

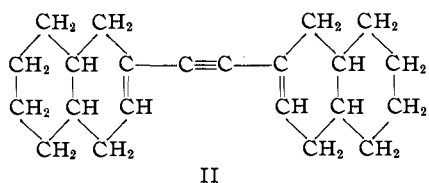
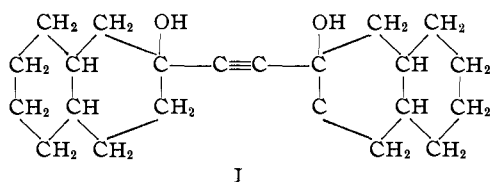
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cyclization of Dienynes. XI.¹ Ring Closures with Di- Δ^2 -2-Octalinylacetylenes. Synthesis of Perhydro-9-phenanthrone

BY C. S. MARVEL AND L. A. PATTERSON

Previous work on di- Δ^2 -2-*cis*-octalinylacetylene² showed that, while it apparently was cyclized by the sulfuric acid treatment, the product would not yield ketonic derivatives. Moreover, dehydrogenation of the cyclized product did not give the expected polynuclear aromatic hydrocarbon but a hydrocarbon richer in hydrogen.

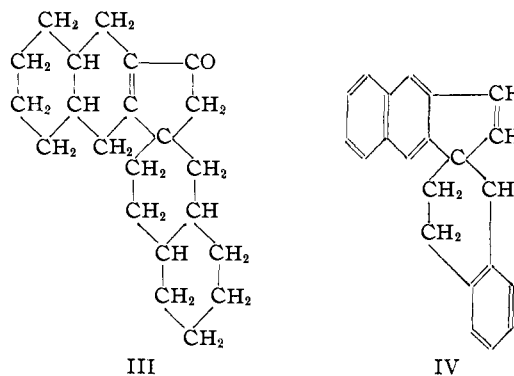
Similar results have been obtained with the di-*trans*- and the *cis-trans*-octalinylacetylenes. The glycols (I) were prepared by adding *trans*-2-decalone to the Grignard reagent of 2-ethynyl-*trans*-2-decalol for the *trans*-isomer and *trans*-2-decalone to 2-ethynyl-*cis*-2-decalol for the *cis-trans* isomer. Both glycols were readily dehydrated to homogeneous dienynes (II); the di-*trans* glycol gave a solid dienyne. The Δ^2 -positions of the double bonds in the octalin ring were assigned on the basis of work previously discussed.²



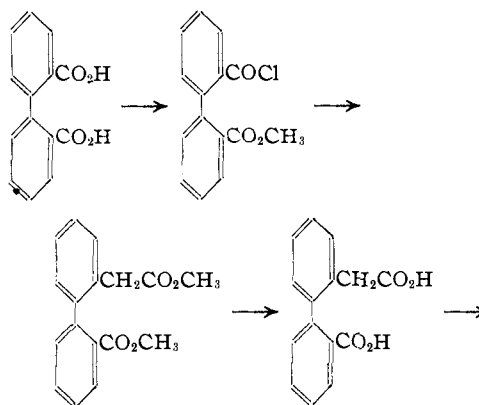
Treatment of either dienyne with sulfuric acid gave a glassy product which had the composition of the expected cyclic ketone. None of the schemes which have been described in earlier papers would convert this glassy product to a crystalline compound or would cause it to yield ketone derivatives. Girard's reagent³ was used on the glassy product but even this failed to give a derivative. Dehydrogenation of either cyclization product over palladized charcoal⁴ at 320°

gave the C₂₂H₁₈ hydrocarbon described previously² as similarly obtained from the di- Δ^2 -2-*cis*-octalinylacetylene.

It is of interest to note that if cyclization of the dioctalinylacetylenes occurs to yield a spiran (III) as suggested by Levitz, Perlman and Bogert⁵ for related dienynes, the product might be expected to dehydrogenate only to the C₂₂H₁₈ stage (IV).



Recently one of the stereoisomers of perhydro-9-phenanthrone was made by the nuclear reduction of 9-phenanthrol followed by oxidation of this alcohol to the ketone.⁶ In search of other of the possible stereoisomers, we have converted diphenic acid (V) to perhydro-9-phenanthrone by the following series of reactions.



