anol and, finally, sublimation *in vacuo* gave colorless feathery needles, m.p. 46–47°. The ultraviolet absorption spectrum of an ethanolic solution displayed a single maximum at 266 mμ (log ε 3.05). The hydrocarbon did not react with 2% potassium permanganate in acetone.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.46; H, 9.01.

Pyracene (I).—2a,3,4,4a-Tetrahydropyracene (4.55 g., 0.025 mole) was heated at 300–320° under a nitrogen atmosphere with 200 mg. of 10% palladium-on-charcoal catalyst until the evolution of hydrogen ceased (*ca.* 90 minutes). The product was dissolved in benzene, the catalyst removed by filtration, and, after removal of most of the solvent, the collected material recrystallized from benzene to give 3.0 g. (67%) of colorless needles which sintered at 206° and melted at 212–216°. Further recrystallization, twice from benzene and once from butanol, followed by sublimation *in vacuo* raised the melting point to 214.5–217.5°.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.38; H, 6.68.

The trinitrobenzene derivative crystallized from benzene as bright orange needles, m.p. 206–207°.

Anal. Calcd. for $C_{20}H_{15}N_3O_6$: C, 61.07; H, 3.84. Found: C, 61.09; H, 3.84.

The picrate was obtained from a benzene solution as dark red needles, m.p. 206–207°.

Anal. Calcd. for $C_{20}H_{15}N_3O_7$: C, 58.68; H, 3.69. Found: C, 59.10; H, 4.01.

Pyracene is only slightly soluble in ethanol, insoluble in hexane, and dissolves in hot benzene to give a solution having a blue fluorescence. The hydrocarbon showed no reaction with 2% potassium permanganate in acetone and was recovered quantitatively from an attempted hydrogenation in ethanol in the presence of a palladium-on-barium sulfate or platinum oxide catalyst at room temperature and atmospheric pressure. The ultraviolet absorption spectrum of an ethanolic solution showed the following peaks: λ_{max} in mμ at 231 (log ε 4.95), 284 (log ε 3.82), 295 (log ε 3.92), 307 (log ε 3.75), 313 (log ε 3.57), 322 (log ε 3.23) and 329 (log ε 3.44). This spectrum, along with that of acenaphthene, is shown in Fig. 1.

1,4,5,8-Naphthalenetetracarboxylic Acid.—Sodium dichromate (25 g.) was added in portions to a solution of pyracene (1.9 g.) in 50 ml. of acetic acid at a temperature of 90° and the resultant mixture heated under reflux for three hours. The cooled reaction mixture was poured into 150 ml. of cold dilute sulfuric acid and the precipitated acid collected by suction filtration. The crude product was then heated for 15 minutes in an alkaline solution containing 0.5 g. of potassium permanganate. On acidification of the decolorized, filtered solution, crystalline 1,4,5,8-naphthalenetetracarboxylic acid precipitated. The yield was 1.12 g. (35%). This acid had no characteristic melting point and was further identified by a series of specific transformations first described by Bamburger and Philip[16] and later confirmed by Fieser and Peters.[9]

SEATTLE 5, WASHINGTON

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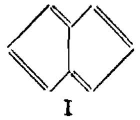
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Syntheses of Some Bicyclo[3.3.0]octane Derivatives

BY JOHN D. ROBERTS AND WILLIAM F. GORHAM[1]

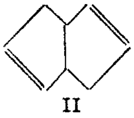
As part of a projected synthesis of pentalene (bicyclo[3.3.0]octatetraene), bicyclo[3.2.0]-2-hepten-6-one prepared by condensation of ketene and cyclopentadiene was converted by the Tiffeneau–Demjanov ring expansion procedure to a mixture of bicyclo[3.3.0]-2-octen-6-one and bicyclo[3.3.0]-2-octen-7-one. The ketonic mixture was reduced with lithium aluminum hydride and the resulting alcohols were converted to a mixture of tetrahydropentalenes by the Chugaev method. Unsuccessful attempts were made to transform the tetrahydropentalene mixture into pentalene by catalytic dehydrogenation procedures. Some of the steps in the Linstead synthesis of *cis*- and *trans*-bicyclo[3.3.0]octanes have been improved.

