[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

# Cyclic Dienes. XXIII. 1,4-Dimethylene-2-cyclohexene[1]

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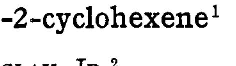
1,4-Dimethylene-2-cyclohexene, isomeric with *p*-xylene, was prepared by a six-step synthesis starting from dimethyl terephthalate. In the last step an unsaturated diacetate, 1,4-di-(acetoxymethyl)-2-cyclohexene, was pyrolyzed at 490° to give a 61% yield of the conjugated triene. Little or no *p*-xylene was formed during the pyrolysis. The structure of the triene was established by determination of its ultraviolet and infrared absorption spectra, isomerization to *p*-xylene and ozonization to formaldehyde and succinic acid.

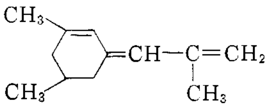
Previous work has shown that the pyrolysis of esters is an excellent method for the synthesis of polyfunctional unsaturated compounds. Thus the pyrolysis of a triacetate produced 2-vinyl-1,3-butadiene,[3] while the pyrolysis of a tetraacetate produced 2,3-di-(acetoxymethyl)-1,3-butadiene.[4] If charring is carefully avoided, highly strained unsaturated compounds that are isomeric with aromatic derivatives can be formed in high yields completely free of their aromatic isomers. Thus the pyrolysis of an unsaturated diacetate produced a 92% yield of 1,2-dimethylene-4-cyclohexene,[5] isomeric with *o*-xylene. This synthesis is quite remarkable in view of the failure of the Hofmann decomposition of a quaternary ammonium hydroxide to produce such an isomer of an aromatic compound. Thus Ladberg and Turner[6] failed to obtain any 1,2-dimethylene-4-cyclohexene but obtained only *o*-xylene from the decomposition of the corresponding unsaturated bis-quaternary ammonium hydroxide. Because of interest in these highly strained isomers of aromatic compounds the pyrolysis procedure was extended to produce an 89% yield of 4-methyl-1,2-dimethylene-4-cyclohexene,[7] isomeric with pseudocumene, and 4,5-dimethyl-1,2-dimethylene-4-cyclohexene, isomeric with durene. More recently this procedure was extended to the synthesis of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene, isomeric with prehnitene, and 2,3-dimethylene-$\Delta^{9(10)}$-octalin, isomeric with 6,7-dimethyltetralin.[8]

In all these trienes only two of the double bonds are in conjugation and rearrangement of both these double bonds into conjugation with the endocyclic double bond is required for aromatization. It was of interest, therefore, to prepare an isomer of an aromatic compound in which all three of the double bonds were in conjugation. One of the simplest trienes with this arrangement of double bonds is 1,4-dimethylene-2-cyclohexene (I), isomeric with *p*-xylene. It was thought that the preparation of this conjugated triene would indeed emphasize the usefulness of the pyrolysis of esters for the synthesis of strained unsaturated compounds.

Grundmann[9] has reported the preparation of a conjugated triene acid that could be isomerized



to an aromatic system by treatment with base. However, in this case the double bonds are stabilized by conjugation with the carbonyl group; there is also no strain of the system from double bonds in the exocyclic position. Auwers and Peters[10] reported also a conjugated triene



which underwent polymerization rather than rearrangement.

The starting material for the preparation of 1,4-dimethylene-2-cyclohexene (I) was the commercially available dimethyl terephthalate (II). Although the reduction of II with a nickel catalyst had been reported previously,[11,12] the reduction in our hands was somewhat erratic, giving in the best runs a 77% yield of a mixture of dimethyl *cis*- and *trans*-1,4-cyclohexanedicarboxylate (III). Even in the best runs considerable hydrogenolysis occurred, producing methyl *p*-toluate and methyl 4-methylcyclohexanecarboxylate. A partial saponification of III to produce methyl hydrogen 1,4-cyclohexanedicarboxylate (IV) was accomplished by a modification of the method of Fichter and Holbro[13] in which milder conditions were employed in order to simplify the purification of the half-ester. This process gave a 63% conversion to IV but, since 32% of the starting diester also was recovered, the yield of IV, based on unrecovered material, was 93%. The half-ester was treated with an excess of thionyl chloride and the resulting acid chloride was brominated at 100°. Esterification of the reaction product with methanol gave an 81% yield of the bromo ester V. An attempt was made to brominate III directly but, although the absorption of bromine was rapid at 130°, the resulting hydrogen bromide cleaved a substantial portion of the ester.

