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

The Condensation of *trans*-1-Phenyl-1,3-butadiene with Acrylonitrile, Acrylyl Chloride, Acrylamide and Propiolic Acid[1]

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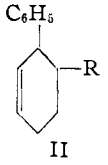
Previous work in our laboratory and elsewhere showed that when *trans*-piperylene was condensed with monosubstituted ethylenes, the major adduct was the *cis*-ortho-tetrahydrotoluene derivative. Recently, it has been found by Alder that *trans*-1-phenyl-1,3-butadiene, when condensed with acrylic acid at room temperature, gave mainly the *cis*-ortho-phenyltetrahydrobenzoic acid, but that significant amounts of the *trans*-isomer were formed at higher reaction temperatures. In our work reported below, evidence is presented to show that with acrylyl chloride and acrylamide, the major adduct formed with *trans*-1-phenyl-1,3-butadiene is the *trans*-ortho-phenyltetrahydrobenzene derivative when condensation temperatures of about 100° were used. The *trans*-ortho adduct of acrylyl chloride may be due to isomerization of the *cis*-ortho adduct which was found to isomerize to the *trans*-isomer when heated at 141°. The adduct of acrylonitrile and I, when treated with alkaline hydrogen peroxide, gave *trans*-2-phenyl-1,2,5,6-tetrahydrobenzamide. Propiolic acid was found to give 2-phenyl-2,5-dihydrobenzoic acid when condensed with *trans*-1-phenyl-1,3-butadiene.

trans-1-Phenyl-1,3-butadiene (I) has been condensed with acrolein,[3-7] acrylic acid,[3,5-8] acrylonitrile,[8] ethyl acrylate[5,8] and methyl vinyl ketone.[8,9] In each case, the major adduct was an ortho-phenyltetrahydrobenzene derivative (II).



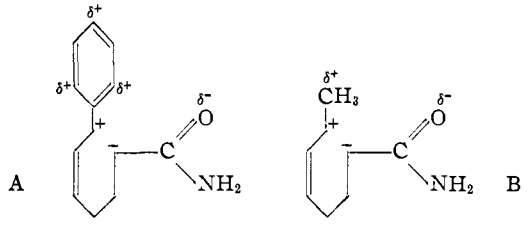
II

The stereoisomerism of the adducts of acrylic acid and acrolein with 1-phenylbutadiene has been determined.[6-8] Alder, Vagt and Vogt, on condensing acrylic acid and I at room temperature, were able to obtain only the *cis*-phenyl-1,2,5,6-tetrahydrobenzoic acid. When the condensation was carried out at 100°, *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid was obtained, and from the residues, the anilide of the *trans*-isomer was obtained. It was estimated that not more than one quarter of the product was the *trans*-adduct. This tendency for the *trans*-isomeric adduct to be favored by higher reaction temperatures was noted before with 1-carboxybutadiene and acrylic acid as well as with the corresponding acid chlorides.[10]

The oil from the condensation of acrolein and *trans*-1-phenyl-1,3-butadiene, after purification *via* the sodium bisulfite addition product, was reported to give both *cis*- and *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid after oxidation with silver oxide.[6] However, the *trans*-product has been shown to result largely, if not entirely, from isomerization of the *cis*-adduct by the sodium bisulfite used in isolating the aldehydes, and Alder, Vagt and Vogt were able to show only the presence of a *cis*-adduct when acrolein and *trans*-1-phenyl-1,3-butadiene were condensed at 100°.[7]

In our laboratory, *trans*-1-phenyl-1,3-butadiene has been condensed with acrylonitrile, acrylyl chloride and acrylamide. In each of these cases, the major adduct appeared to be the *trans*-2-phenyl isomer. The temperatures used in these Diels–Alder reactions were not excessive—being in the neighborhood of 100°. This indicates that *trans*-1-phenylbutadiene has a much greater tendency to form a *trans*-adduct than has *trans*-piperylene. The *cis*-adducts are the chief products of piperylene with all of the above dienophiles even when the condensations are carried out at 100° or higher.[11-13] This is probably due to the greater bulk of the phenyl group and the distribution of any charge in the transition state over a greater area in the larger phenyl group. This would decrease any attraction of the phenyl group for the negative group of the dienophile in comparison with the smaller methyl group.

