222 g. of bromine was added at −10° to a well-stirred mixture of 200 g. of the sodium enolate of ethyl formylacetate in 1500 cc. of absolute ethanol. Anhydrous hydrogen chloride was then passed into the mixture at −10° until 170 g. was absorbed. Stirring was continued for three hours at −10° and for twenty-four hours at room temperature. The mixture was then worked up as described under ethyl α-chloro-β,β-diethoxypropionate, method "a"; yield, 76 g. of product boiling at 112–116° (9 mm.), n^{20}D 1.4412.

On boiling with zinc dust in benzene, the compound readily yielded ethyl β-ethoxyacrylate.

Attempted Reformatsky Reaction between Ethyl α-Bromo-β,β-diethoxypropionate and Aldehydes and Ketones.—A few cc. of a mixture of 0.34 mole each of the bromoacetal and aldehyde or ketone (acetone, acetophenone, β-ionone, butyraldehyde, and benzaldehyde were tried) were added to 100 cc. of dry benzene containing some dissolved iodine and 26.4 g. of dry purified zinc dust. The mixture was partially immersed in an oil-bath at 70°, and stirred. Reaction soon commenced and the addition of reactants was then continued at a rate sufficient to maintain refluxing with the oil-bath at 70°. Refluxing was continued for three hours after complete addition of the reactants. The mixture was worked up in the usual manner and 39 g. of product boiling at 90–96° (16 mm.) was obtained.

The product was unsaturated as shown by a bromine test and, on hydrolysis with 10% caustic, it yielded an unsaturated acid melting at 109–110°. A mixed melting point with β-ethoxyacrylic acid prepared according to Tschitschibabin[3] showed no depression.

Attempted Darzens Reaction with Ethyl α-Chloro-β,β-diethoxypropionate and Acetophenone.—A suspension of dry sodium ethylate prepared from 5.7 g. of sodium wire in 250 cc. of anhydrous ether was added gradually at −10° to a mixture of 56 g. of chloroester and 29.7 g. of acetophenone. After stirring at 0° for eight hours, the dark brown solution was poured into ice-water, the ether layer separated, washed, and dried over anhydrous magnesium sulfate. It yielded a few grams of unreacted chloroacetal and acetophenone. The opaque aqueous layer, after clarification with Norite, gave a blue-red color with ferric chloride solution and deposited a heavy oil on acidification. The precipitated oil was soluble in alkali but insoluble in bicarbonate solution. On attempted distillation at 1 mm., it decomposed and resinified. A sodium fusion test indicated considerable chlorine.

Summary

1. New methods for the synthesis of ethyl α-chloro- and α-bromo-β,β-diethoxypropionates have been developed.

2. These compounds behave like α-haloacetals rather than α-haloesters in respect to their halogen activities.

3. Knoevenagel condensations could not be effected between formylacetic ester or its diethylacetal and aldehydes and ketones.

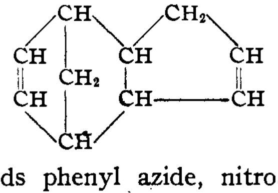
BROOKLYN, N. Y. RECEIVED SEPTEMBER 8, 1944

[CONTRIBUTION FROM RESINOUS PRODUCTS AND CHEMICAL COMPANY AND ROHM AND HAAS COMPANY]

The Chemistry of Dicyclopentadiene. I. Hydration and Rearrangement

BY HERMAN ALEXANDER BRÚSON AND THOMAS W. RIENER

It has been shown by Alder and Stein[1] that dicyclopentadiene possesses an unsymmetrical structure (A)



(A)

which adds phenyl azide, nitrosyl chloride, or hydrogen to the double bond of the bridged cyclohexene ring. In each case the compounds obtained are normal addition products in which no rearrangement of the original ring system has occurred.[2]

We have found that various hydrogen donors notably water, HCl, HBr, HI, alcohols, phenols and carboxylic acids readily add to only one double bond of dicyclopentadiene. During these additions, which require the presence of hydrogen ions or acidic catalysts, for example H_2SO_4 or BF_3, a molecular rearrangement occurs to form an entirely different ring system.

When dicyclopentadiene is stirred rapidly with hot dilute sulfuric acid (20–40% H_2SO_4) it forms an unsaturated, secondary monohydric alcohol $C_{10}H_{13}OH$ in 80–84% yield. We have termed this alcohol hydroxy-dihydro-*nor*-dicyclopentadiene. It is a colorless liquid possessing a musty, somewhat camphoraceous odor, and does not solidify at 0°. With phenyl isocyanate it yields a crystalline phenylurethan melting at 164–165°.

