ment was based upon the assumption that all of the portion to be methylated was α-ethoxypropiovanillone.

Summary

1. All lignin-containing materials appear to undergo the same type of ethanolysis reaction when refluxed with absolute ethanol containing hydrogen chloride. California redwood, Douglas fir, red oak, bamboo, corn stalks, rye straw, and jute are found to give crude oils and crystalline derivatives similar to those obtained previously from spruce and maple woods.

2. A botanical classification of gymnosperms and angiosperms is indicated from results of the present experiments on ethanolysis; the lignin present in materials of the former class contains guaiacyl units only while that in the latter both guaiacyl and syringyl groupings. This is in agreement with similar results obtained in the alkaline degradation of lignin sulfonic acids. On ethanolysis only about one-third of the Klason lignin is removed from gymnosperms and about two-thirds from angiosperms.

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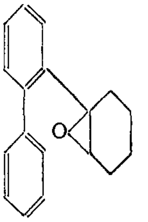
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

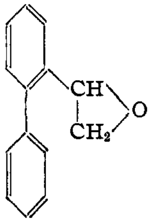
Aromatic Cyclodehydration.[1] VII.[2] Phenanthrene

BY CHARLES K. BRADSHER AND ROBERT W. WERT

The success met with in the synthesis of tetrahydrotriphenylene from the oxide (I) of 1-(2-biphenyl)-cyclohexene-1 suggested that phenanthrene might be prepared from *o*-phenylstyrene oxide (II).

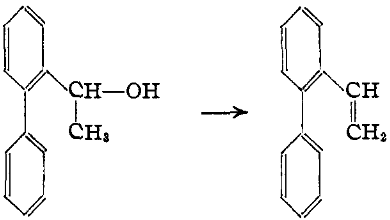


I



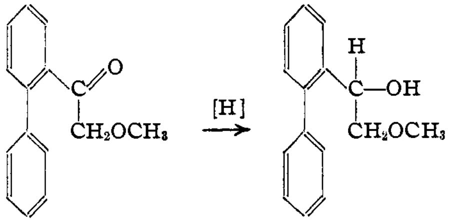
II

A Grignard reagent prepared from 2-iodobiphenyl was treated with acetaldehyde to give 1-(2-biphenyl)-ethanol-1 (III) which upon dehydration gave some *o*-phenylstyrene (IV). The oxide (II) prepared from this by the action of monoperphthalic acid, underwent cyclization in a boiling mixture of hydrobromic acid and acetic acid to give a small amount of phenanthrene.



III IV

In an effort to find a more promising method of synthesis, we decided to attempt the cyclization of 1-(2-biphenyl)-2-methoxyethanol-1 (VI), since it had been shown[2c] that the corresponding propanol gave 9-methylphenanthrene. The crude carbinol (VI) obtained by the aluminum isopropylate reduction of 2-(ω-methoxy)-acetobiphenyl (V), was cyclized by hydrobromic and acetic acids to give the desired hydrocarbon in an overall yield of 46%.



V VI

Although our experiments afford no direct evidence as to the course of the reaction, our belief that the intermediate is 2-biphenylacetaldehyde (VII) gains support from the observation of Tiffeneau[3] that 1-phenyl-2-methoxyethanol-1 (VIII) is converted to phenylacetaldehyde under conditions comparable to those used by us in the cyclization. We predict that the biphenylacetaldehyde, as well as any compound converted to

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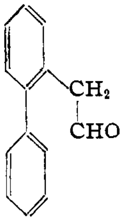
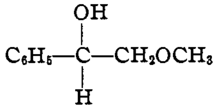
(1) The term "aromatic cyclodehydration" is used here to designate the type of cyclization in which the elements of water are eliminated from a compound with the establishment of a new aromatic ring. This is in contradistinction to the type which leads to the formation of hydroaromatic rings.

