a dioxadiene. The probable intermediate, the diexomethylene compound, is of interest in relation to the general problem of preparing such types as potential mon-omers for polymerization studies.⁹ A closely related compound, 2-exomethylenetetrahydrofuran, had been prepared by Paul and Tchelitcheff¹⁰ from 2-bromomethyltetrahydrofuran by elimination of hydrogen bromide with base. Essentially the same reaction was used by us recently in the preparation in good yield of 2,3-bis-(exomethylene)-p-dioxane.11

This general method of preparing a dioxadiene was attempted in our laboratories some years ago

(7) W. E. Parham and H. E. Reiff, THIS JOURNAL, 77, 6391 (1955).

(8) R. K. Summerbell and J. R. Stephens, *ibid.*, 76, 731, 6401 (1954).

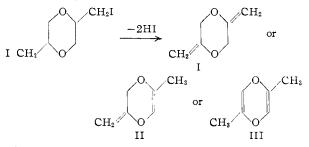
(9) W. J. Bailey and Robert L. Hudson, *ibid.*, 78, 670 (1956).

(10) R. Paul and S. Tchelitcheff, Bull. soc. chim., 17, 520 (1950).
(11) R. K. Summerbell and Gregory J. Lestina, THIS JOURNAL, 79, 3878 (1957).

using ethanolic potassium hydroxide as the base,¹² but although a mixture of several compounds boiling over a wide range was obtained, no single compound of constant properties and acceptable analysis was isolated. We decided to repeat the attempt, using a higher boiling solvent and modern techniques of separation.

Discussion

When the proposed synthesis was performed, there was obtained a clear, sweet-smelling liquid which could be expected to possess any of the structures I, II or III.



The empirical formula of this diene, b.p. 146-147°, was confirmed by analysis. Upon dilute acid hydrolysis and treatment of the hydrolysate with pnitrophenyl
hydrazine, there was obtained the p-nitrophenylos
azone of methylglyoxal in 99% yield, a result consistent with any of the three possible structures. There seems to be no reason to suspect skeletal rearrangement.

It has been shown by Pickett and Sheffield⁴ that dioxadiene possesses a strong ultraviolet absorption at 250 m μ whereas dioxene has none at this wave length. Since the compound b.p. 146-147° does not absorb at or near $250 \text{ m}\mu$ in ethyl ether solution, its structure is not that represented by III.

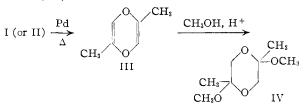
The position of the double bonds was indicated from the results obtained by ozonizing the olefin. There was obtained a 52% yield of the formaldehyde bis-methone condensation product, the calculation assuming that one mole of the diexomethylene compound would yield two moles of formaldehyde. Recorded ozonolysis of related compounds gave comparable results. For instance, the yield of formaldehyde in the case of 2-methylene-tetrahydrofuran was 55%,¹⁰ of 1,2-dimethylenecyelopentane,¹³ 30%. Identical procedures applied by us to divinyl ether gave 43%. In view of these yields obtained by both ourselves and others in the ozonolysis of these closely related compounds, it seemed to us highly unlikely that our compound had structure II, containing only one methylene group, and that we had obtained a formaldehyde yield of 104%. Structure III is eliminated since the ozonolysis of III would be expected to produce only trace quantities of formaldehyde. While structure II cannot be completely set aside as a possibility, the evidence is predominantly in favor of

It was observed that the presence of a small amount of water was necessary in the ozonolysis process for the yield of formaldehyde to be greater

(12) R. R. Umlioefer, M.S. Thesis, Northwestern University, 1936. (13) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald and D. T. Longone, THIS JOURNAL, 78, 6057 (1956).

than trace quantities. It seems possible that in this case the ozonide breaks apart in the reaction and the water is necessary to hydrate the product and prevent it from being further oxidized by the ozone or otherwise lost. Participation of a solvent in an ozonolysis is not new.14 Glycolic acid was also isolated as a product of ozonolysis, thus again excluding III.

The substance b.p. 146-147°, believed to be I, was refluxed in the presence of a palladium-oncharcoal catalyst to yield an isomeric compound, b.p. 122-123°, believed to be 2,5-dimethyl-p-dioxadiene (III).



The double bonds were assumed to be inside the ring since the compound possesses a strong absorption at 252 m μ in ethyl ether solution.⁴ The diene III, upon ozonolysis, yielded only trace amounts of the formaldehyde bis-methone condensation product. This fact eliminates structure II as a possibility

Although dioxane structures have often been assumed for many dimeric hydroxyaldehydes and hydroxyketones, they have been proved in very few cases. Dimeric glycolaldehyde and its derivatives have been definitely related to dioxane.¹⁵ The dimethoxy acetal of dimeric hydroxyacetone has been assumed to be 2,5-dimethoxy-2,5-dimethyl-p-dioxane (IV).¹⁶ The availability of compounds whose formulas could be represented by the structures I or III, offered an opportunity of obtaining supporting evidence of this assumed structure, since either compound I or III would almost certainly add two moles of methanol in the presence of traces of acid to give IV. Both I and III did add methanol in the presence of a trace of acid to form a derivative with the composition of IV and having the melting point reported for IV, thus supporting the assignment of a dioxane structure to IV.

