Carotenoids and Related Compounds. Part 40.[1] Synthesis of Trikentriorhodin and Other β-Diketones

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Three routes to polyene β-diketones are described.

Condensation of 8'-apo-β-carotenal (**4**) and of 8,8'-diapo-carotene-8,8'-dial (**6**) with butylamine in the presence of tri-isobutyl borate gave the Schiff's bases (**5**) and (**7**) respectively. These reacted with the boric oxide complex of acetylacetone to give the polyene β-diketones (**8**) and (**9**).

Reaction of the di-lithium salt of 3-methylpent-1-en-4-yn-3-ol (**32**) with pivalic anhydride (**11**) yielded the acetylenic ketone (**34**), which on hydration furnished the β-diketone (**36**). This was converted into the Wittig salt (**39**) which condensed with the trienedial (**44**) to give the polyene β-diketones (**45**) and (**46**).

Polyene carboxylic esters were found to condense with methyl ketones, in the presence of lithamide, to give β-diketones in high yield. Thus methyl 8'-apo-χ-carotenoate (**59**), for which a synthesis from (**44**) is reported, condensed with the trimethylsilyl derivative of the optically active hydroxy-ketone (**64**) to give, after hydrolysis of the protecting group, trikentriorhodin (**1**). Comparison of the c.d. properties of the synthetic compound, with those reported for the natural pigment, indicate that the latter has the 3*S*, 5*R* configuration.

The formulation of mytiloxanthin,[2,3] trikentriorhodin (**1**)[4] and of two *Wallemia* pigments[5,6] as enols of polyene β-diketones aroused interest in the synthesis of such structures.‡ In this paper we describe three routes, and give details of the use of one of them for the total synthesis of trikentriorhodin.[7] The subsequent extension of this route to the synthesis of mytiloxanthin[3,7] and the *Wallemia* pigments[8,9] is reported elsewhere.

The Aldol Condensation Route.—Curcumin (**3**) and related compounds have been prepared by condensing substituted benzaldehydes with the boric oxide complex of acetylacetone (**2**) in the presence of butylamine and tri-isobutyl borate.[10,11] When this procedure was applied to the 8'-apo-β-carotenal[12] (**4**) the Schiff's base (**5**) was obtained. The same product was formed slowly when the apo-β-carotenal was treated with butylamine alone, but in the presence of tri-isobutyl borate the Schiff's base was formed rapidly. The polyene dial[13] (**6**) similarly gave (**7**). Subsequent reaction of these Schiff's bases with the boric acid complex of acetylacetone, and hydrolysis of the initial product, then furnished the required polyene β-diketones (**8**) and (**9**) in high yield.

The spectral properties of these synthetic compounds lent strong support to key assignments in the spectra of the natural pigments mentioned earlier. However, attempts to extend the synthetic route to β-diketones other than acetylacetone, such as octane-2,4-dione (**10**) and (**14**), were unsuccessful.

Wittig Condensation Route.—Conjugated acetylenic ketones readily undergo nucleophilic addition to give β-diketones, or their derivatives.[14,15] Thus, (**12**) and (**13**), prepared by reaction of pivalic anhydride (**11**) with the appropriate lithium acetylides, were readily converted on treatment with dilute acid into the corresponding β-diketones (**14**) and (**16**) which existed mainly as the enols. On treatment with sodium ethoxide, the acetylenic ketones gave the enol ethers such as (**15**) and (**18**) which on acid hydrolysis again yielded the β-diketones. The introduction of acetylenic ketone moieties into polyenes, or their precursors was, therefore, examined.

Reaction of the di-lithium salt of the readily available *cis*-methylpentenynol[16,17] (**19**) with acetic anhydride gave the required acetylenic ketone (**21**) together with smaller amounts of the furan (**23**). Reaction with propionic anhydride similarly gave the acetylenic ketone (**22**) together with the furan (**24**). However, reaction with pivalic anhydride (**11**) gave the furan (**25**) exclusively. The formation of these cyclic products is rationalised as the result of an intramolecular nucleophilic addition of the type indicated in (**26**), followed by prototropic rearrangement. It is also noteworthy that in the furans (**23**) and (**24**) the α-substituents exist in the enolic forms shown, whereas in (**25**) the α-substituent adopts the di-keto configuration. Presumably, steric interference between the t-butyl groups and the ring methyl in (**25**) inhibits co-planarity of the two carbonyl groups, which is a prerequisite for the formation of the hydrogen bonded enol.

Reaction of the tetrahydropyranyl ether (**20**) of (**19**) with pivalic anhydride gave the acetylenic ketone (**27**). Removal of the protecting group was again accompanied by intramolecular addition to give (**28**).

To avoid cyclisation, pivalic anhydride was treated with the *trans*-methylpentenynol[16,17] (**29**), with the unconjugated isomer[16] (**32**), and with the acetate (**33**) to give the acetylenic ketones (**30**), (**34**) and (**35**) respectively. These, on treatment with triphenylphosphonium bromide gave the Wittig salt (**31**).

Reaction of the acetylenic ketone (**34**) with sodium ethoxide yielded the enol ether (**38**) which was converted into the Wittig salt (**40**) by treatment with triphenylphosphonium bromide; the dihydrofuranone (**41**) was also formed. Treatment of the acetylenic ketone (**34**) with sulphuric acid furnished the β-diketone (**36**) which was similarly converted into the Wittig salt (**39**). The isomeric β-diketone (**43**) could not be obtained by direct hydration of (**30**), but was prepared by reaction of (**30**) with boron trifluoride and hydrolysis of the resulting boron complex (**42**).

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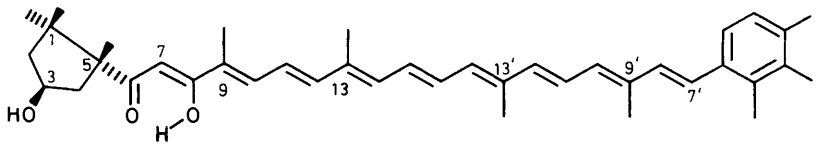
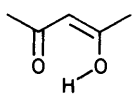
‡ See experimental section for naming of trikentriorhodin and the synthetic polyenes according to the recommendations of the IUPAC-IUB Commission on Biochemical Nomenclature (*Pure Appl. Chem.*, 1975, **41**, 407). The carbon atoms in carotenoids are numbered according to the same recommendations as illustrated in (**1**) and (**4**).



