

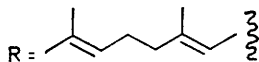
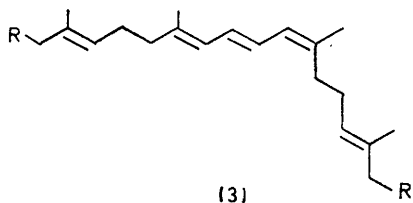
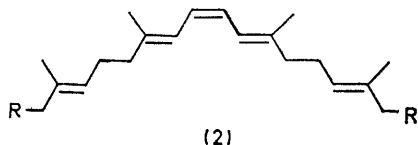
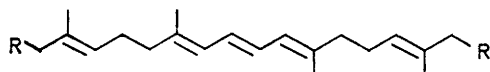
Synthesis of Poly-*Z*-isomers of 2,6,11,15-Tetramethylhexadeca-2,6,8,10,-14-pentaene, a C₂₀ Analogue of Phytoene. Re-examination of the Stereochemistry of a New Isomer of Phytoene from *Rhodospirillum rubrum*

By Linda Barlow and Gerald Pattenden,* Department of Chemistry, The University, Nottingham NG7 2RD

(*Z*)-3,7-Dimethylocta-2,6-dienyltriphenylphosphonium bromide (4) has been prepared, and its condensations with formaldehyde and citral have been shown to proceed with retention of configuration about the α -double bond in the salt. Reaction between compound (4) and (*Z*)-citral gives a mixture of (6*Z*,8*Z*,10*Z*)- (15) and (6*Z*,8*E*,10*Z*)- (14) pentaenes showing retention or configuration about both *Z*-bonds in the starting materials. In a similar manner, compound (4) and (*E*)-citral or the (*E*)-phosphonium salt (5) and (*Z*)-citral give the pentaenes (11) and (12), whereas compound (5) and (*E*)-citral lead to a mixture of (6*E*,8*E*,10*E*)- (9) and (6*E*,8*Z*,10*E*)- (10) pentaenes. Mixtures of (9) and (10) and of (14) and (15) were also obtained, from (*E*)- and (*Z*)-citral respectively, by reductive coupling with titanium trichloride-lithium aluminium hydride. The isomeric pentaenes (9)–(12), (14), and (15) have been separated and characterised.

¹³C N.m.r. data for the isomers of the pentaene (9), the C₂₀ analogue of phytoene, are presented and discussed. The stereochemistry of a new isomer of phytoene from *Rhodospirillum rubrum* is re-examined by using comparative ¹³C n.m.r. data.

PHYTOENE (1) is generally regarded as the first conjugated polyene in the biosynthetic route to carotenoids. A number of naturally occurring geometrical isomers about the central triene system of structure (1) have been reported.^{1a} The main phytoene isomer isolated from carrot oil, commercial tomatoes, *Phycomyces blakesleeanus*, and *Chlorella vulgaris* has been shown to have the *E,Z,E*-configuration (2) about the triene system, whereas phytoene from diphenylamine-inhibited cultures



of *Flavobacterium dehydrogenans* consists principally of the *E,E,E*-isomer [*viz.*(1)].^{2,3} More recently, a third isomer of phytoene, assigned the *E,E,Z*-configuration

¹ See B. C. L. Weedon in 'Carotenoids,' ed. O. Isler, Birkhauser, Basel, 1971, (a) pp. 31 and 268; (b) pp. 269–280.

² J. B. Davis, L. M. Jackman, P. T. Siddons, and B. C. L. Weedon, *J. Chem. Soc. (C)*, 1966, 2154.

³ N. Khatoon, D. E. Loeber, T. P. Toube, and B. C. L. Weedon, *J.C.S. Chem. Comm.*, 1972, 996; *J.C.S. Perkin I*, 1975, 1457.

(3), has been isolated along with compounds (1) and (2) from *Rhodospirillum rubrum* inhibited by 2-hydroxybiphenyl and from *Mucor hiemalis* inhibited by fluoren-9-one.^{4,5}

Z-Isomers of phytoene are probably implicated in the biosynthesis of the intriguing ('poly-*Z*')-lycopenes and other (poly-*Z*)-carotenoids found in nature.^{1b} As part of a programme directed towards the unambiguous synthesis and stereochemical assignment of (poly-*Z*)-carotenoids, we report the synthesis and characterisation of the six geometrical isomers of the C₂₀ analogue (9) of phytoene.

