Endo-Exo-Rearrangement in the Addition of Acids to Dicyclopentadiene

BY PAUL D. BARTLETT AND ABRAHAM SCHNEIDER

In two interesting papers, Bruson and Riener[1] have recently reported the results of a study of the addition of acids, and of water catalyzed by acids, to one double bond of dicyclopentadiene (I). These authors established that the double bond involved was the one in the six-membered ring and showed that the saturated alcohol, ketone and hydrocarbon derived from the hydration product of dicyclopentadiene were not identical with the corresponding derivatives (II, III and IV), previously prepared by Alder and Stein[2] and by Wieland and Bergel,[3] and having the dicyclopentadiene ring structure. Since bicyclo(2,2,1)-2-heptene (V) on hydration yielded "β-norborneol" of known structure (VI), Bruson and Riener


I   II, X = OH   III   V   VI
      IV, X = H
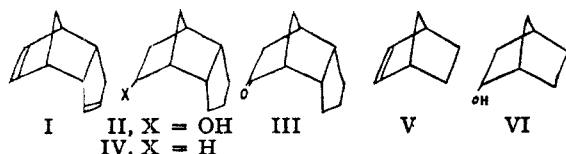
assigned to their hydration product the structure tricyclo(4,2,2,0^{1,6})decen(2 or 3)ol-8 (VII, X = OH), regarding it as the product of a type of molecular rearrangement which was considered to occur also in the case of norborneol but to yield a product identical in ring structure with the starting material.

The conditions of the addition reactions in question are similar to those of known Wagner-Meerwein rearrangements. Now, the structure VII is an expected product of the Wagner-

VII
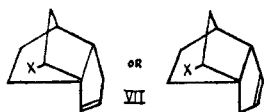
Meerwein rearrangement during addition to I *only* on the basis of the discredited[4] "cyclopropane" mechanism for this rearrangement.[5] Using the "ionic" mechanism[4b,6] which is generally successful in accounting for the course of the Wagner-Meerwein rearrangement, we should ex-

pect the following series of changes (with the same uncertainty with regard to the position of the remaining double bond as in the case of VII). Contrary to the reasoning of Bruson and Riener, the product VIII is not identical with II, for the

VIII
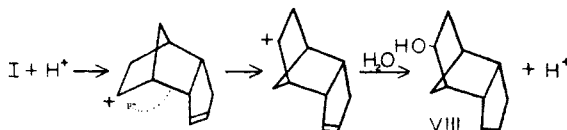
former has the "exo," the latter the "endo," configuration.[7] The rearrangement mechanism postulated here is exactly parallel to that formulated by Alder and Stein[8] to account for the conversion by 50% sulfuric acid of exo-cis-3,6-endomethylene-Δ^4-tetrahydrophthalic acid into a lactonic acid having the *endo* configuration.

It happens that, although Alder and Stein have prepared a number of dicyclopentadiene and related derivatives possessing the *exo* configuration, these did not include any which should be identical with any of the compounds described in the two papers of Bruson and Riener. We have bridged this gap by converting Bruson's "dihydronordicyclopentadiene" by oxidation into Alder's β(exo)cis-3,6-endomethylene-hexahydrophthalic anhydride (XIII) and established its identity by mixed melting point of the anhydride and of the phenylimide with specimens prepared by the method of Alder and Stein[9] from the addition product of maleic anhydride to cyclopentadiene. The steps in the reaction are shown in the accompanying flow-sheet. With this demonstration that "dihydronordicyclopentadiene" is in fact *exo*-dihydrodicyclopentadiene, the need for postulating an unusual course for the original addition of acids and water to the double bond disappears, and it becomes probable that all the analogous addition compounds of Bruson represent the hitherto largely unknown *exo*-series of dicyclopentadiene derivatives.

