same way. Hexane was added and the solution was held at 4°. The yield of crystalline XIV was 4.3 g., m.p. 95–96°.

Anal. Calcd. for $C_{19}H_{15}ClO_4$: C, 66.6; H, 4.41. Found: C, 66.7; H, 4.71.

3-(α-Acetonylbenzyl)-4-methoxycoumarin (XV).—To a stirred benzene solution of 0.015 mole of dimethylcadmium[8] was added 2.7 g. (0.015 mole) of XIV. The mixture was refluxed 15 min. and poured into 100 ml. of 5% hydrochloric acid and 50 ml. of ethyl acetate. The organic phase was separated and washed with 100-ml. portions of water, 5% sodium hydroxide and water. After drying with magnesium sulfate the solution was concentrated under vacuum to a dark oil which was dissolved in the minimum amount of methanol, treated with Darco KB charcoal and held at 4° for several days. The product was collected and recrystallized from methanol, m.p. 125–127°. The m.p. of a mixture with authentic XV[9] was not depressed. The product and authentic XV had essentially identical infrared spectra: $\lambda_{\max}^{CHCl_3}$ 3.29, 5.85, and 6.19 μ.

Warfarin (I).—A solution of 0.5 g. of XV in 5 ml. of acetic acid and 5 ml. of 48% aqueous hydrobromic acid was refluxed 1 hr. and poured into 50 ml. of ice and water. The dark solid was collected, washed with water, and dissolved in 25 ml. of 1% sodium hydroxide. This solution was treated with Darco KB charcoal and acidified with concentrated hydrochloric acid. The gummy product was collected by centrifuging. It crystallized after standing several days at 4° in acetone-water. After recrystallization from acetone-water the product had m.p. 160–161° and an infrared spectrum identical to that of authentic I.

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[8] J. Cason, *J. Am. Chem. Soc.*, **68**, 2080 (1946).

[9] M. Ikawa, Ph.D. thesis, University of Wisconsin (1948).

Pyrolysis of Esters. XXIII. 2,3-Divinyl-1,3-butadiene[1-3]

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Received July 18, 1961

2,3-Divinyl-1,3-butadiene was prepared in a three-step synthesis from commercially available 1,2,3,4-butanetetracarboxylic acid in an over-all yield of 20%. In the key step, pyrolysis of a tetraacetate at 50 mm. pressure and 590° gave a 25% yield of the tetraene. The structure of the tetraene was proved by analysis, hydrogenation to the known 3,4-dimethylhexane, conversion to solid Diels-Alder adducts, infrared and ultraviolet absorption spectra, and NMR spectrum.

In a research program on Diels-Alder polymerization it was necessary to prepare a series of polyfunctional dienes. Initially, 2-vinyl-1,3-butadiene was prepared by the pyrolysis of a triacetate[4] and this triene was used to prepare polymeric Diels-Alder adducts[5] with such bifunctional dienophiles as benzoquinone and the bismaleimides. More recently, we reported the synthesis of the very interesting 2-hydroxymethyl-1,3-butadiene[6] and showed how this polyfunctional compound could be converted to bifunctional dienes[7] for use in the Diels-Alder polymerization.[5] In order to make the Diels-Alder polymerization more general, a trifunctional diene which would produce a three-dimensional polymer was required. The simplest compound containing three diene systems is the tetraene, 2,3-divinyl-1,3-butadiene (I). This tetraene I was also of interest because it contained two overlapping cross-conjugated diene systems and would be of use in the preparation of polynuclear aromatic hydrocarbons through Diels-Alder reactions.[8]

The starting material for the synthesis of 2,3-divinyl-1,3-butadiene (I) was the commercially available 1,2,3,4-butanetetracarboxylic acid, which was esterified in a 72% yield to give tetraethyl 1,2,3,4-butanetetracarboxylate (II). By the method of reductive acetylation[4] with lithium aluminum hydride and acetic anhydride that was developed in this laboratory, the tetraester II was converted to 1,6-diacetoxy-3,4-di(acetoxymethyl)hexane (III) in an 84% yield. This method essentially involves the reduction of the tetraester II, but in place of the usual hydrolysis to the tetraol, which would be very difficult to isolate from the aqueous solution of the lithium and aluminum salts, the reduction product was acetylated to give the ether-soluble tetraacetate III. The structure of the tetraacetate III was indicated by hydrolysis to 3,4-di(hydroxymethyl)-1,6-hexanediol in a 93% yield.