Our previous studies demonstrated the versatility of (*Z*)- α -unsaturated aldehydes in the Wittig synthesis of (*Z*)-polyisoprenoids.⁶ The scope of the Wittig approach to (*Z*)-polyisoprenoids would be enhanced enormously by using (*Z*)- α -unsaturated phosphonium ylides in conjunction with (*Z*)- α -unsaturated aldehydes. Earlier efforts to synthesise (*Z*)- α -unsaturated phosphonium salts from (*Z*)-allylic alcohols were unsuccessful.^{6a} We have now found that the *Z*-salt (4) is easily synthesised from nerol, following bromination with phosphorus tribromide in pyridine at 0 °C in the dark, and reaction of the resulting (*Z*)-bromide with triphenylphosphine. This procedure produces isomerically pure (*Z*)-salt (4) which is readily distinguished by spectral data from the corresponding (*E*)-salt (5), prepared in a similar manner from geraniol. Significantly, in the ¹H n.m.r. spectra of the isomers, those protons orientated *cis* to the bulky triphenylphosphorus group are considerably shielded relative to those orientated *trans* (see τ values on formulae).

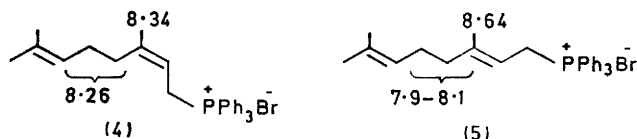
Condensation between the (*Z*)-salt (4) and formaldehyde in benzene, with butyl-lithium as base, proceeded with complete retention of the *Z*-geometry in (4)

⁴ (a) R. Herber, B. Maudinas, and J. Villoutreix, *Compt. rend.*, 1972, 274, 327; (b) B. Maudinas, R. Herber, J. Villoutreix, and P. Granger, *Biochimie*, 1972, 54, 1085.

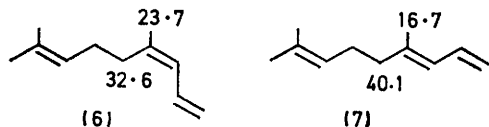
⁵ P. Granger, B. Maudinas, R. Herber, and J. Villoutreix, *J. Magnetic Resonance*, 1973, 10, 43.

⁶ (a) G. Pattenden and B. C. L. Weedon, *J. Chem. Soc. (C)*, 1968, 1984; (b) G. Pattenden, J. E. Way, and B. C. L. Weedon, *ibid.*, 1970, 235.

and led to the (*Z*)-triene (6). In a similar manner, the (*E*)-salt (5) gave the (*E*)-triene (7). The isomeric



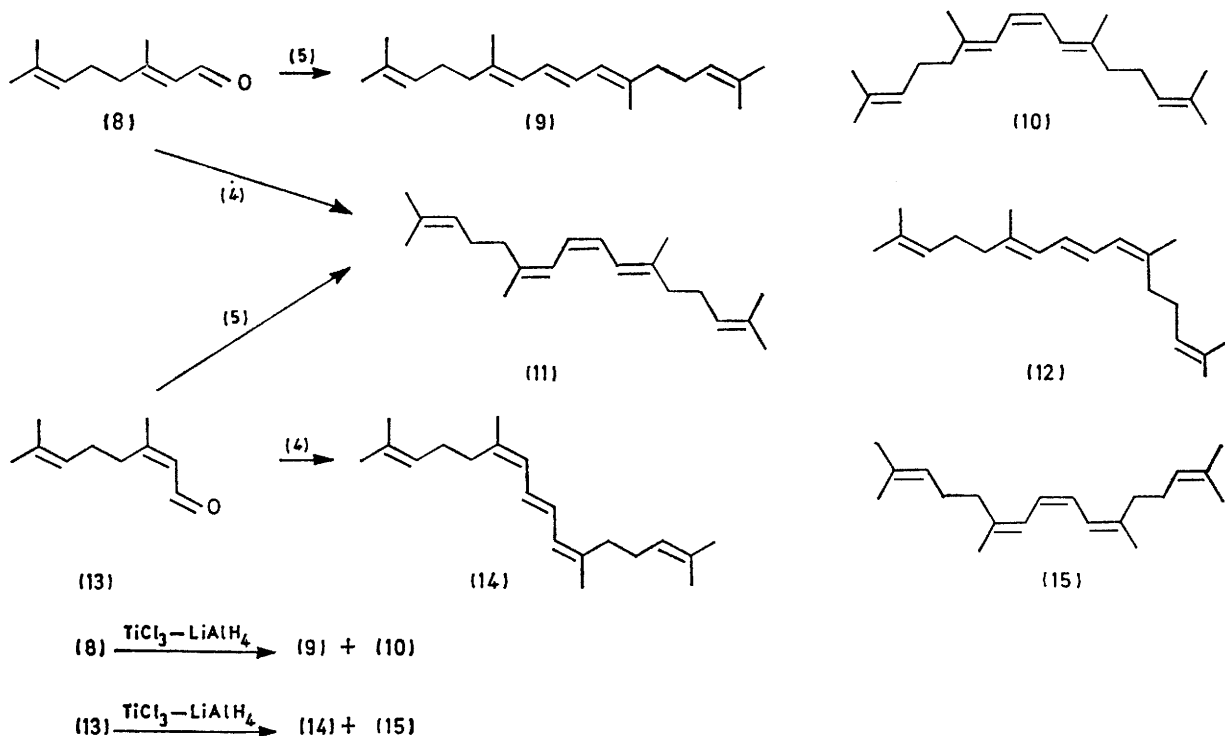
trienes were cleanly resolved in g.l.c. analysis, and each showed i.r. and ^1H n.m.r. data consonant with those reported previously.^{6a} Although the ^1H n.m.r. spectra of compounds (6) and (7) resemble each other very closely, in the corresponding ^{13}C n.m.r. spectra carbon



