aqueous extracts were evaporated to dryness under reduced pressure. Distillation of the residue gave 1.2 g. (73%) of 2-methyl-4-hydroxycyclohexanone (XVIIb), b.p. 119–120° (4 mm.). Benzoylation of this material regenerated the keto-benzoate XVIIa as a mixture of isomers which again only crystallized partially.

Sodium (0.12 g.) was dissolved in 6 cc. of dry methanol and this solution was added to a stirred mixture of 0.77 g. of the above hydroxy-ketone XVIIb and 1-diethylaminobutan-3-one methiodide (prepared from 0.95 g. of IV and 0.9 g. of methyl iodide) in 7 cc. of dry benzene, the operation being conducted under nitrogen. The reaction mixture was stirred overnight at room temperature and then for 1.5 hours under reflux. Acetic acid (1 cc.) was added and the product was then isolated with ether in the usual way. The oily product (0.75 g.) was chromatographed on 30 g. of alumina. The fractions eluted with ether–chloroform (1:1) on crystallization from hexane–benzene gave *ca.* 30 mg. of the unsaturated keto-alcohol XIX, m.p. 102–103°, λ_{max} 242 mμ (ϵ 15,100).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.05; H, 8.96.

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

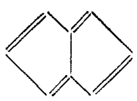
An Attempted Synthesis of the Pentalene Ring System

BY MARSHALL GATES AND S. PAUL MALCHICK[1]

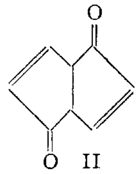
RECEIVED MAY 14, 1957

A synthetic approach to the pentalene ring system starting with dicyclopentadiene has been explored. Two isomeric vinyl substituted bicyclo[3.3.0]octadienes have been shown to yield what appears to be azulene on dehydrogenation.

The as-yet-unknown hydrocarbon pentalene[2] (I) is of great theoretical interest and has been the subject of a number of quantum mechanical treatments,[3] the most refined of which[3c] suggests that the hydrocarbon will not have aromatic stability. In agreement with this conclusion is the failure of a number of attempts to produce it by dehydrogenation of either saturated or unsaturated bicyclo-[3.3.0]octane derivatives[4] and the complete failure of the unsaturated diketone II to exhibit enolic properties.[5]



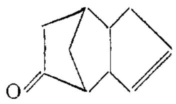
I



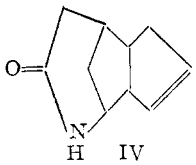
II

We wish to record yet another failure to obtain the pentalene system by dehydrogenation together with the additional observation that ethyl- or vinylpentalene apppears to be thermodynamically unstable relative to azulene.

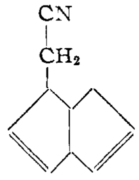
The unsaturated *exo*-ketone III, easily available from dicyclopentadiene (*endo*)[6] and containing the bicyclo[3.3.0]octane system pre-formed,[7] served as starting material. Its oxime[6a] on Beckmann rearrangement yields a mixture of the lactam IV and the nitrile V, the latter the result of second-order Beckmann rearrangement, and both of these substances were used in subsequent operations.[8] As shown below, they have the same carbon skeleton, that with a two carbon atom side chain in the 1-position of the bicyclo[3.3.0]octane system. The isomeric substances with two single carbon atom substituents in the 1- and 3-positions were not encountered.



III



IV



V

The nitrile V, which was characterized by conversion to the corresponding unsaturated and saturated acids, yields the amine VI on reduction with lithium aluminum hydride. Methylation of VI, successively with formaldehyde–formic acid and methyl iodide, yielded the methiodide VIII through the tertiary amine VII. The saturated compounds X and XI were similarly produced from the saturated amine IX obtained by hydrogenation of VI.

Hofmann degradation of the quaternary base corresponding to VIII gave a triply unsaturated hydrocarbon (XII) in insufficient quantity to purify rigorously but which showed infrared maxima at 10.07 and 11.01 μ associated with the vinyl group. Further, the presence of conjugation in the hydrocarbon was clearly shown by its maximum at 238 mμ in the ultraviolet. This conjugation must have been introduced during the degradation inasmuch as the doubly unsaturated amine VII shows no maximum in the ultraviolet.

The unsaturated hydrocarbon XIII produced similarly from XI also exhibits infrared absorption at 10.1 and 11.02 μ attributable to the vinyl group

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[1] Celanese Corporation Fellow, 1951–1952.

[2] J. W. Armit and R. Robinson, *J. Chem. Soc.*, **121**, 827 (1922).