The question of the possible existence and stability of pentalene (bicyclo[3.3.0]octatetraene (I)) is of considerable interest since the substance would be a completely conjugated planar cyclic polyolefin without the (2 + 4 *n*) π-electrons[2] characteristic of the usual stable planar cyclic conjugated systems. The pentalene ring system seems to be known only as various derivatives of 1,2,4,5-dibenzpentalene,[3] and although a number of attempts have been made recently to synthesize 1,2-benzpentalene and its derivatives,[4] only Barrett and Linstead[5] have recorded an attempt to prepare the parent hydrocarbon (by catalytic dehydrogenation of *cis*-bicyclo[3.3.0]octane). Current theoretical opinion seems to be divided as to the possible stable existence of I.[6]

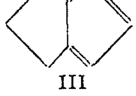


I

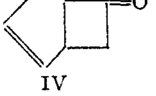
The principal objective of the present investigation was the synthesis and study of a tetrahydropentalene with an unconjugated double bond in each ring. Such a compound (as II) was expected to be somewhat more stable than an isomeric cyclopentanocyclopentadiene like III.[7] The synthesis started with bicyclo[3.2.0]-2-hepten-6-one (IV) which was obtained by addition of ketene to cyclopentadiene.[8] The structure of IV is indicated by the non-identity of its 2,4-dinitrophenylhydrazone with that of dehydronorcamphor[9] (the expected 1,4-adduct), the



II



III



IV

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(1) James Flack Norris Memorial Fellow, 1950–1951.

(2) E. Hückel, "Grundzüge der Theorie ungesättiger and aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 77–85.

(3) The first published report was that of K. Brand, *Ber.*, **45**, 3071 (1912). For references to later work see K. Brand and W. Hennig, *ibid.*, **81**, 382, 387.

(4) (a) W. Baker and W. G. Leeds, *J. Chem. Soc.*, 974 (1948); (b) W. Baker and P. G. Jones, *ibid.*, 787 (1951); (c) G. R. Clemo, L. H. Groves, L. Munday and G. A. Swan, *ibid.*, 863 (1951); (d) L. H. Groves and G. A. Swan, *ibid.*, 867 (1951) and H. Dahn, *Helv. Chim. Acta*, **34**, 1087 (1951).

(5) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

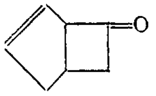
(6) (a) W. Baker, *ibid.*, 258 (1945); (b) C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940); (c) D. P. Craig and A. Maccoll, *Nature*, **161**, 481 (1948); *J. Chem. Soc.*, 964 (1949); (d) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); *ibid.*, **46**, 146 (1950).

(7) Work directed toward the synthesis of III from *cis*-bicyclo[3.3.0]octane-2,4-dicarboxylic acid was done earlier by Miss Winifred Bennett; B.S. Thesis, M.I.T. (1947).

(8) B. T. Brooks and G. Wilbert, THIS JOURNAL, **63**, 870 (1941).

(9) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

band at 5.6 μ in its infrared spectrum (Fig. 1) which is typical of the carbonyl group located on a four-membered ring[10] and degradations to glutaric acid[8] and *cis*-cyclopentane-1,2-dicarboxylic acid.[11] The position of the double bond can be assigned to the 2,3-position (γ,δ to the carbonyl) by analogy to the addition product of ketene and cyclohexadiene[11,12] which assignment (rather than at the 3,4-position and β,γ to the carbonyl, V) is supported by the stability of the 2,4-dinitrophenylhydrazone under



V

conditions which cause the corresponding derivative of a β,γ-unsaturated aldehyde to be readily converted to the α,β-form.[13]

Expansion of the four-membered ring of IV to give the bicyclo[3.3.0]octane ring system was achieved as follows. IV reacted with anhydrous hydrogen cyanide at 0° in the presence of piperidine to give a cyanohydrin which was not isolated but converted directly to the cyanohydrin acetate (VI) with a mixture of acetic anhydride and acetyl chloride in an over-all yield from IV of 67%. In the reduction of VI with excess lithium aluminum hydride, the final product is partly determined by the order in which the groups are reduced. Initial reduction of the nitrile group leads to the desired amino alcohol (VII) while prior reduction of the acetoxyl group can subsequently result in VII or, by reversal of the cyanohydrin formation and further reduction, the alcohol (VIII) corresponding to IV.[14] Reduction of the cyanohydrin acetate VI was found to yield primarily VII although some VIII appeared to be present since, when crude VII was used in the next step, the final product was contaminated with an alcoholic material having about the expected boiling point for VIII. The ring expansion was completed by a semi-pinacolic deamination of VII with nitrous acid. The mixture of ketones (IX and X) produced in 55% yield from VI was analyzed by hydrogenation to a mixture of *cis*-α and *cis*-β-cyclo[3.3.0]octanones (XI and XII) which was shown by its infrared spectrum to contain ~85% of the α-ketone and ~15% of the β-isomer. Explanation of the course of the ring expansion reaction is difficult without knowledge of the stereochemical relationship between the aminomethyl group and the *cis*-hydrogens at the ring junctions of VII. It would be particularly interesting if IX and X were each obtained from a different stereoisomer of VII.

