Constituents of Cigarette Smoke. Part XI.[1] The Isolation and Synthesis of Acenaphthylenes and Macrocyclic Polyolefins

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Acenaphthylene, the monomethylacenaphthylenes, and some dimethylacenaphthylenes have been identified in cigarette smoke condensate. Some of the acenaphthylenes were synthesised, as was also a perhydro-macrocycle (X). The possible formation of aromatic compounds from macrocyclic polyolefins is discussed, and the isolation of such a macrocycle from cigarette smoke is described. The mass spectra of some acenaphthylenes are described.

PREVIOUS work by us [2] described the isolation of naphthalenes and other aromatic hydrocarbons from a neutral fraction of cigarette smoke condensate. On chromatography of the condensate, the fractions eluted immediately after the naphthalenes have now given macrocyclic polyolefins and acenaphthylenes. The pos-

[1] Part X, D. L. Dare, I. D. Entwistle, and R. A. W. Johnstone, *J. Chem. Soc.* (*C*), 1968, 977.

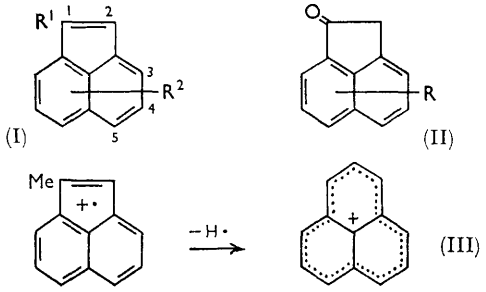
[2] J. W. Cook, R. A. W. Johnstone, and P. M. Quan, *Israel J. Chem.*, 1963, **1**, 356.

sible formation of polycyclic aromatic hydrocarbons from terpenoid constituents of tobacco leaf, notably solanesol, has been discussed with regard to the naphthalenes [2] in which a distribution of methyl substituents was found that strongly suggested a terpenoid origin. Similar reasoning applies to the acenaphthylenes, but although there are substantial quantities of methylacenaphthylenes, the evidence for their terpenoid origin from the pattern of methyl substitution is not nearly so clear-cut. Acenaphthylene itself has been found in the pyrolysates of butadiene and other cigarette smoke components [3] and biacetyl,[3] but very few alkylated polycyclic hydrocarbons were isolated. Interestingly, Prelog [4] has found that dehydrogenation of cycloalkanes gives moderate yields of specific polycyclic aromatic hydrocarbons; in particular, cyclododecane afforded acenaphthylene. Acenaphthylene was identified earlier in cigarette smoke only by ultraviolet spectroscopy.[5]

The formation of aromatic hydrocarbons from linear terpenoid components presumes that these can first be cyclised but there is strong evidence [2,6] that this is the case. For example, the pyrolysis of solanesol [6] gives abundant quantities of cyclic six-membered-ring compounds which have also been isolated from cigarette smoke condensate. Cyclisation to ten-membered and fourteen-membered rings is possible also, and these on dehydrogenation could give rise to polycyclic hydrocarbons. A search was made for such macrocyclic polyolefins, but as the ten-membered-ring unsaturated terpenoid compounds are known to be unstable to heat and acids,[7] the search was concentrated for the larger-ring macrocyclics which would also be present in the less complex C_{20} fraction of smoke condensate. A cyclic polyolefin has now been isolated in small amount, and from its characteristics appears to be a fourteen-membered-ring compound.

The most carcinogenic fraction of cigarette smoke condensate so far discovered contains the polycyclic aromatic hydrocarbons, but from their known concentrations [8] the total calculated carcinogenic activity approximates to only one tenth of the known activity of cigarette smoke. However, with but few exceptions, most previous work on the isolation of aromatic hydrocarbons has relied extensively on only ultraviolet identification, a technique which can reveal the type of ring system but gives little information on alkyl substitution. Methyl substituents in polycyclic hydrocarbons can enhance considerably their carcinogenic action, but the presence of such homologues has usually been ignored or supposed to be zero in much previous work. The evidence that terpenoid compounds can give rise to methyl substituted aromatic compounds suggests that they may also be the precursors of much of the known carcinogenic activity.