atoms [C-5 and 4- CH_3] oriented *cis* to the 1,2-double bond are significantly shielded in comparison with those oriented *trans* (see δ values on formula). The difference

and 40.1). In a similar manner, interaction between the C-2 proton and the C-4 methyl group in (7) results in shielding of the latter relative to the corresponding carbon atom in (6) (δ 16.7 and 23.7); for discussion of this ' γ -effect ' see ref. 7.

With the demonstration of the use of (*Z*)-salt (4) in (*Z*)-isoprenoid synthesis, we next turned to the application of the two salts (4) and (5), and of (*E*)- (8) and (*Z*)-citra (13) as precursors of geometrical isomers of the pentaene (9). Reaction between the (*E*)-salt (5) and (*E*)-citra (8) in the presence of butyl-lithium led to a 65 : 35 mixture of (*E,E,E*)- (9) and (*E,Z,E*)- (10) pentaenes, which were separated by chromatography on silver nitrate-impregnated silica gel. In a similar manner, the (*E*)-salt (5) with (*Z*)-citra (13) or the (*Z*)-salt (4) with (*E*)-citra (8) produced a mixture (*ca.* 3 : 2) of the (*Z,Z,E*)- (11) and (*Z,E,E*)- (12) pentaenes, and condensation between the (*Z*)-salt (4) and (*Z*)-citra (13) gave a mixture (*ca.* 7 : 3) of (*Z,E,Z*)- and (*Z,Z,Z*)-isomers (14) and (15), respectively. In either case preparative layer chromatography on silver nitrate-silica gel gave homogeneous samples of each isomer. We also examined the



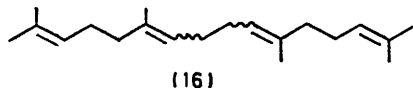
in shifts can be rationalised on the basis of non-bonded interactions between the proton at C-2 and those at C-5 or on the 4-methyl group in the two isomers. Steric interaction between the protons attached to C-2 and C-5 in the (*Z*)-triene (6) places electron density on C-5, with the result that C-5 in structure (6) is shielded relative to the corresponding carbon atom in structure (7) (δ 32.6

synthesis of isomers of (9) by reductive coupling of citra with titanium trichloride-lithium aluminium hydride (TT-LAH).⁸ Reaction of (*E*)-citra with TT-LAH led to a 3 : 2 mixture of (*E,E,E*)- (9) and (*E,Z,E*)- (10) pentaenes in only *ca.* 8% yield; the pentaenes were accompanied by tetraene side-products [*viz.* (16)] resulting from coupling of geraniol produced concurrently. In a similar manner (*Z*)-citra with TT-LAH

⁷ (a) J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 406; (b) F. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315; (c) D. E. Dormon, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, 1971, **36**, 2757.

⁸ J. E. McMurry and M. P. Fleming, *J. Amer. Chem. Soc.* 1974, **96**, 4708.

gave a mixture (*ca.* 4 : 1) of (*Z,E,Z*)- (14) and (*Z,Z,Z*)- (15) pentaenes (*ca.* 8%). In either case the couplings leading to the pentaenes proceeded with preservation of *Z*- or *E*-geometry in the starting citral.



The isomeric pentaenes (9)—(12), (14), and (15) all had u.v. maxima at 274—275, 285—288, and 296—298 nm

Similarly, the vinyl methylene protons in the isomers containing *Z*-trisubstituted double bonds resonate at slightly lower field than the corresponding protons in the isomers containing *E*-trisubstituted double bonds.