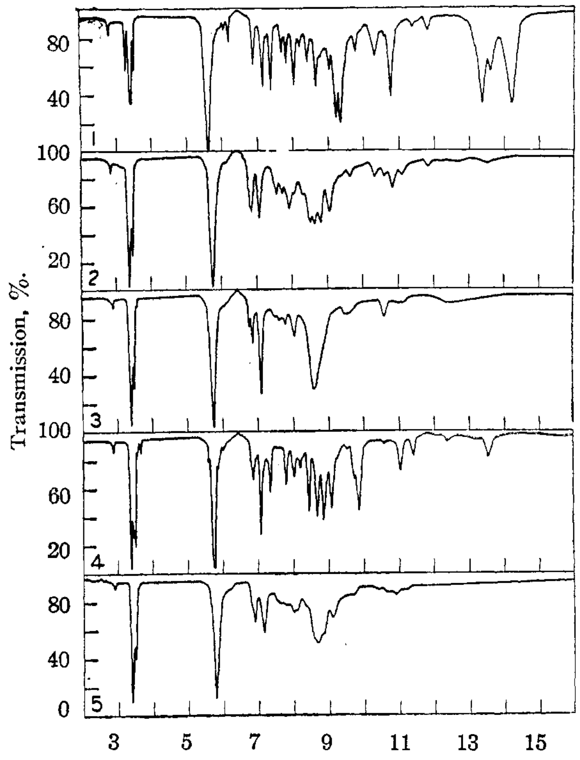
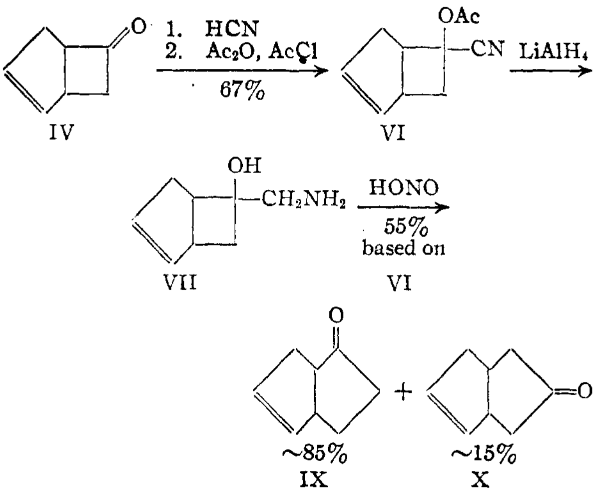


Fig. 1.—Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in regions 4.2–5.0 μ and 6.2–7.4 μ where carbon tetrachloride was used as solvent: (1) bicyclo[3.2.0]-2-hepten-6-one IV, (2) *cis*-α-bicyclo[3.3.0]octanone XI, (3) *cis*-β-bicyclo[3.3.0]octanone XII, (4) *trans*-β-bicyclo[3.3.0]-octanone, (5) ketone mixture from the hydrogenation of IX and X.



Reduction of the mixture of IX and X with lithium aluminum hydride gave a complex mixture of alcohols (XIII) containing both stereo- and position isomers. Dehydration of XIII was achieved in 55% yield by the Chugaev procedure involving pyrolysis of the S-methyl xanthate ester. The product (XIV) was a colorless tetrahydropentalene mixture comprised probably of mostly II and XV with a maximum of 15% of XVI (from the alcohol derived from X). On hydrogenation, XIV absorbed

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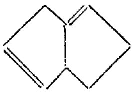
[10] (a) R. S. Rasmussen, "Progress in the Chemistry of Organic Natural Products," Vol. 5, Springer-Verlag, Vienna, 1948, p. 331; (b) compare the spectrum of cyclobutanone, J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[11] A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

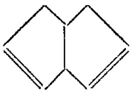
[12] Similar results have been obtained with dimethyl- and diphenylketenes with cyclopentadiene, T. L. Dawson and G. R. Ramage, *J. Chem. Soc.*, 3523 (1950), and J. R. Lewis, G. R. Ramage, J. L. Simonsen and W. G. Wainwright, *ibid.*, 1837 (1937).

[13] W. G. Young and J. D. Roberts, THIS JOURNAL, **68**, 649 (1946).

[14] The low yield obtained by R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948), in the lithium aluminum hydride reduction of mandelonitrile may be partially due to a similar reversal of cyanohydrin formation.



XV



XVI

two moles of hydrogen and yielded pure *cis*-bicyclo[3.3.0]octane. The ultraviolet absorption spectrum of XIV showed no maximum in the region between 220 and 350 mμ indicating the absence of conjugated diolefins such as III. The material was stable and showed no signs of decomposition after several months at 0°.

