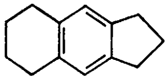
186. *Impurities in Commercial Fluorene and Phenanthrene.*

By E. A. JOHNSON.

Commercial fluorene and phenanthrene have been found to contain small amounts of a number of structurally related compounds which are not readily separated by the usual methods of purification.

DURING work with Beaven *et al.*[1] on the chlorination of fluorene the products were found to contain a compound, m. p. 135°, whose ultraviolet spectrum appeared to be that of a substituted naphthalene. Synthetic fluorene prepared from diphenic acid gave no trace of this material on chlorination, although commercial fluorene recrystallised several times as hydrocarbon and as picrate still gave it in apparently unchanged amount, and zone purification was also almost ineffective. A sharp long-wavelength band at 321 mμ was observed in the spectrum of the commercial fluorene used but not in that of synthetic fluorene (see Askew [2]). Chromatography on silica gel of commercial fluorene showing this band yielded a hydrocarbon, eluted just before fluorene, which on rechromatography was obtained pure, whose melting point (94°), analysis, and ultraviolet spectrum (Fig. 1) suggested that it was probably 5,6-benzindane. Some support was also lent to this by the isolation from the immediately preceding chromatographic fractions of a much smaller quantity of a liquid hydrocarbon identified by ultraviolet [3] and infrared spectra [4] as 4,5-benzindane.

5,6-Benzindane, prepared by Sen Gupta's method (with minor modifications), proved to be identical with the compound isolated from fluorene. Chlorination in acetic acid yielded a dichloro-derivative, m. p. 136°, which from its ultraviolet spectrum (Fig. 1) is likely to be 4,7-dichloro-5,6-benzindane.[6] Under similar conditions 2,3-dimethylnaphthalene gives a dichloro-derivative, m. p. 155°, which has an ultraviolet absorption spectrum very similar to that of the dichlorobenzindane (see also Hebbelynck [7]).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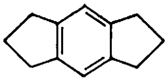
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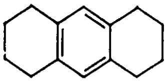
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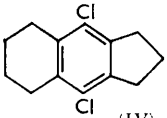
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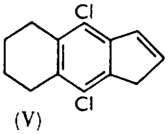
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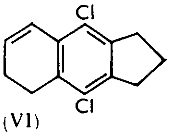
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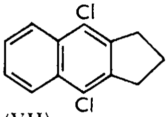
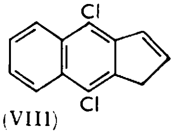

(VII)


(VIII)

More direct evidence for the positions of the chlorine substituents in the dichlorobenzindane was obtained by chlorination of the tetrahydrobenzindane (I) (the penultimate stage in the benzindane preparation) which gave two dichloro-compounds, not very readily separated by crystallisation; these were separable by vapour-phase chromatography on a polyester stationary phase but not on Apiezon M. The major product (IV) had ultraviolet absorption generally similar to that of the parent hydrocarbon, but the other (V) had more intense indene-like absorption and was converted by cautious hydrogenation into the major product (IV). Dehydrogenation of the mixed dichloro-derivatives

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[1] Beaven, de la Mare, Johnson, and Klassen, preceding paper.

[2] Askew, *J.*, 1935, 512.

[3] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951 Nos. 214, 229.

[4] Dannenberg and Rahman, *Chem. Ber.*, 1955, **88**, 1405.

[5] Sen Gupta, *J. Indian Chem. Soc.*, 1939, **16**, 89.

[6] Cf. Mosby, *J. Amer. Chem. Soc.*, 1953, **75**, 3348.

[7] Hebbelynck, *Ind. chim. belge*, 1951, **16**, 483.

with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [8] was incomplete after 5 hr. at 100° (no reaction occurred with chloranil), but two products were obtained, separable by vapour-phase chromatography on a poly(ethylene adipate) stationary phase. One of these was identical, in ultraviolet absorption spectrum and behaviour on vapour-phase chromatography, with the dichlorobenzindane (VII) obtained by direct chlorination of 5,6-benzindane, and its identity was confirmed by a mixed melting point. The second product, formed in somewhat smaller quantity [*i.e.*, in roughly the same proportion as the minor component (V) before dehydrogenation], had a spectrum with three band systems highly suggestive of a 2-vinylnaphthalene-type structure (see Friedel and Orchin [3]). These two products were again not separable on Apiezon M. Dehydrogenation in a similar manner of the dichlorotetrahydrobenzindane (m. p. 133°), purified by cautious hydrogenation to remove the indene-like component, gave almost entirely the dichloro-5,6-benzindane, but a little of the indene-type compound appeared to be re-formed, and an even smaller but detectable amount of the vinylnaphthalene-like compound, which may be assumed to be the corresponding dichlorobenzindene (VIII). The formation of this compound in much greater quantity by dehydrogenation of material containing the indene-like compound suggests that the latter is likely to be a tetrahydrobenzindene (V) rather than a 3′,4′-dihydrobenzindane (VI).