The ^{13}C n.m.r. data of the pentaenes (Table 2) provide the most satisfactory and unambiguous spectroscopic method of distinguishing the isomers. The assignments followed from application of off-resonance techniques and from inspection and comparison of ^{13}C data reported for other poly-isoprenoids.^{5,9} As anticipated, the spectra

TABLE 1

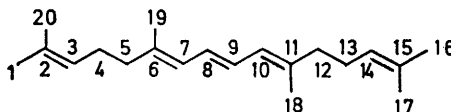
Chemical shifts (τ values) of the isomeric pentaenes (9)—(12), (14), and (15) in the region τ 7.7—8.3

	all- <i>E</i>	6 <i>E</i> ,8 <i>Z</i> ,10 <i>E</i>	6 <i>Z</i> ,8 <i>Z</i> ,10 <i>E</i>	6 <i>Z</i> ,8 <i>E</i> ,10 <i>E</i>	all- <i>Z</i>	6 <i>Z</i> ,8 <i>E</i> ,10 <i>Z</i>
6-Me	8.25	8.25	8.18	8.23	8.18	8.22
11-Me	8.25	8.25	8.25	8.25	8.18	8.22
4-, 5-, 11-, and 12-H ₂	7.9, 7.94	7.86, 7.90	7.83, 7.89	7.84, 7.89	7.83, 7.88	7.84, 7.88

* Resonances are broad; figures show maxima values only.

TABLE 2

^{13}C N.m.r. data (δ_0 in p.p.m. from Me_4Si) of the isomeric pentaenes (9)—(12), (14), and (15)



Carbon atom	all- <i>E</i> (9)	6 <i>E</i> ,8 <i>Z</i> ,10 <i>E</i> (10)	6 <i>Z</i> ,8 <i>E</i> ,10 <i>Z</i> (14)	all- <i>Z</i> (15)	6 <i>Z</i> ,8 <i>E</i> ,10 <i>E</i> (12)	6 <i>Z</i> ,8 <i>Z</i> ,10 <i>E</i> (11)
1	25.67	25.85	25.73	25.73	25.67	25.79
2	131.52	132.57	131.80	131.87	131.75	132.28
3	124.03	123.15	124.10	123.97	124.03	123.39
4	26.67	26.84	26.96	26.90	26.90	27.02
5	40.12	40.58	32.19	32.34	32.63	32.34
6	137.95	139.65	138.30	139.53	137.89	139.53
7	125.44	120.00	126.25	120.87	126.20	120.82
8	127.18	123.27	126.84	122.80	127.01	122.86
9	127.18	123.27	126.84	122.80	127.01	122.86
10	125.44	120.00	126.25	120.87	125.43	120.02
11	137.95	139.65	138.30	139.53	137.66	139.76
12	40.12	40.58	32.69	32.34	40.12	40.53
13	26.67	26.84	26.96	26.90	26.67	27.02
14	124.03	123.15	124.10	123.97	124.03	123.15
15	131.52	132.57	131.80	131.87	131.52	132.51
16	25.67	25.85	25.73	25.73	25.67	25.79
17	17.66	17.89	17.72	17.66	17.66	17.84
18	16.72	16.55	23.98	24.33	16.72	16.49
19	16.72	16.55	23.98	24.33	23.98	24.33
20	17.66	17.89	17.72	17.66	17.66	17.84

but with different relative intensities. In the i.r., isomers (9), (12), and (14) showed a characteristic maxima at *ca.* 960 cm^{-1} , whereas isomers (10), (11), and (15) showed maxima at *ca.* 769 cm^{-1} ; these absorptions are associated with the C-H out-of-plane deformations of the *E*- and *Z*-disubstituted double bonds respectively in the two groups of isomers.

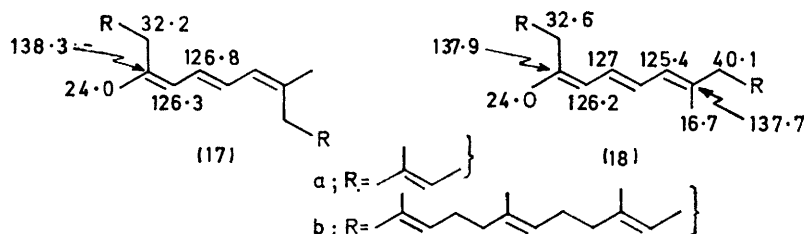
The ^1H n.m.r. spectra of the isomers (9)—(12), containing *E*-(6,7)-trisubstituted double bonds, show that the chemical shift of the methyl groups attached to these bonds (τ 8.25) is independent of the overall geometry of the triene system. By contrast in isomers (11), (12), (14), and (15) containing a *Z*-trisubstituted double bond, the methyl groups are significantly deshielded, depending on the *Z*- ($\Delta\tau$ 0.07) or *E*- ($\Delta\tau$ 0.03) configurations of the adjacent disubstituted double bonds (see Table 1).