Preparative gas chromatography was used to separate the acenaphthylenes into the parent, monomethyl, and dimethyl components. Acenaphthylenes having no substituents on the 1,2-double bond could be separated from isomers by chromatography on argentated silica gel. Acenaphthylene and 1-methylacenaphthylene were identified by comparison with authentic specimens and their *s*-trinitrobenzene adducts. The remaining 3-, 4-, and 5-monomethylacenaphthylenes were isolated as a mixture free from other components but could not be separated individually on a preparative scale. They



were shown to be present in a ratio of 4 : 1 : 1 by gas chromatography and n.m.r. spectrometry. The dimethylacenaphthylenes also were not separated, but analytical gas chromatography and n.m.r. showed the presence of mainly the 1,3-isomer along with smaller amounts of three other unidentified components. All the acenaphthylene fractions had characteristic ultraviolet and mass spectra.

Acenaphthylenes (I; R^1, R^2 = H, Me) were obtained by reduction of the acenaphthenones (II; R = H, Me) to the acenaphthenol followed by dehydration. Introduction of a methyl group at the 1-position was accomplished by treating the acenaphthenone (II; R = H, Me) with methylmagnesium iodide and dehydrating the resulting tertiary alcohol by chromatography through a silica gel column. Although naphthylacetic acid could be cyclised in high yield to acenaphthenone (II; R = H), the corresponding cyclisation of the 2-, 3-, and 4-methylnaphthylacetic acids to the methylacenaphthenones (II; R = Me) could be effected in only moderate yields. 1-Methylacenaphthylene has been reported previously,[9] but of the 16 possible dimethylacenaphthylenes only the 1,2-, 3,8-, and 5,6- [10] isomers are known.

The mass spectra of the acenaphthylenes are particularly simple, with few fragment ions and strong molecular ions (Table 1). The monomethylacenaphthylenes

[3] G. M. Badger and T. M. Spotswood, *J. Chem. Soc.*, 1960, 4420, 4431; J. Lam, *Acta Pathol. Microbiol. Scand.*, 1956, **39**, 198.
[4] V. Prelog, V. Boarland, and S. Polyak, *Helv. Chim. Acta*, 1955, **38**, 434.
[5] See R. A. W. Johnstone and J. R. Plimmer, *Chem. Rev.*, 1959, **59**, 885.
[6] J. D. Grossmann, E. J. Deszyck, R. M. Ikeda, and A. Bavley, *Chem. and Ind.*, 1962, 1950.
[7] *E.g.*, M. Suchy, V. Herout, and F. Sǒrm, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2612.
[8] H. Druckrey, *Acta Med. Scand. Suppl.*, 1961, **369**, 24; E. L. Wynder, *ibid.*, p. 63.
[9] B. R. Brown and D. L. Hammick, *J. Chem. Soc.*, 1948, 1395.
[10] G. Wittig, H. G. Reppe, and T. Eicher, *Annalen*, 1961, **643**, 47; S. Hauptmann and L. Franke, *J. prakt. Chem.*, 1963, **19**, 180.

eliminated a hydrogen atom, and not a methyl radical, to form stable cations. For example, 1-methylacenaphthylene (I; $R^1 = H$, $R^2 = Me$) gives the perinaphthyl cation (III) by ring-expansion similar to the

TABLE 1

Mass spectra of methylacenaphthylenes

	m/e
1-Methyl	166 (52), 165 (100), 164 (12), 163 (16), 139 (8), 86 (8), 85 (16), 84 (12), 83 (8), 69·5 (8)
3-Methyl	166 (98), 165 (100), 164 (15), 163 (18), 139 (9), 83 (6), 82·5 (11), 82 (11), 81·5 (6), 81 (2)
4-Methyl	166 (92), 165 (100), 164 (15), 163 (18), 139 (9), 115 (5), 113 (2), 83 (7), 82·5 (13), 82 (12), 81·5 (6), 81 (3), 69·5 (6), 69 (8), 63 (7)
5-Methyl	166 (90), 165 (100), 164 (15), 163 (17), 139 (11), 83 (19), 82·5 (13), 82 (15), 81·5 (8), 81 (21)
1,3-Dimethyl	180 (87), 179 (60), 178 (26), 165 (100), 152 (14), 151 (5), 150 (3), 89 (10), 88 (4), 76 (9), 75 (3), 63 (5)
1,5-Dimethyl	180 (100), 179 (74), 178 (44), 165 (92), 152 (41), 151 (45), 150 (4), 89·5 (4), 89 (9), 88 (8), 87 (3), 82·5 (7), 76 (114), 75 (6), 74 (3), 63 (7)

electron-impact induced formation of the tropylium ion from toluene. The dimethylacenaphthylenes eliminated one methyl group from the molecular ion but

