[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Tetracyclic Dienes. I. The Diels–Alder Adduct of Norbornadiene and Cyclopentadiene

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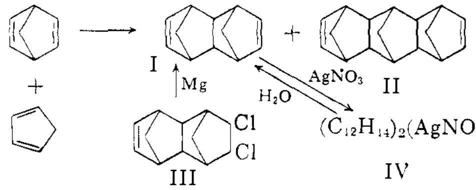
The reaction of norbornadiene with cyclopentadiene affords a good yield of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene, whose configuration was established through semihydrogenation followed by degradation to dicarboxylic acids of known structure, and through complete hydrogenation to the known saturated tetracyclic hydrocarbon. Oxidation of hexahydrodimethanonaphthalene furnished *cis*-bicyclo[3.3.0]octane-*cis,cis,trans,trans*-2,4,6,8-tetracarboxylic acid.

The reaction of norbornadiene with cyclopentadiene was investigated in order to determine the stereochemistry of the resulting tetracyclic diene I. This reaction at 190° provides a 35–40% yield of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (I) and a small amount of 1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1,4,5,8,9,10-trimethanoanthracene (II) in addition to the cyclopentadiene dimer, trimer and tetramer. Compound I also was prepared by the dehalogenation of 2,3-dichloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (III), which is obtained from the reaction of dichloroethylene and cyclopentadiene.[1] The product I was shown to be homogeneous and not a mixture of isomers by purification through formation of a silver nitrate complex[2] IV which, when treated with water, regenerated I. The regenerated olefin's purity was established by vapor chromatography.



The tetracyclic diene I could exist in each of three stereoisomeric forms Ia,b,c. Addition of cyclopentadiene with the methylene group of the diene away from the methano bridge to the less hindered side of norbornadiene would produce the *exo-endo* isomer Ib. This mode of addition of cyclopentadiene is realized in fact with the norbornene dienophile.[3]

Alder, in a series of investigations,[1,4] has shown that the adducts of cyclopentadiene and various substituted norbornenes have the same stereochemistry with respect to the 4a,8a-fusion. Soloway[3] demonstrated later that the stereochemistry of these adducts was *exo-endo*.

Addition of one mole of hydrogen to I gave four products in equal amounts, two of which were identified as starting material and VII as shown by vapor fractometry. Pure VII, which had the same melting point as Alder's product,[4b] was prepared by the complete hydrogenation of I. Permanganate oxidation of the mixture of hydrogenated products produced two known dicarboxylic acids Va and VIa (α- and β-diacids), and bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid (VIII).

An examination of the stereoisomers Ia-c shows that the reaction of one mole of hydrogen with either Ia or Ic would yield only one monoölefin each, in addition to unreacted diolefin and the corresponding saturated product. The semihydrogenation of Ib would give two different monoölefins (V and VI), unreacted starting material and *exo-endo*-decahydro-1,4,5,8-dimethanonaphthalene (VII). Further, oxidation of the remaining double bond in the monoölefin resulting from Ic would furnish a known single dibasic acid, octahydro-*exo*-4,7-methanoindene-*trans,trans*-1,3-dicarboxylic acid (γ-diacid) and in the case of Ia, the unknown δ-diacid. The monoölefin mixture (V and VI) would give two known dibasic acids Va and VIa (α- and β-diacids, respectively).[3] In addition, the *exo-endo* configuration shown (VII) is the correct one for Alder's product as demonstrated by the investigation of Soloway.[3] Thus the stereochemistry of I is *exo-endo* (Ib).

The tetracarboxylic acid VIII, which also was prepared by the ozonolysis of I, formed the anhydride IX, and must have the *cis,cis,trans,trans* configuration shown. This acid evidently is not the same stereochemically as the bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid of unknown configuration prepared by Yates and Bhat,[5] and it may serve as a more easily obtained suitable intermediate for an attempted pentalene synthesis, through conversion to the tetraamine and the subsequent elimination reaction.