(1)



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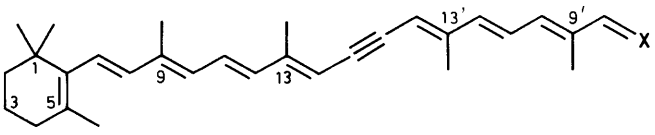
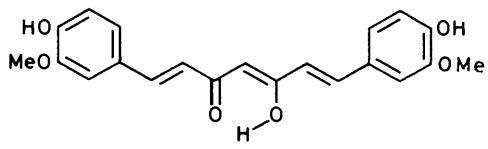


(4) X = O
(5) X = $NCH_2CH_2CH_2CH_3$



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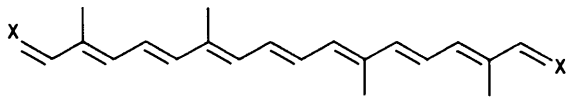
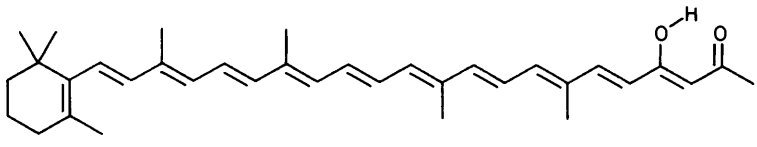


(6) X = O
(7) X = $NCH_2CH_2CH_2CH_3$



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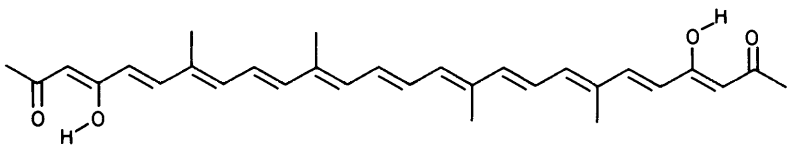

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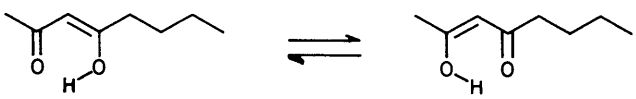


(10)

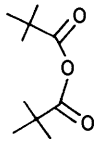
Attempts to carry out Wittig condensations with either (**31**) or (**40**) and polyene aldehydes were unsuccessful. These failures were attributed to deactivation of the intermediate phosphoranes by the strong electron withdrawing properties of the oxygen substituents. However, in keeping with this explanation, treatment of (**39**) with an excess of base gave the corresponding enolate phosphorane which reacted normally with the trienedial[16] (**44**) to give both the mono- and the di-condensation products (**45**) and (**46**) respectively.

Claisen Condensation Route.—The condensation of polyene aldehydes with methyl ketones to give α,β-unsaturated ketones has been used successfully in the synthesis of various carotenoids.[18–21] The condensation of polyene esters with methyl ketones in a similar reaction of the Claisen type[22] was therefore explored as a route to polyene β-diketones.

In model experiments with the apo-carotenoate (**47**)[22] and pinacolone (**48**) no reaction was detected in the presence of such bases as potassium hydroxide, sodium ethoxide, and piperidine. However, with sodium hydride the pinacolone enolate formed irreversibly reacted with (**47**) to give the required β-diketone (**49**) in yields up to 50%, together with other products. These side reactions were avoided by using lithamide as base, and the β-diketone (**49**) was then obtained in almost quantitative yield. The related apo-β-carotenoate (**50**)[22] was similarly condensed with pinacolone and with methyl isopropyl ketone, to give (**51**) and (**52**) respectively, and dimethyl crocetin[23] (**53**) reacted with pinacolone to give the bis-β-diketone (**46**) in high yield. This route was therefore chosen for the synthesis of the natural β-diketone pigments.

The Trikentriorhodin Series.—Partial condensation of the trienedial (**44**)[17] with the Wittig salt (**54**)[24] yielded the aldehydo ester (**55**). Reaction of the ionone analogue (**56**)[25] with vinylmagnesium bromide gave the vinyl alcohol (**57**) which on treatment with triphenylphosphonium bromide furnished the Wittig salt (**58**). The latter, on condensation with the aldehydo ester (**55**), gave the apo-χ-carotenoate (**59**).

Condensation of (**59**) with the methyl ketone (**60**),[26] in the presence of lithamide, gave '(5*R*)-desoxy-trikentriorhodin' (**66**).



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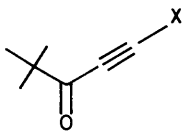
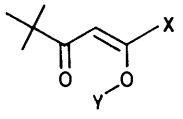
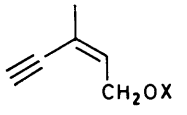


(12) X = Et
(13) X = $CH_2CH_2CH_2CH_3$

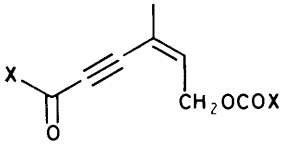


(14) X = Et, Y = H
(15) X = Et, Y = Et
(16) X = $CH_2CH_2CH_2CH_3$, Y = H
(17) X = $CH_2CH_2CH_2CH_3$, Y = Me
(18) X = $CH_2CH_2CH_2CH_3$, Y = Et

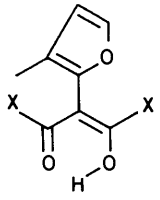


(19) X = H

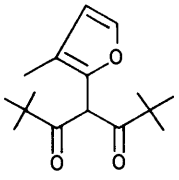
(20) X = 



(21) X = Me
(22) X = Et



(23) X = Me
(24) X = Et



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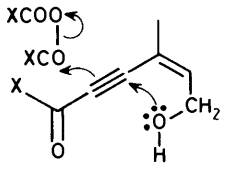

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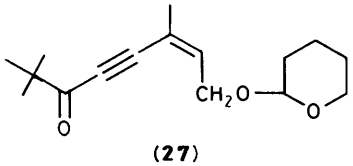

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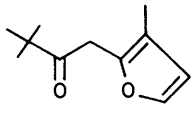

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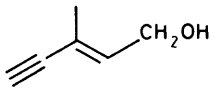

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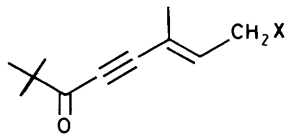
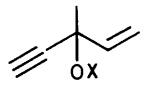
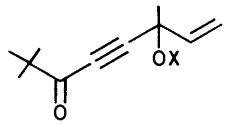


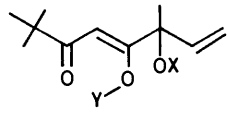
(30) X = OCO+
(31) X = $^+PPh_3Br^-$



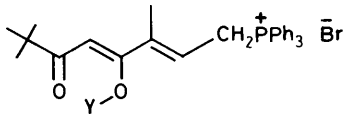
(32) X = H
(33) X = Ac



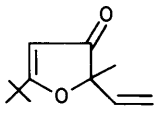
(34) X = CO+
(35) X = Ac



(36) X = CO+, Y = H
(37) X = CO+, Y = Me
(38) X = CO+, Y = Et



(39) Y = H
(40) Y = Et



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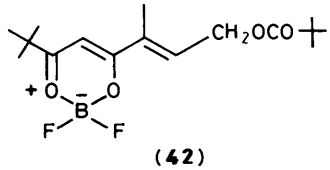

