

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

Reaction of Dipropionylidimide with Compounds Containing an Active Hydrogen.—A solution of dipropionylidimide was prepared by the addition over 45 min. of 0.80 g. (0.005 mole) 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. (0.0003 mole) of nitrogen was evolved; so it was assumed that the solution contained 0.004 mole of dipropionylidimide 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 dipropionylidimide 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. Calcd. for $C_6H_{12}O_2N_2$: 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 *p*-toluidine.

Catalysis of Vinyl Polymerization by Dipropionylidimide.—Solutions containing 0.18 g. (0.0012 mole) of distilled dipropionylidimide and 5 ml. of styrene, acrylonitrile or methyl methacrylate in 10 ml. of benzene were warmed in a water-bath at 75–80° for 2 hr. together with solutions of the vinyl monomers containing no dipropionylidimide. The solution containing styrene and dipropionylidimide 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 dipropionylidimide, 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 dipropionylidimide absorbed strongly at 5.96 μ indicating an amide structure obtained through copolymerization of dipropionylidimide with styrene.

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A New Synthesis of a Dioxadiene

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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 dimeric hydroxyacetone, 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 tetrachlorodioxanes.^{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

probably occasion considerable difficulty. In a recent study, the pyrolysis of 2,5-dimethoxy-*p*-dioxane⁷ 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 monomers 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

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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_D^{20} 1.4880, d_4^{20} 1.048. Repeated distillation of the middle fractions did not produce any change in the refractive index or in the infrared spectrogram.

Anal. Calcd. for $C_6H_8O_2$: 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 I 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 Approximately 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 that it had been partially isomerized on the silica gel.

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 spectrograms showed any change from starting material.

Proof of Structure. 1. The Hydrolysis of I.—There was added 75 ml. of 0.8 *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 flocculent red precipitate of the *p*-nitrophenylosazone of methylglyoxal 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 terminated 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

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

When no water was added to the methylene chloride solution before ozonolysis, the formaldehyde bis-methone condensation 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 described. 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 to yield a white solid, glycolic acid, which, after having 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.

4. 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 bis-methone 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 obtained 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, n_D^{20} 1.4480, d_4^{20} 1.014, m.p. 15.5–16.5°.

Anal. Calcd. for $C_6H_8O_2$: 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), 6.08(m), 7.68(s), 8.13(w), 9.25(s), 9.72(w), 11.79(m), 12.15(s), 12.54(m). Compound III: 3.40(m), 3.44(m), 5.85(sh), 5.95(s), 7.21(s), 7.39(s), 8.09(s), 8.76(s), 9.99(s), 11.21(s), 12.97(s), 13.80(m).

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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 dioxomethylene 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 related compounds have been studied, this evidence is of limited value in confirming our structures.

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

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