Experimental

1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene from Norbornadiene and Cyclopentadiene.—To 138 g. (1.5 moles) of freshly distilled norbornadiene[6] was added 99 g. (1.5 moles) of cyclopentadiene which had been freshly cracked from the dimer,[7] and 0.2 g. of hydroquinone. The mixture was heated in an autoclave (previously swept with nitrogen) for 18 hours at 190°. The resulting mixture was subjected to fractional distillation and gave 63 g. (41.7% based on recovered norbornadiene) of I, b.p. 107–114° (32 mm.). Redistillation affords 55 g. (36.4%) of a product of about 97% purity.

To 7.9 g. (0.05 mole) of I was added slowly with stirring 10 ml. of a saturated solution of silver nitrate.[2] The mixture immediately set up into a hard gel. The solid was removed by filtration and recrystallized from minimum amount

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[1] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

[2] S. Winstein and H. Lucas, THIS JOURNAL, **60**, 836 (1938).

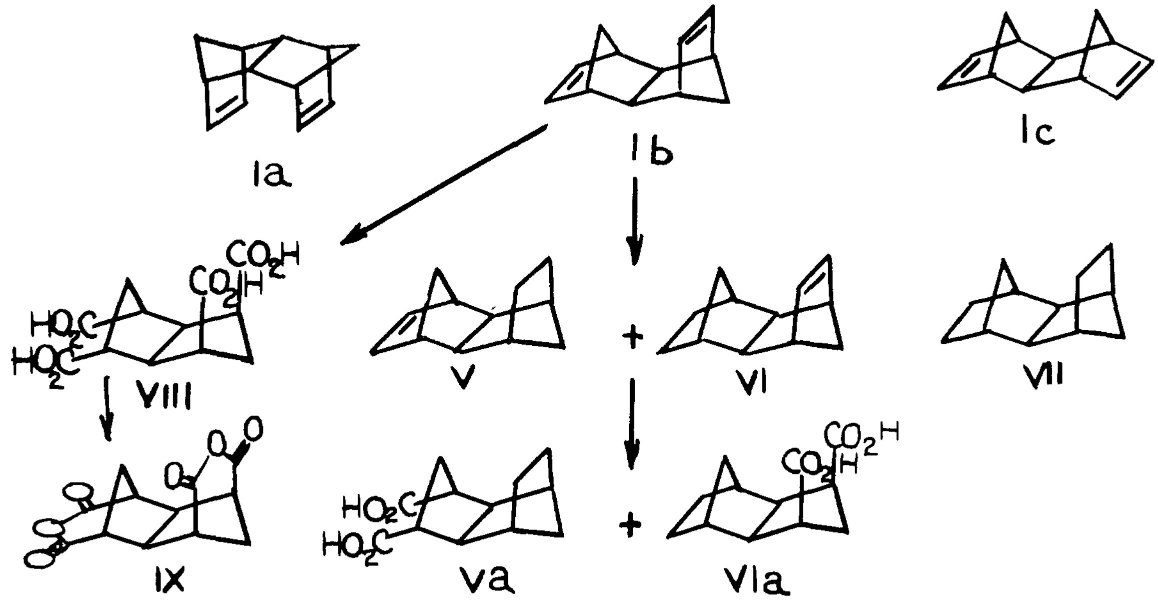
[3] S. B. Soloway, *ibid.*, **74**, 1027 (1952), offers an excellent summary and discussion of the stereochemistry involved in fused norcamphane systems.

[4] (a) K. Alder, G. Stein, J. Reese and W. Grassman, *Ann.*, **496**, 204 (1932); (b) K. Alder and E. Windemuth, *Ber.*, **71**, 2409 (1938); (c) K. Alder and G. Stein, *Angew. Chem.*, **47**, 834 (1934).

[5] P. Yates and G. Bhat, *Chemistry & Industry*, 1237 (1954).

[6] Obtained from the Shell Chemical Corporation.

[7] Obtained from the Enjay Co. See Enjay Technical Bulletin No. 4, *High Purity Dicyclopentadiene and Methyl Cyclopentadiene Dimer.*



of hot absolute ethanol yielding 14.8 g. (72%) of product, m.p. 157–158° dec.

