Summary

Lupinus sericeus var. *flexuosus* contains 0.53% of alkaloids, the principal base being octalupine, $C_{15}H_{22}O_2N_2$, a 2,16-diketosparteine. The base and several of its salts are described.

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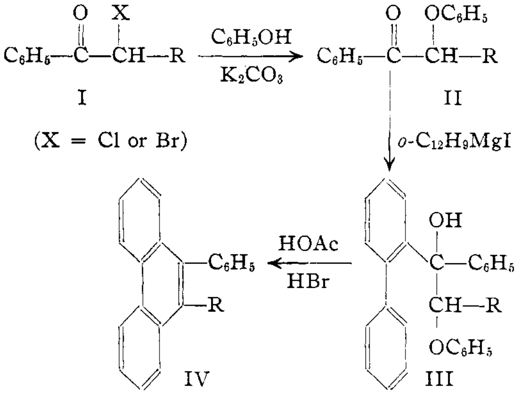
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND DUKE UNIVERSITY]

Synthesis of Phenanthrene Derivatives. II.[1] 9,10-Disubstituted Hydrocarbons

BY CHARLES K. BRADSHER[2,3] AND RONALD ROSHER

The great ease with which 1-phenyl-1-(2-biphenyl)-2-phenoxyethanol-1 (III, R = H) undergoes cyclization to form 9-phenylphenanthrene suggested the possibility that this mode of reaction might be general for carbinols of this type.



(R = H, CH_3, C_2H_5 or C_6H_5)

Should such be the case it would offer a convenient method for the preparation of 9,10-disubstituted phenanthrenes.

Three such carbinols were synthesized. In each case they were prepared by the action of 2-biphenylmagnesium iodide on α-phenoxy ketones of type II.

Of the three α-phenoxy ketones required for this research only one, desyl phenyl ether (II, R = C_6H_5), has been reported previously.[4] The other two, α-phenoxypropio- and α-phenoxybutyro-phenones (II, R = CH_3 and C_2H_5) were prepared by refluxing an acetone solution of the corresponding α-bromo ketones (I, R = CH_3 and C_2H_5; X = Br) with potassium carbonate and phenol. These two, in sofar as we know, constitute the only known compounds of type II in which R is an aliphatic group.

Each of the carbinols (III) may exist in two diastereomeric forms. Since we were primarily interested in obtaining hydrocarbons in good yield, it was considered inadvisable to attempt the purification of the carbinols. The crude products of the Grignard reaction were refluxed directly with a mixture of hydrobromic and acetic acids. In each case the corresponding hydrocarbon (IV) was obtained in good yield. The best results were obtained in the case of 9-methyl-10-phenylphenanthrene (IV, R = CH_3) which was obtained in a yield of 72% from α-phenoxypropiophenone or an over-all yield of 40% from propiophenone.

Although 9,10-diphenylphenanthrene (IV, R = C_6H_5) has been known for some time,[5] the two 9-alkyl-10-phenylphenanthrenes (IV, R = CH_3 or C_2H_5) are not only new, but are the unique examples of a phenanthrene hydrocarbon with two dissimilar substituents in the central nucleus.

Experimental

α-Bromobutyrophenone was prepared in 84% yield by bromination of butyrophenone in chloroform solution. This product boiled at 168–170° (19 mm.).

α-Phenoxybutyrophenone.—To a solution of 38 g. of α-bromobutyrophenone in 200 cc. of acetone was added 15.7 g. of phenol and 22.8 g. of potassium carbonate and the mixture refluxed for five hours. At the end of this period water was added and yellow oil which separated was taken up in ether. The ethereal solution was washed with dilute sodium hydroxide, the ether evaporated and the residue crystallized from ethanol as tiny colorless needles, m. p. 70°; yield 27 g. (66%).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.20; H, 6.82.

1-Phenyl-1-(2-biphenyl)-2-phenoxybutanol-1 (III, R = C_2H_5).—A Grignard reagent was prepared in ether from 28 g. of 2-iodobiphenyl and 2.4 g. of magnesium. To this was added 24 g. of α-phenoxybutyrophenone in dry benzene solution. After one hour the addition product was decomposed with 20% ammonium chloride solution. The ether solution was separated and evaporated. The residue crystallized on standing. Once recrystallized from

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(1) For the first paper of this series see THIS JOURNAL, **60**, 2960 (1938).

(2) Du Pont Post-Doctorate Fellow, 1938.

(3) Author's present address: Duke University, Durham, N. C.

(4) Richard, *Compt. rend.* **198**, 1242 (1934).

(5) Klinger and Lonnes, *Ber.*, **29**, 2152 (1896).

low-boiling petroleum ether it was obtained as an amorphous powder, m. p. 83–91°, yield 19 g. (49%).