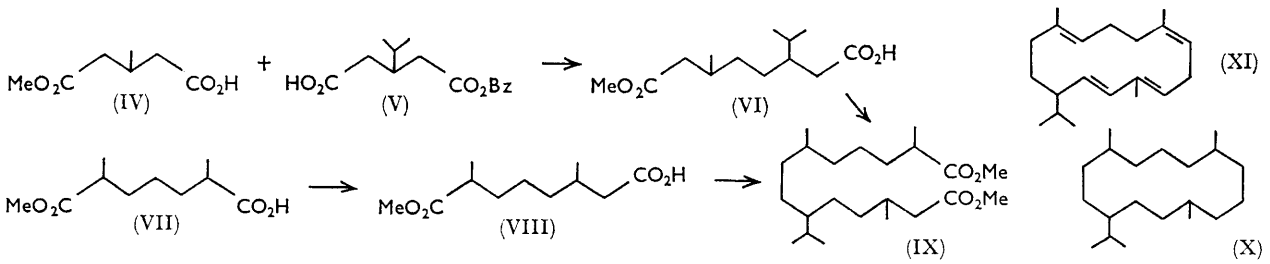
TABLE 2

	m/e	Retention vol. relative to phytane				
Cembrane	280, 278	1·76 (9·7)	1·85 (73·6)	1·93 (12·8)	2·02 (3·7)	
'Synthetic' cembrane	280		1·83 (8·8)	1·93 (88·5)	2·02 (5·8)	
Fraction 'C'	280, 278		1·83 (66·1)	1·94 (21·4)	2·03 (7·1)	2·16 (5·4)

again the elimination of hydrogen was particularly marked.

The fractions of cigarette smoke condensate eluted just before the acenaphthylenes on chromatography consisted mainly of polyolefins, as shown by their infrared spectra. After hydrogenation, samples of some of these fractions on gas chromatography showed peaks corresponding to those of the cembrane (X) obtained either by synthesis or by hydrogenation of cembrene (XI) [11] (Table 2). The richest fractions were combined and rechromatographed on argentated silica gel, to give an oil (W) which on mass spectrometry gave molecular ions at *m/e* 270 and 272. After hydrogenation, molecular ions were found at *m/e* 278 and 280, but these were also found with the cembrane obtained by catalytic reduction of cembrene. As the cembrane obtained by synthesis gave only a molecular ion at *m/e* 280, and there were no unsaturated components in the hydrogenation products, it is concluded that both the oil (W) and natural Cembrene must have suffered partial ring-closure on hydrogenation. However, the results confirmed that the isolated oil was monocyclic and was a mixture of at least two olefins with 4 and 5 double bonds. The nature of the mixture was revealed by analytical gas chromatography, which indicated one main component together with three others in much smaller amount. The mass spectrum of the oil was characteristic of a terpenoid polyolefin with fragment ions corresponding to successive losses of C_5 units, and there was a strong loss of 43 mass units from the molecular ion, characteristic of an isopropenyl group. As the oil had an ultraviolet maximum at 232 mμ, a conjugated diene must have been present, as was also shown by the infrared spectral absorption at 1599 $cm.^{-1}$. The infrared spectrum showed also the presence of trisubstituted methylene, and *trans*-disubstituted double bonds, and the n.m.r. spectrum showed the expected resonances for the various types of proton. After hydrogenation of the oil (W) and of cembrene, their n.m.r. spectra were very similar to that of cembrane. Although the isolated oil was not completely pure, the evidence strongly suggests that the major component is a monocyclic polyolefin similar to cembrene. Some confirmation of the ring size of the polyolefin was obtained by its dehydrogenation to an anthracene, a characteristic product of dehydrogenation of fourteen-membered-ring compounds.[4]