(1) For the tenth communication in this series see THIS JOURNAL, **62**, 2741 (1940).

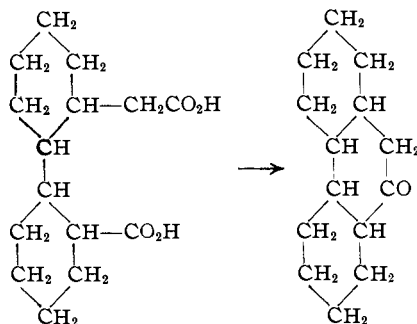
(2) Marvel, Pearson and Patterson, *ibid.*, **62**, 2659 (1940).

(3) Girard and Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

(4) Zelinsky, and Borisoff, *Ber.*, **57**, 150 (1924).

(5) Levitz, Perlman and Bogert, *J. Org. Chem.*, **6**, 105 (1941).

(6) Marvel and White, THIS JOURNAL, **62**, 2739 (1940).



The perhydro-9-phenanthrene thus obtained proved to be identical with the product described earlier.⁶

Experimental

Di-*trans*-2-decalolacetylene.—Essentially the directions described previously² for the preparation of di-*cis*-2-decalolacetylene were followed. Eleven grams of 2-ethynyl-*trans*-2-decalol and 10 g. of *trans*-2-decalone were converted to the glycol. The unreacted starting materials were removed by vigorous steam distillation. Ten grams of the product melting at 143–146° was obtained after crystallizing it from acetone and water. A sample prepared for analysis melted at 151.5–152.5°.

*Anal.*⁷ Calcd. for C₂₂H₃₄O₂: C, 80.00; H, 10.30. Found: C, 79.55; H, 10.49.

***trans*-2-Decalol-*cis*-2-decalolacetylene.**—The same directions were followed to prepare this glycol from 28.5 g. of 2-ethynyl-*cis*-2-decalol and 26 g. of *trans*-2-decalone. The product after crystallization from acetone and water weighed 24.5 g. and melted at 124–126°. A sample prepared for analysis melted at 136.5–137°.

Anal. Calcd. for C₂₂H₃₄O₂: C, 80.00; H, 10.30. Found: C, 79.92; H, 10.35.

Di- Δ^2 -*trans*-octalinylacetylene.—The method described previously² for the preparation of di- Δ^2 -*cis*-octalinylacetylene was followed. From 7 g. of di-*trans*-2-decalolacetylene was obtained 4.7 g. of solid dienyne boiling at 205–215° (3 mm.). The product was crystallized from low-boiling petroleum ether employing a dry-ice-acetone bath. Three grams of white solid melting at 79–81° was obtained. A sample prepared for analysis by crystallizing from low-boiling petroleum ether melted at 80–82°.

Anal. Calcd. for C₂₂H₃₀: C, 89.80; H, 10.20. Found: C, 89.44; H, 10.42.

Δ^2 -*trans*-Octalinylyl- Δ^2 -*trans*-octalinylylacetylene.—The same method was used to prepare 6.3 g. of this dienyne from 9.5 g. of *cis*-2-decalol-*trans*-2-decalolacetylene. The product boiled at 211° (3 mm.), n_D^{20} 1.5615.

Anal. Calcd. for C₂₂H₃₀: C, 89.80; H, 10.20. Found: C, 87.87; H, 10.35.

Cyclization of Di- Δ^2 -*trans*-octalinylylacetylene.—The dienyne was cyclized in the manner described in a previous paper² for the cyclization of di- Δ^2 -*cis*-octalinylylacetylene.

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

Three grams of the dienyne yielded a brown viscous liquid which was subjected to molecular distillation. Two grams of a light yellow very viscous liquid was obtained. This product was dissolved in low-boiling petroleum ether and placed in a dry-ice-acetone bath. A small amount of white solid melting at 85–95° was precipitated. It was recrystallized twice giving 8 mg. of material melting at 112–115°. There was not sufficient material for analysis. The liquid cyclization fraction was analyzed instead. A crystalline 2,4-dinitrophenylhydrazone derivative could not be prepared.

Anal. Calcd. for C₂₂H₃₂O: C, 84.55; H, 10.33. Found: C, 83.05; H, 10.25.

