tallization from water. The yield of VII from III was 40%. Beilstein and Kuhlberg[9] report a m. p. of 77.5° for VII.

Anal. Calcd. for $C_7H_8O_2N_2$ (152): C, 55.3; H, 5.3; N, 18.4. Found: C, 55.2; H, 5.4; N, 18.5.

VII was also prepared from 2,4-dinitrotoluene (VIII). m. p. 70–71°, as described by Beilstein and Kuhlberg,[9] and a mixed m. p. of VII prepared from VI with VII prepared from VIII was 78–79°.

2-Amino-6-nitrotoluene (X).—2,6-Dinitrotoluene (IX), m. p. 65–66°, was obtained in 52% yield from IV using the method described by Kornblum.[10] IX was reduced as described by Bernthsen[11] to give X, m. p. 90–91°, in 80% yield. The m. p. of X is reported[11] to be 90.5°. The m. p. of X was depressed in the presence of VII and *vice versa.*

Summary

2-Amino-4-acetamido-6-nitrotoluene is obtained by the monoacetylation of 2,4-diamino-6-nitrotoluene with acetic anhydride either in acetone solution or in the absence of added solvent.

PASADENA, CALIFORNIA RECEIVED FEBRUARY 20, 1950

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[9] F. Beilstein and A. Kuhlberg, *Ann.*, **155**, 1 (1870).

[10] N. Kornblum, "Organic Reactions," **2**, 278 (1944).

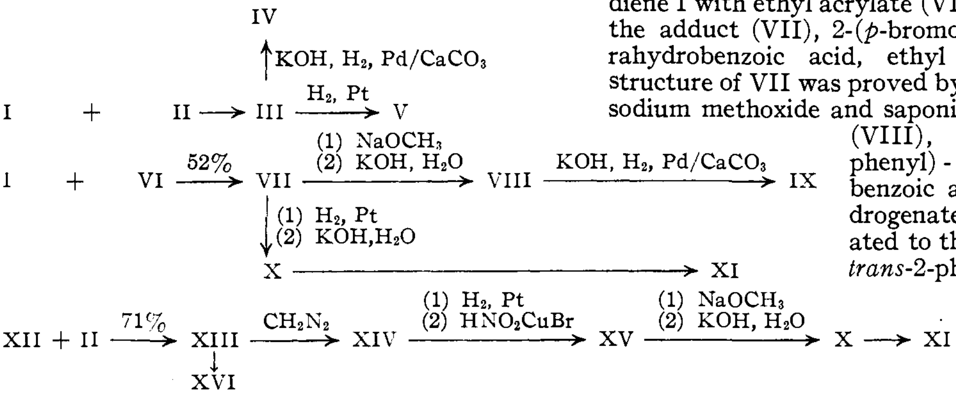
[11] A. Bernthsen, *Ber.*, **15**, 3011 (1882).

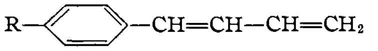
[CONTRIBUTION NO. 76 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Reactions of 1-(*p*-Bromophenyl)-1,3-butadiene[1] and 1-(*p*-Nitrophenyl)-1,3-butadiene with Acrylic Acid and Ethyl Acrylate

BY GUS A. ROPP[2] AND EUGENE C. COYNER[3]

As a continuation of a study[4] of the applicability of the anionoid–cationoid mechanism[5] to Diels–Alder reactions, acrylic acid and ethyl acrylate have now been caused to react with 1-(*p*-bromophenyl)-1,3-butadiene and 1-(*p*-nitrophenyl)-1,3-butadiene, and in all cases *ortho* adducts have been shown to result.

