Pyrolysis of Esters. XXI. 2-Hydroxymethyl-1,2-butadiene[1,2]

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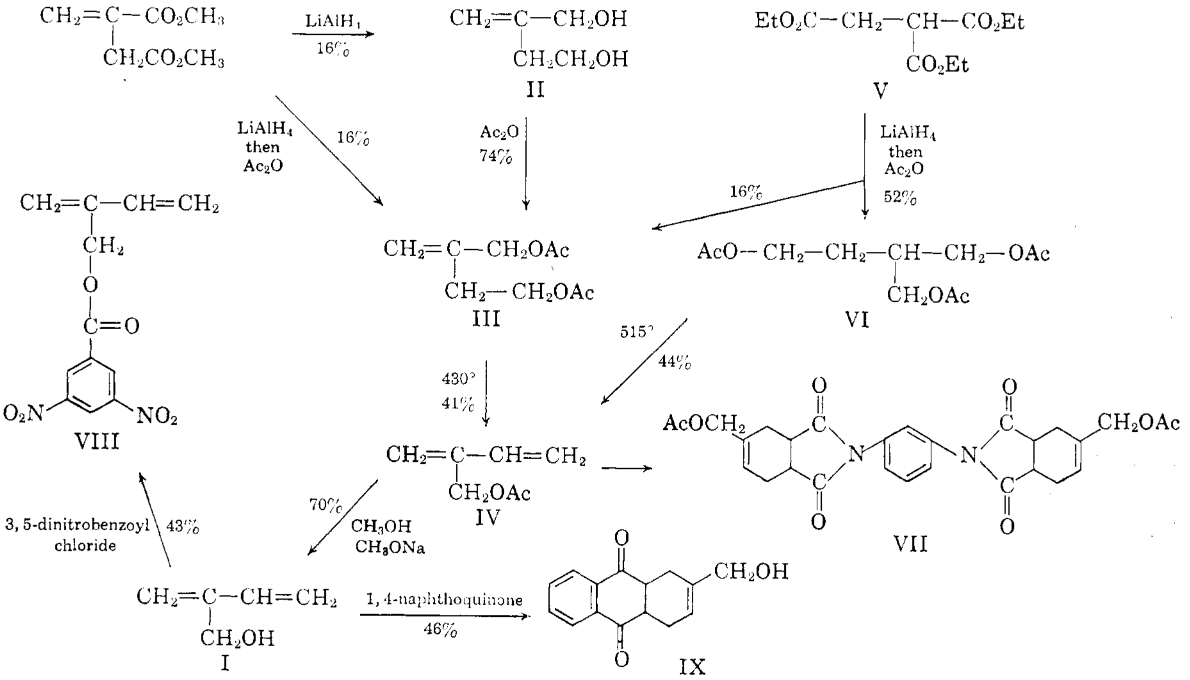
2-Hydroxymethyl-1,3-butadiene was synthesized by two different routes involving the pyrolysis of an ester as the key step. The structure of the hydroxydiene was established by analysis, ultraviolet and infrared absorption spectra, conversion to a solid 3,5-dinitrobenzoate, and conversion to a solid Diels-Alder adduct with 1,4-naphthoquinone.

In conjunction with a research program on Diels-Alder polymers, we recently reported the synthesis of 2-vinyl-1,3-butadiene,[5] which is the simplest bifunctional diene. In order to produce a series of bifunctional dienes, we became interested in dienes with functional groups substituted in the 2- or 3-position. Although there are many dienes containing alkyl groups in the 2-position, very few compounds are known with functional groups in this position. The known compounds in this series include 2-cyano-1,3-butadiene[6] and 2,3-dicyano-1,3-butadiene.[7] Since a convenient synthesis had previously been developed for 2,3-di(hydroxymethyl)-1,3-butadiene,[8] it was of interest to extend this procedure to the synthesis of 2-hydroxymethyl-1,3-butadiene (I). The hydroxymethylbutadiene was expected to be useful not only for the production of bifunctional dienes through its reactive hydroxyl group, but also for the production of oil-resistant polymers.

