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

The Condensation of 1-Phenyl-1,3-butadiene with Acrylic Acid and Acrolein

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Since previous work in our Laboratory had shown that piperylene condenses with acrylonitrile,[2] methyl acrylate,[2] acrylic acid,[3] acrylamide,[3] and acrolein[3] to form the *cis–ortho* isomer in each case, it seemed likely that 1-phenyl-1,3-butadiene (I) might condense with these dienophiles to give *cis–ortho* isomers. Of these, only the condensation of 1-phenyl-1,3-butadiene with acrylic acid (II) and acrolein (III) has been reported in the literature so far.[4,5,6,7]

The work in our Laboratory was begun in an effort to determine the exact structure of the adducts formed from 1-phenyl-1,3-butadiene when condensed with various dienophiles. The liquid adduct (IV) of acrolein and I was first prepared by Lehmann and Paasche who oxidized it to an acid (V) which they reported melted at 105°. From acrylic acid and I they obtained an acid (VI) which melted at 122°.[4] Since our manuscript was first submitted, Ropp and Coyner have reported again the preparation of VI by the condensation of I and III.[7] They have shown conclusively that VI is *cis*-1,2,5,6-tetrahydro-2-phenylbenzoic acid and that V is the *trans* isomer.

In our Laboratory it was found that three acids could be isolated from the adduct mixture of acrylic acid and 1-phenyl-1,3-butadiene. Two of these acids corresponded to V and VI previously reported[4,5,6,7] and melted at 101–102° (V) and 120–121.5° (VI) while the third melted at 65–67° (VII). A fourth component melted sharply at 85–87° but was finally separated into V and VI. It was shown that this was the eutectic mixture of V and VI by mixed melting point experiments. Previous workers have reported isolating only VI from this reaction.

Oxidation of the adduct mixture of acrolein and 1-phenyl-1,3-butadiene produced six to nine parts of V to one part of VI. None of compound VII was isolated but since the original adduct mixture was purified by distillation and conversion to the sodium bisulfite addition products before oxidation to the acids, the relative amounts of isomeric adducts formed in the diene synthesis may have been changed before the isolation of V and VI. The authors believe that both *cis* and *trans*-1,2,5,6-tetrahydro-2-phenylbenzaldehyde are formed directly in the Diels–Alder reaction.

The preparation and isolation of V and VI from the aldehyde adduct mixture does not involve the use of base under conditions which seem likely to cause an appreciable amount of V to be formed from VI. By heating for two hours under reflux in a 10% sodium hydroxide solution, VI was converted largely into V. Similar treatment of V indicated that little if any VI could be formed thus from V. Therefore, the *trans* isomer (V) is the more stable to aqueous sodium hydroxide, although it has a melting point about twenty degrees lower than the *cis* isomer.

The structures of V and VI were confirmed by hydrogenation to *trans*- and *cis*-2-phenylcyclohexanecarboxylic acid, respectively. The S-benzylthiuronium salts of these last two acids were prepared and had melting points corresponding to those reported by Gutsche.[8] Compound VII is believed to be a 3-phenyl-1,2,3,6-tetrahydrobenzoic acid. Since the *cis* and *trans* isomers of 3-phenylhexahydrobenzoic acid are not known, dehydrogenation of VII was tried.

Dehydrogenation of V with sulfur produced about an 80% yield of biphenyl. A similar yield of biphenyl was obtained with VI but in addition a small amount of *o*-phenylbenzoic acid was isolated. Dehydrogenation over palladium gave only biphenyl.

Dehydrogenation of the sodium salt of VII with sulfur gave a trace of biphenyl and a crude acid resembling *m*-phenylbenzoic acid.

The formation of the *o*-type isomers may be explained on the basis of electronic effects with the phenyl ring acting as an electron source as discussed previously for the piperylene adducts.[2] The isolation of both *cis* and *trans* products with phenylbutadiene is different from the piperylene case where only the *cis* form was found. That work was explained on the basis that the positive methyl group of piperylene and the negative end of the dienophile were aligned by electrostatic attractions in the transition state in such a fashion that *cis* isomers were formed. Here steric interaction of the phenyl group with the carboxyl or aldehyde group may be greater than that of a methyl group and may help to overcome the effect of the electrostatic attraction so that the *trans* isomer may be formed directly. Also a positive charge in the phenyl group would be distributed over a larger area than in a methyl group and should attract less strongly the negative end of a dienophile.