The transition states proposed are illustrated by A and B. This type of transition state has been



proposed by Branch and Calvin,[14] Dewar[15] and Remick.[16]

Acrylonitrile and I, when refluxed together, gave a liquid adduct which, when treated with slightly alkaline hydrogen peroxide, gave an excellent yield of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzamide (III). Inversion of the α-carbon atom might have occurred by this treatment, but *cis*-2-methyl-1,2-5,6-tetrahydrobenzonitrile gives the *cis*-ortho-amide under similar conditions without isomerization,[13] and *cis*-2-phenyl-1,2,5,6-tetrahydrobenzamide was found to be fairly stable to alkaline hydrogen

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(2) American Cyanamid Fellow, 1950–1951.

(3) E. Lehmann and W. Paasche, *Ber.*, **68**, 1146 (1935).

(4) J. W. Cook and C. L. Hewitt, *J. Chem. Soc.*, 62 (1936).

(5) G. Blumenfeld, *Ber.*, **74B**, 525 (1941).

(6) J. S. Meek, F. J. Lorenzi and S. J. Cristol, THIS JOURNAL, **71**, 1830 (1949).

(7) K. Alder, H. Vagt and W. Vogt, *Ann.*, **565**, 135 (1949).

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

(9) L. Reich and E. I. Becker, *ibid.*, **71**, 1834 (1949).

(10) K. Alder, M. Schumacher and O. Wolff, *Ann.*, **564**, 79 (1949).

(11) J. S. Meek and J. W. Ragsdale, THIS JOURNAL, **70**, 2502 (1948).

(12) K. Alder and W. Vogt, *Ann.*, **564**, 120 (1949).

(13) Unpublished work of this Laboratory.

(14) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 5th printing, 1946, p. 489.

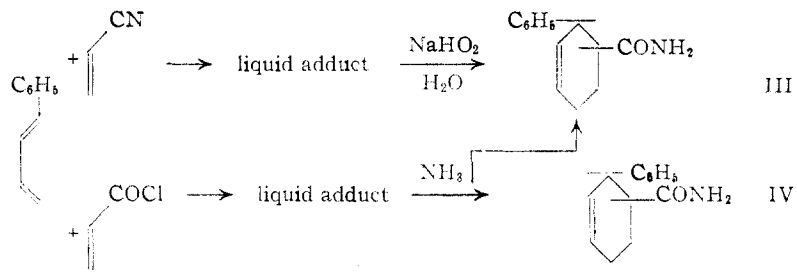
(15) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, England, 1949, p. 151.

(16) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 477.

peroxide under the conditions used in making III. The structure of III was shown by hydrogenation to the known *trans*-2-phenylhexahydrobenzamide.[17]

When acrylonitrile and I were mixed and allowed to stand for 16 days at 10°, no adduct was obtained.

By heating excess acrylyl chloride with I at reflux for 12 hours, a liquid adduct mixture was obtained. After distillation at 123°, this product was treated with ammonia in anhydrous benzene and gave mainly III as well as a little of the *cis*-ortho-isomer (IV). Hydrogenation of IV gave the known *cis*-2-phenylhexahydrobenzamide.[17] Hydrolysis of the adduct with sodium bicarbonate at room temperature was very slow, and only the *trans*-ortho-acid was isolated, although the low melting point of several fractions indicated some *cis*-ortho-acid may have been present. Solvolysis with formic acid of the acrylyl chloride adduct prepared as above led only to *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid.



The possibility exists that isomerization during the preparation of the acrylyl chloride adduct or in its conversion to the amide or acid may have occurred, although the adduct of acrylyl chloride and piperylene, upon similar treatment, has led only to *cis*-2-methyl-1,2,5,6-tetrahydrobenzoic acid and its amide.[13]

Since it has been reported that *cis*-2-phenylhexahydrobenzoic acid, when refluxed with thionyl chloride and then treated with ammonia, gave the *trans* amide,[17] it was decided to try the conversion of *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid to an amide. Treatment of this compound with thionyl chloride at room temperature gave an acid chloride which could be converted to the original *cis* acid by warming with 98–100% formic acid. This showed thionyl chloride did not cause isomerization under the conditions used. Ammonolysis of the acid chloride from the *cis* acid led to a 70% yield of the *cis* amide and no evidence of any isomerization to a *trans* product was found.

When acrylyl chloride and I were mixed and kept below 28° for 1 day, a yield of about 55% of adduct was obtained. This indicates that acrylyl chloride is a more reactive dienophile with I than is acrylonitrile. The acrylyl chloride adduct, prepared below 28° as above without distillation, on solvolysis with formic acid gave almost pure *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid.

