for VIII) and ultraviolet, visible and infrared (except for IV) spectra with those of authentic samples.

B.—A small quantity of the dioxime diacetate VII was applied to a carefully prepared column of acid-washed alumina with dichloromethane. The violet layer which developed slowly turned green as it moved down the column. When none of the violet color remained, the column was washed with acetone and ethanol, the eluate evaporated and the residue rechromatographed. Chloroform eluted a fraction containing 14.3 mg. of 1-acetamido-3-acetylazulene (V), and acetone containing a little ethanol removed a second fraction which yielded 10.4 mg. of 1-acetamido-3-acetylazulene oxime (VIII). The products were identified as in A above. A relatively large amount of brown material remained on the column.

Seattle 5, Wash.

[Contribution from the Department of Chemistry, Wayne State University]

Cyclic Dienes. XXI. Diels–Alder Adducts and Cyclodecane Derivatives from 1,2-Dimethylenecyclohexane[1,2]

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The reaction of 1,2-dimethylenecyclohexane with a wide variety of dienophiles produced a series of $\Delta^{9(10)}$-octalin derivatives. These Diels–Alder adducts were transformed into several other substituted $\Delta^{9(10)}$-octalins by conventional reactions. Ozonization of these octalin derivatives produced directly a series of highly substituted cyclodecane derivatives, which might serve as starting materials for the synthesis of cyclodecapentaene. The diketones containing electron-withdrawing groups were extremely susceptible to intramolecular condensation, but the other derivatives were somewhat more stable.

Cyclic dienes, such as 1,2-dimethylenecyclohexane (I),[5] have attracted interest because they produce multicyclic adducts through the Diels–Alder reaction. Many uses of these interesting dienes and their Diels–Alder adducts already have been reported. For example, 1,2-dimethylenecyclohexane (I) was polymerized to produce the first synthetic all-*cis* diene polymer related in structure to natural rubber.[6] The adduct from benzoquinone and the diene I was shown to be an excellent starting material for the synthesis of pentacene,[7] and the adduct of the diene I and maleic anhydride was shown to be an excellent starting material for the synthesis of 2,3-dimethylenedecalin.[8] Related materials also have been prepared from the series of substituted dimethylenecyclohexanes.[9,10]

Since the Diels–Alder adducts are derivatives of $\Delta^{9(10)}$-octalin, it appeared that these bicyclic compounds could be used as starting materials for the preparation of cyclodecane derivatives. Nametkin and Glagolew[11] and Hückel and Blohm[12] developed a procedure for the synthesis of cyclodecane derivatives through the ozonization of $\Delta^{9(10)}$-octalin. Improved variations of this procedure have been reported more recently.[13-15] Since normal ring closures give poor yields for ten-membered carbocyclic rings,[16] several alternative processes have been developed. The most attractive methods for the preparation of cyclodecane derivatives include the rearrangement of the benzoate of decalin hydroperoxide[17] and the acyloin condensation of diethyl sebacate.[18,19] However, none of these methods is well adapted for the preparation of highly substituted cyclodecane derivatives. These derivatives are of interest as possible starting materials for the preparation of cyclodecapentaene, but the introduction of five double bonds into a ring with only two functional groups would be quite difficult. It seemed reasonable that, since the synthesis of 1,2-dimethylenecyclohexane (I) can be modified to introduce additional functional groups,[20,21] the synthesis of highly substituted cyclodecane derivatives from their intermediate Diels–Alder adducts would be practical. For this reason the preparation of a series of Diels–Alder adducts of 1,2-dimethylenecyclohexane (I) was undertaken and the conversion of these adducts to cyclodecane derivatives was studied.

When nitroethylene, prepared by the pyrolysis of β-nitroethyl acetate, was allowed to react with 1,2-dimethylenecyclohexane (I), an 85% yield of the Diels–Alder adduct, 2-nitro-$\Delta^{9(10)}$-octalin (IIa), was obtained. Since mechanical difficulties were encountered in the ozonization of IIa, several variations were tried. The most satisfactory procedure was to bubble the ozone through a gas-washing bottle containing a solution of IIa in 75% acetic acid at 0°. Under these conditions, the ozone was absorbed slowly, the ozonide was hydrolyzed and the resulting 3-nitro-1,6-cyclodecadione (IIIa) pre-

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[2] Abstracted in part from a Dissertation submitted to the Graduate Council of Wayne State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1950.

