2-Hydroxy-2-methyl-1-phenylpropane.—1-Phenyl-2-propanone, 268 g., was treated with methylmagnesium iodide to give 273 g. (82%) of product,[14] b.p. 98° (10 mm.), n^{20}_{D} 1.5133.

β,β-Dimethylstyrene.—2-Hydroxy-2-methyl-1-phenylpropane was dehydrated with a trace of 85% phosphoric acid in xylene solution to give a 76% yield of product,[14] b.p. 188–189°. Careful fractionation of the reaction mixture gave some 2-methyl-3-phenyl-1-propene, b.p. 177°.

2-(2-Hydroxyphenyl)-2-methyl-1-phenylpropane (X).—β,β-Dimethylstyrene, 132 g., was treated with phenol (4 moles) in the usual manner to give 162 g. (71%) of product, b.p. 147° (1 mm.).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 85.0; H, 8.0.

The infrared spectrum (neat) of this compound exhibited a doublet at 1340 and 1380 cm.$^{-1}$, and none in the 810-cm.$^{-1}$ region.

Oxidation of 2-(2-Hydroxyphenyl)-2-methyl-1-phenylpropane (X) with Potassium Permanganate.—Phenol X, 42.2 g., was dissolved in 1.5 l. of water containing 40 g. of potassium hydroxide, and to the resulting stirred solution was slowly added 216 g. of potassium permanganate at 85°. The reaction mixture was filtered and the filtrate was acidified and extracted with ether. The ether layer was dried and evaporated, and the residue was dissolved in 150 ml. of dry methanol containing 7.5 g. concentrated sulfuric acid and refluxed for 2 hr. The cooled solution was diluted with water, extracted with ether, and the ether extract was washed with sodium bicarbonate and water. The dried ether solution was fractionally distilled to give 5.2 g. (20%) of methyl benzoate, b.p. 71° (10 mm.), 2.6 g. (7%) of methyl 2,2-dimethyl-3-phenylpropionate, b.p. 106°, (10 mm.), and 10.9 g. (27%) of methyl 3,3-dimethyl-2-keto-4-phenylbutanoate, b.p. 141° (10 mm.).

Methyl 2,2-dimethyl-3-phenylpropionate was identified by conversion in 76% yield to the corresponding anilide,[15] m.p. 108–108.5°.

The keto ester was redistilled for analysis.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3; sapon. equiv. 220. Found: C, 71.0; H, 7.3; sapon. equiv. 224.

The n.m.r. spectrum (neat) of this material exhibited sharp peaks at δ = 1.13, 2.93, 3.63, and 7.13.

Reduction of this keto ester with lithium aluminum hydride gave, after chromatography on alumina, the corresponding glycol in 87% yield. The presence of a benzyl group was demonstrated by the presence in its nuclear magnetic resonance spectrum (neat) of a band at δ = 2.55.[8]

Acknowledgment.—The authors are indebted to Dr. C. A. Reilly for the determination and interpretation of the n.m.r. spectra reported in this work. They also wish to acknowledge the initial isolation of bisphenol V by Dr. W. T. Tsatsos.

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Cyclic Dienes. XXVIII. 3,4-Dimethylenetetrahydrofuran[1,2]

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3,4-Dimethylenetetrahydrofuran, which is isomeric with 3,4-dimethylfuran, was prepared in a four-step synthesis from dimalonic ester. The key step involved the pyrolysis of a diacetate at 605° under reduced pressure to produce a 24% yield of the diene. The structure of the diene was indicated by analysis and ultraviolet, infrared, and nuclear magnetic resonance spectra, as well as by conversion to three solid Diels–Alder adducts.