recorded for the symmetrical isomers (9), (10), (14), and (15) show just ten resonance lines, whereas the non-symmetrical isomers (11) and (12) show all twenty carbon absorptions. The ^{13}C shifts of C-1 (C-16), C-2 (C-15), C-3 (C-14), and C-17 (C-20) remain almost constant for all six isomers (see Table 2). Significantly, the ^{13}C resonances of the methyl (C-18 and -19) and methylene (C-5 and -12) carbon atoms associated with the trisubstituted double bonds (6,7- and 10,11-) of the triene systems in the isomers vary dramatically with the

⁹ (a) M. Jautelat, J. B. Grutzner, and J. D. Roberts, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **65**, 288; (b) M. W. Duch and D. M. Grant, *Macromolecules*, 1970, **3**, 165; (c) R. S. Becker, S. Berger, D. K. Dalling, D. M. Grant, and R. J. Pugmire, *J. Amer. Chem. Soc.*, 1974, **96**, 7008; (d) R. Rowan, *tert.*, and B. D. Sykes, *J. Amer. Chem. Soc.*, 1974, **96**, 7000; (e) W. Bremser and J. Paust, *Org. Magnetic Resonance*, 1974, **6**, 433.

geometries of these bonds. The C-18 (C-19) resonance on a *E*-trisubstituted bond occurs between δ 16.55 and 16.72 depending on the configurations of the neighbouring 8,9- and 6,7-(10,11-) double bonds [cf. δ for C-18 (C-19) in isomers (9)–(12)]. The same methyl carbon atoms on *Z*-trisubstituted double bonds, by contrast, are deshielded ($\Delta\delta$ ca. 7), appearing between δ 23.98 and 24.33. In a similar manner, the methylene carbon atoms (C-5 and -12) associated with a *Z*-trisubstituted double bond are shielded ($\Delta\delta$ ca. 8) relative to those associated with an *E*-double bond (δ 32.3 and 40.3). An explanation for the differential shifts of C-18 (C-19) and C-5 (C-12) in the six isomers can be found based on non-bonded interactions between the protons associated with C-5 and C-8 in the isomers containing *Z*-(6,7- or 10,11-) double bonds [cf. the ' γ -effect',⁷ and data presented for (6) and (7)].

A number of the relative shifts of the olefinic carbon atoms (C-6–11) are also reasonable on the basis of increased steric crowding in the *Z*-compounds. For



example the large upfield shift of the C-7 (C-10) signal for isomers (10), (11), and (15) containing *Z*-(8,9-)disubstituted double bonds is most likely due to interactions between the protons at C-7 and C-10, which are not found in the *E*-(8,9-)isomers (δ ca. 120 and ca. 126).

The foregoing ¹³C data of the pentaenes cast some doubt on the assignments made by Granger *et al.*⁵ for certain olefinic carbons in (*E,Z,E*)- (2) and (*E,E,E*)- (1) phytoenes isolated from *Rhodospirillum rubrum* and *Mucor hiemalis*. These two isomers were not available in quantity, and it was not possible to perform single frequency decoupling experiments. It is clear from our own work, however, that the assignments for C-13 and C-15 [\equiv C6 and C8 in (9) and (10)] should be reversed. It is also likely that some of the assignments given for the new isomer of phytoene from *R. rubrum* are in error. Indeed, comparison of our ¹³C data for compounds (14) and (12) with those given for the new phytoene isomer suggest that it has either a *Z,E,Z*- or a *Z,E,E*-configuration about the triene chromophore. The ¹³C resonances at δ 24.14 [¹³-CH₃; \equiv C-19 in (14)] and 32.63 [C-12; \equiv C-5 in (14)] recorded for the new isomer clearly establish the presence of a *Z*-trisubstituted double bond in the triene system. Furthermore, the resonance at δ 127.47 [C-15; \equiv C-8 in (14)] (note that this resonance was wrongly assigned by Granger *et al.*) points to an *E*-disubstituted double bond, and hence to a *Z,E,Z*- or *Z,E,E*-configuration for the new isomer.

The symmetrical *Z,E,Z*-isomer (14) shows only one

resonance due to C-18 (C-19) at δ 24.0 whereas the *Z,E,E*-isomer (12) shows resonances for both C-18 and C-19 at δ 16.70 and 24.0 [see δ values on formulae (17a) and (18a)]. According to Granger *et al.*, the new phytoene isomer shows only one corresponding methyl resonance (δ 24.14), suggesting therefore that it possesses the *Z,E,Z*-configuration (18b) rather than the *Z,E,E*-configuration proposed by the authors. Some caution should be exercised however, since the ¹³C parameters published for the new isomer were deduced from a spectrum recorded for it in the presence of the *E,E,E*-isomer. Since the positions of certain ¹³C resonance lines are common to both *Z,E,E*- and *E,E,E*-isomers (cf. Table 2), conclusions based on these data could lead to an erroneous conclusion.