The rest of the hydration product, in addition to resinous material, is the ether of hydroxy-dihydro-*nor*-dicyclopentadiene (II) having the formula $C_{10}H_{13}$—O—$C_{10}H_{13}$. This ether is a colorless liquid which is extremely autoxidizable. Thin films of it upon exposure to the air rapidly absorb oxygen to form a hard, brittle varnish. The pure di-(dihydro-*nor*-dicyclopentadienyl) ether can be obtained in quantity by treating hydroxy-dihydro-*nor*-dicyclopentadiene with one mole of dicyclopentadiene in the presence of sulfuric acid or boron trifluoride as a catalyst.[3] Upon catalytic hydrogenation this ether takes up four atoms of hydrogen to yield the saturated di-(tetrahydro-*nor*-dicyclopentadienyl) ether, a crystalline solid melting at 59–60°.

That the hydration of dicyclopentadiene by dilute sulfuric acid yields a rearranged alcohol instead of a normal hydration product such as (B) or (C) is borne out by the following discussion.

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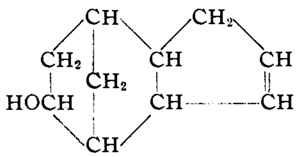
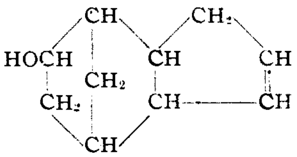
(1) Alder and Stein, *Ann.*, **485**, 223 (1931).

(2) For a comprehensive survey of the present status of dicyclopentadiene chemistry see the review by P. J. Wilson and J. H. Wells, *Chem. Reviews*, **34**, 1–106 (1944).

(3) Bruson, U. S. Patent 2,358,314 (1944).

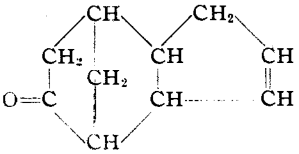


(B)

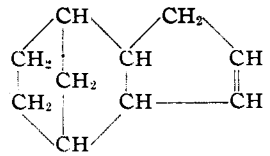


(C)

Upon mild oxidation with chromic anhydride in acetic acid, hydroxydihydro-*nor*-dicyclopentadiene yields the corresponding dihydro-*nor*-dicyclopentadienenone (III). This unsaturated ketone is a colorless liquid, giving a semicarbazone m. p. 200°, an oxime m. p. 105–106°, and a crystalline dibromide m. p. 163–164°. It is entirely different from the known ketone (D) melting at 83–84° (semicarbazone m. p. 216°, oxime m. p. 92°; dibromide m. p. 142°) previously described by Alder and Stein[1] and also by Wieland and Bergel.[4] Furthermore, upon Clemmensen reduction, ketone (III) yields a liquid unsaturated hydrocarbon $C_{10}H_{14}$, namely, dihydro-*nor*-dicyclopentadiene (IV or IV-A) which does not solidify at −80°, and which is not identical with the previously known crystalline dihydro-dicyclopentadiene (E) that is isomeric with it.[1,5]

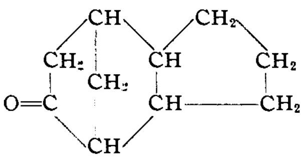


(D)

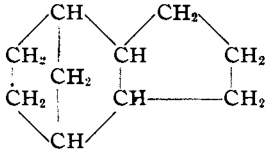


(E)

Catalytic hydrogenation of hydroxy-dihydro-*nor*-dicyclopentadiene yields hydroxy-tetrahydro-*nor*-dicyclopentadiene (V). This saturated alcohol is a crystalline solid, m. p. 53–54°, having a menthol-like odor. It yields a phenylurethan m. p. 107–108°; a *p*-nitrobenzoate m. p. 93–94° and upon mild oxidation gives the corresponding saturated ketone, namely, tetrahydro-*nor*-dicyclopentadienone (VI). This ketone is a colorless liquid giving a semicarbazone m. p. 210°, an oxime m. p. 87–88°, and a mono-benzylidene derivative melting at 88°. It is different from the known isomeric ketone (F) melting at 109–110° (semicarbazone m. p. 229°) described by Alder and Stein.[1] Furthermore upon Clemmensen reduction ketone (VI) yields a liquid hydrocarbon $C_{10}H_{16}$, namely, tetrahydro-*nor*-dicyclopentadiene (VII), solidifying below −80°, which is not identical with the already known crystalline tetrahydro-dicyclopentadiene[5] having formula (G) that is isomeric with it.

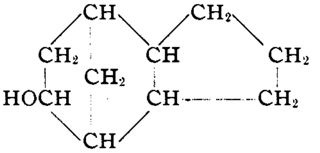


(F)



(G)

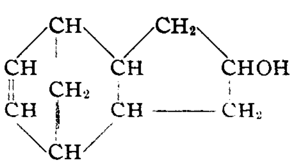
Since an alcohol having formula (VIII) has apparently never been prepared, it was considered expedient to obtain it by reduction of the Wieland and Bergel[4] ketone (D) for purposes of comparison with our hydroxy-tetrahydro-*nor*-dicyclopentadiene (V). Alcohol (VIII) was found to be a crystalline solid m. p. 120–121° entirely different from (V).