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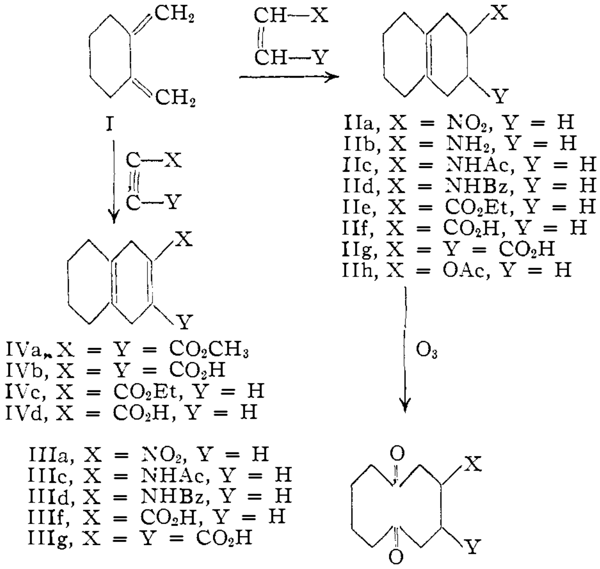
cipitated and could be removed by filtration. IIIa was extremely sensitive to both acidic and basic reagents—so much so that normal carbonyl reagents promoted extensive condensation and tar formation. Apparently the nitro groups activated the ring so that internal condensations, which have been observed in the unsubstituted diketone,[14,22] occur more readily. For this reason the more stable amino derivatives were investigated.

The 2-nitro-$\Delta^{9(10)}$-octalin (IIa) was reduced to 2-amino-$\Delta^{9(10)}$-octalin (IIb) in three different ways. Reduction of IIa with lithium aluminum hydride gave IIb in 80% yield, while reduction with tin and hydrochloric acid gave a 70% yield. IIb could be converted to its acetyl derivative IIc with acetic anhydride and to its benzoyl derivative IId with benzoyl chloride, both in 90% yields, Catalytic reduction of IIa, followed by acetylation with acetic anhydride, gave IIc in an over-all yield of 69%.

Ozonization of 2-acetamido-$\Delta^{9(10)}$-octalin (IIc) in 85% acetic acid at room temperature gave in one step a 49% yield of the very soluble 3-acetamido-1,6-cyclodecadione (IIIc). Although IIIc was extremely sensitive to acids, a dinitrophenylhydrazone derivative could be obtained in dioxane solution. The infrared absorption spectrum of IIIc showed strong bands at 1670 and 1720 cm.$^{-1}$, characteristic for the carbonyl groups, and also a strong band at 1520 cm.$^{-1}$, characteristic of an N-substituted amide.[23] Slightly weaker peaks were observed at 1122, 1152, 1220, 1305, 1378, 1423, 1450, 2950 and 3200 cm.$^{-1}$. Ozonization of 2-benzamido-$\Delta^{9(10)}$-octalin (IId) gave a 62% yield of the less soluble and therefore more easily isolated 3-benzamido-1,6-cyclodecadione (IIId).



IIa, X = NO_2, Y = H
IIb, X = NH_2, Y = H
IIc, X = NHAc, Y = H
IId, X = NHBz, Y = H
IIe, X = CO_2Et, Y = H
IIf, X = CO_2H, Y = H
IIg, X = Y = CO_2H
IIh, X = OAc, Y = H

IVa, X = Y = CO_2CH_3
IVb, X = Y = CO_2H
IVc, X = CO_2Et, Y = H
IVd, X = CO_2H, Y = H

IIIa, X = NO_2, Y = H
IIIc, X = NHAc, Y = H
IIId, X = NHBz, Y = H
IIIf, X = CO_2H, Y = H
IIIg, X = Y = CO_2H

A series of cyclodecane compounds containing carboxyl groups was then prepared. Thus 1,2-dimethylenecyclohexane (I) was treated with ethyl acrylate to obtain an adduct IIe which subsequently was hydrolyzed to the $\Delta^{9(10)}$-octalin-2-carboxylic acid (IIf). Ozonization of IIf produced a 43% yield of 1,6-cyclodecadione-3-carboxylic acid (IIIf). Similarly, the maleic anhydride adduct of 1,2-dimethylenecyclohexane was hydrolyzed to the diacid IIg, which, in turn, was ozonized to give a 58% yield of 1,6-cyclodecadione-3,4-dicarboxylic acid (IIIg).