Dimethyl itaconate was reduced with lithium aluminum hydride to produce a 16% yield of 2-methylene-1,4-butanediol (II). Since the isolation of the water-soluble glycol fom the mixture of salts was very difficult, the essentially one-step reductive acetylation procedure involving reduction with lithium aluminum hydride, followed by direct treatment with acetic anhydride, which was developed in this laboratory,[5,8] was used to obtain a 16% yield of 2-methylene-1,4-diacetoxybutane (III). Even though this procedure was much easier to carry out, the yield still was low, presumably because of polymerization of the itaconate in the presence of the lithium aluminum hydride. The same diacetate III was obtained by esterification



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[1] Previous paper in this series, XX, *J. Org. Chem.*, **27**, 1851 (1962).

[2] Presented before the Division of Polymer Chemistry at the 132nd Meeting of the American Chemical Society, New York, September, 1957.

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[4] Office of Naval Research Fellow, 1956–1957; National Science Foundation Fellow, 1957–1959.

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

[6] A. S. Carter and F. W. Johnson, U. S. Patent 2,205,239 (1940).

[7] E. J. Prill, U. S. Patent, 2,446,167 (1948).

[8] W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, **78**, 2287 (1956).

of the diol II with acetic anhydride. Pyrolysis of the diacetate III at 430°, under conditions that liberated 63% of one molar equivalent of acetic acid, produced a 41% yield of the 2-acetoxymethyl-1,3-butadiene (IV). Even through the diacetate III contains two ester groups, one would normally expect elimination of only one molecule of acetic acid under the pyrolytic conditions used, since only one of these ester groups possesses a beta hydrogen.

Since the starting diacetate III was not easily accessible, an alternative route for the production of the 2-acetoxymethyl-1,3-butadiene (IV) was investigated. Alkylation of diethyl malonate with an equivalent amount of ethyl chloroacetate gave a 62% yield of triethyl 1,1,2-ethanetricarboxylate (V), together with a 21% yield of diethyl 3,3-dicarbethoxyglutarate. The substantial yield of the dialkylation product is not unexpected, since the inductive effect of the carbethoxymethyl group tends to make the monoalkylated product quite acidic. The reductive acetylation procedure, which involved reduction of the triester V with lithium aluminum hydride, followed by direct acetylation with acetic anhydride, produced a 52% yield of 1,4 - diacetoxy - 2 - (acetoxymethyl)butane (VI), along with a 16% yield of 2-methylene-1,4-diacetoxybutane (III). The formation of the unsaturated diacetate III during this reduction with lithium aluminum hydride is probably related to the work of Dreiding and Hartman,[9] who isolated 2-methylenecyclohexanol and 1-hydroxymethylcyclohexene from the reduction of 2-carbethoxycyclohexanone. The production of unsaturated alcohols from the reduction of malonic esters is the subject of a subsequent publication.

When the triacetate VI was dropped through the pyrolysis tube at 515°, under conditions that liberated 71% of two molar equivalents of acetic acid, a 33% conversion to 2-acetoxymethyl-1,3-butadiene (IV) was realized. In addition, a 14% yield of a mixture consisting, presumably, of the two possible olefin diacetates, III plus 2-vinyl-1,3-propanediol diacetate, was obtained, along with a 10% recovery of the starting diacetate VI. The yield of IV was, therefore, 44% based on unrecovered material.

The structure of the 2-acetoxymethyl-1,3-butadiene (IV) was indicated by analysis, ultraviolet and infrared spectra, and conversion to a solid Diels-Alder adduct. The ultraviolet absorption spectrum of IV showed an ϵ_{max} at 222 mμ of 14,200, in accord with Woodward's rules.[10]

The infrared spectrum indicated strong bands at 1737, 1226, 1600, and 906 cm.$^{-1}$, which indicated the presence of an acetate, an acetate, a conjugated diene, and external methylene group, respectively.[11] The diene IV was further characterized by conversion to a solid Diels-Alder adduct, 1,3-di(4-acetoxymethyl-Δ^4-tetrahydrophthalimido)benzene (VII) by treatment with *N,N'-m*-phenylenebismaleimide.[12] Since saponification of the ester IV gave only a 52% yield of 2-hydroxymethyl-1,3-butadiene (I), a procedure involving ester interchange with a tenfold excess of methanol plus a trace of sodium methoxide was investigated. This procedure gave a 70% yield of the diene I. The 2-hydroxymethyl-1,3-butadiene (I) was characterized by its ultraviolet absorption spectrum, which indicated an ϵ_{max} at 222 mμ of 17,900. Treatment of the hydroxymethylbutadiene I with 3,5-dinitrobenzoyl chloride produced a 43% yield of the solid ester, 2-(3,5-dinitrobenzoxymethyl)-1,3-butadiene (VIII), while treatment of the diene I with 1,4-naphthoquinone produced the solid Diels-Alder adduct, 2-hydroxymethyl-1,4,4a,9a-tetrahydroanthraquinone (IX), in a 46% yield.