Acknowledgment.—Our thanks are given to the Abbott Foundation of Northwestern University for financial aid and to the Allied Chemical Dye Corporation for a fellowship held by G.J.L.

Experimental

trans-2,5-Bis-(iodomethyl)-p-dioxane was prepared ac-

trans-2,5-Bis-(10domethyl)-p-dioxane was prepared ac-cording to the procedure of Summerbell and Stephens.⁸ The Preparation of 2,5-Bis-(exomethylene)-p-dioxane (I).—A hot solution (ca. 200-210°) of 44 g. (1.1 moles) of sodium hydroxide in 50 ml. of water and 100 ml. of carbitol was treated with 157 g. (0.427 mole) of 2,5-bis-(iodomethyl)-p-dioxane suspended in 200 ml. of an equivolume water-carbitol mixture added in small portions. Each addition was followed by the ebullition of vapor which condensed to water and impure I. When the addition of iodide was water and impure I. When the addition of iodide was completed, 50 ml. of an equivolume water-carbitol mixture was added, and heating was continued until the distillate became clear. The lower layer was removed, dried by means of anhydrous sodium carbonate and stored at -4°

⁽¹⁴⁾ P. S. Bailey, ibid., 78, 3810 (1956).

⁽¹⁵⁾ R. K. Summerbell and L. K. Rochen, ibid., 63, 3241 (1941).

⁽¹⁶⁾ C. F. Hennion and W. S. Murray, ibid., 64, 1220 (1942).

under a nitrogen atmosphere. There was obtained after quick distillation 39.5 g.(0.353 mole) of liquid, yield 82.6%.

Separation and Analysis.-Distillation accomplished under a nitrogen atmosphere in a 12-inch column packed with base-washed glass helices gave 26.43 g. (0.236 mole) of I, b.p. 146–147° (755.1 mm.), n^{20} D 1.4880, d^{20} , 1.048. Repeated distillation of the middle fractions did not produce any change in the refractive index or in the infrared spectrogram.

Anal. Caled. for C₆H₈O₂: C, 64.27; H, 7.19; MRD, 30.06. Found: C, 64.18; H, 7.05; MRD, 30.8.

In an attempt to obtain further purification, compound 1 was chromatographed on 100–200 mesh high grade silica gel (Davidson Chemical Corp., Baltimore 3, Md., Grade 923) in a column described by Mair and Forziatti.¹⁷ Ap-proximately 1 ml. of compound diluted with 1 ml. of pentane was charged for each separation run. Absolute ethanol was used as an eluent. The separation was followed by the refractive indices. The appearance of new bands in the infrared spectrogram of the diolefin after separation showed

Another sample of I was chromatographed in the same manner, using reagent aluminum oxide (Merck and Co., Inc.). The separation was again followed by the refractive indices. Neither the refractive indices nor the infrared

proof of Structure. 1. The Hydrolysis of I.—There was added 75 ml. of 0.08 N sulfuric acid to 0.1077 g. (0.000961 mole) of I. The mixture was heated on a steam-bath for 1 hr. and 0.92 g. (0.0060 mole) of *p*-nitrophenylhydrazine was added while the solution was vigorously stirred. The mixture was heated for an additional 5 hr. during which time a

ture was heated for an additional 5 hr. during which time a flocculent red precipitate of the *p*-nitrophenylosazone of methylgloxal was formed. The precipitate was collected, washed with cold 2 N hydrochloric acid until the filtrate was colorless, and dried. There was obtained 0.6199 g. (0.00181 mole) of osazone, m.p. 285–289°,¹⁸ for a yield 99.1% (lit.¹⁹ m.p. 282–283° and 302–304°). 2. The Preparation of 2,5-Dimethyl-2,5-dimethoxy-*p*-dioxane (IV).—To a solution of 50 ml. of methyl alcohol containing 1 drop of 12 N hydrochloric acid there was added 1.0 g. (0.0091 mole) of I. The solution was warmed on a steam-bath for 1 hr., and then the excess methyl alcohol was removed under reduced pressure. There was obtained 1.16 g. (0.0066 mole) of IV for a yield 72%, m.p. 126–127° (lit.¹⁶ m.p. 125°)