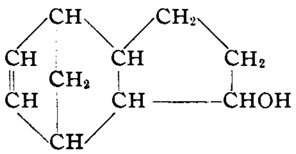
(VIII)

It is thus obvious that hydroxy-dihydro-*nor*-dicyclopentadiene cannot have the formula (B) or (C) since either of these structures upon hydrogenation followed by ketonization would yield the already known ketone (F).

Proof that the hydration of dicyclopentadiene does not occur in the unbridged cyclopentene ring to yield an alcohol having the possible formula (H) or (J) and that the rearrangement does occur in the bridged cyclohexene ring, is afforded by the fact that the Diels–Alder adduct of cyclopentadiene and cyclopentene, namely (IX), upon hydration with dilute sulfuric acid yields a solid alcohol



(H)



(J)

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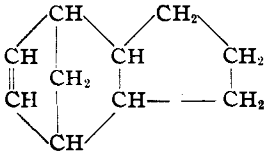
[4] Wieland and Bergel, *Ann.*, **446**, 21 (1926).

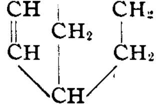
[5] Staudinger and Rheiner, *Helv. chim. acta*, **7**, 28 (1924).



(IX)

m. p. 53–54°, identical with hydroxy-tetrahydro-*nor*-dicyclopentadiene (V) obtained by hydrogenating the hydration product of dicyclopentadiene. Furthermore no trace of an alcohol is obtained by treating dihydro-dicyclopentadiene (E) with dilute sulfuric acid under the same conditions; the hydrocarbon being recovered unchanged.

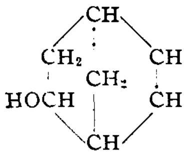
In order to gain an insight into the exact nature of the rearrangement involved, the hydration of bicyclo-(2,2,1)-2-heptene[6] (X) known as "nor-



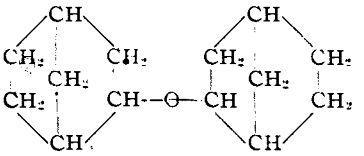
(X)

bornylene" was studied, since it serves as a model for the bridged cycle of the dicyclopentadiene molecule.

Upon treatment of (X) with hot dilute sulfuric acid under the same conditions as employed for the hydration of dicyclopentadiene, two crystalline products,[7] namely, β-norborneol (XI) and dinorbornyl ether (XII) were obtained.



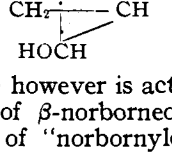
(XI)



(XII)

No trace of the stereoisomeric α-norborneol was found. β-Norborneol has already been described and its structure established by Komppa and Beckmann,[8] who obtained it from β-norbornylamine by diazotization and hydrolysis.

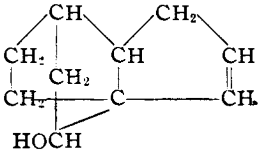
At first glance it thus seems as if "norbornylene" does not rearrange upon hydration, since the elements of water appear to have added directly to the double bond to give β-norborneol. However, a closer inspection demonstrates that if the hydration involves a rearrangement mechanism as above, the hydration product should possess configuration (K).



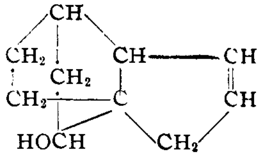
(K)

Formula (K) however is actually identical with formula (XI) of β-norborneol. In other words the hydration of "norbornylene" can involve a rearrangement induced by hydrogen ions, without producing a structurally different alcohol than that obtained without benefit of the rearrangement. This is possible only in the case of "norbornylene" because of its symmetry and the equivalency of its ring methylene groups not only with each other but also with the bridge endomethylene group.

The application of this reasoning by analogy to the hydration of the bridged cyclohexene ring of dicyclopentadiene leads to the conclusion that the logical structure for hydroxy-dihydro-*nor*-dicyclopentadiene is that represented by formula (I) or (I-A)



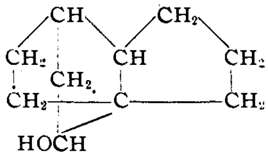
(I)



(I-A)

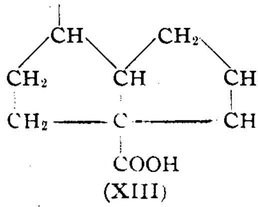
It has, however, not as yet been possible to decide which one of these structures definitely represents the compound, since attempts to obtain breakdown products by oxidation with permanganate or with nitric acid have yielded uncrystallizable sirups from which no pure product could be isolated.