The bromo ester V was dehydrobrominated and saponified by treatment with a hot methanolic potassium hydroxide solution. The crude 1-

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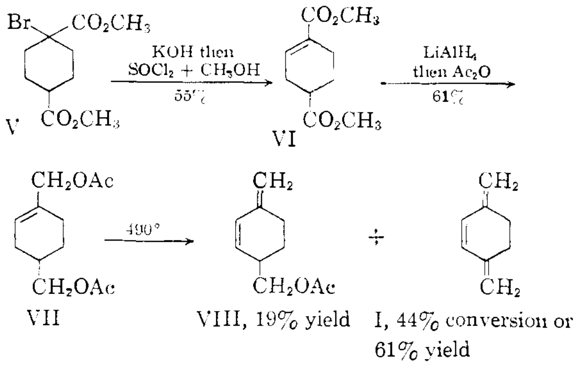

cyclohexene-1,4-dicarboxylic acid was not purified but was directly esterified with thionyl chloride and methanol to produce a 55% yield of dimethyl 1-cyclohexene-1,4-dicarboxylate (VI). An alternative procedure involving treatment with quinoline at 145–155° was less satisfactory since partial hydrolysis occurred and re-esterification of the reaction product gave only a 51% yield of VI.

When the unsaturated ester VI was treated with lithium aluminum hydride, incomplete reduction to the glycol resulted even after 58 hours. Apparently the complex arising from the reduction of one ester group is so insoluble that the reduction of the second ester group is extremely slow. This difficulty was circumvented by esterification of the crude glycol mixture with acetic anhydride, followed by re-treatment of the mixed esters with lithium aluminum hydride. The resulting glycol again was not isolated but was converted directly to 1,4-di-(acetoxymethyl)-2-cyclohexene (VII) in an over-all yield of 61%. The absence of a band at 890 cm.$^{-1}$ in the infrared spectrum of VII indicated that little or no isomerization to the methylene derivative had taken place.

Pyrolysis of the diacetate VII over Pyrex helices at 490° under such conditions that no charring occurred in the tube and 72% of two molar equivalents of acetic acid was liberated resulted in a 44% conversion to 1,4-dimethylene-2-cyclohexene (I). Since a 19% yield of a mixture of diene acetates VIII and a 9% recovery of diacetate also were obtained, the yield of triene I, based on unrecovered VII and VIII, was 61%. On the basis of ultraviolet absorption the mixture of diene acetates was assumed to consist primarily of the 1-methylene-4-acetoxymethyl-2-cyclohexene, together with very little of the isomeric 4-methylene-1-acetoxymethyl-1-cyclohexene.

The structure of 1,4-dimethylene-2-cyclohexene (I) was indicated by the fact that the ultraviolet absorption spectrum exhibited the three prominent maxima that are so characteristic of conjugated trienes.[14] The infrared spectrum is also consistent with a triene structure and indicated that little or no *p*-xylene was present in the pyrolysate. Vapor-phase chromatography showed a single symmetrical peak. Treatment of I with palladium-on-carbon resulted in polymerization plus isomerization to *p*-xylene, which was identified by its physical properties plus conversion to the solid trinitro derivative. Ozonolysis of the triene I gave formaldehyde plus succinic acid. Polymerization of I with either peroxide or boron trifluoride gave an insoluble polymer.

Thus it appears that the pyrolysis of esters is an excellent method for the preparation of strained or highly reactive unsaturated compounds. The application of this pyrolytic process to the preparation of other more demanding examples of reactive dienes and isomers of aromatic systems will be reported later.