The *trans* isomer might also be produced by a rearrangement of the *cis* isomer in the hot reaction mixture. However, when the *cis* isomer (VI) was heated in toluene at 95° for six hours, the isomer

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[1] This paper was taken from the Master's Thesis of Frank J. Lorenzi, University of Colorado, 1948, and was supported in part by the Office of Naval Research.

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

[3] Unpublished work by D. R. Wilgus and C. R. Smith, Jr.

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

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

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

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

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

was recovered almost completely with little indication of any isomerization. In one experiment where a short reaction time had been used, a higher yield of the *cis–ortho* adduct was obtained. Further investigation of this problem is in progress as well as the condensation of 1-phenyl-1,3-butadiene with other dienophiles.

Experimental

1-Phenyl-1,3-butadiene (I).—This was first prepared by the procedure of Coyner and Ropp.[9] In this preparation 4-phenyl-3-buten-2-ol (VIII) was made from benzaldehyde and from allylmagnesium chloride. The alcohol was then converted to the corresponding chloride with phosphorus trichloride. Dehydrohalogenation with pyridine produced I. The second procedure used was that of Grummitt and Becker.[10] Eastman technical grade cinnamic aldehyde was condensed with methylmagnesium bromide obtained from the Arapahoe Chemical Company. The resulting alcohol (VIII) was then dehydrated by distillation.

The third method was to prepare VIII by reduction of benzylideneacetone and the alcohol was then distilled as before to produce I. Meerwein-Ponndorf reductions of benzylideneacetone were tried but were not as convenient as reductions with lithium aluminum hydride.

Thirty-eight grams (0.25 mole) of benzylideneacetone was reduced with 2.8 g. of lithium aluminum hydride in 75 ml. of anhydrous ether in accordance with the directions of Nystrom and Brown.[11] The reduction mixture was decomposed by the addition of first 40 ml. of ice–water and then 200 ml. of 20% sulfuric acid. The ether layer was washed, dried and then concentrated. Thirty-eight grams of an oil[12] was obtained which upon distillation gave 17 g. of I, b.p. 100–130° (20 mm.). This was again distilled before use and the fraction distilling at 80–85° (10 mm.) was used.

Condensation of I and II.—In a round-bottom flask were placed 12.5 g. of I (0.096 mole), 5.5 g. (0.098 mole) of II together with 0.1 g. of phenyl-β-naphthylamine as a polymerization inhibitor. The mixture was heated under a reflux condenser in an atmosphere of nitrogen for six hours. The product was then fractionally distilled, yield 13.0 g. (73%), b. p. 112–119° (10–12 mm.). It was purified further by addition to a rapidly stirred saturated solution of 10.6 g. of sodium bisulfite. After the addition of the aldehyde mixture was completed, an equal volume of ether containing 5 ml. of ethanol was added to secure separation of the salt. The bisulfite addition product was filtered, washed with three small portions of ether and dried, yield 17.5 g. (61%). The salt was decomposed and the aldehyde mixture redistilled, yield 10.5 g. (58%).

Oxidation of the Acrolein Adduct Mixture.—Chromic anhydride was used by Lehmann and Paasche to oxidize their adduct. They obtained a 58% yield of V. Using their procedure and quantities, a trial run gave only a 38% yield (2.5 g.).

