sulfate. Fractional distillation of the crude product through an 8-inch Widmer column at atmospheric pressure yielded 3.94 g. (35%) of an olefin mixture, b.p. 136–137°, $n^{25}\text{D}$ 1.4552. An examination of the infrared spectrum of this material showed considerably less methylenecycloheptane than was present in the sample from thermal dehydration of 1-methylcycloheptanol. However, a small amount of the *exo* double bond absorptions was still apparent in the spectrum. A vapor-phase chromatograph indicated that the amount of methylenecycloheptane (IX) did not exceed 2%.

N-(1-Methylcyclohexyl)-acetamide (XI).—In a 200-ml. flask were placed 22.8 g. (0.20 mole) of 1-methylcyclohexanol, 8.2 g. (0.20 mole) of acetonitrile and 43.5 ml. of glacial acetic acid. To this rapidly stirred mixture was added dropwise 13.5 ml. of concentrated sulfuric acid and the mixture was allowed to stand at room temperature for 8 hours. The contents were poured onto crushed ice and the resulting mixture was neutralized with sodium bicarbonate. After the solid had been removed by filtration, it was washed with three portions of cold water and then dried over calcium chloride in an evacuated desiccator to yield 28.6 g. (92%) of crude N-(1-methylcyclohexyl)-acetamide (XI), b.p. 76–80°. Two recrystallizations of this crude material from *n*-hexane gave analytically pure material, m.p. 85–86°.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04, N, 9.02. Found: C, 69.87; H, 10.97; N, 9.16.

Pyrolysis of N-(Methylcyclohexyl)-acetamide (XI).—The dropping funnel of the pyrolysis apparatus was heated with resistance wire to liquefy the amide and the ground-glass stopcock of the funnel was heated with an infrared lamp to prevent solidification. At a temperature of 570°, 4.5 g. (0.029 mole) of N-(1-methylcyclohexyl)-acetamide (XI) was pyrolyzed at the rate of 1 g. per minute. The receiver for the collection of the pyrolysate was connected directly to the exit end of the pyrolysis tube and was cooled in a Dry Ice–methyl Cellosolve-bath. (After the pyrolysis, there was a small carbonaceous deposit at the top of the helix packing.) The pyrolysate was immediately heated at 100° and 120 mm. and 1.0 g. (37%) of crude olefin was collected in a receiver immersed in a Dry Ice cooling bath. (A vapor-phase chromatograph of this crude olefin indicated the presence of 72% of 1-methylcyclohexene (XII) and 28% of methylenecyclohexane (XIII)). After the solid residue from the distillation had been broken up and mixed with 20 ml. of water, it was heated on the steam-bath for 10 minutes. The mixture was then cooled in ice and filtered to yield, after it was dried, 1.5 g. (34% recovery) of N-(1-methylcyclohexyl)-acetamide (XI), m.p. 84–85°. The filtrate was heated under reduced pressure to remove the water and then dried to yield 0.6 g. (37%) of impure acetamide, m.p. 67–72.5° (reported[19] m.p. 82–83°). After two recrystallizations from a 10:1 mixture of ether and methanol, a melting point of 79.5–81° was obtained for this sample of acetamide. A mixed melting point determination with an authentic sample of acetamide showed no depression. However, when the acetamide from the pyrolysis was mixed with a sample of N-(1-methylcyclohexyl)-acetamide (XI), there was an 11° depression of the melting point of XI. Acetonitrile was found in the volatile portion of the pyrolysate in a 2.5% over-all yield, calculated from the vapor-phase chromatograph.

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[19] E. C. Wagner, *J. Chem. Ed.*, **7**, 1135 (1950).

COLLEGE PARK, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

1,2-Dihydro-*endo*-dicyclopentadiene[1]

BY PELHAM WILDER, JR., CHICITA F. CULBERSON AND GEORGE T. YOUNGBLOOD[2]

RECEIVED JULY 21, 1958

1,2-Dihydro-*endo*-dicyclopentadiene (I), prepared by an unequivocal reaction sequence, is shown to be identical with the dihydrodicyclopentadiene of Bruson and Riener,[3] synthesized by the Diels–Alder addition of cyclopentene and cyclopentadiene. The chemistry of this compound and the stereochemical problem are discussed.