Seventy-eight milligrams of the product was dehydrogenated for twelve hours at 320° over palladium black on asbestos. The solid product obtained from the benzene extract melted at 173–176°. The impurities were removed by dissolving the product in a mixture of benzene and low-boiling petroleum ether and passing the solution through a column of activated aluminum oxide. A few milligrams of a white crystalline product melting at 179–181° was obtained. Mixed melting point with the dehydrogenation product from di- Δ^2 -*cis*-octalinylylacetylene (m. p. 182°) was 181–182°.

Cyclization of Δ^2 -*cis*-Octalinylyl- Δ^2 -*trans*-octalinylylacetylene.—In the same manner 15 g. of dienyne was cyclized. Distillation of the product gave 12.15 g. of a light brown glassy product, b. p. 225–245° (6 mm.). Attempts to crystallize the product were unsuccessful. Six grams of the material was subjected to molecular distillation. A light yellow glassy distillate was obtained and analyzed. Although the product analyzed for the expected ketone, no ketone derivative could be prepared with 2,4-dinitrophenylhydrazine.

Anal. Calcd. for C₂₂H₃₂O: C, 84.55; H, 10.33. Found: C, 84.57; H, 10.24.

Dehydrogenation of 1.17 g. of this product in the usual manner gave a few milligrams of white crystalline material melting at 179–181°. Mixed melting point with the dehydrogenation product from di- Δ^2 -*cis*-octalinylylacetylene (m. p. 182°) was 181–182°.

Acid Chloride of Monomethyl Diphenate.—Twenty-four grams of monomethyl diphenate was dissolved in 100 cc. of dry benzene contained in a 200-cc. round-bottomed flask fitted with a calcium chloride tube. Eight cubic centimeters of thionyl chloride and three or four drops of pyridine were added. The flask as placed in a water-bath at a temperature of 45–50° for forty minutes. The benzene was removed with a water pump at a temperature of 60–65°. An additional 15 cc. of dry benzene was added to the flask and then removed under reduced pressure. The colorless oily product was dissolved in hot benzene and filtered. The solution was concentrated to a volume of 10 cc. and cooled. Low-boiling petroleum ether was added precipitating an oily product which was induced to crystallize by vigorously scratching it. The white solid acid chloride was collected on a filter, washed with cold low-boiling petroleum ether, and then dried in a vacuum desiccator. The product weighed 24 g. and melted at 63–64°.

Anal. Calcd. for C₁₆H₁₁O₃Cl: C, 65.55; H, 4.04. Found: C, 66.27; H, 4.18.

2-Carbomethoxymethyl-2'-carbomethoxybiphenyl.—Ten grams of the acid chloride of monomethyl diphenate dissolved in 60 cc. of dry ether was cooled to a temperature of 0° and added dropwise rather rapidly to 300 cc. of an ice-cooled ether solution of diazomethane prepared from 12 g. of nitrosomethyl urea according to the directions in "Organic Syntheses."⁸ The flask was swirled rather rapidly during the addition of the acid chloride and then allowed to stand in an ice-bath for one hour. It was then allowed to stand at room temperature for three hours. The ether was removed with a water pump at a temperature of 30–33° leaving the diazoketone as a yellow liquid. The diazoketone was treated with 100 cc. of dry methanol and then warmed to a temperature of 50°. Silver oxide prepared from 30 cc. of 10% silver nitrate solution was added in small portions at five-minute intervals. The flask was swirled occasionally, the nitrogen being evolved rapidly as the temperature of the reaction mixture was kept at 50–60°. The addition of nitrogen ceased in thirty minutes. The solution was refluxed with Norite for several hours and then filtered. The liquid residue remaining after removing the alcohol was taken up in ether, washed first with sodium carbonate solution, then with water, and finally dried with anhydrous sodium sulfate. The light brown product left after removing the ether was distilled under reduced pressure. Seven and one-half grams of solid product boiling at 187–189° (7 mm.) was obtained. The product melted at 68–69° after crystallizing it from high-boiling petroleum ether. A sample prepared for analysis, crystallized from alcohol and water, melted at 71–71.5°.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.80; H, 5.67. Found: C, 72.14; H, 5.97.

