[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Cyclization of Dieneynes. V.[1] Hydrophenanthrenes

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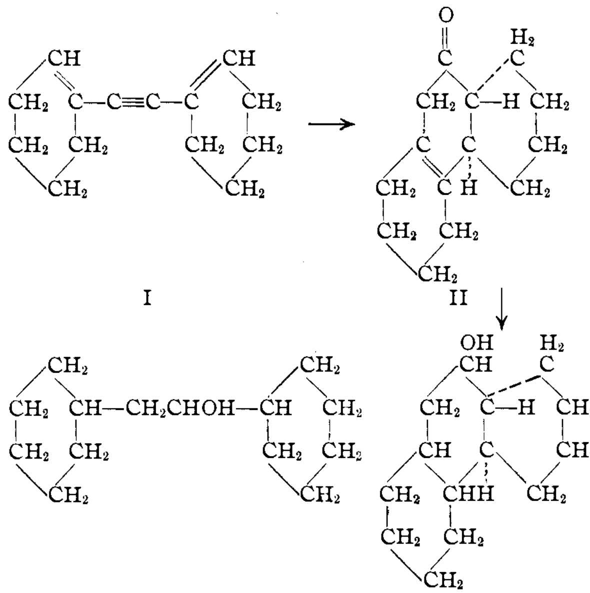
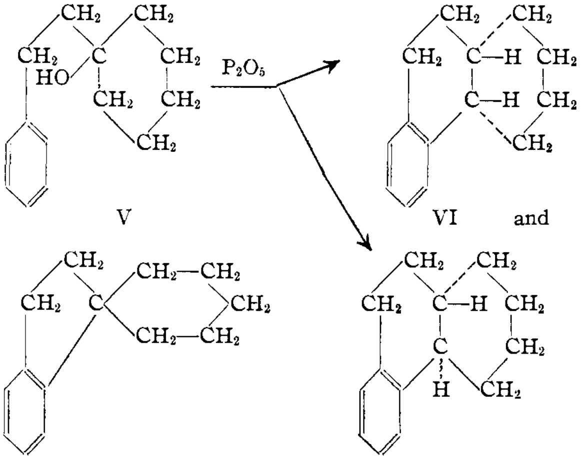
Previous work indicates[1] that the cyclization of dieneynes to produce polynuclear compounds leads to molecules which have the *trans* configuration at the saturated carbon atoms common to the two fused rings. Thus the conversion of di-Δ^1-cyclohexenylacetylene (I) to Δ^{11}-dodecahydrophenanthrone-9 (II) reported earlier[3] would be expected to yield the *trans* isomer.

Since it is important to have a synthetic method which will produce hydrophenanthrenes of known configuration it seemed desirable to have further proof of the cyclic nature of the ketone (II). Catalytic reduction of this ketone with hydrogen over Raney nickel[4] gave an alcohol, tetradecahydrophenanthrol-9 (III) which was entirely different in its physical properties from the open chain alcohol (IV) obtained by the reduction of benzyl Δ^1-cyclohexenyl ketone (X). There can thus be no question that the ketone is the cyclic product indicated.



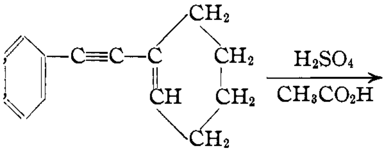
I II IV III

Δ^{11}-Dodecahydrophenanthrene, prepared by the reduction of the cyclic ketone[3] or directly by Clemmensen[5] reduction of the acetylenic glycol, was partially dehydrogenated when it was heated with selenium. The dehydrogenation product was found to be identical with the *trans-as*-octahydrophenanthrene (VII) which has been reported by van de Camp and Mosettig[6] as being formed along with the *cis* isomer (VI) by the phosphorus pentoxide dehydration of 1,β-phenylethylcyclohexanol (V). Perlman, Davidson and Bogert[7] treated this alcohol (V) with sulfuric acid and obtained the spirane (VIII) as well as the mixed octahydrophenanthrenes. Oxidation of the selenium dehydrogenation product prepared in our experiments gave phthalic acid but no α,α-pentamethylenehomophthalic acid. Hence in the cyclization reaction which we used no spirane was formed.

