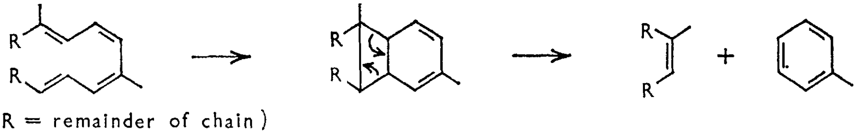
520. *Constituents of Cigarette Smoke. Part IX.*[1] *The Pyrolysis of Polyenes and the Formation of Aromatic Hydrocarbons*

By F. S. Edmunds and R. A. W. Johnstone

Pyrolysis of β-carotene yields mainly 1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene, also isolated from cigarette smoke. The effect of heat on some shorter conjugated systems leads to other cyclic compounds which are readily transformed into hydroaromatic substances. These hydroaromatics have been synthesised, the geometrical isomerism of the intermediate tertiary alcohols being discussed.

Previous work from these laboratories showed how non-conjugated polyenes can form cyclic hydrocarbons on pyrolysis.[2] An extension of this work suggests how some, at least, of the polycyclic aromatic substances in cigarette smoke may originate.[1] Conjugated polyenes, like β-carotene, are present in tobacco leaf,[3] as well as such non-conjugated polyenes as solanesol. The content of conjugated polyenes decreases from a maximum in fresh tobacco leaf to a minimum in fermented tobacco. The pyrolysis of the conjugated polyenes β-carotene and bixin proceeds at quite low temperatures.[4] The previously identified products of the pyrolysis of β-carotene were small amounts of toluene, *m*-xylene, and 2,6-dimethylnaphthalene, which can arise by simple cyclisation and elimination reactions of the polyene. On heating, the individual double bonds of a long conjugated chain can switch readily from *trans* to *cis* and back, and fairly simple reactions can



(R = remainder of chain)

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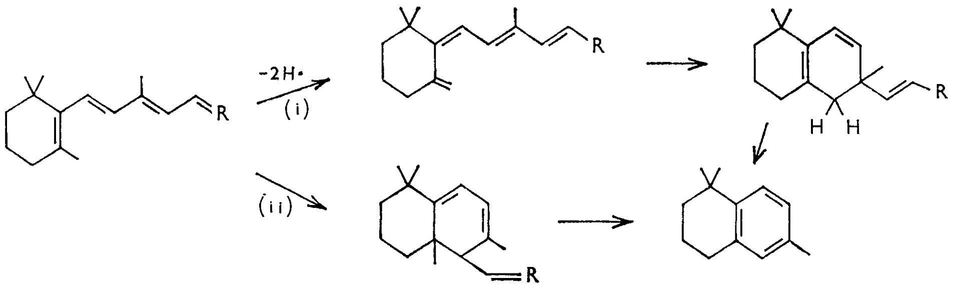
[1] Part VIII, J. W. Cook, R. A. W. Johnstone, and P. M. Quan, *Israel J. Chem,*, 1963, **1**, 356.
[2] R. A. W. Johnstone and P. M. Quan, *J.*, 1963, 2221.
[3] H. E. Wright, W. W. Burton, and R. C. Berry, *Arch. Biochem. Biophys.*, 1959, **82**, 107.
[4] J. F. B. Van Hasselt, *Rec. Trav. chim.*, 1911, **30**, 1; 1914, **33**, 192; R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 1928, **11**, 427; *Ber.*, 1932, **65**, 1873; 1933, **66**, 429, 1733.

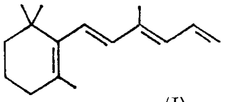
yield, for example, toluene. However, the major portion of the product of pyrolysis of β-carotene has been described as " hydroaromatic."[4,5]

