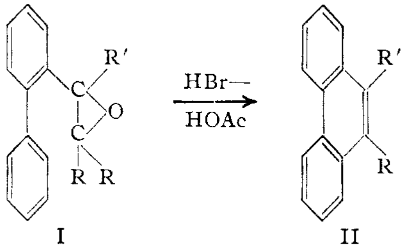
[Contribution from the Chemical Laboratory of Duke University]

Aromatic Cyclodehydration. XX.[1] Elimination of Alkyl Groups in Cyclizations of the Olefin Oxide Type

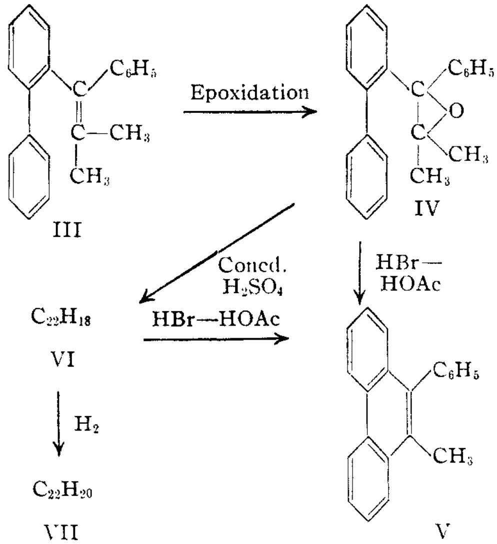
By Charles K. Bradsher, Lorence Rapoport and Powell Anderson

In previous papers of this series,[2] it has been shown that the cyclization of certain 2-biphenylylolefin oxides (I, one or both R groups = H) can lead to the formation of phenanthrene hydrocarbons (II) with substituents in the 9- or 9,10-positions.



As a means for the elucidation of the mechanism of this reaction, a study of oxides of the type illustrated (R = alkyl) seemed particularly promising. Should the cyclization of such an oxide be accomplished, the hydroaromatic compound thus formed would be "blocked," that is to say, it could not achieve aromatic character through the loss of water. It has now been observed that even this "blocking" does not prevent the formation of fully aromatic 9,10-disubstituted phenanthrene derivatives (II). This aromatization evidently involves the loss of the elements of the corresponding alcohol (R = OH), thus, the oxide (I, R = CH_3; R' = C_6H_5) of 1-(2-biphenylyl)-1-phenyl-2,2-dimethylethene gave 9-methyl-10-phenylphenanthrene (II, R' = C_6H_5; R = CH_3) while the oxide (I, R' = C_6H_5; R = C_2H_5) of the corresponding diethylethene yielded 9-ethyl-10-phenylphenanthrene. It was found that the presence of the phenyl group was not essential in this reaction for the oxide (I, R and R' = CH_3) of 1-(2-biphenylyl)-1,2,2-trimethylethene when treated with the usual acid mixture yielded 9,10-dimethylphenanthrene (II, R and R' = CH_3).

A possible clue to the mechanism for these transformations is to be found in the behavior of the oxide (IV) of 1-(2-biphenylyl)-1-phenyl-2,2-dimethylethene when treated with cold concentrated sulfuric acid. Under these conditions, the oxide appears to lose a molecule of water to form an unsaturated hydrocarbon (VI) which may be readily hydrogenated to a compound (VII) having, apparently two more hydrogen atoms. Remarkably, the unsaturated hydrocarbon (VI), upon refluxing in the usual hydrobromic–acetic acid mixture, loses one carbon and two hydrogen atoms to yield 9-phenyl-10-methylphenanthrene.



A brief review of two of the more plausible mechanisms for this cyclization will be of assistance in arriving at a tentative structure for the unsaturated hydrocarbon (VI). On the basis of accepted interpretations[3] for the rearrangement of olefin oxides, it would be expected that addition of a proton (followed by rupture of a carbon-to-oxygen bond) would yield the carbonium ion (VIII). While this ion could undergo a normal pinacolic rearrangement to the conjugate acid XI, an alternative possibility is that attack on the adjacent benzenoid ring might take place yielding the fluorenecarbinol (IX). The latter assumption appeared plausible since evidence at hand indicates that related secondary[4] and primary[5] carbinols undergo dehydration with Wagner–Meerwein rearrangement to yield phenanthrene hydrocarbons. In our case, at the higher temperature, the carbinol (IX) might undergo a similar rearrangement with the loss of the elements of methyl alcohol, while at the lower temperature it would undergo simple dehydration to the olefin (XII), the carbanion X being the intermediate in either reaction.

