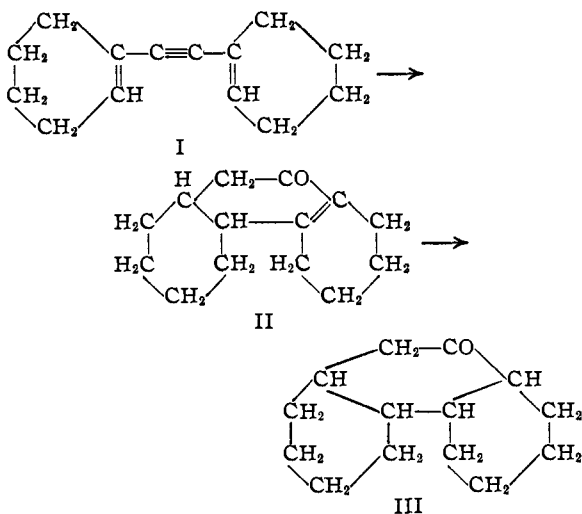


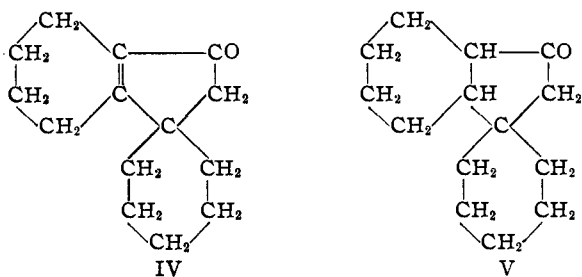
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthesis of a New Perhydro-9-phenanthrene¹By C. S. MARVEL AND RALPH V. WHITE²

Cyclization of di- $\Delta^{1,1'}$ -cyclohexenylacetylene (I) with sulfuric acid³ gives as the main product, a ketone, which has been described as dodecahydro-9-phenanthrone (II). Linstead and Walpole⁴



have shown that the unsaturation is in the 13-14 position and have reduced this ketone to obtain two stereoisomeric perhydro-9-phenanthrones (III). Levitz, Perlman and Bogert⁵ have questioned the phenanthrone structure of these products and have suggested that they may be spiran derivatives (IV and V).



In addition to the two perhydro-9-phenanthrones obtained from the cyclization product, a

(1) This is the ninth paper on cyclization of dienes. For the eighth see *THIS JOURNAL*, **62**, 2659 (1940).

(2) Röhm and Haas Post-Doctorate Special Research Assistant in 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, Mazingo and Kirkpatrick, *ibid.*, **61**, 2003 (1939).

(4) Linstead and Walpole, *J. Chem. Soc.*, 842, 850 (1939).

(5) Levitz, Perlman and Bogert, paper presented before the Organic Division of the 99th American Chemical Society Meeting, Cincinnati, Ohio, April, 1940.

third isomer has been prepared⁴ by the reduction of the $\Delta^{10,11}$ -dodecahydro-9-phenanthrone of Rapson and Robinson.⁶ This ketone is also the result of a cyclization reaction and hence its structure may possibly be questioned. Hence, it has seemed worth while to prepare a perhydro-9-phenanthrone from phenanthrene in order to have it available for comparisons.

This synthesis has been accomplished by using the method of Fieser, Jacobsen and Price⁷ to convert phenanthrene to 9-phenanthrol. This phenol was then reduced with hydrogen over Raney nickel⁸ to perhydro-9-phenanthrol which was readily converted to the ketone. The ketone was obtained as a solid melting at 56-57°, which differs from the melting points of the previously described isomers. Since there are eight racemic isomers of the ketone possible, it is not surprising that a new isomer was obtained in this new method. The derivatives with 2,4-dinitrophenylhydrazine and hydroxylamine also differ from those obtained for any previous isomers.

The new cyclic ketone was readily oxidized to a perhydrodiphenic acid, m. p. 174-175°, which is a different isomer from the four previously obtained by Linstead and Walpole⁴ and the one isomer obtained by Vocke.⁹ Our isomer makes the sixth optically inactive isomer of perhydrodiphenic acid which has been described. Since four racemic and two meso forms are theoretically possible, this must be the final isomer of the series. Our isomer gives a perhydrodiphenic anhydride, m. p. 103-104°, which may be identical with the anhydride, m. p. 104°, which Linstead and Walpole obtained from the acid which melted at 220°. However, we have not been able to convert our anhydride to a perhydrofluorenone whereas Linstead and Walpole did get a perhydrofluorenone from their anhydride. We are therefore inclined to believe that both our anhydride and acid are new isomers in this series.

Experimental

9-Phenanthrol.—Essentially the procedure previously described was used. Our experience showed that the

(6) Rapson and Robinson, *J. Chem. Soc.*, 1285 (1935).