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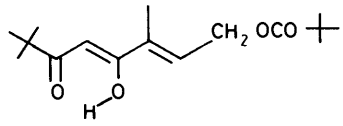


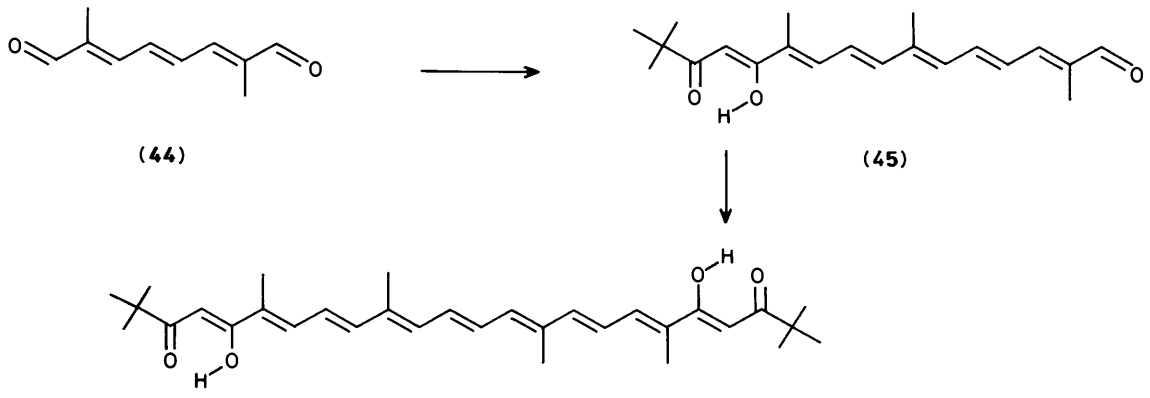
(43)

The dehydro-derivative, 'anhydro-trikentriorhodin' (**67**), was similarly obtained from the methyl-ketone (**61**).[21]

Condensation of the key intermediate (**59**) with (**62**),[21,27] after protecting the hydroxy group by trimethylsilylation, led to '(2*R*,5*R*)-iso-trikentriorhodin' (**68**), whilst a similar series of reactions based on (**64**),[20,21] gave (3*S*,5*R*)-trikentriorhodin (**70**≡**1**). The two synthetic isomers were readily distinguished by their n.m.r. spectra (see Table) and chromatographic behaviour. The physical properties of (**70**) were in good agreement with those reported for the natural pigment[4,28] from which it did not separate in mixed thin layer chromatography. These results confirm the structure proposed for trikentriorhodin,[4,28] in particular the location of a hydroxy group at C-3 and the relative stereochemistry of the substituents on the five-membered ring. Moreover, the c.d. properties reported for the natural pigment[28,29] were qualitatively similar to those of the synthetic material; the natural carotenoid must, therefore, have the same absolute configuration, namely, 3*S*,5*R*.

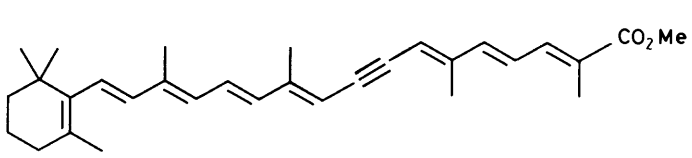
Characteristics of Polyene β-*Diketones.*—The examples reported in this, and the following paper are pseudo-acidic and tenaciously adsorbed on alumina; they are, however, amenable to chromatography on silica gel.

In ethanol, the polyene (mono-) β-diketones exhibit light absorption spectra devoid of fine structure, but with light absorption maxima close to the positions of the principal light absorption maxima of analogous polyene ketones without the β-enolic hydroxy group, such as semi-β-carotenone (5,6-seco-β,β-carotene-5,6-dione)[30] and related models.[31] The bis-β-diketone (**46**) exhibits maximal light absorption at a wavelength *ca.* 10 nm lower than β-carotenone (5,6,5′,6′-diseco-β,β-



(44) (45)

(46)



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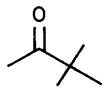

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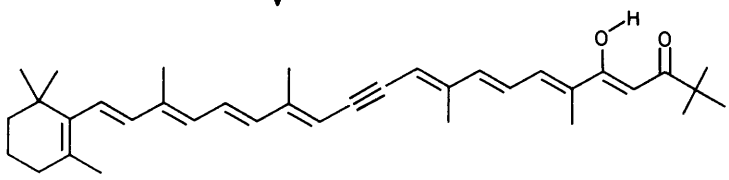

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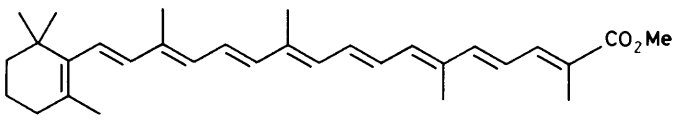

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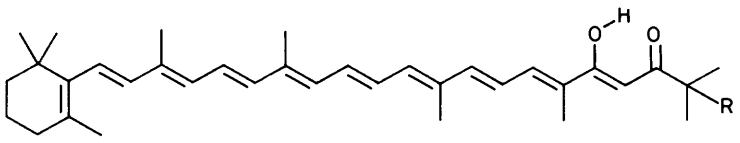
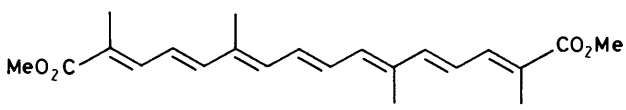