Other interesting adducts were obtained by the treatment of I with vinyl acetate to give 2-acetoxy-$\Delta^{9(10)}$-octalin (IIh), with ethyl propiolate to obtain the ester IVc, which could be saponified to 1,4,5,6,7,8-hexahydronaphthalene-2-carboxylic acid (IVd), and with dimethyl acetylenedicarboxylate to give the dimethyl ester IVa, which, in turn, could be saponified to the corresponding hexahydronaphthalene-2,3-dicarboxylic acid IVb.

Thus it appears that 1,2-dimethylenecyclohexane (I) reacts readily with various dienophiles to produce a series of substituted $\Delta^{9(10)}$-octalins. These octalins can be ozonized to produce highly substituted cyclodecane derivatives, some of which might serve as starting materials for the synthesis of cyclodecapentaene.

Experimental[24]

2-Nitro-$\Delta^{9(10)}$-octalin (IIa).—To a cold solution of 216 g. (2.0 moles) of 1,2-dimethylenecyclohexane (I) in 400 ml. of ether was added 146 g. (2.0 moles) of nitroethylene[25] dissolved in 200 ml. of ether. Such a vigorous exothermic reaction occurred that the reaction flask had to be cooled in ice in order to keep the reaction under control. After the reaction mixture had been heated under reflux for an additional 2 hr., the ether was removed by distillation and the residue was fractionated through a 10-inch, helix-packed column to produce 308 g. (85%) of 2-nitro-$\Delta^{9(10)}$-octalin (IIa), b.p. 128–129° (5 mm.), n^{25}_{D} 1.5112.

Anal. Calcd. for $C_{10}H_{15}NO_2$: C, 66.28; H, 8.34; N, 7.73. Found: C, 66.39; H, 8.20; N, 7.75.

3-Nitro-1,6-cyclodecadione (IIIa).—In a gas-washing bottle equipped with a spiral glass packing was placed a solution of 9.05 g. (0.05 mole) of 2-nitro-$\Delta^{9(10)}$-octalin (IIa) in 100 ml. of a 75% acetic acid solution. (The use of the usual sintered glass disk was unsatisfactory because the precipitate that formed during the ozonization clogged the pores of the disk.) A stream of ozone-enriched oxygen[26] was passed through the solution at 0°, until the rate of absorption decreased. Since the ozone was not absorbed quantitatively under these conditions, the unreacted ozone was passed through a trap containing a 10% potassium iodide solution and by titration of the liberated iodine with a standard potassium thiosulfate solution the amount of absorbed ozone could be determined. After a total of 0.0488 mole of ozone had been absorbed in 4 hr., the reaction mixture was diluted to 500 ml. with ice-water. The precipitate was removed by filtration and washed with water to yield 8.8 g. of crude product, m.p. 100–105°. Evaporation of the filtrate under reduced pressure at room temperature produced an additional quantity of material. Two recrystallizations from acetone produced 8.7 g. (80%) of 3-nitro-1,6-cyclodecadione (IIIa), m.p. 113–113.5°. (The crude dione IIIa quickly turned brown when it was exposed to air, but the pure material could be kept indefinitely without any apparent change.)

Anal. Calcd. for $C_{10}H_{15}NO_4$: C, 56.32; H, 7.09; N, 6.57. Found: C, 56.44; H, 7.37; N, 6.99.

2-Amino-$\Delta^{9(10)}$-octalin (IIb). A. From the Lithium Aluminum Hydride Reduction of 2-Nitro-$\Delta^{9(10)}$-octalin (IIa).—To a slurry of 17.5 g. (0.47 mole) of lithium aluminum hy-

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[24] The authors are grateful to Arthur Tomasewski and Vivian Capucinski for the microanalyses and to Dr. L. Kuentzel of Wyandotte Chemical Co., Wyandotte, Mich., for the infrared absorption spectrum, which was determined on a saturated chloroform solution. All melting points are corrected.