[3] (a) C. A. Coulson and G. A. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940); (b) D. P. Craig and A. Maccoll, *J. Chem. Soc.*, 964 (1949); (c) D. P. Craig, *ibid.*, 3175 (1951); R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).

[4] (a) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936); C. T. Blood and R. P. Linstead, *ibid.*, 2255, 2263 (1952); (b) J. D. Roberts and W. F. Gorham, THIS JOURNAL, **74**, 2278 (1952).

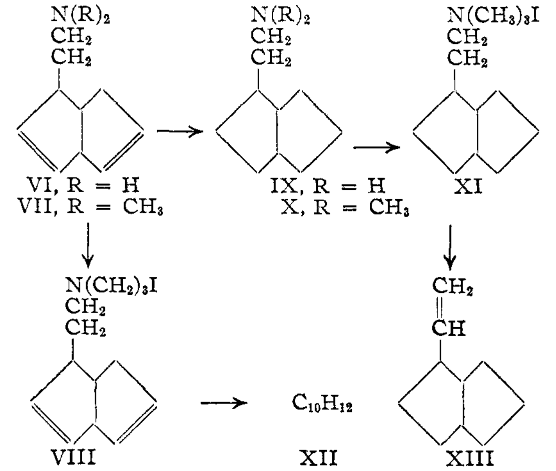
[5] H. J. Dauben, Jr., Victor R. Ben and S. H. K. Chiang, Abstracts of Papers Presented at Los Angeles, Calif., March 15 to March 19, 1953, American Chemical Society.

[6] (a) H. A. Bruson and T. W. Reiner, THIS JOURNAL, **67**, 723 (1945); (b) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

[7] Several other approaches from dicyclopentadiene also appear promising and some have been investigated. The action of performic acid on dicyclopentadiene yields a rearranged glycol of no immediate use; *cf.* M. Gates and S. P. Malchick, *ibid.*, **76**, 1378 (1954).

[8] The double bonds of III and IV and their derivatives have been assigned the position shown on the assumption that the hydration-rearrangement by which the precursor of III is formed from dicyclopentadiene[6b] is favored when the double bond is in the allylic position to that undergoing rearrangement. This assignment is, of course, not rigorous, nor is the assignment of the positions of the double bonds in V.

and these maxima disappear on hydrogenation. The presence of the vinyl group in XII and XIII clearly justifies the assignment of the 1-ethylbicyclo[3.3.0]octane skeleton to the members of this series.[9]

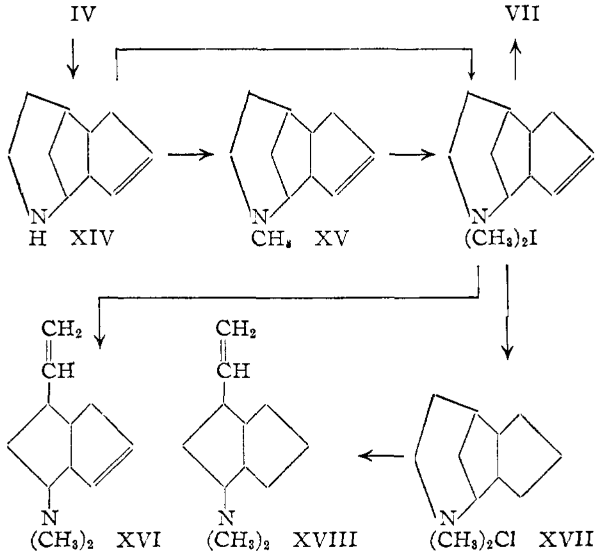


VI, R = H
VII, R = CH$_3$
IX, R = H
X, R = CH$_3$
XI
VIII
XII
XIII

Reduction of the lactam IV with lithium aluminum hydride gave the amine XIV in 80–87% yield, from which the quaternary methiodide could be prepared directly in 96% yield. Hofmann degradation of the quaternary bases below 75°[10] yielded a mixture of amines which could be separated easily through their picrates, one of which (m.p. 156–157°) is sparingly soluble in alcohol, the other of which was too soluble to crystallize from this solvent. The amine recovered from the soluble picrate was identical with the tertiary amine VII from the nitrile series. This identity, which served to demonstrate the common carbon skeleton of the nitrile V and the lactam IV, and which provided additional supplies of VII, was established by the correspondence in m.p. and mixed m.p. of the methiodide and of the tetrahydromethiodide and picrate.