It will be noted that chloro-dihydro-*exo*-dicyclopentadiene is not a compound of the neopentyl type. Its inertness in ionic displacement reactions[1b] is rather to be explained by the very effective shielding against rearward attack upon the carbon holding the chlorine which is afforded by the bicyclo(2,2,1)-heptane ring system.

Experimental

The degradation of the "dihydronordicyclopentadiene" of Bruson and Riener to the dibasic acid was effected by

(1) (a) Bruson and Riener, THIS JOURNAL, 67, 723 (1945); (b) 67, 1178 (1945).

(2) Alder and Stein, Ann., 485, 223 (1931).

(3) Wieland and Bergel, ibid., 446, 21 (1926).

(4) (a) Lipp, Ber., 53B, 769 (1920); (b) Meerwein and van Emster, ibid., 1815 (1920).

(5) This point has been recognized independently by a number of organic chemists including, to the present authors' knowledge, Drs. F. C. Whitmore, C. C. Price, and S. G. Cohen. It was the subject of discussion by Dr. Bruson, Dr. Price, and one of the present authors at a Gibson Island conference in June, 1945. Dr. Bruson kindly welcomed our offer, made at that time, to test the alternative set of structures which is the subject of this paper.

(6) See Whitmore, THIS JOURNAL, 54, 3274 (1932).

(7) Alder and Stein, Ann., 504, 228 (1933).

(8) Alder and Stein, ibid., 514, 9 (1934).

(9) Alder and Stein, ibid., 504, 247 (1933).
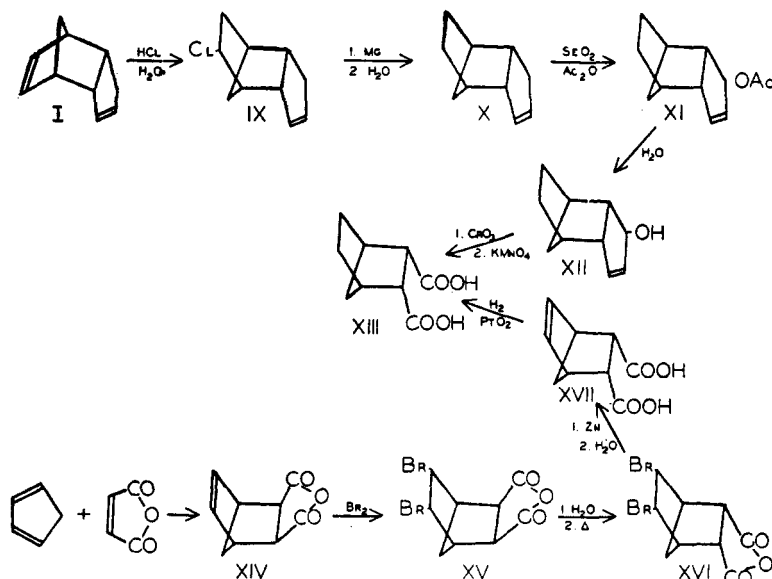
the procedure which Alder and Stein[10] applied to *endo-* and the mixed *endo-* and *exo*-dihydrodicyclopentadienes. Their two final *cis*-dibasic acids and their anhydrides melted as follows:

	Acid	Anhydride
α (*endo*)	165°	170°
β (*exo*)	152°	80°

The "Dihydronordicyclopentadiene" of Bruson and Riener.—A Grignard reagent was made by adding "chloro-dihydronordicyclopentadiene,"[1b] 33 g. (0.197 mole) b. p. (23 mm.) 117–119°, n^{25}D 1.5209, to 7 g. of magnesium chips covered with 35 cc. of ether and 0.5 cc. of ethyl bromide to initiate the reaction. Hydrolysis was effected with 25 cc. of water followed by 25 cc. of 6 *N* hydrochloric acid. The ether solution was washed, dried and distilled. The yield was 74%; b. p. 78–79° (26 mm.); n^{25}D 1.4990. Bruson and Riener[1a] report for the "dihydronordicyclopentadiene" formed from a Clemmensen reduction of "keto-dihydronordicyclopentadiene" a b. p. of 78–79° (27 mm.) and n^{25}D 1.4986.