2-Carboxymethyl-2'-carboxybiphenyl.—Seven and four-tenths grams of pure 2-carbomethoxymethyl-2'-carbomethoxybiphenyl was refluxed for five hours with 50 cc. of 10% sodium hydroxide solution. After the unsaponifiable material was extracted with ether, the solution was heated to boiling and acidified with hydrochloric acid. A mixture of white and brown crystalline material weighing 5.7 g. was obtained. Washing the product with hot benzene removed the brown material leaving 3.1 g. of white product melting at 171–172°. Invariably a considerable amount of brown crystalline material appeared in the crude product even though the ester was very carefully purified before being saponified.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 70.28; H, 4.72. Found: C, 70.75; H, 4.97.

Hydrogenation of Disodium-2-carboxymethyl-2'-carboxybiphenyl.—Two and two-tenths grams of 2-carboxymethyl-2'-carboxybiphenyl was titrated with 10% sodium hydroxide solution until basic to phenolphthalein. The solution was diluted to 20 cc. and hydrogenated with Raney nickel at a pressure of 3000 pounds. The hydrogen intake at a temperature of 200° was slow. After five hours the temperature was raised to 215°. The hydrogenation then proceeded slowly and smoothly to completion in about fifteen hours. The aqueous solution was filtered

free of catalyst, heated to boiling and acidified with hydrochloric acid. A white oil was precipitated; this was extracted with ether. Removal of the ether left a glassy colorless product which could not be crystallized.

2-Carboxymethyl-2'-carboxyhexahydrobiphenyl.—The hydrogenation of 2-carboxymethyl-2'-carboxybiphenyl was stopped at the half-way point. Acidification of the aqueous solution precipitated a colorless oil containing considerable solid material. The material was washed with ether, the solid part being difficultly soluble in ether. Recrystallization of the solid from absolute alcohol gave white cubical crystals melting at 261–263° (with decomposition).

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.94. Found: C, 68.32; H, 6.95.

Perhydro-9-phenanthrone.—Four hundred and seventy milligrams of the glassy, liquid reduction product of 2-carboxymethyl-2'-carboxybiphenyl was placed in a 25-cc. Erlenmeyer flask through which a stream of carbon dioxide was being passed. The flask was heated in a metal bath, the temperature being raised gradually. At 200° carbon dioxide was evolved. The temperature was maintained finally at 300–320°. The acid refluxed slightly but a stream of air directed against the outside of the flask prevented loss of any material. The flask was cooled and the brown viscous residue taken up in ether, washed twice with sodium carbonate solution and then with water. The removal of the ether from the dried ether extract left two hundred and twenty milligrams of impure brown liquid containing perhydro-9-phenanthrone. The product was dissolved in alcohol, treated with Norite and filtered. Concentration of the solution to a volume of 1–2 cc. and cooling caused a few white crystals to form. They were too few to isolate. The entire crude product was refluxed with 0.25 g. of hydroxylamine hydrochloride, 0.25 g. of sodium acetate, 6 cc. of alcohol and 3 cc. of water. White fluffy crystals of the oxime separated upon cooling the solution. These were collected on a filter and washed with cold alcohol. The oxime melted at 198–200°. Two crystallizations raised the melting point to 218–219.5°. A sample prepared for analysis melted at 219–220.5°. The oxime prepared was identical with the one obtained from a perhydro-9-phenanthrone melting at 57°. A mixture of the oxime (m. p. 218–219.5°) previously described⁶ and the new oxime, melted at 219–220°.

Anal. Calcd. for $C_{14}H_{22}ON$: C, 76.29; H, 10.04. Found: C, 76.42; H, 10.04.

Summary

1. Cyclization of *di-trans*- and the *di-cis-trans*- Δ^2 -2-octalinylacetylenes and subsequent dehydrogenation over palladium has given a $C_{22}H_{18}$ hydrocarbon which can be accounted for by assuming spiran formation in the cyclization reaction.

2. A new synthesis for perhydro-9-phenanthrone has led to the same stereoisomer which was previously prepared.

URBANA, ILLINOIS

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(8) Arndt, "Organic Syntheses," Vol. XV, John Wiley and Sons, Inc., New York, N. Y., 1935, p. 3.