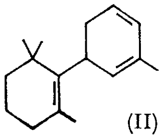
We heated β-carotene *in vacuo* at 300° for 2 hr., and obtained a thin, mineral-like oil which could be distilled readily at atmospheric pressure with little residue. Analytical gas chromatography showed that the distillate was mainly one compound, with much smaller amounts of toluene, *m*-xylene, 2,6-dimethylnaphthalene, and other unknown substances. The whole mixture was separated by preparative gas chromatography. The major-component peak overlapped those of much smaller amounts of two other components, which were separated from each other and the main component by thin-layer chromatography. The major component of the pyrolysis was 1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene (ionene), as shown by the identity of its infrared and ultraviolet spectra, and gas chromatographic retention times, with those of an authentic specimen prepared from β-ionone.[6] Ionene may be formed in one of two ways [(i) and (ii)], as shown. The components immediately following the ionene peak separated on thin-layer chromatography into three bands which proved to be 1,2-dihydro-1,1,6-trimethylnaphthalene, ionene, and 3-(2,2,6-trimethylcyclohexyl)toluene (III). The proportions of the substances isolated in this pyrolysis are given in the Experimental section. Examination of the relevant part of the neutral fraction of cigarette smoke condensate by preparative gas chromatography yielded ionene (estimated concentration 8 μg./cigarette). Since toluene, *m*-xylene, and 2,6-dimethylnaphthalene have been isolated previously from cigarette smoke,[7,8] it is reasonable to assume that part of the total of these substances, along with ionene, is formed on pyrolysis of the tobacco leaf conjugated polyenes.

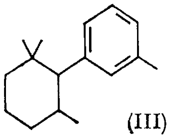
To examine this type of reaction further, two conjugated polyenes of different chain-length were pyrolysed. Vitamin A alcohol on pyrolysis yielded ionene, possibly following an elimination of water, and then following the reaction mechanism (i).



Attempts to prepare the shorter conjugated system, 3-methyl-1-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-triene (I) using the Wittig reaction between β-ionone and allylidenetriphenylphosphorane yielded only small amounts of a hydrocarbon, eventually shown to be the bicyclic triene (II). The hydrocarbon (II) was evidently formed by the ready


(I)


(II)


(III)

cyclisation of the *trans*-1,*cis*-3-form of the tetraene (I). The absence of any *trans*-1,*trans*-3-isomer of this tetraene is possibly due to rapid polymerisation. In the presence of iodine

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[5] J. G. Erdman, *Geochim. e Cosmochim. Acta*, 1961, **22** (1), 16; R. N. Jones and R. W. Sharpe, *Canad. J. Res.*, 1948, *B*, **26**, 728.

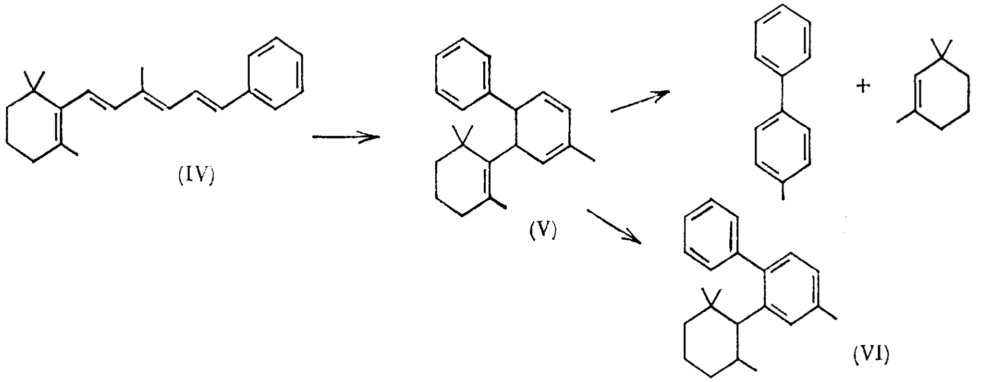
[6] M. T. Bogert and V. G. Fourman, *J. Amer. Chem. Soc.*, 1933, **55**, 4670.

[7] R. A. W. Johnstone, P. M. Quan, and W. Carruthers, *Nature*, 1962, **195**, 1267.

[8] R. A. W. Johnstone and P. M. Quan, *Nature*, 1963, **199**, 1184.

and daylight, or on brief heating with palladium–charcoal, the cyclic diene (II) was converted into the aromatic compound (III). This same substance was one of the products of pyrolysis of β-carotene.