In a study of the acid-catalyzed hydration and rearrangement of *endo*-dicyclopentadiene, Bruson and Riener reported a dihydrodicyclopentadiene prepared by the reaction of cyclopentene and cyclopentadiene at elevated temperature and pressure.[3,4]

The synthetic method used by Bruson and Riener suggests that the adduct has a norbornylene ring, and by application of Alder's empirical rules concerning the stereochemical course of the diene synthesis it may be inferred that the adduct has the *endo*-configuration. However, no statement concerning the stereochemistry of the cyclopentyl ring was made. In the present paper the stereochemical problem is solved by identifying Bruson and Riener's olefin with an authentic sample of 1,2 - dihydro - *endo* - dicyclopentadiene (I). The chemistry of the olefin is described.

The synthesis of 1,2-dihydro-*endo*-dicyclopentadiene (I) described here is shown schematically in Fig. 1. From *endo*-dicyclopentadiene the dimeric nitroso chloride II is prepared with nitrosyl chloride by the method of Kraemer and Spilker.[5] On reduction with zinc and acetic acid in isoamyl alcohol, the dimeric nitroso chloride gives two products, the unsaturated monomeric oxime III and derived ketone which is then reconverted to the ketoxime with hydroxylamine. The saturated ketoxime IV, obtained by the catalytic hydrogenation of III, is then converted into 9-aminotetrahydro-*endo*-dicyclopentadiene (V) by a sodium-alcohol reduction. The tertiary amine, 9-dimethylaminotetrahydro - *endo* - dicyclopentadiene (VI), prepared by treating the primary amine with formalin in a formic acid medium, is converted with methyl iodide into the quaternary salt, trimethyl-9-tetrahydro-*endo*-dicyclopentadienyl ammonium iodide (VII). Treatment of the methiodide with silver oxide and decomposition at elevated temperature yield the olefin, 1,2-dihydro-*endo*-dicyclopentadiene (I). This olefin is identical with the adduct of Bruson and Riener.

The formation of an addition product with phenyl azide,[6,7] and the method of synthesis show

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[1] Taken in part from a dissertation submitted by G. T. Youngblood to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, October, 1956. For the previous paper in this series, see G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **21**, 1436 (1956).

[2] American Cyanamid Pre-doctoral Fellow, 1955–1956.

[3] H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723 (1945).

[4] P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

[5] G. Kraemer and A. Spilker, *Ber.*, **29**, 552 (1896).

[6] K. Alder and G. Stein, *Ann.*, **485**, 211 (1931).

[7] K. Alder, G. Stein and H. Finzerhagen, *ibid.*, **485**, 223 (1931).

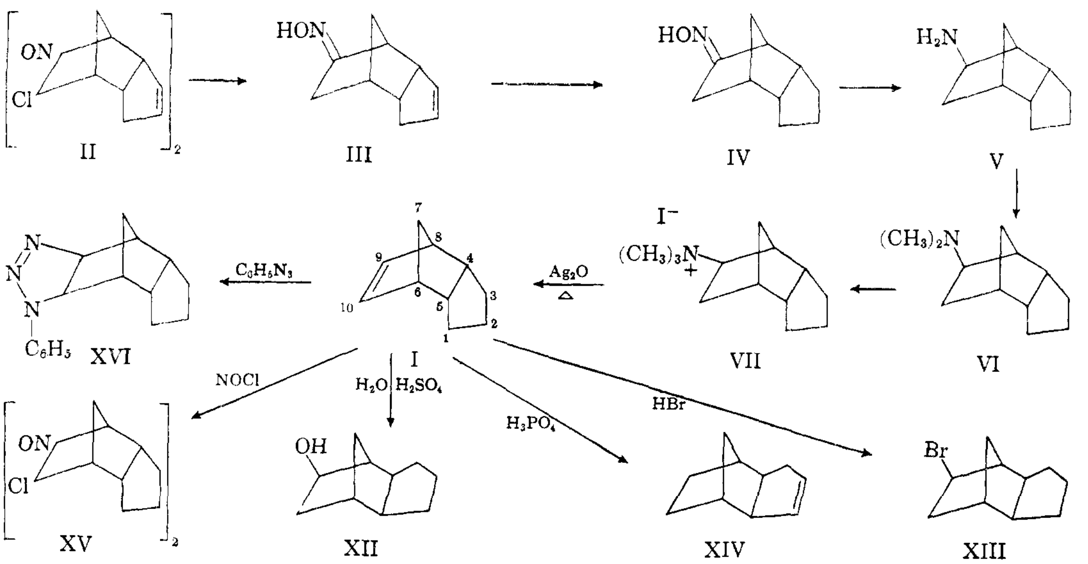
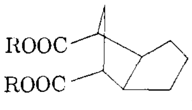