It is interesting that 1,4-dimethylene-2-cyclohexene (I) is one of the few 1,3,5-hexatrienes for which the configurations of the groups around the double bonds are known with any degree of certainty.[15] The groups attached to the central double bond in the triene I must have the *cis* configuration, while many of the conventional methods of preparation of trienes would be expected to produce the *trans* configuration.

## Experimental[16]

**Dimethyl 1,4-cyclohexanedicarboxylate** (III).—A mixture of 643 g. (3.31 moles) of dimethyl terephthalate (II), 40 ml. of absolute ethanol and 36 g. of W-2 Raney nickel catalyst was hydrogenated for 1.8 hours at 140–185° and a hydrogen pressure of 35 atmospheres. After the reaction mixture was dissolved in hot ethanol, the solution was filtered to remove the catalyst and then chilled overnight at about 5°. Filtration of the cold slurry produced 48 g. (7%) of unreacted dimethyl terephthalate (II). After the ethanol had been removed from the filtrate by distillation under reduced pressure through a 12-inch, helix-packed column, the residue was fractionally distilled through the same column to give 54 g. of a forerun, b.p. 68–119° (7 mm.), and 512 g. (77%) of a mixture of dimethyl *cis*- and *trans*-1,4-cyclohexanedicarboxylate (III), b.p. 122.5–126.5° (6–7 mm.), $n^{31}\text{D}$ 1.4560 [reported[12] for dimethyl *cis*-1,4-cyclohexanecarboxylate, b.p. 110° (1 mm.), $n^{16}\text{D}$ 1.4595; reported[17] for dimethyl *trans*-1,4-cyclohexanecarboxylate, m.p. 71°].

Refractionation of the forerun through a 6-inch, helix-packed column yielded 15 g. (3%) of impure methyl 4-methylcyclohexanecarboxylate, b.p. 50–58.5° (3.0 mm.), $n^{25}\text{D}$ 1.4490 (reported[18] for the *cis* isomer, b.p. 198–198.5°, $n^{20}\text{D}$ 1.4459; for the *trans* isomer, b.p. 197–197.5°, $n^{20}\text{D}$ 1.4451); 26 g. (5%) of impure methyl *p*-toluate, b.p. 77–80° (3.7–4.0 mm.), $n^{25}\text{D}$ 1.5120; and 11 g. (2%) of impure dimethyl 1,4-cyclohexanedicarboxylate, b.p. 104.5–117.5° (3.6–3.8 mm.), $n^{25}\text{D}$ 1.4579. The crude methyl *p*-toluate was crystallized at low temperature from petroleum ether (b.p. 30–60°) to yield the pure ester, m.p. 32–35° (reported[19] m.p. 34–35°). The methyl *p*-toluate fraction (4.7 g.) was saponified to yield 3.12 g. (73%) in *p*-toluic acid, m.p. 180–181° (reported[20] m.p. 181°).

**Methyl Hydrogen 1,4-Cyclohexanedicarboxylate** (IV).—A mixture of 522 g. (2.61 moles) of refractionated III ($n^{25}\text{D}$ 1.4573, containing less than 2.4% of dimethyl terephthalate as indicated by ultraviolet analysis), 200 ml. of water and 4500 ml. of methanol was treated, over a period of 7.5 hours with stirring, with a solution of 121 g. of potassium hydroxide in 300 ml. of water. The temperature did not rise noticeably. After this solution had been stirred for an additional 13.5 hours, about 4000 ml. of solvent was removed by distillation under slightly reduced pressure. When the residue was diluted with 1300 ml. of water, an oil separated and

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(15) H. H. Inhoffen and G. Quinkert, *Chem. Ber.*, **87**, 1418 (1954).

(16) The authors are grateful to Dr. Mary H. Aldrich and Miss M. Kathryn Gerdeman for the microanalyses and to Miss Gerdeman and Dr. Joseph Wenograd for the infrared spectra. The infrared spectra were determined with a Beckman IR-4 infrared spectrometer on the pure liquids. The ultraviolet absorption spectra were determined on a Beckman D. U. spectrophotometer. All melting points are corrected.