As the natural cembrene was available in very small amounts and gave a hydrogenation product having two molecular ions in the mass spectrum, a synthesis of cembrane was undertaken.[12] Electrolytic coupling of



the half-esters (IV) and (V) afforded, after hydrogenation, the half-ester (VI) which was coupled electrolytically with a second half-ester (VIII). The resulting mixture of diesters was separated by preparative gas chromatography into its three components, one of which was the required diester (XI). Much better yields were

[11] W. G. Dauben, W. E. Thiessen, and P. R. Resnick, *J. Amer. Chem. Soc.*, 1962, **84**, 2015.

[12] I. D. Entwistle and R. A. W. Johnstone, *Chem. Comm.*, 1966, 136.

obtainable by coupling the two fairly equally sized half-esters (VI) and (VIII) and separating the resulting mixture than by building up specifically the required diester (IX) by coupling small and large components. The diester (IX) was cyclised to a mixture of acyloins which were then reduced to the saturated cycloalkane (X). The gas-chromatographic analyses (Table 2) of the cycloalkane obtained by this synthesis and of that obtained by reduction of cembrene and the oil (W) showed that, although the same peaks were present, the relative amounts were very different in the synthetic and hydrogenated materials, and suggest different proportions of diastereoisomers.

EXPERIMENTAL

All mass spectra were determined on an AEI MS 9 mass spectrometer at 70 ev, with a source temperature of 250°. Preparative gas chromatography was done on a column 10 ft. × ⅜ in. packed with Chromosorb W coated with 30% silicone elastomer. Analytical work was carried out with a 100 ft. × 0·01 in. capillary column coated with Apiezon L.