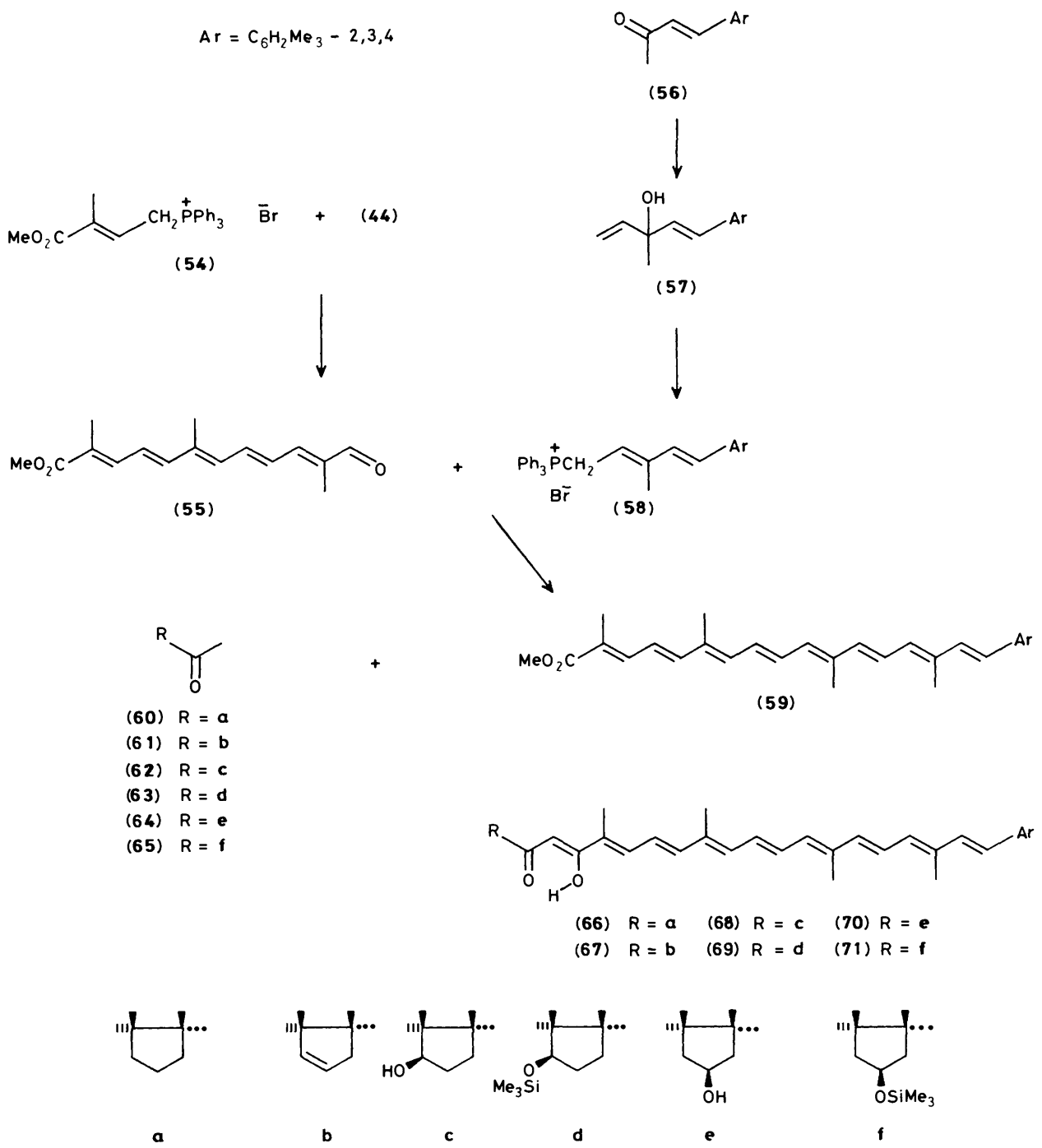
(51) R = Me
(52) R = H



(53)

carotene-5,6,5′,6′-tetraone)[30] and related models.[32] In ethanolic sodium hydroxide the polyene β-diketone is converted into the corresponding mono- or bis-enolate. The typical mono-enolate has a light absorption maximum at a wavelength some 14—18 nm below that of the parent compound. On the evidence of two examples, the difference in the case of bis-enolates is greater, 20—30 nm.

Treatment of an alcoholic solution of a polyene β-diketone with sodium borohydride results in reduction of both carbonyl groups to give a product with light absorption properties



corresponding to the basic polyene chromophore attached to the original β-diketone grouping.

The i.r. spectra (KBr disc) of the polyene β-diketones include bands due to the enolic hydroxy, and strong absorption in the range 1 580—1 660 cm^{-1} attributable to a hydrogen-bonded carbonyl group.

The n.m.r. spectra of the polyene β-diketones contain a band in the range δ 15—19 associated with the protons in enolic hydroxyls,[33] and a singlet in the range δ 5.54—5.94 attributable to the C_α-proton in the enol (see Table). The intensities of these and other n.m.r. bands indicate that the polyene β-diketones examined exist exclusively, or predominantly, in the enolic form. However, the spectra of (**46**) and (**52**), like that of acetylacetone,[34] also include weak bands indicating the presence in solution of *ca.* 10—20% of a (non-enolic) diketo tautomer.

Experimental

All operations were carried out in an inert atmosphere, and direct exposure to bright light was avoided. Solutions of carotenoids were evaporated at *ca.* 30—45 °C in a rotary evaporator. Light petroleum refers to the fraction b.p. 60—80 °C, unless indicated to the contrary. Melting points of carotenoids were determined for samples in evacuated capillary tubes and are uncorrected. Silica gel for thin layer chromatography (t.l.c.) was Merck Kieselgel Hf_{254}; eluants are given in parentheses.

Table. Principal ^1H n.m.r. bands of polyene β-diketones (in C^2HCl_3)

Compound	1-Me(s)	5-Me	9-Me	13-Me	13′-Me	9′-Me	COC*H*=COH	Enolic –OH	Other bands
β-Diketone (**8**)	1.03, 1.03	1.70	1.96	2.10	2.10	1.96	5.64	15.38[b]	2.10 (MeCO)
Bis-β-diketone (**9**)			1.94	1.97	1.97	1.94	5.54	15.53[b]	2.10 (both MeCO, 5.92 (d, *J*, 15 Hz, 2 H, 7- and 7′-H, 7.31 (d, *J* 15 Hz, 2 H; 8- and 8′-H)
β-Diketone (**45**)			2.00	2.04	1.88		5.92	16.10[b]	1.20 (9 H, CMe_3), 9.46 (1 H, CHO)
Bis-β-diketone[c] (**46**)			2.00	2.00	2.00	2.00	5.94	16.12[b]	1.22 (18 H, both CMe_3)
β-Diketone (**49**)	1.04, 1.04	1.72	1.98	2.10	2.10	1.98	5.92	16.08[b]	1.21 (9 H, CMe_3)
β-Diketone (**51**)	1.04, 1.04	1.71	1.97	1.97	1.97	1.97	5.90	16.16[b]	1.21 (9 H, CMe_3)
β-Diketone[d] (**52**)	1.04, 1.04	1.71	1.98	1.98	1.98	1.98	5.82	15.98[b]	1.19(d,*J*7Hz,6H,$CHMe_2$),2.60(m,1H,$CHMe_2$)
β-Diketone (**66**)	0.87, 1.08	1.14	2.00	2.00	2.00	2.06	5.68	15.26[b]	2.20 (3 H and 2.28 (6 H)[e]
β-Diketone (**67**)	0.85, 1.14	1.14	1.97	1.97	1.97	2.04	5.90	16.24[b]	2.20 (3 H) and 2.27 (6 H),[e] 3.90 (d, *J* 16 Hz, 1 H)
β-Diketone (**69**)	0.80, 0.98	1.24	2.00	2.00	2.00	2.06	5.87	16.34[b]	2.20 (3 H) and 2.30 (6 H)[e]
β-Diketone (**68**)	0.84, 1.04	1.28	1.98	1.98	1.98	2.05	5.85	16.36[b]	2.19 (3 H) and 2.28 (6 H)[e]
Trikentriorhodin									
synthetic (**70**)	0.85, 1.20	1.34	1.97	1.97	1.97	2.09	5.85	16.28[b]	2.20 (3 H) and 2.30 (6 H)[e]
natural[29] (**1**)	0.85, 1.19	1.35	1.99	1.99	1.99	2.07	5.86	16.30	2.20 (3 H) and 2.29 (6 H)[e]

[a] Unless indicated to the contrary all bands quoted (δ values) were singlets and had the expected relative intensities. The assignment of bands differing by less than 7 p.p.m. is arbitrary, and may have to be revised. [b] Band due to enolic hydroxy proton(s); removed after shaking the solution of the sample with deuterium oxide. [c] A weak band at 3.74 indicated the presence of 10—20% of the isomer in which one end group exists in the di-keto form. [d] A weak band at 3.84 indicated the presence of 10—20% of the di-keto tautomer. [e] Bands due to the 3 methyl groups attached to the benzene ring in the χ-end group.