In previous articles in this series the synthesis of isomers of aromatic compounds, such as 4,5-dimethylenecyclohexene[3] isomeric with *o*-xylene, 3,6-dimethylenecyclohexene[4] isomeric with *p*-xylene, and 5-methylene-1,3-cyclohexadiene[5] isomeric with toluene, have been reported. It was of interest to extend this series to include the preparation of some isomers of aromatic heterocycles. In view of Marvel's[6,7] failure to obtain 3,4-dimethylenethiophane by pyrolysis of the corresponding diacetate, the more stable furan system was studied. Thus the synthesis of 3,4-dimethylenetetrahydrofuran (I), which is isomeric with 3,4-dimethylfuran (I), was investigated. The diene I, also, can be regarded as an isostere of 4,5-dimethylenecyclohexene. This diene I was of additional interest for the preparation of a cyclic all-*cis* polymer[8] that could be opened under basic conditions to a noncyclic all-*cis* polymer. A method for the reductive cleavage of the tetrahydrofuran ring with lithium aluminum hydride and aluminum chloride was previously reported.[9]

Since the pyrolysis of esters had been successful for the preparation of other isomers of aromatic compounds,[3] this method was selected for the preparation of 3,4-dimethylenetetrahydrofuran (I). The required diacetate II was prepared in three steps from dimalonic ester III in an over-all yield of 17%. Thus ethyl 1,1,2,2-ethanetetracarboxylate (III) was dialkylated with α,α'-dichloromethyl ether with sodium hydride to give ethyl 3,3,4,4-tetrahydrofurantetracarboxylate (IV) in a 48% yield. (The formation of substantial quantities of a high boiling residue suggests the competing formation of a polymer or a larger ring.) Hydrolysis of IV, followed by decarboxylation, gave the solid 3,4-tetrahydrofurandicarboxylic acid (V); however, because of the high water solubility of V, it was usually not isolated but was directly esterified to give a 37% over-all yield of ethyl 3,4-tetrahydrofurandicarboxylate (VI). By the method of one-step reduction and acetylation with lithium aluminum hydride and acetic anhydride,[10] VI was converted to the diacetate II in a 60% yield. When these three steps were carried out without the isolation of any of the intermediates, a 17% yield of II from III was obtained.

When 3,4-di(acetoxymethyl)tetrahydrofuran (II) was added dropwise to a Vycor tube packed with glass helices at temperatures of 445 to 605°, the yield of 3,4-dimethylenetetrahydrofuran (I) was only 1 to 4%. Since pyrolysis under reduced pressure had been shown to increase dramatically the yields in the preparation of

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[1] Previous paper in this series, *J. Org. Chem.*, **27**, 3479 (1962).

[2] This work was supported in part by a grant from the National Science Foundation.

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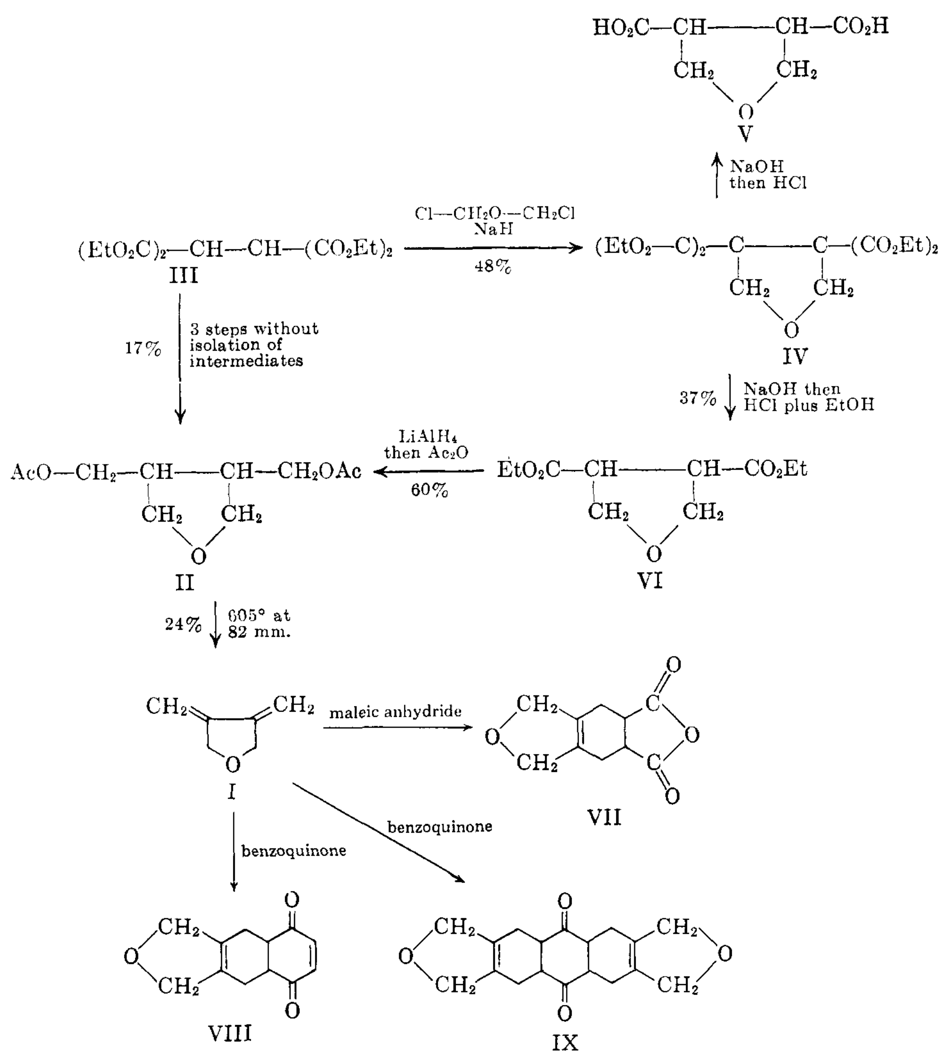