We have demonstrated that this "fluorenecarbinol" mechanism is incorrect for the hydrogena-

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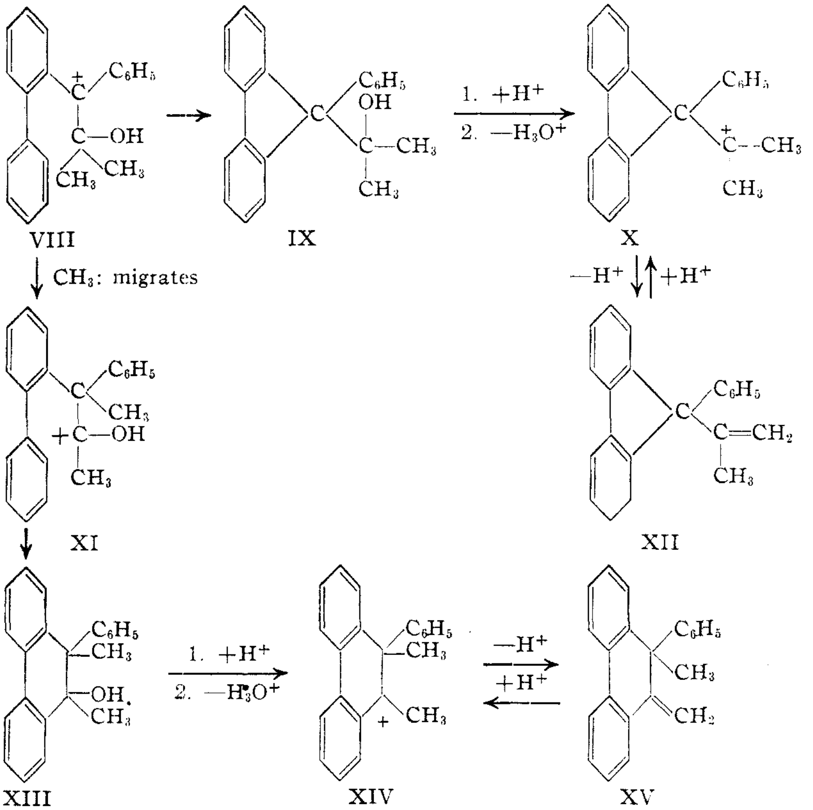
[1] For the preceding communication of the series see This Journal, **68**, 2149 (1946).

[2] *E. g.*, (a) Bradsher, *ibid.*, **61**, 3131 (1939); (b) Bradsher and Amore, *ibid.*, **63**, 493 (1941); (c) **65**, 2016 (1943); (d) **66**, 1280 (1944).

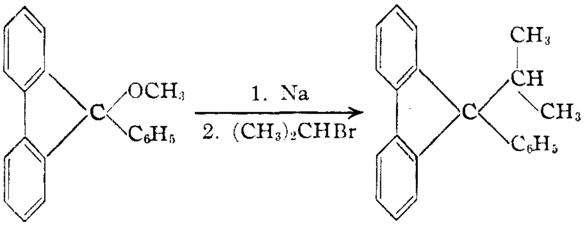
[3] Ingold, "Annual Reports on the Progress of Chemistry," The Chemical Society, London, **25**, 135 (1928); Wallis, "Organic Chemistry, An Advanced Treatise," Vol. I, Henry Gilman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 787.

[4] Werner and Grob, *Ber.*, **37**, 2894 (1904); Meerwein, *Ann.*, **405**, 129, 173 (1914).

[5] Brown and Bluestein, This Journal, **62**, 3256 (1940); **65**, 1235 (1943).



tion product (VII) of the unknown olefin was not identical with a sample of 9-phenyl-9-isopropylfluorene (XVI) prepared by the action of isopropyl bromide on 9-phenylfluorenylsodium.



Returning to the possibility that normal rearrangement takes place,[6] cyclization of the resulting conjugate acid[7] would yield a 9,10-dihydrophenanthrene derivative (XIII) which in the acidic medium would be transformed into the carbonium ion (XIV). At the lower temperatures of the sulfuric acid reaction, this ion might simply undergo the reversible loss of a proton to yield the unsaturated hydrocarbon (XV) while at a higher temperature the irreversible loss of a methyl ion may take place to yield the fully aromatic 9-methyl-10-phenylphenanthrene. It appears reasonable that the correct structure for the dehydration product (VI) of the olefin oxide is 9-methyl-9-phenyl-10-methylene-9,10-dihydrophenanthrene (XV), but this formulation is as yet tentative, pending further study.

