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# 1,2,3,4-Dibenzphenanthrene and its Derivatives. II. Some New Synthetic Attempts[1]

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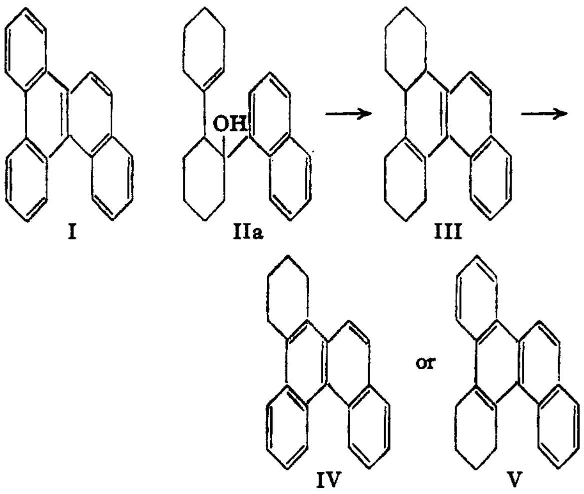
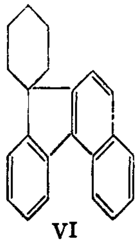
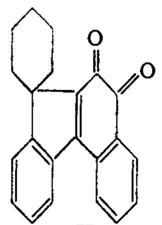
Amongst the several possible approaches to the synthesis of 1,2,3,4-dibenzphenanthrene (I) by cyclization, we have investigated more thoroughly the reaction of cyclohexenylcyclohexanone with $\alpha$-naphthylmagnesium bromide, following the method of Rapson[2] for the synthesis of triphenylene. The carbinol II(a or b) could be cyclized by aluminum or stannic chloride in benzene rather than in carbon disulfide solution, but the reaction product, expected to correspond to III, was not homogeneous. This, however, is not surprising for a structure like III, which should be able to undergo a disproportionation. Dehydrogenation of III with selenium at 320–340° proceeded with extreme difficulty and yielded an oily product, which on the basis of the analytical results was considered to be one of the tetrahydro derivatives IV or V. No further aromatization could be achieved by palladium asbestos at 350°. This resistance to complete aromatization was not understood, until it was observed by R. N. Jones,[3] that the ultraviolet absorption spectrum suggests that the product is a derivative of 3,4-benzfluorene and therefore must be represented by formula VI. The red quinone, which is obtained from it, probably is the *o*-quinone VII, although the two *p*-quinoid structures VIII and IX cannot be excluded. It is hoped that further experiments on model substances will decide this question.



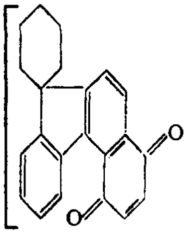
I IIa III IV V

The formation of analogous spirane structures is probable also in the experiments of Rapson.[2] When he started with the oily portion of the cyclization product, he always found appreciable amounts of oily dehydrogenation products besides triphenylene, whereas in the case of crystalline octahydro-triphenylene, "an almost quantitative yield of triphenylene" was obtained with a palladium–charcoal catalyst. But it is strange that no trace of I was detected in our reaction mixture, especially in view of the results from the corresponding reaction of cyclohexenylcyclohexanone with 9-phenanthrylmagnesium bromide. In this case two products could be isolated after aromatization. A small amount of tetrabenznaphthalene (X) was identified as its black picrate. Besides that another picrate was obtained, differing from the former by four to six hydrogen atoms. In analogy with the above results the spirane structure XI is ascribed to it.