To obtain a suitable tetraene in good yield, β-ionone was treated with the ylide of cinnamyltriphenylphosphonium bromide, to give a mixture of 3-methyl-6-phenyl-1-(2,6,6-trimethylcyclohex-1-enyl)hexa-*trans*-1,*trans*-3,*trans*-5- and -*trans*-1,*cis*-3,*trans*-5-triene (IV), which were separated by chromatography on alumina. The pyrolysis of the tetraene (IV) yielded a small amount of ionene, some 4-methylbiphenyl, but mainly a mixture of 2-methyl-5-phenyl-6-(2,6,6-trimethylcyclohex-1-enyl)cyclohexa-1,3-diene (V), and 4-methyl-2-(2,2,6-trimethylcyclohexyl)biphenyl (VI). The hydrocarbon (V) is a simple cyclisation product of the tetraene (IV), the biphenyls arising by simple 1,3-hydrogen shifts, and an elimination in the case of 4-methylbiphenyl. In the polyolefin (IV), cyclisation to a monocyclic diene predominates over the formation of a bicyclic diene as in the case of β-carotene.



The pyrolysis of conjugated polyenes can give rise therefore to different types of cyclised products depending on the length and nature of the chain of double bonds.

The hydrocarbons (III) and (VI) were synthesised by other routes. Treatment of 2,2,6-trimethylcyclohexanone with either *m*-tolyl-lithium or *m*-tolylmagnesium bromide yielded a mixture of isomeric tertiary alcohols (VII; R = *m*-tolyl) which, in the presence of concentrated hydrochloric acid, were catalytically hydrogenated to the mixture of isomeric hydrocarbons (III). The mixture of isomers (III) could not be separated by gas chromatography. Dehydration of the alcohols (VII; R = *m*-tolyl) with potassium hydrogen sulphate yielded the unsaturated hydrocarbon (VIII; R = *m*-tolyl), but left some of the alcohol unaffected even when subjected to a second dehydration. Only 20% of the alcohol (VII) prepared from *m*-tolylmagnesium bromide was dehydrated, as compared to 70% in the case of the same alcohol prepared from *m*-tolyl-lithium. These differences can be ascribed to the differences in the ratios of *cis*- and *trans*-alcohols.* Consideration of non-bonded interactions suggests that the *m*-tolyl-lithium should produce more of the *trans*-alcohol than *m*-tolylmagnesium bromide. Gas chromatography of the alcohols showed that the proportions of the two alcohols were, (i) from *m*-tolyl-lithium, 40 : 60 (*cis* : *trans*), and (ii) from *m*-tolylmagnesium bromide, 80 : 20. Similar tertiary alcohols, difficult to dehydrate, have been described,[9] and are probably the isomers in which the hydroxyl group and the adjacent hydrogen are *cis* to each other. The infrared spectra of both the mixture of isomeric alcohols and the isomer not dehydrated with potassium hydrogen sulphate showed bands at 1160 cm.$^{-1}$, characteristic of an axial tertiary alcohol and indicating that the *m*-tolyl group had taken up an equatorial position.

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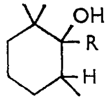
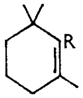
* *cis* and *trans* in this Paper refer to the relative orientations of the hydroxyl group and the hydrogen on the next carbon atom in the cyclohexane ring.

[9] R. E. Carlin and D. A. Constantine, *J. Amer. Chem. Soc.*, 1947, **69**, 50.

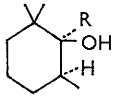
Treatment of 2,2,6-trimethylcyclohexanone with 4-methylbiphenyl-2-yl-lithium gave a mixture of the isomeric alcohols (VII; R = 4-methylbiphenyl-2-yl) which were separated by chromatography on alumina. Again, one of the alcohols was readily dehydrated with potassium hydrogen sulphate to the unsaturated hydrocarbon (VIII; R = 4-methylbiphenyl-2-yl), but the other isomer was almost completely unaffected on similar treatment.



