1079. *Carotenoids and Related Compounds. Part X.* Synthesis of Renieratene, Isorenieratene, Renierapurpurin, and other Aryl-polyenes.*

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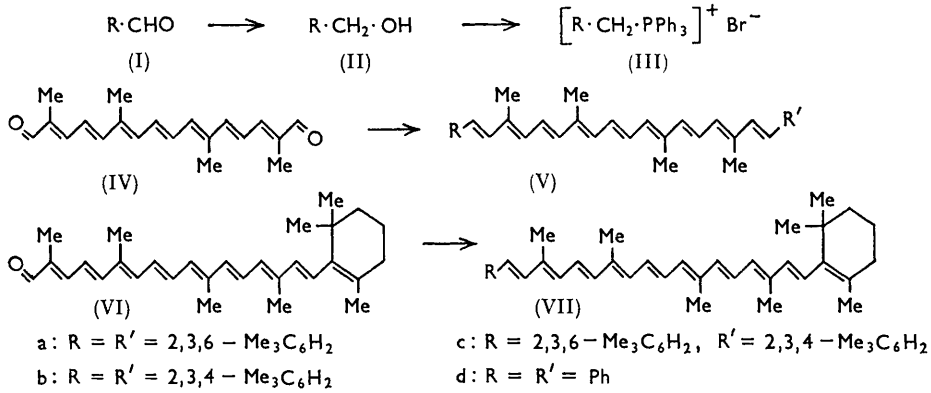
A series of aromatic carotenoids (V and VII) has been synthesised in high yield by reaction of crocetindial (IV) and β-apo-2-carotenal (VI) with appropriate benzyl Wittig reagents.

Yamaguchi's studies on the pigments of a Japanese sea sponge, *Reniera japonica*, led to the discovery of a novel class of natural carotenoids containing aryl end-groups. Renieratene, isorenieratene, and renierapurpurin were shown to have structures (Vc), (Va), and (Vb), respectively,[1,3] and these structures were confirmed by syntheses [2,3] (albeit in low yields) from oct-4-ene-2,7-dione [4] and aryl analogues of β-ionone,[3,5] following a route developed earlier for phenyl [6] (Vd) and β-naphthyl [7] analogues of β-carotene. A similar synthesis of isorenieratene has also been reported by Khosla and Karrer.[8] We now describe syntheses of the three aryl-carotenoids in high yield from crocetindial (IV).[9]



Reduction of 2,3,6- and 2,3,4-trimethylbenzaldehyde (Ia and b) with lithium aluminium hydride gave the alcohols (IIa and b) which were converted into the triphenylphosphonium bromides (IIIa and b). Wittig reactions of these intermediates with crocetindial (IV) then gave isorenieratene (Va) and renierapurpurin (Vb), respectively, in *ca.* 90% yield. The benzyl reagent (IIId) similarly gave the diphenyl analogue (Vd) of β-carotene. When the Wittig reaction was repeated starting with an equimolar mixture of (IIIa and b) a product was obtained from which renieratene (Vc) was isolated in 42% yield, together with the two symmetrical carotenoids (Va and b). On chromatography the three synthetic compounds (Va, b, and c) separated readily from one another, but not from authentic specimens of isorenieratene, renierapurpurin, and renieratene, respectively, which were kindly provided by Professor M. Yamaguchi.

Since related trimethylphenyl analogues of vitamin A acid have slight growth-promoting properties [5,10] synthetic samples of both isorenieratene and renierapurpurin

* Part IX, *J.*, 1961, 4019.

[1] Yamaguchi, *Bull. Chem. Soc. Japan*, 1957, **30**, 111, 979; 1958, **31**, 51, 739.
[2] Yamaguchi, *Bull. Chem. Soc. Japan*, 1959, **32**, 1171.
[3] Yamaguchi, *Bull. Chem. Soc. Japan*, 1960, **33**, 1560.
[4] Cf. Ahmad, Sondheimer, Weedon, and Woods, *J.*, 1952, 4089.
[5] Lowe, Torto, and Weedon, *J.*, 1958, 1855.
[6] Garbers, Eugster, and Karrer, *Helv. Chim. Acta*, 1952, **35**, 1179.
[7] Linner, Eugster, and Karrer, *Helv. Chim. Acta*, 1955, **38**, 1869.
[8] Khosla and Karrer, *Helv. Chim. Acta*, 1960, **43**, 453.
[9] Isler, Gutmann, Lindlar, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1956, **39**, 463.
[10] Bharucha and Weedon, *J.*, 1953, 1571.