If the adduct prepared below 28° was distilled at 144°, then either acidolysis or ammonolysis gave the *trans* derivative. This shows that isomerization of the *cis*-adduct occurs on heating, probably as a result of acid catalysis and that the formation of a *trans*-adduct of I and acrylyl chloride at elevated temperatures may be due to direct condensation or to isomerization of any *cis*-adduct formed.

In the condensation of acrylamide with I, the products might isomerize, but this does not seem likely to occur in the course of their preparation or recrystallization. It was found that the *trans*-2-phenyl adduct predominated over the *cis*-2-phenyl adduct. These isomers melted very close together and were difficult to separate. Refluxing toluene and benzene as well as other solvents for the condensation were tried, but the *trans*-isomer appeared to predominate in each case.

Propiolic acid was also condensed with I. In this case, no *cis–trans* isomerism is possible in a one-to-one adduct since only one asymmetric atom would be present. The ultraviolet absorption spectrum of the product indicated that no rearrangement of the double bonds had occurred. Dehydrogenation of the adduct gave 2-phenylbenzoic acid in good yield.

Experimental

***trans*-1-Phenyl-1,3-butadiene (I).**—The 1-phenyl-1,3-butadiene was prepared from *trans*-cinnamaldehyde by the procedure of Grummitt and Becker.[18] This method has been reported to give only the *trans* isomer.[19]

Acrylonitrile Adduct (V).—One-tenth of a mole each of I and acrylonitrile were refluxed vigorously together for 12 hours in the presence of one gram of hydroquinone. The reaction mixture was very dark and quite viscous. No unreacted acrylonitrile was recovered. A clear yellow oil (V) distilled at 120–125° (3–4 mm.), and was obtained in a yield of 60%. The yield and physical properties were comparable to those reported by Reich and Becker.[9] Treatment of V with concentrated sulfuric acid gave only tar. Attempts to hydrate the nitrile to an amide with boron trifluoride as the catalyst were also unsuccessful.

When 4.24 g. (0.032 mole) of phenylbutadiene and 1.71 g. (0.032 mole) of acrylonitrile were mixed and allowed to stand 16 days in an ice-box at 10°, and this material was treated as below with alkaline hydrogen peroxide, no trace of an amide was obtained.

Conversion of V to an Amide (III).—Alkaline hydrogen peroxide was allowed to react with 0.183 g. of V by the method of Noller.[20] The temperature was not allowed to exceed 50° and the steam distillation was omitted. After acidification to neutralize the sodium hydroxide, the mixture was allowed to stand overnight. A quantitative yield of white needles (III) was obtained, m.p. 161–163°. Recrystallization from aqueous methanol raised the melting point to 165–166°. No other substance was found.

Anal. Calcd. for $C_{13}H_{15}NO$: N, 6.96. Found: N, 7.07.

Treatment of this amide with nitrous acid failed to give a reaction.

Hydrogenation of III to *trans*-2-Phenylhexahydrobenzamide.—One hundred and seventy-six milligrams of III and 224 mg. of platinum oxide in 20 ml. of ethanol were shaken at room temperature and pressure in an atmosphere of hydrogen. The theoretical amount of hydrogen was absorbed in 30 minutes. After removal of the catalyst and most of the solvent, small white plates crystallized. The crude yield was 95%, m.p. 134–135°, which checks the reported melting point of 135–136° for *trans*-2-phenylhexahydrobenzamide.[17]

(17) C. D. Gutsche, THIS JOURNAL, **70**, 4150 (1948).

(18) O. Grummitt and E. I. Becker, *ibid.*, **70**, 144 (1948).

(19) O. Grummitt and F. J. Christoph, *ibid.*, **71**, 4157 (1949); **73**, 3479 (1951).

(20) C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 586.

Acrylyl Chloride.—This was prepared from β-propiolactone by converting it into β-chloropropionyl chloride and then dehydrohalogenating over barium chloride in an overall yield of 57%.[21]

Preparation of 2-Phenyl-1,2,5,6-tetrahydrobenzoyl Chloride (VI). Method A.—Thirteen grams (0.1 mole) of *trans*-1-phenyl-1,3-butadiene, 18.1 g. (0.2 mole) of acrylyl chloride and 0.2 g. of phenyl-beta-naphthylamine were heated at reflux for 12 hours. The temperature of the reaction mixture while refluxing was about 114–117°. At the end of this time, the excess acrylyl chloride was removed by distillation at atmospheric pressure, and the residual liquid was distilled under reduced pressure. A 66% yield of colorless liquid was obtained, b.p. 120–123° (5 mm.), or 126–129° (7 mm.), $n^{20}D$ 1.5521.