When the tetraacetate III was dropped through the pyrolysis tube at 540°, a complex mixture of at least twenty products resulted. Gas phase chromatography indicated that only two of these components had a boiling point in the range of 105–123° by comparison of their retention times on a silicone column with those of octene-1, 4,4-dimethyl-1-hexene, toluene, and tetrachloroethylene. The materials corresponding to both of these peaks were collected from the chromatograph and one was tentatively assigned the structure of 2,3-divinyl-1,3-butadiene (I) on the basis of its absorption maximum in the ultraviolet at 217 mμ. Since this

[1] Previous paper in this series, *J. Org. Chem.*, **27**, 2732 (1962).

[2] Presented before the Division of Polymer Chemistry at the 140th Meeting of the Am. Chem. Soc., Chicago, Illinois, September, 1961.

[3] This work was supported in part by a grant from the National Science Foundation and by a grant from the Petroleum Research Fund of the American Chemical Society.

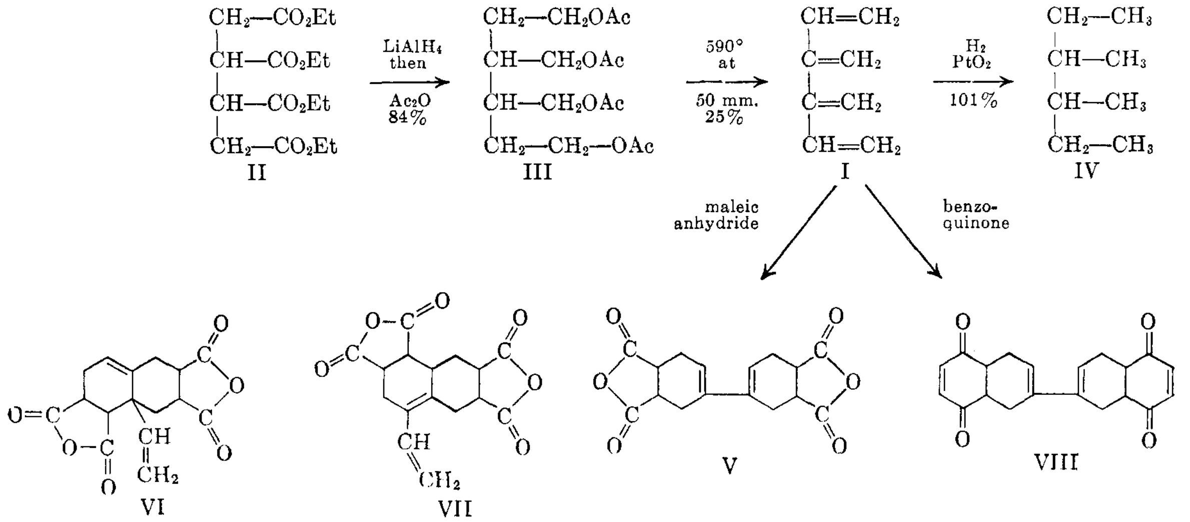
[4] W. J. Bailey and J. Economy, *J. Am. Chem. Soc.*, **77**, 1133 (1955).

[5] W. J. Bailey, J. Economy, and M. E. Hermes, *J. Org. Chem.*, **27**, 3295 (1961).

[6] W. J. Bailey, W. G. Carpenter, and M. E. Hermes, *ibid.*, *Chem.*, **27**, 1975 (1962).

[7] W. J. Bailey and M. E. Hermes, *ibid.*, **27**, 2732 (1962).

[8] W. J. Bailey and C.-W. Liao, *J. Am. Chem. Soc.*, **77**, 992 (1955).