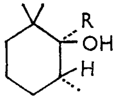
(VII)



(VIII)



(IX)



(X)

(R = 4-methylbiphenyl-2-yl)

The infrared spectra of the alcohols (VII; R = 4-methylbiphenyl-2-yl) indicate axial hydroxyl groups in each case, and this fact, taken in conjunction with the *cis*- and *trans*-arrangements discussed above, fixes the configuration of these alcohols as (IX) and (X) for the lower and higher melting forms, respectively. Their ultraviolet spectra show no peak corresponding to a biphenyl, showing that the planes of the benzene rings are twisted considerably.[10] The crude tertiary chlorides, obtained by treating the alcohols (IX) and (X) with dry hydrogen chloride in ether, were catalytically hydrogenated to the hydrocarbons (VI). Unlike (VII; R = *m*-tolyl), the alcohols (IX) and (X) could not be separated by gas chromatography.

EXPERIMENTAL

Neutral alumina (Brockmann Grade I), washed with ethyl acetate, was used. Light petroleum had b. p. 40—60°.

Preparative Gas Chromatography.—Samples (100 mg.) were placed on a 6 ft. × 0·5 in. column of Celite (30—60 mesh) coated with 25% (w/w) of silicone elastomer E301 (Imperial Chemical Industries), and eluted at a nitrogen flow of 120 ml./min. at the temperatures indicated.

Analytical Gas Chromatography.—Column 1; 4 ft. × 0·25 in. packed with Celite (80—100 mesh) coated with polyethylene glycol adipate (15% w/w). Column 2, 100 ft. × 0·02 in. stainless steel capillary coated with silicone gum SE-30.

Pyrolysis of β-*Carotene.*—In a typical experiment, β-carotene was heated in a sealed tube, *in vacuo*, at 300° for 2 hr. The resulting oil was distilled, to yield a pale yellow liquid, b. p. 20—300° (air-bath) (69%). To remove a small amount of oxygenated material, the liquid was eluted from a short column of alumina with light petroleum. Analytical gas chromatography on column 1 at 180° gave the following percentages (from β-carotene) of components: toluene and *m*-xylene, 1·3; unknowns, 6·3; ionene, 49·5; 1,2-dihydro-1,1,6-trimethylnaphthalene, 3·8; 3-(2,2,6-trimethylcyclohexyl)toluene, 1·7; 2,6-dimethylnaphthalene, 6·4. Preparative gas chromatography at 180° afforded toluene, *m*-xylene, ionene, a mixture of hydrocarbons (A), and 2,6-dimethylnaphthalene. The mixture of hydrocarbons (A) was separated by thin-layer chromatography on silica-gel into ionene, 1,2-dihydro-1,1,6-trimethylnaphthalene, and 3-(2,2,6-trimethylcyclohexyl)toluene. All substances were identified by comparison of infrared and ultraviolet spectra, and gas-chromatographic retention times, with those of authentic specimens. In one experiment when air was present in the tube during the pyrolysis of β-carotene, the yield of hydrocarbon was reduced considerably.

Pyrolysis of Vitamin A Alcohol.—Under the same conditions used for β-carotene, water was split off, to yield a mixture of hydrocarbons consisting mainly (50—60%) of ionene, with small amounts of unidentified, mostly oxygenated, substances.

Pyrolysis of 3-*Methyl*-6-*phenyl*-1-(2,6,6-*trimethylcyclohex*-1-*enyl*)*hexa*-1,3,5-*triene* (IV).—The triene, after heating to 250° for 2 hr. *in vacuo*, yielded a colourless oil which, on preparative gas chromatography, gave ionene (1·0%), 4-methylbiphenyl (4·0%), 4-methyl-2-(2,2,6-trimethylcyclohexyl)biphenyl (48·0%), and 2-methyl-5-phenyl-6-(2,6,6-trimethylcyclohex-1-enyl)cyclohexa-1,3-diene (46·0%) in the yields indicated. There were small amounts of other unidentified

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[10] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, 1962, p. 384.

components. Each substance, apart from the hydrocarbon (V) was identified by comparison of its infrared and ultraviolet spectra, and gas-chromatographic retention times, with those of authentic specimens. The *hydrocarbon* (V) had $\nu_{max.}$ 745, 690 (monosubstituted benzene), and 825 cm.$^{-1}$ (trisubstituted double bond), $\lambda_{max.}$ 259 mμ (log ε 4·05) (monocyclic conjugated diene) (Found: C, 90·5; H, 9·7. $C_{22}H_{28}$ requires C, 90·4; H, 9·6%). When heated with 10% palladium–charcoal catalyst at 200° for 30 min. it was converted in good yield into the biphenyl (VI).