were fed to vitamin-A-deficient rats. No biological activity was observed with doses which would have revealed a potency of about 10% of that of β-carotene. Yamaguchi has reported that both renieratene and isorenieratene are inactive.[1]

It is tempting to suggest that the 2,3,6- and 2,3,4-trimethylphenyl ring systems present in renieratene, isorenieratene, and renierapurpurin are formed in Nature by aromatisation, accompanied by methyl migration, of the 2,2,6-trimethylcyclohexenyl ring systems (or their oxygenated derivatives) commonly encountered in other carotenoids. It may be significant that the three aryl-carotenoids occur in *Reniera japonica* in association with

TABLE 1.

Visible-light absorption properties of aryl-carotenoids.

Diaryl-carotenoids	Ref.	Solvent	Maxima (mμ), with intensities ($10^{-3}\varepsilon$) in parentheses		
Diphenyl analogue (Vd)		C_6H_6	517 (138)	482 (157)	455 (107)
,, ,, ...	6	C_6H_6	517 (132)	482 (152)	455 (102)
,, ,, ...	6	CS_2	536 (102)	501 (120)	475 (85)
Isorenieratene (Va)		C_6H_6	493 (106)	465 (123)	443 * (95)
,, ...	1 †	C_6H_6	492 (104)	463 (123)	430 *
,, ...	1	CS_2	520	484	452
Renieratene (Vc)	1 †	C_6H_6	507	476	457 *
,, ...		CS_2	532 (103)	497 (113)	467 * (84)
,, ...	1	CS_2	532	496	463
Renierapurpurin (Vb)		C_6H_6	519	487	464 *
,, ...		CS_2	544 ‡ (88)	504 (109)	477 * (83)
,, ...	1, 3 †	CS_2	544 ‡ (97)	504 (119)	475 (88)
Monoaryl-carotenoids					
Phenyl analogue (VIId)		C_6H_6	508 (95)	476 (116)	453 (88)
β-Isorenieratene (VIIa)		CS_2	508 (107)	487 (118)	456 (88)
β-Renierpurpurin (VIIb)		CS_2	521 (100)	497 (115)	469 (92)

* Inflexion. † Wavelengths and/or intensities estimated from published curves. ‡ Observed variations (536—544 mμ) in the position of the longest-wavelength maximum may be due to small differences in stereochemical purity of various samples.

TABLE 2.

Nuclear magnetic resonance spectra.*

Compound	Geminal	End-of-chain (cyclohexenyl)	In-chain	Aryl	Rel. intensities (approx.)
β-Carotene [14]	8·97	8·28	8·03		2 : 1 : 2
Phenyl analogue (VIId) ...	8·97	8·28	8·02, 7·96		2 : 1 : 3 : 1
Isorenieratene (Va)			8·02, 7·93	7·78, 7·73	1 : 1 : 1 : 2
β-Isorenieratene (VIIa) ...	8·97	8·28	8·03, 7·92	7·78, 7·73	2 : 1 : 3 : 1 : 1 : 2
β-Renierapurpurin (VIIb)	8·97	8·29	8·03, 7·96	7·81, 7·72	2 : 1 : 3 : 1 : 1 : 2
1,2,4-Trimethylbenzene ...				7·78, 7·73	2 : 1
1,2,3-Trimethylbenzene ...				7·84, 7·72	1 : 2

* Spectra were determined on a Varian A60 spectrometer, for dilute solutions in deuteriochloroform, with tetramethylsilane as an internal reference. Methyl bands only are quoted. Figures are on the τ scale.

α- and β-carotene.[1] An aromatisation of the above type has previously been suggested to account for the presence of the 2,3,6-trimethylphenyl analogue of β-ionone in the urine of pregnant mares,[11] and a similar transformation can be effected *in vitro*.[8,12] However, the formation of a 2,3,4-trimethylphenyl ring in a similar way would, as far as we are aware, be without precedent. In view of these considerations it was of interest to synthesise and characterise " β-isorenieratene " (VIIa) and " β-renierapurpurin " (VIIb) which might conceivably be intermediates in the biosynthesis of the *Reniera* pigments. The desired compounds were readily obtained (90%) from β-apo-2-carotenal [13] (VI) and the appropriate Wittig reagents. The phenyl analogue (VIId) was similarly prepared.

[11] Prelog, Führer, Hagenbach, and Schneider, *Helv. Chim. Acta*, 1948, **31**, 1799.