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dride in 250 ml. of anhydrous ether was added dropwise a solution of 44.0 g. (0.243 mole) of 2-nitro-$\Delta^{9(10)}$-octalin (IIa) in 200 ml. of ether. After the mixture had been stirred for 12 hr. at room temperature, 700 ml. of 10% hydrochloric acid was added slowly to decompose the excess hydride and to dissolve the aluminum complex. The aqueous layer was mixed with 1000 ml. of a 20% solution of sodium potassium tartrate, and the resulting mixture was made strongly alkaline with an excess of 25% sodium hydroxide solution. After the thick gel that formed initially had completely dissolved, the mixture was exhaustively extracted with ether for 14 hr. The ether extracts were dried over anhydrous magnesium sulfate and the ether was removed by distillation. Distillation of the residue through an 8-inch, helix-packed column produced 30.5 g. (80%) of the colorless 2-amino-$\Delta^{9(10)}$-octalin (IIb), b.p. 106–107° (9 mm.), $n^{25}\text{D}$ 1.5132. (This amine rapidly darkened on standing.)

B. **From the Reduction of 2-Nitro-$\Delta^{9(10)}$-octalin (IIa) with Tin and Hydrochloric Acid.**—To a mixture of 18.1 g. (0.10 mole) of 2-nitro-$\Delta^{9(10)}$-octalin (IIa), 50 g. of granulated tin and 50 ml. of 95% ethanol, heated under reflux, was added 110 ml. of concentrated hydrochloric acid at a rate sufficient to maintain a vigorous but controllable reaction. After the reaction mixture had been cooled, 250 ml. of 50% sodium hydroxide solution was added. The basic solution was then steam distilled until 500 ml. of distillate was collected. This distillate was exhaustively extracted with ether, and the resulting ether solution was dried over anhydrous potassium carbonate. After the ether was removed by distillation, the residue was fractionated through an 8-inch, helix-packed column to yield 22.0 g. (70%) of 2-amino-$\Delta^{9(10)}$-octalin (IIb), b.p. 100–101° (7 mm.), $n^{25}\text{D}$ 1.5130.

2-Acetamido-$\Delta^{9(10)}$-octalin (IIc). A. From 2-Amino-$\Delta^{9(10)}$-octalin (IIb).—To a mixture of 15.1 g. (0.10 mole) of 2-amino-$\Delta^{9(10)}$-octalin (IIb) and 8.3 ml. of concentrated hydrochloric acid in 250 ml. of water was added 16.7 g. (0.16 mole) of acetic anhydride. To the cold reaction mixture was added a cold 10% sodium hydroxide solution until the mixture became strongly alkaline. The resulting precipitate was removed by filtration, washed with ice-water and recrystallized from alcohol to produce 17.4 g. (90%) of 2-acetamido-$\Delta^{9(10)}$-octalin (IIc), m.p. 130–131°.

Anal. Calcd. for $C_{12}H_{19}NO$: C, 74.61; H, 9.84. Found: C, 74.43; H, 9.71.

B. **From 2-Nitro-$\Delta^{9(10)}$-octalin (IIa).**—A solution of 1.81 g. (0.010 mole) of 2-nitro-$\Delta^{9(10)}$-octalin (IIa) in 5 ml. of absolute ethanol was hydrogenated at low pressure in the presence of 1.0 g. of 5% palladium-on-carbon catalyst. The reaction mixture absorbed 91% of three molar equivalents of hydrogen. After the catalyst was removed by filtration and the alcohol was removed by distillation, the residue was dissolved in 25 ml. of dilute hydrochloric acid. The mixture was cooled in ice and 2 ml. of acetic anhydride was added slowly. The reaction mixture was worked up as described above to yield 1.55 g. (69%) of 2-acetamido-$\Delta^{9(10)}$-octalin (IIc), m.p. 130–131°.

3-Acetamido-1,6-cyclodecadione (IIIc).—Ozone was bubbled through a solution of 7.65 g. (0.030 mole) of 2-acetamido-$\Delta^{9(10)}$-octalin (IIc) in 25 ml. of 85% acetic acid for 2.5 hr. at room temperature until 0.0292 mole of ozone had been absorbed. The reaction mixture was diluted with 250 ml. of ether, and this solution was allowed to stand at 0° for 2 hr. The precipitate was removed by filtration and washed with ether to yield 4.2 g. (49%) of 3-acetamido-1,6-cyclodecadione (IIIc), m.p. 155–157°.

