61. *Polycyclic Aromatic Hydrocarbons. Part XXIII.*

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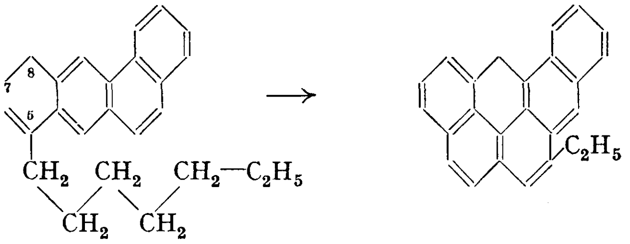
The 5-methyl, 5-ethyl, 5-*n*-propyl, and 5-*iso*propyl derivatives of 1 : 2-benzanthracene have carcinogenic properties and it seemed of interest to determine to what extent the length of the carbon chain could be increased without loss of activity.

The 5-n-*butyl*, 5-n-*amyl*, 5-n-*hexyl*, and 5-n-*heptyl* derivatives of 1 : 2-benzanthracene have been prepared by the action of alkylmagnesium bromides on 5-keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, followed by dehydration of the tertiary carbinols to 5-*alkyl*-7 : 8-*dihydrobenzanthracenes*, which were subsequently dehydrogenated to the completely aromatic state. These new homologues of 1 : 2-benzanthracene are undergoing biological test. Preliminary results of tests by Professor E. L. Kennaway suggest that there is a steady decline in carcinogenic activity with increasing length of chain. In experiments in which the hydrocarbons in dilute benzene solution were applied to the skin of mice the 5-*n*-butyl compound has given three malignant tumours after 347 days, the 5-*n*-amyl compound has given two malignant tumours after 294 days, whereas the 5-*n*-hexyl and the 5-*n*-heptyl compound have not yet given malignant tumours after 262 and 294 days, respectively.

In the case of the hexyl and the heptyl compound dehydrogenation of the dihydro-derivatives gave by-products in addition to the alkylbenzanthracenes. The pure *by-product* was isolated from the heptyl compound (I). Its high carbon content showed that the intact side chain was no longer present and a possible formulation is (II). This structure accords with the analytical values for carbon and hydrogen and, as it is a benzanthrene type of structure, it would account for the relative instability of the compound, which became discoloured on heating to 80° or on keeping for some weeks. The ultraviolet absorption spectrum, examined by Dr. E. Roe, showed that the compound was not a simple derivative of 1 : 2-benzanthracene or of chrysene.

(I.)



(II.)

EXPERIMENTAL.

Grignard Condensations.—Finely powdered 5-keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (Haworth and Mavin, J., 1933, 1012) (0·1 g.-mol.) was added to an ice-cold Grignard solution prepared from the appropriate alkyl bromide (0·11 g.-mol.) in ether (100 c.c.) and benzene (165 c.c.). The suspension was kept at room temperature for 18 hours and then decomposed with ice and ammonium chloride.

5-*Alkyl*-7 : 8-*dihydro*-1 : 2-*benzanthracenes.*—The crude tertiary carbinol was obtained by evaporation of the benzene–ether solution and was dehydrated by an hour's boiling with picric acid (25 g.) in alcohol (165 c.c.). The picrate of the hydrocarbon separated on cooling; it was freed from picric acid, and the hydrocarbon purified by distillation at 0·2—0·4 mm., followed by crystallisations from methyl or ethyl alcohol.

5-*Alkyl*-1 : 2-*benzanthracenes.*—Dehydrogenation of the dihydro-compound was effected by heating with platinum-black at 300—310° for 24 hours, the product being purified through its picrate, distilled in a vacuum, and then recrystallised from alcohol.

The following table gives the m. p.'s and analytical figures of the individual compounds :

	Hydrocarbon.					Picrate.				
		Found.		Theo.			Found.		Theo.	
Derivative of 1 : 2-benzanthracene.	M. p.	C, %.	H, %.	C, %.	H, %.	M. p.	C, %.	H, %.	C, %.	H, %.
5-*Ethyl*-7 : 8-*dihydro*-, $C_{20}H_{18}$	109—110°	92·7	7·2	93·0	7·0	159—160°	64·0	4·6	64·0	4·3
5-n-*Butyl*-7 : 8-*dihydro*-, $C_{22}H_{22}$	69—70	92·2	7·65	92·3	7·7	124—125	65·3	4·9	65·2	5·0
5-n-*Butyl*-, $C_{22}H_{20}$	81	92·6	7·3	92·9	7·1	116—117	65·6	4·5	65·5	4·5
5-n-*Amyl*-7 : 8-*dihydro*-, $C_{23}H_{24}$	59—60	92·0	8·0	92·0	8·0	90—91	65·3	4·9	65·7	5·1
5-n-*Amyl*-, $C_{23}H_{22}$	93	92·6	7·6	92·55	7·45	85—86	66·4	5·4	66·0	4·8 *
5-n-*Hexyl*-7 : 8-*dihydro*-, $C_{24}H_{26}$	47—48	91·4	8·5	91·7	8·3	86—87	66·3	5·6	66·3	5·3
5-n-*Hexyl*-, $C_{24}H_{24}$	72—73	92·3	7·6	92·25	7·75	90—91	66·9	5·15	66·5	5·0 *
5-n-*Heptyl*-7 : 8-*dihydro*-, $C_{25}H_{28}$ .... [gave *dipicrate*]	53—54	91·2	8·4	91·4	8·6	80	75·8	6·6	75·9	6·7
5-n-*Heptyl*-, $C_{25}H_{26}$	68	91·9	8·0	92·0	8·0	82—83	67·0	5·4	66·9	5·3

* Characterisation in these two cases was better made by the *s*-trinitrobenzene complexes, which gave more satisfactory analyses than the picrate. The trinitrobenzene *complex* of 5-*n*-amyl-1 : 2-benzanthracene crystallised in orange-yellow needles (from alcohol), m. p. 112—113° (Found : C, 68·2; H, 4·9. $C_{23}H_{22},C_6H_3O_6N_3$ requires C, 68·1; H, 4·9%). The trinitrobenzene *complex* of 5-*n*-hexyl-1 : 2-benzanthracene formed vermilion prisms (from alcohol), m. p. 116—117° (Found : C, 68·7; H, 5·2. $C_{24}H_{24},C_6H_3O_6N_3$ requires C, 68·5; H, 5·2%).

Hydrocarbon obtained as a By-product in the Dehydrogenation of 5-n-*Heptyl*-7 : 8-*dihydro*-1 : 2-*benzanthracene* (I).—The crude dehydrogenation product gave a small amount of material which was considerably less soluble in alcohol than the main fraction. This material, m. p. 115—116°, was treated in alcoholic solution with *s*-trinitrobenzene, and gave a complex which, after recrystallisation from benzene, formed orange needles, m. p. 159—160°. The trinitrobenzene was removed from this by reduction with stannous chloride in aqueous alcoholic solution, and the regenerated hydrocarbon was sublimed in a high vacuum and recrystallised from alcohol. This *hydrocarbon* (possibly II) formed colourless leaflets, m. p. 116·5—117·5° (Found : C, 94·0; H, 5·8. $C_{25}H_{18}$ requires C, 94·3; H, 5·7%). It dissolved in concentrated sulphuric acid with a reddish-brown coloration.

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