[12] Karrer and Ochsner, *Helv. Chim. Acta*, 1948, **31**, 2093; Büchi, Seitz, and Jeger, *ibid.*, 1949, **32**, 39; Bächli and Karrer, *ibid.*, 1955, **38**, 1863; Braude, Jackman, Linstead, and Lowe, *J.*, 1960, 3123.

[13] Rüegg, Montavon, Ryser, Saucy, Schwieter, and Isler, *Helv. Chim. Acta*, 1959, **42**, 854.

The visible-light absorption properties of the carotenoids described above are summarised in Table 1. Despite the three methyl substituents on their aryl rings, both isorenieratene and β-isorenieratene absorb at appreciably lower wavelengths than their phenyl analogues. Similar effects have been noted previously with other 2,3,6-trimethylphenyl polyenes [5] and may be ascribed to steric interference between the polyene chain and the 2- and 6-methyl groups, the effect of the 2-methyl group being enhanced by the " buttressing effect " of the 3-methyl group. The consequent non-planarity of the molecule limits the overlap of the π-orbitals associated with the aryl rings and the polyene chain, resulting in the observed hypsochromic shift of the light-absorption maxima. Renierapurpurin and β-renierapurpurin exhibit maximal absorptions at wavelengths very similar to those of their phenyl analogues. Apparently the severe steric hindrance associated with one of the two possible planar arrangements of each 2,3,4-trimethylphenyl polyene end-group limits the probability of planar conformations to an extent which offsets the bathochromic influence normally shown by methyl substituents. As expected, the light-absorption properties of renieratene are intermediate between those of isorenieratene and renierapurpurin.

Of the diaryl-carotenoids, only isorenieratene was sufficiently soluble for its nuclear magnetic resonance spectrum to be measured. However, the compounds possessing a 2,2 6-trimethylcyclohexenyl ring at one end of the molecule were more soluble and allowed the methyl absorption bands associated with the aromatic systems to be determined (Table 2). It is clear that an aryl group deshields slightly the " in-chain " methyl nearest to it, giving rise to a band at 7·96 which can be resolved from the usual band at *ca.* 8·03 owing to the more remote " in-chain " methyl groups.[14] The 2,3,6-trimethylphenyl end group has methyl bands at 7·78 and 7·73 (relative intensities 1 : 2), whereas the 2,3,4-trimethylphenyl end-group has two bands at 7·81 and 7·72 (relative intensities 1 : 2).

Experimental

As far as possible, operations were carried out in an inert atmosphere, usually of nitrogen. Alumina for chromatography was pre-treated as described by Cheeseman *et al.*[15] and was graded according to Brockmann and Schodder.[16]

M. p.s of polyenes were determined in evacuated capillary tubes unless otherwise stated.

The purity of ψ-cumene and hemimellitene was confirmed by gas–liquid chromatography, which readily separated these from one another and from mesitylene.

Nuclear magnetic resonance and visible-light absorption data are given in the Tables.

2,3,6- *and* 2,3,4-*Trimethylbenzaldehyde* (Ia and b).—2,3,6-Trimethylbenzaldehyde was prepared from ψ-cumene by the method of Lowe *et al.*[5] 2,3,4-Trimethylbenzaldehyde was prepared (50%) similarly from hemimellitene through 1-bromo-2,3,4-trimethylbenzene [17] and had b. p. 120—122°/0·8 mm., n_D^{22} 1·5495, $\lambda_{max.}$ (in EtOH) 265 and 214·5 mμ ($10^{-3}\varepsilon$ 11·5 and 18·6, respectively), $\nu_{max.}$ (in CCl_4) 2858, 2720 (aldehydic CH), and 1698 cm.$^{-1}$ (aryl CH=O). The 2,4-dinitrophenylhydrazone (84%) crystallised from chloroform–ethanol in red needles, m. p. 230—231° (Yamaguchi [1] gives m. p. 229°), $\lambda_{max.}$ (in $CHCl_3$) 388 mμ ($10^{-3}\varepsilon$ 28·8); the semicarbazone (77%) had m. p. 240—241° (decomp.) (Yamaguchi [1] gives m. p. 240—242°).