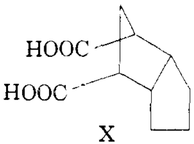
Fig. 1.

that the olefin I has the gross structure of a 1,2-dihydrodicyclopentadiene.

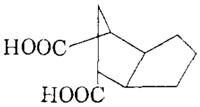
The olefin is synthesized from *endo*-dicyclopentadiene by a series of reactions precluding rearrangement of the carbon skeleton. Oxidation to the same dicarboxylic acid X, m.p. 230°, obtained by oxidation of 9-ketotetrahydro-*endo*-dicyclopentadiene and comparison of the olefin with the known isomeric 1,2-dihydro-*exo*-dicyclopentadiene[1,8,9] require assignment of the *endo* configuration to olefin I. On alkaline permanganate oxidation the *exo*-ketone yields a dicarboxylic acid VIII, m.p. 181-182°. When either dibasic acid is converted into the methyl ester with diazomethane and that ester, in turn, is subjected to the action of sodium methoxide in methanol, the product is *trans* - bicyclo[3.3.0]octane - 2,4 - dicarboxylic acid (XI), m.p. 176-177°.



VIII, R = H
IX, R = CH_3



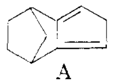
X



XI

The chemistry of 1,2-dihydro-*endo*-dicyclopentadiene (I) is essentially that of a highly reactive norbornylene system. Like *endo*-dicyclopentadiene[3,10] itself, the dihydro- compound reacts readily in the presence of acidic reagents to give derivatives of the *exo* configuration. With dilute aqueous sulfuric acid the olefin I gives 9-*exo*-hydroxytetrahydro-*exo*-dicyclopentadiene[3] (XII); with hydrobromic acid the product is 9-*exo*-bromotetrahydro - *exo* - dicyclopentadiene (XIII). With sirupy phosphoric acid at elevated temperature a transformation occurs, in which the double bond migrates from the norbornylene ring to the cyclopentyl ring to yield 9,10-dihydro-*exo*-dicyclopentadiene (XIV). This rearrangement, known to occur in the case of 1,2-dihydro-*exo*-dicyclopentadiene and also in the dehydration of 9-hydroxytetrahydro - *exo* - dicyclopentadiene, is now being studied. Some reactions of the olefin proceed without rearrangement. Catalytic hydrogenation with Adams oxide yields the expected tetrahydro-*endo*-dicyclopentadiene; treatment with phenyl azide gives an adduct (XVI) preserving the *endo* configuration[11]; and addition of nitrosyl chloride yields the dimeric nitroso chloride XV.

Bruson and Riener's early synthesis and the present characterization of 1,2-dihydro-*endo*-dicyclopentadiene complete the list of the dihydrodicyclopentadienes,[12] the others previously reported and characterized being 9,10-dihydro-*endo* - dicyclopentadiene,[7] 1,2 - dihydro - *exo*-dicyclopentadiene[1,8,9] and 9,10-dihydro-*exo*-dicyclopentadiene.[3,4,8,9]



A

Note added in proof.—The yield of olefin I obtained by the method of Bruson and Riener is improved by employing an excess of cyclopentene, and the product olefin is essentially free of dicyclopentadiene and 1,2-dihydro-*exo*-dicyclopentadiene contamination. When 10 g. of cyclopentene and 3.0 g. of cyclopentadiene were heated in a sealed tube and the crude reaction mixture was treated with an ether solution of phenyl azide, the entire yield of solid adduct (12% on the basis of cyclopentadiene) was identical with the phenyl azide adduct of an authentic sample of 1,2-dihydro-*endo*-dicyclopentadiene.

Experimental[13]

Dihydrodicyclopentadiene was prepared from cyclopentene and cyclopentadiene according to the directions of

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[8] P. Wilder, Jr., and G. T. Youngblood, THIS JOURNAL, **78**, 5706 (1956).