Attempted Preparation of 3-*Methyl*-1-(2,6,6-*trimethylcyclohex*-1-*enyl*)*hexa*-1,3,5-*triene* (I).—A solution of β-ionone (4·1 g.) in dry ether (20 ml.) was added dropwise, with cooling, to a stirred solution of allylidenetriphenylphosphorane (prepared from 8·1 g. of allyltriphenylphosphonium bromide and one equivalent of *n*-butyl-lithium in ether) under nitrogen. The white precipitate was stirred for 18 hr., and the mixture filtered. The residue from the distillation of the ether from the filtrate was chromatographed on alumina. Elution with light petroleum afforded 2-*methyl*-6-(2,6,6-*trimethylcyclohex*-1-*enyl*)*cyclohexa*-1,3-*diene* (II) (586 mg.), b. p. 140° (air-bath)/17 mm., $\lambda_{max.}$ 272 mμ (log ε 3·74), $\nu_{max.}$ 724 cm.$^{-1}$ (Found: C, 88·6; H, 11·3. $C_{16}H_{24}$ requires C, 88·8; H, 11·2%). It absorbed 2·9 mol. of hydrogen in the presence of platinic oxide in glacial acetic acid, to give 1,1,3-*trimethyl*-2-(3-*methylcyclohexyl*)*cyclohexane*, b. p. 120° (air-bath)/0·4 mm. (Found: C, 86·5; H, 13·4. $C_{16}H_{30}$ requires C, 86·4; H, 13·6%). Either under the action of iodine in light petroleum and daylight, or on heating with 10% palladium–charcoal at 180° for 20 min., the triene (II) gave a high yield (80%) of 3-(2,2,6-trimethylcyclohexyl)toluene (III), b. p. 145° (air-bath)/15 mm., $\lambda_{max.}$ 261, 267, 275 mμ (log ε 2·39, 2·46, 2·39), $\nu_{max.}$ 780, 709 cm.$^{-1}$ (Found: C, 89·1; H, 10·7. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%). The ultraviolet and infrared spectra, and gas-chromatographic retention times, were identical with those of a sample prepared by another route (see under).

3-*Methyl*-6-*phenyl*-1-(2,6,6-*trimethylcyclohex*-1-*enyl*)*hexa*-1,3,5-*triene* (IV).—Cinnamylidenetriphenylphosphorane (1 mol., prepared as above) in ether was treated dropwise with β-ionone (1·2 mol.) in ether and stirred for 18 hr. under nitrogen at room temperature. The mixture was filtered, and the filtrate evaporated on a water-bath to yield a pale yellow oil. Chromatography of the oil on alumina gave, on elution with light petroleum, the trans-1,cis-3,trans-5-*triene* (9%) as a pale yellow oil, b. p. 135° (air-bath)/0·04 mm., $\lambda_{max.}$ 338 mμ (log ε 4·58), $\nu_{max.}$ 960, 744, 688 cm.$^{-1}$ (Found: C, 89·8; H, 9·8. $C_{22}H_{28}$ requires C, 90·3; H, 9·7%). Further elution with light petroleum–ether (99 : 1) afforded pale yellow crystals of the trans-1,trans-3,trans-5-*triene* (16%), m. p. 79—81° (from ethanol), $\lambda_{max.}$ [323], 337, 345 mμ (log ε 4·59, 4·69, 4·69), $\nu_{max.}$ 965, 747, 686 cm.$^{-1}$ (Found: C, 90·6; H, 9·4%).