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was extracted with four 300-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and the ether was removed by evaporation on a steam-bath in a current of air to yield 165 g. (32% recovery) of unreacted dimethyl 1,4-cyclohexanedicarboxylate (III).

After the aqueous solution had been cooled to 15° and acidified with 180 ml. of concentrated hydrochloric acid, the resulting mixture was extracted with 1100 ml. of ether in four portions. The combined ether solutions were dried over magnesium sulfate and the ether was removed by evaporation on a steam-bath to yield 310 g. (63%) of a crude solid mixture of methyl hydrogen *cis-* and *trans*-1,4-cyclohexanedicarboxylate (IV), melting over a wide range. The yield of IV, based on unrecovered III, was, therefore, 93%. A sample which was dried over calcium chloride and potassium hydroxide in a vacuum desiccator had a neutral equivalent of 185 (calcd. for $C_9H_{14}O_4$, 186).

**Dimethyl 1-Bromo-1,4-cyclohexanedicarboxylate (V).**—To 380 g. (2.04 moles) of methyl hydrogen 1,4-cyclohexanedicarboxylate (IV) was added 450 ml. (6.2 moles) of thionyl chloride (b.p. 75.8°, distilled from quinoline). Although the mixture initially became quite cold, when it was warmed slightly and stirred, a vigorous reaction ensued. The temperature gradually was raised to 87° over a period of 2.2 hours. After the solution was heated an additional 1.75 hours at 87–96°, it became clear. To the solution of the ester acid chloride was added, over a period of about 8 hours, 110 ml. (2.1 moles) of bromine (dried with sulfuric acid), while the temperature was maintained at 96–103°. The stirring was then continued for an additional 9 hours at 100–105°. After the reaction mixture had been cooled, the excess thionyl chloride and bromine were removed by distillation under slightly reduced pressure.

To 300 ml. of anhydrous methanol was added the crude bromination product over a period of 28 minutes. (The solution boiled gently even though the reaction flask was immersed in an ice-bath.) After the solution was heated under reflux for 1 hour, the cooled reaction mixture was poured into about 2 liters of water. The aqueous phase was extracted with ether and the combined organic layers were washed successively with 100 ml. of water, 500 ml. of a 2% sodium hydrogen sulfite solution, two 500-ml. portions of a 4% potassium carbonate solution and two 50-ml. portions of water. After the solution was dried over magnesium sulfate, the ether was removed by distillation at atmospheric pressure. The residue was distilled through a Claisen head to yield 520 g. (91%) of a crude mixture of dimethyl *cis-* and *trans*-1-bromo-1,4-cyclohexanedicarboxylate (V), b.p. 99–127° (0.3–0.9 mm.), $n^{25}D$ 1.4930. Refractionation through a 8.5-inch, helix-packed column produced an analytically pure sample, b.p. 92.5–99° (0.12–0.25 mm.), $n^{25}D$ 1.4914 (reported[17] for the *trans* isomer, m.p. 70–71°; *cis* isomer, a liquid with no physical constants reported).

**Dimethyl 1-Cyclohexene-1,4-dicarboxylate (VI).**—To a stirred solution of 528 g. (8 moles) of potassium hydroxide pellets in 1500 ml. of methanol, heated under reflux, was added 553 g. (1.98 moles) of crude dimethyl 1-bromo-1,4-cyclohexanedicarboxylate (V) over a period of 6.3 hours. After the heating had been continued for an additional 50 minutes, the suspension was allowed to stand overnight. About 700 ml. of solvent was removed by distillation under slightly reduced pressure, and the pasty residue was dissolved in 2 liters of water. The solution was acidified with 800 ml. of concentrated hydrochloric acid and cooled to about 27°. The precipitate, which was removed by filtration, was washed with three 500-ml. portions of water and dried overnight at about 75° to yield 250 g. (74%) of crude 1-cyclohexene-1,4-dicarboxylic acid.