The sparingly soluble picrate yielded a base whose infrared spectrum again shows the absorption bands (10.08 and 11.01 μ) attributable to the vinyl group, and which therefore must have the structure XVI.[11]

Hydrogenation of the quaternary methochloride of XIV gave the saturated substance XVII which on degradation yielded an olefinic base XVIII again showing the vinyl absorption in the infrared. Both XVI and XVIII can be hydrogenated to the corresponding saturated substance with loss of the vinyl absorption.

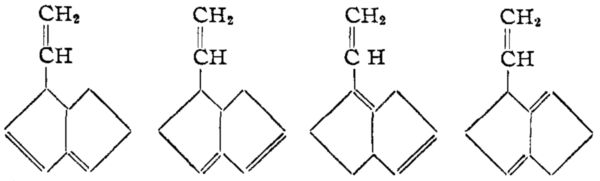


XIV
XV
XVI
XVIII
XVII

The quaternary methiodide of XVI on Hofmann degradation yields a second triply unsaturated hydrocarbon $C_{10}H_{12}$ (XIX), again obtained in too small amount for rigorous purification. It exhibits an absorption maximum in the ultraviolet at 247 mμ.[12]

Small samples of both hydrocarbons XII and XIX were subjected to dehydrogenation over palladized asbestos at 300°. XIX yielded a small amount of deep blue-green oil which could be separated by chromatography on alumina into a deep blue fraction and a deep green fraction. Neither fraction was obtained in sufficient quantity to characterize or identify, although the ultraviolet spectrum of each had broad maxima at 240, 281 and about 342–348 mμ, and was in general similar to that of azulene, but with the fine structure absent. XII yielded two substances, a yellow hydrocarbon, $C_{10}H_{12}$, λ_{max} 252 mμ,[13] isomeric with XII; and a deep

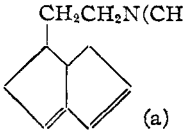
(9) There are not enough ultraviolet data on suitably selected model substances containing five-membered rings to allow the assignment of structure to XII to be made with confidence on the basis of its absorption at 238 mμ. About all that can be said is that application of the Woodward rules (THIS JOURNAL, **64**, 72 (1942)) suggests that XII, if homogeneous, has one of the structures



the first three on the assumption that a double bond exocyclic to a five membered ring exerts a bathochromic shift of 5 mμ, the last on the assumption that no such effect is produced.

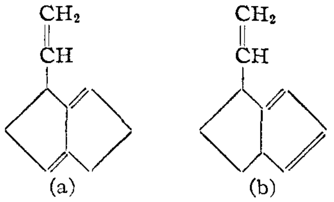
(10) At higher temperatures appreciable amounts of undegraded tertiary amine were formed.

(11) VII and XVI are the only substances expected from the Hofmann degradation, inasmuch as the formation of the remaining structure possibility (a) would involve the bridgehead hydrogen which is *cis* to the amino group in XIV (the original ketone has the *exo* configuration).



(a)

(12) This value suggests structures (a), assuming an exocyclic effect (*vide supra*), or (b) (no exocyclic effect) inasmuch as this absorption



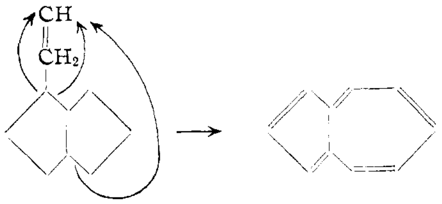
(a) (b)

is well beyond that expected of any substance in which conjugation involves the vinyl group (≤237 mμ). Five-membered rings containing two double bonds absorb at longer wave lengths than the conjugated systems originally treated by Woodward (ref. 9). Thus cyclopentadiene absorbs at 241 mμ and 1-methyl-1,3-cyclopentadiene at 247 mμ. The bathochromic shift produced by the methyl group in the latter case corresponds to the substitution effect of the Woodward rules.

(13) If this substance retains the carbon skeleton of XII, it must be one of the isomeric triolefins containing two double bonds in one of the five-membered rings.

blue partially crystalline substance whose ultraviolet spectrum (maxima at 240, 270, 274, 282, 328, 342 and 354) was essentially superimposable on that of azulene.

Although none of the dehydrogenation products was conclusively identified, the conclusion that azulene is formed from both triply unsaturated hydrocarbons XII and XIX, perhaps in larger quantities from XII, seems inescapable.



If this is so, the results clearly indicate that an ethyl- or vinylpentalene is thermodynamically unstable relative to azulene.

