a high vacuum (0.05 mm.), bath-temperature 280–300°. A drop of yellowish oil was obtained which could not be induced to crystallize. Because of the small amount of material available, the oil could not be purified satisfactorily; therefore, no definite conclusions can be drawn regarding the sterical relation of the ketone II to IIIa or IIIb.

## Summary

The steric aspects of the Diels–Alder reaction have been studied as regards the formation of stereoisomers, particularly in the condensation of dicyclohexenyl with ketonic compounds. Certain general rules are proposed, the first being well established: (1) the structure of the philodienic component is preserved unchanged in the adduct with no *cis-trans* isomerization; (2) no isomerism is caused by different spatial arrangements at carbons 3 and 6 of the new ring; (3) no isomerism is caused by the relative arrangement of substituents at carbons 1 and 6 (or 2 and 3); (4) isomeric adducts differ in the position of the double bond only. Dicyclohexenyl has been condensed with cinnamic acid, benzalacetone, benzalacetophenone, *trans*-dibenzoylethylene, *trans*-benzoylacrylic acid, and the properties and reactivities of the addition products studied. In general, they proved to be very resistant to attack by ordinary ketone reagents.

REHOVOTH, PALESTINE RECEIVED MARCH 2, 1942

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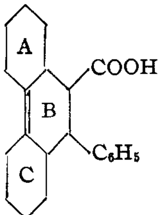
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

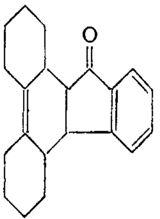
# Friedel–Crafts Reactions of 9-Phenyl-dodecahydrophenanthrene-10-carboxylic Acid

BY H. EMILE ESCHINAZI AND FELIX BERGMANN

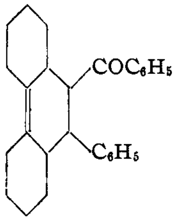
In continuation of our previous experiments with the adduct of dicyclohexenyl and cinnamic acid (I),[1] we attempted to cyclize the acid (I) to the dibenzfluorenone derivative III. When the acid chloride II[2] was treated with aluminum chloride in boiling benzene solution, the benzoyl derivative IV of m. p. 198–199° was isolated as the only reaction product. IV proved to be different from both the isomeric condensation products of dicyclohexenyl with benzalacetophenone, of m. p. 216 and 153°, respectively.[1] The most probable explanation for the occurrence of a third isomer is that aluminum chloride causes a shift of the 12,13-double bond in IV.



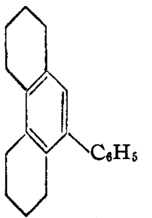
I



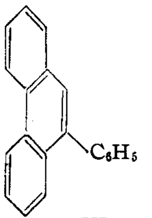
III



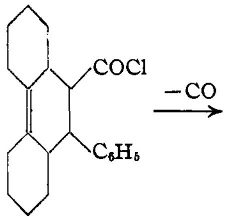
IV



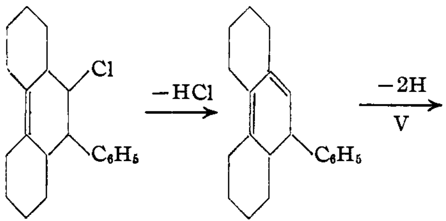
V



VI



II



VII VIII

In boiling carbon disulfide no clear results were obtained and no definite reaction product could be isolated. In boiling petroleum ether (80°), however, stannic chloride gave immediately a green-blue complex with the acid chloride II. After decomposition with sodium hydroxide, a hydrocarbon $C_{20}H_{22}$ was isolated, which is derived from the acid I by elimination of carbon dioxide and aromatization of ring B. Its structure as 9-phenyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (V) is proved by its dehydrogenation to 9-phenylphenanthrene (VI)[3] by means of sulfur or selenium.

Although the exact mechanism for the formation of V was not elucidated, we believe that first CO is split off and that the remaining chloride VII loses a molecule of hydrogen chloride to yield the dihydrobenzene derivative VIII. This intermediate stage may then be converted to V by disproportionation or autoxidation.

It is of interest that the selective dehydrogenation of ring B in I, which is effected by reaction with stannic chloride, could not be achieved with sulfur or selenium, the former agent leading directly

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(1) F. Bergmann and Eschinazi, THIS JOURNAL, **64**, 1405 (1942).

(2) Previous attempts to prepare this chloride by means of thionyl chloride were unsuccessful: T. Berlin, Dissertation, Jerusalem, 1939.

(3) Koelsch, THIS JOURNAL, **56**, 480 (1934); E. Bergmann and F. Bergmann, *ibid.*, **59**, 1443 (1937).

to VI, the latter to 9-phenylphenanthrene-10-carboxylic acid.[4] It should be noted, also, that the high-melting isomer of I[1] was not attacked at all when subjected to the same reaction conditions as described above.