It is not clear whether the new (*Z,E,Z*- or *Z,E,E*-) isomer of phytoene from *R. rubrum* is a genuine natural product or an artefact formed from the *E,Z,E*- or *E,E,E*-isomer during isolation. If it is a genuine natural product, it is probable that its biosynthesis proceeds *via*

(*Z*)-2-geranylgeranyl pyrophosphate rather than *via* the preformed *E,E,E*- (or *E,Z,E*-) isomer by enzymic isomerisation of the 14,15-trisubstituted double bond(s).

EXPERIMENTAL

¹H N.m.r. spectra were determined with a Perkin-Elmer R10 spectrometer, with tetramethylsilane as internal standard. ¹³C N.m.r. data were recorded with a JEOL JNM-PS-100 spectrometer operating at 25.15 MHz interfaced with a Nicolet 1085 20K computer. Deuterium lock was provided by the sample (solvent CDCl₃). The pulse width was 3 μ s (22° tip) and the FIDs were compiled by using 8K data points over a spectral width of 600 Hz.

As far as possible all operations were carried out in an atmosphere of nitrogen, at room temperature or below, and in diffuse light or in the dark. All solvents for chromatography were redistilled. Solutions were dried over magnesium sulphate and evaporations were carried out under reduced pressure.

G.l.c. analysis was performed with a Pye 104 instrument (50 ft SCOT capillary columns at 160–180°C). Proportions of geometrical isomers in mixtures were calculated from g.l.c. data. For preparative layer chromatography, layers of silica gel impregnated with silver nitrate (30%) on 20 \times 20 cm plates were employed.

Geraniol and nerol (Fluka) were isomerically homogeneous in g.l.c. analysis (OV 225; 112°C).

(*Z*)-3,7-Dimethylocta-2,6-dienyltriphenylphosphonium Bromide (4).—Bromination of nerol with phosphorus tribromide in ether in the presence of pyridine at 0 \pm 1°C and with the rigorous exclusion of light gave (72%) the

corresponding bromide, identical with that described previously.¹⁰ A solution of the bromide (11 g) and triphenylphosphine (16 g) in dry benzene (150 ml) was stirred at 20 °C in the dark for 24 h, and the resulting solid (14.7 g) was filtered off and washed with dry ether. Crystallisation from ethanol gave the salt, m.p. 192–193°, mixed m.p. 166–168° with the corresponding (*E*)-salt, ν_{\max} (KBr) 898 and 857 cm^{-1} , τ 2.1–2.4 (15 H, m), 4.9br ($\text{C}\cdot\text{H}$), 5.5dd (J 7 and 14 Hz, $\text{CH}_2\cdot\text{P}^+$), *ca.* 8.28br (4 H), *ca.* 8.34 (d, J 6 Hz, $\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{P}^+$), *ca.* 8.39 (Me), and *ca.* 8.50 (Me) [the resonances between τ 8.28–8.50 were only fully resolved after addition of $\text{Eu}(\text{hfd})_3$ (shift reagent)], δ_{C} 17.72, 23.51, 24.97, 25.55, 31.87, 108.36, 108.77, 116.14, 119.53, 123.21, 130.06, 130.58, 131.87, 133.45, 133.80, 135.03, 146.19, and 146.72 (Found: C, 68.3, 68.5; H, 6.7, 6.5; Br, 16.7, 17.1. $\text{C}_{28}\text{H}_{32}\text{BrP}\cdot 0.7\text{H}_2\text{O}$ requires C, 68.4; H, 6.5; Br, 16.3%).

(*E*)-3,7-Dimethylocta-2,6-dienyltriphenylphosphonium Bromide (5).—The salt was prepared from geraniol as described for the (*Z*)-salt; m.p. 187–188° (lit.,¹¹ 188–189°), ν_{\max} (KBr) 878 and 818 cm^{-1} , τ 1.9–2.4 (15 H, m), 4.9br ($\text{C}\cdot\text{H}$), 5.5dd (J 7 and 14 Hz, $\text{CH}_2\cdot\text{P}^+$), 7.9–8.1 (4 H, m), 8.42 (Me), 8.48 (Me), and 8.64 (d, J 4 Hz, $\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{P}^+$), δ_{C} 17.08, 17.72, 23.33, 25.61, 39.59, 107.95, 108.30, 116.37, 119.76, 123.39, 130.11, 130.58, 131.93, 133.56, 133.91, 135.08, 146.60, and 147.13.

