

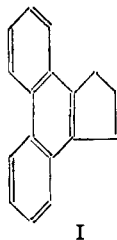
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Synthesis of Phenanthrene Derivatives. IV.¹ 9,10-Cyclopenteno- and 9,10-Cyclohexenophenanthrene

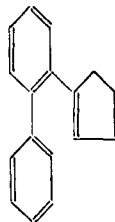
BY CHARLES K. BRADSHER

The first synthesis of 9,10-cyclopentenophenanthrene (I) was that by Bachmann and Kloetzel² who obtained this hydrocarbon, together with the isomeric 5,6-benzo-2,3-dihydrobenzophenanthrene, upon reduction of the mixture of ketones formed by the cyclization of β -(9-phenanthryl)-propionic acid.

A more convenient route, and one which suggested itself to the aforementioned authors, is that through the cyclization of 1-(2-biphenyl)-cyclopentene-1 (II). They found, however, that the cyclopentene (II), upon treatment with



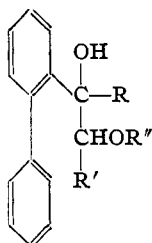
I



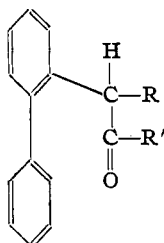
II

aluminum chloride, gave not the desired 9, 0-cyclopentano-9,10-dihydrophenanthrene, but the corresponding spiran.

In the preceding papers of this series, we have described a general method for the synthesis of 9- and 9,10-substituted phenanthrene hydrocarbons. This method involves the cyclization of carbinols of type III by hydrobromic acid.



III



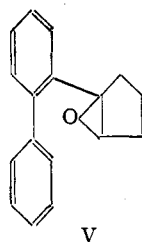
IV

(R' = alkyl, aryl, or H)

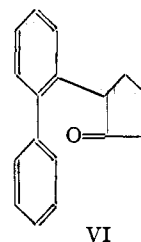
Although the evidence does not as yet amount to a demonstration, it has appeared increasingly probable that a carbonyl compound of type IV, or its enol form, is an intermediate in this cycliza-

tion. It should then follow that any carbonyl compound of type IV, or any substance capable of being converted by acids to such a carbonyl compound, would undergo cyclization to give a phenanthrene derivative.

For our purposes, the most satisfactory compound fulfilling the latter requirement seemed to be the cyclopentene oxide (V).



V



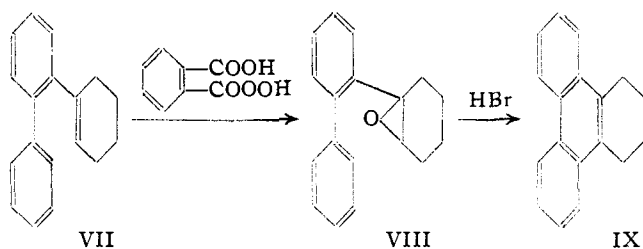
VI

Such a compound could be formed readily by the action of monoperphthalic acid on the cyclopentene and would be expected to isomerize under the influence of acids to give 2-(2-biphenyl)-cyclopentanone-1 (VI). Whether or not this was the mechanism of the reaction, when 1-(2-biphenyl)-cyclopentene-1 (II) was oxidized with monoperphthalic acid, and the crude oxide (V) thus afforded refluxed with a mixture of acetic and hydrobromic acids, 9,10-cyclopentenophenanthrene was obtained.

The synthesis of 9,10-cyclohexenophenanthrene (1,2,3,4-tetrahydrotriphenylene (IX)) has been accomplished previously by Bergmann and Blum-Bergmann³ both by partial dehydrogenation of dodecahydrotriphenylene and by the reduction of the ketone obtained when γ -(9-phenanthryl)-butyric acid was cyclized.

The hydrocarbon (IX) was synthesized by us in a manner analogous to that employed in the case of 9,10-cyclopentenophenanthrene. The Grignard reagent from 2-iodobiphenyl was treated with the cyclohexanone and the crude carbinol dehydrated with potassium bisulfate to give 1-(2-biphenyl)-cyclohexene-1 (VII). The cyclohexene (VII) was treated with monoperphthalic acid to give the corresponding oxide (VIII) and the crude oxide cyclized to 1,2,3,4-tetrahydrotriphenylene by the action of hydrobromic acid.