peak represented less than a 1% yield of the tetraene I, a systematic investigation of the conditions necessary to produce the maximum yield of the tetraene was undertaken. For the preliminary screening of conditions for the optimum yields, 0.05-g. samples of the tetraacetate III were injected into a micropyrolysis apparatus from which the hot pyrolysates were introduced directly onto a gas-phase chromatograph. Changes in temperature of pyrolysis, packing, contact time, or rate of addition had little effect on the yield of tetraene I. Although dilution of the tetraacetate with mesitylene improved the yield somewhat, quite startling results were obtained when the pyrolysis was carried out under reduced pressure. When the system was partially evacuated to a pressure of 50 mm. with the tube at 590°, a 25% yield of 2,3-divinyl-1-3-butadiene (I) resulted. Under these conditions, 62% of four molar equivalents of acetic acid was liberated and very little charring resulted. In a large scale preparation the low boiling flash distillate from the pyrolysate, after removal of the acetic acid by extraction, was shown to contain 49% tetraene as well as smaller amounts of fourteen other materials. By comparison of retention times on several different gas chromatographic columns with those of authentic samples, the presence of styrene, *o*-xylene, *p*-xylene, *m*-xylene, and ethylbenzene was indicated. The pure 2,3-divinyl-1,3-butadiene (I) was most conveniently obtained on a small scale preparative gas chromatograph. The high boiling residue from the pyrolysate presumably can be repyrolyzed to produce additional tetraene.

The structure of the divinylbutadiene I was indicated by catalytic hydrogenation to the known 3,4-dimethylhexane (IV) with the absorption of four moles of hydrogen. Infrared absorption and gas-phase chromatography indicated that IV was identical in all respects with an authentic sample of the hydrocarbon prepared by the Wurtz reaction.

The ultraviolet absorption spectrum of the 2,3-divinyl-1,3-butadiene (I) in isooctane showed an ϵ_{max} of 28,500 at 217 mμ. Since the spectrum of 2-vinyl-1,3-butadiene had an ϵ_{max} of 20,500[9] at 231 mμ,[4] the maximum at 217 mμ was surprising. In fact, Woodward's rules[10] would also have led one to expect a maximum at a longer wave length. A study of the Fisher-Hirschfelder models shows that 2-vinyl-1,3-butadiene may have all its double bonds coplanar, but that 2,3-divinyl-1,3-butadiene (I) in strain-free conformations does not have all of its double bonds in one plane. The infrared spectrum was consistent with the assigned structure of the tetraene I. The NMR spectrum of I showed only bands that could be assigned to vinyl hydrogens—four triplets at 3.44, 3.64, 3.74, and 3.90 p.p.m. that could be assigned to the secondary or internal vinyl hydrogens and three complex bands at 4.74, 4.85, and 5.00 p.p.m. that could be assigned to the terminal methylene hydrogens. Furthermore, the ratio of the area under the four triplets to the area under the other three peaks was 1 to 3.85.

When 2,3-divinyl-1,3-butadiene (I) was treated with maleic anhydride, a 1:2 adduct was formed. Of the three possible adducts, V, VI, and VII, formed from one tetraene and two maleic anhydride molecules, the adduct was assumed to be only V or at least mostly V on the basis that its ultraviolet absorption spectrum showed an ϵ_{max} at 242 mμ and that its infrared absorption spectrum failed to show any evidence for a terminal methylene or a vinyl group. The tetraene I with an excess of benzoquinone formed a 1:2 Diels-Alder adduct which was assigned the structure VIII by analogy with the maleic anhydride adduct.

The use of this interesting diene for Diels-Alder polymerization and in organic syntheses will be reported separately.

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[9] The value of ϵ_{max} originally reported for 2-vinyl-1,3-butadiene[4] was in error by a factor of ten.

[10] R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941).

Experimental[11]

Tetraethyl 1,2,3,4,-Butanetetracarboxylate (II).[12]—In a 12-liter, three-necked flask, fitted with two Dean-Stark traps and a mechanical stirrer, were placed 1000 g. (4.27 moles) of 1,2,3,4-butanetetracarboxylic acid, 2700 ml. of absolute ethanol, 7500 ml. of benzene, and 11 ml. of concentrated sulfuric acid. The mixture was heated under reflux, with vigorous stirring, until no further separation of the ternary azeotrope was observed in the Dean-Stark traps. Solvent was removed by distillation at atmospheric pressure until nearly 4 l. had been removed. After the concentrated mixture was washed consecutively with water, a saturated sodium bicarbonate solution, and again with water, the organic layer was dried over magnesium sulfate and the remaining solvent was removed by distillation under reduced pressure through a 10-in. Vigreux column. The brown residue was then distilled through the same column to yield 1066 g. (72%) of the tetraethyl 1,2,3,4-butanetetracarboxylate (II), b.p. 186° (5.0 mm.), n^{25}_D 1.4551, d^{25}_4 1.1288, M_D 81.68 (calcd. 82.72) [reported[12] b.p. 201 (13 mm.)].