Experimental

1-(2-Biphenylyl)-1-phenyl-2,2-dimethylethene Oxide Series

Phenyl-(2-biphenylyl)-isopropylcarbinol.—A lithium reagent was prepared from 28 g. of 2-iodobiphenyl in dry ether and 16 g. of isobutyrophenone in 60 ml. of dry ether added at such a rate as to maintain vigorous refluxing. After the addition was complete, the mixture was refluxed overnight and decomposed with ice and water in the usual way. The residue obtained by evaporation of the ethereal solution solidified on standing, was triturated with 20 ml. of ice-cold ethanol and collected, yielding 24.6 g. (81.5%) of colorless crystals, m. p. 103–105°. An analytical sample, obtained by recrystallization from ethanol, melted at 104–105°.

Anal.[8] Calcd. for $C_{22}H_{20}O$: C, 87.37; H, 7.33. Found: C, 87.25; H, 7.11.

1-(2-Biphenylyl)-1-phenyl-2,2-dimethylethene (III).—The above carbinol (23.6 g.) was heated for one hour at 170° with 60 g. of potassium bisulfate. After cooling, the organic material was extracted with ether and purified by vacuum distillation. The product was a colorless viscous oil, b. p. 184–185° (6–7 mm.); yield, 18.4 g. (83%). This oil which crystallized on standing, was pure enough for further reactions, but a sample recrystallized from ethanol as hexagonal prisms melted at 57.5–58.5°.

Anal.[8] Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 93.02; H, 6.90.

1-(2-Biphenyl)-1-phenyl-2,2-dimethylethene Oxide (IV).—The above olefin (4.6 g.) was dissolved in 60 ml. of ether containing 4.0 g. of monoperphthalic acid. The solution was allowed to stand at room temperature for forty hours, at the end of which time, analysis showed that the theoretical quantity of peracid had been consumed. After extraction of the acid with bicarbonate solution, the ether was evaporated. The residue crystallized as a white powder, m. p. 115–125°; yield 4.8 g. (99%). An analytical sample prepared by crystallization from ethanol gave square white plates, m. p. 127.5–128.5°.

Anal.[8] Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.90; H, 6.34.

Hydrobromic–Acetic Acid Cyclization.—One gram of the oxide above was refluxed in a mixture of 8 ml. of 48% hydrobromic acid and 15 ml. of glacial acetic acid for twenty-four hours. At the end of this period, the product was taken up in ether and the ethereal solution washed and evaporated. The residue was crystallized from ethyl alcohol as flat glistening white needles, m. p. 97–99°; yield 0.50 g. (56%). A mixed melting point determination (98–99°) with an authentic sample[9] showed this material to be **9-phenyl-10-methylphenanthrene.**

Sulfuric Acid Cyclization.—One gram of the oxide (IV) was added in portions to 5 ml. of ice-cold concentrated

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(6) Ramart-Lucas and Salmon-Legagneur (*Bull. soc. chim.*, [4] **45**, 718 (1929)) have shown that the oxide of unsymmetrical diphenyldimethylethylene, on treatment with concentrated sulfuric acid, yields α-methyl-α,α-diphenylacetone.

(7) It has been demonstrated (Bradsher and Wissow, THIS JOURNAL, **68**, 2149 (1946)) that related biphenylyl methyl ketones may be cyclized to phenanthrene derivatives, evidently through the conjugate acid.

(8) Analyses by T. S. Ma, University of Chicago.

(9) Bradsher and Rosher, THIS JOURNAL, **61**, 1524 (1939).

sulfuric acid. A deep purple color developed immediately and the material slowly went into solution. After standing for one-half hour, the solution was poured into 200 ml. of ice and water. A white precipitate formed and was collected. On warming on the filter, this material became gummy. Crystallization from ethyl alcohol yielded flat white needles, m. p. 88–90°; yield 0.55 g. (58%). An analytical sample melted at 89–90°.

Anal.[8] Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.19; H, 6.76.

This unsaturated hydrocarbon (VI) presumably **9-methylene-10-methyl-10-phenyl-9,10-dihydrophenanthrene (XV)** gave an immediate purple solution when treated with concentrated sulfuric acid.

Hydrogenation of the Unsaturated Hydrocarbon (VI).—The above hydrocarbon (0.35 g.) was reduced in quantitative yield by shaking in alcoholic solution for one-half hour with platinum oxide catalyst under hydrogen pressure of three atmospheres. Crystallized from alcohol, the product formed fine white needles, m. p. 114–115° with immediate resolidification and remelting at 124–125°. The more stable (higher melting) form was obtained after drying an analytical sample *in vacuo* for four hours at 100°.

Anal.[8] Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.76; H, 7.26.

