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

Cyclization of Dienynes. X.[1] The Dodecahydrophenanthrone Obtained from Dicyclohexenylacetylene

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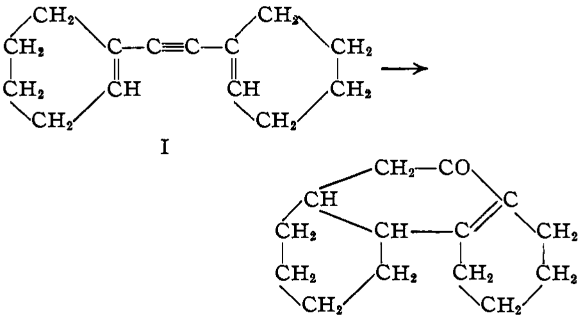
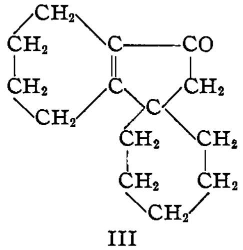
Treatment of di-$\Delta^{1,1'}$-cyclohexenylacetylene(I) with sulfuric acid or formic acid[3] produces two isomeric unsaturated ketones (II) which can be converted by various hydrogenation and dehydrogenation reactions to known phenanthrene derivatives. The principal product of the cyclization was first described[3a] as a β,γ-unsaturated ketone since it could be reduced by the Clemmensen[4] method without reducing the carbon–carbon double bond or dimerizing. Linstead and Walpole[5] have studied the ultraviolet absorption of this ketone and also certain reduction products and have concluded that the unsaturation is α,β to the carbonyl group and that it occurs in the 13–14 position. Recently Levitz, Perlman and Bogert[6] have questioned that this ketone is a phenanthrone and have suggested that it may be a spiran derivative (III).



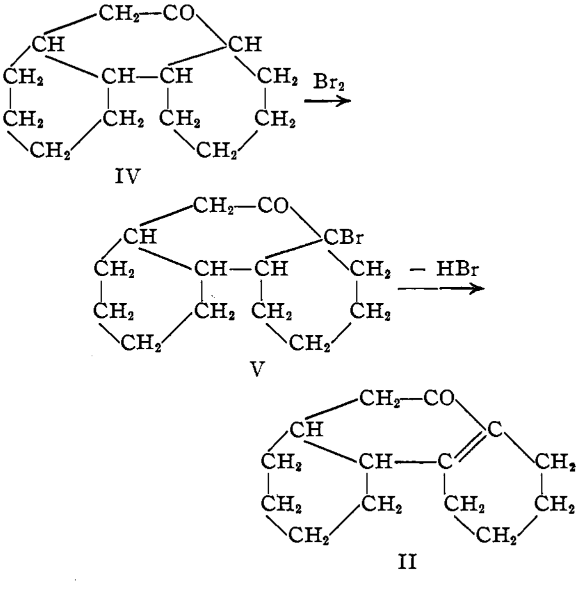
I

II



III

We have studied some further reactions of this cyclic ketone in order to establish the position of the carbon–carbon double bond and to show that the ketone was a 9-dodecahydrophenanthrone. A convenient method of converting the impure liquid ketone to a pure solid ketone by removing the impurities by zinc and acetic acid has been found. The position of the double bond has been definitely located in the α,β-position. The liquid and the solid isomers of perhydro-9-phenanthrone (IV) which Linstead and Walpole[5] obtained by hydrogenation of our unsaturated ketone were brominated to mono-bromo ketones (V). Elimination of hydrogen bromide from each of these mono-bromo derivatives has given an unsaturated ketone (II) which gives the same solid derivatives that are obtained from the cyclization product. Obviously very little bromination can have occurred at the —CH_2— group adjacent to the carbonyl as dehydrohalogenation of this product would lead to the $\Delta^{10,11}$-dodecahydro-9-phenanthrone of Rapson and Robinson.[7] It is interesting to note that when the perhydro-9-phenanthrone, m. p. 51°, was treated with two moles of bromine and then with pyridine the product isolated contained one bromine atom and apparently



IV

V

II

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[1] For the ninth communication in this series see THIS JOURNAL, **62**, 2739 (1940).