1,6-Diacetoxy-3,4-di(acetoxymethyl)hexane (III).[13]—A mixture of 113.8 g. (3 moles) of lithium aluminum hydride and 5 l. of anhydrous ethyl ether was placed in a 12-l., three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. A solution of 346.2 g. (1 mole) of tetraethyl 1,2,3,4-butanetetracarboxylate (II) in 1 l. of anhydrous ether was added dropwise, with stirring, to the hot mixture at a rate sufficient to maintain reflux. When the addition was complete, the reaction mixture was heated under reflux for 11 days. After 5 l. of *n*-butyl ether (dried over anhydrous sodium sulfate) was added, the ethyl ether was removed by distillation at atmospheric pressure until the temperature of the mixture in the reaction flask reached 140°. Glacial acetic acid (300 ml.) was then added dropwise to the mixture to decompose the excess lithium aluminum hydride. Dropwise addition of 4 l. of acetic anhydride to the hot reaction mixture was carried out over 2 days. After about 1 l. of acetic anhydride had been added, the mixture became quite viscous and stirring was difficult, but as the heating and addition of acetic anhydride were continued, the mixture became thinner and stirring was facilitated. After the stirring and heating under reflux was continued for 10 days, the mixture was allowed to cool and the lithium and aluminum salts were removed by filtration. The solvent was removed by distillation under reduced pressure; the residue was dissolved in ether and the resulting solution was washed consecutively with water, a saturated sodium bicarbonate solution, and a saturated sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate and the ether was removed by distillation at atmospheric pressure. Reduced pressure distillation of the residue through a 10-in. Vigreux column yielded 292 g. (84%) of 1,6 - diacetoxy - 3,4 - di(acetoxymethyl)hexane (III), b.p. 190.5° (0.7 mm.), n^{25}_D 1.4523.

Anal. Calcd. for $C_{16}H_{26}O_8$: C, 55.48; H, 7.57. Found: C, 55.46; H, 7.36.

3,4-Di(hydroxymethyl)-1,6-hexanediol.[13]—To 50 ml. of methanol in a 100-ml. flask were added 0.01 g. (0.0004 g.-atom) of sodium and 10.0 g. (0.0289 mole) of 1,6-diacetoxy-3,4-di(acetoxymethyl)hexane (III). After this mixture was heated under reflux for 30 min., the methyl acetate plus excess methanol were removed by slow distillation at atmospheric pressure and then the residue was heated at 100° and 20 mm. pressure for 30 min. When a solution of this residue in an 80–20 mixture of toluene and absolute alcohol was cooled at −20° overnight, 4.8 g. (93%) of crude 3,4-di(hydroxymethyl)-1,6-hexanediol, m.p. 86–89°, was obtained. Recrystallization from a mixture of xylene and *n*-butyl ether plus a small amount of absolute ethanol gave a white crystalline solid, m.p. 89.5–91°.

Anal. Calcd. for $C_8H_{18}O_4$: C, 53.91; H, 10.18. Found: C, 54.14; H, 10.21.

2,3-Divinyl-1,3-butadiene (I).—By a method similar to that described by Bailey and King,[14] 17.6 g. (0.167 mole) of 1,6-diacetoxy-3,4-di(acetoxymethyl)hexane (III) was added dropwise at a rate of 0.4 g. per min. to a vertical 3-cm. Vycor tube packed to a depth of 20 cm. with 3/16-in. glass helices and externally heated at 590°. Two receivers connected in series and cooled in a methyl Cellosolve–Dry Ice bath were used to collect the pyrolysate. Throughout the entire pyrolysis a reduced pressure of 50 mm. was maintained by means of a water aspirator system placed after the second receiver in order to remove the pyrolysis products from the tube as quickly as possible. The volatile products were flash distilled from the pyrolysate and the flash distillate was washed with four 20-ml. portions of ice water to remove the acetic acid. (Titration of an aliquot of the aqueous extracts with standard sodium hydroxide solution indicated that 61.5% of 4 mol. equiv. of acetic acid had been liberated.) The crude tetraene I was extracted with a saturated solution of sodium bicarbonate and a saturated solution of sodium chloride and then dried over potassium carbonate. Fractionation of the crude material was accomplished by a gas chromatograph equipped with a 7.5-foot U-tube of 10-mm. Pyrex glass, packed with 15% silicone grease on 30–60 mesh Chromosorb support. The eluted tetraene I, as indicated by its peak on the chromatogram, was collected in a U-tube attached to the exit port of the chromatograph and cooled in a methyl Cellosolve–Dry Ice bath. Collection of the tetraene I from repeated 1-ml. sample injections yielded a quantity of a pure colorless liquid, 2,3-divinyl-1,3-butadiene (I), b.p. 122.5° (746 mm.) (by microcapillary method), n^{20}_D 1.4850.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50; mol. wt., 106.2. Found: C, 90.70; H, 9.31; mol. wt., 103.5.