Acknowledgment.—We gratefully acknowledge the aid of the Celanese Corporation of America, whose grant to the Department of Chemistry of this University supported a part of this work.

Experimental[14]

Beckmann Rearrangement of the Oxime of III.—The oxime of the ketone III was prepared according to Bruson and Riener.[6a] It was found that the crude distillate of the oxime contained a considerable quantity of ketone and that crystallization was therefore necessary in order to obtain reasonably pure material.

A solution of 34.6 g. (0.22 mole) of the crude solid oxime, m.p. 94–104°, in 300 ml. of 5 *N* sodium hydroxide was treated with 39 g. (0.22 moles) of C.P. benzenesulfonyl chloride added in small portions. After a short induction period the reaction began. (It is not necessary to cool the reaction mixture, but large excesses of benzenesulfonyl chloride should be avoided.)

The mixture gradually became cloudy and turned light brown. Stirring was continued until the reaction mixture cooled almost to room temperature. The products were taken up in chloroform, washed with water, dried, and the solvent removed. The residue was a thick sweet-smelling liquid which on distillation gave two fractions, the first a light yellow oil, b.p. 103–106° (6 mm.), 136–140° (24 mm.) (6.15 g.); the second a very viscous almost colorless liquid, b.p. 156–160° (1 mm.), which slowly solidified (22.4 g.).

The first of these was largely the **nitrile V** (infrared max. 4.49 μ) but was seriously contaminated by some carbonyl-containing substance, possibly starting ketone, as shown by its infrared spectrum (strong band at 5.75 μ). It was used without further purification in the work to follow. A sample for analysis was obtained by heating it under reflux with Girard reagent T in alcohol containing a small amount of acetic acid for 1 hr. The nitrile was extracted from the diluted reaction mixture with ether, the ether extract was washed, dried and concentrated, and the residue was distilled to give the nitrile, essentially free of carbonyl impurities, as a colorless mobile oil (5.55 g. from 6.15 g. crude b.p. 109–111° (5 mm.), $n^{29}\mathrm{D}$ 1.4976.

Anal. Calcd. for $C_{10}H_{11}N$: N, 9.65. Found: N, 9.55.

The second fraction was recrystallized from ether. Large rhombohedra of the **lactam IV**, m.p. 80–81°, were obtained.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.58; H, 8.03; N, 8.58. Found: C, 73.58; H, 8.17; N, 8.73.

Benzylthiouronium Salt of 1-Bicyclo[3.3.0]-2,4-octadienylacetic Acid.—A solution of 2.7 g. of crude nitrile V in 100 ml. of alcohol was added to a concentrated aqueous sodium hydroxide solution and the mixture was heated under reflux for 16 hours. The alcohol was removed, water was added, and the solution was extracted with ether to remove neutral material. The basic solution was acidified and extracted with ether. The ether solution was extracted with bicarbonate solution, the extract acidified and then extracted again with ether. The ether was evaporated leaving 0.5 g. of a strong-smelling oil. It formed a benzylthiouronium salt, m.p. 155–155.5°.

Anal. Calcd. for $C_{18}H_{22}N_2O_2S$: C, 65.42; H, 6.71. Found: C, 65.86; H, 6.97.

Benzylthiouronium Salt of 1-Bicyclo[3.3.0]octanylacetic Acid.—An alcoholic solution of 0.8 g. of the unsaturated acid was hydrogenated over platinum oxide at atmospheric pressure. The compound took up 81% of the theoretical amount of hydrogen in 7 hours. The catalyst and solvent were removed and the benzylthiouronium salt of the residual oil was prepared. Recrystallization from dilute alcohol gave material of m.p. 159.5–160°.

Anal. Calcd. for $C_{18}H_{26}N_2O_2S$: C, 64.64; H, 7.86. Found: C, 64.90; H, 7.90.

β-(1-Bicyclo[3.3.0]-2,4-octadienyl)-ethylamine (VI).—A solution of lithium aluminum hydride in ether was added to the nitrile in dry ether at 0°. After short standing, the complex was decomposed carefully with water. Excess dilute hydrochloric acid was added and the acid layer was slowly dropped into a solution of 20% sodium hydroxide and 5% sodium potassium tartrate. The liberated oil was taken into ether, dried and concentrated, and the amine was distilled, b.p. 114° (12 mm.), $n^{20}\mathrm{D}$ 1.5050.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.73; H, 10.32.