2,3,6- *and* 2,3,4-*Trimethylbenzyl Alcohol* (IIa and b).—2,3,6-Trimethylbenzaldehyde (5·7 g.) in ether (15 ml.) was added during 15 min. to a cold (0°) suspension of lithium aluminium hydride (448 mg.) in ether (20 ml.). The mixture was stirred at 20° for 7 hr., and moist ether was added, followed by ammonium chloride (650 mg.) in water (1·6 ml.). The ethereal solution was filtered, dried, and evaporated. Crystallisation of the residue (5·9 g.) from light petroleum (b. p. 40—60°) gave 2,3,6-trimethylbenzyl alcohol (4·4 g., 76%), m. p. 84·5—85° (Found: C, 79·7; H, 9·3. Calc. for $C_{10}H_{14}O$: C, 79·95; H, 9·4%), $\nu_{max.}$ (in CCl_4) 3614, 3468 cm.$^{-1}$ (OH), $\nu_{max.}$ (in KBr) 804 cm.$^{-1}$ (2 adjacent ring H) (Smith and Agre [18] report m. p. 83·5—85° for an alcohol believed to have this constitution). The 3,5-*dinitrobenzoate* (70%) crystallised from

[14] Barber, Davis, Jackman, and Weedon, *J.*, 1960, 2870.
[15] Cheeseman, Heilbron, Jones, and Weedon, *J.*, 1949, 3120.
[16] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.
[17] Martin, *J.*, 1943, 239; cf. Smith and Agre, *J. Amer. Chem. Soc.*, 1938, **60**, 648.
[18] Smith and Agre, *J. Amer. Chem. Soc.*, 1938, **60**, 652.

aqueous ethanol in needles, m. p. 147·5—148·5° (corr.) (Found: C, 59·6; H, 4·9. $C_{17}H_{16}N_2O_6$ requires C, 59·3; H, 4·7%).

Similar reduction of the isomeric aldehyde (8·15 g.) gave 2,3,4-trimethylbenzyl alcohol which crystallised from light petroleum (b. p. 40—60°) in needles (5·0 g., 60%), m. p. 48·5—49·5° (Found: C, 79·9; H, 9·2), $\nu_{max.}$ (in CCl_4) 3614, 3468 (OH), 1010, and 815 cm.$^{-1}$ (2 adjacent ring H) (Reichstein *et al.*[19] give m. p. 49—50°). Alkaline permanganate oxidation [19] of the alcohol gave (60%) 2,3,4-trimethylbenzoic acid which crystallised from light petroleum (b. p. 100—120°) as prisms, m. p. 165—166°, $\nu_{max.}$ (in CCl_4) 1687 cm.$^{-1}$ (CO_2H) (Reichstein *et al.*[19] give m. p. 166—168°; Jacobson [20] gives m. p. 167·5°).

Triphenyl-2,3,6- and -2,3,4-trimethylbenzylphosphonium Bromide (IIIa and b).—A solution of phosphorus tribromide (0·31 ml.) in light petroleum (b. p. 40—60°) (2 ml.) was added during 30 min. to a cold (−30°) suspension of 2,3,6-trimethylbenzyl alcohol (1·22 g.) in light petroleum (b. p. 40—60°) (25 ml.), carbon tetrachloride (40 ml.), and pyridine (0·08 ml.). The mixture was stirred at −25° for 30 min. and then allowed to warm to 20° during 1 hr. The mixture was poured into cold (0°) water, and the product was isolated in the usual way with light petroleum. The resulting crude, lachrymatory oil (1·73 g.) in benzene (2 ml.) was added to a solution of triphenylphosphine (2·13 g.) in benzene (8 ml.). The mixture was warmed and kept at 20°. The solid (3·72 g., 97%) which separated was collected and had m. p. 242·5°—245° (corr.) Repeated crystallisation from propan-2-ol–light petroleum (b. p. 60—80°) for analysis gave *triphenyl-2,3,6-trimethylbenzylphosphonium bromide*, m. p. 243—245° (corr.) (Found: C, 70·3; H, 5·9; P, 6·25. $C_{28}H_{28}BrP$ requires C, 70·7; H, 5·9; Br, 16·8; P, 6·5%).

2,3,4-Trimethylbenzyl alcohol (1·22 g.) was similarly converted in almost quantitative yield into the corresponding *phosphonium bromide*, 222—223° (corr.) (Found: C, 70·3; H, 5·95; Br, 17·1; P, 6·6%).