However the hydrogenation product of (I) or (I-A), namely, hydroxytetrahydro-*nor*-dicyclopentadiene (V)



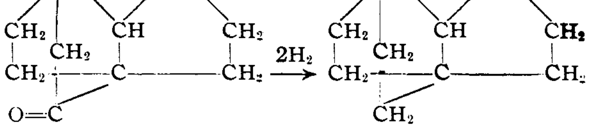
(V)

yields, upon oxidation with nitric acid, a crystalline dicarboxylic acid $C_{10}H_{14}O_4$ melting at 182–184°, presumably (XIII)



(XIII)

In view of the foregoing discussion, the liquid hydrocarbon $C_{10}H_{16}$ obtained from ketone (VI) by Clemmensen reduction and which is designated tetrahydro-*nor*-dicyclopentadiene possesses formula (VII)



(VI) (VII)

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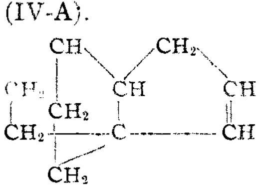
[6] Joshel and Butz, THIS JOURNAL, 63, 3351 (1941).

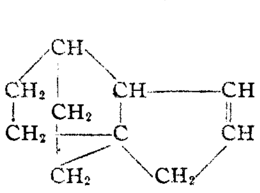
[7] Bruson, U. S. Patent 2,345,573 (1944).

[8] Komppa and Beckmann, *Ann.*, 512, 172 (1934).

In the same way the liquid hydrocarbon $C_{10}H_{14}$ obtained from ketone (III) by Clemmensen reduction and which is designated dihydro-*nor*-dicyclopentadiene possesses formula (IV) or (IV-A).



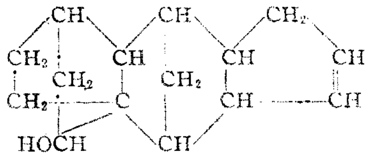
(IV)



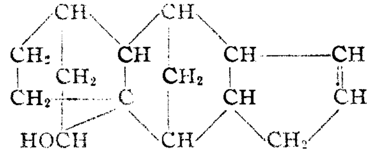
(IV-A)

Upon treating hydroxy-dihydro-*nor*-dicyclopentadiene with phosphorus trichloride, the corresponding chloro-dihydro-*nor*-dicyclopentadiene (XIV) is obtained. It is extremely resistant to hydrolysis and replacement reactions. For example, it withstands boiling for twenty hours with 10% alcoholic potassium hydroxide solution, and remains unaffected upon boiling with zinc in glacial acetic acid. This behavior is characteristic of the neopentyl chloride system[9] and lends additional support to the formulation of hydroxy-dihydro-*nor*-dicyclopentadiene as a substituted neopentyl alcohol as in (I) or (I-A).

The hydration of tricyclopentadiene[10] proceeds in a manner similar to that of dicyclopentadiene to yield an unsaturated, secondary monohydric alcohol $C_{15}H_{19}OH$ (XV or XV-A), namely, hydroxy-dihydro-*nor*-tricyclopentadiene.

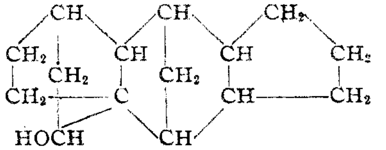


(XV)



(XV-A)

Upon catalytic hydrogenation it yielded hydroxy-tetrahydro-*nor*-tricyclopentadiene (XVI).



(XVI)

Experimental

Hydroxy-dihydro-*nor*-dicyclopentadiene (I or I-A).—A rapidly stirred mixture of 264 g. of dicyclopentadiene (purified by redistillation *in vacuo*) and 800 g. of aqueous 25% sulfuric acid was boiled under reflux for five hours at 104–107°. The oil layer was separated, washed with hot water, then with dilute sodium hydroxide solution and again with hot water. The oil was then distilled *in vacuo*. The fraction boiling at 105–115° (6–7 mm.) was a faintly yellow liquid; yield 250 g. or 83.4%. The analytical sample obtained by redistillation *in vacuo* (nitrogen through capillary) was a colorless oil boiling at 102–104° (7 mm.) or 239–240° (770 mm.) having $n^{25}\text{D}$ 1.5246; d^{25}_4 1.0773.[11] It does not solidify at 0°.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.39; iodine no., 169. Found: C, 79.80; H, 9.53; iodine no., 164 (Wijs).

The compound is miscible with methanol, acetone, dioxane, benzene and petroleum ether.

Its phenylurethan was prepared by heating 5 g. each of the alcohol and phenyl isocyanate on a steam-bath for fifteen minutes, triturating the cooled viscous product with petroleum ether, and recrystallizing the solid material from ethanol: m. p. 164–165°. *Anal.* Calcd. for $C_{17}H_{19}NO_2$: C, 75.79; H, 7.12; N, 5.20. Found: C, 75.90; H, 6.86; N, 5.15.

The *p*-nitrobenzoate of hydroxy-dihydro-*nor*-dicyclopentadiene melted at 130–131° (recryst. from ethanol). *Anal.* Calcd. for $C_{17}H_{17}NO_4$: C, 68.19; H, 5.72; N, 4.68. Found: C, 67.80; H, 6.03; N, 4.73.