Acenaphthylenes.—4-Methylnaphthylacetic acid (10 g.) was converted with thionyl chloride into 4-methylnaphthylacetyl chloride (9·7 g.), b.p. 145—148°/0·5 mm. The acid chloride (2 g.) in dry methylene chloride (40 ml.) was added to a stirred solution of aluminium chloride (1·2 g.) in methylene chloride (300 ml.), and the mixture stirred overnight, to yield *5-methylacenaphthenone* (0·8 g.), m.p. 103—104° (from light petroleum–benzene), $\nu_{max.}$ 1690, 1600, 910, 830, 812, and 760 cm.$^{-1}$ (Found: C, 85·7; H, 5·5. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%). Similarly were prepared *3-methylacenaphthenone* (0·6 g.), m.p. 115—116°, $\nu_{max.}$ 1705, 1620, 1595, 985, 835, 825, 780, and 770 cm.$^{-1}$ (Found: C, 85·7; H, 5·7%), and *4-methylacenaphthenone* (0·58 g.), m.p. 129—130°, $\nu_{max.}$ 1700, 1615, 1590, 1040, 880, 850, 765 cm.$^{-1}$ (Found: C, 85·9; H, 5·6%). Reduction of 5-methylacenaphthenone with lithium aluminium hydride in ether afforded *1-hydroxy-5-methylacenaphthene*, m.p. 142—143° (from light petroleum–benzene), $\nu_{max.}$ 3350, 3250, 1050, 822, 815, 800, and 765 cm.$^{-1}$ (Found: C, 84·7; H, 6·4. $C_{13}H_{12}O$ requires C, 84·8; H, 6·6%). Dehydration, by distillation over potassium hydrogen sulphate at 130—140°/20 mm., followed by chromatography on alumina, yielded *5-methylacenaphthylene* as a yellow oil, b.p. 136°/20 mm., $\nu_{max.}$ 1080, 838, 825, 765, and 730 cm.$^{-1}$, $\lambda_{max.}$ 253, 270, 281, (319), 327, 339, and 335 mμ [log ε 4·96, 3·48, 3·4, (4·27), 4·34, 4·04, and 4·04], δ(CH_3) 2·70 (Found: C, 93·9; H, 6·1. $C_{13}H_{10}$ requires C, 93·9; H, 6·1%); *s*-trinitrobenzene *complex*, m.p. 209—210° (from ethanol) (Found: C, 60·0; H, 3·5; N, 11·2. $C_{19}H_{13}N_3O_6$ requires C, 60·2; H, 3·5; N, 11·1%). Similarly, from *1-hydroxy-3-methylacenaphthene*, m.p. 138—139°, $\nu_{max.}$ 3350, 3250, 1060, 875, 840, 810, 780, and 765 cm.$^{-1}$ (Found: C, 85·5; H, 6·7%), was prepared *3-methylacenaphthylene*, b.p. 134°/20 mm., m.p. 27°, $\nu_{max.}$ 855, 832, 760, and 765 cm.$^{-1}$, $\lambda_{max.}$ 233, (319), 328, and (344) mμ [log ε 4·97, (4·28), 4·38, and (4·08)], δ 2·60 (Found: C, 93·6; H, 6·4%); *s*-trinitrobenzene *complex*, m.p. 206—206·5° (Found: C, 60·2; H, 3·6; N, 10·8%), and from *1-hydroxy-4-methylacenaphthene*, m.p. 121—122°, $\nu_{max.}$ 3350, 3250, 1060, 850, and 767 cm.$^{-1}$ (Found: C, 84·5; H, 6·7%), was prepared *4-methylacenaphthylene*, b.p. 133°/20 mm., $\nu_{max.}$ 910, 860, 815, 765, and 725 cm.$^{-1}$, $\lambda_{max.}$ 233, 268, 277, 315, 327, and 345 mμ (log ε 4·86, 4·03, 3·99, 4·18, 4·29, and 3·85), δ 2·48 (Found: C, 93·8; H, 6·12%); *s*-trinitrobenzene complex, m.p. 191—192° (Found: C, 60·3; H, 3·6; N, 11·4%). Treatment of acenaphthenone with methylmagnesium iodide followed by dehydration gave 1-methylacenaphthylene, b.p. 132°/20 mm., $\nu_{max.}$ 838, 805, and 770 cm.$^{-1}$, $\lambda_{max.}$ 230, 270, 279, 313, 323, (333), and 340 mμ [log ε 4·5, 4·04, 4·0, 4·51, 4·58, (4·31), and 4·24], δ 2·35 and 2·37. Similar reactions of 3- and 5-methylacenaphthenone with methylmagnesium iodide afforded *1,3-dimethylacenaphthylene*, b.p. 143—146°/20 mm., m.p. 25°, $\nu_{max.}$ 835, 810, 780, and 755 cm.$^{-1}$, $\lambda_{max.}$ 233, 270, 323, and 334 mμ (log ε 4·92, 3·88, 4·21, and 4·04), δ 2·32, 2·34, and 2·51 (Found: C, 93·3; H, 6·7. $C_{14}H_{12}$ requires C, 93·3; H, 6·7%); *s*-trinitrobenzene complex, m.p. 198—200° (Found: C, 61·2; H, 3·9; N, 10·9. $C_{20}H_{15}N_3O_6$ requires C, 61·1; H, 3·8; N, 10·7%), and *1,5-dimethylacenaphthylene*, b.p. 142—145°/20 mm., m.p. 65—67°, $\nu_{max.}$ 995, 845, 815, and 760 cm.$^{-1}$, $\lambda_{max.}$ 234, (316), 327, 333, and 345 mμ [log ε 4·45, (4·06), 4·14, 4·05, and 3·87], δ 2·35, 2·37, and 2·65 (Found: C, 93·4; H, 6·5%); *s*-trinitrobenzene complex, m.p. 192—193° (Found: C, 61·4; H, 4·2; N, 10·8%).

3-Isopropyl-7-methoxycarbonyl-6-methylheptanoic acid (VI).—A solution of methyl hydrogen β-methylglutarate (5 g.) [13] and benzyl hydrogen β-isopropylglutarate (15 g.) [14] in methanol (35 ml.) containing some sodium methoxide (0·3 g.) was electrolysed for 4½ hr. at 30—35°, to afford, after fractional distillation, benzyl 3-isopropyl-6-methyl-7-methoxycarbonylheptanoate, b.p. 180—200°/0·5 mm. (3·5 g.). Hydrogenation over palladium–charcoal in methanol gave the *acid* (VI) (2·75 g.), b.p. 165°/0·3 mm. (Found: C, 63·7; H, 9·9. $C_{13}H_{24}O_4$ requires C, 63·9; H, 9·9%).