Dimethyl-β-(1-bicyclo[3.3.0]-2,4-octadienyl)-ethylamine (VII).—The primary amine VI (1.3 g., 0.009 mole) was dissolved in 2.24 g. of 90% formic acid and 1.64 g. (0.02 mole) of 35% formalin solution was added. The reaction mixture was refluxed for 12 hours, diluted with water, neutralized with sodium hydroxide and the liberated oil taken into ether. The ether was dried and concentrated and the residual liquid distilled to give 0.99 g. (0.0055 mole, 63%) of a colorless amine, $n^{20}\mathrm{D}$ 1.4881. The substance exhibits no absorption maximum in the ultraviolet.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.80. Found: C, 80.95; H, 11.15.

Its methiodide VIII on recrystallization from alcohol–ethyl acetate gave colorless cubes, m.p. 152.4–155°.

Anal. Calcd. for $C_{13}H_{22}NI$: C, 48.91; H, 6.95. Found: C, 48.55; H, 7.05.

β-(1-Bicyclo[3.3.0]octanyl)-ethylamine (IX).—The unsaturated amine VI (3.85 g., 0.026 mole) was dissolved in ethanol and hydrogenated over platinum oxide at atmospheric pressure. After one hour 1250 cc. of hydrogen (99%) had been taken up. The catalyst and solvent were removed and the product was distilled in a molecular still to give 3.59 g. (0.0234 mole, 91%) of colorless liquid, $n^{20}\mathrm{D}$ 1.4891.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50. Found: C, 77.96; H, 12.63.

The amine reacted with phenyl isothiocyanate to form a substituted **phenylthiourea** which was recrystallized from alcohol, m.p. 141–142°.

Anal. Calcd. for $C_{17}H_{24}N_2S$: C, 70.78; H, 8.39. Found: C, 70.62; H, 8.58.

Dimethyl-β-(1-bicyclo[3.3.0]octanyl)-ethylamine (X).—The saturated amine (3.59 g., 0.0234 mole) was dissolved in 6 g. of 90% formic acid, 4.42 g. of 35% formalin was added and the mixture was refluxed for about 12 hours. After dilution with water the mixture was made alkaline with sodium hydroxide and extracted with chloroform. The chloroform solution was dried, the solvent removed and the residue was distilled in a molecular still giving 2.65 g. (0.0146 mole, 62.4%) of colorless tertiary amine, $n^{20}\mathrm{D}$ 1.4740.

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.78. Found: C, 79.42; H, 12.79.

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[14] Melting points are corrected, boiling points are uncorrected. Most of the analyses were carried out by Miss Claire King and Miss Annette Smith. The infrared spectra were carried out by Mr. Carl Whiteman on Nujol mulls or on homogeneous liquid samples with a Perkin–Elmer infrared spectrophotometer, model 12c, equipped with sodium chloride optics. Ultraviolet spectra were carried out on a Beckman ultraviolet spectrophotometer, model DU, cell 1 cm., in alcohol.

Its picrate was recrystallized from a small amount of alcohol, m.p. 113.7–114.4°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.67; H, 6.39. Found: C, 53.07; H, 6.65.

Its methiodide XI formed readily and was recrystallized from ethanol–ethyl acetate, m.p. 236–238°.

Anal. Calcd. for $C_{13}H_{26}NI$: C, 48.30; H, 8.11. Found: C, 48.49; H, 8.34.

1-Vinyltetrahydropentalene (XII).—A solution of 1.46 g. (0.0045 mole) of the methiodide VIII in methanol was passed over a column of Amberlite IRA-400 ion exchange resin which had previously been converted to the hydroxide form. The methanol was removed carefully under reduced pressure and the residue was transferred to a molecular still and heated to 90–110° at 12 mm. The distillate was a colorless liquid which was dissolved in pentane and extracted with dilute aqueous hydrochloric acid. The pentane solution was dried and the solvent distilled leaving a colorless liquid with a typical olefinic odor, which was distilled in a molecular still giving 0.2 g. (33%) of the triolefin, n^{20}D 1.5156; ultraviolet max. 238 mμ; infrared max. 10.07 and 11.01 μ.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.15; H, 9.34.

1-Vinylbicyclo[3.3.0]octane (XIII).—The methiodide XI (3.6 g.) was converted to the hydroxide by passing a methanolic solution over IRA-400 resin. Methanol was removed carefully under reduced pressure and the residue was distilled in a molecular still at 100° and 15 mm. The colorless distillate was taken up in petroleum ether (30–60°), washed with dilute hydrochloric acid, dried and the solvent evaporated. The product was redistilled through a short-path still at atmospheric pressure (block temp. 100°); yield 0.3 g., infrared max. 10.1 and 11.02 μ.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.15; H, 11.84. Found: C, 88.51; H, 12.31.