Di-(dihydro-*nor*-dicyclopentadienyl) Ether (II).—The crude still residues from several preparations of hydroxy-dihydro-*nor*-dicyclopentadiene were combined and distilled in high vacuum. The crude ether $C_{10}H_{13}—O—C_{10}H_{13}$ distilled over at 180–190° (2 mm.) as a faintly yellow oil. The analytical sample (distilled in an atmosphere of nitrogen) was a colorless oil boiling at 185–188° (3 mm.). $n^{25}\text{D}$ 1.5372; d^{25}_4 1.077. *Anal.* Calcd. for $C_{20}H_{26}O$: C, 85.04; H, 9.29; iodine no., 180. Found: C, 84.80; H, 9.14; iodine no., 179 (Wijs).

A better method for preparing the above ether in quantity is the following:

A mixture of 132 g. of dicyclopentadiene and 150 g. of hydroxy-dihydro-*nor*-dicyclopentadiene was heated to 70° and stirred while 15 g. of boron fluoride-diethyl ether $BF_3 \cdot O(C_2H_5)_2$ was added dropwise. The mixture was stirred for six hours at 70°, then washed with hot water and soda solution, dried, and distilled *in vacuo*, using nitrogen through the capillary. The yield of di-(dihydro-*nor*-dicyclopentadienyl) ether boiling at 180–185° (2 mm.) was 108 g.

Di-(tetrahydro-*nor*-dicyclopentadienyl) Ether.—A mixture of 200 g. of di-(dihydro-*nor*-dicyclopentadienyl) ether and 10 g. of Raney nickel catalyst was heated in a shaking autoclave at 120–125° for six hours with hydrogen at a pressure of 1,400 lb. per sq. in. The filtered product upon distillation *in vacuo* yielded 169 g. of colorless oil boiling at 182–185° (2 mm.). The analytical sample boiled at 222–223° (13 mm.) and solidified to a crystalline mass, which after recrystallization from 1-nitropropane melted at 59–60°. *Anal.* Calcd. for $C_{20}H_{30}O$: C, 83.84; H, 10.56. Found: C, 83.60; H, 10.77.

Oxidation of Hydroxy-dihydro-*nor*-dicyclopentadiene to Ketone (III).—To a stirred solution of 500 cc. glacial acetic acid and 300 g. of hydroxy-dihydro-*nor*-dicyclopentadiene maintained at 40°, there was added dropwise a solution of 160 g. chromic anhydride, 500 cc. of glacial acetic acid and 100 g. of water during the course of two hours. The mixture was then heated at 90–95° for two and one-half hours. The product was diluted with much water, the oil was taken up in toluene, washed well with water and dilute sodium carbonate solution, and the toluene was then removed under reduced pressure. The residual oil (250 g.) upon distillation *in vacuo* yielded 193 g. of crude ketone boiling at 126–133° (29 mm.). Upon redistillation a heart cut (100 g.) boiling at 130–132° (29 mm.) was collected as the ketone. It was a colorless oil having a pleasant odor; $n^{25}\text{D}$ 1.5140; d^{25}_4 1.0749.

For conversion to its semicarbazone, 33.3 g. of the above ketone in 330 cc. of ethanol, was mixed with a solution of 50 g. semicarbazide hydrochloride, 58 g. of sodium acetate and 165 cc. of water, and heated on a steam-bath under

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(9) Whitmore and Fleming, THIS JOURNAL, **55**, 4162 (1933).

(10) Staudinger and Bruson, *Ann.*, **447**, 109 (1926).

(11) We have observed slight deviations in refractive index in various close cuts of a 400-pound batch of this alcohol indicating the possible presence of a stereoisomer therein.

reflux for one hour. The product was allowed to crystallize overnight in the ice box at 5°, and the crystalline semicarbazone was filtered off, washed with water, and recrystallized from 50% ethanol; m. p. 199–200°. *Anal.* Calcd. for $C_{11}H_{15}N_3O$: C, 64.35; H, 7.32; N, 20.48. Found: C, 64.28; H, 7.65; N, 20.56.

A sample of this semicarbazone was reconverted to the ketone by boiling with excess of a 10% aqueous oxalic acid solution. The purified ketone thus obtained boiled at 109° (13 mm.) and possessed the following constants: $n^{25}D$ 1.5146; d^{25}_4 1.0759. *Anal.* Calcd. for $C_{10}H_{12}O$: C, 81.03; H, 8.16. Found: C, 80.80; H, 8.29.

The oxime was prepared by heating at 95° for one hour, 193 g. of the ketone with a solution prepared from 180 g. of hydroxylamine sulfate, 180 cc. of water and 440 g. of 20% sodium hydroxide solution. The crude oxime separated as an oil. It was distilled *in vacuo* to yield 110 g. of oxime boiling at 136–139° (4–5 mm.), as a very viscous, colorless oil which gradually crystallized. After recrystallization from petroleum ether it formed colorless crystals, m. p. 105–106°. *Anal.* Calcd. for $C_{10}H_{13}NO$: N, 8.58. Found: N, 8.47.