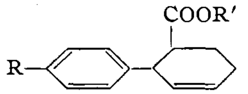




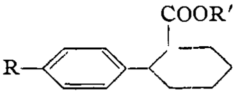
I R = Br
XII R = NO_2

$CH_2 = CHCOOR$

II R = H
VI R = C_2H_5



	R =	R′ =
III(*cis*)	Br	H
VII	Br	C_2H_5
VIII(*trans*)	Br	H
XIII	NO_2	H
XIV	NO_2	CH_3



	R =	R′ =
IV(*cis*)	H	H
V(*cis*)	Br	H
IX(*trans*)	H	H
X(*trans*)	Br	H
XI(*trans*)	Br	$NH_3CH_2C_6H_5$
XV	Br	CH_3
XVI	OH	H

1-(*p*-Bromophenyl)-1,3-butadiene (I) and acrylic acid (II) formed the adduct (III), *cis*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, for which both the *ortho* structure and the *cis* configuration were shown by hydrogenation and dehalogenation to the known acid (IV), *cis*-2-phenylhexahydrobenzoic acid.[4,6] The adduct III was also hydrogenated to the acid (V), *cis*-2-(*p*-bromophenyl)-hexahydrobenzoic acid. The diene I with ethyl acrylate (VI) gave in 52% yield the adduct (VII), 2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, ethyl ester. The *ortho* structure of VII was proved by isomerization with sodium methoxide and saponification to the acid (VIII), *trans*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid which was hydrogenated and dehalogenated to the known acid (IX), *trans*-2-phenylhexahydrobenzoic acid.[7] The adduct VII was also hydrogenated and saponified to form (X), *trans*-2-(*p*-bromophenyl)-hexahydrobenzoic acid, which was converted to its benzylamine salt (XI).

1-(*p*-Nitrophenyl)-1,3-butadiene (XII) and acrylic acid yielded 71% of the adduct (XIII), 2-(*p*-nitrophenyl)-1,2,5,6-tetrahydrobenzoic acid.

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[1] Presented in part at the 114th National Meeting of the American Chemical Society, St. Louis, Mo., September, 1948.

[2] Oak Ridge National Laboratory, Oak Ridge, Tennessee (Research Corporation Fellow 1946–1948).

[3] Mallinckrodt Chemical Works, St. Louis, Mo.

[4] Ropp and Coyner, THIS JOURNAL, **71**, 1832 (1949).

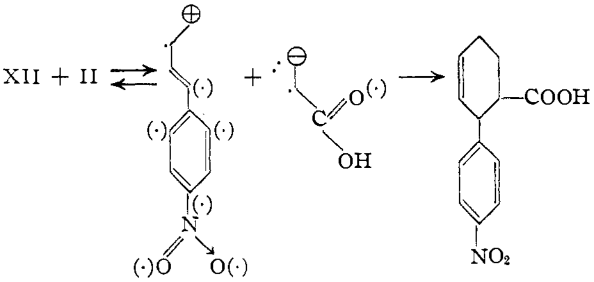
[5] Meek and Ragsdale, *ibid.*, **70**, 2502 (1948).

[6] Gutsche, *ibid.*, **70**, 4150 (1948).

[7] Fujise, *Ber.*, **71B**, 2461 (1938).

To prove the *ortho* structure of XIII, its methyl ester (XIV) was reduced to the saturated amino ester and converted via the Sandmeyer reaction to the methyl ester (XV) of 2-(*p*-bromophenyl)-hexahydrobenzoic acid. The *ortho* structure of the ester XV was shown by treatment with sodium methoxide and saponification to the previously described bromoacid X which was also converted to the previously described benzylamine salt XI. An attempt to prove the structure of the adduct XIII by reduction to the saturated amino acid and deamination resulted in the isolation of 2-(*p*-hydroxyphenyl)-hexahydrobenzoic acid (XVI).

Since the simple anionoid-cationoid mechanism would point to the formation of the *meta* adduct from 1-(*p*-nitrophenyl)-1,3-butadiene and since it fails to explain the greater ease of formation of a high yield of *p*-nitro adduct as compared to the *p*-bromo adduct, some such modification as the electron-pairing mechanism of Woodward[8] seems more probable



Following transfer of an electron from the diene to the dienophile, the charged intermediates shown could be stabilized as resonance hybrids, the odd electrons residing at the positions indicated by (·) with corresponding shifts in the bond structures. 1-(*p*-Bromophenyl)-1,3-butadiene could also form the *ortho* adduct according to this mechanism, but the lesser degree of resonance stabilization of the odd electron which is possible with the *p*-bromo intermediate could explain the observed fact that the Diels–Alder reaction of the *p*-bromo diene is less facile than that of the *p*-nitrodiene.