After a mixture of the crude acid, 240 ml. (3.3 moles) of purified thionyl chloride and 300 ml. of anhydrous chloroform was heated under reflux for 5.8 hours, the resulting slurry was cooled in an ice-bath, 300 ml. of anhydrous methanol was added over a period of 40 minutes, and a violent reaction took place. When the resulting mixture was heated, a large amount of solid, possibly unreacted acid, remained undissolved. Therefore, a solution of 10 ml. of concentrated sulfuric acid in 200 ml. of anhydrous methanol was added, and the mixture was heated under reflux for 11 hours. The almost clear solution was cooled and poured into 1.5 liters of water. The aqueous phase was separated and extracted with 400 ml. of chloroform in three portions. The combined organic layers were washed with three 500-ml. portions of a 5% sodium bicarbonate solution, while the combined aqueous layers were extracted with 100 ml. of chloroform. After the combined chloroform solutions had been dried over magnesium sulfate, the chloroform was removed by distillation through a 12-inch, helix-packed column, first at atmospheric pressure and then under reduced pressure. The residue was fractionally distilled through the same column to yield 233 g. of a semi-solid product, b.p. 119–124.5° (3.5–4.2 mm.). This product was recrystallized from 500 ml. of petroleum ether (b.p. 30–60°) at −20° to yield 208 g. of dimethyl 1-cyclohexene-1,4-dicarboxylate (VI), m.p. 34–36° (reported[17] m.p. 39°). By concentration of the mother liquors, an additional 9 g. of product, m.p. 31–33°, was obtained. The total yield was 217 g. (55% over-all yield from V). The ultraviolet spectrum of VI, determined in absolute ethanol (0.011 g./liter), gave an $\epsilon_{max}$ at 217 m$\mu$ of 10,400.

**1-Cyclohexene-1,4-dimethanol Diacetate (VII).**—To a slurry of 62 g. (1.63 moles) of lithium aluminum hydride and 1800 ml. of anhydrous ether was added a solution of 220 g. (1.11 moles) of dimethyl 1-cyclohexene-1,4-dicarboxylate (VI) in 600 ml. of anhydrous ether over a period of 6 hours and heating was continued for an additional 58 hours. The excess lithium aluminum hydride was destroyed by the dropwise addition of 120 ml. of water, and the complexes were decomposed by the addition of 250 ml. of a saturated aqueous solution of potassium sodium tartrate. After the slurry had been stirred for 2.5 hours, the crystalline precipitate was removed by filtration and washed with several portions of ether. The combined filtrate and washings were dried over magnesium sulfate, and the ether was removed by distillation through a 12-inch Vigreux column. The residue was then fractionally distilled through the same column to yield 142 g. of impure diol, b.p. 115–148° (3.2–3.8 mm.).

To 525 ml. (5.5 moles) of refluxing acetic anhydride was added a solution of the crude reduction product in 65 ml. (1.1 moles) of acetic acid, over a period of 55 minutes. After the solution had been heated under reflux for an additional 9.4 hours, the excess acetic acid and acetic anhydride were removed by distillation through a 12-inch Vigreux column under reduced pressure. The residue was fractionally distilled through a 12-inch, helix-packed column to give 177 g. of a mixture of acetates, b.p. 115.5–139° (3.5–3.7 mm.).

The mixture of acetates was reduced with 40 g. (1.05 moles) of lithium aluminum hydride and the crude reaction product was acetylated with acetic anhydride (426 ml.) and acetic acid (55 ml.), essentially as described above. The yield of 1-cyclohexene-1,4-dimethanol diacetate (VII), b.p. 133–133.5° (3.0 mm.), $n^{25}D$ 1.4679, was 154 g. (61%). (Ultraviolet analysis indicated the absence of the partially reduced impurity.) The infrared spectrum of VII included the bands: 2879(s), 1730(vs), 1438(s), 1369(vs), 1270–1213(vs), 1177(w), 1150(w), 1130(vw), 1094(shoulder), 1052–1020(vs), 962(s), 927(vw), 900(m), 844.5(m), 811(m) and 767(vw) cm.$^{-1}$.