(3) Bergmann and Blum-Bergmann, *ibid.*, 59, 1441 (1937).(1) For the preceding paper of this series see *THIS JOURNAL*, 61, 2184 (1939).(2) Bachmann and Kloetzel, *ibid.*, 59, 2207 (1937). Weizmann, Bergmann, and Berlin likewise prepared this hydrocarbon by a similar method, *ibid.*, 60, 1331 (1938).



The yield of the hydrocarbon from the cyclohexene was 30%.

The importance of this method is that it is applicable to the synthesis of alkyl tetrahydro-triphenylenes which would be expected to give alkyltriphenylenes upon dehydrogenation.

The author is indebted to Dr. W. E. Bachmann for the gift of a sample of 9,10-cyclopentenophenanthrene.

Experimental

1-(2-Biphenyl)-cyclopentene-1 (II).—A Grignard reagent was prepared from 30.8 g. of 2-iodobiphenyl and 3.74 g. of magnesium. To this was added 8.4 g. of cyclopentanone in ethereal solution. The mixture was refluxed for a half hour and then decomposed by the addition of a 20% solution of ammonium chloride. The ether layer was dried, the ether distilled off and the residue heated for one hour at 160° with 30 g. of powdered potassium bisulfate. At the end of this period, water and benzene were added. The benzene layer was separated, concentrated to a small volume and the residue distilled under reduced pressure. After a large fore-run, consisting chiefly of biphenyl, the desired cyclopentene (II) came over as a colorless oil, b. p. 150–159° (5 mm.); yield 4.0 g.

Monoperphthalic acid was prepared by the action of an alkaline solution of hydrogen peroxide on phthalic anhydride by a method essentially that of Böhme.⁴ We found, however, that satisfactory yields of the acid could be obtained only when the alkaline solution of hydrogen peroxide was stirred vigorously with a mechanical stirrer and when the solution was cooled by the addition of crushed ice. In every case the yields of monoperphthalic acid obtained were verified by iodimetric titration.

9,10-Cyclopentenophenanthrene (I).—The cyclopentene (II) (2 g.) was dissolved in ether, cooled in an ice-

bath and poured into an ice-cold ether solution containing 0.019 mole of monopero-phthalic acid. The mixture was allowed to stand for twelve hours at room temperature, after which the acids were extracted from the solution with sodium bicarbonate solution. The ether was evaporated off and the crude cyclopentene oxide (V) was dissolved in 25 cc. of acetic acid. To this was added 25 cc. of 34% hydrobromic acid and the mixture refluxed for twenty-four hours. Upon cooling, the hydrocarbon

solidified, but contained some resinous material which made crystallization impossible. The hydrocarbon was, therefore, purified by vacuum sublimation. The sublimation product, once recrystallized from acetic acid, was obtained pure as long slender needles, m. p. 150–151°; yield, 0.31 g. It showed no depression of melting point when mixed with an authentic sample of 9,10-cyclopentenophenanthrene.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.5; H, 6.4.

The picrate prepared in alcohol was obtained as red needles, m. p. 164–165° (Bachmann,² 161.5–162°).

1-(2-Biphenyl)-cyclohexene-1 (VII).—A Grignard reagent was prepared from 14 g. of 2-iodobiphenyl and 4.9 g. of cyclohexanone added. The mixture was decomposed with ammonium chloride solution and the crude carbinol dehydrated as in the preparation of the corresponding cyclopentene (II). Upon distillation, 3.4 g. (29%) of a yellowish oil was obtained, b. p. 183–193° (23 mm.).

9,10-Cyclohexenophenanthrene (IX).—The cyclohexene (VII) (3.4 g.) obtained above was dissolved in ether and oxidized with an ether solution containing 0.024 mole of monopero-phthalic acid. After sixteen hours, the acids were extracted with bicarbonate solution, the ether evaporated and the crude oxide (VIII) cyclized by refluxing for twenty-four hours in a mixture of hydrobromic and acetic acids. Upon cooling, the hydrocarbon crystallized from the solution. Twice recrystallized from acetic acid, it was obtained as pure, colorless needles, m. p. 122–123° (Bergmann,³ 120–121°); yield, 1.0 g. (30%).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.1; H, 6.9. Found: C, 92.9; H, 6.9.

Summary

By the use of a new modification of the ring closure, 9,10-cyclopenteno- and cyclohexeno-phenanthrene have been synthesized.

DURHAM, N. C.

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(4) Böhme, *Ber.*, **70**, 379 (1937).