Anal. Calcd. for $C_{12}H_{19}NO_3$: C, 63.97; H, 8.50; N, 6.22. Found: C, 63.80; H, 8.53; N, 6.46.

To a hot solution of 0.225 g. (0.001 mole) of 3-acetamido-1,6-cyclodecadione (IIIc) and 0.594 g. (0.003 mole) of 2,4-dinitrophenylhydrazine in 5 ml. of dioxane was added one drop of concentrated hydrochloric acid. After 0.5 ml. of water was added, the mixture was allowed to cool to room temperature. The resulting precipitate was removed by filtration and washed with dioxane, ethanol and then with ether until the wash liquid was no longer colored. This process produced 0.15 g. of a dinitrophenylhydrazone, m.p. 313° dec.

Anal. Calcd. for $C_{24}H_{25}N_9O_9$: C, 49.39; H, 4.30; N, 21.61. Found: C, 49.15; H, 4.09; N, 21.76.

Catalytic hydrogenation of IIIc resulted in the absorption of only 1 mole of hydrogen, which suggests the usual internal bimolecular reduction.[22]

2-Benzamido-$\Delta^{9(10)}$-octalin (IId).—A mixture of 1.51 g. (0.010 mole) of 2-amino-$\Delta^{9(10)}$-octalin (IIb) dissolved in 25 ml. of dilute hydrochloric acid and 2 ml. of benzoyl chloride was made strongly basic with a 5% sodium hydroxide solution. After the mixture had been shaken vigorously for 5 min., the resulting precipitate was removed by filtration and washed with a 5% sodium carbonate solution. Recrystallization from alcohol produced 2.30 g. (90%) of 2-benzamido-$\Delta^{9(10)}$-octalin (IId), m.p. 169–170°.

Anal. Calcd. for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.82; H, 8.08; N, 5.53.

3-Benzamido-1,6-cyclodecadione (IIId).—Ozone was bubbled through a solution of 1.28 g. (0.005 mole) of 2-benzamido-$\Delta^{9(10)}$-octalin (IId) in 75 ml. of 90% acetic acid for 20 minutes at 0° until 0.0046 mole of ozone had been absorbed. The solvent was removed by evaporation under reduced pressure and the residue was recrystallized from alcohol to yield 0.90 g. (62%) of 3-benzamido-1,6-cyclodecadione (IIId), m.p. 174–175°.

Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 71.05; H, 7.37. Found: C, 70.90; H, 7.21.

$\Delta^{9(10)}$-Octalin-2-carboxylic Acid (IIf).—A mixture of 17.2 g. (0.20 mole) of ethyl acrylate, 21.6 g. (0.20 mole) of 1,2-dimethylenecyclohexane (I), 50 ml. of benzene and a trace of *p*-*t*-butylcatechol was heated under reflux for 24 hours. After the benzene was removed by distillation under reduced pressure, the residue was fractionated through an 8-inch, helix-packed column to yield 31 g. (74%) of ethyl $\Delta^{9(10)}$-octalin-2-carboxylate (IIe), b.p. 103° (2 mm.).

A mixture of 5 g. of IIe and 30 ml. of 10% alcoholic potassium hydroxide was heated under reflux for 2 hr. The reaction mixture was acidified with concentrated hydrochloric acid, and the precipitated acid was removed by filtration. Recrystallization from 10 ml. of glacial acetic acid produced 2.8 g. (65%) of $\Delta^{9(10)}$-octalin-2-carboxylic acid (IIf), m.p. 112–113°.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.33; H, 8.88. Found: C, 73.17; H, 8.80.

1,6-Cyclodecadione-3-carboxylic Acid (IIIf).—Ozone was bubbled through a solution of 1.80 g. (0.010 mole) of $\Delta^{9(10)}$-octalin-2-carboxylic acid (IIf) in 25 ml. of 80% acetic acid for 40 minutes at room temperature until 0.0088 mole of ozone had been absorbed. The solvents were removed by evaporation under reduced pressure and the residue was recrystallized from aqueous methanol to yield 0.85 g. (43%) of 1,6-cyclodecadione-3-carboxylic acid (IIIf), m.p. 135–136°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55. Found: C, 62.47; H, 7.72.