*Anal.* Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.89; H, 8.16.

**1,4-Dimethylene-2-cyclohexene (I).**—Over a period of 32 minutes, 21.1 g. (0.0933 mole) of 1-cyclohexene-1,4-dimethanol diacetate (VII) was dropped through a pyrolysis tube packed with $^1/_8$-inch Pyrex helices and externally heated at 490–495°, as described previously.[21] An ether solution of the pyrolysate was extracted several times with water to remove the acetic acid. (Titration of aliquots of the aqueous extract showed that 72% of two molar equivalents of acetic acid had been liberated.) The resulting solution was combined with the washed pyrolysate solutions obtained from two parallel batches. [The total amount of ester pyrolyzed was 63.1 g. (0.279 mole).] After the combined solutions had been dried over magnesium sulfate and a small amount of N-phenyl-2-naphthylamine had been added, the ether was removed by distillation through a 12-inch Vigreux column at atmospheric pressure. The residue was then fractionally distilled through the same column under reduced pressure to yield 13.0 g. (44%) of 1,4-dimethylene-2-cyclohexene (I), b.p. 57° (47 mm.), $n^{25}D$ 1.5398; 8.8 g. (19%) of a mixture of diene acetates, b.p. 73.5–79.5° (3.0–3.2 mm.), $n^{25}D$ 1.4795; and 5.6 g. (9%) of a mixture of olefin diacetates, b.p. 128.5–136° (3.0–3.3 mm.) (largely solidi-

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fied). Since the diene acetates and olefin diacetates could be repyrolyzed, the yield of I, based on unrecovered material, was 61%.

*Anal.* Calcd. for $C_8H_{10}$: C, 90.50; H, 9.50. Found: C, 90.70; H, 9.55.

The ultraviolet spectrum of a sample of the mixture of diene acetates showed an $\epsilon_{max}$ at 232 m$\mu$ of 11,700 (0.0166 g./liter in cyclohexane).

The ultraviolet spectrum of I, which was determined in cyclohexane solution (0.00129 g./liter). possessed three absorption maxima: $\epsilon_{max}$ at 274.5 m$\mu$ of 21,200, $\epsilon_{max}$ at 264 m$\mu$ of 30,000 and $\epsilon_{max}$ at 256 m$\mu$ (inflection) of 25,200. The infrared spectrum of I included the bands: 2917(s), 1771(m), 1622(s), 1438(s), 1382(w), 1315(vw), 1208(vw), 1167(vw), 1144(m), 978(w), 962(vw), 916(w), 891–875(vs), 820(s), 784(vw) and 733.5(m) cm.$^{-1}$. The absence of specific absorption at 795 cm.$^{-1}$, at which wave number (reported[22] 799 cm.$^{-1}$) *p*-xylene absorbs very strongly, indicated that no appreciable amount of *p*-xylene was present.

By the use of a model 154 Perkin–Elmer vapor fractometer with the "A" column at a temperature of 125°, the triene I gave a single symmetrical peak, with a retention time of 12.2 minutes. Since the retention time for *p*-xylene under the same conditions was 12.4 minutes, the infrared spectrum was used to indicate the absence of *p*-xylene.

