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

Some Diels–Alder Reactions of 2-Phenyl-1,3-butadiene

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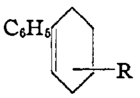
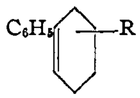
Previous work on 2-substituted butadienes has shown that their Diels–Alder condensations with mono-substituted dienophiles result in 1,4-disubstituted cyclohexenes as the major products rather than the 1,5-disubstituted cyclohexenes. 2-Phenyl-1,3-butadiene was chosen for study in an effort to clarify the role of aryl groups in determining the orientation of adducts obtained from mono-substituted ethylenes. The dienophiles, acrolein, acrylic acid, acrylamide, acrylonitrile, methyl acrylate, phenylacetylene and 2-vinylpyridine, when condensed with 2-phenyl-1,3-butadiene, were shown to give, in each case, a 1,4-disubstituted adduct as the major product. With acrylic acid, acrylamide and acrylonitrile, the other possible isomeric adduct was also shown to be formed. With allyl alcohol and propargyl alcohol, the only product isolated was a dimer of 2-phenyl-1,3-butadiene.

2-Phenyl-1,3-butadiene (phenoprene) has been condensed in the Diels–Alder reaction with α-naphthoquinone,[2–4] maleic anhydride,[3–5] acrylic acid,[5] acrolein,[5] propiolic acid[5] and styrene.[5] The recent publication of the work of Alder and Haydn has prompted us to report our work with 2-phenyl-1,3-butadiene. These workers found, as did we, that the major adduct in each case with 2-phenyl-1,3-butadiene was the para-type (I) isomer. In no case did they show that a meta-type isomer (II) was formed.



I



II

Our work showed that 2-phenyl-1,3-butadiene and acrylic acid gave both possible adducts which were obtained in a ratio of about five parts of I (R = CO_2H) to two parts of II. The structures of these adducts were established by dehydrogenation to para- and meta-phenylbenzoic acid. With acrylamide, again two isomeric adducts were obtained in a ratio of about 7 parts of I (R = $CONH_2$) to two parts of II. These adducts, on hydrolysis, gave the corresponding acids obtained from 2-phenyl-1,3-butadiene and acrylic acid. Acrylonitrile and 2-phenyl-1,3-butadiene gave an oil which, upon treatment with alkaline hydrogen peroxide, gave the same two amides obtained from 2-phenyl-1,3-butadiene and acrylamide. The ratio of the acrylonitrile adducts appeared to be four to one with the major adduct again being of type I (R = CN).

Methyl acrylate and 2-phenyl-1,3-butadiene gave a solid adduct which was shown to be methyl 4-phenyl-1,2,5,6-tetrahydrobenzoate by hydrolysis to the acid of type I. This same acid was obtained by the oxidation of the acrolein–2-phenyl-1,3-butadiene adduct with silver oxide. No acid of type II was obtained from either the acrolein or methyl acrylate adduct.

Attempts to condense 2-phenyl-1,3-butadiene with allyl alcohol and propargyl alcohol led only to high yields of a solid dimer of 2-phenyl-1,3-butadiene which has been shown by Alder and Haydn to be 1,4-diphenyl-4-vinylcyclohexene.[5] Even when these alcohols were used in large excess no adduct was obtained. It thus appears that 2-phenyl-1,3-butadiene is a more active dienophile with itself than is allyl or propargyl alcohol.

The condensation of 2-phenyl-1,3-butadiene with phenylacetylene gave a 5% yield of a solid which appeared to be a mixture of 1,4-diphenyl-1,4-cyclohexadiene and its dehydrogenation product, para-terphenyl. Treatment of this mixture with boiling nitrobenzene gave a high yield of para-terphenyl.

2-Vinylpyridine was condensed with 2-phenyl-1,3-butadiene and gave a 26% yield of a solid adduct. This was dehydrogenated to the known solid 2-(4-biphenylyl)-pyridine.

Experimental

Starting Materials.—2-Phenyl-1,3-butadiene (phenoprene) was prepared by pyrolysis of 2-phenyl-4-acetoxy-1-butene, by the method of Price, Benton and Schmidle,[4] with slight modifications. The acetoxy compound, prepared from α-methylstyrene, formaldehyde, acetic anhydride and acetic acid, was distillled slowly at 20 mm. pressure upward through an "Inconel" tube packed with 0.25-inch Raschig rings. The tube was 630 mm. by 15 mm. (inside diameter), but only 330 mm. of its length (middle section) was heated in an electric furnace. The temperature of the heated portion of the tube was maintained at 700–750°, and the rate of distillation through the tube was regulated by cooling coils around both ends of the tube. There was about 49 ml. of free space in the heated portion of the tube. At the average rate of distillation of 5 g. of acetate per hour, contact time was 2.1 seconds. Under these conditions, about 50% of the acetate was converted to the diene in one pass, and the unchanged ester was recycled, so that an almost quantitative yield of 2-phenyl-1,3-butadiene was obtained. This was purified by distillation at reduced pressure and was not kept for more than 24 hours before use. Longer storage, even with inhibitors present and at ice-box temperature, resulted in considerable polymerization.