3. The Ozonolysis of I.—The ozonizer was modeled after one described by Henne.²⁰

(a) A solution of 0.1943 g. (0.00173 mole) of I in 30 ml. of methylene chloride to which 2 drops of water had been added was cooled to 0° , and an oxygen stream containing ozone was passed through slowly. The reaction was terozone was passed through slowly. minated when the exit gases liberated iodine from acidic potassium iodide. The ozonized mixture was added to 25 ml. of 25% acetic acid containing 0.3 g. of zinc dust. The mixture was shaken vigorously and 0.3 g. of silver nitrate and 0.2 g. of hydroquinone were added. After 30 minutes of vigorous shaking, the methylene chloride was removed by heating. The residual solution was cooled to 0° and made basic with 3 N sodium hydroxide. The zinc hydroxide precipitate was removed by filtration. The precipitate was washed twice with 10-ml. portions of water and the washings were added to the filtrate. The filtrate was neutralized with acetic acid and 1.5 g. (0.0107 mole) of methone was added. The mixture was warmed for 15 minutes on a steam-bath and then allowed to stand overnight at room

(17) B. J. Mair and A. F. Forziatti, J. Research Natl. Bur. Standards, 32, 151, 165 (1944).

(18) All melting points were taken on a Fisher-Johns block unless otherwise indicated.

(19) N. Ariyama, J. Biol. Chem., 77, 399 (1928)

(20) A. L. Henne, THIS JOURNAL, 51, 2676 (1929).

temperature. The resulting precipitate was collected and dried to yield 0.5256 g. (0.00181 mole) of formaldehyde bismethone condensation product, m.p. 189-191°, yield 52.0%.

When no water was added to the methylene chloride solu-

tion before ozonolysis, the formaldehyde bis-methone con-densation product was obtained in only 7% yield. (b) A solution of 0.210 g. (0.00187 mole) of I in 30 ml. of wet methylene chloride was ozonized as previously de-scribed. When the reaction was completed, the ozonized solution was added to 5 ml. of water and the mixture heated to 54° until all of the methylene chloride was removed. The resulting liquid was evaporated under reduced pressure been dried on a clay plate, weighed 0.10 g. (0.0013 mole), m.p. 77-78°, yield 35%. The compound did not depress the melting point of authentic glycolic acid in a mixed melting point determination.

The Ozonolysis of Divinyl Ether .--- A solution of 0.176 g. (0.00235 mole) of divinyl ether in 30 ml. of wet methylene chloride was cooled to -70° and an oxygen stream containing ozone was passed slowly through the solution. The reaction was terminated when the exit gases liberated iodine from an acidic potassium iodide solution. The mixture was worked up as described previously. After the addition of 1.5 g. (0.0108 mole) of methone, there was collected 0.587 g. (0.00201 mole) of the formaldehyde bismethone condensation product, m.p. 188-189°, yield 43%. The Preparation of 2,5-Dimethyl-p-dioxadiene (III).—To

a mixture of 2 g. of biphenyl, 1.0 g. of hydroquinone and 0.62 g. of 5% palladium-on-charcoal catalyst, there was added 9.1 g. (0.081 mole) of I. The mixture was refluxed for 24 hr. under a nitrogen atmosphere. There was ichned by tained on distillation 4.0 g. (0.030 mole) of III, yield 44%, b.p. 122-123° (756.2 mm.). Redistillation through a 12-inch glass packed column, followed by a chromatographic separation on high grade silica gel on a 1-ml. sample of III gave the pure diolefin, n²⁰D 1.4480, d²⁰, 1.014, m.p. 15.5-16.5°.

Anal. Calcd. for C₆H₈O₂: C, 64.27; H, 7.19; MRD, 30.06. Found: C, 63.99; H, 6.95; MRD, 29.6.

The Determination of the Structure of III. 1. The Ozonolysis of III.-Ozonolysis of 0.2109 g. (0.00188 mole) of III was conducted as described previously. There was obtained 0.0314 g. (0.00011 mole) of the formaldehyde adduct of methone, m.p. 180-187

2. The Formation of IV from III.—To a solution of 50 ml. of methyl alcohol containing 1 drop of 12 N hydrochloric acid there was added 1.0 g. (0.0091 mole) of III. The solution was warmed on a steam-bath for 1 hr., and then the excess methyl alcohol was removed under reduced pressure. There was obtained 1.10 g. (0.0062 mole) of IV, m.p. 126-127°, for a 68% yield. In a mixed melting point determination with IV prepared from I, the mixture melted at 126-127

Infrared Spectra.^{21,22}—Compound I: 3.49(w), 5.95(m), $\begin{array}{l} \text{Linking by Constants} & \text{Linking in the set of a state o$

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(21) See G. D. Meakins, J. Chem. Soc., 4170 (1953), for a discussion of the infrared spectra of unsaturated ethers. He has proposed that the 11.2 band characteristic of terminal methylene groups in hydrocarbons is shifted to about 12.5 in the corresponding ethers. Our supposed diexomethylene compound I does possess a medium band at 12.54 and a strong band at 12.15, while our supposed dioxadiene III does not absorb in this region. Due to the fact that only a few re-lated compounds have been studied, this evidence is of limited value in confirming our structures.

(22) Y. Mikawa, Bull. Chem. Soc. Japan 29, 110 (1956).