This hydrocarbon (VII) is probably **9,10-dimethyl-10-phenyl-9,10-dihydrophenanthrene.**

Action of Hydrobromic–Acetic Acid on the Unsaturated Hydrocarbon (VI).—The unsaturated hydrocarbon (0.2 g.) was dissolved in 10 ml. of acetic acid, 5 ml. of 48% hydrobromic acid added, and the mixture refluxed for twenty-four hours. The mixture was diluted with water, extracted with ether–benzene, dried and the solvent removed. The residue was vacuum sublimed, yielding 0.12 g. of white needles, m. p. 97–98.5°. This gave no depression of melting point when mixed with an authentic sample of 9-methyl-10-phenylphenanthrene.

9-Phenyl-9-isopropylfluorene (XVI).—An ethereal solution of 2.71 g. of 9-phenyl-9-methoxyfluorene[10] was shaken for three days with an excess of sodium wire (0.75 g.) yielding a deep orange colored solution. At the end of this period 5 ml. of isopropyl bromide was added, discharging the color. After washing and drying, the ethereal solution was evaporated and the residue crystallized from alcohol as white prisms, m. p. 125–127°; yield 1.8 g. An analytical sample melted at 128–129° and was not identical (mixed m. p. 101–119°) with the hydrogenation product (VII).

Anal.[8] Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.82; H, 6.90.

1-(2-Biphenylyl)-1-phenyl-2,2-diethylethene Oxide Series

1-(2-Biphenylyl)-1-phenyl-2,2-diethylethene.—This olefin was prepared essentially as was the dimethyl derivative (III) except that the carbinol was not isolated. The lithium reagent prepared from 30 g. of 2-iodobiphenyl was allowed to react with an ethereal solution containing 17.6 g. of ω,ω-diethylacetophenone and after decomposition as in the previous case, the resulting crude carbinol was heated directly with 100 g. of potassium bisulfate. Purified as previously by vacuum distillation and crystallization from alcohol 10 g. (33%) of white irregular flat needles was obtained, m. p. 107–108°. An analytical sample melted at 107.5–108.5°.

Anal.[11] Calcd. for $C_{24}H_{24}$: C, 92.25; H, 7.75. Found: C, 92.41; H, 7.79.

1-(2-Biphenylyl)-1-phenyl-2,2-diethylethene Oxide (I, R = C_2H_5; R′ = C_6H_5).—The above olefin (3.12 g.) was oxidized as in the previous series using 1.5 mole equivalents of perbenzoic acid. The crude oxide obtained by evaporation of the washed ether solution was twice crystallized from ethanol to yield 2.45 g. (75%) of small white cubes, m. p. 100.5–101.5°. An analytical sample melted at 100.5–101.5°.

Anal.[11] Calcd. for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.88; H, 7.22.

9-Ethyl-10-phenylphenanthrene (II, R = C_2H_5; R′ = C_6H_5).—The oxide (0.5 g.) was refluxed for twenty-three hours with a mixture containing 5 ml. of acetic acid and 5 ml. of 48% hydrobromic acid. The gummy solid which collected on cooling was recrystallized from acetic acid to yield 0.26 g. (60%) of flat white needles, m. p. 162–164°. Once recrystallized from acetic acid, it melted at 164–164.5° and gave no depression when mixed with an authentic sample[9] of 9-ethyl-10-phenylphenanthrene.

9,10-Dimethylphenanthrene.[12]—Crude 1-(2-biphenylyl)-1,2,2-trimethylethene (4.1 g.) obtained in 24% yield from methyl isopropyl ketone by the method used in the preceding cases, was oxidized with an excess of monoperphthalic acid and the resulting oxide cyclized by refluxing for twenty-four hours with hydrobromic–acetic acid. The crude product was purified by vacuum distillation, followed by crystallization from ethanol yielding 0.3 g. (8%) of nearly white needles, m. p. 141–142°. This did not depress the melting point of an authentic[2d] sample of 9,10-dimethylphenanthrene.

Summary

By the cyclization of 1-(2-biphenylyl)-olefin oxides of such structure that the primary cyclization product cannot achieve aromatic character through loss of water, it has been shown that, under normal conditions for the cyclization, aromatic character is achieved through the loss of the elements of an alcohol (ROH) from the molecule.

Under less drastic conditions, in one instance an unsaturated hydrocarbon, probably a 9,10-dihydrophenanthrene derivative, was obtained.

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[10] Schlenk and Bergmann, *Ann.*, **463**, 98 (1928).

[11] Analyses by Arlington Laboratories.

[12] Experiment by Shirley Davie.