isolated and no better results were obtained by using the minimum temperature at which hydrogen sulfide was evolved.

One-tenth of a gram of crude VII was converted to its sodium salt and dried. Upon heating at 225–235° with a 50% excess of sulfur, a steady evolution of gas was maintained and only a trace of biphenyl was isolated. Acidification of the dehydrogenated salt gave brownish material melting at 165–175°, lit. 166° for *m*-phenylbenzoic acid.[17]

Hydrogenation of V and VI.—Twenty milligrams of platinum oxide, 0.763 g. of VI in 20 ml. of ethanol were shaken for two hours and fifteen minutes under an atmosphere of hydrogen at room temperature. At the end of this time the theoretical amount of hydrogen was absorbed. The product melted at 76–80°; reported for *cis*-2-phenylcyclohexanecarboxylic acid 76–77°.[8]

In an identical experiment with V, twelve hours of shaking led to the absorption of only about 15% of the theoretical amount of hydrogen and only the original compound could be isolated.

One gram of the pure sodium salt of V was dissolved in 50 ml. of water and refluxed for two hours with an excess of W-6 Raney nickel.[18]

The nickel was filtered and the filtrate was acidified carefully with 6 *N* hydrochloric acid. Upon cooling, crystals appeared and 0.85 g. of acid (94%), m. p. 103–107°, was obtained. The reported melting point of *trans*-2-phenylcyclohexanecarboxylic acid is 106–107°. The S-benzylthiuronium salt of the hydrogenated product was obtained in good yield by the procedure outlined by Donleavy.[19] The shiny, needle-like crystals obtained melted at 123–125°. One recrystallization from ethyl acetate raised the melting point to 124–126°, reported m. p. 126.5–127°.[8]

One gram of pure VI was converted to its sodium salt and reduced by refluxing as before with Raney nickel. When refluxed for one hour, the chief product was an acid, m. p. 76–79°, reported m. p. 76–77° for *cis*-2-phenylcyclohexanecarboxylic acid.[8] The S-benzylthiuronium salt of this product melted at 148–152°, reported m. p. 152–153°.[8] When the period of heating with Raney nickel was extended to two hours, nearly equal amounts of *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids were obtained. Longer periods of heating results in almost complete conversion to the *trans* product.

Isomerization of V, VI and VII.—When pure V was heated under reflux in an excess of 10% sodium hydroxide for two hours over 90% of V could be recovered with its melting point depressed about one degree. When a sample of VI melting at 120–121.5° was similarly treated, the product melted at 96–113° and chiefly V and some VI were isolated. When VII was treated in the same manner with alkali, it was recovered quantitatively and only a slight depression of its melting point was noted. When VI was heated at 95° for six hours in toluene no significant change was observed.

Acknowledgment.—The authors wish to thank the Shell Development Company for a generous sample of acrolein used in this research. The analysis of VII was performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

Summary

The condensation of 1-phenyl-1,3-butadiene with acrolein and acrylic acid has led mainly to the *trans-ortho* adduct and some of the *cis–ortho* isomer in each case.

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[17] Jacobson and Lischke, *Ber.*, **28**, 2547 (1895).

[18] Adkins and Billica, THIS JOURNAL, **70**, 695 (1948).

[19] Donleavy, *ibid.*, **58**, 1004 (1936).

[CONTRIBUTION NO. 58 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Reactions of 1-Phenyl-1,3-butadiene[1] with Acrylic Acid, Ethyl Acrylate and Methyl Vinyl Ketone

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

The reaction of 1-phenyl-1,3-butadiene (I) with ethyl acrylate (V) has been found to give in 78% yield an adduct which when saponified yields an acid (VI), m. p. 102°, which Lehmann and Paasche[4] and Blumenfeld[5] proved to be a 2-phenylcyclohexenecarboxylic acid. The adduct (III), m. p. 120°, from acrylic acid (II) and 1-phenyl-1,3-butadiene was considered by Lehmann and Paasche to be a 3-phenylcyclohexenecarboxylic acid. Cook and Hewitt,[6] however, hydrogenated a crude sample of the acid (III) and obtained in low yield the acid (VII), m. p. 105–107°, which they independently synthesized to show that it was 2-phenylhexahydrobenzoic acid. Since their sample of III was not pure, the possibilities remained (1) that the acid m. p. 120° was a 3-phenylcyclohexenecarboxylic acid, (2) that III and VI were 2-phenylcyclohexenecarboxylic acids differing only in position of the double bond, or (3) that III and VI were *cis* and *trans* forms of 2-phenylcyclohexenecarboxylic acid.