Selenium Dioxide Oxidation of "Dihydronordicyclopentadiene" to the Acetyl Derivative of 3-Hydroxy-dihydro-*exo*-dicyclopentadiene.—"Dihydronordicyclopentadiene" (15 g., 0.112 mole) dissolved in 45 cc. of acetic anhydride was shaken with a suspension of 12.5 g. of selenium dioxide in 3 cc. of water. The mixture warmed up slowly and deposited the bright red precipitate of selenium. After two hours of shaking, the mixture was filtered and the excess anhydride destroyed by warming with water on the steam cone. The mixture was extracted with ether and the ether washed with dilute base and evaporated. The residue was distilled at 25 mm. to give 3 g. of starting hydrocarbon, 8 g. of the desired ester boiling at 132–135° with n^{25}D 1.5008, and a solid residue.

Hydrolysis of the Ester to 3-Hydroxydihydro-*exo*-dicyclopentadiene.—Sixteen grams (0.0835 mole) of 3-acetoxydihydro-*exo*-dicyclopentadiene obtained as above was heated under reflux with 50 cc. of 15% methyl alcoholic potassium hydroxide for two hours. The mixture was diluted with water, extracted with ether and the ether layer distilled. The yield of the alcohol was 96%; b. p. 136–138° (30 mm.); n^{25}D 1.5218.

Oxidation of the Alcohol to 3-Keto-dihydro-*exo*-dicyclopentadiene.—The alcohol 3-hydroxydihydro-*exo*-dicyclopentadiene (6 g.) in 25 cc. of acetic acid was treated while stirring with a solution of 3.2 g. of chromic anhydride in

2.5 cc. of water and 5 cc. of acetic acid, the temperature being kept at 20°. After dilution with water, extraction into ether, bicarbonate washing and drying, the material was distilled. The yield was 4.48 g.; b. p. 133.5–135° (27 mm.); n^{25}D 1.5242.

Oxidation of the Ketone to *cis-exo*-Endomethylene Hexahydrophthalic Acid.—The 3-ketodihydro-*exo*-dicyclopentadiene (1.5 g.) dissolved in 30 cc. of acetone was treated while stirring with 8 g. of powdered potassium permanganate in small portions. The reaction was instantaneous. After two hours, 10 cc. of water was added and this caused further warming. The mixture was filtered, the acetone boiled off and the remaining aqueous solution acidified and extracted twice with ether. On evaporation of the ether a solid remained which was decolorized with charcoal and recrystallized twice. The yield was 0.68 g., m. p. 151–152° (dec.) (cor.).

Anhydride of *cis-exo*-Endomethylene Hexahydrophthalic Acid.—A solution of *cis-exo*-endomethylene hexahydrophthalic acid (0.2 g.) in 2 cc. of acetic anhydride was heated under reflux for one hour. The excess acetic anhydride was removed *in vacuo* leaving an oil which soon crystallized and on recrystallization from ligroin melted without decomposition at 77.5–78.5° (cor.). There was no change in melting point after resolidification.

Synthesis of *cis-exo*-3,6-Endomethylene Hexahydrophthalic Acid:[9] 4,5-Dibromo-*endo-cis*-3,6-endomethylene Hexahydrophthalic Anhydride.—*Endo-cis*-3,6-endomethylene-Δ⁴-tetrahydrophthalic anhydride (25 g.) dissolved in 100 cc. of c. p. chloroform was treated with 8.5 cc. of bromine dissolved in 100 cc. of chloroform. Illumination initiated vigorous reaction and a solid separated. This was recrystallized from ethyl acetate. The yield was 36.7 g.; m. p. 210–211° (cor.) (reported by Alder and Stein, 206°).