$\Delta^{9(10)}$-Octalin-2,3-dicarboxylic Acid (IIg).—After 10.0 g. (0.048 mole) of $\Delta^{9(10)}$-octalin-2,3-dicarboxylic anhydride[5] had been saponified with 100 ml. of 10% alcoholic potassium hydroxide, the reaction mixture was acidified with concentrated hydrochloric acid. The resulting precipitate was removed by filtration and recrystallized from acetic acid to yield 8.0 g. (74%) of $\Delta^{9(10)}$-octalin-2,3-dicarboxylic acid (IIg), m.p. 203–205° (sealed tube).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.49; H, 7.02.

1,6-Cyclodecadione-3,4-dicarboxylic Acid (IIIg).—Ozone was bubbled through a solution of 2.24 g. (0.01 mole) of $\Delta^{9(10)}$-octalin-2,3-dicarboxylic acid (IIg) in 50 ml. of glacial acetic acid for 45 min. until 0.0097 mole of ozone had been absorbed. The solution was diluted with 25 ml. of water and cooled at 0° for 30 min. The resulting precipitate was removed by filtration, washed with water and dried to yield 1.5 g. (58%) of 1,6-cyclodecadione-3,4-dicarboxylic acid (IIIg), m.p. 198–199°. A mixed melting point determination with the original octalin derivative IIg showed a large depression. IIIg was insoluble in alcohol but was soluble in warm acetic acid.

Anal. Calcd. for $C_{12}H_{16}O_6$: C, 56.24; H, 6.29. Found: C, 56.52; H, 6.17.

2-Acetoxy-$\Delta^{9(10)}$-octalin (IIh).—A mixture of 10.8 g. (0.10 mole) of 1,2-dimethylenecyclohexane (I), 12.9 g. (0.15 mole) of vinyl acetate and 0.1 g. of *p*-*t*-butylcatechol was heated for 6 hr. at 170–180° in a heavy-walled tube, which was sealed under vacuum. The reaction mixture was quickly distilled through an 8-inch, helix-packed column and the fraction, b.p. 120–130° (10 mm.), was refractionated through the same column to yield 3 g. (15%) of 2-acetoxy-$\Delta^{9(10)}$-octalin (IIh), b.p. 130–131° (12 mm.), n^{25}_{D} 1.4940.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.27. Found: C, 74.48; H, 9.48.

1,4,5,6,7,8-Hexahydronaphthalene-2,3-dicarboxylic Acid (IVb).—After a mixture of 10.8 g. (0.10 mole) of 1,2-dimethylenecyclohexane (I) and 14.2 g. (0.10 mole) of dimethyl acetylenedicarboxylate in 25 ml. of ether had been heated under reflux for 1 hr., the solvent was removed by distillation under reduced pressure. The residue was fractionated through an 8-inch, helix-packed column to yield 20 g. (80%) of dimethyl 1,4,5,6,7,8-hexahydronaphthalene-2,3-dicarboxylate (IVa), b.p. 168° (3 mm.), n^{25}_{D} 1.5110.

A mixture of 1 g. of IVa and 20 ml. of 10% alcoholic potassium hydroxide was heated under reflux for 2 hr. The reaction mixture was acidified with concentrated hydrochloric acid, and the precipitated acid was removed by filtration. Recrystallization from 50 ml. of 70% ethanol produced 0.55 g. (62%) of 1,4,5,6,7,8-hexahydronaphthalene-2,3-dicarboxylic acid (IVb), m.p. 223–225°.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.86; H, 6.35. Found: C, 64.70; H, 6.59.

1,4,5,6,7,8-Hexahydronaphthalene-2-carboxylic Acid (IVd).—After 5.0 g. (0.021 mole) of ethyl 1,4,5,6,7,8-hexahydronaphthalene-2-carboxylate (IVc)[5] had been saponified with 50 ml. of 10% alcoholic potassium hydroxide, the solution was acidified with concentrated hydrochloric acid. The resulting precipitate was removed by filtration and recrystallized from acetic acid to yield 3 g. (78%) of 1,4,5,6,7,8-hexahydronaphthalene-2-carboxylic acid (IVd), m.p. 165–166°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 73.90; H, 7.67.

DETROIT 1, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CHAS. PFIZER AND CO., INC.]

