[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XIX.[1] Use of Intermediates Obtained by the Diene Addition Reaction

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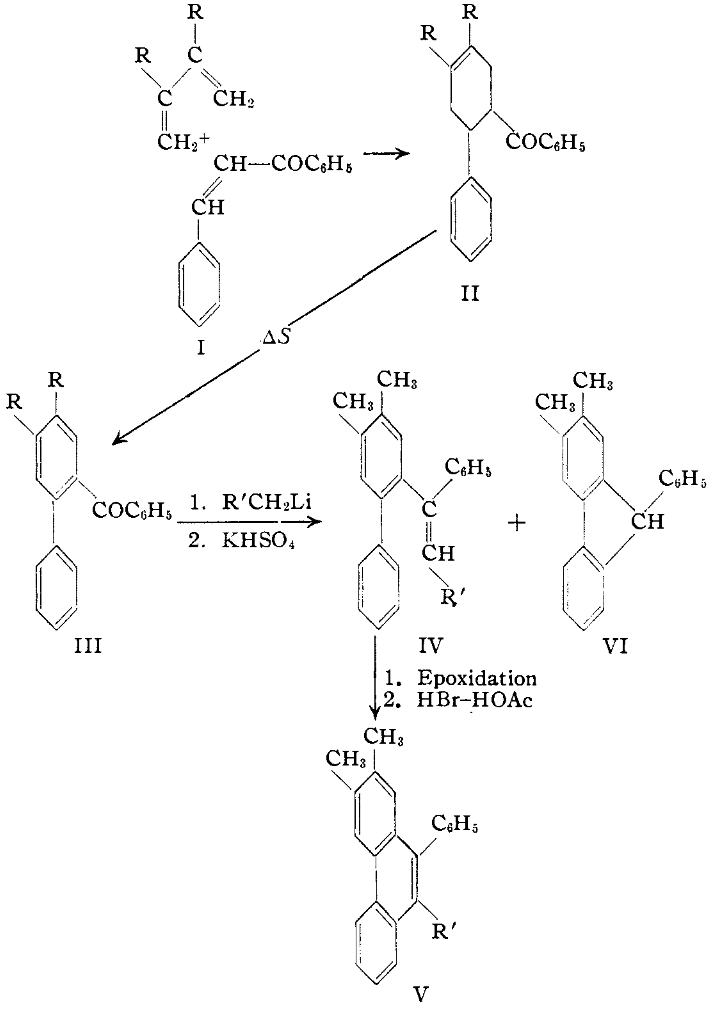
Biphenyl derivatives of certain types undergo aromatic cyclodehydration readily to yield phenanthrene derivatives with substituents on the central ring.[1,2] The extension of this general synthesis to the preparation of phenanthrenes having additional substituents on the terminal rings may follow at least two general plans. The first, illustrated in the preceding communication involves the use of intermediates obtained originally by the substitution of biphenyl: the other, as exemplified in the present paper involves the preparation of biphenyl intermediates from phenyl derivatives. One method by which such a transformation may be accomplished is through the use of the Diels–Alder reaction. It has been shown[3] that chalcone (I) reacts with butadiene to yield 4-phenyl-5-benzoylcyclohexene (II, R = H), but our attempts to dehydrogenate the hydroaromatic ketone yielded only traces of the desired 2-benzoylbiphenyl (III, R = H). The 1,2-dimethyl-4-phenyl-5-benzoylcyclohexene (II, R = CH_3), obtained in 90% yield from chalcone and dimethylbutadiene, was found to undergo dehydrogenation to the aromatic ketone (III, R = CH_3) more readily (45%). Treatment of the aromatized ketone with ethyl- or propyllithium resulted in reduction as well as the normal addition, for dehydration of the crude carbinols yielded 9-phenyl-2,3-dimethylfluorene (VI) as well as the expected olefin (IV).

On oxidation with monoperphthalic acid and cyclization with boiling hydrobromic–acetic acid, the olefins yielded what are believed to be 10-phenyl-2,3,9-trimethylphenanthrene (V, R′ = CH_3) and 9-ethyl-10-phenyl-2,3-dimethylphenanthrene (V, R′ = C_2H_5).