It is now shown that acid III is *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid by isomerization with sodium methoxide to VI which is therefore *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid. The possibility that III and VI are double bond position isomers was eliminated by hydrogenation of acid VI to acid VII which must therefore be *trans*-2-phenylhexahydrobenzoic acid, and hydrogenation of acid III to acid IV which must therefore be *cis*-2-phenylhexahydrobenzoic acid. Isomerization of acid IV yielded acid VII which is identical with *trans*-2-phenylhexahydrobenzoic acid[7] prepared by reduction of *o*-phenylbenzoic acid (VIII).

The reaction of 1-phenyl-1,3-butadiene and methyl vinyl ketone (X) yielded an adduct (XI), 2-phenyl-1,2,5,6-tetrahydroacetophenone, which,

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

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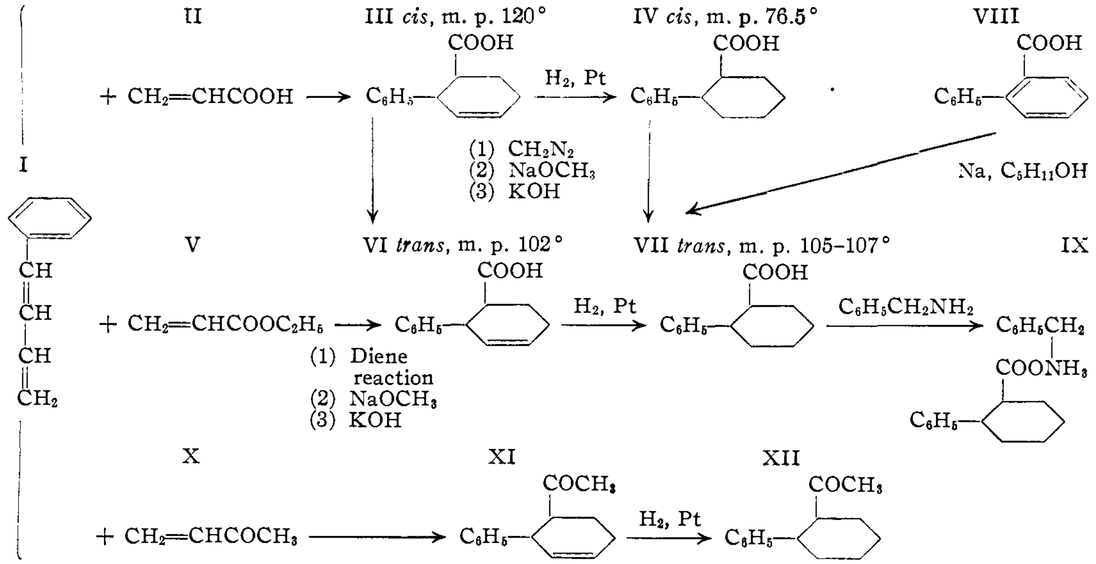
[3] Present address: Mallinckrodt Chemical Works, St. Louis, Mo.

[4] Lehmann and Paasche, *Ber.*, **68**, 1146 (1935).

[5] Blumenfeld, *ibid.*, **74**, 524 (1941).

[6] Cook and Hewitt, *J. Chem. Soc.*, 62 (1936).

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



upon hydrogenation, gave the previously reported 2-phenylhexahydroacetophenone (XII).

The reaction of 1-phenyl-1,3-butadiene with ethyl acrylate, acrylic acid or methyl vinyl ketone to give an adduct in which the carbethoxy, carboxyl, or acetyl group is *ortho* to the phenyl group is explained by the usually advanced anionoid–cationoid mechanism[8] for the Diels–Alder reaction.

Diels–Alder reactions with the *p*-bromo and *p*-nitro derivatives of 1-phenyl-1,3-butadiene will be reported in a separate publication.

Experimental

Reaction of 1-Phenyl-1,3-butadiene (I) and Acrylic Acid (II).—Ten grams (0.077 mole) of diene,[9] b. p. 62–72° at 4–5 mm., and 7 g. (0.092 mole) of acrylic acid were heated with approximately 0.05 g. of hydroquinone in a sealed Pyrex tube at 100° for two and one-fourth hours. The reaction mixture from the tube solidified when cooled. It was recrystallized from 25 cc. of hot 80% methanol and a coarse white solid was obtained. This solid was triturated in water, collected on a filter, and dried thoroughly to yield 4.9 g. of white powder, m. p. 95–110°, which was recrystallized from 15 cc. of ligroin, b. p. 90–120°, then from 23 cc. of 80% methanol. The white crystalline product weighed 2.4 g. (15.5%), m. p. 114.5–118.5°. Repeated recrystallizations from the same solvents yielded a small amount of very pure *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid (III) which crystallized as white needles, m. p. 120–121°.