1-Ethylbicyclo[3.3.0]octane.—About 200 mg. of the unsaturated hydrocarbon XIII was hydrogenated over platinum oxide in pentane at atmospheric pressure. After uptake of hydrogen had ceased, the catalyst was removed and the solvent evaporated to leave 150 mg. of product which was redistilled through a short-path still at atmospheric pressure (block temp., 100–110°); no infrared max. at 10 or 11 μ.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 87.18; H, 13.08.

Lithium Aluminum Hydride Reduction of Lactam IV.—An anhydrous solution of 5.35 g. (0.033 mole) of IV in ether was added to 60 ml. of 1 *M* lithium aluminum hydride in ether and the mixture was refluxed for 24 hours. The excess reagent was decomposed carefully with water, and then excess dilute hydrochloric acid was added to dissolve the alumina. The acidic layer was dropped slowly into a concd. sodium hydroxide–Rochelle salt solution. The liberated amine was taken into ether, dried, the solvent removed and the residual liquid distilled to give 4.27 g. (0.029 mole, 87.2%) of pure colorless amine XIV, b.p. 128° (25 mm.), n^{20}D 1.5260.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.94; H, 9.99.

An alcoholic solution of 4.10 g. (0.0275 mole) of amine and 2.0 g. of potassium hydroxide was treated with excess methyl iodide. The solid **methiodide** precipitated gradually and when collected and dried amounted to 8.04 g. (0.0264 mole, 95.6%) of colorless crystals which on recrystallization from water gave large needles, m.p. 275° dec.

Anal. Calcd. for $C_{12}H_{20}NI$: C, 47.22; H, 6.72. Found: C, 47.52; H, 6.84.

Methylation of Amine XIV.—One gram of the amine was dissolved in 1.9 g. of 90% formic acid and 0.7 g. of 35% formalin added. The mixture was refluxed several hours, made alkaline with sodium hydroxide solution and extracted with ether. The ether solution was dried and the solvent removed. The residual oil was distilled in a molecular still at 12 mm. (block temp. 100–120°) to give 0.7 g. of the tertiary amine XV as a colorless liquid, n^{20}D 1.5099.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50. Found: C, 80.95; H, 10.49.

Its picrate, recrystallized from ethanol, melted at 223–224°.

Anal. Calcd. for $C_{17}H_{20}N_4O_7$: C, 52.04; H, 5.14. Found: C, 51.57; H, 5.10.

Hydrogenation of XV.—The tertiary amine XV (100 mg.) was hydrogenated over platinum oxide in ethanol at atmospheric pressure. The catalyst and solvent were removed and the product converted to the picrate and the methiodide. **Its picrate** was recrystallized from ethanol, m.p. 219–220°.

Anal. Calcd. for $C_{17}H_{22}N_4O_7$: C, 51.77; H, 5.62. Found: C, 52.09; H, 5.99.

The methiodide was recrystallized from ethanol–ethyl acetate, m.p. 251–252°.

Anal. Calcd. for $C_{12}H_{22}NI$: C, 46.91; H, 7.22. Found: C, 46.71; H, 7.26.

1-Vinyl-3-dimethylaminobicyclo[3.3.0]octene-4 (XVI) and Dimethyl-β-(1-bicyclo[3.3.0]-2,4-octadienyl)-ethylamine (VII).—A solution of 8 g. (0.0262 mole) of the methiodide of XIV in methanol was passed over an ion exchange column (IRA-400) to convert it to the methohydroxide. The solvent was removed carefully under reduced pressure, and the residue was transferred to a molecular still and heated to 73–75°[15] at 1–2 mm. pressure. The product distilled as a colorless liquid, n^{27}D 1.4934, 284 g. (0.016 mole, 61%).

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80. Found: C, 81.32; H, 10.86.

Addition of this substance to an ethanolic solution of picric acid caused the deposition of a solid picrate which was recrystallized from ethanol, m.p. 157–158°; yield of pure picrate, 3.08 g.

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.48; H, 5.62; N, 14.12.

The amine XVI was recovered from this pure picrate by liberation with aqueous lithium hydroxide and extraction with chloroform. The distilled amine, n^{20}D 1.4946, gave a **methiodide**, m.p. 220–222°, long needles from ethanol–ethyl acetate.