Anal. Calcd. for $(C_{12}H_{14})_2(AgNO_3)_3$: C, 34.89; H, 3.42. Found: C, 34.35; H, 3.27.

The complex was dissolved in 150 ml. of warm water and the aqueous solution was subjected to a continuous ether extraction. The ether extract was dried, the ether was removed under reduced pressure and the residue distilled to give 4.2 g. (53% recovery) of pure I, b.p. 108° (25 mm.), $n^{26}\text{D}$ 1.5324, d^{25}_4 1.038. Vapor fractometry revealed a pure product. The infrared spectrum of I[8] showed absorption maxima at 2940 (-C-H str.), 3050 (=C—H str.), 1570 (C=C)[9] and 712 cm.$^{-1}$ (*cis*-CH=CH).[10] Quantitative hydrogenation of I with palladium catalyst showed the absorption of 2.02 moles of hydrogen.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92; mol. wt., 158.23. Found: C, 90.78; H, 9.30; mol. wt. (ebullioscopic), 157.

1,4a,5,8,8a.9,9a,10,10a-Decahydro-1,4,5,8,9,10-trimethanoanthracene (II).—The fraction obtained at 95–105° (0.25 mm.) (32.9 g., 9.8%) was recrystallized from ethanol giving 32 g. (9.5%) of pure II, m.p. 139.5°. The infrared spectrum showed bands at 3050 (=C-H str.), 2925 (C-H str.), 1575 (C=C) and 712 cm.$^{-1}$ (CH=CH *cis*).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99; mol. wt., 224. Found: C, 90.56; H, 8.69; mol. wt. (ebullioscopic), 231.

The Diolefin I from 2,3-Dichloro-1,2,3,4,4a,5,8,8a-1,4,5,-8-dimethanonaphthalene (III).—The reaction of *trans*-1,2-dichloroethylene and cyclopentadiene was carried out as described,[1] except that 110 g. (1.65 moles) of cyclopentadiene and 97 g. (1.0 moles) of *trans*-1,2-dichloroethylene were employed in order to afford a higher yield (40%) of the desired product. The method employed for dehalogenation is described by Schmerling, Luvisi and Welch.[11] To 3.8 g. (0.015 mole) of iodine and 9.12 g. (0.375 g. atom) of magnesium in 200 ml. of ether was added slowly a solution of 57.25 g. (0.25 mole) of III in 50 ml. of ether so as to maintain a gentle reflux. At the end of the addition, the mixture was heated to the reflux temperature for 3 hr. after which time the reaction mixture was decomposed with ice to which 1 ml. of sulfuric acid had been added. The ether layer was washed with water and dried. The ether was removed under reduced pressure and the residue distilled to yield 12.4 g. (31.4%) of I which was identical to the product described above.

Decahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (VII).—A solution of 7.9 g. (0.05 mole) of I in 100 ml. of absolute ethanol was hydrogenated at 20° and 1 atm. with a platinum catalyst. After the addition of 0.1 mole of hydrogen, the reaction stopped and the catalyst was removed by filtration. The solution was concentrated to 75 ml. and on cooling, white plates formed. Additional product was obtained by successive concentration and cooling. Recrystallization was effected from methanol, yielding 5.5 g. (70%) of VII, m.p. 35.5–36.5°, reported[1] 36–37°; VII was shown by the vapor fractometer to be about 95% pure. The infrared spectra revealed the absence of those bands characteristic of I.

Semihydrogenation of I.—A solution of 7.9 g. (0.05 mole) of I in 100 ml. of absolute ethanol was hydrogenated at 15° and 1 atm. with a palladium catalyst and 0.05 mole of hydrogen. The catalyst was removed by filtration and the ethanol solvent was removed under reduced pressure leaving the hydrocarbon mixture. This mixture showed four peaks of equal height on a vapor chromatogram,[12] the first and fourth peaks of which were identified as I and VII, respectively, by comparison with pure samples.