Attempts were made to catalytically dehydrogenate the tetrahydropentalene mixture XIV by passing the vaporized material over platinized asbestos and platinized charcoal. In no case did it appear that dehydrogenation occurred although the conditions used were sufficiently drastic to dehydrogenate cyclohexene to benzene and tetralin to naphthalene. The results are consistent with the observation of Barrett and Linstead[1] that *cis*-bicyclo[3.3.0]octane is resistant to catalytic dehydrogenation. Analogous results have been obtained in attempts to synthesize 1,2-benzpentalene[4] by dehydrogenation procedures. Preliminary experiments on the conversion of XIV to pentalene or a dihydropentalene by halogenation–dehydrohalogenation methods similar to those used by Cope and Bailey[15] for the synthesis of cycloöctatetraene and cycloöctatriene from 1,5-cycloöctadiene were unsuccessful.

The previously reported syntheses[5] of *cis*- and *trans*-bicyclo[3.3.0]octanes have been repeated to obtain reference samples for infrared analyses. The key intermediates are the *cis*- and *trans*-cyclopentane-1,2-diacetic acids which were obtained from α-carbethoxycyclopentanone *via* ethyl 2-ketocyclopentaneacetate (XVII).[16]

The second acetic acid group was introduced by condensation of XVII with ethyl cyanoacetate in piperidine at room temperature over a period of 15 days.[17] The condensation product (XVIII) which was obtained in 40% yield was then reduced with aluminum amalgam (catalytic hydrogenation was reported to be generally ineffective) and the reduction product hydrolyzed and decarboxylated to a 3:1 mixture of the *cis*- and *trans*-cyclopentane-1,2-diacetic acids.[14] We find that the condensation of XVII with ethyl cyanoacetate gives a 68% yield of XVIII in 15 hours using the conditions employed by Cope and co-workers[18] for condensation of unreactive ketones with ethyl cyanoacetate. Catalytic reduction of XVIII occurred smoothly over a freshly prepared palladium-on-charcoal catalyst.[18] Hydrolysis and decarboxylation of the reduction product gave an approximately 1:1 mixture of the *cis*- and *trans*-diacids. This procedure therefore is to be preferred if the *trans*-diacid is desired.

The remainder of the preparations was as described previously[17] except that it was found convenient to use the Huang-Minlon[19] modification of the Wolff–Kishner reduction for the conversion of the *cis*- and *trans*-β-bicyclo[3.3.0]octanones to the corresponding hydrocarbons.

Experimental[20]

Bicyclo[3.2.0]-2-hepten-6-one (IV).—The addition of ketene to cyclopentadiene was carried out much as described by Blomquist and Kwiatek.[11] The product was purified through the semicarbazone, m.p. 221–222° dec. (lit. 221–222° dec.,[3] 219–220°[11]), which was decomposed by steam distillation from oxalic acid. Pure IV had b.p. 83–84° (51 mm.), $n^{25}\mathrm{D}$ 1.4801 (lit.[11] b.p. 62–63.5° (20 mm.), $n^{20}\mathrm{D}$ 1.4819). The infrared spectrum is given in Fig. 1.

The **2,4-dinitrophenylhydrazone** of IV had m.p. 114–115° after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{12}O_4N_4$: C, 54.15; H, 4.17; N, 19.45. Found: C, 54.35; H, 4.35; N, 19.30.

6-Acetoxy-6-cyanobicyclo[3.2.0]-2-heptene (VI).—A mixture of 84.5 g. (0.78 mole) of IV and 32 ml. (0.83 mole) of anhydrous hydrogen cyanide[21] was cooled to 0° and 0.25 ml. of piperidine added. The flask was stoppered and left in an ice-bath for 24 hours. The piperidine was neutralized with 0.25 ml. of concd. sulfuric acid and the crude cyanohydrin acetylated by addition of 50 ml. of anhydrous ether, 150 ml. of acetic anhydride and 5 ml. of acetyl chloride. The acetylation mixture was kept at 0° for 24 hours and then allowed to stand at room temperature for a week. The excess hydrogen cyanide and ether were removed by distillation at atmospheric pressure and the acetic acid and acetic anhydride by distillation through a 20-cm. Vigreux column under reduced pressure. Fractionation of the residue gave 95 g. (67%) of VI, b.p. 106–110° (3 mm.), $n^{25}\mathrm{D}$ 1.4785.

Anal. Calcd. for $C_{10}H_{11}O_2N$: C, 67.80; H, 6.22; N, 7.91. Found: C, 67.80; H, 6.44; N, 7.77.

6-Aminomethyl-6-hydroxybicyclo[3.2.0]-2-heptene (VII).—In a 2-l. three-necked flask equipped with stirrer, dropping funnel, reflux condenser and protected from atmospheric moisture was placed 16 g. (0.42 mole) of lithium aluminum hydride in 400 ml. of dry ether. The mixture was stirred and a solution of 42.5 g. (0.24 mole) of VI in 75 ml. of dry ether was added dropwise over 40 minutes. The reaction mixture was then heated under reflux for 45 minutes, cooled in an ice-bath and treated cautiously with 25 ml. of water to destroy the excess hydride. Eight hundred milliliters of 20% sodium potassium tartrate solution was added, the mixture stirred for 15 minutes and transferred to a separatory funnel. The ether layer was removed and the aqueous layer extracted continuously with ether for 3 days. The combined extracts were dried over calcium oxide and the ether removed under reduced pressure. One-tenth of the residual crude VII (40 g.) was set aside for purification and the remainder was used directly in the next step.