2,3-divinyl-1,3-butadiene[11] and 1,2,4,5-tetramethylenecyclohexane,[12] II was pyrolyzed at 605° under a pressure of 82 mm. to produce a 24% yield of the diene I. A preparative gas chromatograph facilitated the isolation and purification of the diene.

The ultraviolet absorption spectrum of 3,4-dimethylenetetrahydrofuran (I) showed an $\epsilon_{\max}$ of 9820 at 244 mμ. Although Woodward's rules[13] would predict a maximum at 237 mμ, cyclic dienes with coplanar methylene groups have been shown to absorb at longer wave lengths; 1,2-dimethylenecyclopentane[14] at 243 mμ and 2,3-dimethylenebicyclo[2.2.1]heptane[15] at 248 mμ. In contrast, simple derivatives of furan have practically no absorption above 220 mμ.[16] The infrared spectrum of I, which had strong bands at 890, 1065, 1725, and 2940 cm.$^{-1}$ and moderate bands at 770, 917, 1128, 1175, 1224, 1425, and 1685 cm.$^{-1}$, was consistent with the assigned structure. Finally, the n.m.r. spectrum of I in carbon tetrachloride with tetramethylsilane as a reference showed peaks at 4.62, 5.07, and 5.60 p.p.m. with the relative peak areas in the ratio of 1:1:2. The first two peaks were assigned to the terminal methylene hydrogens and the last peak to the methylene hydrogens adjacent to the ether oxygen. One would expect the hydrogen atoms of the terminal methylene to be nonequivalent because of the rigid planar structure of the diene I. The 3,4-dimethylenetetrahydrofuran (I) was further characterized by conversion to a Diels–Alder adduct, $\Delta^{3a(7a)}$-hexahydrobenzo[c]furan-5,6-dicarboxylic anhydride (VII), with maleic anhydride and to both a monoadduct VIII and a diadduct IX with benzoquinone.

The chemistry of this interesting diene will be reported separately.

Experimental[17]

Tetraethyl 3,3,4,4-Tetrahydrofurantetracarboxylate (IV).—To 1850 ml. of dry dioxane (purified and dried according to the procedure of Fieser[18]) were added 318 g. (1.0 mole) of tetraethyl 1,1-2,2-ethanetetracarboxylate (III) and 48 g. (2.0 moles) of sodium hydride. After the reaction mixture was heated and stirred under reflux for 1 hr., 115 g. (1.0 mole) of *sym*-chloromethyl ether[19] was added dropwise over a period of 1 hr. The mixture was allowed to stir under reflux for an additional 24 hr. and then cooled to 50°. After the white precipitate of sodium chloride was removed by filtration, the filtrate was concentrated by removal of solvent by distillation under reduced pressure. The residue was then fractionally distilled through a 10-in. Vigreux column to yield 173 g.