Anal. Calcd. for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94. Found: C, 70.38; H, 5.99.

Method B.—Precooled quantities of 7.02 g. (0.054 mole) of I and 10.28 g. (0.108 mole) of acrylyl chloride were mixed in a round-bottomed flask and cooled in ice-water. The initial temperature on mixing was 10° which dropped slowly. The bath and the contents of the flask were allowed to stand for 24 hours while warming up to room temperature. Then the excess acrylyl chloride was removed at room temperature by the use of a water aspirator.

Method C.—A 0.61-g. (0.003 mole) sample of *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid and 2 ml. (0.023 mole) of thionyl chloride were allowed to react at room temperature. Then the excess thionyl chloride was removed by means of a jet of air.

Ammonolysis and Acidolysis of VI.—Dry ammonia was bubbled for 4 hours into 100 ml. of benzene containing 4.46 g. of VI prepared by method A. Although ammonolysis appeared complete in less than 30 minutes, treatment was continued to ensure complete reaction. The benzene solution was heated and filtered. The ammonium chloride was extracted three times with 125-ml. portions of hot benzene, and the extracts were combined with the original filtrate. On concentration of the solvent and filtration of the solid, there were obtained four fractions: 2.45 g., m.p. 160–162°; 0.28 g., m.p. 140–152°; 0.28 g., m.p. 140–145° and 0.10 g., m.p. 135–140°. The combined yield was 3.11 g. or 76%. Fractional recrystallization from benzene gave 1.94 g. (48%) of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzamide (III) melting at 165–165.8° and 0.02 g. (0.5%) of the *cis* isomer (IV), m.p. 169–170°.

Anal. of IV: Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51. Found: C, 77.66; H, 7.65.

One-tenth of a gram (0.005 mole) of IV was dissolved in 40 ml. of anhydrous benzene and placed in a 50-ml. hydrogenation flask with 0.0028 g. of Adams catalyst and shaken under an atmosphere of hydrogen. After 10% more than the theoretical amount of hydrogen was absorbed, the hydrogenation was stopped. Concentration of the benzene solution after removal of the catalyst failed to give crystals. Aqueous methanol was next used as a solvent and upon standing overnight in the ice-box, crystals separated. Recrystallization from methanol with a small amount of water gave 0.06 g. (60%) of a white solid, m.p. 80–80.7°, which checks with the melting point of 80–80.5° reported for *cis*-2-phenylhexahydrobenzamide.[17]

Hydrogenation of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzamide in a similar manner gave a 65% yield of *trans*-2-phenylhexahydrobenzamide, m.p. 136.5°, which corresponds closely to the previously reported m.p. of 135–136°.[17]

When 0.0096 g. of pure *cis*-2-phenyl-1,2,5,6-tetrahydrobenzamide was treated with alkaline hydrogen peroxide as in the hydration of the acrylonitrile adduct, 0.0057 g. (59%) was recovered unchanged without any indication of isomerization of the amide.

2.21 grams (0.01 mole) of VI from method A and 20 ml. of Matheson 98–100% formic acid were stirred for 10 minutes with no apparent reaction. The liquid was heated on a steam-bath until it just began to boil and was removed. After stirring for 5 minutes, a white solid precipitated. Filtration gave 1.69 g. of material melting at 98–101° in a yield of 83.1%. Crystallization gave 1.40 g. of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid, m.p. 100.5–101.2°, in a yield of 69%.

When VI prepared by method A was shaken with 5% sodium bicarbonate at room temperature, the hydrolysis was slow and about half complete after 2 days. The crude acid melted at 80–83° and upon recrystallization, only *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid was obtained.

When VI, prepared by method B without purification by distillation, was warmed with formic acid as above, 4.54 g. (41%) of solid acid was obtained, m.p. 116–118°. This was recrystallized from a mixture of petroleum ether (b.p. 60–71°) and ethyl acetate, and there was isolated 2.65 g. of *cis*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid, m.p. 119–120.5°.