Isorenieratene (Va).—Ethereal butyl-lithium (0·60N; 5·5 ml.) was added during 1 min. to a stirred suspension of finely powdered triphenyl-2,3,6-trimethylbenzylphosphonium bromide (1·43 g.) in ether (25 ml.). The mixture was stirred for 90 min., then methylene chloride (0·5 ml.) was added to destroy the excess of butyl-lithium. After 5 min., a solution of crocetindial [9] (294 mg.) in methylene chloride (12 ml.) was added in 5 min. and the mixture was stirred under reflux in the dark for 4 hr. [Analysis of a test sample on a chromatoplate of calcium hydroxide–kieselgel (4 : 1) impregnated with paraffin, and with aqueous acetone (1 : 3) as eluent, indicated that reaction was complete; under these conditions the required product and crocetindial have R_F 0·0 and 0·85, respectively.] The mixture was cooled (0°), diluted with methanol (30 ml.) and methylene chloride (10 ml.), and kept at 0° overnight. The product (470 mg.) which had separated was collected, washed thoroughly with methanol, and dried; it had m. p. 205—206° (corr.) and $\lambda_{max.}$ (in benzene) 494 and 465·5 mμ. Crystallisation from chloroform–ethanol gave isorenieratene as purple needles, m. p. 207—208° (corr.) (undepressed on admixture with a natural sample which had the same m. p.) [Yamaguchi [1] gives m. p. 199° (uncorr.; evac. cap.)] (Found: C, 90·8; H, 9·1. Calc. for $C_{40}H_{48}$: C, 90·85; H, 9·15%), $\nu_{max.}$ (in Nujol) 964 (*trans*-CH=CH), 815, and 810 cm.$^{-1}$ (2 adjacent ring H). Natural and synthetic isorenieratene had identical infrared spectra, and on chromatography on a thin layer of calcium hydroxide–kieselgel (4 : 1), with benzene–light petroleum (b. p. 60—80°) (1 : 4) as eluent, both had R_F 0·71.

Renierapurpurin (Vb).—By the general procedure of the previous experiment, triphenyl-2,3,4-trimethylbenzylphosphonium bromide (800 mg.) was treated with ethereal propyl-lithium (1·0N; 2·5 ml.), and the resulting phosphoran was caused to react with crocetindial (206 mg.). More ethereal phosphoran (from 160 mg. of the phosphonium bromide) was added, and the mixture was boiled under reflux for 5 hr. and then kept at 20° overnight. The mixture was diluted with methanol (30 ml.) and stored at −20°. The solid (335 mg.), m. p. 232—234° (corr.), which separated crystallised from chloroform–ethanol, giving renierapurpurin as purple plates, m. p. 237—238° (corr.) (Found: C, 90·8; H, 9·1. Calc. for $C_{40}H_{48}$: C, 90·85; H, 9·15%) [Yamaguchi [1] gives m. p. 230° (uncorr.)], $\nu_{max.}$ (in Nujol) 1007, 973, 966 (*trans*-CH=CH), 883, 836, and 813 cm.$^{-1}$. Thin-layer chromatography of the product with an authentic sample of renierapurpurin on Merck aluminium oxide G (acc. to Stahl) and 0·5% of acetone in light petroleum (b. p. 60—80°) as eluent revealed no separation (R_F *ca.* 0·5). Under similar conditions isorenieratene and renieratene had R_F 0·78 and 0·69, respectively.

[19] Reichstein, Cohen, Ruth, and Meldahl, *Helv. Chim. Acta*, 1936, **19**, 412.
[20] Jacobson, *Ber.*, 1886, **19**, 1214.

Renieratene (Vc).—A mixture of triphenyl-2,3,4- and -2,3,6-trimethylbenzylphosphonium bromide (400 mg. of each) was treated with ethereal propyl-lithium (2·0N; 1·8 ml.), and the resulting phosphorans were treated (15 hr.) with crocetindial (200 mg.), according to the general procedure described for isorenieratene. The mixture was diluted with methanol (30 ml.) and chloroform (10 ml.) and kept at −20°. The red solid (284 mg.) was collected. Chromatography on alumina (grade IV) from light petroleum (b. p. 60—80°)–benzene (1 : 1), and then on alumina (grade I) from benzene, gave three main bands. Elution of the middle band, and evaporation, gave a solid (145 mg.), m. p. 184—185° (corr.). Crystallisation from benzene–ethanol gave renieratene as purple needles, m. p. 191—192° (corr.) (Found: C, 90·8; H, 9·1. Calc. for $C_{40}H_{48}$: C, 90·85; H, 9·15%) [Yamaguchi [1] gives m. p. 184—185° (uncorr.)], $\nu_{max.}$ (in Nujol) 962 and 802 cm.$^{-1}$. A mixed chromatogram with authentic renieratene on a thin layer of alumina, as described above for renierapurpurin, revealed no separation. From the first and the last of the three main bands to be eluted, isorenieratene (70 mg.) and renierapurpurin (70 mg.) were isolated, respectively.