Distillation of the crude VII gave material of b.p. 80–83° (0.9 mm.) which contained only 90% of the theoretical amount of nitrogen. The impurities appeared to be neutral since they were removed by continuous ether extraction of a dilute sulfuric acid solution of the impure distillate. The aqueous residue was basified, extracted continuously with ether and the extract dried over calcium oxide. Distillation through a semi-micro column[22] gave pure VII, b.p. 83–84° (1.5 mm.).

Anal. Calcd. for $C_8H_{13}ON$: C, 69.10; H, 9.34; N, 10.07. Found: C, 69.41; H, 9.50; N, 9.62.

The **picrate** of VII was prepared by evaporation of a benzene solution of equivalent amounts of the amino alcohol and picric acid. It was recrystallized from a benzene–ethanol–hexane mixture and had m.p. 137–138°.

Anal. Calcd. for $C_{14}H_{16}O_8N_4$: C, 45.65; H, 4.35; N, 15.20. Found: C, 45.76; H, 4.30; N, 15.17.

Bicyclo[3.3.0]-2-octen-6-one and Bicyclo[3.3.0]-2-octen-7-one (IX and X).—The crude amino alcohol (VII) (36 g.) from the preceding preparation was dissolved in 225 ml. of water containing 15 g. of acetic acid. The solution was then cooled in an ice-bath and 16 g. (0.23 mole) of sodium ni-

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(15) A. C. Cope and W. J. Bailey, This Journal, **70**, 2305 (1948).

(16) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

(17) J. W. Barrett and R. P. Linstead, *ibid.*, 436 (1935).

(18) A. C. Cope, C. M. Hofmann, C. Wyckoff and E. Hardenbergh, This Journal, **63**, 3452 (1941).

(19) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(20) Analyses by Dr. S. M. Nagy and his associates.

(21) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 314.

(22) C. W. Gould, G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

trite dissolved in 50 ml. of water was added over 5 minutes. The mixture was stirred in the ice-bath for 40 minutes, heated on a steam-cone for 40 minutes and then allowed to stand overnight. The mixture was steam distilled and the steam distillate (450 ml.) was extracted continuously with ether. The extract was dried over magnesium sulfate and on distillation yielded 14.5 g. (55% based on VI) of a mixture of IX and X, b.p. 80–82.5° (17 mm.), $n^{25}\text{D}$ 1.4902. The infrared spectrum showed weak hydroxyl absorption indicating the presence of VIII. The material was purified by conversion to the semicarbazone which was then decomposed by steam distillation in the presence of oxalic acid. The recovery of the purified ketone was 80%; b.p. 81–83° (17 mm.), $n^{25}\text{D}$ 1.4880.

Anal. Calcd. for $C_8H_{10}O$: C, 78.70; H, 8.20. Found: C, 78.39; H, 8.30.

The **2,4-dinitrophenylhydrazone** from the ketone mixture had a long m.p. range (120–155°) after crystallization from ethanol but had a satisfactory analysis.

Anal. Calcd. for $C_{14}H_{14}O_4N_4$: C, 55.60; H, 4.65; N, 18.65. Found: C, 55.92; H, 5.05; N, 18.33.

The **semicarbazone** was also prepared and after recrystallization from ethanol–water had m.p. 164–166° dec.

Anal. Calcd. for $C_9H_{13}ON_3$: C, 60.30; H, 7.25; N, 23.50. Found: C, 60.30; H, 7.51; N, 23.20.

Hydrogenation of 3 g. of the mixture of IX and X in ethanol over platinum oxide gave 1 g. of reduced ketone mixture, b.p. 84–86° (18 mm.), $n^{25}\text{D}$ 1.4758. The infrared curve of the product (Fig. 1) was almost identical with that of a synthetic mixture containing 85% of α-bicyclo[3.3.0]-octanone and 15% of β-bicyclo[3.3.0]octanone.

Catalytic hydrogenation of 1.5 g. of the mixture of IX and X followed by Wolff–Kishner reduction of the crude product by the procedure used for the preparation of *cis*- and *trans*-bicyclo[3.3.0]octanes from the β-ketones (see later) yielded 0.5 g. of crude hydrocarbon, b.p. 110–125°, which after purification by passage over silica gel[23] had $n^{24}\text{D}$ 1.4590 and an infrared spectrum identical with that of an authentic sample of *cis*-bicyclo[3.3.0]octane.