If VI was prepared by method B, distillation gave 8.67 g. (55%) of 2-phenyl-1,2,5,6-tetrahydrobenzoyl chloride, b.p. 166–170° (25 mm.). Redistillation gave 6.7 g., b.p. 134–137° (3–6 mm.). When 4.0 g. of this last fraction was warmed with formic acid as before, 2.77 g. of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzoic acid was obtained, m.p. 100–101°.

When a distilled sample of VI, prepared by method B, was dissolved in benzene and treated with gaseous ammonia, a 67% yield of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzamide, m.p. 164.6–165.3°, was isolated.

The ammonolysis of VI, prepared without distillation by method C, gave a 70% yield of *cis*-2-phenyl-1,2,5,6-tetrahydrobenzamide, m.p. 169.8–170.4°.

Acidolysis with formic acid of VI, prepared by method C, gave a 67% yield of the starting *cis*-acid, m.p. 120°.

Condensation of Acrylamide with I.—Acrylamide was prepared by ammonolysis of acrylyl chloride with ammonia in benzene at 5°.[22]

One and four-tenths grams (0.02 mole) of acrylamide, 2.9 g. (0.222 mole) of *trans*-1-phenyl-1,3-butadiene, 0.02 g. of phenyl-β-naphthylamine and 5 ml. of anhydrous benzene were refluxed for 3 days. The resulting solution was diluted with benzene and filtered to remove traces of insoluble polymer. Fractional crystallization gave 0.21 g. (5%) of *trans*-2-phenyl-1,2,5,6-tetrahydrobenzamide, m.p. 165–166°, and 0.03 g. (1%) of the corresponding *cis*-isomer, m.p. 169–170°. These compounds were identical to those derived from the ammonolysis of VI.

In a similar run using toluene as a solvent to increase the temperature, a yield of 0.5 g. of the *trans*-ortho-adduct (13%) and 0.11 g. (3%) of the *cis*-ortho-adduct was obtained. Crude yields of up to 45% were obtained by refluxing in 10 ml. of toluene for 72 hours with the above amounts of reactants.

Adduct of I and Propiolic Acid.—Propiolic acid was prepared from acetylenedicarboxylic acid.[23] Some of the acetylenedicarboxylic acid was purchased from Farchan Research Laboratories and some was prepared according to directions in reference 24.

Two and six-tenths grams (0.02 mole) of I and 1.75 g. (0.025 mole) of propiolic acid were heated under reflux for 33 hours with 0.02 g. of hydroquinone. On cooling, crystals (VII) formed and were filtered and dried. The yield was 1.21 g. (30.2%), m.p. 193–194°. Subsequent recrystallization from benzene or a petroleum ether (b.p. 60–71°)-benzene mixture failed to raise the melting point. The material dissolved on warming in 5% sodium bicarbonate. Elemental analyses were not quite satisfactory until the compound was dried at room temperature and kept under nitrogen until analyzed. Possibly this dihydrobenzene underwent a slow oxidation in air.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04; neut. equiv., 200. Found: C, 78.30; H, 5.89; neut. equiv., 202.

The ultraviolet absorption spectrum for this compound is reported elesewhere.[25] On the basis of this spectrum, the structure assigned is 2-phenyl-2,5-dihydrobenzoic acid rather than that of an isomeric acid resulting from a double bond shifting to give a conjugated system.

Dehydrogenation of VII.—One gram (0.005 mole) of VII and 0.16 g. (0.005 mole) of sulfur were heated in a sublimator at 230° for 30 minutes and then at 250° for 5.5 hours. Dur-

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

(23) W. H. Perkins, Jr., and J. L. Simonsen, *J. Chem. Soc.*, **91**, 833 (1907).

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(25) H. E. Ungnade and I. Ortega, THIS JOURNAL, **73**, 1564 (1951).

ing the course of the dehydrogenation, some material collected on the cold finger. The remaining brown tar was sublimed and eventually 0.56 g. of crude product was collected, m.p. 107°. This was washed once with petroleum ether (b.p. 60–71°) to remove sulfur and, on drying, melted at 110–111°, yield 0.49 g.