***cis*-2-Phenylhexahydrobenzoic Acid (IV).**—One-half gram of *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid (III), m. p. 119–120°, 19 cc. of absolute ethyl alcohol, 0.03 g. of platinum oxide, and 2 drops of glacial acetic acid were shaken under hydrogen at 1 atm. pressure. Approximately the theoretical volume of hydrogen was absorbed in thirty minutes. The catalyst was removed by filtration, and the product was precipitated by addition of 20 cc. of water and collected on a filter. This sample was twice recrystallized from aqueous methanol, then sublimed *in vacuo* to give very small hexagonal crystals, m. p. 76.0–76.5°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.60, 76.38; H, 8.18, 8.36.

Reaction of 1-Phenyl-1,3-butadiene (I) and Ethyl Acrylate (V).—Twenty-five and one-half grams (0.195 mole) diene, b. p. 93–96.5° at 15–16 mm., 20 g. (0.20 mole) ethyl acrylate and 0.1 g. of hydroquinone were heated nineteen hours at 100° in an open flask. From the clear, light yellow, slightly viscous solution, unreacted material was distilled by heating to 150° at 25–35 mm., and 40 g. of oil remained. Distillation in nitrogen atmosphere yielded 35.5 g. (78%) of clear, pale yellow, viscous 2-phenyl-1,2,5,6-tetrahydrobenzoic acid ethyl ester, b. p. 154–157° at 0.5–17 mm., n^{25} 1.5283.

Saponification of the ester to *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid (VI) was effected by refluxing for periods up to seventy hours with aqueous ethanolic potassium hydroxide. The highest recoveries of pure acid were of the order of 25%, obtained by refluxing the ethyl ester with sodium methoxide solution in methanol before saponification in order to isomerize, at least partially, *cis* ester to *trans*. In one case where this preliminary isomerization was omitted, recovery of pure acid amounted to less than 1%. The writers believe that the Diels–Alder reaction probably produces *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid ethyl ester, but that partial isomerization to the *trans* ester takes place at the temperature of the reaction.

Hydrogenation of *trans*-2-Phenyl-1,2,5,6-tetrahydrobenzoic Acid (VI).—One half gram of VI, m. p. 101.5–102.5°, from saponification of the adduct from 1-phenyl-1,3-butadiene and ethyl acrylate, 19 cc. of absolute ethyl alcohol, 0.035 g. of platinum oxide, and 2 drops of glacial acetic acid were shaken under hydrogen at 1 atm. pressure. About 90% of the calculated volume of hydrogen was absorbed in twenty minutes. The catalyst was removed by filtration and washed with 25 cc. of methanol. Addition of 50 cc. of distilled water precipitated the product, *trans*-2-phenylhexahydrobenzoic acid (VII), m. p. 107–109°.

Benzylamine Salt[10] of *trans*-2-Phenylhexahydrobenzoic Acid (IX).—This salt was obtained as white flakes, m. p. 182.5–185° by two recrystallizations from ethyl acetate.

Anal. Calcd. for $C_{20}H_{25}O_2N$: C, 77.13; H, 8.09. Found: C, 76.82, 77.00; H, 8.18, 8.01.

Reduction of *o*-Phenylbenzoic Acid (VIII).—*o*-Phenylbenzoic acid was reduced with sodium and amyl alcohol according to the procedure of Ranedo and Léon[11] to *trans*-2-phenylhexahydrobenzoic acid. The product showed no depression of its melting point when mixed with the acid VII produced by hydrogenation of VI. For con-

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[8] Meek and Ragsdale, THIS JOURNAL, **70**, 2502 (1948).

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

[10] Buehler, Carson and Edds, *ibid.*, **57**, 2181 (1935).

[11] Ranedo and Léon, *Anal. fis. quim.*, **23**, 113 (1925).

firmation the benzylamine salt of the acid prepared by sodium and amyl alcohol reduction was made and gave no melting point depression when mixed with IX.

Isomerization of *cis*-2-Phenyl-1,2,5,6-tetrahydrobenzoic Acid (III).—The adduct of 1-phenyl-1,3-butadiene with acrylic acid, 0.2 g., m. p. 120–122°, was methylated in ether solution with diazomethane. After excess diazomethane was decomposed with glacial acetic acid, the ether and methyl acetate were distilled *in vacuo*. A solution of 0.1 g. of sodium in 10 cc. of methanol was added. After the solution was refluxed for seven and one-half hours, an equal volume of water containing 2 g. of potassium hydroxide was added. Refluxing was then continued for thirteen and one-half hours. Two volumes of water was added and the solution was treated with charcoal while hot. The solution was filtered and acidified, and the white solid, *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid, was separated by filtration, m. p. 101.5–102.5°. This product gave no melting point depression when mixed with the acid prepared by saponification of the adduct (VI) of 1-phenyl-1,3-butadiene and ethyl acrylate.