The α-Diacid Va and the β-Diacid VIa.[1,3]—To a stirred suspension of the mixed hydrocarbons in 750 ml. of water was added 20 g. (1 g. less than theoretical) of solid potassium permanganate in portions over a period of 6 hr., keeping the temperature below 35°. The mixture was stirred overnight, after which time the manganese dioxide was removed by filtration and washed with hot water. The combined filtrates were concentrated to 100 ml., treated with Norite, filtered, and acidified with 6 *N* hydrochloric acid. The crystals which formed were removed by filtration and the filtrate was further concentrated to 50 ml. in order to obtain a second crop. Fractional recrystallization was effected by dissolving the combined crops in hot acetone followed by addition of acetonitrile to the cloud point. The first fraction was identified as the β-diacid, m.p. 254°, reported[3] 256°; anhydride, m.p. 178°, reported[3] 179–179.5°.

The filtrate from the fractional crystallization was evaporated to dryness. The residue was precipitated once from a benzene solution by addition of "Skelly B" and subsequently recrystallized from acetonitrile, which afforded the α-diacid, m.p. 217–218°, reported[1] 216–217°; anhydride, m.p. 154°, reported[1] 154°. The infrared spectra of both acids (KBr pellet) were nearly identical, showing broad bands at 2500–3200 (-O-H bonded) and 1710–1725 cm.$^{-1}$ (C=O str.).

***cis*-Bicyclo[3.3.0]octane-*cis,cis,trans,trans*-2,4,6,8-tetracarboxylic Acid (VIII).**—The aqueous filtrate from the oxi-

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[8] The infrared spectra were run on a Perkin-Elmer model 21 spectrophotometer obtained in part through the assistance of the National Science Foundation.

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

[10] S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958).

[11] L. Schmerling, J. P. Luvisi and R. Welch, *ibid.*, **78**, 2819 (1956).

[12] Perkin-Elmer high temperature vapor fractometer column *Q* at 215°.

dation above was further concentrated to 15 ml. to yield the crude tetracarboxylic acid VIII, which was recrystallized from water with the aid of decolorizing carbon, m.p. 268–271° dec. (block preheated to 260°).

This acid also was prepared by ozonolysis of I.[13] To 3.95 g. (0.025 mole) of I was added 50 ml. of methanol and enough methylene chloride to effect solution at 0°. This solution was treated with a stream of ozonized oxygen[14] (8% O_3 in O_2) for 5.5 hours (twice theoretical). At the end of this time, the solvent was removed under reduced pressure leaving a glassy polymeric methoxy peroxide. To the peroxide was added 35 ml. of 98% formic acid and 17 ml. of 30% hydrogen peroxide. On gentle warming, a vigorous reaction took place (CAUTION!) which ceased after 15 minutes. The solution was heated under reflux for an additional 15 minutes, during which time white crystals formed and a test for peroxides with a potassium iodide solution was negative. The mixture was cooled to 0° and the crystalline precipitate was removed by filtration, yielding 4.1 g., 57%, of crude tetracarboxylic acid VIII, which was recrystallized from water to give 3.6 g. (50%) of pure VIII, m.p. 268–271° dec. (block preheated to 260°).

Anal. Calcd. for $C_{12}H_{14}O_8$: C, 50.35; H, 4.93. Found: C, 50.29; H, 5.01.

The titration of this acid with 0.1 *M* potassium hydroxide gave a smooth curve which did not distinguish the individual carboxyl groups but gave a sharp end-point; neut. equiv. 70.1, calcd. 71.5. The infrared spectra (KBr pellet) showed absorption maxima 2500–3200 (O–H bonded) and 1695–1720 cm.$^{-1}$ (C=O str.).

The Anhydride IX.—A solution of 0.8 g. (0.0028 mole) of VIII in 20 ml. of acetic anhydride was heated at the reflux temperature for 6 hr. The excess acetic anhydride and some acetic acid then was distilled from the reaction mixture and the residue was taken up in hot ethyl acetate. The solution was treated with charcoal, filtered, and the anhydride was crystallized by the addition of benzene, m.p. 239–240°. The infrared spectra showed bands at 1810 and 1765 cm.$^{-1}$ (C=O anhydride).

Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03. Found: C, 57.18; H, 3.76.