Allyl-*p*-bromophenylcarbinol was prepared in 95% yield by the Grignard reaction from *p*-bromobenzaldehyde and converted to 1-(*p*-bromophenyl)-1,3-butadiene in 25–50% yields by a series of reactions analogous to those used to prepare 1-phenyl-1,3-butadiene.[9] An attempted diene preparation by dehydrohalogenation[10] of 1-chloro-4-(*p*-bromophenyl)-butene-2, which was prepared by the Meerwein reaction[10] from *p*-bromoaniline, was unsuccessful although dehydrohalogenation was previously found[10] to be successful with the *p*-nitro analog. The greater ease of dehydrohalogenation of the nitro compound is readily explained by the greater electron withdrawing effect of the *p*-nitro group with respect to the *p*-bromo group; extraction of a proton from the *alpha* carbon atom is facilitated by the withdrawal of electrons from the side chain.

Experimental

1. **Preparation of 1-(*p*-Bromophenyl)-1,3-butadiene (I) (a) Preparation from Allyl-*p*-bromophenylcarbinol (1) Preparation of Allyl-*p*-bromophenylcarbinol.**—To a solution of allylmagnesium bromide which had been prepared from 242 g. (2.0 moles) of freshly distilled allyl bromide, 73 g. (3.0 moles) of magnesium and 750 ml. of ether, and had been filtered by forcing through a filter stick with nitrogen pressure, there was added during two hours a dry ethereal (650 ml.) solution of 88 g. (0.5 mole) of *p*-bromobenzaldehyde. The Grignard addition product was decomposed at 0° with saturated ammonium chloride solution, and the ether layer was separated, washed twice with water, and dried over anhydrous magnesium sulfate. The ether was distilled at room temperature *in vacuo*, and the carbinol distilled as a clear, colorless, viscous oil weighing 107.8 g. (95% yield), b. p. 133–135° at 3 mm.

Anal. Calcd. for $C_{10}H_{11}OBr$: Br, 35.19. Found: Br, 35.51, 35.75.

(2) **Reaction of Allyl-*p*-bromophenylcarbinol with Hydrogen Bromide.**—Twenty-three grams (0.10 mole) of allyl-*p*-bromophenylcarbinol was stirred forty-five minutes while anhydrous hydrogen bromide was introduced with cooling to below 50°. When there was no longer a tendency of the temperature to rise, and the oil layer was extracted with benzene, the extract was washed four times with water and dried over anhydrous magnesium sulfate. The solvent was distilled and the residual oil was vacuum distilled several times in nitrogen atmosphere. The final distillate was a pale yellow, viscous oil, b. p. 108–117° at 2 mm., $n^{31.5}$ 1.5813.

(3) **Dehydrohalogenation of Crude 1-Bromo-1-(*p*-bromophenyl)-butene-3.**—To a solution in 250 ml. of dry benzene of the 1-bromo-1-(*p*-bromophenyl)-butene-3 concentrate obtained from 0.1 mole of carbinol, 12 g. of C. P. pyridine and 0.01 g. of hydroquinone were added, and the solution was stirred twenty-three hours under reflux. A light colored gum which collected and was separated and washed with benzene (wt. 20 g.) was found to contain 73% of the theoretical amount of bromide ion. The benzene solution was dried over anhydrous magnesium sulfate in a refrigerator, benzene was distilled *in vacuo*, and 10.2 g. of diene (50% yield) distilled as a pale yellow oil, b. p. 99–109° at 1 mm. A small sample was redistilled to give a viscous colorless oil, b. p. 121–124° at 7 mm. (Braude, Jones and Stern[11] give 88° at 1 micron), n^{23} 1.6368. In batches of larger size lower yields were obtained; in a preparation from 0.36 mole of carbinol, the yield was 26%.