N.m.r. spectra were recorded at 60 or 100 MHz for solutions in deuteriochloroform, with tetramethylsilane as an internal standard, unless indicated to the contrary; doublets are indicated by d, triplets by t, quartets by q, and multiplets by m; broad bands are indicated by b; all other bands were observed as singlets (s). Mass spectra were determined by direct insertion with an A.E.I. MS902 instrument (ionization potential 70 eV); selected lines only are quoted, assignments and the intensity of the lines relative to that of the base peaks are given in parentheses. Selected bands only are quoted for the i.r. spectra.

N-*Butyl*-15,15′-*didehydro*-8′-*apo*-β-*caroten*-8′-*imine* (**5**).—A solution of butylamine (0.5 ml) in ethyl acetate (10 ml) was added over 5 min to a solution of 15,15′-didehydro-8′-apo-β-caroten-8′-al[12] (414 mg) and tri-isobutylborate (364 mg) in ethyl acetate (15 ml), and the reaction was monitored by t.l.c. After 2 h, water (20 ml) was added and the product was isolated with ether. Recrystallisation from ethyl acetate gave the *imine* (446 mg) as brick red crystals, m.p. 100—101 °C; $\lambda_{max.}$(ethanol) 426 and 444infl nm; $\lambda_{max.}$(ethanolic HCl) 484 nm; $\nu_{max.}$(KBr) 2 958, 2 142w, 1 618, 965, and 955 cm^{-1}; δ 0.92 (t, *J* 7 Hz, 3 H), 1.03 (s, 6 H), 1.20—1.68 (m, 10 H), 1.70 (s, 3 H), 1.96 (s, 3 H), 2.01 (s, 3 H), 2.10 (s, 6 H), 2.0—2.15 (m, 2 H), and 5.60—6.84 (m, 11 H); *m/z* 469.370 ($M^{+\cdot}$; Calc. for $C_{34}H_{47}N$: *m/z* 469.371, 74), 454 (*M* − 15, 20), 403 (11), 377 (*M* − 92, 5), 368 (7), 342, (5), 337 (4), 183 (50), 93 (100), and 91 (100). An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 454 and 410 nm.

N,N′-*Dibutyl*-8,8′-*diapocarotene*-8,8′-*di-imine* (**7**).—Condensation of 8,8′-diapo-carotene-8,8′-dial[13] (292 mg) with butylamine (1.0 ml) in ethyl acetate (15 ml) containing tri-isobutyl borate (730 mg), as in the previous experiment, gave the *di-imine* (395 mg) as red crystals, m.p. 143—145 °C; $\lambda_{max.}$(ethanol) 458, 440, and 414 nm; $\lambda_{max.}$(ethanolic HCl) 536 and 520 nm; $\nu_{max.}$(KBr) 1 625, 965, and 958 cm^{-1}; δ 0.92 (t, *J* 7 Hz, 6 H), 1.20—1.80 (m, 8 H), 1.98 (s, 6H), 2.01 (s, 6 H), 3.80 (t, *J* 7 Hz, 4 H), 5.80—6.80 (m, 10 H), and 6.81 (s, 2 H); *m/z* 406.333 ($M^{+\cdot}$; Calc. for $C_{28}H_{42}N_2$: *m/z* 406.334, 100), 391 (*M* − 15, 3), 364 (*M* − 42, 3), 349 (*M* − 57, 5), and 151 (85).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 15 min the solution had $\lambda_{max.}$ 426, 401, and 368 nm.

6′-*Hydroxy*-15,15′-*didehydro*-18′-*nor*-3′-*apo*-β,χ-*caroten*-4′-*one* (**8**).—15,15′-Didehydro-8′-apo-β-caroten-8′-al (414 mg) was treated with butylamine as described above. The resulting solution of the imine was heated under reflux and the acetylacetone–boric oxide complex (prepared by shaking 1.0 g of acetylacetone with 0.5 g of boric oxide for 2 h) was added in small portions over 2 h. The mixture was boiled for 14 h, then cooled to 50 °C, and poured into 2M hydrochloric acid at 60 °C. The mixture was cooled to 20 °C and the red solid which had separated was collected and dried. Crystallisation from ethyl acetate gave the β-diketone (406 mg), m.p. 178—180 °C; $\lambda_{max.}$(ethanol) 460 nm; $\lambda_{max.}$(ethanolic NaOH) 475 and 441 nm; $\nu_{max.}$(KBr) 2 920, 2 145w, 1 610, 1 580, 1 520, and 960 cm^{-1}; δ, see Table; *m/z* 496.333 ($M^{+\cdot}$; Calc. for $C_{35}H_{44}O_2$: *m/z* 496.334, 55), 478 (*M* − 18, 1), 411 (6), 195 (71), 180 (*M* − 195 − 15, 55; *m** 166.5, $180^2/195$ = 166.5), 158 (75), 118 (38), 106 (48), 105 (59), and 91 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 15 min the solution had $\lambda_{max.}$ 452 and 426 nm.

6,6′-*Dihydroxy*-18,18′-*dinor*-3,3′-*diapo*-χ,χ-*carotene*-4,4′-*dione* (**9**).—Prepared from 8,8′-diapo-carotene-8,8′-dial and acetylacetone by the procedure described in the previous experiment, the bis-β-diketone (80%) had m.p. 225 °C (with decomp.); $\lambda_{max.}$(ethanol) 500 nm; $\lambda_{max.}$(ethanolic NaOH) 516infl, 472 and 460infl nm; $\nu_{max.}$(KBr) 1 618, 1 540, and 965 cm^{-1}; δ, see Table; *m/z* 460.262 ($M^{+\cdot}$; Calc. for $C_{35}H_{44}O_2$: *m/z* 460.262, 38), 442 (*M* − 18, 6), 417 (*M* − 43, 6), 369 (*M* − 91, 10), 354 (*M* − 106, 15), 106 (100), 105 (100), 98 (80), 92 (100), 91 (100), and 85 (100).