Pure acrylic acid was made from the 60% technical product by azeotropic distillation of the water with benzene using a Barrett type moisture test receiver obtained from Ace Glass, Inc., Vineland, New Jersey. Eastman Kodak Co. practical grade acrylonitrile, acrolein and methyl acrylate were used as obtained; acrylamide was prepared from the acid chloride by ammonolysis.[6]

Phenylacetylene was prepared by bromination of styrene, followed by two dehydrobromination steps. Styrene dibromide was converted to α-bromostyrene by refluxing with alcoholic potassium hydroxide.[7] The second mole of hydrogen bromide was eliminated[8] by dropping the α-bromostyrene onto molten potassium hydroxide at 200° in a distillation flask.

2-Vinylpyridine was obtained from Reilly Tar and Chemi-

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(1) This work was supported by the Office of Naval Research and was taken mainly from the Doctor's Thesis of Raymond T. Merrow, University of Colorado, 1951.

(2) W. H. Carothers and G. J. Berchet, THIS JOURNAL, **55**, 2813 (1933).

(3) H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934).

(4) C. C. Price, F. L. Benton and C. J. Schmidle, THIS JOURNAL, **71**, 2860 (1949).

(5) K. Alder and J. Haydn, *Ann.*, **570**, 201 (1950).

(6) D. M. Jones, J. Zomlefer and K. Hawkins, *J. Org. Chem.*, **9**, 506 (1944).

(7) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(8) J. C. Hessler in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 438.

cal Corporation and tended to become colored and to polymerize on standing, so that it was necessary to steam distil this compound immediately before use. The water-white distillate was dried over magnesium sulfate.

The Reaction of 2-Phenyl-1,3-butadiene with Acrylic Acid.—Thirteen grams (0.1 mole) of 2-phenyl-1,3-butadiene and 7.2 g. (0.1 mole) of purified acrylic acid were mixed and 0.2 g. of phenyl-β-naphthylamine was added as a polymerization inhibitor. The mixture was heated under reflux. As soon as the mixture became warm, it began to boil vigorously, and the heating was stopped. After being cooled to room temperature, the reaction mixture set to a solid crystalline mass. The solid was dissolved in 10% sodium hydroxide solution, extracted with ether to remove the amine inhibitor and the aqueous layer was acidified with concentrated hydrochloric acid. The solid acid was filtered and dried at 100°. The crude adduct weighed 15.5 g. (76.7%) and melted at 142–145° after some softening at 125°.

After several recrystallizations from benzene, two acids were obtained: (III) m.p. 157–158°, weight, 8.2 g.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.48; H, 7.17.

(IV) m.p. 87–88°, weight, 3.1 g. *Anal.* Found: C, 77.03; H, 7.04. The melting points of these acids were not changed by sublimation.

Dehydrogenation of 4-Phenyl-1,2,5,6-tetrahydrobenzoic Acid (III).—In the dehydrogenation tube were placed 0.93 g. (0.005 mole) of (III) and 0.32 g. (0.01 gram-atom) of sulfur. The tube was heated to 160–200° for 3 hours, during which time hydrogen sulfide was being evolved copiously. White crystalline material which had sublimed out of the heated part of the tube was washed down with benzene, and, after evaporation of the solvent, heating was continued for two hours longer, until no more gas came off. After addition of 0.1 g. of zinc dust, the tube was heated for another 30 minutes.

The mixture was extracted with hot benzene. Besides a small amount of zinc, the benzene-insoluble residue consisted of 0.65 g. of crude *p*-phenylbenzoic acid, m.p. 221–222.5°. By sublimation, there was obtained 0.50 g. of pure acid, m.p. and mixed m.p. 222.5–223°.[9] No acidic material was obtained from the benzene solution.

Dehydrogenation of 3-Phenyl-1,2,5,6-tetrahydrobenzoic Acid (IV).—An attempt to dehydrogenate this acid with sulfur resulted in the evolution of hydrogen sulfide, but no acidic material could be isolated from the tarry residue in the reaction vessel.