Recrystallization from petroleum ether gave 0.40 g. of product, m.p. 113–113.5°, reported for 2-phenylbenzoic acid, 113–113.5°.[26] The melting point was not depressed when mixed with a sample of 2-phenylbenzoic acid prepared from 2-aminobiphenyl by a method similar to that used in converting *o*-toluidine to *o*-toluic acid *via* the nitrile.[27,28]

One-tenth of a gram of dehydrogenated VII was heated with 1 ml. of thionyl chloride for 10 minutes on a steam-bath cooled in ice, and then treated with 25 ml. of aqueous ammonia containing some ice. After standing 15 minutes, the solid material was collected and dried; yield 0.08 g. (80%), m.p. 173–174°. This melting point was not lowered by mixing with a known sample of 2-phenylbenzamide prepared from 2-phenylbenzonitrile by the method previously used.[20]

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(27) H. T. Clarke and R. R. Read, "Organic Syntheses," Coll. Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 514.

(28) H. T. Clarke and E. R. Taylor, *ibid.*, Coll. Vol. II, 1943, p. 588.

Acknowledgment.—All micro-analyses were performed by the Clark Microanalytical Laboratories, Urbana, Illinois. The authors are indebted to B. F. Goodrich Chemical Company for a generous sample of β-propiolactone, and to Mr. E. R. Hardwick, Jr., and Mr. H. L. Hill of our Laboratory, for a sample of *o*-phenylbenzoic acid and its amide.

BOULDER, COLORADO RECEIVED OCTOBER 1, 1951

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Reaction of N-Methylpiperidine with Alkyl Durenecarboxylates

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A pronounced solvent effect on the position of equilibrium between *n*-methylpiperidine, methyl durenecarboxylate and *n*-dimethylpiperidinium durenecarboxylate has been discovered. Other aspects of the reaction between esters of durenecarboxylic acid and *n*-methylpiperidine are described.

The reaction of esters with *t*-amines has been known for some time but has received little attention. Since the discovery of the reaction,[2] only one study has appeared.[3] In this it was shown that the rate of reaction (1) was first order with respect to ester and amine and that the equation $\log k =$

$$RCOOCH_3 + N(CH_3)_3 \xrightarrow{k} R\,COON(CH_3)_4 \quad (1)$$

$-1.81 - 0.81 \log K$, where K was the ionization constant of the acid RCOOH, was obeyed for aliphatic and aromatic acids, including *o*-substituted acids. More recently, the formation of quaternary salts from esters and *t*-amines has been postulated as a step in certain alkylations[4] and in the disproportionations observed in the reaction of benzyldimethylamine with methyl esters.[5]

The reverse reaction, the decomposition of quaternary ammonium salts into esters and *t*-amines has been known even longer[6] and has been applied to the esterification of hindered acids.[7] When *d*-(+)-α-phenethyltrimethylammonium acetate was pyrolyzed, *l*-(−)-α-phenethyl acetate of 98–100% optical purity was isolated.[8] This shows that inversion had occurred and suggests an SN2 type of mechanism. A related reaction, the thermal rearrangement of betaines into esters of amino-acids[2,9] has received some attention.

We became interested in the reactions of *t*-amines with esters because it seemed to offer the opportunity to study certain steric factors in a typical SN2 type reaction. The present study is a preliminary semiquantitative study of the reaction between N-methylpiperidine with alkyl durenecarboxylates. Durenecarboxylic acid was chosen as an easily prepared hindered acid which we desired in order to avoid complications that might arise from carbonyl addition side reactions. N-Methylpiperidine was chosen in preference to quinuclidine because of its greater ease of preparation and because the F-strain[10] in its reaction with esters should be low.

In this work we have observed a number of interesting facts listed below.

(1) The reaction between methyl durenecarboxylate and N-methylpiperidine to form N-dimethylpiperidinium durenecarboxylate is reversible.

$$2,3,5,6\text{-}(CH_3)_4C_6HCOOCH_3 + CH_2N(CH_2)_5 \rightleftarrows 2,3,5,6\text{-}(CH_3)_4C_6HCOO^-(CH_3)_2\overset{+}{N}(CH_2)_5 \quad (2)$$

(2) Solvents have a profound effect on the position of this equilibrium at 140°: alcoholic solvents favor a position far to the right; non-hydroxylic solvents, such as benzene, nitrobenzene and dioxane, favor a position far to the left.

(3) The rate of reaction to the right in the case of various alkyl esters falls off in the order $CH_3 >> C_2H_5 > CH_3CH_2CH_2- > (CH_3)_2CH-$.

(4) The *t*-butyl ester is thermally unstable at 140° and its decomposition into durenecarboxylic acid is not affected by amine.

(5) The rate of the salt forming reaction in meth-

(1) Taken from the Ph.D. Thesis of H. A. Lloyd, The Ohio State University, 1951.

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