(*E*)- and (*Z*)-Citral [(8) and (13)].—(*E*)-Citral was obtained (75%) from geraniol by oxidation with Collins reagent. (*Z*)-Citral was obtained from nerol by oxidation with manganese dioxide in methylene chloride (^1H n.m.r. monitoring); the oxidation was interrupted when 50% nerol remained, and (*Z*)-citral was separated by chromatography in light petroleum on silica gel. Both isomers showed one peak on g.l.c. analysis (PEGA, 100 °C) and exhibited spectral data (i.r. and n.m.r.) identical with those reported.^{6a}

Condensations with (*Z*)- [and (*E*)-]3,7-Dimethylocta-2,6-dienyltriphenylphosphonium Bromide. General Procedure.—An equivalent of *n*-butyl-lithium in hexane was added, during 2 min, to a stirred suspension of the salt (4.8 g) in tetrahydrofuran (150 ml) under nitrogen. The mixture was stirred at 20 °C for 0.5 h, and then the aldehyde [freshly purified (*Z*)- or (*E*)-citral or formaldehyde gas from paraformaldehyde] was introduced. The resulting suspension was stirred at 20 °C for 1 h, then diluted with water and extracted with ether (3 \times 50 ml). The extracts were washed (H_2O), dried, and evaporated. The residual oil was triturated with light petroleum (b.p. 60–80°), and the supernatant liquid was decanted from the solid residue and then evaporated.

Isomerically pure samples of 2,6,11,15-tetramethylhexadeca-2,6,8,10,14-pentaene were obtained by preparative layer chromatography on 30% silver nitrate–silica gel with the eluants specified; purities were monitored by g.l.c. analysis on a SCOT OV-1 capillary column (150 °C).

(*Z*)-4,8-Dimethylnona-1,3,7-triene (6).—By the general procedure, the (*Z*)-salt and formaldehyde produced the triene (0.97 g, 65%), which was purified by chromatography in ether on silica gel (50 g); g.l.c. (SE-30; 80 °C) showed only one peak. The hydrocarbon showed spectral data (u.v., i.r., ^1H n.m.r.) identical with those published;^{6a} δ_{C} 17.6 (8-Me), 23.7 (4-Me), 25.6 (C-9), 27.0 (C-6), 32.6 (C-5), 114.3

(C-1), 124.15 (C-7), 126.7 (C-3), 131.6 (C-8), 133.21 (C-2), and 139.3 (C-4).

(*E*)-4,8-Dimethylnona-1,3,7-triene (7).—By the general procedure, the (*E*)-salt (5) and formaldehyde produced the triene (0.92 g, 61%), which was purified by chromatography as above; g.l.c. showed only one peak, with a retention time longer than that of the (*Z*)-triene. The hydrocarbon showed spectral data (u.v., i.r., ^1H n.m.r.) identical with those published;^{6a} δ 16.7 (4-Me), 17.7 (8-Me), 25.6 (C-9), 26.8 (C-6), 40.1 (C-5), 114.4 (C-1), 124.3 (C-7), 125.8 (C-3), 131.5 (C-8), 133.5 (C-2), and 139.1 (C-4).

(6*E*,8*Z*,10*E*)- and (all-*E*)-2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene [(10) and (9)].—By the general procedure, the (*E*)-salt (5) and (*E*)-citral produced a 65 : 35 mixture (by g.l.c. analysis) of (*E*,*Z*,*E*)- and (all-*E*)-pentaenes (2.1 g, 75%). Chromatography in benzene–ethyl acetate–methanol (20 : 1 : 1) gave: (i) the (all-*E*)-pentaene (eluted first on $\text{AgNO}_3\text{-SiO}_2$; >95% isomerically pure in g.l.c. analysis), λ_{\max} (hexane) 269nm, 274, 285, and 298 nm, ν_{\max} 961 cm^{-1} , τ 3.5–4.3 (4 H, m), 4.9br (2 H), 7.7–8.0 (8 H, m), 8.25 (2 \times Me), 8.33 (2 \times Me), and 8.41 (2 \times Me), M^+ 272; and (ii) the (*E*,*Z*,*E*)-pentaene [eluted second on $\text{AgNO}_3\text{-SiO}_2$; g.l.c. showed one major peak (>94%), with a retention time shorter than that of the (all-*E*)-pentaene], λ_{\max} (hexane) 262nm, 275, 285, and 296nm, ν_{\max} 768 cm^{-1} , τ 3.65–3.9 (4 H, m), 4.9br (2 H), 7.7–8.0 (8 H, m), 8.25 (2 \times Me), 8.33 (2 \times Me), and 8.41 (2 \times Me), M^+ 272.