Anal. Calcd. for $C_{13}H_{22}NI$: C, 48.91; H, 6.95; N, 4.39. Found: C, 48.96; H, 6.77; N, 4.57.

The mother liquor from the solid picrate was concentrated, dilute lithium hydroxide solution was added and the liberated oil taken up in chloroform. The solution was dried, the solvent removed and the residual liquid distilled. The product formed a **methiodide**, m.p. 152–155°, from ethanol–ethyl acetate, mixed melting point with methiodide of VII, 152–155°. The amine was hydrogenated over platinum oxide in ethanol, and the product converted to its **picrate**, m.p. 113–114°, mixed m.p. with picrate of X, 113–114°; and a **methiodide**, m.p. 236–238°, mixed m.p. with methiodide of X, 236–238°.

1-Ethyl-3-dimethylaminobicyclo[3.3.0]octane.—An alcoholic solution of 0.6 g. of unsaturated amine XVI was hydrogenated over platinum oxide at atmospheric pressure. After one hour uptake of hydrogen ceased at 96.4% of the theory for two double bonds. The product was a colorless liquid, n^{20}D 1.4794.

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.78. Found: C, 79.5; H, 12.77.

Its picrate crystallized as needles from ethanol, m.p. 157–158°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.67; H, 6.39. Found: C, 52.85; H, 6.57.

Its methiodide crystallized from ethanol–ethyl acetate, m.p. 264° dec.

Anal. Calcd. for $C_{13}H_{26}NI$: C, 48.29; H, 8.11. Found: C, 48.39; H, 8.11.

1-Vinyl-3-dimethylaminobicyclo[3.3.0]octane (XVIII).—A solution of 2.5 g. of the methiodide of XIV in ethanol was converted to the chloride by passing over an IRA-400 column and the solution directly hydrogenated over platinum oxide at atmospheric pressure; 98% of the theoretical amount of hydrogen was taken up in 50 minutes. The

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[15] If the degradation is carried out above 75°, another compound distils with the other products. Its picrate is difficult to separate from that of the degraded amine. Hydrogenation of the mixture of amines and subsequent formation of the picrates gave a relatively insoluble picrate, m.p. 219–220° from ethanol, mixed m.p. with the picrate of hydrogenated XV, 219–220°.

catalyst was removed and the solution passed over another IRA-400 column to convert the methochloride to the methohydroxide. The solvent was carefully removed under reduced pressure, and the residue transferred to the molecular still and heated to 75° at 1–2 mm. A colorless liquid distilled at this temperature, $n^{20}\text{D}$ 1.4810, infrared max. 10.08 and 11.01 μ.

Anal. Calcd. for $C_{12}H_{21}N$: C, 80.38; H, 11.81. Found: C, 80.33; H, 11.89.

Its picrate, recrystallized from alcohol, melted at 170.4–171.2°.

Anal. Calcd. for $C_{18}H_{24}N_4O_7$: C, 52.93; H, 5.92. Found: C, 53.23; H, 6.11.

Its methiodide crystallized from alcohol–ethyl acetate and gave the same range after repeated recrystallization, m.p. 186–200°.

Anal. Calcd. for $C_{13}H_{24}NI$: C, 48.60; H, 7.52. Found: C, 48.78; H, 7.55.

1-Vinyltetrahydropentalene (XIX).—A methanolic solution of 425 mg. (0.0014 mole), of the methiodide of XVI was passed over an IRA-400 column (hydroxide form), the solvent distilled carefully under reduced pressure, and the residue transferred to the molecular still and heated to 100–130° at 15 mm. The distillate was taken into pentane, washed with dilute hydrochloric acid, dried and the pentane evaporated leaving 74 mg. (0.00056 mole, 41%) of the hydrocarbon, ultraviolet max. 247 mμ.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 89.72; H, 9.19.

The picrate of trimethylamine was formed from the products in the Dry Ice trap of the distillation system, m.p. 216–223°, from alcohol.

Attempted Dehydrogenation of XII.—A stream of nitrogen was passed over the 1-vinyltetrahydropentalene (XII) and the vapors were passed through a tube packed with 5% palladinized asbestos and 10% palladium-on-charcoal at 300–310°. The product was a deep blue oil which collected at the end of the tube. The oil was washed out with pentane and chromatographed on alumina in pentane. The first band gave about 30 mg. of a yellow liquid after evaporation of the solvent. Its infrared and ultraviolet spectra were different from those of the starting material (ultraviolet max. 252 mμ).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.64; H, 9.39.

