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The Isomeric Phenylpyrenes

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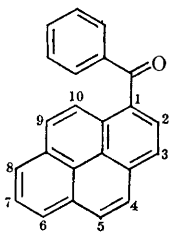
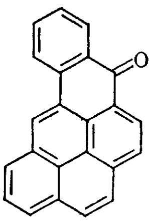
In connection with another investigation we required authentic samples of the three phenylpyrenes. During the synthesis of these compounds we discovered several erroneous assignments of structure which have created a confused situation. For example, Jensen and Berg[1] have recently reported the "first" synthesis of 2-phenylpyrene. However, this isomer was described thirty years ago as "4-phenylpyrene" and has masqueraded in this guise ever since.[2]

Our sample of 1-phenylpyrene was prepared as described by Norman, Thompson, and Waters[3] and has a melting point of 82—83° and an ultraviolet absorption spectrum that is essentially identical with the values reported by these workers. Furthermore, Jensen and Berg have prepared this isomer by two additional methods.[1]

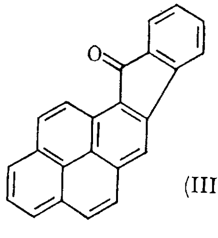
2-Phenylpyrene was synthesized from 2-aminopyrene[4] by diazotization and arylation of benzene. The melting point of our sample (173—175°) and its ultraviolet spectrum are in good agreement with the melting point, 166—167°, and the ultraviolet data reported for 2-phenylpyrene by Jensen and Berg. This isomer (m.p. 169°) was described initially as "4-phenylpyrene" by Vollmann *et al.*[2] who prepared it from 1-benzoylpyrene (I) by cyclodehydrogenation to ketone,[5] alkaline fusion to acid(s) and decarboxylation. Twenty years later, Lang and Buffleb[6] isolated two phenylpyrenes from a pyrolysate of pyrene and benzene. One of these isomers, m.p. 170—171°, was identified as Vollmann's "4-phenylpyrene." However, the ultraviolet absorption spectrum reported by these workers confirm that this compound is the 2-isomer.



(I)



(II)



(III)

We prepared the real 4-phenylpyrene from 4-aminopyrene[7] by the route described above for the 2-isomer. The melting point (133—134°) and ultraviolet spectrum of this compound are essentially identical with the corresponding data given by Lang and Buffleb[6] for the second phenylpyrene (m.p. 132°) isolated from their pyrolysate. These workers assigned the "1-phenylpyrene" structure to this compound since they demonstrated that it must be either the "4"- or the "1"-isomer.

Obviously, the original error is in the work of Vollmann *et al.*[2] who made the erroneous assumption that cyclodehydrogenation of 1-benzoylpyrene (I) gave ketone (II). We have repeated this reaction and found that the earlier workers actually isolated a ketone which exhibits carbonyl absorption in the infrared (1695 cm.$^{-1}$, $CHCl_3$) that is characteristic of 9-fluorenones,[8] *i.e.*, ketone (III). Although (III) is the major product of the reaction, we have also isolated ketone (II) which exhibits carbonyl absorption at the expected frequency (1642 cm.$^{-1}$ in $CHCl_3$).[9]

Wolff–Kishner reduction of ketone (III) affords hydrocarbon (III; CH_2 for CO). Previously, Clar had reduced the product of cyclodehydrogenation of (I) to a hydrocarbon which was assigned structure (II; CH_2 for CO).[10] However, the physical properties and ultraviolet absorption spectrum of authentic (III; CH_2 for CO) are virtually identical with those reported for (II; CH_2 for CO). Thus, Clar's sample of "8*H*-dibenzo[*b,f,g*]pyrene" is in reality 11*H*-indeno-[2,1-*a*]pyrene (III; CH_2 for CO).

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[3] R. O. C. Norman, G. A. Thompson, and W. A. Waters, *J. Chem. Soc.*, 1958, 175.

[4] A. Streitwieser, Jr., R. Lawler, and P. Schwaab, *J. Org. Chem.*, 1965, **30**, 1470; A. Jensen and A. Berg, *Acta Chem. Scand.*, 1965, **19**, 520.

[5] For a recent Review of the cyclodehydrogenation or Scholl reaction, see: A. T. Balaban and L. D. Nenitzescu in "Friedel–Crafts and Related Reactions," Vol. II, Part 2, G. A. Olah, ed., Wiley–Interscience, New York, 1964, ch. XXIII.

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