(2) The preceding papers of this series are: (a) Bradsher and Schneider, THIS JOURNAL, **60**, 2960 (1938); (b) Bradsher and Rosher, *ibid.*, **61**, 1524 (1939); (c) Bradsher and Tess, *ibid.*, **61**, 2184 (1939); (d) Bradsher, *ibid.*, **61**, 3131 (1939); (e) Bradsher, *ibid.*, **62**, 486 (1940); (f) Bradsher, *ibid.*, **62**, 1077 (1940).

(3) Tiffeneau, *Compt. rend.*, **145**, 811 (1907).



VII



$$C_6H_5-\overset{OH}{\underset{H}{C}}-CH_2OCH_3$$

VIII

it under the conditions of the cyclization, can be made to yield phenanthrene.

The extension of this general method of synthesis to the preparation of phenanthrene opens the way for further extension to the synthesis of derivatives without substituents in the central nucleus.

Experimental

1-(2-Biphenyl)-ethanol-1 (III).—A Grignard reagent was prepared in ether from 30.8 g. of 2-iodobiphenyl and 3.74 g. of magnesium. To this was added 8 g. of acetaldehyde in ether solution and the mixture allowed to stand overnight. The mixture was decomposed with an ammonium chloride solution and after evaporation of the ether the product was crystallized from benzene–ligroin as slightly colored needles, m. p. 110–112°; yield 12.1 g. (56%). An analytical sample purified by recrystallization melted at 110.5–111.5° and was colorless.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.93; H, 7.42.

***o*-Phenylstyrene.**—Ten grams of the carbinol described above was mixed intimately with 30 g. of finely ground potassium bisulfate and heated at 160° for one hour. The mixture was extracted with benzene and water. The benzene layer was concentrated and the residue distilled under reduced pressure. The olefin was obtained as a light yellow oil, b. p. 127–130° (5 mm.); yield 2.2 g. (24%).

Preparation and Cyclization of *o*-Phenylstyrene Oxide.—The olefin described above (2.2 g.) was dissolved in ether and this was added to an ether solution containing 0.036 mole of monoperphthalic acid.[2d] After the mixture had stood for twelve hours, the acids were extracted with a solution of sodium bicarbonate and the ether finally evaporated. The residue was dissolved in 30 cc. of acetic acid, 20 cc. of 34% hydrobromic acid added and the mixture refluxed for twenty-four hours. At the end of this period, the mixture was cooled in ice and the crude hydrocarbon collected. This was dissolved in alcohol and an alcoholic solution of picric acid added. Upon standing, 0.7 g. of crude picrate precipitated. This was decomposed by suspending it in ether and shaking with dilute ammonium hydroxide. After evaporation of the ether, the residue was crystallized from alcohol as irregular plates, m. p. 98–99°; yield 0.05 g. This material gave no depression of melting point when mixed with phenanthrene.

Preparation of Phenanthrene from 2-(ω-Methoxyaceto)-biphenyl.—The 2-(ω-methoxyaceto)-biphenyl[2a] (19.9 g.) was reduced with aluminum isopropylate by the method of Lund.[4] The crude **1-(2-biphenyl)-2-methoxyethanol-1** thus obtained was dissolved in 200 cc. of acetic acid, 66 cc. of 34% hydrobromic acid added and the mixture refluxed for twenty-four hours. After cooling, the crude hydrocarbon was collected and purified by vacuum distillation and recrystallization from ethanol. The phenanthrene obtained in this way consisted of irregular plates with a faint yellow color, m. p. 97.5–99°; yield 7.3 g. (46%). An analytical sample twice recrystallized melted at 99–100° and was colorless.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.33; H, 5.76. Found: C, 94.17; H, 5.79.

The picrate crystallized from alcohol as orange needles, m. p. 145–146°.

A sample of the hydrocarbon was oxidized with chromic oxide to give the orange quinone which, once recrystallized from acetic acid, melted at 207–208°.

Summary

The new type of ring closure has been extended to the synthesis of phenanthrene.

DURHAM, N. C. RECEIVED JULY 29, 1940

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[4] Lund, *Ber.*, **70B**, 1521 (1937).