The resistance of acid I to cyclization contrasts sharply with the smooth formation of hexahydrofluorenone from 2-phenylhexahydrobenzoic acid by aluminum chloride at 0°[5]. In the latter case, no information is available regarding the relative position of carboxyl and phenyl groups. Therefore, one cannot be sure that cyclization of the acid I is prevented by the *trans*-arrangement of the two substituents, which has been proved in our previous work.[1]

## Experimental Part

1. **9-Phenyl-10-benzoyldodecahydrophenanthrene (IV).**—The low-melting isomer of I (m. p. 231°, 10g .) was suspended in benzene (50 cc.) and phosphorus pentachloride (7 g.) added at once, causing a smooth reaction. After refluxing for one hour, the phosphorus oxychloride was distilled off *in vacuo;* 2 g. of the remaining chloride was heated with aniline and the anilide of I precipitated by dilute hydrochloric acid. From glacial acetic acid it was obtained as long needles, m. p. 307–308°.

*Anal.* Calcd. for $C_{27}H_{31}ON$: C, 84.2; H, 8.1; N, 3.6. Found: C, 84.3; H, 8.3; N, 3.9.

To a suspension of aluminum chloride (10 g.) in boiling benzene (50 cc.) was added dropwise a solution of the chloride II[2] (8 g.) in benzene (25 cc.). A strong evolution of hydrogen chloride set in, the deep-brown mixture becoming homogeneous. After one hour of boiling, it was decomposed and the reaction product fractionated in a high vacuum. Three fractions were obtained.

(a) b. p. 220° (0.05 mm.), thick yellow liquid, 1 g.
(b) b. p. 260° (0.05 mm.), thick yellow oil, 3.5 g.
(c) b. p. 320–360° (0.005 mm.), brown oil, 2 g.

Only fraction (b) gave a crystalline material, after treatment with glacial acetic acid for four days. The solvent was then decanted and the semicrystalline mass triturated with petroleum ether. After two recrystallizations from high-boiling petroleum ether and three from isopropanol, about 1 g. of long white needles was obtained, m. p. 198–199°; mixed m. p. with the isomer of IV, m. p. 216°,[1] 184°.

*Anal.* Calcd. for $C_{27}H_{30}O$: C, 87.6; H, 8.1. Found: C, 87.3; H, 7.8.

At room temperature, aluminum chloride led only to unidentifiable sirupy products.

2. **9-Phenyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (V).**—To a boiling solution of stannic chloride (20 g.) in petroleum ether, b. p. 80° (100 cc.), was added slowly a solution of the chloride II (12 g.) in the same solvent. Every drop produces a deep green-blue color. After two hours of boiling, the complex was decomposed with sodium hydroxide, whereby a small amount of an insoluble sirup separated. The soluble part was distilled, b. p. 186° (0.2 mm.), and the yellow mass (6 g.), so obtained, was dissolved in acetone–isopropanol 1:1. By slow evaporation of the solvent, crystallization could be effected: from isopropanol as rods, m. p. 94° (V).

*Anal.* Calcd. for $C_{20}H_{22}$: C, 91.6; H, 8.4. Found: C, 91.6, 91.7; H, 8.3, 8.2.

The insoluble part was washed with sulfuric acid and triturated with methanol. After recrystallization from glacial acetic acid, 2 g. of the starting material (I) was obtained.

Dehydrogenation of (V) (5 g.) with sulfur (2.5 g.) set in at 200° and was finished by raising the temperature to 260° during thirty minutes. The product was dissolved in benzene and distilled. The fraction of b. p. 190–200° (0.2 mm.) crystallized on treatment with isopropanol. From the same solvent, plates were obtained, m. p. 105–106°, which did not depress the m. p. of authentic 9-phenylphenanthrene.[3] The two picrates, m. p. 115–116°, were likewise identical.

Dehydrogenation with selenium required a much higher temperature, 320–340°, during twenty hours and gave an 80% yield of the hydrocarbon VI.

3. **Reactions of the High-melting Isomer of I,** m. p. **281°.**—The chloride of this acid was prepared in quantitative yield by the method described for the lower melting isomer and was identified by conversion into the corresponding anilide. From glacial acetic acid clusters of long needles, m. p. 247–248°, were obtained.

*Anal.* Calcd. for $C_{27}H_{31}ON$: C, 84.2; H, 8.1. Found: C, 84.0; H, 8.2.

No reaction occurred when the acid chloride was heated with stannic chloride in petroleum ether.

## Summary

The chloride of 9-phenyldodecahydrophenanthrene-10-carboxylic acid failed to undergo cyclization under various conditions of the Friedel–Crafts reaction. With stannic chloride a curious reaction occurs, leading to 9-phenyloctahydrophenanthrene.

Rehovoth, Palestine Received July 13, 1942

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[4] Weizmann, E. Bergmann and Berlin, This Journal, **60**, 1331 (1938).

[5] Cook and Hewett, *J. Chem. Soc.*, 62 (1936).