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[17] The authors are indebted to Dr. Franz Kasler, Mrs. Kathryn Baylouny, Mrs. Jane Ratka, and Mrs. Christine Nielsen for the microanalyses and to Dr. Edwin Becker of the National Institutes of Health for the n.m.r. spectrum and aid in its interpretation.

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(48%) of tetraethyl 3,3,4,4-tetrahydrofurantetracarboxylate (IV), b.p. 166° (1.5 mm.), n^{25}D 1.4532.

Anal. Calcd. for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.48; H, 6.98.

Infrared spectrum of the liquid tetraester IV showed strong bands at 862, 948, 1020, 1087, 1125, 1220–1300, 1372, 1720–1750, and 3020 cm.$^{-1}$ and medium bands at 769, 788, 810, 1177, 1400, 1450, 1488, 1640, and 1800 cm.$^{-1}$.

3,4-Tetrahydrofurandicarboxylic Acid (V).—After a mixture of 368 g. (1.02 moles) of tetraethyl 3,3,4,4-tetrahydrofurantetracarboxylate (IV), 100 ml. of absolute ethyl alcohol, and a solution of 204 g. (5.10 moles) of sodium hydroxide in 1350 ml. of distilled water was heated under reflux for 40 hr., the reaction mixture was cooled to room temperature and acidified by the slow addition of 425 ml. of 37% hydrochloric acid. The aqueous solution was then exhaustively extracted with ether for 60 hr. After the ether was removed by evaporation, the residual product was used in the subsequent reaction. However, a small portion of this material was concentrated to give an orange-colored viscous oil. Distillation of this material under reduced pressure gave only a small amount of distillable material and a solid. Recrystallization of this solid material from ethyl acetate gave the 3,4-tetrahydrofurandicarboxylic acid (V), m.p. 120–121°.

Anal. Calcd. for $C_6H_8O_5$: C, 45.00; H, 5.04. Found: C, 44.99; H, 4.92.

Diethyl 3,4-Tetrahydrofurandicarboxylate (VI).—The brownish orange oil which was obtained in the experiment described above was added to 4450 ml. of dry benzene, 1025 ml. of absolute ethyl alcohol, and 30 ml. of concentrated sulfuric acid in a 12-l., three-necked flask, equipped with a stirrer, a condenser protected with a drying tube containing calcium chloride, and a Dean–Stark trap for the removal of the ternary azeotrope. After the mixture was heated under reflux for 168 hr. (until the formation of the additional second layer was negligible), the material was concentrated to approximately 1 l. by removal of the solvents by distillation under atmospheric pressure. An ether solution of the residue was washed with water and then with a 10% aqueous solution of sodium bicarbonate. After the ether layer was dried over magnesium sulfate and the ether was removed by evaporation, the residue was fractionated through a 10-in. Vigreux column to give 81.6 g. (37% based on IV) of diethyl 3,4-tetrahydrofurandicarboxylate (VI), b.p. 84–85° (0.3 mm.), n^{25}D 1.4438.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.70; H, 7.59.

3,4-Bis(acetoxymethyl)tetrahydrofuran (II). A. **From Diethyl 3,4-Tetrahydrofurandicarboxylate** (VI).—To a 3-l., three-necked flask, equipped with a stirrer, a dropping funnel, and a condenser protected with a drying tube containing calcium chloride, were added 68.5 g. (1.80 moles) of lithium aluminum hydride and 2 l. of anhydrous ether. While the slurry was heated under reflux, a solution containing 65.0 g. (0.30 mole) of diethyl 3,4-tetrahydrofurandicarboxylate (VI) dissolved in 250 ml. of anhydrous ether was added during a 1-hr. period. After the mixture had been heated under reflux for 24 hr., the excess lithium aluminum hydride was decomposed by the dropwise addition of 360 g. of glacial acetic acid. The anhydrous ether was replaced by *n*-butyl ether by concurrent removal of the former by distillation and the addition of the latter. While the mixture was heated under the reflux temperature of *n*-butyl ether, 612 g. of acetic anhydride (tenfold excess) was added, and the mixture was heated under reflux for 125 hr. The inorganic salts were removed from the cooled reaction mixture by filtration through a Büchner funnel, followed by washing of the solid with two 200-ml. portions of *n*-butyl ether. The combined organic solutions were concentrated to a smaller volume by removal of excess acetic anhydride and *n*-butyl ether under reduced pressure, and the residue was fractionated through a 10-in. Vigreux column to afford 39.0 g. (60%) of 3,4-bis(acetoxymethyl)tetrahydrofuran (II), b.p. 96° (0.2 mm.), n^{25}D 1.4492.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.46; H, 7.58.