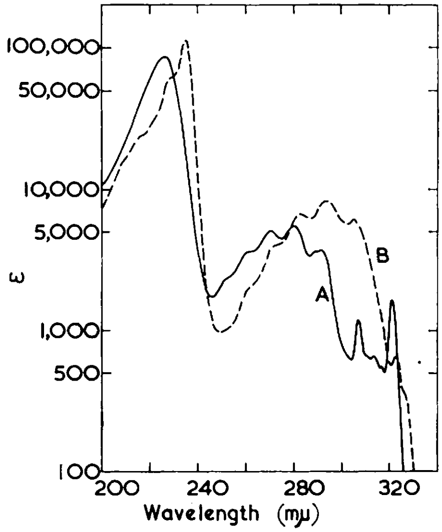

FIG. 1. A, 5,6-Benzindane, B, 4,7-Dichloro-5,6-benzindane (VII). Both in light petroleum (b. p. 100—120°).

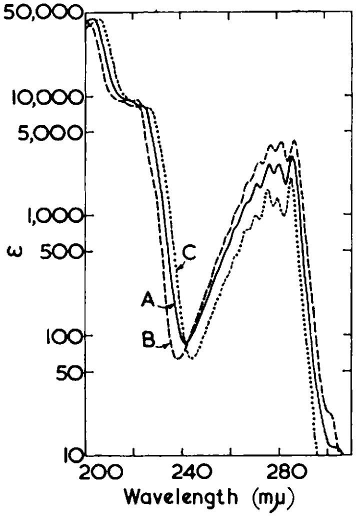

FIG. 2. A, 3′,4′,5′,6′-Tetrahydro-5,6,-benzindane (I). B, Hydrindacene (II). C, 1,2,3,4,5,6,7,8-Octahydroanthracene (III). All in light petroleum (b. p. 100—120°).

Six commercial samples of fluorene, of British and German origin, all contained 5,6-benzindane, in amounts varying from 0·3% to 3% as estimated from the intensity of the band at 321 mμ. Another contaminant which appears to be almost universally present in comparable quantities is dibenzofuran, which is readily detected and separated from fluorene by vapour-phase chromatography on a stationary phase of Apiezon M; the sharp and intense dibenzofuran band at 249 mμ may appear as an inflection on the ultraviolet absorption curve of fluorene, which is itself smooth in this region. One published

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[8] Braude, Brook, and Linstead, *J.*, 1954, 3569.

fluorene spectrum[9] shows this feature clearly; although free from benzindane the sample used evidently contained 4—5% of dibenzofuran. If spectral data for a pure substance are known, the best check for the absence of absorbing impurities is a determination of maximum-to-minimum absorbance ratios rather than of absolute intensity values. For fluorene the max. : min. ratios are $\varepsilon_{301}/\varepsilon_{297} = 2{\cdot}7$, and $\varepsilon_{261}/\varepsilon_{231} = 9{\cdot}5$; the latter value is especially sensitive to traces of impurity. Reliable values for $\varepsilon_{\text{min.}}$ are however required; these are often not determined or reported.

Phenanthrene appears often to be contaminated with dibenzothiophen as well as with the much more readily detected anthracene, and again crystallisation is ineffective for purification. Commercial products such as individual coal-tar hydrocarbons are isolated from complex industrial mixtures, and among the wide diversity of compounds present it is to be expected that some will readily form mixed crystals. Hence a sharp melting point unchanged by recrystallisation is not an adequate criterion of purity for such compounds.

EXPERIMENTAL

5,6-Benzindane was prepared from indane by Sen Gupta's route,[5] with the following modifications. Clemmensen reduction of the γ-indanyl-γ-oxobutyric acid was carried out in toluene (Vogel[10]). Ring closure of the indanylbutyric acid was effected in polyphosphoric acid at 100°, and the resulting ketonic products were reduced by the Huang-Minlon method. In each case the yield was substantially improved; from indane the overall yield of tricyclic hydrocarbons was 34%.

Vapour-phase chromatography of the tricyclic ketone showed that about a fifth of the indanylbutyric acid had cyclised in the 4- instead of the 6-position; the major product was low-melting solid and was separated and reduced separately, yielding 3′,4′,5′,6′-*tetrahydro*-5,6-*benzindane* (I). This was recrystallised twice from ethanol at about −40° and, redistilled, had b. p. 150° (bath)/15 mm., m. p. 10°, n_D^{20} 1·5590, d_4^{20} 1·0080. In Fig. 2 and the annexed Table its ultraviolet absorption spectrum is compared with those of related compounds kindly supplied by Dr. B. M. Wepster and Professor E. E. Turner.