Three-tenths gram of IV was dissolved in 10 ml. of *p*-cymene and heated under reflux with 0.1 g. of 10% palladium–charcoal catalyst for 6.5 hours. The mixture was diluted with benzene, filtered, and extracted with 10% sodium hydroxide solution. The alkaline solution was acidified and ether-extracted. Evaporation of the ether yielded 0.3 g. of a crude acid, m.p. 135–140°. Recrystallization from benzene gave 0.20 g. of acid melting at 153–154° and showing no depression when mixed with *m*-phenylbenzoic acid, m.p. 162–163°.

The unknown acid was converted to the S-benzylthiuronium salt which was recrystallized from ethyl acetate and then melted at 158–159°. This salt appeared to be identical with that obtained from an authentic sample of *m*-phenylbenzoic acid. The S-benzylthiuronium salt was waxy in appearance and texture and since it seemed difficult to dry it was not analyzed and was hydrolyzed back to the acid by heating with 5% aqueous sodium hydroxide. The purified acid now weighed 0.15 g. and melted at 162–163° with no change on mixing with an authentic sample of *m*-phenylbenzoic acid.[10]

Adducts of 2-Phenyl-1,3-butadiene and Acrylamide.—A mixture of 6.5 g. (0.05 mole) of 2-phenyl-1,3-butadiene, 3.55 g. (0.05 mole) of acrylamide and 0.2 g. of phenyl-β-naphthylamine was dissolved in 25 ml. of benzene, and the solution was heated under reflux for 5.5 hours. The mixture became a solid mass on cooling. Extraction with hot water removed a trace of acrylamide, and the water-insoluble residue was recrystallized from benzene. Two grams (20%) of crude adduct was obtained, m.p. 180–185°. Fractional crystallization from benzene yielded 1.45 g. of an isomer (V), m.p. 194–195°, and 0.40 g. of an isomer (VI), m.p. 144–145°. The melting points of these compounds were not changed by sublimation.

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found (V): C, 77.99; H, 7.83; N, 6.87. Found (VI): C, 77.71; H, 7.53.

Hydrolysis of (V).—Two-tenths gram of amide (V) was refluxed with 8 ml. of 20% sodium hydroxide solution for 4.5 hours. Acidification with dilute hydrochloric acid gave 0.15 g. of 4-phenyl-1,2,5,6-tetrahydrobenzoic acid (III), m.p. and mixed m.p. 156–157°.

Hydrolysis of (VI).—One-tenth gram of amide (VI) was refluxed for 2 hours with 5 ml. of 20% sodium hydroxide solution. Forty milligrams of unreacted amide was filtered off and the filtrate acidified. Fifty milligrams of 3-phenyl-1,2,5,6-tetrahydrobenzoic acid (IV) was obtained, m.p. and mixed m.p. 87–88°.

Condensation of 2-Phenyl-1,3-butadiene with Acrylonitrile.—Six and one-half grams (0.05 mole) of 2-phenyl-1,3-butadiene and 2.65 g. (0.05 mole) of acrylonitrile were heated under reflux with 0.2 g. of phenyl-β-naphthylamine for 12 hours. The temperature of the liquid rose gradually from the boiling point of acrylonitrile to about 95° after four hours, and remained at 95–100° during the remaining time. Distillation of the mixture yielded 3.0 g. (32.8%) of a yellow oil, b.p. 125–128° (9 mm.); $n^{20}D$ 1.5741. No effort to purify this further and separate the possible isomeric adducts was made. The crude mixture was converted directly to the amide.

Hydration to the Amide.—A vigorous reaction occurred at once when 1.37 g. (0.0075 mole) of the crude adduct was treated with alkaline hydrogen peroxide in ethanol by the procedure of Noller.[11] The yield of crude amide was 1.3 g. (86%), m.p. 165–170°. By fractional crystallization from benzene, there were isolated 0.75 g. of 4-phenyl-1,2,5,6-tetrahydrobenzamide (V), m.p. and mixed m.p. 194–195°, and 0.20 g. of 3-phenyl-1,2,5,6-tetrahydrobenzamide (VI), m.p. and mixed m.p. 144–145°.