(b) **1-Chloro-4-(*p*-bromophenyl)-butene-2.**—Thirty-four and one-half grams (0.2 mole) of C. P. *p*-bromoaniline was diazotized using 75 ml. of C. P. hydrochloric acid, 75 ml. of water, and 14 g. of sodium nitrite. Two hundred milliliters of acetone, 16 g. of sodium acetate, 6 g. of cupric chloride, 30 ml. of water, and 18 ml. of liquid butadiene were stirred in an ice–salt-bath and the diazonium salt solution was added dropwise during twenty minutes at −2 to +1°. The mixture was allowed to warm to room temperature while stirring four hours. An ether extract of the oil layer was washed three times with water and dried over anhydrous magnesium sulfate. When the ether was distilled in nitrogen atmosphere, 32 g. of deep brown oil remained as a residue. A sample of this concentrate was not affected by cold alcoholic potassium hydroxide at 30–32°, but the unreacted 1-chloro-4-(*p*-bromophenyl)-butene-2 was recovered as a clear white oil after distilling three times, b. p. 118–122° at 0.5 mm., n^{25} 1.5720.

Anal. Calcd. for $C_{10}H_{10}ClBr$: C, 48.99; H, 4.10. Found: C, 48.62, 48.74; H, 4.02, 4.09.

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[8] Woodward, This Journal, **64**, 3058 (1942).

[9] Coyner and Ropp, *ibid.*, **69**, 2231 (1947).

[10] Coyner and Ropp, *ibid.*, **70**, 2283 (1948).

[11] Braude, Jones and Stern, *J. Chem. Soc.*, 1087 (1947).

II. **Diels–Alder Reactions of 1-(*p*-Bromophenyl)-1,3-butadiene and Structural Proof of the Adducts: (a) *cis*-2-(*p*-Bromophenyl)-1,2,5,6-tetrahydrobenzoic Acid** (III).—Five and eight-tenths grams (0.028 mole) of 1-(*p*-bromophenyl)-1,3-butadiene, 2.1 g. of acrylic acid (0.030 mole) and a trace of hydroquinone were heated at 100° in a sealed tube seventeen hours. Acidic components of the reaction mixture were extracted with excess aqueous sodium bicarbonate, the extract was acidified with C. p. hydrochloric acid, and a white gum which separated was collected and treated with charcoal in hot ligroin (b. p. 90–120°), then recrystallized from cyclohexane and from ligroin. Approximately 10 mg. of white flakes of *cis*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, m. p. 135–137° was obtained.

Anal. Calcd. for $C_{13}H_{13}O_2Br$: C, 55.53; H, 4.66. Found: C, 55.20, 55.32; H, 4.54, 4.62.

(1) **Hydrogenation and Dehalogenation.**—Two-tenths gram of *cis*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, 0.2 g. of potassium hydroxide, 2 g. of palladium on calcium carbonate catalyst, and 10 ml. of absolute ethyl alcohol were shaken forty-four hours in hydrogen[12] at 55 pounds pressure at room temperature. The catalyst was removed by filtration, and the filtrate was acidified with nitric acid and cooled in ice. A gray solid was collected on a filter and recrystallized from aqueous methanol to give 20 mg. of white solid, m. p. 65–71°, which caused no mixed melting point depression with *cis*-2-phenylhexahydrobenzoic acid[6] (IV) when the two acids were mixed.

(2) *cis*-**2-(*p*-Bromophenyl)-hexahydrobenzoic Acid** (V).—A solution of 0.63 g. (0.0023 mole) of *cis*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid in 10 ml. absolute ethanol was shaken in hydrogen at 1 atm. pressure at room temperature with 0.01 g. of platinum oxide and a drop of acetic acid. After two hours shaking, the catalyst was removed by filtration, and water was added to the filtrate to precipitate a white solid which was collected on a filter and recrystallized three times from aqueous methanol to give 10 mg. of white crystalline *cis*-2-(*p*-bromophenyl)-hexahydrobenzoic acid, m. p. 105.5–108°.