Bicyclo[3.3.0]-2-octen-6-ol and Bicyclo[3.3.0]-2-octen-7-ol Mixture (XIII).—In a 500-ml. three-necked flask equipped with stirrer, dropping funnel, reflux condenser and in an atmosphere of dry nitrogen was placed 3.8 g. (0.1 mole) of lithium aluminum hydride and 200 ml. of dry ether. The mixture of ketones IX and X (21.6 g., 0.18 mole) dissolved in 50 ml. of dry ether was added over 25 minutes. The stirred mixture was refluxed for 40 minutes, then cooled in an ice-bath and 20 ml. of water added cautiously followed by 150 ml. of 12% sulfuric acid. The mixture was extracted continuously with ether for 48 hours, the extract dried over magnesium sulfate and the ether removed. Distillation of the residue yielded 18.4 g. (84%) of the alcohol mixture XIII, b.p. 91–94° (17 mm.), $n^{25}\text{D}$ 1.5025.

Anal. Calcd. for $C_8H_{12}O$: C, 77.42; H, 9.69. Found: C, 76.93; H, 9.77.

Solid derivatives of XIII were difficult to crystallize and had wide m.p. ranges as might be expected for a mixture of position and stereoisomers. The acetate mixture, b.p. 91–94° (16 mm.), $n^{25}\text{D}$ 1.4675, was prepared from XIII and acetyl chloride in pyridine.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.43. Found: C, 72.04; H, 8.69.

Dehydration of Alcohol Mixture XIII by the Chugaev Procedure.—The alcohol mixture XIII (2.7 g.) was converted to the S-methyl xanthate by the method previously employed for O-cyclobutyl S-methyl xanthate.[10b] The crude xanthate was transferred to a 50-ml. distilling flask and pyrolyzed by heating the flask to 180–220° with a Wood's metal bath over 40 minutes. Gas was evolved and organic material distilled smoothly. The distillate was taken up in 25 ml. of ether and shaken thoroughly with 50 ml. of 20% sodium hydroxide solution. The ethereal solution was dried over calcium chloride, the ether removed and the residue fractionated through a semi-micro column.[22] The yield of a mixture (XIV) of tetrahydropentalenes (presumably II, XV and XVI), b.p. 129–131°, $n^{25}\text{D}$ 1.4852, was 1.23 g. (53%). After passage over silica gel, the material had $n^{25}\text{D}$ 1.4865. The infrared spectrum is given in Fig. 2. XIV had no ultraviolet absorption maxima between 220 and 350 mμ.

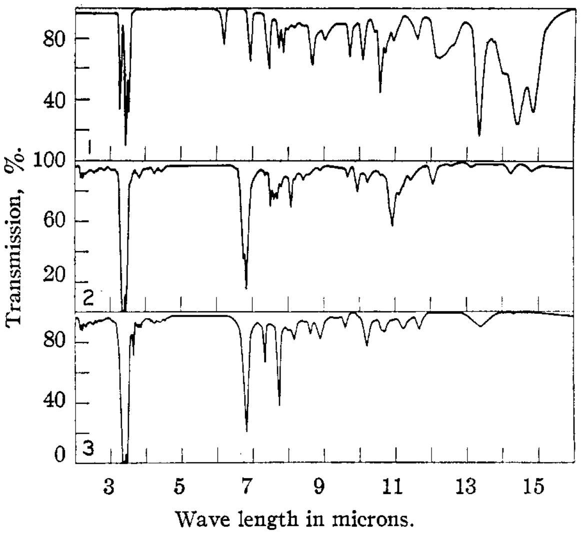

Fig. 2.—Infrared spectra: Baird spectrograph with NaCl prism, pure liquids in 0.025-mm. cell; (1) mixture of tetrahydropentalenes XIV, (2) *cis*-bicyclo[3.3.0]octane, (3) *trans*-bicyclo[3.3.0]octane.

Anal. Calcd. for C_8H_{10}: C, 90.57; H, 9.43. Found: C, 90.28; H, 9.62.

On catalytic hydrogenation in acetic acid over prereduced Adams catalyst, XIV absorbed 102–103% of the theoretical quantity of hydrogen for a diene and yielded *cis*-bicyclo-[3.3.0]octane, b.p. 135–137°, $n^{25}\text{D}$ 1.4584. After several passages over silica gel to remove the last traces of ether and acetic acid, the product had $n^{25}\text{D}$ 1.4593 and an infrared spectrum identical with that of *cis*-bicyclo[3.3.0]octane.

In an attempt to dehydrate 4 g. of XIII by heating it with 25 ml. of 98–100% formic acid at 100° for one hour, 3.4 g. (75%) of the formate was obtained, b.p. 98–100° (28 mm.), $n^{25}\text{D}$ 1.4838.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.07; H, 7.83. Found: C, 71.17; H, 8.07.