[2] Röhm and Haas Post-Doctorate Special Research Assistant in Organic Chemistry, 1939–1940.

[3] (a) Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, **58**, 972 (1936); (b) Pinkney, Nesty, Pearson and Marvel, *ibid.*, **59**, 2666 (1937); (c) Marvel, Mozingo and Kirkpatrick, *ibid.*, **61**, 2003 (1939).

[4] Clemmensen, *Ber.*, **46**, 1837 (1913).

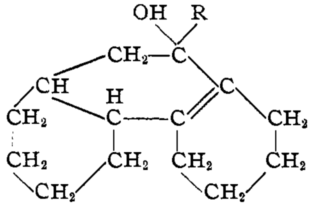
[5] Linstead and Walpole, *J. Chem. Soc.*, 842 (1939).

[6] Levitz, Perlman and Bogert, paper presented before the Organic Division of the 99th American Chemical Society Meeting, Cincinnati, Ohio, April, 1940.

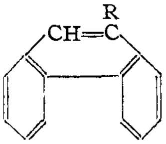
[7] Rapson and Robinson, *J. Chem. Soc.*, 1285 (1935).

one of the rings was aromatized in the reaction. The structure of the new bromo compound was not determined.

Further evidence for the phenanthrone structure has been obtained by condensing the unsaturated cyclic ketone obtained by a cyclization reaction with methylmagnesium chloride and ethylmagnesium bromide. The two carbinols (VI, R = CH_3 and C_2H_5) thus obtained were readily dehydrated and on dehydrogenation of these hydrocarbons 9-methyl- and 9-ethylphenanthrene (VII, R = CH_3 and C_2H_5) were obtained, respectively. While dehydrogenation is not a conclusive proof of structure, these experiments do contribute additional evidence for the phenanthrone structure as it would be unlikely that an alkyl group would retain its position in the rearrangement of a spiran to a phenanthrene under dehydrogenation conditions.



VI



VII

When phenylmagnesium bromide was condensed with our cyclic unsaturated ketone, a carbinol was obtained which was readily dehydrated to a phenyl decahydrophenanthrene derivative. Dehydrogenation of this hydrocarbon over platinum on charcoal[8] gave a solid hydrocarbon, m. p. 95.5–96°, which analysis indicated to be a phenyloctahydrophenanthrene. Further attempts to convert this hydrocarbon to 9-phenylphenanthrene were unsuccessful.

Experimental

Purification of $\Delta^{13,14}$-Dodecahydro-9-phenanthrone.—A solution of 5 g. of the crude ketone, b. p. 118–119° (1.5 mm.), n^{20}D 1.5321, m. p. 17–20°, in 100 cc. of acetic acid was refluxed vigorously for six hours with 6 g. of zinc dust. About half of the acetic acid was removed by distillation and the remaining solution was poured into water. The ketone was collected in benzene, washed with sodium bicarbonate solution and water and then distilled. The recovered ketone boiled at 113–115° (1.5 mm.); n^{20}D 1.5290. It was dissolved in 10 cc. of low-boiling petroleum ether and cooled in dry-ice. The ketone separated as crystals melting at 37°. The oxime prepared from this ketone melted at 186°. Linstead and Walpole report the melting points as 39° and 183–184°, respectively.

The liquid portion of the ketone obtained from the mother liquors boiled at 117–118° (1.5 mm.), n^{20}D 1.5230, and gave an oxime, m. p. 124.5–126.5°. This does not agree with any of the known reduction products of the ketone. This portion was not investigated further.