The dibromide of the ketone was prepared by adding a solution of 27 g. bromine in 25 cc. of ethylene dichloride to a solution of 25 g. of the ketone in 25 cc. of ethylene dichloride at 0°. The ethylene dichloride was then distilled off *in vacuo* and the residual viscous oil was crystallized from ethanol. The product formed long colorless needles, m. p. 163–164°. *Anal.* Calcd. for $C_{10}H_{12}OBr$: C, 38.97; H, 3.91; Br, 51.90. Found: C, 39.10; H, 4.07; Br, 51.50.

Dihydro-*nor*-dicyclopentadiene (IV or IV-A).—A mixture of 200 g. of mossy zinc, 300 cc. of water, 20 g. of mercuric chloride and 10 g. of concentrated hydrochloric acid was shaken for five minutes and the amalgamated zinc separated from the supernatant liquid. To the zinc thus prepared, there was added 100 cc. of glacial acetic acid, 300 cc. of concentrated hydrochloric acid, 150 cc. of toluene and 100 g. of ketone (III). The mixture was stirred and boiled under reflux for nine hours during which time two 100-cc. portions of concentrated hydrochloric acid were added at the end of the sixth and eighth hours of boiling. The product was cooled and diluted with water, the toluene layer was separated and the remainder was extracted with toluene. The combined toluene extracts were washed with water, sodium carbonate solution and again with water. After removal of the toluene *in vacuo,* 95 g. of oil was obtained. This after several distillations *in vacuo*, yielded 20 g. of the pure hydrocarbon boiling at 79–80° (27 mm.). It is a colorless thin liquid having $n^{25}D$ 1.4986; d^{25}_4 0.9610. It does not solidify at −80°. *Anal.* Calcd. for $C_{10}H_{14}$: C, 89.48; H, 10.52; iodine no., 189.5. Found: C, 89.60; H, 10.51; iodine no., 191 (Wijs).

Hydroxy-tetrahydro-*nor*-dicyclopentadiene (V).—A mixture of 214 g. of hydroxy-dihydro-*nor*-dicyclopentadiene and 10 g. of Raney nickel catalyst was heated in a shaking autoclave at 120–125° for seven hours with hydrogen at a pressure of 1500 lb. per sq. in. The product was taken up in benzene, filtered, and distilled *in vacuo* to yield 187 g. of a viscous colorless oil b. p. 120–123° (13 mm.) which crystallized on standing in the ice box. After recrystallization from nitromethane it melted at 53–54°. *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.88; H, 10.60. Found: C, 78.90; H, 10.58.

Its *p*-nitrobenzoate after recrystallization from ethanol melted at 93–94°. *Anal.* Calcd. for $C_{17}H_{19}NO_4$: C, 67.74; H, 6.36; N, 4.65. Found: C, 67.40; H, 6.48; N, 4.54.

Its phenylurethan was prepared by warming 5 g. each of the alcohol and phenyl isocyanate for ten minutes on a steam-bath, triturating the viscous product with petroleum ether and crystallizing the solid material from ethanol; m. p. 107–108°.

Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.23; H, 7.80; N, 5.16. Found: C, 75.40; H, 7.58; N, 5.12.

Oxidation of (V) to Saturated Ketone (VI).—To a stirred solution of 250 cc. of glacial acetic acid and 152 g. of hydroxy-tetrahydro-*nor*-dicyclopentadiene (V) maintained at 45° there was added dropwise a solution of 80 g. of chromic anhydride, 250 cc. of glacial acetic acid and 50 cc. of water during the course of one hour. The mixture was then heated at 95° for five hours, cooled and poured into one liter of water. The oil layer was separated and combined with a toluene extract of the aqueous layer. The product was washed with water and soda solution, and distilled *in vacuo.* The saturated ketone (VI) distilled at 129–132° (29 mm.) as a colorless liquid; $n^{25}D$ 1.4995; d^{25}_4 1.0446; yield 105 g.

The semicarbazone of this ketone melted at 210° (from ethanol). *Anal.* Calcd. for $C_{11}H_{17}N_3O$: C, 63.72; H, 8.27; N, 20.27. Found: C, 63.90; H, 8.12; N, 20.22.

The oxime of ketone (VI) distilled at 130–135° (4 mm.) as a colorless oil which gradually crystallized on standing in petroleum ether. The analytical sample melted at 87–88° after recrystallization from petroleum ether. *Anal.* Calcd. for $C_{10}H_{15}NO$: C, 72.67; H, 9.16; N, 8.48. Found: C, 72.80; H, 8.88; N, 8.52.