Attempted Dehydrogenation of Tetrahydropentalene Mixture XIV.—The details of one typical experiment will be given. The tetrahydropentalene mixture (1.0 g.) was vaporized in a preheater at 200° and passed through a bed of platinized asbestos at 360–380° over a period of 75 minutes. No more than 20 ml. ($\sim$ 5%) of the theoretical amount of hydrogen was liberated and the refractive index of the product was not significantly different from the starting material. Under similar conditions, cyclohexene liberated more than 50% of the theoretical amount of hydrogen in one passage over the catalyst. With platinized charcoal at 320–340°, XIV evolved less than 5% of the theoretical quantity of hydrogen while, with the same catalyst, tetralin liberated $\sim$ 90% of the theoretical amount of hydrogen.

Ethyl α-(Carbethoxymethyl)-cyclopentylidenecyanoacetate XVIII.—The following procedure is adapted from those of Cope and co-workers.[18] A mixture of 17.3 g. (0.10 mole) of ethyl 2-ketocyclopentaneacetate (XVII),[16] 4.8 g. (0.08 mole) of acetic acid, 1.93 g. (0.025 mole) of ammonium acetate, 11.3 g. (0.10 mole) of ethyl cyanoacetate and 30 ml. of benzene was heated in a 100-ml. flask equipped with water separator and reflux condenser for 15 hours with a bath at 130–140°. The mixture was cooled, 50 ml. of benzene and 30 ml. of ether were added and the whole washed with three 40-ml. portions of water. The solution was dried over magnesium sulfate and distilled. The yield of XVIII was 18 g. (68%); b.p. 172–174° (2.8 mm.), $n^{25}\text{D}$ 1.4831 (lit.[17] b.p. 177°, 2 mm.).

Preparation of *cis*- and *trans*-Cyclopentane-1,2-diacetic Acids.—A solution of 104 g. (0.39 mole) of XVIII in 300 ml. of 95% ethanol was shaken with hydrogen at 1–2 atm. over 2.5 g. of freshly prepared palladium-on-charcoal[24] for

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[23] A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950), describe a procedure particularly applicable to small quantities of hydrocarbons.

[24] *Org. Syntheses*, **26**, 78 (1946).

5 hours at the end of which time the theoretical amount of hydrogen had been absorbed. The catalyst was removed, the ethanol distilled under reduced pressure and the residue (110 g.) heated under reflux for 15 hours with 450 ml. of concd. hydrochloric acid. The hot solution was filtered and then steam distilled at constant volume until one liter of distillate was collected. The still residue was allowed to cool and 58 g. of crude product was obtained. Recrystallization from 500 ml. of boiling water (carbon) gave 35.5 g. of *cis-* and *trans*-cyclopentane-1,2-diacetic acids, m.p. 149.5°. A second crop had m.p. 138° and amounted to 3 g. From the m.p.-composition diagram,[17] the first crop contained 45% of the *trans-* and 55% of the *cis*-isomer. The second crop was 70% *trans-* and 30% *cis*-diacid. The yield was 38.5 g. (53% from XIX).

In some preparations, the intermediate reduction product was isolated. Thus, 24.2 g. of XIX yielded 17.4 g. (71%) of ethyl α-(carbethoxymethyl)-cyclopentylcyanoacetate, b.p. 150–153° (1.5 mm.), $n^{25}\text{D}$ 1.4599 (lit.[17] b.p. 172°, 2 mm.).

cis- **and** ***trans*-Bicyclo[3.3.0]octanes.**—The *cis-* and *trans-* β-bicyclo[3.3.0]octanones were prepared as described by Barrett and Linstead.[17] The *cis*-ketone, b.p. 88° (17 mm.), $n^{25}\text{D}$ 1.4772 (lit.[17] b.p. 78°, 10 mm., $n^{18}\text{D}$ 1.4811) was identified as the semicarbazone, m.p. 194–195° dec. (lit.,[17] m.p. 197–198° dec.) and yielded a **2,4-dinitrophenylhydrazone**, m.p. 115–116° (after crystallization from ethanol).

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.30; H, 5.26; N, 18.42. Found: C, 55.61; H, 5.29; N, 18.39.

The *trans*-ketone, b.p. 87–88° (22 mm.), $n^{25}\text{D}$ 1.4755 (lit.[17] b.p. 61–62°, 10 mm., $n^{18}\text{D}$ 1.4791) gave a semicarbazone, m.p. 243–244° dec. (lit.[17] m.p. 248–249° dec.), and a **2,4-dinitrophenylhydrazone** which had m.p. 156.5–157.5° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.30; H, 5.26; N, 18.42. Found: C, 55.22; H, 5.32; N, 18.66.