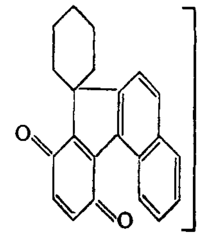

VI



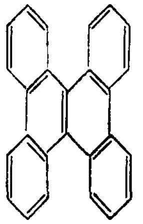
VII

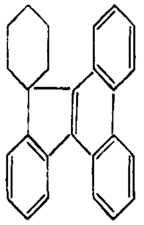


VIII



IX


X


XI

It is usually supposed, that spirane formation competes with the cyclization to a six-membered ring in all those cases where dehydration may lead to isomeric olefins.[4] In the present case, a diene is formed during dehydration, which may have either of two structures, and, accordingly, may give rise to two different cyclization products. However, in view of the fact that there was no indication of a second product another mechanism must be considered: the cyclization catalyst as an electrophilic reagent liberates a carbonium ion from the carbinol, and this ion is a resonance hybrid and

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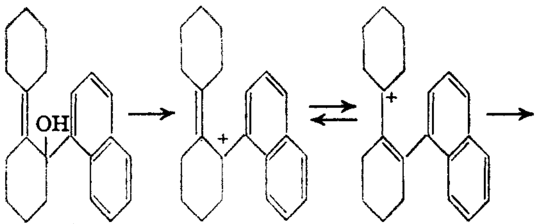
[1] Part I. F. Bergmann and Eschinazi, THIS JOURNAL, 65, 1413 (1943).

[2] Rapson, *J. Chem. Soc.*, 15 (1941).

[3] See Jones, THIS JOURNAL, 66, 185 (1944).

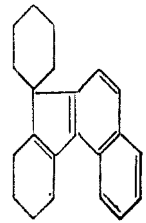
[4] Perlmann, Davidson and Bogert, *J. Org. Chem.*, 1, 288 (1936).

therefore able only to form a five-membered ring. This mechanism will be discussed in a future paper.



IIb

XIII



XII

## Experimental Part

1. **9,9-Spirocyclohexanyl-3,4-benzfluorene (VI).**—To a Grignard solution, prepared from α-bromonaphthalene (0.1 mole) and magnesium (0.1 mole) an equivalent amount of cyclohexenylcyclohexanone in benzene was added, the mixture refluxed for four hours and worked up as usual. Distillation yielded 13 g. (42%) of a fraction b. p. 225–230° (0.8 mm.) (II).

*Anal.* Calcd. for $C_{22}H_{26}O$: C, 86.2; H, 8.5. Found: C, 85.6; H, 8.2.

For the cyclization of II, benzene proved the most suitable solvent. Twelve grams of carbinol II in benzene (50 cc.) was added dropwise to a suspension of aluminum chloride (15 g.) in benzene at 0°. The color turned quickly to red-violet. After six hours at 0°, the reaction was continued for twelve hours at room temperature, after which time all the aluminum chloride had passed into solution and two layers were formed. The reaction product was divided into three fractions by distillation: (a) b. p. 210–230° (0.1 mm.); thick yellow oil, 4.5 g. Its picrate was prepared in isopropanol solution and crystallized from glacial acetic acid as fine brown needles, m. p. 160–161° (XII?).

*Anal.* Calcd. for $C_{28}H_{27}O_7N_3$: C, 65.0; H, 5.2; N, 8.1. Found: C, 64.9; H, 5.2; N, 8.0.

(b) B. p. 230–240° (0.1 mm.). This fraction (4 g.) proved to be a mixture of (a) and (c), because its picrate consisted of a mixture of the two respective picrates.

(c) B. p. 250–270° (0.1 mm.); yellow-reddish oil, 1.5 g. The picrate was prepared as described under (a) and crystallized from glacial acetic acid as golden rods, m. p. 169–170°.

*Anal.* Found: C, 65.3; H, 5.1; N, 8.2.

This substance, according to its analysis, is isomeric with the product, yielding the picrate of m. p. 160–161°. A mixture of both picrates melts at 150–152°.

Dehydrogenation was best attained with fraction (c); the other fractions gave essentially the same end-product, but less pure and in poorer yields.

15 g. of (c) and selenium (25 g.) were heated to 320° for thirty hours. The hot mixture was then stirred carefully into petroleum ether (80°), the solution washed with sodium hydroxide and distilled. The main fraction (9.5 g.) had b. p. 220–240° (0.1 mm.) and consisted of a reddish oil with green fluorescence. This product was purified via its picrate, which was prepared in glacial acetic acid with addition of a little petroleum ether, in order to obtain a homogeneous solution. The picrate crystallizes from glacial acetic acid in red rods, m. p. 141–142°; 7 g of crude hydrocarbon yielded about 8 g. of picrate.