The benzylidene derivative was prepared by adding a mixture of 32.3 g. of ketone (VI) and 22.8 g. of benzaldehyde to a cooled, stirred mixture of 50 g. of ethanol, 98 g. of water and 11 g. of sodium hydroxide at 15°, and stirring for twenty-four hours. The oil was then separated, washed with water and distilled *in vacuo* to yield 13 g. of the monobenzylidene derivative boiling at 180–220° (6 mm.), which crystallized on standing. After recrystallization from petroleum ether, the analytical sample melted at 88°. *Anal.* Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.48. Found: C, 85.70; H, 7.72.

The pure ketone (VI) regenerated from 28 g. of its semicarbazone by steam distillation from a solution of 27 g. of oxalic acid and 300 cc. of water was a colorless liquid boiling at 132° (30 mm.) and having the following constants: $n^{25}D$ 1.4993; d^{25}_4 1.0443. *Anal.* Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.40. Found: C, 79.80; H, 9.21.

Tetrahydro-*nor*-dicyclopentadiene (VII).—A mixture of 200 cc. of glacial acetic acid, 100 cc. of toluene, 300 cc. of concentrated hydrochloric acid, 100 g. of ketone (VI) and 200 g. of amalgamated mossy zinc was stirred and boiled under reflux for twelve hours during which time additional hydrochloric acid was added after three hours (100 cc.), seven hours (50 cc.) and eight hours (100 cc.). The toluene layer was separated and combined with a toluene extract of the aqueous layer. The combined toluene layer and extract was washed with water, soda, and again with water. The toluene was stripped off under reduced pressure (100 mm.) on a steam-bath. The residual oil (71 g.) was distilled *in vacuo* and the cut boiling at 75–90° (28 mm.) was redistilled *in vacuo* over sodium. The purified product (30 g.) boiled at 83.5–84.5° (28 mm.). It was a colorless, thin liquid with a root-like odor having the constants: $n^{25}D$ 1.4868; d^{25}_4 0.9314. It did not solidify at −80°.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.15; H, 11.85. Found: C, 88.30; H, 12.00.

Hydroxy-tetrahydro-dicyclopentadiene (VIII).—A mixture of 5 g. of Raney nickel, 50 cc. of ethanol and 10 g. of ketone (D) prepared from dicyclopentadiene nitrosochloride[1] was shaken at 125–150° with hydrogen under a pressure of 1500 lb. per sq. in. for six hours. The filtered product upon distillation *in vacuo* came over at 110–120° (3 mm.) and solidified in the receiver; yield 8.5 g. The product after several recrystallizations from nitromethane melted at 120–121°. It possessed a camphor-like odor entirely different from the menthol-like odor of (V). *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.88; H, 10.60. Found: C, 78.80; H, 10.33.

Its *p*-nitrobenzoate melted at 98–99°. *Anal.* Calcd. for $C_{17}H_{19}NO_4$: C, 67.74; H, 6.36; N, 4.65. Found: C, 67.70; H, 6.51; N, 4.69.

A mixed m. p. with the *p*-nitrobenzoate of (V) gave a 20–30° depression.

Adduct of Cyclopentadiene and Cyclopentene (IX).—A mixture of 66 g. of cyclopentadiene and 81 g. of cyclopentene was heated in a sealed bomb for five hours at 200°. The partially solid product containing polymers of cyclopentadiene, was fractionally distilled *in vacuo* to yield 30 g. of crude (IX) as a colorless liquid boiling at 92–94° (40 mm.). It was purified by a slow atmospheric distillation through a Podbielniak column in order to depolymerize any dicyclopentadiene present. The product was redistilled once more. It boiled at 173–175° (764 mm.) without decomposition. Its odor resembles that of dicyclopentadiene: $n^{25}D$ 1.5001; d^{25}_4 0.9581. *Anal.* Calcd. for $C_{10}H_{14}$: C. 89.48; H. 10.52. Found: C, 90.01; H, 10.23.

Hydration of (IX).—A mixture of 30 g. of (IX) and 88 g. of aqueous 25% sulfuric acid was rapidly stirred and boiled under reflux for three hours at 102–105°. The oil was separated, washed with water, soda solution and finally again with water, then distilled *in vacuo*. The fraction boiling at 110–113° (7 mm.) weighed 15 g. and solidified to a crystalline mass. After two recrystallizations from nitroethane it melted at 51°. One more crystallization from nitromethane yielded the purified product in the form of colorless needles m. p. 53°. A mixed melting point with compound (V) gave no depression. *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.88; H, 10.60. Found: C, 79.00; H, 10.63.

Hydration of "Norbornylene."—Cyclopentadiene and ethylene were heated together in a sealed bomb as described by Joshel and Butz[6] to yield the "norbornylene" used. A more convenient method is to heat dicyclopentadiene with ethylene[12] at 200° in a high pressure autoclave.