The infrared spectrum of the diacetate II showed strong bands at 930, 977, 1032–1050, 1085, 1220–1260, 1362, 1715–1730, 2845, and 2930 cm.$^{-1}$ and weak bands at 832, 1430, 1645, and 3280 cm.$^{-1}$.

B. **From Tetraethyl 1,1,2,2-Ethanetetracarboxylate** (III).—After a mixture of 2500 ml. of dry dioxane, 642 g. (2.02 moles) of tetraethyl 1,1,2,2-ethanetetracarboxylate (III), and 97 g. (4.04 moles) of sodium hydride was heated and stirred under reflux for 1 hr., the enolate was alkylated with 232 g. (2.02 moles) of *sym*-chloromethyl ether, as described above. After the sodium chloride was removed by filtration through a Büchner funnel, the filtrate was concentrated by removal of the solvent by distillation under reduced pressure. After the residue, along with 200 ml. of absolute ethyl alcohol and a solution of 404 g. (10.1 moles) of sodium hydroxide dissolved in 2500 ml. of distilled water, was heated under reflux for 60 hr., the reaction mixture was cooled to room temperature and made acidic by the slow addition of 840 ml. of 37% hydrochloric acid. After the aqueous solution was exhaustively extracted with ether for 72 hr., the ether was removed by evaporation and the residual product (541 g.) was esterified with 3250 ml. of dry benzene, 700 ml. of absolute ethyl alcohol, and 35 ml. of concentrated sulfuric acid. The mixture was concentrated to approximately 1 l. by removal of the solvents by distillation under atmospheric pressure. An ether solution of the residue was washed with water and then with a 10% aqueous sodium bicarbonate solution. After the ether layer was dried, the crude material was distilled through a 10-in. Vigreux column to give 105 g. of crude diethyl 3,4-tetrahydrofurandicarboxylate (VI), b.p. 100–130° (1 mm.), n^{25}D 1.4427. This material was reduced with 112 g. (2.94 moles) of lithium aluminum hydride and 2500 ml. of anhydrous ether, and the reaction product was acetylated with 588 g. of glacial acetic acid and 100 g. of acetic anhydride (tenfold excess) in 125 hr. Fractionation of the crude product through a 10-in. Vigreux column afforded 73 g. (17.4% based on III) of 3,4-bis(acetoxymethyl)tetrahydrofuran (II).

3,4-Dimethylenetetrahydrofuran (I).—At the rate of 1 g. per min., 18.5 g. of 3,4-bis(acetoxymethyl)tetrahydrofuran (II) was dropped into a Vycor tube packed to a depth of 10 in. with $^1/_8$-in. Pyrex helices and externally heated at a temperature of 605°, as previously described.[20] While a slow stream of purified nitrogen was continuously introduced into the system, a pressure of 82 mm. was maintained during the course of the pyrolysis to remove the pyrolysis products from the tube as quickly as possible and to prevent any charring. With the pyrolysate initially condensed by a 6-in., water-cooled spiral condenser, 15.2 g. of pyrolysate was collected in a flask immersed in a Dry Ice–acetone bath. By allowing the pyrolysate to come to room temperature under reduced pressure (0.3 mm.), 8.4 g. of volatile products was distilled from the pyrolysate and collected in a second flask immersed in a Dry Ice–acetone bath to leave 6.8 g. of recovered material in the first flask. Acetic acid was removed from the 8.4 g. of flash distillate by extraction with two portions of cold saturated sodium bicarbonate solution to leave 2.2 g. of acid-free material which was then fractionated by vapor chromatography in an 8-ft. U-tube of 10-mm. Pyrex glass, packed with 20% Carbowax 20-M on 20–40-mesh Chromosorb support. As indicated by its peak on the chromatogram, the eluted diene I amounted to 58% of the flash distillate (or 1.28 g.) and was collected in an apparatus attached to the exit port of the chromatograph and cooled in a Dry Ice–acetone bath.