The mol. wt. was determined by the Beckmann cryoscopic method with cyclohexane as the solvent. The chromatogram of the crude pyrolysate, which contained fourteen distinct peaks, showed the pyrolysate to be a complex mixture of at least that number of components. Calculations were made of a percentage of 2,3-divinyl-1,3-butadiene (I) in the flash-distilled acid-free pyrolysate by weighing the paper under the peaks on the chromatogram and by the use of mesitylene as an internal standard in the mixture. Both of these methods indicated that the mixture contained 49.2% of the tetraene I. This percentage corresponds to a 24.7% yield of 2,3-divinyl-1,3-butadiene, based on the quantity of ester pyrolyzed.

Gas chromatographic retention times of authentic samples of styrene, *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene were determined and these were compared to those of peaks in the chromatogram of the crude pyrolysate. It was observed that each of the retention times of these compounds was the same as a peak from the chromatogram of the pyrolysate. When Carbowax 20-M or di-*n*-decyl phthalate was used as the stationary phase in the chromatographic column, the same correspondence of retention times of these known compounds to those of pyrolysate peaks was observed.

With a Beckman IR-5 spectrophotometer and gas cell, the infrared absorption spectrum of the tetraene I was obtained. The gas cell was evacuated (0.1 mm.) and 0.004 ml. of 2,3-divinyl-1,3-butadiene was injected into the cell and allowed to vaporize. The spectrogram obtained from this sample exhibited two very strong bands at 906 and 908 cm.$^{-1}$; strong bands at 990, 1400, 1590, 3030, and 3100 cm.$^{-1}$; and a moderate band at 1814 cm.$^{-1}$.

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[11] The authors are grateful to Dr. Franz Kasler and Mrs. Christine Nielsen for the microanalyses, to Mr. Thomas Kenny for the infrared spectra, and to Dr. Edwin Becker of the National Institutes of Health for the NMR spectrum.

[12] C. K. Ingold, *J. Chem. Soc.*, **119**, 348 (1921).

[13] The authors are grateful to Dr. Warren F. Hale for the preparation of these compounds.

[14] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

A 2.179×10^{-5} *M* solution of 2,3-divinyl-1,3-butadiene in isoöctane (spectro grade) was prepared by the weighing of 0.01155 g. of the tetraene I into a sealed capillary bulb and then the crushing of the bulb in the appropriate quantity of isoöctane. With a Beckman DK-1 recording spectrophotometer the ultraviolet absorption spectrum on the tetraene I showed an ϵ_{max} of 28,500 at 217 mμ.

The NMR spectrum of the tetraene I was obtained with a Varian HR-60 NMR spectrometer (electromagnet frequency of 60 Mc.) with purified carbon tetrachloride as the solvent and a drop of tetramethylsilane as an internal reference. Assignment of band positions on the resulting spectrogram was accomplished by use of an audio sideband of known frequency. Peak distances on the spectrogram were measured in c.p.s. from the tetramethylsilane peak and then converted to τ values (p.p.m.). Four triplets were observed at 3.44, 3.64, 3.74, and 3.90 p.p.m. and three bands, with as many as ten distinct structural elements in each, were observed at 4.74, 4.85, and 5.00 p.p.m. The ratio of peak area under the four triplets to the area under the other three bands, determined by weighing the paper under the peaks, was found to be 1 to 3.85.