One must conclude from this work that the pyrolysis of esters is a very convenient route for the preparation of polyfunctional compounds. The chemistry of this interesting 2-hydroxymethyl-1,3-butadiene (I) will be reported in subsequent publications.

Experimental[13]

2-Methylene-1,4-butanediol (II).—To a 5-l., three-necked flask, containing 98.6 g. (2.6 moles) of lithium aluminum hydride and 4 l. of anhydrous ether at room temperature was added dropwise over a period of 3.25 hr. a solution of 316 g. (2.00 moles) of dimethyl itaconate in 800 ml. of anhydrous ether. After the addition was complete, the slurry was heated under reflux with stirring for an additional 48 hr. After 100 ml. of water had been added cautiously to the cooled mixture to decompose the excess hydride, 400 ml. of a saturated potassium sodium tartrate solution was added rapidly to form a complex with the salts. After the complex had been stirred for 1 hr., the mixture was filtered. No aqueous layer was observed in the filtrate. The precipitate was digested with 2 l. of absolute alcohol for 24 hr. at room temperature to extract any residual 2-methylene-1,4-butanediol (II). After the salts were removed by filtration, the alcohol solution was concentrated to approximately 100 ml. by distillation under reduced pressure to leave a heavy, dark brown polymeric residue. This residue was distilled under a reduced pressure of 0.3 to 0.4 mm. from an oil bath heated from 150° to 205° to yield 23.4 g. of crude 2-methylene-1,4-butanediol (II) and 10.5 g. of a hard, brown polymeric residue. The original ether solution, after being dried over magnesium sulfate, was concentrated by distillation under reduced pressure to about 200 ml. and this residue was combined with the residue

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[9] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

[10] R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 76 (1942).

[11] H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, 1953, p. 140.

[12] The authors are indebted to Dr. Eugene Kraiman of the Union Carbide Plastics Co., Bound Brook, N. J., for the sample of the bismaleimide.

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from the alcohol extraction. The combined concentrates were fractionated through a 6-in., helix-packed column to yield 33.2 g. (16%) of 2-methylene-1,4-butanediol (II), a colorless, viscous liquid, b.p. 86° (0.3 mm.), $n^{25}\mathrm{D}$ 1.4680.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.64; H, 10.06.

2-Methylene-1,4-diacetoxybutane (III). A. By Acetylation of 2-Methylene-1,4-butanediol (II).—After a solution of 67.2 g. (0.658 mole) of 2-methylene-1,4-butanediol (II), 620 ml. (6.58 moles) of acetic anhydride, and 114 ml. of acetic acid had been heated under reflux for 48 hr., the excess acetic anhydride and acetic acid were removed by distillation under reduced pressure. The residue was dissolved in 500 ml. of ether, and the ether solution was washed consecutively with three 250-ml. portions of water, three 250-ml. portions of a saturated sodium bicarbonate solution, and, finally, with 250 ml. of a saturated sodium chloride solution. After the solution was dried over magnesium sulfate, the ether was removed by distillation under reduced pressure. The residue, to which had been added a trace of *N*-phenyl-β-naphthylamine, was fractionated through a 6-in., helix-packed column to yield 90.8 g. (74%) of 2-methylene-1,4-diacetoxybutane (III), a colorless liquid, b.p. 86.0° (2.3 mm.), $n^{25}\mathrm{D}$ 1.4351.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.00; H, 7.65.