Anal. Calcd. for $C_{13}H_{15}O_2Br$: C, 55.14; H, 5.34. Found: C, 55.18, 55.29; H, 5.42, 5.36.

(b) **2-(*p*-Bromophenyl)-1,2,5,6-tetrahydrobenzoic Acid, Ethyl Ester** (VII).—Five and eight-tenths grams (0.028 mole) of 1-(*p*-bromophenyl)-1,3-butadiene, 3.0 g. (0.03 mole) of freshly distilled ethyl acrylate, and approximately 0.01 g. of hydroquinone were heated twenty-one hours in a sealed tube at 160–180°. Excess ethyl acrylate was distilled by heating to 100° at 12 mm. and the product, 4.5 g. (52% yield) of viscous water-white 2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, ethyl ester, boiled at 158–160° at 0.5 mm., n^{23} 1.5495.

Anal. Calcd. for $C_{15}H_{17}O_2Br$: C, 58.26; H, 5.54. Found: C, 58.20, 58.20; H, 5.45, 5.45.

(1) *trans*-**2-(*p*-Bromophenyl)-1,2,5,6-tetrahydrobenzoic Acid** (VIII).—Three milliliters of methanol containing 0.1 g. of dissolved sodium[13] and 0.5 g. of the ethyl ester of 2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid was refluxed twenty-three hours on a steam-bath. Five grams of potassium hydroxide and 15 ml. of water were added, and the solution was stirred twenty-one hours at reflux in a bath heated to 140°. The solution was acidified, and a solid was removed by filtration. About 50 mg. of white granular *trans*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, m. p. 114–115.5°, was obtained by recrystallization from ligroin (b. p. 70–90°) then from cyclohexane.

Anal. Calcd. for $C_{13}H_{13}O_2Br$: C, 55.53; H, 4.66. Found: C, 55.82, 55.60; H, 4.79, 4.61.

Hydrogenation and Dehalogenation.—Two-tenths gram of *trans*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, 2 g. of palladium on calcium carbonate catalyst,[12] 0.2 g. of potassium hydroxide, and 10 ml. of absolute ethyl alcohol were shaken forty-nine hours in hydrogen at 62 pounds pressure. The solution was stirred with charcoal and filtered. Acidification of the filtrate precipitated a solid which when dried in a vacuum desiccator, weighed 0.09 g., m. p. 104–105.5°. The acidic filtrate was found to contain bromide ion equivalent to the organic acid used. The melting point of the product was not depressed by mixing with a sample of *trans*-2-phenylhexahydrobenzoic acid[6] (IX).

(2) *trans*-**2-(*p*-Bromophenyl)-hexahydrobenzoic Acid** (X).—Eighty-four one-hundredths gram (0.0027 mole) of the ethyl ester of 2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, 5 ml. of absolute ethyl alcohol, and 0.05 g. platinum oxide were shaken in hydrogen at 1 atm. pressure at 32.5°. After one hour, the catalyst was removed by filtration, the alcohol was distilled from the filtrate, 7 ml. of methanol containing 0.1 g. of dissolved sodium was added, and the solution was heated under reflux fifteen hours on a steam-bath. Thirty-five milliliters of water and 2 g. of potassium hydroxide were added, and the mixture was stirred four and one-half hours at 100°. The solution was diluted and treated with charcoal. The filtrate was acidified and cooled in ice and a yellow solid which crystallized was purified by charcoal treatment in aqueous methanol. Air-dried product, *trans*-2-(*p*-bromophenyl)-hexahydrobenzoic acid, 0.77 g., m. p. 130–137°, was recrystallized twice from aqueous methanol to give 10 mg. of white powder, m. p. 138.5–140°.

Anal. Calcd. for $C_{13}H_{15}O_2Br$: C, 55.15; H, 5.34. Found: C, 55.35; H, 5.29.

Benzylamine Salt (XI).—The benzylamine salt[14] was prepared and recrystallized from absolute alcohol, then from ethyl acetate, to give a flaky white solid salt m. p. 188–190°.