1,18-*Diphenyl*-3,7,12,16-*tetramethyloctadeca*-1,3,5,7,9,11,13,15,17-*nonaene* (Vd).—Benzyltriphenylphosphonium bromide [21] (886 mg.) was treated with ethereal phenyl-lithium (1·0N; 1·96 ml.), and the resulting phosphoran was treated (24 hr.) with crocetindial (186 mg.). The mixture was diluted with methanol (50 ml.) and kept at 0°. The red solid (213 mg.), m. p. 225—228° (Kofler block), which separated was collected. (A further 20 mg. of product, m. p. 228—232°, was obtained by keeping the mother-liquors in bright daylight in the presence of a trace of iodine, evaporation, and crystallisation of the residue from benzene–methanol.) Crystallisation of the crude product (82%) from benzene and from chloroform–ethanol gave the diphenylnonaene as copper-red plates, m. p. 230—231°, 234—235° (Kofler block) (Found: C, 91·3; H, 7·75. Calc. for $C_{34}H_{36}$: C, 91·85; H, 8·15%), $\nu_{max.}$ (in KBr) 964 (*trans*-CH=CH), 747, and 690 cm.$^{-1}$ (Garbers *et al.*[6] give m. p. 209—210°).

β-*Isorenieratene* (VIIa).—Ethereal propyl-lithium (0·75N; 3·0 ml.) was added during 1 min. to a stirred suspension of finely powdered triphenyl-2,3,6-trimethylbenzylphosphonium bromide (300 mg.) in ether (20 ml.). The mixture was stirred for 30 min., and then methylene chloride (1 ml) was added to destroy the excess of propyl-lithium. After 5 min., a solution of β-apo-2-carotenal [13] (300 mg.) in methylene chloride (3 ml.) was added slowly and the mixture was stirred under reflux for 1 hr. The solvent was removed *in vacuo* and the residue was chromatographed on alumina (grade I). Elution of the main band with benzene and crystallisation of the product from benzene–ethanol gave β-*isorenieratene* (350 mg.) as red crystals, m. p. 128° (corr.) (Found: C, 90·2; H, 9·85. $C_{40}H_{52}$ requires C, 90·15; H, 9·85%), $\nu_{max.}$ (in Nujol) 961, 805, and 793 cm.$^{-1}$

β-*Renierapurpurin* (VIIb). By following the general procedure of the previous experiment, triphenyl-2,3,4-trimethylbenzylphosphonium bromide (230 mg.) was treated with ethereal propyl-lithium (0·75N; 2·5 ml.), and the resulting phosphoran was treated with β-apo-2-carotenal (200 mg.). The mixture was stirred under reflux for 1 hr., the solvent was removed *in vacuo*, and the residue was chromatographed on alumina (grade I). Elution of the main band with benzene and crystallisation of the product from benzene–ethanol gave β-*renierapurpurin* (265 mg.) as red crystals, m. p. 164° (corr.) (Found: C, 90·4; H, 9·65. $C_{40}H_{52}$ requires C, 90·15; H, 9·85%), $\nu_{max.}$ (in Nujol) 962 and 802 cm.$^{-1}$.

18-*Phenyl*-1-(2,2,6-*trimethylcyclohex*-6-*enyl*)-3,7,12,16-*tetramethyloctadeca*-1,3,5,7,9,11,13,15,17-*nonaene* (VIId).—Benzyltriphenylphosphonium bromide (330 mg.) was treated with ethereal propyl-lithium (0·75N; 2 ml.), and the resulting phosphoran was treated (1 hr.) with β-apo-2-carotenal (300 mg.). The solvent was removed *in vacuo* and the residue was chromatographed on alumina (grade I). Elution of the main band with benzene and crystallisation of the product from benzene–methanol gave the *polyene* (290 mg., 74%) as red crystals, m. p. 158° (corr.) (Found: C, 90·0; H, 9·45. $C_{37}H_{46}$ requires C, 90·55; H, 9·45%), $\nu_{max.}$ (in CCl_4) 964 cm.$^{-1}$.

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[21] Wittig and Haag, *Chem. Ber.*, 1955, **88**, 1654.