Stereochemistry of the Itaconic Acid–Cyclopentadiene Adduct

BY BRYCE E. TATE AND A. BAVLEY

RECEIVED JULY 2, 1957

The adduct of itaconic acid and cyclopentadiene prepared in refluxing aqueous isopropyl alcohol is a mixture of isomers. The isomers were converted to the iodolactones which were separated by recrystallization. Treatment of the iodolactones with zinc and acetic acid regenerated the isomeric acids. The ratio of the isomer with an *exo*-carboxyl to that with the *endo*-carboxyl was about three.

The reaction of itaconic anhydride and cyclopentadiene was reported in 1928.[1] The resulting adduct, which was hydrolyzed to the acid but was not investigated further, appeared to consist of a single isomer.[2] The present paper describes the preparation of the adduct from cyclopentadiene and itaconic acid and the separation of the product *via* the iodolactones into two geometric isomers for which structures are assigned. The adduct I was obtained in 84% yield by heating the reactants in aqueous isopropyl alcohol. The wide melting range of I, even after several recrystallizations, indicated that it was a mixture. The neutral equivalent and hydrogen uptake of the product indicated it was a mixture of isomers.

Acid-catalyzed lactonization[3] of the mixture in an attempt to prepare the lactones IIa and IIb gave a viscous non-crystallizing sirup which exhibited a five-membered lactone band[4] at 5.63 μ, and a possible six-membered lactone band[4] at 5.83 μ. An attempt to prepare the bromolactones (IIIa and IIIb)[3,5] also resulted in a viscous sirup which did not crystallize. The infrared spectrum indicated a mixture similar to that obtained in lactonization, since five- and possibly six-membered lactone bands were observed at 5.57 and 5.78 μ. The possible occurrence of Wagner–Meerwein rearrangements during these reactions makes the evidence inconclusive as to the nature of the components of the original acid adduct.[3,5b,6]

The iodolactonization reaction which is milder than the bromolactonization reaction,[7] has been utilized as a method for characterization of unsaturated acids[8] and for separation of *exo–endo* isomers.[9] When the acid adduct I was treated with iodine in alkaline solution, two crystalline iodolactones were obtained. The major isomer, which melted at 208–209°, was isolated in about three times the amount of the minor isomer, which melted at 168–169°. Some infrared spectral data for these compounds are summarized in Table I. The data collected there indicate the important effect of the phase in which these compounds are examined. In potassium bromide the six-membered lactone band and the acid band of IVa absorb at the expected wave lengths,[4] while in dioxane only a single broad band appears, presumably from a shift of the acid carbonyl absorption. Isomer IVb in potassium bromide exhibits a poorly resolved doublet, while in dioxane both the five-membered lactone and the acid bands are observed.

The unrearranged lactone formulas IVa and IVb have been proposed for the two substances obtained from the iodolactonization reaction. In these structures the adjacent iodo- and ester oxygen

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[1] O. Diels and K. Alder, *Ann.*, **460**, 117 (1928).

[2] Dr. R. Hill and Mr. T. van Auken at Princeton University have also observed the formation of a single isomer from itaconic anhydride and cyclopentadiene (private communication). The iodolactone resulting from this isomer was apparently identical to our IVa.

[3] K. Alder and G. Stein, *Ann.*, **514**, 7 (1934).

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 152–163.

[5] (a) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); (b) R. B. Woodward and H. Baer, THIS JOURNAL, **70**, 1161 (1948); (c) H. Kwart and L. Kaplan, *ibid.*, **76**, 4078 (1954); (d) J. A. Berson, *ibid.*, **76**, 5748 (1954); (e) K. Alder and F. Brochhagen, *Chem. Ber.*, **87**, 167 (1954).

[6] (a) K. Alder, F. W. Chambers and W. Trimborn, *Ann.*, **566**, 27 (1950); (b) S. Beckmann, R. Schaber and R. Bamberger, *Chem. Ber.*, **87**, 997 (1954); (c) see also, J. A. Berson and R. Swidler, THIS JOURNAL, **76**, 4060 (1954), and ref. 2 for a summary of rearrangements in other bicyclic systems.

[7] C. D. Ver Nooy and C. S. Rondestvedt, Jr., THIS JOURNAL, **77**, 3583 (1955).

[8] (a) J. Bougault, *Ann. chim. et phys.*, **14**, 145 (1908); **15**, 296 (1908); (b) E. E. van Tamelen and M. Shamma, THIS JOURNAL, **76**, 2315 (1954).

[9] C. D. Ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 4878 (1955).