B. By Reductive Acetylation of Dimethyl Itaconate.—To a 12-l., three-necked flask, containing 83.5 g. (2.2 moles) of lithium aluminum hydride and 4000 ml. of anhydrous ether, maintained at −10°, was added with stirring over a period of 10 hr. 316 g. (2.0 moles) of dimethyl itaconate dissolved in 1000 ml. of anhydrous ether. After the mixture had been stirred for a week at 0°, 4000 ml. of *n*-butyl ether was added. The ethyl ether was removed by distillation through a Dean-Stark trap until the temperature of the mixture increased to 120°. After the residue had cooled to room temperature, 458 ml. (8.0 moles) of acetic acid was added dropwise to destroy the excess lithium aluminum hydride. Stirring had to be discontinued during the addition because the salts became quite thick. Without further heating or stirring of the mixture, 1400 ml. of acetic anhydride was added and the mixture was heated under reflux with stirring for a week. After the salts had been removed by filtration, the acetic acid, acetic anhydride, and *n*-butyl ether were removed by distillation under reduced pressure. The distillation residue was dissolved in 1 l. of ether, and the ether solution was washed consecutively with three 250-ml. portions of water, three 250-ml. portions of a saturated sodium bicarbonate solution, and 250 ml. of a saturated sodium chloride solution. After 0.2 g. of *N*-phenyl-β-naphthylamine had been added to the dried ether solution, the ether was removed by distillation under reduced pressure. The residue was then fractionated through a 6-in., helix-packed column to yield 61.5 g. (16%) of 2-methylene-1,4-diacetoxybutane (III), b.p. 68.5° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4325.

2-Acetoxymethyl-1,3-butadiene (IV). A. From 2-Methylene-1,4-diacetoxybutane (III).—By the apparatus and procedure described previously,[14] 90.9 g. of 2-methylene-1,4-diacetoxybutane (III) was dropped through the hot tube at 430° while the pyrolysis system was continuously flushed with a stream of oxygen-free nitrogen. In order to minimize charring, 0.01 g. of hydroquinone was added to the diacetate III, and the pyrolysis tube was changed four times during the total addition. The clear, pale yellow pyrolysate, which weighed 84.2 g., was dissolved in 300 ml. of ether, and the ether solution was washed consecutively with three 250-ml. portions of water, three 250-ml. portions of a saturated sodium bicarbonate solution, and three 200-ml. portions of a saturated sodium chloride solution. (Titration of an aliquot of the aqueous extracts with a standard solution of sodium hydroxide indicated the liberation of 63% of 1 mol. equiv. of acetic acid.) After the ether extract was dried over magnesium sulfate and 0.2 g. of *N*-phenyl-β-naphthylamine had been added, the ether was removed by distillation under reduced pressure. The residue was then fractionated through a 6-in., helix-packed column to give 19.4 g. (32%) of 2-acetoxymethyl-1,3-butadiene (IV), b.p. 51° (35 mm.), $n^{25}\mathrm{D}$ 1.4515, and 21.6 g. of recovered 2-methylene-1,4-diacetoxybutane (III). The yield, based on unrecovered starting material, was, therefore, 41%.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.59; H, 8.09.

B. From 1,4-Diacetoxy-2-(acetoxymethyl)butane (VI).—By use of the pyrolysis apparatus previously described, 67.0 g. (0.272 mole) of 1,4-diacetoxy-2-(acetoxymethyl)butane (VI) was pyrolyzed at 515° at the rate of 1 ml./min. To the orange-colored pyrolysate was added 50 ml. of ether and 0.01 g. of *N*-phenyl-β-naphthylamine. This solution was extracted with seven portions (total 250 ml.) of water. (Titration of an aliquot of these aqueous extracts showed that 0.384 mole or 71% of 2 mol. equiv. of acetic acid had been eliminated.)

The ether solution was dried over anhydrous sodium sulfate, and, after the ether was removed at atmospheric pressure, the residue was fractionated under partial vacuum through a 6-in., helix-packed column to yield 11.38 g. (33%) of 2-acetoxymethyl-1,3-butadiene (IV), b.p. 60–65° (30 mm.), $n^{25}\mathrm{D}$ 1.4515.

Continued distillation gave 7.25 g. (14%) of a mixture consisting of, presumably, the two possible olefin diacetates, 2-methylene-1,4-butanediol diacetate and 2-vinyl-1,3-propanediol diacetate, b.p. 82–85° (2.2 mm.), $n^{25}\mathrm{D}$ 1.4421–1.4465, and 6.8 g. (10%) of recovered 1,4-diacetoxy-2-(acetoxymethyl)-butane, b.p. 124° (0.2 mm.). The yield of 2-acetoxymethyl-1,3-butadiene (IV), based on unrecovered material, was 44%.

Vapor phase chromatography of the 2-acetoxymethyl-1,3-butadiene (IV) at 128° with the A column of the Perkin-Elmer Model 154 vapor phase fractometer gave only one peak. Similarly, chromatographic analysis of the mixture of olefin diacetates on an instrument constructed in these laboratories[15] and a column made by the absorption of silicone grease on Chromosorb at 170° gave two peaks whose area ratios were about 2:1, the peak with the larger area corresponded in retention time with an authentic sample of 2-methylene-1,4-butanediol diacetate.