(7) Fieser, Jacobsen and Price, *THIS JOURNAL*, **58**, 2163 (1936).

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

(9) Vocke, *Ann.*, **508**, 1 (1934).

preparation of the complex of one mole of bromomethoxyphenanthrene with phenanthrene dibromide was the difficult step. We had better luck when we used 25 g. of phenanthrene and 75 cc. of 20% sodium acetate solution in 900 cc. of methanol and treated with 15 cc. of bromine in 50 cc. of methanol than when the amounts previously described were used. From this amount we obtained 32–35 g. of the complex melting at 104–106° with decomposition. The remaining steps were carried out exactly as previously described. Our crude phenol melted at 146–150° and was used directly in the subsequent experiments. Some of this phenol was converted to the methyl ether and reductions with Raney nickel were tried. This treatment seemed to remove most of the oxygen from the molecule.

Perhydro-9-phenanthrol.—A solution of 10 g. of 9-phenanthrol in 10 cc. of absolute ethanol was reduced with hydrogen at 4000 lb. (267 atm.) pressure and 150° over a Raney nickel catalyst. About two-thirds of the calculated amount of hydrogen was absorbed rapidly. Hydrogenation then ceased. The product was isolated, put in fresh solvent with fresh catalyst and hydrogenation continued at 4000 lb. (267 atm.) pressure and 200°. The product was then isolated and the portion weighing 6.3 g. which boiled at 110–128° (3.5 mm.) was again hydrogenated. The product from this treatment boiled at 115–120° (3.5 mm.). The yield was 4.7 g. (44%). On standing the product solidified to a hard, waxy solid, m. p. 66.5–67.5°.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.78; H, 11.61. Found: C, 80.84; H, 11.54.¹⁰

Perhydro-9-phenanthrone.—To a solution of 8.5 g. of perhydro-9-phenanthrol in 25 cc. of glacial acetic acid was added dropwise a solution of 2.75 g. of chromic anhydride in 15 cc. of acetic acid. The mixture was cooled slightly so that the temperature did not go much above room temperature. When heat was no longer generated by the oxidation, the mixture was heated on a steam-bath for thirty minutes. Then excess water was added and the ketone was collected in ether. The ether extract was washed with aqueous sodium carbonate solution to remove acid and then distilled. The perhydro-9-phenanthrone boiled at 110–115° (3.5 mm.); n_D^{20} 1.5125. The yield was 7 g. It was dissolved in 3 cc. of low-boiling petroleum ether and cooled in dry-ice. The crude ketone melted at 51–54° and after one recrystallization from low-boiling petroleum ether it melted at 56–57°.

(10) We are indebted to Mr. L. G. Fauble and Miss Mary Kreger for the microanalyses reported in this paper.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.76; H, 10.83.

The 2,4-dinitrophenylhydrazone was obtained as orange red plates melting at 232–233° and the oxime after two crystallizations from ethanol melted at 210–212°.

Anal. Calcd. for (2,4-dinitrophenylhydrazone) $C_{20}H_{26}N_4O_4$: N, 14.50. Found: N, 14.43.

Anal. Calcd. for (oxime) $C_{14}H_{23}NO$: N, 6.34. Found: N, 6.28.

Oxidation of Perhydro-9-phenanthrone.—One and one-half grams of the ketone was added to 10 cc. of a nitric acid mixture (3 cc. fuming nitric acid and 7 cc. of nitric acid, sp. gr. 1.42). The mixture was cooled as long as heat was evolved spontaneously. When the initial reaction slowed down the oxidation mixture was heated on a steam-bath for twenty minutes. Excess water was then added and the ether extract prepared. The ether was washed with water to remove mineral acid and then extracted with sodium carbonate solution. Acidification of the alkaline extract gave a semi-solid acid. This was taken up in ether and again washed repeatedly with water. Evaporation of the ether left an oil. This was dissolved in a mixture of benzene and petroleum ether (b. p. 90–100°) and on cooling the perhydrodiphenic acid crystallized, m. p. 174–175°. The yield was 0.205 g.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.75. Found: C, 66.43, 66.30; H, 8.73, 8.86.

Perhydrodiphenic Anhydride.—To 0.175 g. of the above acid was added 4 cc. of acetic anhydride and the solution was refluxed for four hours. The excess acetic anhydride was removed under reduced pressure and the residue was recrystallized from benzene and petroleum ether mixture. The product melted at 103–104°.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.55. Found: C, 71.33; H, 8.65.

About 0.075 g. of this anhydride was heated to 250–350° in an effort to obtain a perhydrofluorenone.⁴ Some gas evolution occurred but no semicarbazone derivative could be obtained from the residue.

Summary

A new perhydro-9-phenanthrone has been synthesized from 9-phenanthrol. Oxidation of this ketone gives a new perhydrodiphenic acid which presumably is the last of the six possible optically inactive isomers of this compound.

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