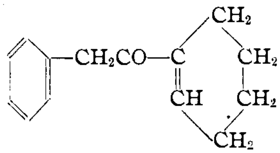


V VI and VIII VII

An attempt was made to synthesize the *as*-octahydrophenanthrene by cyclization and reduction of 1-phenyl-2-Δ^1-cyclohexenylethyne (IX).



IX



X

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(1) For the fourth paper in this series see Nesty and Marvel, THIS JOURNAL, **59**, 2662 (1937).

(2) Chemical Foundation Fellow in Organic Chemistry.

(3) Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, **58**, 972 (1936).

(4) Covert and Adkins, *ibid.*, **54**, 4116 (1932).

(5) Clemmensen, *Ber.*, **46**, 1837 (1913).

(6) Van de Camp and Mosettig, THIS JOURNAL, **58**, 1062 (1936).

(7) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1936).

In this case, however, cyclization did not occur. The only product which could be isolated was benzyl Δ^1-cyclohexenyl ketone (X). Cook and Hewett[8] have already shown that this ketone does not undergo ring closure. The results of our experiment are not surprising, since from stereochemical considerations it is evident that ring closure cannot take place until the triple bond has been attacked. The experiment shows that cyclization is not to be expected in dieneynes in which one of the double bonds is a part of the benzenoid system.

In the course of this work it has been observed that treatment of 1,1′-ethynylenebiscyclohexanol or di-Δ^1-cyclohexenylacetylene (I) with zinc amalgam and concentrated hydrochloric acid gives Δ^{11}-dodecahydrophenanthrene (II) but the method of preparation is not as satisfactory as the method previously published.[1] Also 1,1′-ethynylenebiscyclohexanol has been reduced with hydrogen in the presence of platinum oxide–platinum black catalyst[9] to give the olefinic and saturated glycols.

Experimental

Di-Δ^1-Cyclohexenylacetylene.—This dieneyne which has been described[3] before was obtained in a very pure form and in 88% yields by heating 1,1′-ethynylenebiscyclohexanol with about one-seventh its weight of potassium acid sulfate at 200–205° for ten minutes. The water was distilled at 17 mm. and the hydrocarbon was then distilled directly from the sulfate at 1.5 mm. The product on redistillation boiled at 105–110° at 1.5 mm.; n^{20}D 1.5549. This hydrocarbon solidified as white needles when cooled in a solid carbon dioxide–acetone bath but the crystals melted much below room temperature.

Δ^{11}-Dodecahydrophenanthrene.—According to the general procedure described for related reactions,[1] 20 g. of 1,1′-ethynylenebiscyclohexanol was refluxed with a mixture of 75 g. of zinc amalgam and 100 cc. of concentrated hydrochloric acid for about four days. During this period, additional acid was added whenever needed to maintain the steady evolution of hydrogen. On working up the reaction mixture there were obtained 7 g. of di-Δ^1-cyclohexenylacetylene and 0.7 g. of Δ^{11}-dodecahydrophenanthrene; n^{20}D 1.5098.

A similar treatment of 22 g. of di-Δ^1-cyclohexenylacetylene gave 0.5 g. of the cyclized hydrocarbon (n^{20}D 1.5067) and 7.5 g. of the dieneyne was recovered.

***trans-as*-Octahydrophenanthrene.**—A mixture of 10 g. of Δ^{11}-dodecahydrophenanthrene and 25 g. of powdered selenium was heated at 300–335° for about twenty-three hours. After about seventeen hours very little further evolution of hydrogen selenide was noted. The mixture was cooled, extracted with ether and the solution was distilled. In the first distillation 8 g. of liquid, b. p. 92–110° at 1.5 mm., was obtained. Redistillation gave 7 g. of *trans-as*-octahydrophenanthrene; b. p. 94–95° at 1.5 mm.; n^{15}D 1.5452; $d^{25}{}_4$ 0.9840.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.25; H, 9.75. Found: C, 90.15; H, 9.86.