Anal. Calcd. for $C_{23}H_{26}O_2$: C, 85.25; H, 6.62. Found: C, 84.62; H, 6.60.

9-Ethyl-10-phenylphenanthrene.—The carbinol (III, R = C_2H_5) (8 g.) was dissolved in acetic acid (40 cc.) and concentrated hydrobromic acid (22 cc.) added. After the mixture had been refluxed for a few hours, crystals started to separate. After twenty-two hours the crystals were collected and recrystallized from methyl alcohol as small plates, m. p. 161°; yield 4 g. (70%).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.38; H, 6.35.

α-Bromopropiophenone was prepared in the same manner as the α-bromobutyrophenone. It was obtained in 90% yield as a yellow oil, b. p. 141° (18–20 mm.).

α-Phenoxypropiophenone was prepared in a manner analogous to that used in the case of α-phenoxybutyrophenone except that a slight excess of phenol and potassium carbonate was used. From 38 g. of α-bromopropiophenone 25 g. (62%) of colorless, silky needles was obtained, m. p. 79–80°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.55; H, 6.41.

1-Phenyl-1-(2-biphenyl)-2-phenoxypropanol-1 (III, R = CH_3) was prepared from 10 g. of α-phenoxypropiophenone by addition to an excess of 2-biphenylmagnesium iodide in a manner analogous to that used in the preparation of III (R = C_2H_5). No attempt was made to purify the crude product from the Grignard reaction. The ether was merely evaporated off and the residue used in the following reaction.

9-Methyl-10-phenylphenanthrene.—The crude carbinol was refluxed with hydrobromic and acetic acids for twenty-four hours. At the conclusion of this period the acid was neutralized and the product extracted with ether. The ether was evaporated and the residue crystallized from ethanol, as colorless flat needles, m. p. 99–100°; yield 8.5 g. (72%, calculated from α-phenoxypropiophenone used).

Anal. Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.00. Found: C, 93.96; H, 6.17.

This hydrocarbon formed an orange picrate, m. p. 131–133°.

Desyl phenyl ether (II, R = C_6H_5) was prepared from desyl chloride[6] in a manner analogous to that used in the preparation of α-phenoxybutyrophenone from α-bromobutyrophenone. From 11.5 g. of the desyl chloride 8.5 g. (59%) of desyl phenyl ether, m. p. 85° was obtained. The product described by Richard[4] melted at 85.5°.

1,2-Diphenyl-1-(2-biphenyl)-2-phenoxyethanol-1 (III, R = C_6H_5) was prepared by the action of 2-biphenylmagnesium iodide on desyl phenyl ether. The reaction was carried out as described previously (III, R = CH_3 or C_2H_5). The carbinol was not purified.

9,10-Diphenylphenanthrene.—The impure carbinol was refluxed with a mixture of acetic and hydrobromic acids. The hydrocarbon crystallized from the reaction mixture and was recrystallized from acetic acid as long needles, m. p. 234°; yield 6 g. (62%).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.24; H, 5.50.

Summary

A convenient method for the preparation of α-phenoxy ketones has been devised.

By a suitable extension, the new type of ring closure has been used to prepare phenanthrene hydrocarbons with substituents in both the 9- and 10-positions.

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(6) Ward, *Org. Syntheses*, **12**, 20 (1932).

DURHAM, N. C. RECEIVED APRIL 15, 1939

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Relations between Rotatory Power and Structure in the Sugar Group. XXXII. The Rotations of the Aldonic Gamma Lactones[1]

BY C. S. HUDSON

The lactone rule of rotation[2] is a qualitative expression; it correlates the sign of rotation with the stereoconfiguration of the gamma lactone ring, but the magnitude of the rotation is not disclosed. The extensive data from which the rule was inferred have always seemed to preclude the possibility that the principle of optical superposition can hold in this group of lactones; thus, as one example, the specific rotations ($[\alpha]_D$ in water) of the gamma lactones of D-ribonic (+18), D-arabonic (+72) and D-xylonic (+92) acids require by this principle that the value for D-lyxonic lactone be +146, but its observed value is +82. It has long seemed strange to me that superposition and also isorotation hold fairly closely among the alpha and beta forms of many sugars and glycosides, and among the aldonic amides, but have appeared to fail completely in the lactone group. Lately I have observed that the more extensive and more accurate data that are now available give good evidence that superposition and isorotation may hold, provided the

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. No. XXXI was published in THIS JOURNAL, **61**, 1268 (1939). Presented at the Baltimore meeting of the Amer. Chem. Soc., April 6, 1939.

[2] Hudson, THIS JOURNAL, **32**, 338 (1910).