Triethyl 1,1,2-Ethanetricarboxylate (V).—To 1600 ml. of anhydrous ethanol (dried by treatment with sodium metal, followed by addition of diethyl phthalate) contained in a 5-l., three-necked flask fitted with a reflux condenser, a dropping funnel, and a stirrer was added 92 g. (4.0 g.-atoms) of sodium at a rate such as to maintain reflux. Heating was necessary to effect the reaction of the last few pieces of sodium. To the sodium ethoxide solution was added quickly 704 g. (4.4 moles) of diethyl malonate. The yellow solution became cloudy with the diethyl sodiomalonate formation.

To the resulting solution was then added 488 g. (4.0 moles) of ethyl chloroacetate dropwise over a 6-hr. period. After the reaction mixture was heated under reflux for 11 hr. and then cooled, the sodium chloride was removed by filtration. Ethanol was removed by distillation and the residue was fractionated through a 12-in., helix-packed column to yield 604 g. (62%) of triethyl 1,1,2-ethanetricarboxylate (V), b.p. 111° (0.7 mm.), $n^{25}\mathrm{D}$ 1.4263 (reported,[16] $n^{20}\mathrm{D}$ 1.4215), and 138.5 g. (21%) of diethyl 3,3′-dicarbethoxyglutarate, b.p. 143° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4368 [reported[17] b.p. 178–180° (12 mm.)].

1,4-Diacetoxy-2-(acetoxymethyl)butane (VI).—A slurry of lithium aluminum hydride was prepared by the addition of 55.3 g. (1.47 moles) of the hydride to 2000 ml. of dry

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(14) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(15) W. J. Bailey and W. F. Hale, *J. Am. Chem. Soc.*, **81**, 647 (1959).

(16) C. A. Bischoff and A. von Kuhlberg, *Ber.*, **23**, 634 (1890).

(17) H. Lund, *ibid.*, **67B**, 935 (1934).

ethyl ether in a 5-l., three-necked flask equipped with a condenser, a Hershberg stirrer, and a dropping funnel, protected from atmospheric water by drying tubes containing Drierite. A solution of 159 g. (0.65 mole) of triethyl 1,1,2-ethanetricarboxylate (V) in 400 ml. of dry ether was added to the flask at a rate such as to keep the ether refluxing briskly. After the 5-hr. addition period, the dark gray mixture was heated under reflux for 8 days.

Ethyl ether was removed by distillation through a Dean-Stark separator and 1600 ml. of dry di-*n*-butyl ether was added. This distillation was continued until the temperature of the reaction mixture reached 120°. After the reaction mixture was allowed to cool, 120 ml. of glacial acetic acid was slowly added. The reaction mixture heated spontaneously and the solvent refluxed without external heating. Following this addition the reaction was stirred at 100° for a day.

As 1600 ml. of acetic anhydride was added slowly, the solvent again refluxed spontaneously and, as the addition of the anhydride was nearly completed, the reaction mixture became very pasty and difficult to stir. By switching to a heavy duty Bodine motor and working the stirrer through the pasty mass from the top down, along with strong heating, it was possible to loosen this mass so that it flowed quite freely and was easily agitated.

After the mixture was heated under reflux for 6 days, it was cooled and filtered to remove the precipitated salts. The salt cake was triturated with about 400 ml. of dry di-*n*-butyl ether and the resulting slurry was filtered. Butyl ether, acetic acid, and acetic anhydride were removed by distillation from the combined filtrates under partial vacuum. Distillation of the residue through a 12-in., helix-packed column gave 82.5 g. (52%) of 1,4-diacetoxy-2-(acetoxymethyl)butane (VI), b.p. 132–133° (1.0 mm.), $n^{25}\text{D}$ 1.4390, and 19 g. (16%) of 2-methylene-1,4-butanediol diacetate (III), b.p. 80–82° (1 mm.), $n^{25}\text{D}$ 1.4346.

Anal. Calcd. for $C_{11}H_{18}O_6$: C, 53.65; H, 7.36. Found: C, 53.88; H, 7.28. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.14; H, 7.67.