[9] P. R. Schleyer and M. M. Donaldson, *ibid.*, **78**, 5702 (1956).

[10] H. A. Bruson and T. W. Riener, *ibid.*, **67**, 1178 (1945); **68**, 8 (1946).

[11] This adduct was previously prepared even though the olefin was unknown. Alder, *et al.* [*Ann.*, **504**, 216 (1933)] added phenyl azide to a mixture of *exo*- and *endo*- dicyclopentadiene, separated the isomers, and then reduced catalytically the adducts to the dihydro-derivatives.

[12] The preparation of iso-dicyclopentadiene (A) has been reported by Alder, *et al.* [*Ber.*, **89**, 2689 (1956)]. The list does not include dihydro-iso-dicyclopentadiene.

[13] Melting points, except micro melting points, and boiling points, are uncorrected. Infrared spectra were obtained with a Perkin–Elmer model 21 double beam recording spectrophotometer with sodium

Bruson and Riener, b.p. 88–89° (40 mm.), n^{25}_{D} 1.5022 (reported[3] 92–94° (40 mm.), n^{25}_{D} 1.5001).

To 3.0 g. (0.024 mole) of the olefin was added 4.0 g. of phenyl azide. After 36 hours the solid was washed with 95% ethanol and recrystallized from absolute ethanol yielding 3.5 g. (0.014 mole, 58%) of adduct, m.p. 128.5–129° (reported[11] 128–129°).

Dimeric nitroso chloride of *endo*-dicyclopentadiene (II) was prepared in 81% yield by the method of Kraemer and Spilker,[5] m.p. 181–182.5° (reported 181–182°).

9-Keto-9,10-dihydro-*endo*-dicyclopentadiene oxime (III) was prepared by an extensive modification of the method of Wieland and Bergel.[14] One hundred grams (0.253 mole) of the nitroso chloride dimer, suspended in 750 ml. of isoamyl alcohol, was heated slowly to reflux with vigorous stirring. As soon as all the solid had disappeared, the darkened solution was cooled in an ice-bath and 250 ml. of absolute ethanol, 125 ml. of glacial acetic acid and 60 g. (0.92 mole) of zinc dust were added. After heating for 1 hr., the zinc was removed by filtration, the ethanol distilled under diminished pressure, and the dark residue poured into 2.5 l. of ether in a 4-l. erlenmeyer flask. After 10 hr. the ether solution was decanted from the precipitate, washed with aqueous Na_2CO_3 and with water, and dried over $MgSO_4$. Removal of the ether under diminished pressure and distillation of the dark viscous residue yielded 8.8 g. (0.0595 mole, 8.5%) of the ketone of the oxime, b.p. 110° (14 mm.) reported 177–178° (140 mm.)) and 34.7 g. (0.213 mole, 42%) of the oxime b.p. 110° (0.3 mm.) (reported 135° (2 mm.)).

To convert the ketone to the desired oxime, 90 g. (0.61 mole) of ketone, 90 g. (1.3 moles) of hydroxylamine hydrochloride, 360 g. of KOH and 1800 ml. of 95% ethanol were mixed and heated under reflux for 3 hr. The KCl was separated by filtration and the solution reduced to 800 ml. by removing alcohol under diminished pressure. The residue was poured into 7 l. of water, acidified with 1:1 aqueous hydrochloric acid, and extracted with ether. The extracts were washed with aqueous Na_2CO_3 and with water and dried over $MgSO_4$. Ether was removed and the residue distilled under reduced pressure. From the reaction, 16 g. of unreacted ketone and 50 g. (61%, on the basis of starting material used) of oxime were obtained. The total yield of oxime calculated from 100 g. of nitroso chloride dimer was 48%.

9-Ketotetrahydro-*endo*-dicyclopentadiene Oxime (IV).—Two hundred thirty-three grams (1.4 moles) of the unsaturated oxime was divided into five parts and each was dissolved in 200 ml. of absolute ethanol and reduced with PtO_2 catalyst at an average pressure of 45 p.s.i. of hydrogen. The catalyst was removed by filtration and ethanol evaporated under diminished pressure. Distillation of the combined residues yielded 217 g. (1.3 mole, 93%) of the saturated oxime, b.p. 124–126° (3.3 mm.), which solidified in the receiving flask. A sample was recrystallized from nitroethane, m.p. 93–94.5°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15. Found: C, 72.54; H, 9.30.