Van de Camp and Mosettig[6] report the physical properties of the *trans* isomer as: b. p. 135.5–135.7° at 10.5–10.8 mm.; n^{15}D 1.5460; $d^{25}{}_4$ 0.9828.

No phenanthrene was obtained in this dehydrogenation.

Oxidation of *trans-as*-Octahydrophenanthrene.—A 1.2-g. sample of the above hydrocarbon was oxidized with 15 g. of potassium permanganate in 60 cc. of water containing a few drops of strong potassium hydroxide solution as described for a similar oxidation by Perlman, Davidson and Bogert.[7] No evidence of the presence of α,α-pentamethylenehomophthalic acid in the oxidation product could be obtained. By repeated ether extraction of the acidified oxidation mixture, 0.3 g. of phthalic acid melting at 185–187° with decomposition was obtained. This acid was converted to the anhydride which melted at 130–131.5°.

1-Phenylethynylcyclohexanol.—A solution of phenylethynylmagnesium bromide was prepared by adding 51.3 g. of phenylacetylene in 50 cc. of ether to a solution of ethylmagnesium bromide prepared from 12.2 g. of magnesium, 54.5 g. of ethyl bromide and 250 cc. of ether. After the mixture was warmed to complete the reaction, a solution of 50 g. of cyclohexanone in 10 cc. of ether was added over a period of forty-five minutes and the mixture was stirred for about twelve hours at room temperature.

The reaction mixture was decomposed with cold dilute hydrochloric acid in the usual manner. The ether layer was washed with sodium carbonate to remove any acid and was then evaporated and the residue distilled with steam to remove the unreacted cyclohexanone and phenylacetylene. On cooling the mixture in the distillation flask the carbinol crystallized. The crude yield was 66 g. (66%). Recrystallization from high boiling petroleum ether gave a product melting at 58–59°. Hurd and Cohen[10] report the melting point at 58–60° for a product prepared from the sodium salt of phenylacetylene.

Phenyl-Δ^1-cyclohexenylacetylene.—Hurd and Jones[11] have obtained this hydrocarbon by the action of phosphorus pentachloride on the above alcohol. Dehydration of 66 g. of the alcohol by heating it with 15 g. of potassium acid sulfate at 170–185° until no more water was evolved gave 45 g. (75%) of hydrocarbon boiling at 120–125° at 2 mm. Redistillation gave a pure product; b. p. 117–118.5° at 1.5 mm.; n^{20}D 1.6033; $d^{20}{}_4$ 0.9391.

Attempted Cyclization of 1-Phenyl-2-Δ^1-cyclohexenylethyne.—Thirty-six grams of hydrocarbon was added dropwise to a cooled, well-stirred solution of 100 cc. of sulfuric acid in 200 cc. of glacial acetic acid. After stirring for three hours, the mixture was poured into ice water and worked up as usual for the cyclization reaction. On distillation 21 g. (55%) of benzyl Δ^1-cyclohexenyl ketone boiling at 125–127° at 1.5 mm. and melting at 45–46°

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(8) (a) Cook and Hewett, *J. Chem. Soc.*, 1098 (1933); (b) Bergs, Wittfeld and Wildt, *Ber.*, **67**, 238 (1934).

(9) Adams, Voorhees, and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(10) Hurd and Cohen, THIS JOURNAL, **53**, 1068 (1931); see also ref. 11.

(11) Hurd and Jones, *ibid.*, **56**, 1924 (1934).

was obtained. The semicarbazone of the ketone melted at 170–171°. Oxidation of the ketone with potassium permanganate gave benzoic acid, m. p. 121°.

Bergs, Wittfeld, and Wildt[8b] report this ketone as melting at 47° and Cook and Hewett[8a] report the melting point of the ketone as 46–48° and of the semicarbazone of the ketone as 168–169°.