3-(2,6,6-*Trimethylcyclohex*-1-*enyl*)*toluene* (VIII; R = *m*-tolyl).—To a solution of *m*-tolylmagnesium bromide (1 mol.) in ether was added a solution of 2,2,6-trimethylcyclohexanone (1·1 mol.) in ether. The mixture was refluxed for 16 hr., and worked up in the usual way, to give a colourless oil which was chromatographed on alumina. Elution with light petroleum yielded toluene, and further elution with ether–light petroleum (1 : 10) gave first 2,2,6-trimethylcyclohexanone and then 2,2,6-*trimethyl*-1-m-*tolylcyclohexanol* (VII; R = *m*-tolyl) (6%), b. p. 108° (air-bath)/0·4 mm., $\nu_{max.}$ 1160, 785, 706 cm.$^{-1}$ (Found: C, 82·7; H, 10·7. $C_{16}H_{24}O$ requires C, 82·7; H, 10·4%). On heating with 5% (w/w) of potassium hydrogen sulphate at 140° for 15 min., the alcohol gave approximately 20% of 3-(2,6,6-*trimethylcyclohex*-1-*enyl*)-*toluene* (VIII; R = *m*-tolyl), b. p. 120° (air-bath)/15 mm., $\lambda_{max.}$ [266], 272 mμ (log ε 2·93, 2·84), $\nu_{max.}$ 782, 705 cm.$^{-1}$ (Found: C, 89·8; H, 10·4. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%). The remainder of the alcohol was recovered unchanged.

Similarly, 2,2,6-trimethylcyclohexanone was treated with *m*-tolyl-lithium (prepared by exchange between n-butyl-lithium and *m*-bromotoluene),[11] to yield 2,2,6-trimethyl-1-*m*-tolylcyclohexanol (36%). On dehydration with potassium hydrogen sulphate at 140°, 70% of this alcohol was converted into 3-(2,6,6-trimethylcyclohex-1-enyl)toluene, the remainder of the alcohol being unchanged. On gas chromatography of the alcohols on column 2 at 134° the relative retention times of the *cis*- and *trans*-alcohols (VII; R = *m*-tolyl) were 1·00 : 1·03.

Hydrogenation of the above alcohols with 10% palladium–charcoal in ethanol–10N-hydrochloric acid (2 : 1) for 6 hr. yielded 3-(2,2,6-trimethylcyclohexyl)toluene (Found: C, 88·8; H, 11·0. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%). The relative gas-chromatographic retention times of 3-(2,2,6-trimethylcyclohexyl)toluene and 3-(2,6,6-trimethylcyclohex-1-enyl)toluene were 1·09 : 1·00 at 120° on column 2.

[11] H. Gilman, W. Langham, and F. W. Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.

