LXV.—Polycyclic Aromatic Hydrocarbons. Part II. The Non-existence of 1:2:7:8-Dibenzanthracene.

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By pyrolysis of 2-methyl-1: 1'-dinaphthyl ketone (I) and 2-methyl-1: 2'-dinaphthyl ketone (II), Clar (*Ber.*, 1929, **62**, 350) and Fieser and Dietz (*ibid.*, p. 1827) obtained compounds which they believed to be respectively 1:2:7:8-dibenzanthracene (III) and 1:2:5:6dibenzanthracene (IV):



The two products had practically the same m. p., alone or mixed, as was also the case with their respective picrates and guinones, and they were indistinguishable in their physical properties (solubility, absorption spectra, and the oxidation-reduction potentials of the quinones). The only apparent difference was one of colour, but whereas Clar observed that the hydrocarbon from (I) was more highly coloured than that from (II), Fieser and Dietz found the This difference is of no significance, as it has been found reverse. that in both cases the colour is due to an impurity which can be removed by suitable treatment with sulphuric acid. The above authors commented on the great resemblance between the pyrolysis products of (I) and (II), but do not appear to have considered the possibility that they are identical; nevertheless, it is evident from the experiments described in the following paper that this is so. \mathbf{It} was found that the two substances have the same fluorescence spectrum (Hieger, Biochem. J., 1930, 24, 505) and both produce cancer in mice (Kennaway and Hieger, Brit. Med. J., 1930, I, 1044), and the following derivatives of the supposed 1:2:7:8-dibenzanthracene were found to be identical in all respects with the corresponding derivatives of the supposed 1:2:5:6-dibenzanthracene: 2'-methyl- (m. p. 256-257.5°), 3'-methyl- (m. p. 245°), 9:10dimethyl- (m. p. $205 \cdot 5$ — $206 \cdot 5^{\circ}$), 9:10-di-*n*-butyl- (m. p. 143 $\cdot 5$ —144 $\cdot 5^{\circ}$), and octahydro- (m. p. 188—190°).

In no case has there been any suggestion of difference in properties or reactivity between corresponding compounds in the two series and there can be no doubt that these are all derivatives of the same parent hydrocarbon. Whether this is represented by structure (III) or by structure (IV) can be answered at once, since the substance is identical with the 1:2:5:6-dibenzanthracene (IV) of Weitzenböck and Klinger (*Monatsh.*, 1918, **39**, 315), who synthesised it by a method which establishes its constitution.

Transformation of the ketone (I) into the hydrocarbon (IV) probably proceeds through the intermediate formation of ketone (II). It was found that neither $\alpha\alpha'$ -dinaphthyl ketone nor $\alpha\beta'$ -dinaphthyl ketone was isomerised by the conditions used for the pyrolysis (heating at 440—450° for 1—2 hours) and it may be that the conversion of the α -naphthyl ketone (I) into the isomeric β -ketone (II) is associated with a tautomerism dependent on the presence of the ortho-methyl group, since 1-phenylacetylnaphthalene,



which has the properties of a tautomeric substance, is readily converted into the isomeric β -ketone by simple pyrolysis (future communication). The observation of Fieser and Dietz (*loc. cit.*) that complete conversion of (I) into the hydrocarbon requires 10 times as long as when (II) is used is consistent with the view here expressed as to the mechanism of the production of (IV) from (I).

Since the pyrolysis product of (I) is not 1:2:7:8-dibenzanthracene, it became necessary to examine the claim of Homer (J., 1910, **97**, 1148) that this hydrocarbon is formed by the action of aluminium chloride on naphthalene in the presence of tetrachloroethane. Repetition of Homer's experiment showed that her product is, in fact, perylene,* which was first described by Scholl, Seer, and Weitzenböck in the same year in which Homer's paper appeared (*Ber.*, 1910, **43**, 2202). The tetrachloroethane is thus merely a solvent and takes no part in the reaction.

It appears, therefore, that 1:2:7:8-dibenzanthracene has not yet been prepared. It should be obtainable from 1:1'-dinaphthyl ketone-2-carboxylic acid. Attempts are being made to prepare this

* Identified by direct comparison with an authentic sample kindly supplied by Imperial Chemical Industries, Limited.

acid by oxidation of the ketone (I) or by condensation of naphthalene-1: 2-dicarboxylic anhydride with naphthalene (compare Waldmann, J. pr. Chem., 1930, **127**, 195), although so far the results have not been promising.

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