Treatment of the hydrocarbon (5 g.) with formic acid which is also a good reagent for cyclization of dieneynes gave no cyclic products and 55% of the theoretical amount of the ketone (3 g.) was isolated.

1,2-Dicyclohexylethanol.—Four grams of the above ketone in 60 cc. of methylcyclohexane[12] was shaken with 8 g. of Raney nickel catalyst[4] at 170° and under a hydrogen pressure of 2000–2400 pounds per square inch (136–163 atm.) for ten hours. After filtering the catalyst and evaporating the solvent, the residue (4 g.) was recrystallized from ether by cooling in an acetone–solid carbon dioxide bath. The product melted at 64–65° which checks the melting point reported for this alcohol by Venus-Danilowa.[13]

Tetradecahydrophenanthrol-9.—A similar reduction of 6 g. of Δ^{11}-dodecahydrophenanthrone-9 with 7 g. of Raney nickel catalyst[4] gave 3.5 g. of a clear, colorless, very viscous liquid; b. p. 122–125° at 1.5 mm.; n^{20}_{D} 1.5130. It did not crystallize when cooled in an acetone–solid carbon dioxide bath.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.79; H, 11.61. Found: C, 80.13; H, 11.99.

No crystalline derivatives were obtained by treating the alcohol with *p*-nitrobenzoyl chloride or phenyl isocyanate. The presence of the hydroxyl was shown by the liberation of ethane when the alcohol was added to ethylmagnesium bromide solution.

1,1′-Vinylenebiscyclohexanol.—A solution of 11 g. of 1,1′-ethynylenebiscyclohexanol in 150 cc. of glacial acetic acid was shaken with 0.1 g. of platinum oxide–platinum black[9] for three hours under a hydrogen pressure of 40–50 pounds per square inch (3–3.5 atm.). In three hours the pressure drop indicated that 90% of the theoretical amount of hydrogen for the reduction of the triple bond to the double bond had been absorbed. The catalyst was removed by filtration and the glycol was precipitated as a white solid by pouring the solution into 5 liters of water. After recrystallization from dilute alcohol, the product melted at 154–155°. Zal'kind[14] reports the melting point of this compound as 152°.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 74.93; H, 10.80. Found: C, 74.40; H, 10.80.

***sym*-1,1′-Dicyclohexanolethane.**—A solution of 11 g. of 1,1′-ethynylenebiscyclohexanol in 150 cc. of 95% alcohol containing 0.2 cc. of 48% hydrobromic acid[15] was shaken with 0.1 g. of platinum oxide catalyst[9] under 45–50 pounds per square inch pressure for thirty minutes, when the drop in pressure indicated complete reduction. Without the hydrobromic acid the second mole of hydrogen was not absorbed until the mixture was heated to 70° and shaken for two hours. The catalyst was removed and the solution heated to boiling and diluted with water to incipient turbidity. On cooling, 9 g. (81%) of colorless crystals melting at 128–129° was obtained.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.27; H, 11.58. Found: C, 74.47; H, 11.65.

Summary

1. Δ^{11}-Dodecahydrophenanthrone-9 obtained by cyclization of 1,1′-ethynylenebiscyclohexanol or di-Δ^1-cyclohexenylacetylene has been converted into *trans-as*-octahydrophenanthrene.

2. Attempts to cyclize 1-phenyl-2-Δ^1-cyclohexenylethyne in which one double bond of the dieneyne system is part of a benzene ring, resulted in the formation of benzyl Δ^1-cyclohexenyl ketone.

3. Some reduction products of the various ketones and unsaturated glycols have been prepared.

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[12] The authors acknowledge their indebtedness to the Hooker Electro-Chemical Company for this material.

[13] Venus-Danilowa, *Ber.*, **61**, 1954 (1928).

[14] Zal'kind, *J. Gen. Chem.* (U. S. S. R.), **5**, 1723 (1935); *C. A.*, **30**, 3407 (1936).

[15] Brown, Durand and Marvel, THIS JOURNAL, **58**, 1594 (1936).