An excess of borohydride was added to a sample of the product in ethanol. After 15 min the solution had $\lambda_{max.}$ 462, 434, and 418infl nm.

2,2-*Dimethylhept*-4-*yn*-3-*one* (**12**).—Butyl-lithium (0.12 mol) in pentane (1.64M) was added slowly to a solution of but-1-yne (5.4 g, 0.1 mol) in ether (200 ml) at 0 °C. The mixture was stirred at 20 °C for 2 h, and then again cooled to 0 °C. Pivalic anhydride (22 g, 0.12 mol) in ether (150 ml) was added slowly and the mixture was then stirred at 20 °C for 2 h. Water (200 ml) was added, and the product was isolated in the usual way giving the acetylenic ketone (9.3 g), b.p. 40—42 °C/0.2 mmHg, n_D^{20} 1.4390; $\lambda_{max.}$(ethanol) 222 nm; $\nu_{max.}$(liq. film) 2 945, 2 210, 1 660,

and 1 150 cm^{-1}; δ 1.19 (s, 9 H), 1.22 (t, *J* 7 Hz, 3 H), and 2.40 (q, *J* 7 Hz, 2 H); *m/z* 138 ($M^{+\cdot}$; Calc. for $C_9H_{14}O$: *m/z* 138).

2,2-*Dimethylnon*-4-*yn*-3-*one* (**13**).—Reaction of hex-1-yne (1.64 g) with pivalic anhydride (4.0 g), as in the previous experiment, gave the acetylenic ketone (2.8 g), b.p. 50—55 °C/0.2 mmHg, n_D^{20} 1.4430; $\lambda_{max.}$(ethanol) 223 nm; $\nu_{max.}$(liq. film) 2 950, 2 210, 1 660, and 1 150 cm^{-1}; δ 0.96 (t, *J* 7 Hz, 3 H), 1.20 (s, 9 H), 1.4—1.6 (m, 4 H), and 2.42 (t, *J* 7 Hz, 2 H); *m/z* 166 ($M^{+\cdot}$; Calc. for $C_{11}H_{18}O$: *m/z* 166).

cis-7-*Acetoxy*-5-*methylhept*-5-*en*-3-*yn*-2-*one* (**21**).—Butyllithium in pentane (1.64M; 2 molar proportions) was added slowly to *cis*-3-methylpent-2-en-4-yn-1-ol[16] (1.92 g, 0.02 mol) in ether (40 ml) at 0 °C.

The solution was stirred at 20 °C for 2 h to complete the formation of the dianion, and then again cooled to 0 °C. Acetic anhydride (2.5 g, 2 molar proportions) in ether (30 ml) was added slowly, and the mixture was stirred at 20 °C for 2 h. Water (20 ml) was added and the products were isolated with ether. Preparative t.l.c. (3% acetone in light petroleum) gave the following.

(i) The acetylenic ketone (1.8 g), as the more polar product; $\lambda_{max.}$(ethanol) 267, 258 and 225 nm; $\nu_{max.}$(liq. film) 2 912, 2 190, 1 748, 1 670, and 1 230 cm^{-1}; δ 1.94 (m, 3 H), 2.04 (s, 3 H), 2.36 (s, 3 H), 4.76 (dq, J_1 7 Hz, J_2 1 Hz, 2 H) and 6.00 (tq, J_1 7 Hz, J_2 1 Hz, 1 H); *m/z* 180 ($M^{+\cdot}$; Calc. for $C_{10}H_{12}O_3$: *m/z* 180, 20), 138 (*M* − 42, 90; *m** 105.8, $138^2/180$ = 105.6), 109 (55), 95 (45), and 43 (100). An excess of sodium borohydride was added to a sample of the product in ethanol; after 10 min the solution had $\lambda_{max.}$ 228 nm.

(ii) 4-*Hydroxy*-3-(3-*methylfuryl*)*pent*-3-*en*-2-*one* (**23**) (0.75 g) as a colourless liquid; $\lambda_{max.}$(ethanol) 280 and 220 nm; $\lambda_{max.}$(ethanolic NaOH) 292 nm; $\nu_{max.}$(liq. film) 2 600, 1 600b, 1 480, 1 210, 1 152, and 1 085 cm^{-1}; δ 1.90 (s, 9 H), 6.20 (d, *J* 2 Hz, 1 H), 7.34 (d, *J* 2 Hz, 1 H), and 16.74 (s, 1 H; lost on deuteriation); *m/z* 180 ($M^{+\cdot}$; Calc. for $C_{10}H_{12}O_3$: *m/z* 180). An excess of sodium borohydride was added to a sample of the product in ethanol; after 15 min the solution had no u.v. light absorption maximum above 220 nm.

cis-6-*Methyl*-8-*propionyloxyoct*-6-*en*-4-*yn*-3-*one* (**22**).—Substitution of propionic anhydride (2 molar proportions) for acetic anhydride in the previous experiment gave the following.

(i) The acetylenic ketone (**22**) (1.1 g), as the more polar product; $\lambda_{max.}$(ethanol) 268, 258, and 225 nm; $\nu_{max.}$(liq. film) 2 978, 2 184, 1 745, 1 675, and 1 178 cm^{-1}; δ 1.14 (t, *J* 7 Hz, 3 H), 1.15 (t, *J* 7 Hz, 3 H), 1.97 (m, 3 H), 2.34 (q, *J* 7 Hz, 2 H), 2.62 (q, *J* 7 Hz, 2 H), 4.20 (dq, J_1 7 Hz, J_2 1 Hz, 2 H), and 6.22 (tq, J_1 7 Hz and J_2 1 Hz, 1 H); *m/z* 208 ($M^{+\cdot}$; Calc. for $C_{12}H_{16}O_3$: *m/z* 208). An excess of sodium borohydride was added to a sample of the product in ethanol; after 10 min the solution had $\lambda_{max.}$ 230 nm.

(ii) 5-*Hydroxy*-4-(3-*methylfuryl*)*hept*-4-*en*-3-*one* (**24**) (0.7 g) as a colourless liquid; $\lambda_{max.}$(ethanol) 280 and 220 nm; $\lambda_{max.}$(ethanolic NaOH) 294 nm; $\nu_{max.}$(liq. film) 2 980, 2 930, 1 600b, 1 462, 1 400, and 1 180 cm^{-1}; δ 1.04 (t, *J* 7 Hz, 6 H), 1.88 (s, 3 H), 2.10 (q, *J* 7 Hz, 4 H), 6.25 (d, *J* 2 Hz, 1 H), 7.34 (d, *J* 2 Hz, 1 H), and 16.86 (s, 1 H; lost on deuteriation); *m/z* 208.109 ($M^{+\cdot}$; Calc. for $C_{12}H_{16}O_3$: *m/z* 208.110), 190 (*M* − 18, 10; *m** 173.5, $190^2/208$ = 173.5), 179 (*M* − 29, 25), 151 (*M* − 57, 36; *m** 127.3, $151^2/208$ = 127.3), and 133 (80; *m** 117.2, $133^2/151$ = 117.1). An excess of sodium borohydride was added to a sample of the product in ethanol; after 10 min the solution had no u.v. light absorption maximum above 220 nm.