Dr. Marcus E. Hobbs and Mr. E. J. Hackney of this Laboratory have kindly undertaken a comparison of the new phenanthrene hydrocarbons (V) with 9-phenylphenanthrene and of 2,3-dimethyl-9-phenylfluorene (VI) with 9-phenylfluorene. They report as follows:

"In Figure 1 the curves giving $\log_{10}$ of molecular extinction (ϵ) *vs.* wave length (mμ) for the three phenanthrene hydrocarbons show that the absorption for the trimethyl- and ethyldimethyl-phenanthrenes (V, R′ = CH_3 and C_2H_5) is essentially the same for the spectral region shown. The separation of the benzenoid peak near 255 mμ and the phenanthrene peak near 300 mμ is 43 mμ for the 9-phenylphenanthrene and 46 mμ for the two alkyl derivatives (V, R = CH_3 and C_2H_5). The latter two compounds seem well enough defined to show that they are both derivatives of the parent substance 9-phenylphenanthrene.



In Fig. 2 the curves for the two fluorene derivatives differ from the curves for the phenanthrene derivatives (Fig. 1) both as to qualitative and quantitative aspects. The similarity of the curves

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[1] For the preceding communication of this series see THIS JOURNAL, **68**, 1094 (1946).

[2] *E. g.*, Bradsher and Rosher, *ibid.*, **61**, 1524 (1939); Bradsher and Tess, *ibid.*, **61**, 2184 (1939); Bradsher and Amore, *ibid.*, **63**, 493 (1941); **65**, 2016 (1943); **66**, 1280 (1944).

[3] Natsynskaya and Petrov, *J. Gen. Chem., U. S. S. R.*, **11**, 665 (1941); *C. A.*, **35**, 6934 (1941).

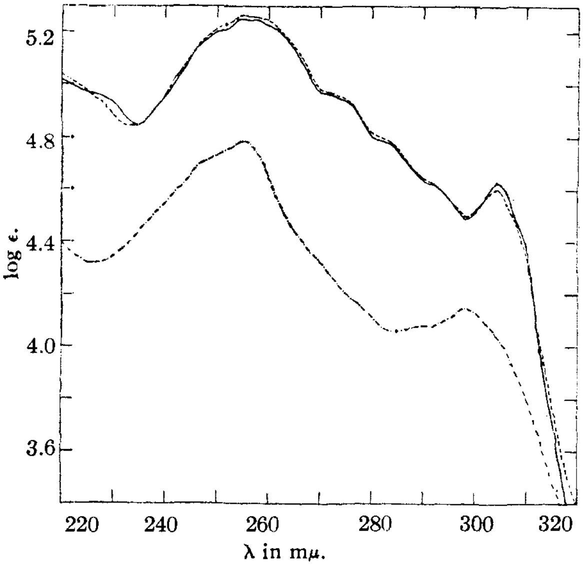


Fig. 1.—9-Phenylphenanthrene-·-·-; dimethyl-ethyl-9-phenylphenanthrene——; trimethyl-9-phenylphenanthrene - - - -

for the two fluorene derivatives as to wave length separation of the peaks and minima indicate rather well that VI is definitely a fluorene derivative.[4]"

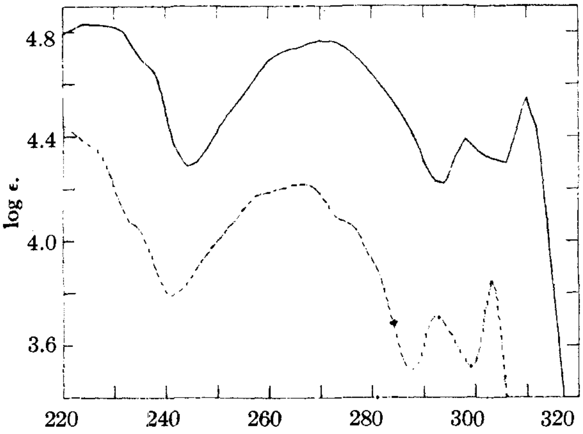
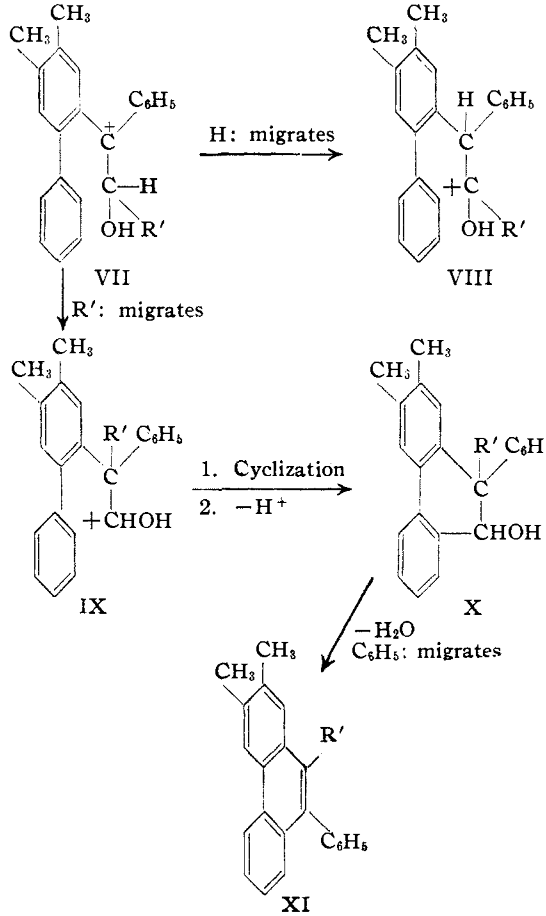