4,5-Dibromo-*endo-cis*-3,6-endomethylene Hexahydrophthalic Acid.—The anhydride (39.4 g.) was dissolved in 350 cc. of acetone and 80 cc. of water. After fourteen hours at 25° the solution was warmed to 50° for two hours. The acetone was removed on the steam-bath and the free acid crystallized on cooling, m. p. 184° (cor.) (dec.); yield 35 g.

4,5-Dibromo-*exo-cis*-3,6-endomethylene Hexahydrophthalic Anhydride.—The *endo*-dibromo acid (12 g.) was added in small portions to a flask immersed in a metal bath at 215°. Steam was evolved and then hydrogen bromide. After fourteen minutes the reaction ceased and, on cooling, the material was dissolved in ethyl acetate. The ethyl acetate solution was washed with dilute sodium carbonate to remove the bromo-*trans*-lactonic acid (5.4 g., m. p. 182–185°, from petroleum ether and ethyl acetate). After neutralizing and drying over sodium sulfate, the ethyl acetate solvent was removed leaving a crystalline solid which was recrystallized from acetonitrile. The yield was 3.1 g.; m. p. 244–245° (uncor.) (reported by Alder and Stein, 248–249°).

exo-cis-3,6-Endomethylene-Δ⁴-tetrahydrophthalic Acid. —The dibromo-*exo*-anhydride dissolved in 25 cc. of glacial acetic acid was warmed for two hours with 2 g. of zinc dust. The solution was decanted from the metal and evaporated *in vacuo*. On addition of water a precipitate formed which dissolved in boiling water. Acidification and extraction into ether gave the bromine-free acid which, on recrystallization from water, melted at 148–149° (dec.). The reported melting point is 148°.

exo-cis-3,6-Endomethylene Hexahydrophthalic Acid.— The unsaturated acid (0.75 g.) dissolved in 25 cc. of ether was hydrogenated at room temperature using 0.08 g. of platinum oxide catalyst. A solid remained after the ether

(10) Alder and Stein, *Ann.*, 504, 212 (1933).

was removed which on recrystallization from water melted with decomposition at 152–153°. This acid was converted into its anhydride in the same way as the acid obtained from Bruson's hydrochloride. The specimens of this anhydride from both sources melted without decomposition at 77.5–78.5°, alone and when mixed.

Preparation of the Acid Anilide and Phenylimide of the Synthetic β-Anhydride.—On addition of 0.1 g. of the anhydride dissolved in 1 cc. of benzene to 0.4 cc. of aniline a precipitate formed rapidly. This was filtered, washed with benzene and recrystallized twice from acetonitrile. It melted at 157.5–158°.

Anal. Calcd. for $C_{18}H_{17}O_3N$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.86; H, 6.58; N, 4.98.

The acid anilide was heated in a metal bath at 170° for five minutes. Steam was evolved and, on cooling, the sample solidified. It was crystallized three times from water–ethanol and melted at 169–170°. On resolidification, there was no change in melting point.

Anal. Calcd. for $C_{18}H_{15}O_2N$: C, 74.66; H, 6.26; N, 5.81. Found: C, 74.28; H, 6.02; N, 5.37.

Mixed Melting Points.—The phenylimide of the anhydride from Bruson's compound, made in the same way, melted at 169–170°. There was no depression in a mixed melting point with the synthetic phenylimide.

Summary

The addition of strong acids, or the acid-catalyzed hydration, of dicyclopentadiene involves a normal Wagner–Meerwein rearrangement to yield derivatives of the *exo*-isomer of dihydrodicyclopentadiene and requires no modification of the current ionic interpretation of that rearrangement. This conclusion has been established by the oxidation of the "dihydro-*nor*-dicyclopentadiene" of Bruson and Riener[1] to the *exo-cis*-3,6-endomethylenehexahydrophthalic acid of Alder and Stein.