4-(3-*Methylfuryl*)-2,2,6,6-*tetramethylheptane*-3,5-*dione* (**25**).—Substitution of pivalic anhydride (2 molar proportions) for the anhydride used in the two previous experiments gave the *diketone* (2.4 g) which had b.p. 84—86 °C/0.01 mmHg and crystallised from ether as needles, m.p. 83—84 °C; $\lambda_{max.}$(ethanol) 220 nm; $\nu_{max.}$(Nujol) 2 960, 1 710, 1 360, 1 270, 1 140, and 965 cm^{-1}; δ 1.22 (s, 18 H), 1.98 (s, 3 H), 5.68 (s, 1 H), 6.18 (d, *J* 2 Hz, 1 H), and 7.28 (d, *J* 2 Hz, 1 H); *m/z* 264.172 ($M^{+\cdot}$; Calc. for $C_{16}H_{26}O_3$; *m/z* 264.173, 51), 249 (*M* − 15, 3), 207 (*M* − 57, 5), 180 (95), 165 (15; *m** 151.2, $150^2/180$ = 151.2), and 123 (100).

Tetrahydropyranyl Ether (**27**) *of* cis-8-*Hydroxy*-2,2,6-*trimethyloct*-6-*en*-4-*yn*-3-*one*.—Reaction of the tetrahydropyranyl ether (1.8 g) of *cis*-3-methylpent-2-en-4-yn-1-ol with pivalic anhydride, as in the preparation of (**21**), gave the acetylenic ketone (1.4 g) as a colourless oil; $\lambda_{max.}$(ethanol) 268, 260, and 220 nm; $\nu_{max.}$(liq. film) 2 925, 2 190, 1 660, 1 460, 1 193, 1 118, and 1 025 cm^{-1}; δ 1.24 (s, 9 H), 1.4—1.7 (m, 6 H), 1.96 (d, *J* 1 Hz, 1 H), 3.6 (m, 1 H), 4.30 (dq, J_1 7 Hz, J_2 1 Hz, 2 H), 4.61 (m, 1 H), and 6.08 (tq, J_1 7 Hz, J_2 1 Hz, 1 H).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 228 nm.

3,3-*Dimethyl*-1-(3-*methylfuryl*)*butan*-2-*one* (**28**).—A mixture of the preceding acetylenic ketone (100 mg) in ether (15 ml) and 2M hydrochloric acid (10 ml) was stirred for 3 h. Isolation of the product in the usual way, and preparative t.l.c. (2% acetone in light petroleum), gave the ketone as a colourless liquid (65 mg); $\lambda_{max.}$(ethanol) 224 nm; $\nu_{max.}$(liq. film) 2 950 and 1 705 cm^{-1}; δ 1.16 (s, 9 H), 1.95 (s, 3 H), 3.62 (s, 2 H), 6.08 (d, *J* 2 Hz, 1 H), and 7.15 (d, *J* 2 Hz, 1 H); *m/z* 180 ($M^{+\cdot}$; Calc. for $C_{11}H_{16}O_2$: *m/z* 180).

trans-2,2,6-*Trimethyl*-8-*pivaloyloxyoct*-6-*en*-4-*yn*-3-*one* (**30**).—Reaction of *trans*-3-methylpent-2-en-4-yn-1-ol[16] (0.96 g) with pivalic anhydride, as described above for the 2-*cis* isomer, gave the *acetylenic ketone* (0.8 g) as a colourless oil; $\lambda_{max.}$(ethanol) 269 nm; $\nu_{max.}$(liq. film) 2 980, 2 200, 1 730, 1 660, and 1 150 cm^{-1}; δ 1.21 (s, 9 H), 1.22 (s, 9 H), 1.94 (m, 3 H), 4.66 (dm, J_1 7 Hz, 2 H) and 6.14 (tm, J_1 7 Hz, 1 H); *m/z* 264 ($M^{+\cdot}$; Calc. for $C_{16}H_{24}O_3$: *m/z* 264). An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 228 nm.

2,2,6-*Trimethyl*-6-*pivaloyloxyoct*-7-*en*-4-*yn*-3-*one* (**34**).—3-Methylpent-1-en-4-yn-3-ol[16] (0.98 g) in ether (10 ml) was added slowly to butyl-lithium in pentane (1.56M; 15 ml) and ether (20 ml) at −30 °C. The mixture was stirred at 20 °C for 1 h and then again cooled to −30 °C. Pivalic anhydride (4.0 g) in ether (10 ml) was added slowly, and the mixture was stirred at 20 °C for 2 h. Water (30 ml) was added cautiously, and the product was isolated with ether. Distillation gave the acetylenic ketone (2.2 g), b.p. 85—90 °C/0.2 mmHg; $\lambda_{max.}$(ethanol) 220 nm; $\nu_{max.}$(liq. film) 2 962, 2 215, 1 740, 1 673, and 1 132 cm^{-1}; δ 1.21 (s, 18 H), 1.74 (s, 3 H), 5.26 (d, *J* 9 Hz, 1 H), 5.50 (d, J 9 Hz, 1 H), and 5.90 (dd, J_1 15 Hz, J_2 9 Hz, 1 H); *m/z* 264 ($M^{+\cdot}$; Calc. for $C_{16}H_{24}O_3$: *m/z* 264, 40), 249 (*M* − 15, 2), 207 (5), 180 (100), and 57 (100).

3-*Acetoxy*-3-*methylpent*-1-*en*-4-*yne* (**33**).—3-Methylpent-1-en-4-yn-3-ol (0.98 g) in ether (10 ml) was added slowly to butyllithium in pentane (1.56M; 7.5 ml, 1.1 mol equiv) in ether (20 ml) at −30 °C, and the mixture was stirred at 20 °C for 1 h. Acetyl chloride (0.7 g, 1.1 mol equiv.) in ether (10 ml) was added slowly, and the mixture was stirred at 20 °C for 2 h. Water (20 ml) was added and the product was isolated with ether giving 3-acetoxy-3-methylpent-1-en-4-yne (1.3 g), b.p. 24—26 °C/0.3 mmHg; $\nu_{max.}$(liq. film) 2 100w, 1 740 and 1 230 cm^{-1}; δ 2.14 (s, 3 H), 2.48 (s, 3 H), 2.94 (s, 1 H), 5.64 (d, *J* 9 Hz, 1 H), 5.92 (d, *J* 15 Hz, 1 H), and 6.50 (dd, J_1 9 Hz, J_2 15 Hz, 1 H).