Fig. 2.—9-Phenylfluorene - · - · -; 2,3-dimethyl-9-phenylfluorene ——

Since substituted chalcones may be prepared with great ease, this synthesis should make possible the preparation of fairly complex phenyl phenanthrene derivatives with a wide choice of substituents in the central and one of the terminal rings, and with the possibility of further modification of the other terminal ring through a suitable choice of dienes.

While it is believed that the phenanthrene derivatives (V) have the assigned structure, a consideration of the mechanism will reveal that the hydrocarbon may possibly have the alternate structure in which the position of the substituents on the central nucleus is reversed (XI). Accepting the hypothesis that the acid-catalyzed rupture of a carbon-to-oxygen bond takes place at that carbon atom bearing the most potent electron releasing groups,[5] the product of this rupture would be the carbonium ion (VII). Next might be expected the migration of either a hydrogen or an alkyl group with a pair of electrons. In the former case, the product is the conjugate acid (VIII) of a ketone, the cyclization of which should follow a previously considered pattern.[1] If the alkyl group migrates, the product is the conjugate acid (IX) of a trisubstituted acetaldehyde. While cyclization (IX → X) could be expected in the usual way, dehydration of the resulting carbinol must be accompanied by a retropinacolone rearrangement. If the migrating group is the same as that in the first instance (VII → IX), the structure of the final hydrocarbon will be that originally represented (V), while if the phenyl group migrates, the isomeric 2,3-dimethyl-9-phenyl-10-alkyl-phenanthrene (XI) will be obtained.

A further extension of this synthesis is being undertaken.



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[4] A more complete discussion of absorption curves for the above and some related compounds will be reported from this Laboratory at a later date.—M. E. H.

[5] Ingold, *Ann. Rept. Progress Chem.*, **35**, 135 (1938), The Chemical Society, London.

Experimental

Absorption Spectra.—The ultraviolet absorption spectra were measured in 95% ethyl alcohol solution using a Beckman Model DU Quartz Spectrophotometer. The phenanthrene derivatives were measured at a concentration of 1.1×10^{-5} *M* and the fluorene derivatives at a concentration of 2.0×10^{-5} *M*. One centimeter silica cells were used in all measurements. The "nominal"[6] spectral regions isolated at the wave lengths of chief interest were: at 255 mμ — 1.7 mμ, at 258 mμ — 1.7 mμ, at 266 mμ — 1.6 mμ, at 270 mμ — 1.1 mμ, at 292 mμ — 1.5 mμ, at 298 mμ — 1.6 mμ, at 303 mμ — 1.7 mμ, and at 310 mμ — 1.8 mμ.

2-Benzoylbiphenyl (III, R = H) was obtained by heating 4-benzoyl-5-phenylcyclohexene[3] (4.53 g.) for one and one-half hours with sulfur (1.11 g.) at 230–240°. Distillation of the crude product followed by sublimation *in vacuo* gave a small amount of solid (m. p. 87–89°) which was shown to be 2-benzoyl-biphenyl by comparison with an authentic sample.[7]

Attempts at dehydrogenation of the hydroaromatic ketone using chloranil[8] or bromine[9] were unsuccessful.

4-Benzoyl-5-phenyl-1,2-dimethylcyclohexene (II, R = CH_3).—A mixture of benzalacetophenone (20 g.), ethanol (20 ml.) and 2,3-dimethylbutadiene[10] (19 g.) was heated for ten hours in a steel reactor at 150°. The hot solution crystallized on cooling to give 25.7 g. (90%) of almost white crystals, m. p. 83–86°. An analytical sample was prepared by recrystallization from ethanol, m. p. 85–86°.

Anal. Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found[11]: C, 86.86; H, 7.91.

2-Benzoyl-4,5-dimethylbiphenyl (III, R = CH_3).—A mixture of the hydroaromatic ketone above (25.6 g.) with sulfur (5.67 g.) was heated at 200–230° for one hour, followed by heating at 250° for one additional hour. The product was distilled *in vacuo*, and crystallized from methanol as small yellow crystals, m. p. 99–100°; yield 11.3 g. (45%).