7-Methoxycarbonyl-3,7-dimethylheptanoic acid (VIII).—Dimethyl αα′-dimethylpimelate (80 g.) was refluxed with sodium hydroxide (14·5 g.) for 3 hr., cooled, and extracted with light petroleum (b.p. 60—80°). The aqueous layer was acidified and again extracted with light petroleum, to give crude methyl hydrogen αα′-dimethylpimelate (18 g.), b.p. 120°/0·3 mm. The aqueous layer was extracted with ether, the extracts were added to the first petroleum extracts, and the whole was evaporated, to yield a mixture of αα′-dimethylpimelic acid and its dimethyl ester. The latter mixture was re-esterified and hydrolysed, to yield more methyl hydrogen αα′-dimethylpimelate, and the process was continued until a good overall conversion (40 g.) had been obtained. A solution of this half-ester (35 g.) in thionyl chloride was allowed to stand at 40° for 3 hr. and refluxed for 5 min., to yield 6-methoxycarbonyl-2,6-dimethylhexanoyl chloride (36 g.), b.p. 120°/14 mm. A solution of the acid chloride (9 g.) in dry ether was added dropwise during 30 min. to a solution of diazomethane (8 g.) in ether, and the solution allowed to stand overnight, to give 5-methoxycarbonyl-1,5-dimethylpentyl diazomethyl ketone (8 g.), $\nu_{max.}$ 2300, 1720, and 1650 cm.$^{-1}$. A solution of this crude diazo-ketone (6 g.), in a mixture of benzyl alcohol (60 ml.) and collidine (60 ml.), was heated during 30 min. to 180°, and then maintained at 180—190° until evolution of nitrogen had ceased (about 15 min.). Distillation yielded benzyl 7-methoxycarbonyl-3,7-dimethylheptanoate (9·3 g.),

[13] R. P. Linstead, J. C. Lunt, and B. C. L. Weedon, *J. Chem. Soc.*, 1950, 3331.

[14] W. A. Noyes and H. W. Doughty, *J. Amer. Chem. Soc.*, 1905, **27**, 238.

b.p. 168°/0·9 mm., $\nu_{max.}$ 1710, 1150, 750, 740, and 690 cm.$^{-1}$, which on hydrogenation gave the *acid* (VIII), b.p. 135°/0·6 mm. (Found: C, 61·3; H, 9·0. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%).

Methyl 9-Isopropyl-13-methoxycarbonyl-2,6,12-trimethyltridecanoate (IX).—A solution of 3-isopropyl-7-methoxycarbonyl-6-methylheptanoic acid (13 g.) and 7-methoxycarbonyl-3,7-dimethylheptanoic acid (16·5 g.) in methanol (40 ml.) containing sodium methoxide (1 g.) was electrolysed for 6 hr. at 30—35°, to yield a mixture of diesters (20 g.). The required *ester* (IX), b.p. 170—172°/0·6 mm., *M*, 370 (Found: C, 71·0; H, 11·3. $C_{22}H_{42}O_4$ requires C, 71·3; H, 11·4%), was isolated by preparative gas chromatography at 250°.

12-Isopropyl-1,5,9-trimethylcyclotetradecane (*Cembrane*).—A solution of the ester (IX) (2 g.) in dry toluene (20 ml.) was added dropwise during 2¼ hr. to a vigorously stirred suspension of finely divided sodium in refluxing toluene (100 ml.) under nitrogen. The mixture was stirred for a further ¾ hr., and then treated successively with methanol (20 ml.), water (100 ml.), and dilute hydrochloric acid, to yield, as a viscous yellow oil, a mixture of 12-isopropyl-1,5,9-trimethyl-4-hydroxy-3-oxo- and -3-hydroxy-4-oxocylotetradecane (1·65 g.), $\nu_{max.}$ 3400 and 1700 cm.$^{-1}$. This mixture of acyloins (1·5 g.) was reduced by the Clemmensen method (amalgamated zinc and conc. hydrochloric acid) during 3 days, to give, after chromatography on alumina, a mixture of cycloalkene and cycloalkane (600 mg.). Reduction over palladium–charcoal afforded *cembrane* (500 mg.), b.p. 136—138°/0·35 mm., $\nu_{max.}$ 2900, 1450, 1365, and 725 cm.$^{-1}$, δ 0·82, 0·88, 1·25, 1·62, and 1·70, *M*, 280 (Found: C, 85·9; H, 14·3. $C_{20}H_{40}$ requires C, 85·6; H, 14·4%). A sample of cembrene (3 mg.) [11] was hydrogenated over palladium–charcoal, to give cembrane.