2-Phenyl-1,3-butadiene–Methyl Acrylate Adduct.—Six and one-half grams (0.05 mole) of 2-phenyl-1,3-butadiene was mixed with 4.3 g. (0.05 mole) of methyl acrylate, 0.2 g. of hydroquinone was added, and the mixture was refluxed for 26 hours. After 20 hours, the temperature of the condensing vapors remained steady at 95–100°. The mixture was distilled, with the recovery of 1.0 g. of 2-phenyl-1,3-butadiene and 2.0 g. of methyl acrylate. There was also obtained 2.90 g. of adduct distilling at 118–120° (3 mm.), m.p. 45–48°. The crude yield was 50% based on unrecovered methyl acrylate. Repeated recrystallization from methanol and water gave 2.00 g. of pure adduct, m.p. 57–58° (lit. 58°[6]).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.74; H, 7.46. Found: C, 77.90; H, 7.45.

One hundred sixty-seven milligrams of ester was refluxed with 25 ml. of methanolic potassium hydroxide for 1.5 hours. From the reaction mixture, by acidification and evaporation of the alcohol, there was obtained 0.155 g. (100%) of 4-phenyl-1,2,5,6-tetrahydrobenzoic acid, m.p. and mixed m.p. 156–157°.

Condensation of 2-Phenyl-1,3-butadiene and Acrolein.—Six and one-half grams (0.05 mole) of 2-phenyl-1,3-butadiene was heated under reflux with 2.8 g. (0.05 mole) of acrolein and 0.2 g. of phenyl-β-naphthylamine for 20 hours. The temperature of the liquid rose to 150–155° after the first 3 hours and remained there for the duration of the heating period. Distillation of the mixture (after evaporation of the acrolein in an air jet) gave 4.0 g. (43%) of crude adduct, b.p. 142–145° (6 mm.); redistillation at 3 mm. yielded 2.8 g. of purified adduct, b.p. 121–122° [lit. b.p. 170–190° (13 mm.)[5]].

One gram of the adduct was dissolved in 10 ml. of ethanol and an aqueous solution of 2.90 g. of silver nitrate was added. To this mixture was added a solution of 1.95 g. of potassium hydroxide in 10 ml. of water, dropwise with cooling and shaking, over a period of an hour. After standing for 72 hours at room temperature, the mixture was shaken me-

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[9] An authentic sample of *p*-phenylbenzoic acid was obtained from Dr. George B. Payne, University of California, and it was prepared according to the method of H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 498 (1929).

[10] This sample was obtained from D. J. Mann, University of Illinois.

[11] C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 586.

chanically for six hours and filtered. The precipitate was washed with ethanol, and the combined filtrate and washings were evaporated and acidified. Fifty-five hundredths of a gram of a waxy solid acid precipitated. Recrystallization from benzene yielded 0.35 g. of 4-phenyl-1,2,5,6-tetrahydrobenzoic acid, m.p. 157–158°. This was the only acidic substance isolated from the oxidation mixture. The filtrate from the crude acid gave 0.2 g. of unreacted aldehyde adduct, and traces of aldehyde were obtained from the benzene used to recrystallize the crude acid.

Attempted Condensation of 2-Phenyl-1,3-butadiene with Allyl Alcohol and Propargyl Alcohol.—Twenty-six grams (0.2 mole) of 2-phenyl-1,3-butadiene, 23.2 g. (0.4 mole) of allyl alcohol and 0.2 g. of hydroquinone were heated in a sealed tube at 100° for 12 hours. The resulting mixture was purified by fractional distillation. A total of 21.1 g. (91%) of the allyl alcohol was recovered along with 8 g. of 2-phenyl-1,3-butadiene. In addition, 11.2 g. of material, b.p. 180–190° (4 mm.), was obtained. This material solidified after standing a few days. After recrystallization twice from ethanol, 10.1 g. of material was obtained, m.p. 61–62° (lit. 62°[2] and 60°[5]). This compound has been identified by Alder and Haydn as 1,4-diphenyl-4-vinylcyclohexene.

A mixture of 13 g. (0.1 mole) of 2-phenyl-1,3-butadiene, 116 g. (2 moles) of allyl alcohol and 0.2 g. of hydroquinone was refluxed for about 24 hours. Distillation of the mixture gave an almost complete recovery of unreacted allyl alcohol, and no alcohol adduct was obtained even with this large excess of allyl alcohol.

A mixture of 22.4 g. (0.4 mole) of propargyl alcohol, 26 g. (0.2 mole) of 2-phenyl-1,3-butadiene and 0.2 g. of hydroquinone was heated at 105–110° under a reflux condenser for 24 hours. Distillation led to the recovery of 21.3 g. of propargyl alcohol and 14.2 g. of 2-phenyl-1,3-butadiene. Two grams of material boiling between 55–180° (4 mm.) was obtained but gave no test for alcohols with phenyl isocyanate or with sodium.