**Isomerization of 1,4-Dimethylene-2-cyclohexene (I) to *p*-Xylene.**—In a test-tube fitted with an air-cooled condenser were placed 2.72 g. (0.0256 mole) of 1,4-dimethylene-2-cyclohexene (I), 0.20 g. of 10% palladium-on-carbon and 0.19 g. of hydroquinone. The test-tube was heated in an oil-bath, the initial temperature being 135°. After the initial vigorous reaction had subsided, the temperature was raised to 180° over a period of 2.25 hours and then maintained at 174–180° for 10.75 hours. After the reaction mixture was allowed to cool somewhat, it was distilled at a pressure of about 2 mm. The distillate was collected in two traps cooled in a Dry Ice–chloroform bath to yield 0.79 g. (29%) of crude *p*-xylene, $n^{24}_{D}$ 1.4890, m.p. approximately 5.3–11.2° (reported[23] $n^{25}_{D}$ 1.49319, f.p. 13.233°). The residue was apparently polymeric. The *p*-xylene was further characterized by comparison of its ultraviolet spectrum with that reported[24] for authentic *p*-xylene. The *p*-xylene also was converted to the trinitro derivative, m.p. 137.5–141° (reported[25] m.p. 139°). The melting point was not depressed by admixture with authentic trinitro-*p*-xylene.

**Ozonolysis of 1,4-Dimethylene-2-cyclohexene (I).**—A solution of 1.08 g. (0.0102 mole) of 1,4-dimethylene-2-cyclohexene (I) in 100 ml. of ethyl acetate was ozonized at 0°. A stream of oxygen containing 0.0013 mole of ozone per liter was passed through the sample for 8 hours at an average rate of 6.8 liters per hour. Formaldehyde that evolved during ozonization was collected in a water trap and identified as the dimethone derivative, m.p. 190.5–191.5° (reported[26] m.p. 191–191.5°). The melting point was not depressed by admixture with an authentic sample of the derivative.

The ethyl acetate was removed by distillation under reduced pressure, and the residual ozonide was decomposed by heating for 5 hours on a steam-bath with 25 ml. of 30% hydrogen peroxide and 40 ml. of glacial acetic acid. After a platinum wire had been added in order to catalyze the decomposition of the excess peroxide, the hot solution was stirred for 40 hours; water was added at intervals to maintain the volume. The water was removed by evaporation at atmospheric pressure to leave a gummy residue. This residue was extracted with several portions of aqueous acetone (a small amount was insoluble). After the solvent had been removed by evaporation, the residue was recrystallized from a very small amount of water to yield 0.32 g. (27%) of slightly impure succinic acid, m.p. 179–183° (reported[25] m.p. 185°); the melting point of a mixture with authentic succinic acid was 180.5–184.5°. The succinic acid was converted to N,N'-di-*p*-tolylsuccinamide, m.p. 255.5–259.5° (reported[27] m.p. 260°); the melting point of a mixture with an authentic sample was 256.5–260°.

**Polymerization of 1,4-Dimethylene-2-cyclohexene (I).**—A mixture of 0.48 g. (0.0045 mole) of 1,4-dimethylene-2-cyclohexene (I), 0.0077 g. (0.000033 mole) of benzoyl peroxide and 7 ml. of benzene was heated under reflux for 46 hours. An additional 0.0303 g. (0.000131 mole) of benzoyl peroxide was added in four portions during the heating. The solution was filtered, and the filtrate was poured slowly into 100 ml. of methanol. After a small amount of N-phenyl-2-naphthylamine was added, the solution was allowed to stand for 3 days. The coagulated polymer was then removed by filtration, washed with methanol and dried in a vacuum desiccator at about 2 mm. pressure for 2 days. The yield of dry polymer was 0.018 g. (4%). The polymer, softening point about 150–155°, was insoluble in boiling benzene.

To a mixture of 0.45 g. (0.0042 mole) of 1,4-dimethylene-2-cyclohexene (I) and 5 ml. of carbon disulfide, thoroughly cooled in a Dry Ice–acetone bath, was added a small amount of boron trifluoride gas. The mixture was allowed to remain in the bath for 19.5 hours with occasional shaking. To the solution was added 1 ml. of cold methanol, and the system (one solid and two liquid phases) was stirred while it was allowed to warm to room temperature. After the reaction mixture was poured into 55 ml. of methanol, the resulting polymer was removed by filtration, washed with methanol and dried at about 2 mm. pressure for 36 hours to yield 0.08 g. (18%) of a white polymer. The polymer did not dissolve to any visible extent in either hot benzene or diphenyl ether.

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