9-Aminotetrahydro-*endo*-dicyclopentadiene (V).—To a solution of 26.4 g. (0.16 mole) of the saturated oxime in 600 ml. of absolute ethanol under slow reflux, 35 g. (1.3 g. at.) of sodium was added in small portions with vigorous stirring. After three hours, the addition was completed; the reaction was cooled, acidified with 1:1 HCl and the alcohol removed under diminished pressure. The solution was made alkaline with dilute NaOH and extracted several times with ether. The ether extracts were combined, washed with water, and dried over $MgSO_4$. The ether was removed and distillation of the residue under reduced pressure yielded 24 g. (99%) of the primary amine, b.p. 97–99° (10 mm.), n^{26}_{D} 1.5135.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.40; H, 11.34. Found: C, 79.62; H, 11.54.

A picrate was prepared according to the procedure of Wieland,[15] m.p. 195–196°.

Anal. Calcd. for $C_{16}H_{20}N_4O_7$: C, 50.53; H, 5.30. Found: C, 50.59; H, 5.44.

9-Dimethylaminotetrahydro-*endo*-dicyclopentadiene (VI).—To 70 g. (0.46 mole) of primary amine, 280 g. (2.5 moles) of 88% formic acid and 95 g. (1.1 moles) of formalin were successively added with stirring and cooling. The mixture was heated under slow reflux for 24 hr. and then treated with 56 ml. of 36% hydrochloric acid. After the formic acid and some of the formalin were removed under diminished pressure, the residue was made alkaline with 25% NaOH and extracted with ether. The ether extracts were washed with water and dried over $MgSO_4$. Removal of ether and distillation of the residue under reduced pressure yielded 40.2 g. (0.224 mole, 48%) of the crude tertiary amine, b.p. 104–110° (10 mm.). A second distillation gave 34.7 g. (0.194 mole, 42%), b.p. 105–109° (10 mm.), n^{26}_{D} 1.4903.

Anal. Calcd. for $C_{12}H_{21}N$: C, 80.37; H, 11.80. Found: C, 80.18; H, 11.74.

A picrate was prepared by the method of Wieland,[15] m.p. 193–194.°

Anal. Calcd. for $C_{18}H_{24}N_4O_7$: C, 52.93; H, 5.92. Found: C, 52.76; H, 6.06.

Trimethyl-9-tetrahydro-*endo*-dicyclopentadienyl Ammonium Iodide (VII).—Twenty-seven grams (0.15 mole) of the tertiary amine, mixed with 58 ml. of acetonitrile was cooled in an ice-bath and 67.5 ml. (0.47 mole) of methyl iodide was added slowly with swirling. After 1 hr. the reaction mixture was filtered to remove most of the salt. The addition of anhydrous ether to the mother liquor precipitated additional salt which was collected by filtration. The product was dissolved in absolute ethanol and reprecipitated by anhydrous ether. The solid was dried in a vacuum desiccator over P_2O_5 for 5 days. The yield of the salt was 25.9 g. (0.081 mole, 54%), m.p. 214–215.5° dec.

Anal. Calcd. for $C_{13}H_{24}NI$: C, 48.61; H, 7.53. Found: C, 48.60, H, 7.31.

1,2-Dihydro-*endo*-dicyclopentadiene (I).—Twenty-four grams (0.075 mole) of the methiodide was mixed in 200 ml. of water with Ag_2O prepared from 27.2 g. (0.16 mole) of $AgNO_3$ and 6.4 g. (0.16 mole) NaOH. The mixture was heated on a steam-bath with stirring for 1 hr. Solid materials were removed by filtration and the aqueous solution of the quaternary ammonium hydroxide was distilled to remove water. After the residue was heated to decompose the hydroxide, the product was distilled. The total distillate was extracted with ether and the combined ether extracts were washed with water and dried over $MgSO_4$. The ether was removed and distillation of the residue yielded 7.0 g. (0.052 mole, 69%) of olefin boiling at 90–92° (40 mm.), n^{26}_{D} 1.5005 (reported[3] 92–94° (40 mm.), n^{25}_{D} 1.5001).