A different procedure patterned after that used by Delépine and Bonnet[13] was then tried. Five grams (0.0286 mole) of adduct in 12 ml. of 75% ethanol containing 5.1 g. (0.03 mole) of silver nitrate were placed in a three-necked round-bottom flask equipped with a Hershberg stirrer and dropping funnel. The flask was immersed in an ice-bath and 30 ml. of 10% sodium hydroxide was added with vigorous stirring over a two-hour interval. After an additional fifteen minutes, the stirrer and dropping funnel were removed and the mixture was allowed to stand for two and a half days. The silver and silver oxide precipitate was filtered and washed with alcohol. The filtrates were taken up in 10% sodium hydroxide and extracted with four 50-ml. portions of ether. The solution was then acidified with 6 *N* hydrochloric acid. This was added slowly with stirring which was continued until the acid crystallized. The acid was filtered, washed with very dilute hydrochloric acid and dried, yield 5.1 g. (93%), m. p. 98–102°. The compound was recrystallized from Skellysolve B and gave 4.3 g. (78.5%) of white crystals melting at 99–101°. Another recrystallization gave crystals melting at 100–102°. In other similar experiments a small amount of acid was isolated which melted at 120–121.5° (VI) when fully purified. It amounted to perhaps as much as 10 to 15% of the total adduct mixture.

Condensation of I and III.—Acrylic acid was prepared by fractionating a 60% technical grade obtained from the Eastman Kodak Company. Thirty grams (0.23 mole) of freshly prepared I[9] and 21 g. (0.29 mole) of III containing 0.2 g. of phenyl-β-naphthylamine were heated under reflux condenser for six hours. The resulting adduct mixture was divided into two equal parts. Part A was taken up in a 10% solution of sodium bicarbonate and part B in a 10% solution of sodium hydroxide. The two fractions were treated alike and the procedure used in the isolation of the oxidation product of the previous adduct was followed. Fraction A yielded 14.5 g. of acid (62%), m. p. 66–115°, while 12.5 g. of acid (54%), m. p. 60–115°, was obtained from B. Later yields up to 75% were obtained using I prepared by Grummitt and Becker's method.

Isolation of V, VI and VII.—A systematic fractional crystallization in petroleum ether similar to that used by Miller and Adams[14] was first tried with the acrylic acid adduct mixture. Three fractions were isolated which melted at 85–87°, 101–102° and 115–119°. Subsequent recrystallizations showed that the lowest melting fraction could be separated into the two higher melting components. It was also shown by mixed melting point experiments that this fraction melting at 85–87° was a eutectic mixture of V and VI.

Using Skellysolve B for the recrystallization, the adduct mixture separated into three compounds melting at 101–102° (V), 120–121.5° (VI), and 65–67° (VII). The compound VII was the most soluble of the three and VI was also highly soluble whereas V was only slightly soluble. The original mixtures were approximately 50–62% V, 11–14% VI and 22–31% VII.

The analysis of compound VII indicates it was isomeric with V and VI.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.04; H, 7.20.

Dehydrogenations of V, VI and VII.—One gram (0.05 mole) of V and 0.5 g. of 10% palladium-on-charcoal were placed in a Heymann type dehydrogenating tube.[15] This was mounted in a glas-col heating mantle, enveloped in sand and fitted with a gas delivery tube which could be inverted under a nitrometer. The mixture was heated under a nitrogen atmosphere and at 180° hydrogen evolution commenced. The mixture was heated for four hours at 215–225° until no more gas was evolved. The product was taken up in 10% sodium hydroxide, ether extracted and filtered. Biphenyl was obtained from the ether extract. Acidification of the alkaline solution produced a small amount of clear oil. All attempts to crystallize this oil failed.

A similar dehydrogenation of V was tried using the calculated amount of sulfur. An excess of the calculated amount of gas was obtained and upon cooling the dehydrogenation apparatus slowly an 80% yield of biphenyl was sublimed out of the reaction mixture. A small amount of flat crystalline plates of an acid melting at 113–116° was obtained.

The melting point of *o*-phenylbenzoic acid is reported to be 113.5–114.5°.[16]

An identical dehydrogenation with VI produced biphenyl in about an 80% yield. No other compound was

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

[10] Grummitt and Becker, *ibid.*, **70**, 149 (1948).

[11] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

[12] The authors are indebted to J. R. Dann for this preparation.

[13] Delépine and Bonnet, *Compt. rend.*, **149**, 39 (1909).

[14] Miller and Adams, This Journal, **58**, 787 (1936).

[15] Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath, Boston, Mass., 1941, p. 462.

[16] Weger and Döring, *Ber.*, **36**, 880 (1903).

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.

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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

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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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[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).