4-*Methyl*-2-(2,2,6-*trimethylcyclohexyl*)*biphenyl* (VI).—A solution of 2-bromo-4-methylbiphenyl[12] (1·2 g.) in dry ether (10 ml.) was treated with a solution of n-butyl-lithium (1 equiv.) and refluxed under nitrogen for 15 min. The solution was allowed to cool for 10 min., and then treated dropwise with a solution of 2,2,6-trimethylcyclohexanone (1·5 g.) in ether (10 ml.). After working up in the usual way, the product was heated to 100°/15 mm. to remove excess 2,2,6-trimethylcyclohexanone. The residual oil was chromatographed on alumina; elution with light petroleum afforded (i) 4-methylbiphenyl, (ii) a solid alcohol (0·59 g.), and (iii) a gummy alcohol (0·63 g.). The alcohol (ii) was cis-2,2,6-*trimethyl*-1-(4-*methylbiphenyl*-2-*yl*)*cyclohexanol* (X), m. p. 133° (from ethanol), $\lambda_{max.}$ 261, 269, 279 mμ (log ε 2·97, 2·92, 2·77), $\nu_{max.}$ 3600(sharp), 1165, 1160, 815, 771, 711, 701 cm.$^{-1}$ (Found: C, 85·8; H, 9·3. $C_{22}H_{28}O$ requires C, 85·7; H, 9·2%). When heated with potassium hydrogen sulphate to 185° for 30 min. in a sealed tube, less than 5% of the alcohol was dehydrated to 4-*methyl*-2-(2,6,6-*trimethylcyclohex*-1-*enyl*)-*biphenyl*, b. p. 140° (air-bath)/0·4 mm., $\lambda_{max.}$ 248 mμ (log ε 4·28), $\nu_{max.}$ 800, 771, 762, 742, 698 cm.$^{-1}$ (Found: C, 91·5; H, 8·6. $C_{22}H_{26}$ requires C, 91·0; H, 9·0%). The gummy alcohol (iii) was distilled, to give a small amount of 1-n-butyl-2,2,6-trimethylcyclohexanol (VII; R = n-butyl) but mainly trans-2,2,6-*trimethyl*-1-(4-*methylbiphenyl*-2-*yl*)*cyclohexanol* (IX), m. p. 102—103° (from methanol), $\lambda_{max.}$ 263, 269, 279 mμ (log ε 2·79, 2·79, 2·69), $\nu_{max.}$ 3540(sharp), 1150, 824, 768, 712, 699 cm.$^{-1}$ (Found: C, 85·1; H, 8·8. $C_{22}H_{28}O$ requires C, 85·7; H, 9·2%). The alcohol was completely dehydrated when heated to 185° with potassium hydrogen sulphate for 30 min., to yield 4-methyl-2-(2,6,6-trimethylcyclohex-1-enyl)biphenyl (VIII; R = 4-methylbiphenyl-2-yl). A solution of the alcohol in dry ether over anhydrous calcium chloride was saturated with dry hydrogen chloride. After being allowed to stand overnight, the ether was evaporated, to give the crude 2,2,6-trimethyl-1-(4-methylbiphenyl-2-yl)cyclohexyl chloride which was immediately hydrogenated with platinic oxide catalyst in ethyl acetate, to yield 4-*methyl*-2-(2,2,6-*trimethylcyclohexyl*)*biphenyl* (VI), b. p. 195° (air-bath)/10 mm., $\lambda_{max.}$ 245 mμ (log ε 3·84), $\nu_{max.}$ 820, 771, 765, 741, 697 cm.$^{-1}$ (Found: C, 90·5; H, 9·5. $C_{22}H_{28}$ requires C, 90·4; H, 9·6%). The relative gas-chromatographic retention times of the hydrocarbons (VIII; R = 4-methylbiphenyl-2-yl) and (VI) were 1·00 : 1·06.

1,2,3,4-*Tetrahydro*-1,1,6-*trimethylnaphthalene* (Ionene).—Prepared from β-ionone.[6] The crude product was chromatographed on alumina, to yield ionene, $\lambda_{max.}$ 272, 279 mμ (log ε 2·74, 2·75), $\nu_{max.}$ 815 cm.$^{-1}$.

1,2-*Dihydro*-1,1,6-*trimethylnaphthalene*.—A solution of ionene (800 mg.) in carbon tetrachloride (10 ml.) was treated with *N*-bromosuccinimide (900 mg.) and refluxed for 30 min. with a few crystals of benzoyl peroxide. The solution was cooled, filtered, and the solution evaporated. The residual crude bromide was refluxed with a dilute solution of potassium hydroxide in ethanol for a short time, and poured into water. Extraction with light petroleum, and chromatography on alumina, yielded 1,2-*dihydro*-1,1,6-*trimethylnaphthalene*[13] (216 mg.), $\lambda_{max.}$ 265 mμ (log ε 3·72), $\nu_{max.}$ 814, 695 cm.$^{-1}$ (Found: C, 89·9; H, 10·1. Calc. for $C_{13}H_{16}$: C, 90·6; H, 9·4.

Ionene in Cigarette Smoke.—The neutral portion of cigarette smoke condensate eluted from an alumina column with light petroleum[14] was distilled, and a fraction, b. p. 220—280°, was gas-chromatographed on the preparative column at 160°. A substance, giving a peak with the same retention time as ionene, was collected by cooling the effluent to −70°. The infrared and ultraviolet spectra of this substance were identical with those of ionene. The estimated (by gas chromatography) concentration of ionene in cigarette smoke condensate was 8 μg./cigarette (average weight 1·1 g.).

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[12] M. Gomberg and J. C. Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.
[13] R. A. Barnes and G. R. Buckwalter, *J. Amer. Chem. Soc.*, 1951, **73**, 3858.
[14] R. A. W. Johnstone and P. M. Quan, *J.*, 1963, 5706.