A phenyl azide adduct was prepared, m.p. 128–129° (reported[11] 128–129°); mixed m.p. with the phenyl azide adduct of the olefin prepared from cyclopentene and cyclopentadiene, 128–129°.

Dimeric nitroso chloride of 1,2-dihydro-*endo*-dicyclopentadiene (XV) was prepared by the method of Kraemer and Spilker.[5] A solution of 2 ml. of 95% ethanol and 2 ml. of concentrated hydrochloric acid was added dropwise with stirring to 2.68 g. (0.020 mole) of the olefin in 2.5 g. (0.021 mole) of isoamyl nitrite and 2 ml. of 95% ethanol cooled in an ice-bath. After 1 hr. the product, separated by filtration, was washed with 95% ethanol and with ether, yielding 3.2 g. (0.012 mole, 63%) of a white crystalline solid. A sample was recrystallized from chloroform, m.p. 185–186° dec.

Anal. Calcd. for $C_{20}H_{20}N_2O_2Cl_2$: C, 60.45; H, 6.59. Found: C, 6032, H, 6.75.

9-Bromotetrahydro-*exo*-dicyclopentadiene (XIII).—A mixture of 13.4 g. (0.10 mole) of olefin and 32.4 g. (0.20 mole) of 48.8% hydrobromic acid was heated under slow reflux with stirring for 5 hr. After addition of 200 ml. of water, the mixture was extracted with ether. The ether extract was washed with water and dried over $MgSO_4$. Removal of ether and distillation of the residue under reduced pressure yielded 13.9 g. (0.065 mole, 65%) of the bromide, b.p. 110–113° (10 mm.), n^{25}_{D} 1.5355 (reported[1] b.p. 79° (0.5 mm.), n^{25}_{D} 1.5359).

9,10-Dihydro-*exo*-dicyclopentadiene (XIV).—After standing 30 minutes, 28 g. (0.21 mole) of olefin and 25 g. of 85% H_3PO_4, were heated to boiling and the distillate of water and organic material was extracted with ether. The extract was dried over $MgSO_4$ and the ether was removed. Distillation under reduced pressure yielded 3.2 g. (0.024 mole, 11%) of the rearranged olefin, b.p. 88° (39 mm.), n^{25}_{D} 1.4995 (reported[9] b.p. 180.1° (760 mm.), n^{25}_{D} 1.4985).

***exo-cis*-Bicyclo[3.3.0]octane-2,4-dicarboxylic acid** (VIII) was prepared by the oxidation of 9-ketotetrahydro-*exo*-

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chloride prism. A solution of the substance in a suitable solvent in a 1-mm. sodium chloride cell was used. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(14) H. Wieland, and F. Bergel, *Ann.*, **446**, 20 (1926).

(15) H. Wieland, *Ber.*, **39**, 1497 (1906).

dicyclopentadiene[3] with alkaline permanganate by the method of Bergel and Widman,[16] micro m.p. 181–182° (reported 182–184°).

***exo-cis*-Bicyclo[3.3.0]octane-2,4-dicarboxylic Acid Dimethyl Ester (IX).**—A solution of 10.0 g. (0.051 mole) of dicarboxylic acid VIII in 50 ml. of ether was added to a solution of diazomethane in ether cooled in a Dry Ice–acetone-bath. After 30 minutes the excess diazomethane was destroyed with formic acid. Removal of ether and methyl formate yielded a sirupy residue which on distillation gave 9.9 g. (76%) of colorless dimethyl ester, b.p. 135–137° (2 mm.). An additional distillation gave a sample, b.p. 122° (1 mm.), d^{20}_4 1.101, n^{25}_D 1.4711.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.00. Found: C, 63.90; H, 8.27.

***trans*-Bicyclo[3.3.0]octane-2,4-dicarboxylic Acid (XI).**—A solution of 10.0 g. (0.044 mole) of the dimethyl ester IX in 200 ml. of ethanol in which 10.0 g. (0.43 g. at.) of sodium had been dissolved was heated under reflux for 4 hours. Methanol was then removed under diminished pressure on a steam-bath and the residue dissolved in water. The aqueous solution was washed twice with ether and the ether discarded. The aqueous solution, acidified with 6 *M* hydrochloric acid, was extracted continuously with ether for 36 hours. Evaporation of the ether gave a brown solid material which was treated in hot water for 4 hours with 1 g. of charcoal. Removal of the charcoal yielded a clear solution from which 4.5 g. (59%) of *trans*-bicyclo[3.3.0]octane-2,4-dicarboxylic acid, m.p. 175–176° (reported[16] 178°), slowly crystallized.