Reaction of (*E*)-citral with the species produced from titanium trichloride (0.8 g) and lithium aluminium hydride (0.2 g) ⁸ in tetrahydrofuran (100 ml) under reflux for 4 h, followed by chromatography (silica gel; chloroform) led to a mixture (0.2 g, *ca.* 28%) of isomeric pentaenes and tetraenes [*viz.* (16), *m/e* 274], present in the approximate proportions 1 : 3 (by g.l.c.). Comparison with authentic specimens (by g.l.c. and ^{13}C n.m.r.) showed that the only isomeric pentaenes formed were (9) and (10), in the proportion 3 : 2. Reaction of geranyl bromide with nickel carbonyl also led to a mixture of tetraenes (16).

(6*Z*,8*Z*,10*E*)- and (6*Z*,8*E*,10*E*)-Isomers of 2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene [(11) and (12)].—By the general procedure, the (*Z*)-salt (4) and (*E*)-citral produced a 57 : 43 mixture (by g.l.c. analysis) of (*Z*,*Z*,*E*)- and (*Z*,*E*,*E*)-pentaenes (1.9 g, 70%). Chromatography in benzene–ethyl acetate (10 : 1) gave: (i) the (*Z*,*E*,*E*)-pentaene (eluted first on $\text{AgNO}_3\text{-SiO}_2$; >95% isomerically pure in g.l.c. analysis), λ_{\max} (hexane) 269sh, 275, 288, and 298 nm, ν_{\max} 960 cm^{-1} , τ 3.6–4.4 (4 H, m), 4.9br (2 H), 7.8–8.0 (8 H, m), 8.23 (Me), 8.25 (Me), 8.33 (2 \times Me), and 8.41 (2 \times Me), M^+ 272; and (ii) the (*Z*,*Z*,*E*)-pentaene [eluted second on $\text{AgNO}_3\text{-SiO}_2$; g.l.c. showed one major peak (>80%) with a retention time shorter than that of the (*Z*,*E*,*E*)-pentaene], λ_{\max} (hexane) 262sh, 275, 285, and 298 nm, ν_{\max} 768 cm^{-1} , τ 3.6–4.4 (4 H, m), 4.95br (2 H), 7.8–8.0 (8 H, m), 8.18 (Me), 8.25 (Me), 8.33 (2 \times Me), and 8.41 (2 \times Me), M^+ 272.

A similar condensation between the (*E*)-salt (5) and (*Z*)-citral led to similar proportions (60 : 40) of isomeric (*Z*,*Z*,*E*)- and (*Z*,*E*,*E*)-pentaenes.

(6*Z*,8*E*,10*Z*)- and (all-*Z*)-Isomers of 2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene [(14) and (15)].—By the general procedure, the (*Z*)-salt (4) and (*Z*)-citral produced a 68 : 32 mixture (by g.l.c. analysis) of (*Z*,*E*,*Z*)- and (all-*Z*)-pentaenes (68%). Chromatography in benzene–ethyl

¹¹ O. Isler, H. Gutmann, H. Lindlar, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, 1956, **39**, 463.

¹⁰ R. V. M. Campbell, L. Crombie, D. A. R. Findley, R. W. King, G. Pattenden, and D. A. Whiting, *J.C.S. Perkin I*, 1975, 897.

acetate (16:1) gave: (i) the (*Z,E,Z*)-pentaene (eluted first on $\text{AgNO}_3\text{-SiO}_2$; >99% isomerically pure in g.l.c. analysis), λ_{max} 262sh, 275, 285, and 298 nm, ν_{max} 959 cm^{-1} , τ 3.6—4.4 (4 H, m), 4.95br (2 H), 7.8—7.9 (8 H, m), 8.22 (2 \times Me), 8.33 (2 \times Me), and 8.41 (2 \times Me), M^+ 272; and (ii) the (all-*Z*)-pentaene [eluted second on $\text{AgNO}_3\text{-SiO}_2$; g.l.c. showed one major peak (>85%) with a retention time shorter than that of the (*Z,E,Z*)-pentaene], λ_{max} 262sh, 275, 286, and 298 nm, ν_{max} 770 cm^{-1} , τ 3.6—4.4 (4 H, m), 4.9br (2 H), 7.8—7.9 (8 H, m), 8.18 (2 \times Me), 8.33 (2 \times Me), and 8.41 (2 \times Me), m/e 272.2485 (Calc. for $\text{C}_{20}\text{H}_{32}$: M 272.2504).

Reaction of (*Z*)-citral with titanium trichloride–lithium aluminium hydride, as described for *E*-citral, produced similar proportions of pentaene and tetraene products. G.l.c. analysis and ^{13}C n.m.r. data showed that the only isomeric pentaenes formed were (14) and (15), in the proportion 4:1.

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