Perhydro-9-phenanthrone.—Following the directions of Linstead and Walpole,[5] 30 g. of the crude dodecahydro-9-phenanthrone from the cyclization reaction was reduced by hydrogen over palladium. The first one-sixth of the hydrogen was absorbed in ten minutes and the remaining five-sixths required fifty-six hours. It seems probable that in the first stage the reduction attacks the same compound in the unsaturated ketone which is removed by the zinc and acetic acid reduction. The perhydro-9-phenanthrone thus obtained melted at 47–48°; its oxime melted at 161–162.5°. The reported melting points of these products[5] are 51° and 163–164°, respectively.

14(?)-Bromo-perhydro-9-phenanthrone.—To a solution of 4.77 g. of perhydro-9-phenanthrone in 50 cc. of chloroform was added dropwise 3.7 g. of bromine in 40 cc. of chloroform. The reaction started slowly but soon the evolution of hydrogen bromide proceeded rapidly. The chloroform was removed under reduced pressure and the residue distilled under 1.5 mm. pressure. The yield was 3.5 g. of product boiling at 125–126° (1.5 mm.). It was not further characterized but used directly in the next reaction.

Dehydrobromination of 14(?)-Bromo-perhydro-9-phenanthrone.—A solution of 3 g. of the above bromo compound was refluxed with 50 cc. of pyridine for six hours. About half of the pyridine was removed by distillation under reduced pressure and the remaining solution was poured into iced dilute hydrochloric acid. The ketone was collected in benzene, washed thoroughly with water and then distilled. The yield of halogen-free ketone was 2 g., b. p. 117–121° (1.5 mm.). This ketone gave a 2,4-dinitrophenylhydrazone, m. p. 227–228°, which when mixed with a sample of the 2,4-dinitrophenylhydrazone of the original cyclization product, m. p. 227–228°, showed no depression of melting point. Treatment of the debrominated ketone with zinc and acetic acid as described for the purification of the cyclization product gave a ketone melting at 36–37° which did not depress the melting point of the purified cyclization product, m. p. 36–37°. The oxime melted at 182–183° and did not depress the melting point of the oxime of the original cyclization product, m. p. 183–184°.

Dibromination and Dehydrohalogenation of Perhydro-9 Phenanthrone.—A solution of 8 g. of perhydro-9-phenanthrone in 50 cc. of chloroform was treated with 12.5 g. of bromine in 50 cc. of chloroform. When the bromination was complete as indicated by the disappearance of the bromine color, the chloroform was removed by distillation. The residue without purification was refluxed with 120 cc. of dry pyridine for about eight hours. The product was isolated as in the previous case. The principal product of the reaction boiled at 120–138° (1.5 mm.) and solidified. After one crystallization from dilute alcohol with the use of some Norit, white, shiny bromine-containing platelets were obtained; m. p. 186–188°.

Anal.[9] Calcd. for $C_{14}H_{15}OBr$: C, 60.22; H, 5.42. Found: C, 60.38; H, 5.69.

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[8] Linstead, Millidge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).

[9] The authors are indebted to Mr. L. G. Fauble and Mr. W. H. Taylor for the microanalyses reported in this paper.

This obviously is not the $C_{14}H_{18}O$ which was expected. One ring must have been converted to an aromatic ring to give the product isolated.

Bromination and Dehydrobromination of Liquid Perhydro-9-phenanthrone.—Seven grams of the liquid isomer of perhydro-9-phenanthrone, b. p. 116–118° (1.5 mm.), which gave an oxime, m. p. 137–142°, was dissolved in 50 cc. of chloroform and treated with 6 g. of bromine in 50 cc. of chloroform. This bromination and dehydrobromination was carried out as with the solid isomer. The yield was 4 g. of product boiling at 115–120° (1.5 mm.). This ketone gave an oxime, m. p. 183–184°, which did not depress the melting point of the oxime, m. p. 182–184°, obtained from the ketone isolated from the cyclization reaction.