The infrared spectra of the *cis-* and *trans*-ketones as well as that for the *cis*-α-bicyclo[3.3.0]octanone (kindly supplied by Drs. A. C. Cope and W. R. Schmitz) are given in Fig. 1.

The procedure for the reduction of the ketones follows. A mixture of 1.8 g. of *cis*-β-bicyclo[3.3.0]octanone, 1.8 g. of hydrazine hydrate, 2.5 g. of potassium hydroxide and 24 ml. of *n*-butylcarbitol contained in a 50-ml. flask equipped with a 10-cm. Vigreux column was heated with a metal-bath to 200° over 90 minutes. The distillate was taken up in ether, washed with dilute hydrochloric acid and water, dried over magnesium sulfate and the ether removed. The residue was distilled through a micro-column[22] and yielded 1.2 g. (75% of *cis*-bicyclo[3.3.0]octane, b.p. 135–136°, $n^{25}\text{D}$ 1.4580 (lit.[17] b.p. 136–136.5°, $n^{18}\text{D}$ 1.4629). Passage over silica gel gave material of $n^{25}\text{D}$ 1.4598 presumably by removal of traces of ether. The infrared spectrum of the final product is given in Fig. 2.

trans-Bicyclo[3.3.0]octane was similarly prepared in 65% yield; b.p. 136–136.5°, $n^{25}\text{D}$ 1.4568 (lit.[17] b.p. 132°, $n^{18}\text{D}$ 1.4625). After passage over silica gel, the product had $n^{25}\text{D}$ 1.4592. The infrared spectrum is given in Fig. 2.

CABMRIDGE 39, MASSACHUSETTS

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Intramolecular Character of the Benzidine Rearrangement

BY D. H. SMITH, J. R. SCHWARTZ AND G. W. WHELAND

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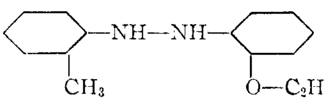
In an experiment designed to establish unambiguously whether the benzidine rearrangement is intra- or intermolecular, non-radioactive 2,2′-dimethylhydrazobenzene was rearranged in the presence of a comparable amount of 2-methylhydrazobenzene which had C^{14} in the side-chain. The radioactivity of the resulting 3,3′-dimethylbenzidine was so low that only a negligible part, and possibly none, of it could have been formed in an intermolecular reaction. It is therefore concluded that the rearrangement is intramolecular. In the search for a pair of hydrazo compounds which would be suitable for a study of the type just described, a number of hitherto unreported members of this class were prepared and rearranged. With the use of C^{14} as a tracer, the relative rates with which several different pairs of hydrazo compounds rearrange to the corresponding benzidines was measured.

The benzidine rearrangement is commonly believed to be intramolecular since it has never been found to give rise to cross products.[1] Thus, in 1922, Jacobson[2] listed all the previously reported rearrangements of unsymmetrical hydrazo compounds Ar–NH–NH–Ar′; in no one of these 65 different reactions had the formation of a symmetrical benzidine with two like radicals Ar or Ar′ been observed. Since, however, the presence of considerable quantities of such cross products might easily have been missed in this earlier work, Wheland and Schwartz[3] have more recently studied, with the aid of C^{14} as a tracer, the rearrangement of 2-methyl-2′-ethoxyhydrazobenzene (I). In this way, they showed that less than about 0.3%, and possibly none, of the cross product, *o*-tolidine (II), was formed. Such reactions as these, however, cannot provide conclusive evidence that the rearrangements are purely intramolecular, since the fact that they give no detectable cross products is not necessarily inconsistent with the belief that they proceed by a dissociation into fragments, which subsequently recombine. Indeed, if the postulated dissociation leads to two dissimilar fragments (say, a cation and a neutral molecule), and if it leads always to exactly the same two fragments, then cross products would not be expected since they could then be formed only by the combination of two like fragments. In order to avoid this difficulty, Ingold and Kidd[4] rearranged mixtures of 2,2′-dimethoxyhydrazobenzene and 2,2′-diethoxyhydrazobenzene. Here, regardless of the detailed mechanism, the cross product, 3-methoxy-3′-ethoxybenzidine, should accompany the two symmetrical benzidines if any



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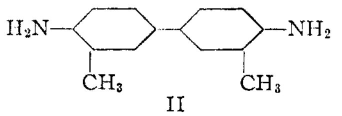

II

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[1] The term "cross product" is here used to signify a benzidine, the molecule of which contains one aryl group derived from each of two different hydrazo molecules. Clearly, a cross product can be formed only in an *inter*molecular reaction.

[2] P. Jacobson, *Ann.*, **428**, 76 (1922).

[3] G. W. Wheland and J. R. Schwartz, *J. Chem. Phys.*, **17**, 425 (1949).

[4] C. K. Ingold and H. V. Kidd, *J. Chem. Soc.*, 984 (1933).