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.39. Found: C, 74.88; H, 8.39.

Based on a 37% recovery of material (assumed to be recovered diacetate II and presumably the monoölefin acetate), 3,4-dimethylenetetrahydrofuran (I) was obtained in a 24.4% yield.

When 23.0 g. of the residue from the flash distillation described above, which was assumed to be mostly 3,4-bis(acetoxymethyl)-tetrahydrofuran (II) and monoölefin acetate, was dropped through a Vycor tube under the identical conditions described above, with only moderate charring, 8 g. of flash distillate and 11 g. of recovered material were obtained. Acetic acid was extracted from the flash distillate with portions of cold sodium bicarbonate solution to leave 1.8 g. of the diene-enriched layer. Fractionation of this layer by gas chromatography with the column described under identical conditions showed the diene to comprise 1.04 g. (58%) of this layer. Based on a 48% recovery of material assumed to be recovered diacetate II and possibly monoölefin acetate, a 20% yield of 3,4-dimethylenetetrahydrofuran was obtained.

With a Beckman DK-1 recording spectrophotometer the ultraviolet absorption spectrum (between 210 and 360 mμ) was run on a 1.271×10^{-5} M solution of 3,4-dimethylenetetrahydrofuran in isoöctane to give an $\epsilon_{\max}$ of 9820 at 244 mμ. The infrared absorption spectrum of the diene was obtained with a film technique on a Beckman IR-5 spectrophotometer.

With a Varian HR-60 nuclear magnetic resonance spectrom-

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eter the n.m.r. spectrum of 3,4-dimethylenetetrahydrofuran (I) in purified carbon tetrachloride containing a drop of tetramethylsilane as an internal standard was obtained at an electromagnet frequency of 60 Mc. Assignment of band positions on the spectrogram was accomplished by use of an audio side band of known frequency. Peak distances on the spectrogram were measured in cycles per second from the tetramethylsilane peak and then converted to τ values (p.p.m.). Three peaks were observed at 4.62, 5.07, and 5.60 p.p.m., with relative peak area ratios of 1:1:2, respectively.

$\Delta^{3a(7a)}$-**Hexahydrobenzo[*c*]furan-5,6-dicarboxylic Anhydride (VII).**—A small amount (*ca.* 0.5 g.) of the diene-enriched fraction (described above) was added to a small amount (*ca.* 0.3 g.) of sublimed maleic anhydride. Immediately the mixture generated considerable heat and upon cooling deposited a solid material which was collected on a Büchner funnel and washed with copious amounts of anhydrous ether. The solid was recrystallized from an ethyl alcohol–ether mixture (1:9 by volume) and then from a benzene–petroleum ether mixture containing a few drops of acetic anhydride to obtain 0.6 g. of the white, crystalline $\Delta^{3a(7a)}$-hexahydrobenzo[*c*]furan-5,6-dicarboxylic anhydride (VII), m.p. 118–121°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 61.85; H, 5.19. Found: C, 61.84; H, 5.34.

$\Delta^{3a(9a),6(7)}$-**Octahydronaphtho[2,3-*c*]furan-5,8-dione (VIII).**—A small amount (*ca.* 0.5 g.) of the diene-enriched fraction (described above) was added to a small amount (*ca.* 0.5 g.) of *p*-benzoquinone. After the mixture was allowed to stand overnight, crystals which had deposited were collected on a Büchner funnel and washed with anhydrous ether to give approximately 0.4 g. of the 1:1 adduct of *p*-benzoquinone and 3,4-dimethylenetetrahydrofuran, $\Delta^{3a(9a),6(7)}$-octahydronaphtho[2,3-*c*]furan-5,8-dione (VIII), m.p. 129–131°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93. Found: C, 70.80; H, 6.20.