	$\lambda_{\text{max.}}$	ε	$\lambda_{\text{min.}}$	ε	$\lambda_{\text{max.}}$	ε	$\lambda_{\text{max.}}$
s-Hydrindacene (II)	200	42,000	238	64·5	287	4200	272, 277, 281·5
Tetrahydrobenzindane (I)	203·5	45,000	242	87	286	3100	271, 276, 280·5
Octahydroanthracene (III)	205·5	45,000	244	64	285·5	2020	267, 270·5, 275·5, 279·5

Reduction of the remaining mixed liquid ketone yielded compound (I) together with a second hydrocarbon, separable with difficulty from it by vapour-phase chromatography on polar stationary phases. This had ultraviolet absorption maxima at 270 and 279·5 mμ (ε of the order of 700). Dehydrogenation of the mixed hydrocarbon yielded a mixture of 4,5- and 5,6-benzindane.

A near-saturated solution of 5,6-benzindane in acetic acid, treated at room temperature with approximately the theoretical volume of chlorine, afforded 4,7-*dichloro*-5,6-*benzindane*, needles (from ethanol), m. p. 136° (Found: C, 65·8; H, 4·5; Cl, 29·1. $C_{13}H_{10}Cl_2$ requires C, 65·8; H, 4·3; Cl, 29·9%).

1,4-*Dichloro*-2,3-*dimethylnaphthalene*, prepared in a similar way from 2,3-dimethyl-naphthalene, was less free from isomers and required several crystallisations to constant m. p. 155° (Found: C, 63·8; H, 4·5; Cl, 31·0. $C_{12}H_{10}Cl_2$ requires C, 64·0; H, 4·5; Cl, 31·5%). The ultraviolet absorption spectra of the benzindane and its dichloro-derivative (Fig. 1) were as follows:

	$\lambda_{\text{max.}}$	ε	$\lambda_{\text{min.}}$	ε	$\lambda_{\text{max.}}$	ε	$\lambda_{\text{min.}}$
5,6-Benzindane	226·5	88,000	246	1700	280	5500	270, 291, 313·5
					307	1200	
					321	1650	
4,7-Dichloro-deriv. (IV)	235	11,400	249	960	293·5	8400	283, 305·5, 322·5
1,4-Dichloro-2,3-dimethylnaphthalene	233·5	88,000	251	1100	293·5	7600	284, 323·5

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[9] American Petroleum Institute, Research Project No. 44, Ultraviolet Spectral Data No. 401 (Shell Development Co.).

[10] Vogel, "Practical Organic Chemistry," Longmans, London, 1948, p. 701.

Chlorination in a similar manner of compound (I) gave a crystalline product which, by vapour-phase chromatography, proved to be a mixture of compounds (IV) (60%) and (V) (40%) (m. p. 122—126°) (Found: C, 64·7; H, 5·9; Cl, 29·4. $C_{13}H_{14}Cl_2$ requires C, 64·7; H, 5·9; Cl, 29·4. Calc. for $C_{13}H_{12}Cl_2$: C, 65·3; H, 5·1; Cl, 29·6%). Cautious hydrogenation at room temperature and atmospheric pressure in light petroleum in presence of palladised barium sulphate converted compound (V) almost completely into (IV) without removal of chlorine; the product, 4,7-*dichloro*-3′,4′,5′,6′-*tetrahydro*-5,6-*benzindane*, had m. p. 133°.

The mixture of compounds (IV) and (V) was heated with about 2½ times its weight of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (generously given by Dr. D. T. Thompson) in benzene in a sealed, partially evacuated, ampoule for 5 hr. at 100°. The product was run through a short alumina column and evaporated to dryness. By vapour-phase chromatography it appeared that about half the material had been dehydrogenated to a mixture of two compounds in a similar proportion. The first of these appeared to be identical with 4,7-dichloro-5,6-benzindane (VII) prepared by chlorination of 5,6-benzindane, and the second possessed a characteristic ultraviolet absorption spectrum quite closely resembling that of 2-vinylnaphthalene [3] but shifted to longer wavelengths. The three band-systems, of progressively greater intensity, had maxima at 348, 343, 328 mμ, at 313, 301, 289 mμ, and at 259, 251 mμ, respectively. It was therefore assumed to be 4,7-dichloro-5,6-benzindene (VIII). An attempt at hydrogenation unfortunately resulted in reduction to apparently pure hydrocarbon (I).

Dehydrogenation of the dichloro-compound (IV) [purified by hydrogenation of the compound (V) present] with a slightly greater excess of the same quinone for 16 hr. at 100° resulted in ~70% conversion into compound (VII). On isolation by vapour-phase chromatography this melted at 132—134°, mixed m. p. 133—135° with material prepared from 5,6-benzindane. A mixture of materials (IV) and (VII) melted at 115—120°.

The vapour-phase chromatography of compounds (IV), (V), (VII), and (VIII) on polar and non-polar stationary phases was of value, not only analytically, but also as a guide to their structural relationship.

Medical Research Council Laboratories,
Holly Hill, London, N.W.3.

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