Anal. Calcd. for $C_{20}H_{24}O_2NBr$: Br, 20.48. Found: Br, 20.50, 20.32.

III. **Diels–Alder Reaction of 1-(*p*-Nitrophenyl)-1,3-butadiene (XII) and Structural Proof of the Adduct: (a) 2-(*p*-Nitrophenyl)-1,2,5,6-tetrahydrobenzoic Acid** (XIII).—Recrystallized 1-(*p*-nitrophenyl)-1,3-butadiene[10] was caused to react with a slight excess of acrylic acid by refluxing a solution of the reactants and a trace of hydroquinone in xylene two to three hours in a nitrogen atmosphere. The solution was cooled and all acidic material was extracted with saturated sodium bicarbonate. The aqueous layer was acidified and diluted, and the precipitated oil crystallized after several hours. The resulting pale yellow solid was ground in fresh water, collected on a filter, and washed thoroughly with water to remove acrylic acid. Dried adduct (71%) m. p. 111–114°, was further purified by three recrystallizations from ligroin (b. p. 90–120°) containing 10% benzene. Pale yellow crystalline 2-(*p*-nitrophenyl)-1,2,5,6-tetrahydrobenzoic acid was obtained, m. p. 116.5–118.0°.

Anal. Calcd. for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30. Found: C, 62.90, 62.97; H, 5.17, 5.21.

In large scale preparations a deeply yellow crystalline by-product obtained from the toluene layer by evaporation after all the acidic material had been removed by extraction with sodium bicarbonate solution was purified by recrystallization from ethanol, and a pale yellow solid, m. p. 145.2–147.4°, was obtained. The same compound was obtained from an attempted reaction of 1-(*p*-nitrophenyl)-1,3-butadiene and ethyl acrylate; no melting point depression resulted from mixing of these materials from different sources. This fact, the analysis of the material, and its melting point led to the belief that this substance was a dimer of 1-(*p*-nitrophenyl)-1,3-butadiene; however, molecular weight determination by use of a differential thermometer[15] did not support this belief with certainty.

Anal. Calcd. for $C_{20}H_{18}O_4N_2$: C, 68.56; H, 5.19; mol. wt., 350.4. Found: C, 68.40, 68.20; H, 4.85, 4.85; mol. wt., 392, 394.

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[12] Busch and Stoeve, *Ber.*, **49**, 1063 (1916).

[13] Linstead and Doering, THIS JOURNAL, **64**, 2000 (1942); Cook and Linstead, *J. Chem. Soc.*, 946 (1934).

[14] Buehler, Carson and de Edds, THIS JOURNAL, **57**, 2181 (1935).

[15] Menzies and Wright, *ibid.*, **43**, 2314 (1921).

(1) **2-(*p*-Nitrophenyl)-1,2,5,6-tetrahydrobenzoic Acid Methyl Ester (XIV).**—A diazomethane in ether solution prepared from 15 g. of nitrosomethylurea was added to a solution of 10 g. of 2-(*p*-nitrophenyl)-1,2,5,6-tetrahydrobenzoic acid. Excess reagent was decomposed by addition of a few drops of glacial acetic acid; the ether solution was washed with potassium hydroxide solution and with water, dried over anhydrous magnesium sulfate, and distilled *in vacuo* in nitrogen atmosphere. 2-(*p*-Nitrophenyl)-1,2,5,6-tetrahydrobenzoic acid, methyl ester, b. p. 120–138° at less than 1 mm., was collected.

Anal. Calcd. for $C_{13}H_{13}O_4N$: C, 64.35; H, 5.79, Found: C, 64.07, 64.17; H, 5.61, 5.71.