***endo-cis*-Bicyclo[3.3.0]octane-2,4-dicarboxylic Acid.**—9-Keto-tetrahydro-*endo*-dicyclopentadine was prepared from the oxime III and oxidized with alkaline permanganate solution to the diacid, m.p. 230° (reported[17] 232°). The methyl ester was prepared as described above, b.p. 111–113° (12 mm.), m.p. 76–77° (reported[16] 77.5–78°), and was, in turn, converted in 47% yield into *trans*-bicyclo [3.3.0] octane-2,4-dicarboxylic acid, m.p. 176–177° (reported[16] 178°); mixed m.p. with the sample from the *exo* isomer, 176–176.5°. The infrared traces of these acids are identical.

For comparison olefin I was oxidized in acetone with potassium permanganate, by the method of Youngblood and Wilder,[17] to the same *endo-cis*-bicyclo [3.3.0] octane-2,4-dicarboxylic acid, m.p. 228–230°; mixed m.p. with the sample from the oxidation of 9-ketotetrahydro-*endo*-dicyclopentadiene, 228–230°.

Acknowledgment.—This work was supported by a grant from the Research Corporation and by a Grant-in-Aid from Allied Chemical and Dye Corporation.

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[16] F. Bergel and E. Widman, *Ann.*, **467**, 76 (1928).

[17] G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **21**, 1436 (1956).

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Reactions of 1-Substituted Cyclohexenes with Peracids[1-3]

BY ROBERT FILLER, BELEN R. CAMARA AND SAIYID M. NAQVI

RECEIVED AUGUST 1, 1958

1-Alkyl- and 1-phenylcyclohexenes react with perbenzoic and monoperphthalic acids to give the 2-substituted cyclohexanones in addition to or instead of the expected epoxide. In some cases, the *trans*-1,2-diol is also isolated. Pure 1-methylcyclohexene oxide does not rearrange to 2-methylcyclohexanone in the presence of perbenzoic acid, but does give the ketone and the hydroxybenzoate with benzoic acid. While some ketone may be formed by thermal rearrangement of epoxide, it is demonstrated that the reaction also occurs in the cold. The mechanism of ketone formation is discussed.

Introduction

The preparation of epoxides is most frequently accomplished by the reaction of olefins with peracids, such as perbenzoic and monoperphthalic acids.[4] There have been a number of cases reported,[5-8] however, in which carbonyl-containing products were formed in addition to or to the exclusion of the expected oxirane, particularly when perbenzoic acid is the reagent.

In the course of preparing 1-substituted cyclohexene oxides for rearrangement studies,[9] we isolated carbonyl and hydroxyl-containing by-products as well as the epoxide. In most cases, these results differed from those reported in the literature.[4] We therefore examined this reaction in further detail.

Results

The substituted cyclohexenes were generally prepared by dehydration of the tertiary alcohol resulting from reaction of cyclohexanone with the appropriate Grignard reagent. In this way, the 1-methyl, -ethyl, -isopropyl and -phenyl analogs were obtained. 1-*t*-Butylcyclohexene failed to give a hydroxyl-free product by this method[10] and was ultimately prepared in low yield by alkylation of cyclohexene in the presence of bismuth trichloride.[11] Attempts to obtain the isopropyl and *t*-butyl compounds by a Birch-type reduction of the alkylbenzene using lithium–ethylamine,[12] gave inconsistent results with part of the product appearing to be the dihydro product, a conjugated diene (ultraviolet absorption). 1-Acetylcyclohexene was best prepared by acylation of cyclohexene,[13] in preference to the rearrangement of 1-ethynylcyclohexanol.[14] Even after recycling, the ketone obtained by

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[1] Abstracted from the thesis submitted to the Graduate School of Illinois Institute of Technology by Belen R. Camara in partial fulfillment of the requirements for the degree of Master of Science.

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