A fourth fraction of 7.8 g., b.p. 180–190° (4 mm.), was obtained. After its solidification, it was recrystallized twice from ethanol and gave 6.0 g. of solid 1.4-diphenyl-4-vinylcyclohexene, m.p. and mixed m.p. 61.5–62°.

Other temperatures and concentrations of 2-phenyl-1,3-butadiene with allyl alcohol and propargyl alcohol were tried but no alcohol adduct was obtained.

Condensation of 2-Phenyl-1,3-butadiene and Phenylacetylene.—Ten grams (0.077 mole) of 2-phenyl-1,3-butadiene, 7.85 g. (0.077 mole) of phenylacetylene and 0.2 g. of phenyl-β-naphthylamine were heated under reflux for 24 hours. The temperature of the liquid remained at 165–167° after the first 4 hours. Distillation of the mixture gave 4.6 g. of 2-phenyl-1,3-butadiene mixed with phenylacetylene. The residue was dissolved in benzene. On evaporation of the benzene solution, there was obtained 0.90 g. of adduct, m.p. 205–206°. This substance sublimed in 95% yield to give very thin white plates, with no change in the melting point. The compound decolorized permanganate very slowly in acetone solution.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.38; H, 6.51 (calcd. for terphenyl, $C_{18}H_{14}$: C, 93.87; H, 6.13).

The analysis would seem to indicate that partial dehydrogenation had occurred during the reaction and the product may have been a mixture.

Heating of 0.133 g. of the above product with 0.045 g. of selenium at 225–230° for 3 hours gave a trace of *p*-terphenyl, but sublimation of the adduct and the selenium in the dehydrogenation tube prevented complete aromatization. The mixture was taken up in 20 ml. of nitrobenzene and heated under reflux for 3 hours. A few water droplets appeared in the nitrobenzene and were distilled out. The nitrobenzene was removed by vacuum distillation, leaving 0.11 g. of *p*-terphenyl, m.p. 210–211°. This product did not decolorize permanganate. It did not depress the melting point of the adduct but spread the melting point over the range from 205–210°.

α-(4-Phenyl-1,2,5,6-tetrahydrophenyl)-pyridine (VII).—Thirteen grams (0.1 mole) of 2-phenyl-1,3-butadiene, 10.5 g. (0.1 mole) of 2-vinylpyridine and 0.4 g. of phenyl-β-naphthylamine were heated under reflux for 24 hours. The temperature of the liquid rose gradually to 140–145°. Distillation of the reaction mixture gave 4.5 g. of unreacted starting materials and 6.2 g. of crude adduct, b.p. 165–167° (7 mm.), m.p. 74–76°. Recrystallization from benzene–petroleum ether gave nearly quantitative recovery of VII, m.p. 75–76°.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.76; H, 7.28. Found: C, 86.60; H, 7.26.

The adduct readily formed a picrate from ethanol solution, which crystallized as fine needles from ethanol and as transparent prisms from acetone, m.p. 171–172°.

Anal. Calcd. for $C_{23}H_{20}N_4O_7$: C, 59.48; H, 4.34. Found: C, 59.62; H, 4.25.

Dehydrogenation.—Two-tenths gram of the adduct was dissolved in 5 ml. of *p*-cymene and heated under reflux with 0.1 g. of 10% palladium–charcoal catalyst for 24 hours. The mixture was diluted with 10 ml. of benzene, filtered, and the filtrate was evaporated to dryness. A dark mixture of tar and crystals remained. From this residue, by extraction with a mixture of benzene and ligroin, 0.1 g. of 2-(4-biphenylyl)-pyridine was obtained, m.p. 141–142° (lit. 141–142°[12]). This compound was converted quantitatively to the picrate, m.p. 186–187° (lit. 186–187°[12]).

Acknowledgment.—The authors wish to thank Dr. C. C. Price for giving directions for the preparation of 2-phenyl-1,3-butadiene before their publication. The authors are also indebted to Rohm & Haas Company for a generous sample of technical acrylic acid, and to General Aniline and Film Corporation for a gift of propargyl alcohol.

The analyses reported were performed by The Clark Microanalytical Laboratory, Microchemical Specialties Company, Galbraith Microanalytical Laboratories and Mrs. Patricia Ramey.

BOULDER, COLORADO RECEIVED MARCH 5, 1951

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[12] I. M. Heilbron, D. H. Hey and A. Lambert, *J. Chem. Soc.*, 1279 (1940).