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[13] P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

[14] L. I. Smith and F. L. Greenwood, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 673.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Nitrous Acid Deamination of *cis*-Cyclohexylamine-2-*d*

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cis-Cyclohexylamine-2-*d* was obtained in low over-all yield by the reaction of cyclohexene oxide with lithium aluminum deuteride to yield *trans*-cyclohexanol-2-*d*, the tosylate of which was displaced by sodium azide to yield *cis*-cyclohexyl-2-*d* azide which was reduced with lithium aluminum hydride. The reaction of *trans*-cyclohexanol-2-*d* *p*-toluenesulfonate with potassium acetate gave a low yield of *cis*-cyclohexanol-2-*d* acetate which was hydrolyzed to the corresponding alcohol. The alcohol produced by the reaction of *cis*-cyclohexylamine-2-*d* with aqueous nitrous acid was *cis*-cyclohexanol-2-*d*; the solvolytic deamination proceeded with almost complete retention of configuration.

The deamination of aliphatic amines generally proceeds with solvolysis and elimination and often rearrangement. The unrearranged solvolysis products of monofunctional acyclic amines have been found generally to be racemized partially with net inversion of configuration.[1–3] The contrasting results afforded by cyclohexylamines must be considered by any comprehensive mechanism of the reaction. Generalizations derived from simple cyclohexylamines and from decalylamines are that axial amines give extensive elimination but form equatorial alcohol (with inversion) although equatorial amines give equatorial alcohol (with retention) and little or no olefin.[4–6] These results have an important bearing on the reaction mechanism. The difference in the amount of olefin formed from axial and equatorial amines is difficult to explain by the "hot carbonium ion" mechanism.[7–11] The same hot carbonium ion which should be formed from both amines would be expected to give identical products. Because of the significance of these results and the importance of conformational considerations in nitrous acid deamination of other systems,[3,8,12] we thought it desirable to study the stereochemistry of the deamination of a cyclohexylamine containing no additional substituents which could stabilize a particular conformation. For this purpose *cis*-cyclohexylamine-2-*d* and *cis*- and *trans*-cyclohexanol-2-*d* were prepared.

The syntheses of the starting amine and of the two possible alcohol products followed from analogous syntheses of deuterioalcohols in the cyclopentane series.[13] Unfortunately, the various displacement reactions involved were accompanied by extensive elimination and over-all yields were low. The reduction of cyclohexene oxide with excess lithium

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[1] K. B. Wiberg, Dissertation, Columbia University, July, 1950.

[2] P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold and P. A. D. S. Rao, *Nature*, **166**, 179 (1950).

[3] A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 2888 (1957).

[4] (a) A. K. Bose, *Experientia*, **9**, 256 (1953); (b) J. A. Mills, *J. Chem. Soc.*, 260 (1953).

[5] (a) W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954); (b) W. G. Dauben and J. Jiu, *ibid.*, **76**, 4426 (1954); (c) W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 48 (1955).

[6] These generalizations apparently do not apply to axial-steroidal amines, in which elimination and retention of configuration seem to be the rule; *cf.* C. W. Shoppee, D. E. Evans and G. H. R. Summers, *J. Chem. Soc.*, 97 (1957), and C. W. Shoppee, R. J. W. Cremlyn, D. E. Evans and G. H. R. Summers, *ibid.*, 4364 (1957).

[7] (a) J. D. Roberts and M. Halmann, THIS JOURNAL, **75**, 5759 (1953); (b) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); (c) A. W. Fort and J. D. Roberts, *ibid.*, **78**, 584 (1956).

[8] D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

[9] (a) L. S. Ciereszko and J. G. Burr, *ibid.*, **74**, 145 (1952); (b) J. G. Burr and L. S. Ciereszko, *ibid.*, **74**, 5431 (1952); (c) P. S. Bailey and J. G. Burr, *ibid.*, **75**, 2591 (1953).

[10] D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

[11] D. Semenov, C.-H. Shih and W. G. Young, *ibid.*, **80**, 5472 (1958).

[12] A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957).

[13] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, THIS JOURNAL, **80**, 2326 (1958).