A mixture of 35 g. of "norbornylene" and 148 g. of aqueous 25% sulfuric acid was rapidly stirred and boiled under reflux for four and one-half hours. The oil layer was separated, the aqueous layer was extracted with ether and the combined ether extract and the oil was washed with water and soda solution and distilled at atmospheric pressure. Two main cuts were obtained, namely, (a) 10 g. boiling at 184–194° and (b) 10 g. boiling at 240–270° both of which solidified. Fraction (a) was crude β-norborneol (XI). After recrystallization from nitromethane it formed colorless crystals, m. p. 126°. Its phenylurethan melted at 147° as described by Komppa and Beckmann.[8] Fraction (b) upon recrystallization from nitromethane formed colorless needles m. p. 67–68° corresponding to dinorbornyl ether (XII). *Anal.* Calcd. for $C_{14}H_{22}O$: C, 81.48; H, 10.75. Found: C, 81.90; H, 10.81.

Oxidation of (VI) to Dicarboxylic Acid (XIII).—Five grams of ketone (VI) was mixed with 15 g. of fuming nitric acid (sp. gr. 1.49–1.50). A homogeneous solution was obtained and heat was evolved. The mixture was then heated in an open Erlenmeyer flask on a steam-bath until the red fumes ceased. This required about one and one-half hours. Two phases were then present. Additional nitric acid (15 cc.) was added and the procedure repeated. The oil which separated was removed. The aqueous layer was diluted with water and extracted with ether. Evaporation of the ether extract yielded a partially crystalline mass which was treated first with petroleum ether and then recrystallized twice from toluene; m. p. 179–181°. After one more recrystallization from water. the acid formed large white needles, m. p. 182–184°. *Anal.* Calcd. for $C_{10}H_{14}O_4$: C, 60.57; H, 7.12. Found: C. 60.50; H, 6.90.

Chloro-dihydro-*nor*-dicyclopentadiene (XIV).—Phosphorus trichloride (41.2 g.) was added dropwise to 75 g. of hydroxydihydro-*nor*-dicyclopentadiene while stirring and cooling to 5°. After all had been added the mixture was gradually warmed to 40–45° and held at that temperature for three hours. The product was cooled, poured on ice, and separated by means of toluene from the water. The toluene solution was washed with sodium carbonate solution, and with water; and distilled *in vacuo*. The pure product boiled at 100–102° (10 mm.). It is a colorless oil with a characteristic odor having the following constants: $n^{25}D$ 1.5203; d^{25}_4 1.1121. *Anal.* Calcd. for $C_{10}H_{13}Cl$: Cl, 21.03. Found: Cl, 20.90.

Hydroxy-dihydro-*nor*-tricyclopentadiene (XV or XV-A).—A mixture of 114 g. of α-tricyclopentadiene[13] (m. p. 60°) and 150 g. of 40% sulfuric acid was stirred rapidly and heated under reflux for five hours at 115–125°. The dark viscous mass was stirred with hot water and the oil layer was separated with the aid of toluene. The toluene solution was washed, first with hot water, then with caustic soda solution and finally with hot water. The toluene was evaporated off and the residual dark, very viscous mass distilled *in vacuo*. The product distilled as a colorless viscous oil at 150–170° (2 mm.); yield 41 g. Upon redistillation at 11 mm. it boiled at 180–185° and crystallized on standing to a wax-like solid. After recrystallization from nitroethane the analytical sample formed colorless needles m. p. 115°. *Anal.* Calcd. for $C_{15}H_{20}O$: C, 83.27; H, 9.33. Found: C, 83.10; H, 9.35.

Hydroxy-tetrahydro-*nor*-tricyclopentadiene (XVI).—A mixture of 28.5 g. of hydroxy-dihydro-*nor*-tricyclopentadiene, 72 cc. of ethanol, and 10 g. of Raney nickel catalyst was heated in a shaking autoclave at 150–190° for six hours at 1470 lb. per sq. in. pressure of hydrogen. The filtered product upon evaporation *in vacuo* yielded an oil which crystallized when stirred with 75 cc. of petroleum ether. After three recrystallizations from nitromethane the analytical sample melted at 99–100°. *Anal.* Calcd. for $C_{15}H_{22}O$: C, 82.50: H, 10.16. Found: C, 81.90; H, 10.18.

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Summary

1. The hydration of dicyclopentadiene and tricyclopentadiene by means of aqueous sulfuric acid yields unsaturated, secondary monohydric alcohols having a different ring system than the original dienes, due to a molecular rearrangement in the terminal bridged cyclohexene ring.

2. The hydration-rearrangement of dicyclopentadiene yields hydroxy-dihydro-*nor*-dicyclopentadiene and the ether thereof. The latter is obtainable by the reaction of dicyclopentadiene with hydroxy-dihydro-*nor*-dicyclopentadiene in the presence of acidic condensing agents.

3. Hydroxy-dihydro-*nor*-dicyclopentadiene has been converted into its corresponding unsaturated ketone, saturated alcohol, saturated ketone, unsaturated chloride and parent saturated and unsaturated hydrocarbons.

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[12] Thomas, U. S. Patent 2,340,908 (1944).

[13] Alder and Stein, *Ann.*, **496**, 204 (1932).