1,3-Bis(4-acetoxymethyl-Δ⁴-tetrahydrophthalimido)benzene (VII).—To a solution of 0.606 g. (0.00226 mole) of *N,N'-m*-phenylenebismaleimide[12] in 90 ml. of toluene was added 0.57 g. (0.0045 mole) of 2-acetoxymethyl-1,3-butadiene (IV). After the solution had been heated under reflux for 3 hr., it was cooled to −20° and filtered. The filtrate was then heated under reflux for an additional 10 hr., cooled, and filtered to yield a total 0.21 g. (18%) of the crude Diels-Alder adduct, m.p. 500° dec. Recrystallization of this crude adduct from 10 ml. of nitrobenzene and 30 ml. of toluene gave an analytically pure sample of 1,3-bis(4-acetoxymethyl-Δ⁴-tetrahydrophthalimido)benzene (VII), m.p. 500° dec.

Anal. Calcd. for $C_{28}H_{28}N_2O_8$: C, 64.61; H, 5.42. Found: C, 64.70; H, 5.22.

2-Hydroxymethyl-1,3-butadiene (I).—To a 100-ml. flask were added 20.0 g. (0.159 mole) of 2-acetoxymethyl-1,3-butadiene (IV), 60 ml. of methanol, 0.43 g. (5 mole %) of commercial sodium methoxide, and 0.1 g. of *N*-phenyl-β-naphthylamine. By use of a 10:1 reflux ratio, 14.6 g. of a methanol–methyl acetate azeotrope, b.p. 54–63° (reported,[18] b.p. 54°), was removed through a 6-in., helix-packed column. The excess methanol was then removed at room temperature under reduced pressure until the weight of the residue was 14.7 g. This residue was flash distilled under 6 mm. of pressure from an oil bath at 100° into a 50-ml. receiving flask immersed in a Dry Ice–methyl Cellosolve bath to yield 9.3 g. (70%) of crude distillate. After the addition of 0.2 g. of *N*-phenyl-β-naphthylamine, the crude product was fractionated under nitrogen through a 24-in. Podbielniak column to yield an analytically pure sample of 2-hydroxymethyl-1,3-butadiene (I), b.p. 56–57° (30 mm.), $n^{25}\text{D}$ 1.4777.

Anal. Calcd. for C_5H_8O: C, 71.40; H, 9.58. Found: C, 71.58; H, 9.87.

2-(3,5-Dinitrobenzoxymethyl)-1,3-butadiene (VIII).—After a mixture of 8 g. (0.095 mole) of 2-hydroxymethyl-1,3-butadiene (I), 0.1 g. of *N*-phenyl-β-naphthylamine, 10 g. of dry pyridine, 26 g. (0.113 mole) of 3,5-dinitrobenzoyl chloride, and 300 ml. of dry benzene had stood at room temperature for 12 hr., an ether solution of the mixture was washed consecutively with three 100-ml. portions of a 5% hydrochloric acid solution, three 100-ml. portions of a 5% sodium hydroxide solution, and three 100-ml. portions of distilled water. After the solvents were removed from the ether solution by distillation under reduced pressure, the residue was recrystallized from 800 ml. of petroleum ether (b.p. 30–60°) to give 11.3 g. (43%) of 2-(3,5-dinitrobenzoxymethyl)-1,3-butadiene (VIII) in orange, needlelike crystals, m.p. 89–90°.

Anal. Calcd. for $C_{12}H_{10}N_2O_6$: C, 51.81; H, 3.62. Found: C, 52.07; H, 371.

2-Hydroxymethyl-1,4-4a,9a-tetrahydroanthraquinone (IX).—A mixture of 0.24 g. (0.00152 mole) of freshly sublimed 1,4-naphthoquinone and 0.20 g. (0.00238 mole) of 2-hydroxymethyl-1,3-butadiene (I) in 75 ml. of toluene was heated under reflux for 12 hr. Since no solid separated when the reaction mixture was cooled, the mixture was concentrated to about 5 ml. by distillation under reduced pressure. When this residue was cooled, a crop of finely divided, light tan crystals, m.p. 80°, was collected. Further cooling of the mother liquor gave a second batch of white, needlelike crystals. The combined crops were recrystallized from a mixture of ether and petroleum ether (90–100°) to yield 0.16 g. (46%) of 2-hydroxymethyl-1,4,4a,9a-tetrahydroanthraquinone (IX), m.p. 87°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.82. Found: C, 74.08; H, 5.85.

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[18] L. H. Horsley, "Azeotropes," American Chemical Society, Washington, D. C., 1952, p. 29.