(2) **2-(*p*-Bromophenyl)-hexahydrobenzoic Acid, Methyl Ester (XV).**—Six grams (0.024 mole) of the adduct from 1-(*p*-nitrophenyl)-1,3-butadiene and acrylic acid was treated with diazomethane in ether solution and the reaction was completed by boiling the solution to remove excess diazomethane. An equal volume of 95% ethyl alcohol was added to the ether solution. The solution was shaken three hours in hydrogen at 45 pounds pressure with 0.1 g. of platinum oxide. Eighty-eight per cent. of the theoretical amount of hydrogen calculated for the reduction to the methyl ester of 2-(*p*-aminophenyl)-hexahydrobenzoic acid was absorbed. The catalyst was removed by filtration and the solvent was distilled *in vacuo*. The concentrate was dissolved in 20 ml. of 48% hydrobromic acid and diazotized, and the diazonium salt separated as a solid. The mixture was stirred vigorously in an ice-bath at +4 to +6° while a solution of 3 g. of cuprous bromide in 10 ml. of 48% hydrobromic acid was added. After stirring twenty-two hours at room temperature, 60 ml. of benzene was added and the mixture was stirred at reflux one hour. Two homogeneous layers separated; the upper benzene layer was removed and washed with dilute potassium hydroxide, then with water, and dried over anhydrous magnesium sulfate. When the solvent was distilled *in vacuo*, 4.6 g. of light red oil which remained was distilled in nitrogen atmosphere, and 1.5 g. of viscous yellow oil, b. p. 160–169° at 2.5 mm., was collected.

Anal. Calcd. for $C_{14}H_{17}O_2Br$: C, 56.57: H, 5.76. Found: C, 57.12, 57.17; H, 6.00, 5.89.

Sodium Methoxide Treatment and Saponification.—A sample of the distilled methyl ester was heated with a methanol solution of sodium methoxide at reflux temperature three hours. The ester was saponified by stirring twenty hours with aqueous alcoholic potassium hydroxide and crystals were obtained of a white solid, m. p. 137.5–139°, which mixed with the previously described 2-(*p*-bromophenyl)-hexahydrobenzoic acid (X) gave no melting point depression. When the benzylamine salt was prepared, a sample mixed with the independently prepared benzylamine salt (XI) of 2-(*p*-bromophenyl)-hexahydrobenzoic acid caused no melting point lowering.

(3) **2-(*p*-Hydroxyphenyl)-hexahydrobenzoic Acid (XVI).**—A solution of 5.2 g. of 2-(*p*-nitrophenyl)-1,2,5,6-tetrahydrobenzoic acid in ethanol was shaken with 0.1 g. of platinum oxide in hydrogen at 37 lb. pressure. After fifty-three minutes the pressure had decreased 6.7 lb. as compared with 6.8 lb. calculated for reduction to 2-(*p*-aminophenyl) - hexahydrobenzoic acid. The reduction product separated from the alcohol as a gray solid which was collected on a filter and oven-dried. A sample proved to be soluble in aqueous hydrochloric acid and ammonium hydroxide and insoluble in organic solvents. Attempted hypophosphorous acid deamination of the reduction product yielded about 5 mg. of white powder, m. p. 178.7–179.6°, which was separated by extraction and sublimation from the bulk of the reaction mixture. Analysis indicated that this product was the phenol, 2-(*p*-hydroxyphenyl)-hexahydrobenzoic acid.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.38, 70.22; H, 7.03, 7.29.

Acknowledgments.—The writers express their appreciation for grants from the Research Corporation which supported this investigation and are indebted to Rohm and Haas Company for research samples of acrylic acid and ethyl acrylate. They also wish to thank Mr. J. W. Holding for his assistance in preparing a supply of allyl-*p*-bromophenylcarbinol.

Summary

A new synthesis of 1-(*p*-bromophenyl)-1,3-butadiene has been described; this diene has been caused to undergo Diels–Alder reactions with acrylic acid and ethyl acrylate, and the adducts have been shown to be *cis*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid and the ethyl ester of 2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, respectively.

1-(*p*-Nitrophenyl)-1,3-butadiene has been caused to react with acrylic acid to form in 71% yield an adduct in which the carboxyl and *p*-nitrophenyl groups are *ortho*.

Knoxville, Tennessee Received October 24, 1949