$\Delta^{3a(12a),6a(9a)}$-**Tetradecahydroanthra[2,3-*c*:6,7-c′]difuran-5,11-dione (IX).**—When the filtrate from which the 1:1 adduct of *p*-benzoquinone and 3,4-dimethylenetetrahydrofuran (I) had been isolated was cooled, an additional adduct (*ca.* 0.1 g.) was deposited as the 1:2 adduct, $\Delta^{3a(12a),6a(9a)}$-tetradecahydroanthra-[2,3-*c*: 6,7-*c*′]difuran-5,11-dione (IX), which sublimed at 185° (cor.).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.18; H, 7.00.

Paracyclophane Derivatives by the Dieckmann Cyclization

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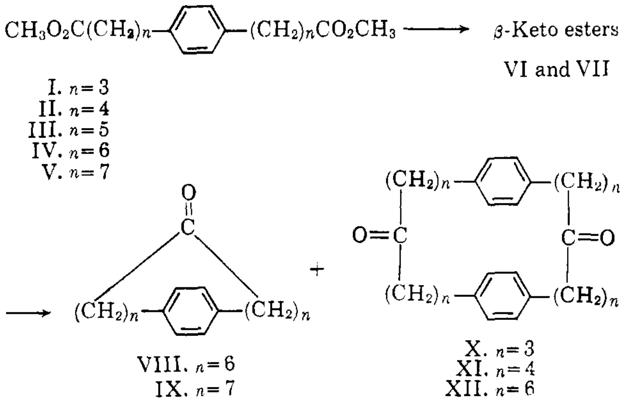
The Dieckmann condensation under conditions of high dilution has been used with the esters of *p*-phenylenedicarboxylic acids. The products, several ketone derivatives of [*n*]paracyclophanes and [*n.n*]paracyclophanes, are described.

Ever since it was shown that macrocycles could be prepared by the Dieckmann cyclization,[2,3] we have wondered if this reaction might be used to prepare derivatives of paracyclophanes. This reaction appeared to be desirable for making compounds with odd-numbered carbon bridges from symmetrical *p*-phenylenedicarboxylic esters, which have led to compounds with even-numbered carbon bridges in the acyloin cyclization.[4] Moreover, it was believed that dimeric derivatives might be made in cases where intramolecular cyclization proved to be impossible.

Precursor diesters were prepared by standard methods; each of the previously known diesters possessed physical properties which agreed with those earlier described.[5–7] *p*-Bis(3-carboxypropyl)benzene was prepared from 4-(*p*-succinylphenyl)butyric acid by the catalytic method of Horning and Reisner.[8] Methyl esters were made by the method of Clinton and Laskowski.[9] *p*-Bis(4-carboxybutyl)benzene was prepared by the action of sodium cyanide on *p*-bis(4-bromobutyl)benzene followed by hydrolysis. *p*-Bis(5-carboxypentyl)benzene was prepared by a malonic ester synthesis with *p*-bis(4-bromobutyl)benzene. In order to prepare *p*-bis(6-carboxyhexyl)benzene, it was necessary to treat *p*-bis(5-carbomethoxypentyl)benzene with lithium aluminum hydride, treat the glycol with hydrogen bromide, allow the dibromide to react with cyanide, and then hydrolyze the dinitrile. This same dibromide was part of a malonic ester synthesis to produce *p*-bis-(7-carboxyheptyl)benzene.

It was found possible to prepare ketone derivatives of paracyclophanes by the method of Dieckmann, although in low yields. From the mixtures, following hydrolysis and decarboxylation of the β-keto esters formed during the reactions, four products were obtained by fractional crystallization and one product was obtained by distillation. No attempts were made to isolate the intermediates VI ($C_{9+2n}H_{6+4n}O_3$) and VII ($C_{18+4n}H_{12+8n}O_6$). From I was produced 4,17-diketo[7.7]paracyclophane (X) in 11.1% yield; from II was produced 5,20-diketo[9.9]paracyclophane (XI)



I. $n = 3$
II. $n = 4$
III. $n = 5$
IV. $n = 6$
V. $n = 7$

VIII. $n = 6$
IX. $n = 7$

X. $n = 3$
XI. $n = 4$
XII. $n = 6$

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