The second fraction gave 3.5 mg. of a deep blue partially crystalline material. No infrared curve was obtained. Its ultraviolet spectrum (arbitrary extinction scale) was essentially identical with that of azulene, showing maxima at 240, 270, 274, 282, 328, 342 and 354 mμ.

Attempted Dehydrogenation of XIX.—A stream of nitrogen was passed slowly over 40 mg. of XIX and the vapors were passed through a tube containing 5% palladinized asbestos at 300–310°. Blue crystals began to form at the end of the tube, but these soon disappeared in the wake of a deep green oil. The product was washed out of the tube with pentane and passed over an alumina column. Elution with pentane gave a pale blue band, which passed readily into the filtrate to yield less than 1 mg. of material, ultraviolet max. 240, 281, 342–348 mμ. The bright green band was eluted with benzene. Evaporation of the solvent gave 3 mg. of a deep green oil. This compound gave an ultraviolet spectrum almost identical with that of the blue material.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY]

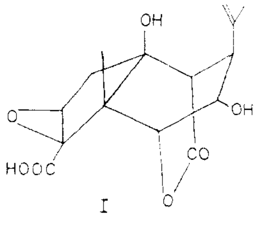
Picrotoxin. V. Conformational Analysis and Problems of Structure[1]

BY HAROLD CONROY

RECEIVED MAY 7, 1957

Conformational analytic principles are employed to account for reactivities in the picrotoxinin series. Structural expressions are proposed for picrotoxinin itself, and for those of its transformation products known as bromopicrotoxinin, picrotoxic acid, Schlittler's "Compound C," picrotoxinindicarboxylic acid and its esters.

In part III[1c] of this series we outlined the development of structural formulas for the α-picrotoxininic and bromopicrotoxininic acids (I and II). This and subsequent papers will show that the conclusions presented there can be broadened to include all other substances in the picrotoxin group and most particularly, the parent naturally occurring compounds, picrotoxinin and picrotin.



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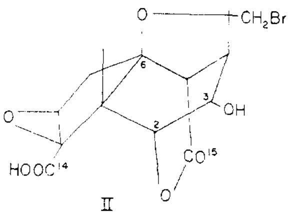

II

β-Bromopicrotoxininic acid (II) is prepared[2,3] by the action of aqueous alkali upon the dilactone, β-bromopicrotoxinin, but the process does not involve merely the opening of a lactone to the corresponding hydroxy-acid; we see that the dilactone formally derived from II by abstraction of the elements of water from the C-14 carboxyl and the C-3 hydroxyl is sterically impossible. The infrared spectra[1a,1c] suggest that the brominated derivative contains two somewhat strained five-membered lactones (absorption near 1790 cm.$^{-1}$) neither of which is present in the acid (1742 and 1705 cm.$^{-1}$ or 1769 and 1745 cm.$^{-1}$; *cf.* ref. 1c, footnote 13); moreover the bromodilactone shows no hydroxyl absorption in the infrared. *The formulation for β-bromopicrotoxinin is given in III.*[4] The action of alkali upon III, in striking contrast to the result with picrotoxinin itself (*vide infra*), then must involve transesterification, probably through the intermediate IV; the driving force for the formation of this lactonic acid (II) with one equivalent[6] of base is considered to be due both to the more effective inductive sta-

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[1] The previous articles in this series appear in (a) THIS JOURNAL, **74**, 491 (1952); (b) **74**, 3046 (1952); (c) **79**, 1726 (1957); (d) *Chemistry & Industry*, 704 (1957). In a brief preliminary report ((e) THIS JOURNAL, **73**, 1889 (1951)), structures for picrotoxinin and picrotoxic acid were proposed on the basis of the more limited evidence then available.

[2] R. J. Meyer and P. Bruger, *Ber.*, **31**, 2985 (1898).

[3] P. Horrmann, *ibid.*, **45**, 2090 (1912); *ibid.*, **46**, 2793 (1913); *Ann.*, **411**, 273 (1916).

[4] The reservations of footnote 11, ref. 1c, with regard to the precise formulation of the β-bromoether linkage still apply. We do not find the arguments of the New Zealand group[5] convincing on this score.

[5] R. B. Johns, S. N. Slater, R. J. Woods, D. Brasch and R. Gee, *J. Chem. Soc.*, 4715 (1956).

[6] The reaction with excess of hot aqueous base upon II or III leads ultimately to opening of the oxide ring; *cf.* ref. 1c.