A sample purified by vacuum sublimation and crystallization gave flat white needles from methanol, m. p. 102–103°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found[12]: C, 87.85; H, 6.66.

1-(4,5-Dimethylbiphenyl-2)-1-phenylpropene-1 (IV, R′ = CH_3).—The crude carbinol obtained by the action of the ethyllithium (prepared from 9.3 ml. of ethyl bromide) on 9.83 g. of the above ketone (III, R = CH_3) was heated with 27 g. of potassium bisulfate at 170° for one hour. The product was extracted with benzene–water. The benzene layer was washed and concentrated and the residue distilled under reduced pressure. The pale yellow oil on addition of petroleum ether deposited 1.1 g. of **2,3-dimethyl-9-phenylfluorene (VI)** which upon recrystallization from ethanol gave white crystals, m. p. 147.5–148°.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found[11]: C, 93.09; H, 6.75.

The remaining oil (7 g., 68%) could not be crystallized and was used directly in the next step without further purification.

2,3,9-Trimethyl-10-phenylphenanthrene (V, R′ = CH_3).—A portion (1.57 g.) of the crude olefin prepared above was dissolved in an ether solution containing a 50% excess of monoperphthalic acid and the solution allowed to stand for twenty-four hours; iodimetric titration of an aliquot showed almost complete oxidation. The acids were removed by washing with sodium bicarbonate solution and the ethereal layer concentrated. The residue was refluxed for ninety-six hours in a mixture containing 50 ml. of acetic acid and 20 ml. of hydrobromic acid. After cooling, the solid which collected was removed, dried, distilled under reduced pressure, and crystallized from ethanol to give 0.5 g. (32%, calculated from olefin) of small white granules, m. p. 131–133°. Repeated recrystallization raised the melting point to only 132–133°. In ethanol it formed a picrate, m. p. 164–165.5°.

Anal. Calcd. for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found[11]: C, 93.37; H, 6.87.

1-(4,5-Dimethylbiphenyl-2)-1-phenylbutene-1 (IV, R′ = C_2H_5).—To the lithium reagent prepared from 5.5 g. of *n*-propyl chloride, 10 g. of 4,5-dimethyl-2-benzoylbiphenyl was added in dry ether and the mixture refluxed for three hours. After decomposition of the mixture in the usual way, the ethereal layer was dried and concentrated. Addition of petroleum ether (b. p. 30–60°) caused the precipitation of 2.2 g. of the original ketone. The purified carbinol was heated with potassium bisulfate at 150° for one hour and the product worked up as in the preceding series (R′ = CH_3). Addition of petroleum ether precipitated 2,3-dimethyl-9-phenylfluorene as in the preceding series. The crude residue olefin, purified in no other way, was used directly in the following cyclization.

2,3-Dimethyl-9-ethyl-10-phenylphenanthrene (V, R′ = C_2H_5).—A portion (1.85 g.) of the crude olefin prepared above was added to an excess of monoperphthalic acid in ether solution. At the end of twenty-four hours, when titration showed that the theoretical amount of oxidant had been consumed, the acids were removed by extraction with sodium bicarbonate solution and the ethereal solution concentrated on the steam-bath. The residue refluxed for five days in the usual hydrobromic–acetic acid mixture, gave a solid which, when vacuum-distilled and crystallized from ethanol, gave pale yellow needles, m. p. 152–155°; yield 0.8 g. (43.5% calculated from the olefin).

Recrystallization from ethanol gave white, well-defined needles, m. p. 154–156°. In ethanol it formed a picrate, m. p. 139.5–140°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.85; H, 7.15. Found[11]: C, 92.64; H, 7.15.

Summary

The possibility of using the diene addition reaction in conjunction with olefin oxide cyclization has been explored. Two new phenanthrene hydrocarbons have been prepared by this combination of reactions.

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[6] Fig. DD25 dated 7-15-41, National Technical Laboratories, South Pasadena, California.

[7] Bradsher, THIS JOURNAL, **66**, 45 (1944).

[8] Clar and John, *Ber.*, **62**, 3021 (1929); Arnold and Collins, THIS JOURNAL, **61**, 1407 (1939); Arnold, Collins and Zenk, *ibid.*, **62**, 983 (1940).

[9] *Cf.* Adams and Geissman, *ibid.*, **61**, 2083 (1939); Adams and Gold, *ibid.*, **62**, 56 (1940).

[10] Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 383.

[11] Analysis by Arlington Laboratories.

[12] Analysis by Dr. T. S. Ma, University of Chicago.