Isolation of Acenaphthylenes and Macrocyclic Polyolefins from Cigarette Smoke Condensate.—The distillate, b.p. 120—150°/0·5 mm. (22 g.),[1] obtained from the neutral fraction of cigarette smoke condensate, was chromatographed on neutral alumina with light petroleum and light petroleum–benzene (1 : 1), and the fractions were combined, according to their gas chromatograms, into six major fractions (H 1—5, 8·7 g.; H6, 3·7 g.).

Fractions H 1—5. A sample (0·5 g.) of fraction H2, after catalytic hydrogenation, was separated, by preparative gas chromatography at 210°, into three main components A, B, and C; the major component (A) contained over 90% of phytane. On analytical gas chromatography, component C showed peaks with retention times identical with those of cembrane, and on mass spectrometry showed molecular ions at *m/e* 278 and 280, but mainly at *m/e* 280. Most of the required cyclic polyolefin was present in fractions H4 and H5, which were therefore combined (0·7 g.) and chromatographed on argentated silica gel (100 g.). Elution with light petroleum–benzene (1 : 0 to 0 : 1) yielded fractions, samples of which were hydrogenated and compared with cembrane by gas chromatography. Those fractions giving peaks corresponding to cembrane were combined and rechromatographed on preparative thin-layer plates of argentated silica gel, to give a colourless oil (W; R_F ~0·5 in benzene), b.p. 130—140°/0·3 mm. (air-bath), $\nu_{max.}$ 1630, 1590, 965, 890, and 820 cm.$^{-1}$, δ 5·0, 1·4, and 1·9, *M*, 270, 272, $\lambda_{max.}$ 232 mμ (log ε 4·3). Analytical gas chromatography of the oil (W) showed one main component (retention volume relative to phytane, 1·15), along with small amounts (~15%) of three closely separated components. On heating the oil (W) (10 mg.) with palladium–charcoal (30 mg.) in a sealed tube at 270° for 12 hr., it gave a product which, on thin-layer chromatography, showed only one fluorescent band (ultraviolet spectrum in ethanol, $\lambda_{max.}$ 254, 341, 358, and 374·5 mμ).

Fraction H6. Chromatography on alumina (60 g.) in light petroleum gave several bright yellow fractions which were combined and evaporated, to yield an oil (2 g.). The oil, in ethanol (5 ml.), was heated to boiling together with a saturated solution of *s*-trinitrobenzene in ethanol, allowed to cool, and filtered, to yield orange-red crystals. The filtrate was evaporated and the residual oil chromatographed on alumina to separate the hydrocarbons from *s*-trinitrobenzene. The eluted hydrocarbons were again complexed with *s*-trinitrobenzene, to yield a second crop of crystals. The whole process was repeated until no further crystalline complex could be obtained. At this stage, the combined lots of crystals were recrystallised from ethanol, to give a main crop of pale orange crystals (500 mg.), m.p. 120—130°, followed by further crops (60 mg.), m.p. 140—170°, and (50 mg.), m.p. 100—120°. A combination of gas- (190°) and thin-layer chromatography on the preparative scale afforded acenaphthylene and 1-methylacenaphthylene, identified by comparison with authentic specimens. A mixture of the 3-, 4-, and 5-monomethylacenaphthylenes could not be separated preparatively but was separated on an analytical scale. The dimethylacenaphthylene fraction consisted mostly of the 1,3-isomer along with one other unidentified major component.

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