Isomerization of *cis*-2-Phenylhexahydrobenzoic Acid (IV).—The acid prepared by hydrogenation of the adduct of 1-phenyl-1,3-butadiene and acrylic acid was methylated and treated with sodium methoxide by the methods previously described. The crude product was treated with charcoal in hot ligroin (b. p. 90–120°) to give a white product, m. p. 105–107°. This melting point was not depressed by mixing with the product of hydrogenation of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid (VI).

2-Phenyl-1,2,5,6-tetrahydroacetophenone (XI).—Methyl vinyl ketone (X), b. p. 35–40° at 120–130 mm., was prepared by cooling the du Pont azeotrope in Dry Ice–acetone, treating with potassium carbonate and anhydrous calcium chloride to remove acetic acid and water, and distilling *in vacuo* into a receiver cooled by Dry Ice–acetone. Twelve grams of ketone, 20 g. of 1-phenyl-1,3-butadiene (I), b. p. 64–72° at 4 mm., and 0.05 g. of hydroquinone were heated for seventeen hours at 100–130° in a sealed tube. The reaction mixture was dissolved in ether and the ether solution was washed with water, dried over anhydrous magnesium sulfate and distilled. Nineteen and one-half grams (62%) of a colorless viscous oil, b. p. 118–122° at 1 mm., was obtained.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.39, 84.26; H, 8.11, 8.38.

Hydrogenation of 2-Phenyl-1,2,5,6-tetrahydroacetophenone (XI).—Ten grams of 2-phenyl-1,2,5,6-tetrahydroacetophenone, 100 cc. of absolute alcohol and 0.1 g. of platinum oxide were shaken under hydrogen at 10 pounds pressure. The theoretical amount of hydrogen was absorbed in twenty minutes. The catalyst was removed by filtration, and 2-phenylhexahydroacetophenone (XII) was distilled as 9 g. of clear water-white oil, b. p. 115–120° at 1.5 mm., $n^{28.5}$ 1.5261. The distillate solidified and was recrystallized from methanol to give a white solid, m. p. 78–78.5°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12, H, 8.97. Found: C, 82.97, 83.07; H, 8.78, 8.82.

This melting point corresponds to that of the 2-phenylhexahydroacetophenone produced by Kipping and Perkin[12] by acetoacetic ester synthesis from 1-phenyl-1,5-dibromopentane.

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 ethyl acrylate and aqueous acrylic acid and to the du Pont Company for a sample of methyl vinyl ketone azeotrope.

Summary

Adducts of 1-phenyl-1,3-butadiene with acrylic acid, ethyl acrylate and methyl vinyl ketone are shown to be 1-substituted-2-phenylcyclohexene-3 derivatives.

[12] Kipping and Perkin, *J. Chem. Soc.*, 304–323 (1890).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Diene Synthesis of 1-Phenyl-1,3-butadiene with Acrylonitrile and Methyl Vinyl Ketone

BY LEO REICH[1] AND ERNEST I. BECKER

The conflicting literature concerning *cis–trans versus ortho–meta* isomerism in the addition of 1-phenyl-1,3-butadiene to unsymmetrical dienophiles has been reviewed by Ropp and Coyner.[2] In view of the proof by Ropp and Coyner that only *ortho*-substitution results, it seemed unusual to find that the addition of *trans*-piperylene to acrylonitrile gives about 10% of *meta*-substituted product in addition to the major *ortho*-substituted product,[3] while in the addition of methyl acrylate,[4] acrolein[5] and crotonaldehyde[5] to piperylene only the products with the diene methyl ortho to the aldehyde or ester group were found. In view of these results, it seemed desirable to extend the diene synthesis with 1-phenyl-1,3-butadiene to acrylonitrile and methyl vinyl ketone.

The condensation of acrylonitrile with 1-phenyl-1,3-butadiene gives a colorless, viscous liquid (I-1) (see Chart I) in 60% yield. The product is unsaturated with respect to bromine in carbon tetrachloride, and its analysis is in accord with an adduct consisting of one molecule each of 1-phenyl-1,3-butadiene and acrylonitrile.

The attempted hydrolysis of this nitrile with alkali took place only very slowly, so that an alternate proof of structure was adopted. This very slow hydrolysis suggests that the compound may be the *cis*-ortho-derivative. The nitrile was aromatized in 32% yield with sulfur and then

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[1] Taken from the thesis submitted by L. Reich in partial fulfillment of the requirements for the degree of Master of Science.

[2] G. A. Ropp and E. C. Coyner, THIS JOURNAL, **71**, 1832 (1949).

[3] R. L. Frank, R. D. Emmick and R. S. Johnson, *ibid.*, **69**, 2313 (1947).

[4] J. S. Meek and J. W. Ragsdale, *ibid.*, **70**, 2502 (1948).

[5] H. L. Holmes, K. Alcock, D. G. Demianiw, J. W. Robinson, C. E. S. Rooney and F. A. Sundberg, *Can. J. Research*, **26B**, 248 (1948).