The Chemistry of Dicyclopentadiene. III. Addition of Alcohols and Phenols

BY HERMAN ALEXANDER BRUSON AND THOMAS W. RIENER

When methanol reacts with dicyclopentadiene in the presence of an acidic catalyst such as sulfuric acid or boron trifluoride, an unsaturated methyl ether, CH_3—O—$C_{10}H_{13}$, is obtained which possesses an intense fragrant odor. The same ether is formed by warming methyl iodide with the sodium alcoholate of the acid catalyzed hydration product of dicyclopentadiene, previously referred to as hydroxy-dihydro-*nor*-dicyclopentadiene.[1] The latter has recently been shown by Bartlett and Schneider,[2] to be the *exo*-isomer of hydroxy-dihydro-dicyclopentadiene. Thus the same type of *endo–exo* addition–rearrangement involved in the acid-catalyzed reaction of dicyclopentadiene with water and with organic acids, occurs also with alcohols.

In accordance with Bartlett and Schneider's formulation for the rearrangement, the addition of methanol to dicyclopentadiene may be written as follows (assuming that the remaining double bond in the cyclopentene ring does not wander).
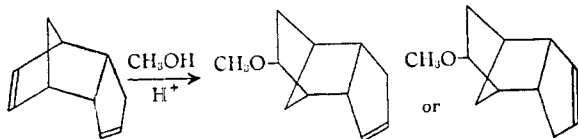
The residual double bond in the methoxy-dihydro-*exo*-dicyclopentadiene although quite inert toward the addition of a second molecule of methanol does, however, add halogen. Chlorine, for example, readily combines with methoxydihydro-*exo*-dicyclopentadiene to give the corresponding dichloro derivative.

In the same manner, it is possible to add a variety of other alcohols or hydroxy compounds to dicyclopentadiene to form the corresponding ethers of hydroxy-dihydro-*exo*-dicyclopentadiene. The ethers derived in this way from the lower aliphatic alcohols (ethyl, isopropyl, allyl, butyl) also possess strong floral odors. Other alcohols which add to dicyclopentadiene with *endo–exo* rearrangement of the ring system include the halogenated alcohols, nitro-alcohols, cyano-alcohols, hydroxycarboxylic acid esters and polyhydric alcohols, as shown in Table I. In the latter case mono- or poly-ethers are obtained depending upon the conditions.

Those ethers of hydroxy-dihydro-*exo*-dicyclopentadiene which possess at least two double bonds in the molecule as for example the allyl ether C_3H_5—O—$C_{10}H_{13}$, the ethylene glycol di-ether $C_{10}H_{13}$—O—CH_2CH_2—O—$C_{10}H_{13}$, the diethylene glycol di-ether $C_{10}H_{13}$—O—C_2H_4—O—C_2H_4—O—$C_{10}H_{13}$, and the ether ester of lactic acid CH_3—CH(O—$C_{10}H_{13}$)COO—$C_{10}H_{13}$ or of glycolic acid $C_{10}H_{13}$—O—CH_2COO—$C_{10}H_{13}$, rapidly absorb oxygen from the air particularly in the presence of siccatives such as manganese or cobalt naphthenate to give hard, insoluble, varnish-like films, behaving in this respect like drying oils. They can also be polymerized by heating with peroxides to viscous autoxidizable oils.

Similar drying properties were shown by di-(dihydro-*exo*-dicyclopentadienyl) ether[3] $C_{10}H_{13}$—O—$C_{10}H_{13}$ obtained by adding hydroxy-dihydro-*exo*-dicyclopentadiene in the presence of sulfuric acid,[1] to dicyclopentadiene.

(1) Bruson and Riener, THIS JOURNAL, 67, 723, 1178 (1945).

(2) Bartlett and Schneider, *ibid*, 68, 6 (1946).

(3) Previously referred to as "di-(dihydro-*nor*-dicyclopentadienyl) ether" in reference 1.