Conversion of $\Delta^{13,14}$-Dodecahydro-9-phenanthrone to 9-Methylphenanthrene.—By the usual procedure 20 g. of the ketone was treated with the methylmagnesium chloride obtained from 4 g. of magnesium. The product of this reaction was distilled at 1 mm. and boiled at 94–96°. The yield was 14 g. An analysis indicated that it was a mixture of the expected carbinol and the hydrocarbon which would result on dehydration. Consequently it was heated for twenty minutes at 150° under 16 mm. pressure with an equal weight of fused potassium bisulfate. On distillation the product boiled at 78–80° (1 mm.); $n^{20}\text{D}$ 1.5389.

Anal. Calcd. for $C_{15}H_{22}$: C, 89.03; H, 10.97. Found: C, 88.68; H, 10.71.

Two grams of this hydrocarbon was dehydrogenated over a platinum on charcoal catalyst[8] at 320° for three hours. The resulting oil was dissolved in ethanol and on standing crystals separated. After two recrystallizations from ethanol, 0.24 g. of crystalline product melting at 91–92° was obtained.

Anal. Calcd. for $C_{15}H_{12}$: C, 93.70; H, 6.30. Found: C, 93.58; H, 6.45.

An orange picrate melting at 154–155° was prepared. The literature[10] reports 9-methylphenanthrene melting at 91° and its picrate at 152–153°.

Conversion of $\Delta^{13,14}$-Dodecahydro-9-phenanthrone to 9-Ethylphenanthrene.—In a similar manner 20 g. of the unsaturated ketone and the ethylmagnesium bromide prepared from 4 g. of magnesium gave 11 g. of hydrocarbon $C_{16}H_{24}$; b. p. 117–118° (2 mm.), $n^{20}\text{D}$ 1.5350.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.81; H, 11.19. Found: C, 88.65; H, 11.09.

Dehydrogenation of 2 g. of this hydrocarbon over platinum-black at 320° gave an oily product. After distillation at 2 mm. the higher boiling part crystallized from alcohol when cooled in an acetone–dry-ice-bath. This product melted at 58–60° and gave a picrate, m. p. 118–120°. These results indicate that our 9-ethylphenanthrene is not quite pure as Pschorr[11] reports the melting point as 61–63° and its picrate at 124°.

Reaction of $\Delta^{13,14}$-Dodecahydro-9-phenanthrone with Phenylmagnesium Bromide.—Twenty grams of ketone and 0.15 mole of phenylmagnesium bromide gave 16.4 g. of viscous yellow oil, b. p. 138–140° (1 mm.), $n^{20}\text{D}$ 1.6142.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.84; H, 9.16. Found: C, 90.47; H, 9.31.

Four grams of this hydrocarbon was heated with platinum[8] at 320° for four and one-half hours in a current of carbon dioxide. The organic material was then separated from the catalyst by dissolving in acetone. This solvent was evaporated and the oily residue was crystallized from glacial acetic acid. The product, m. p. 95.5–96°, weighed 0.775 g.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.54; H, 8.46. Found: C, 91.46; H. 8.47.

This compound when mixed with pure phenanthrene, m. p. 98–99°, melted at about 68°. When mixed with authentic 9-phenylphenanthrene,[12] m. p. 105–106°, the mixture melted at 73°. Our hydrocarbon is apparently a 9-phenyloctahydrophenanthrene. It did not give a picrate under the standard conditions for the preparation of such a derivative.

Summary

Evidence has been presented to show that the ketone obtained by the cyclization of dicyclohexenylacetylene with sulfuric acid has an α,β-unsaturation as suggested by Linstead and Walpole. This ketone has been converted into 9-methylphenanthrene and 9-ethylphenanthrene by standard procedures to furnish further proof that it is a hydrophenanthrone and not a spiran derivative.

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[10] Windaus, Jensen and Schramme, *Ber.*, **57**, 1875 (1924).

[11] Pschorr, *ibid.*, **39**, 3128 (1906).

[12] We are indebted to Professor C. F. Koelsch for this sample.