3,4-Dimethylhexane (IV). A. From Wurtz Synthesis.—A quantity of 3,4-dimethylhexane was prepared by an adaptation of the Wurtz synthesis previously described.[15] The reaction of 50.0 g. (2.18 g.-atoms) of sodium metal with 300 g. (2.18 moles) of *sec*-butyl bromide in refluxing ether for 4 days, with subsequent distillation of the product, gave 16.5 g. (11%) of the hydrocarbon, b.p. 117°, n^{25}D 1.4040 (reported[15] b.p. 116.5°, n^{25}D 1.4058). An infrared spectrum run with the Beckman IR-5 spectrophotometer on this material was identical with the published spectrogram for 3,4-dimethylhexane (IV).[16]

B. From the Hydrogenation of 2,3-Divinyl-1,3-butadiene (I).—To a 125-ml. glass hydrogenation vessel containing 30 ml. of ethanol (95%) and 0.1 g. of prereduced platinum oxide catalyst was added a sealed capillary bulb containing 0.0279 g. (0.263 mmole) of 2,3-divinyl-1,3-butadiene. Gentle shaking of the flask was performed until the hydrogen buret again indicated that the system was saturated with hydrogen. At this time the shaker was started with sufficient intensity to cause the capillary bulb to break against the walls of the vessel. Absorption of hydrogen began immediately, and complete absorption [25.6 ml., 4.05 mol. equiv. (101%)] was indicated by the hydrogen buret after 15 min. (Several runs with 1-octene as a standard showed that the method described gave reproducible results accurate within 1%.) By use of the hydrogenation apparatus previously described, 0.35 g. (0.0033 mole) of 2,3-divinyl-1,3-butadiene (I) in 3 ml. of ethanol (95%) was subjected to catalytic hydrogenation with platinum oxide. After absorption of the calculated quantity of hydrogen had taken place over a 2-hr. period, the resulting ethanol solution and a synthetic mixture of ethanol and authentic 3,4-dimethylhexane (IV) (prepared by the Wurtz reaction) were analyzed with the gas chromatograph. Gas chromatograms of the hydrogenation solution and the synthetic mixture were identical for runs with silicone grease, di-*n*-decyl phthalate, and Carbowax 20-M packed chromatographic columns. Only two peaks, ethanol and the hydrocarbon, were observed on the chromatograms. Repeated collection of the eluted hydrocarbon in the hydrogenation mixture from the gas chromatograph yielded a small quantity of a colorless liquid, n^{25}D 1.4044. The infrared spectrum of this hydrocarbon was identical with that of the authentic 3,4-dimethylhexane (IV).

Diels-Alder Adducts of 2,3-Divinyl-1,3-butadiene (I).—A. With Maleic Anhydride.—To a solution of 0.15 g. (0.0014 mole) of 2,3-divinyl-1,3-butadiene (I) in 2.5 ml. of anhydrous peroxide–free ether was added 0.25 g. (0.0026 mole) of maleic anhydride dissolved in 5 ml. of ether. Immediately upon mixing a warming of the reaction mixture was observed and precipitation of a white solid began after the mixture had stood at room temperature for about 4 hr. The white precipitate was removed by filtration after 12 hr. and dried on a porcelain plate. Recrystallization of this crude material from boiling methyl ethyl ketone yielded a small amount of white crystals of 2:1 adduct (V) of maleic anhydride and 2,3-divinyl-1,3-butadiene (I), which did not melt sharply but decomposed slowly from 230° to 240°.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.80; H, 4.60.

After a mixture of the above-described diadduct with excess maleic anhydride in chlorobenzene was heated under reflux for 7 days, an attempted isolation of a triadduct was unsuccessful.

B. With *p*-Benzoquinone.—A solution of 0.15 g. (0.0014 mole) of the tetraene I and 3 ml. of anhydrous, peroxide-free ether was thoroughly mixed with a solution of 0.25 g. (0.0023 mole) of *p*-benzoquinone in 7 ml. of ether. A small quantity of yellow crystals which had appeared after 48 hr. was removed by filtration and dried on a porcelain plate. The crystals were triturated thoroughly with ether in a small test tube several times, and the solvent was decanted from the solid each time. The solid material was again dried to give a yellow powder of a 2:1 adduct (VIII) of *p*-benzoquinone and 2,3-divinyl-1,3-butadiene, m.p. 181°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.51; H, 5.63. Found: C, 74.16; H, 5.81.

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[15] J. F. Norris and E. H. Green, *Am. Chem. J.*, **26**, 313 (1901).

[16] "Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pennsylvania, 1957, Spectrum No. 11832.