

The True Nature of "Dibenzo[*a,l*]pyrene" and its Known Derivatives

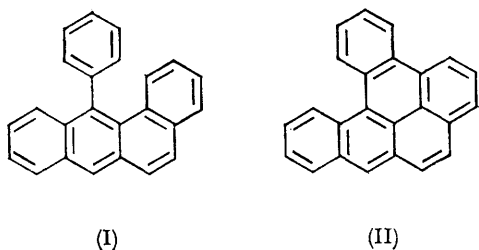
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"DIBENZO[*a,l*]PYRENE" (II) is one of the oldest recognised potent carcinogenic hydrocarbons,¹ and has been identified in tobacco smoke. It was first prepared by Clar from *o*-(1-naphthoyl)benzoic acid by a multi-step synthesis²; simpler methods of preparation are the aluminium chloride-catalysed dehydrogenation of 12-phenylbenz[*a*]anthracene (I) in benzene,³ and direct reaction of benzene

with benz[*a*]anthracene in similar experimental conditions.⁴ Several homologues of "dibenzo[*a,l*]pyrene" have been reported in the literature, and were prepared either from the hydrocarbon itself, as in the case of "10-methyl-" and "10-formyl-dibenzo[*a,l*]pyrene",⁵ or by syntheses based on the same principles as for the preparation of the non-substituted compounds.⁶

The surprisingly low degree of reactivity of the *meso*-anthracene position in "dibenzo[*a,l*]pyrene", observed in the Vilsmeier-Haack reaction⁶ (in contrast with the very high free-valence index assigned to that position⁷) led us to doubt the structure hitherto accepted for this hydrocarbon.

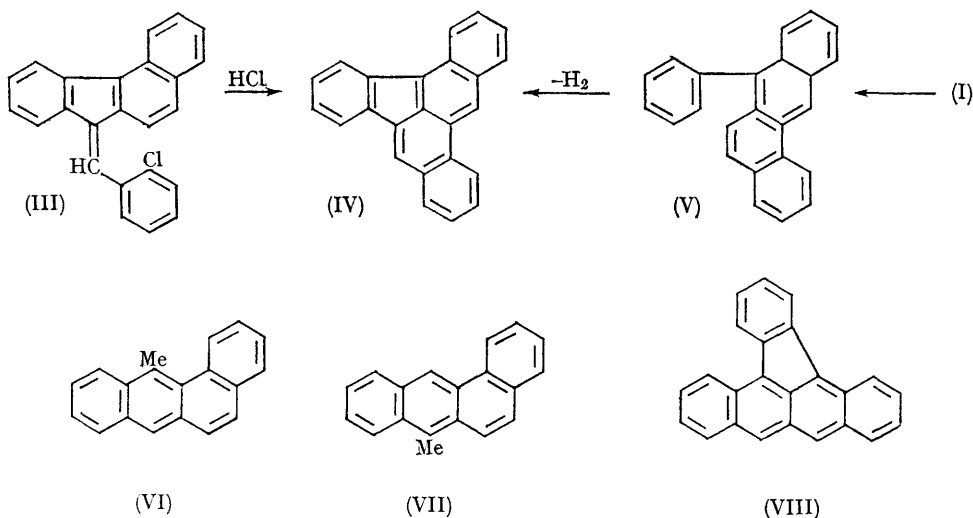


We now report that what has been considered as "dibenzo[*a,l*]pyrene" is in fact identical (m.p. 232°, mixed m.p., properties of the picrate, absorption spectra, halochromism in sulphuric acid) with

reaction mechanism was proved (a) by the isolation of substantial amounts of dibenzo[*a,f*]fluoranthene (VIII) from among the reaction products, and (b) by the easy formation of dibenzo[*a,e*]fluoranthene (IV) by treatment of (V) with aluminium chloride in benzene.

The rearrangement (I)→(V) appears to be only one instance of a general phenomenon, as we were also able to convert 12-methylbenz[*a*]anthracene (VI) into the 7-methyl isomer (VII), although with smaller yields. The mechanism of these rearrangements seems definitely to involve the benz[*a*]anthracene skeleton rather than a simple displacement of substituents, as (VIII) is a side-product in Clar and Stewart's synthesis, and benz[*a*]anthracene itself has shown to rearrange into chrysene in very similar circumstances in low yield.⁸

The reformulation of (II) as dibenzo[*a,e*]fluoranthene should certainly be extended to the products from direct substitution of "dibenzo[*a,l*]pyrene" ("10-formyldibenzo[*a,l*]pyrene") is in



dibenzo[*a,e*]fluoranthene (IV), which we synthesised unequivocally from 7*H*-benzo[*c*]fluorene, by condensation with *o*-chlorobenzaldehyde to its 7-*o*-chlorobenzal derivative (III), and cyclisation of the latter by means of potassium hydroxide in quinoline (in this cyclisation reaction, dibenzo[*b,j*]fluoranthene, m.p. 170–171°, was a by-product.)

In Clar and Stewart's synthesis,³ (IV) arises from a rearrangement of 12-phenylbenz[*a*]anthracene (I) to the 7-phenyl isomer (V), with subsequent cyclodehydrogenation of the latter. This

reality 5-formyldibenzo[*a,e*]fluoranthene (IX), in the formula of which the sterically hindered

position occupied by the formyl group accounts for the difficulties encountered in the preparation of this aldehyde), and probably to many if not all of those homologues of "dibenzo[*a,l*]pyrene" which

had been synthesised by procedures involving the use of aluminium chloride.

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¹ Cf. W. E. Bachmann, J. W. Cook, A. Dansi, C. G. M. deWorms, G. A. D. Haslewood, C. L. Hewett, and A. M. Robinson, *Proc. Roy. Soc.*, 1937, B, **123**, 343.

² E. Clar, *Ber.*, 1930, **63**, 112.

³ E. Clar and D. Stewart, *J. Chem. Soc.*, 1951, 687; E. Clar, "Polycyclic Hydrocarbons", Academic Press, London and New York, 1964.

⁴ M. Zander, *Chem. Ber.*, 1959, **92**, 2749.

⁵ N. P. Buu-Hoï and D. Lavit-Lamy, *Compt. rend.*, 1962, **255**, 2614.

⁶ F. A. Vingiello and W. W. Zajac, *J. Org. Chem.*, 1961, **26**, 2228.

⁷ A. Pullman and B. Pullman, "Cancérisation par les substances chimiques et structure moléculaire", Masson, Paris, 1955; for correlation between free valence indices and Vilsmeier-Haack reaction, see N. P. Buu-Hoï, D. Lavit, and O. Chalvet, *Tetrahedron*, 1960, **8**, 7.

⁸ N. P. Buu-Hoï and D. Lavit-Lamy, *Bull. Soc. chim. France*, 1962, 1398.