*Anal.* Calcd. for $C_{28}H_{23}O_7N_3$: C, 65.5; H, 4.45; N, 8.2. Found: C, 65.8; H, 4.2; N, 8.0.

Five grams of this picrate yielded 2.5 g. of spirane VI, b. p. 225–230° (0.05 mm.) as a thick yellow oil with strong green fluorescence. It dissolves readily in petroleum ether or acetone, but sparingly in acetic acid. With concd. sulfuric acid a pink solution is obtained on gentle heating, which turns slowly to green. After long standing, the substance tends to crystallize, but because of its low melting point could not yet be recrystallized satisfactorily.

*Anal.* Calcd. for $C_{22}H_{20}$: C, 93.0; H, 7.0. Found: C, 93.4; H, 6.9.

Oxidation to the quinone (VII?): 0.25 g. of VI in acetic acid (5 cc.) was boiled with $K_2Cr_2O_7$ (0.5 g.) for five minutes and the quinone precipitated by water. After two crystallizations from high-boiling petroleum ether, it formed beautiful long red plates, m. p. 228° (VIII?). Concd. sulfuric acid dissolves it with cherry-red color.

*Anal.* Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.7. Found: C, 84.0; H, 5.8.

**Tetrabenznaphthalene (X) and Spirane XI.**—The Grignard reaction between 9-bromophenanthrene (26 g.), magnesium (2.5 g.) and cyclohexanylcyclohexanone (18 g.) in benzene, after ten hours of boiling, gave a mixture which after decomposition and distillation yielded 17 g. of a bright yellow sirup, b. p. 270–290° (0.1 mm.). Cyclization of this carbinol (16 g.) was carried out as described above, with aluminum chloride in benzene solution, and gave as the main product a fraction b. p. 320–360° (0.1 mm.), (yield, 10 g.), which was used directly for dehydrogenation.

Ten grams of the cyclization product and selenium (12 g.) were heated to 350° for twenty hours, the mass extracted with hot carbon tetrachloride, washed with sodium hydroxide and fractionated.

(a) B. p. 230–260° (0.2 mm.), reddish oil, 3 g. In acetic acid solution, a plastic picrate was formed. The solvent was decanted and the product kneaded in a mortar with petroleum ether. Thereafter, it could be recrystallized from isopropanol; brown leaflets, m. p. 157–159° (XI).

*Anal.* Calcd. for $C_{32}H_{25}O_7N_3$: C, 68.2; H, 4.4. Found: C, 68.0; H, 4.0.

(b) B. p. 290–320° (0.1 mm.); dark-red resin, 1.5 g. Here again the picrate which was prepared in acetic solution, first formed a black plastic mass and acquired granular consistency only after trituration with butyl acetate and petroleum ether; yield, 1.8 g. It was dissolved in isopropanol (50 cc.) and nitrobenzene (2 cc.) by prolonged boiling and then crystallized in red-black rods, m. p. 210–212°[5] (X).

This procedure had to be repeated two or three times.

*Anal.* Calcd. for $C_{32}H_{19}O_7N_3$: C, 68.9; H, 3.4; N, 7.5. Found: C, 68.6; H, 3.2; N, 7.4.

**Acknowledgment.**—The authors wish to thank Prof. R. N. Jones for his kind coöperation and his help in the discussion of the theoretical problems met with in the present work.

## Summary

Cyclization of 1-(α-naphthyl)-2-cyclohexenylcyclohexanol-1 yields a 9,9-spirane derivative of 3,4-benzfluorene instead of the expected 1,2,3,4-dibenzphenanthrene skeleton. The mechanism of this "cyclodehydration" is discussed.

The analogous reaction between cyclohexenylcyclohexanone and 9-phenanthrylmagnesium bromide yielded, besides the corresponding spirane, a small amount of tetrabenznaphthalene.

REHOVOTH, PALESTINE RECEIVED SEPTEMBER 10, 1943

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(5) E. Bergmann and Fujise, *Ann.*, **483**, 65 (1930), report a m. p. of 200°.