6-*Acetoxy*-2,2,6-*trimethyloct*-7-*en*-4-*yn*-3-*one* (**35**).—Butyllithium in pentane (1.56M; 7 ml, 0.9 mol equiv.) was added dropwise to the preceding acetate (1.48 g) in ether (20 ml) at 0 °C, and the mixture was then stirred at 20 °C for 2 h. Pivaloyl chloride (1.2 g; or 1.86 g of pivalic anhydride) in ether (10 ml) was added at 0 °C and the mixture was stirred at 0 °C for 30 min, and then at 20 °C for 1 h. Water was added, and the product was isolated with ether giving the acetylenic ketone (1.4 g), b.p. 80—85 °C/2 mmHg; $\lambda_{max.}$(ethanol) 222 nm; $\nu_{max.}$(liq. film) 2 962, 2 215w, 1 740, 1 672, and 1 098 cm^{-1}; δ 1.22 (s, 9 H), 1.76 (s, 3 H), 2.04 (s, 3 H), 5.30 (d, *J* 9 Hz, 1 H), 5.52 (d, *J* 15 Hz, 1 H) and 6.0 (dd, J_1 9 Hz, J_2 15 Hz, 1 H); *m/z* 222 ($M^{+\bullet}$; Calc. for $C_{14}H_{18}O_3$: *m/z* 222).

(3,7,7-*Trimethyloct*-2-*en*-4-*ynyl*)*triphenylphosphonium Bromide* (**31**).—Treatment of the acetylenic ketones (**30**), (**34**), and (**35**) with triphenylphosphonium bromide in chloroform for 24 h, evaporation of the solvent, and trituration of the residue with ether, gave the Wittig salt as a yellow solid. Attempts to condense this salt with 2,7-dimethylocta-2,4,6-triene-1,8-dial in 1,2-epoxybutane, or in propan-2-ol containing potassium hydroxide, were unsuccessful.

2,2,6-*Trimethyl*-6-*pivaloyloxyoct*-7-*en*-4-*yn*-3-*ol*.—Sodium borohydride (0.3 g) was added in small portions to a solution of the acetylenic ketone (**34**) (1.0 g) in methanol (20 ml). The mixture was stirred at 20 °C for 2 h, and water (20 ml) was then added. Isolation of the product with ether, and preparative t.l.c. (6% acetone in light petroleum)gave the acetylenic alcohol (0.9 g) as a colourless liquid; $\nu_{max.}$(liq. film) 3 490, 2 998, 1 730, and 1 150 cm^{-1}; δ 0.98 (s, 9 H), 1.18 (s, 9 H), 1.66 (s, 3 H), 2.08 (br s, 1 H; disappears on deuteriation), 4.02 (s, 1 H), 5.16 (d, *J* 9 Hz, 1 H, and 5.90 (dd, J_1 9 Hz, J_2 15 Hz, 1 H); *m/z* 266 ($M^{+\bullet}$, calc. for $C_{16}H_{26}O_3$ *m/z*, 266), 248 (*M* − 18, 22), 230 (15), and 219 (100).

The acetylenic alcohol was treated with triphenylphosphonium bromide in dichloromethane for 24 h. Attempts to condense the resulting salt with 2,7-dimethylocta-2,4,6-triene-1,8-dial gave only small amounts of the required products.

5-*Methoxy*-2,2-*dimethylnon*-4-*en*-3-*one* (**17**).—2,2-Dimethylnon-4-yn-3-one (1.9 g) in methanol was added to sodium methoxide (2 molar proportions, from sodium) in methanol at 0 °C. The mixture was stirred at 20 °C for 3 h and the reaction was monitored by u.v. light absorption spectroscopy. Water (20 ml) was added, and the product isolated with ether to give, after preparative t.l.c. (2% acetone in light petroleum), the enol ether (1.7 g); $\lambda_{max.}$(ethanol) 262 nm; $\nu_{max.}$(liq. film) 2 963, 1 675, 1 585, and 1 096 cm^{-1}; δ 0.92 (t, *J* 7 Hz, 3 H), 1.17 (s, 9 H), 1.2—1.5 (m, 4 H), 2.70 (t, *J* 7 Hz, 2 H), 2.64 (s, 3 H), and 2.62 (s, 1 H); *m/z* 198 ($M^{+\bullet}$; Calc. for $C_{12}H_{22}O_2$: *m/z* 198, 10), 166 (*M* − 31, 5), 151 (*M* − 31 − 15, 5), 141 (*M* − 57, 100), and 57 (8).

5-*Ethoxy*-2,2-*dimethylnon*-4-*en*-3-*one* (**18**).—Substitution of ethanol for methanol in the previous experiment gave the enol ether (2.2 g); $\lambda_{max.}$(ethanol) 262 nm; $\nu_{max.}$(liq. film) 2 960, 2 940, 1 725, 1 580, and 1 100 cm^{-1}; δ 0.92 (t, *J* 7 Hz, 3 H), 1.14 (s, 9 H), 1.2—1.5 (m, 4 H), 1.36 (t, *J* 7 Hz, 3 H), 2.71 (t, *J* 7 Hz, 2 H), 3.70 (q, *J* 7 Hz, 2 H), and 5.6 (s, 1 H); *m/z* 212 ($M^{+\bullet}$; Calc. for $C_{13}H_{24}O_2$: *m/z* 212, 11), 183 (*M* − 29, 1), 155 (*M* − 57, 100), and 127 (*M* − 85, 32; *m** 104, $127^2/155 = 104$).

5-*Ethoxy*-2,2-*dimethylhept*-4-*en*-3-*one* (**15**).—Reaction of 2,2-dimethylhept-4-yn-3-one (1.4 g) with sodium ethoxide in ethanol, as in the previous experiment, gave the enol ether (1.7 g); $\lambda_{max.}$(ethanol) 260 nm; $\nu_{max.}$(liq.film) 2 950, 1 670, 1 580, 1 470, 1 392, 1 218, and 1 100 cm^{-1}; δ 1.10 (t, *J* 7 Hz, 3 H), 1.14 (s, 9 H), 1.30 (t, *J* 7 Hz, 3 H), 2.7 (t, *J* 7 Hz, 2 H), 3.70 (q, *J* 7 Hz, 2 H), and 5.58 (s, 1 H); *m/z* 184 ($M^{+\bullet}$; Calc. for $C_{11}H_{20}O_2$: *m/z* 184).

5-*Methoxy*-2,2,6-*trimethyl*-6-*pivaloyloxyocta*-4,7-*dien*-3-*one* (**37**).—2,2,6-Trimethyl-6-pivaloyloxyoct-7-en-4-yn-3-one (2.8 g) in methanol (10 ml) was added to a solution of sodium methoxide (from 460 mg of sodium) in methanol (15 ml) at 0 °C. The mixture was stirred at 20 °C and the reaction was monitored by u.v. light absorption spectroscopy. After 3 h water (15 ml) was added, and the product was isolated with ether. Preparative t.l.c. (2% acetone in light petroleum) gave the *enol ether* (1.6 g) as a mixture of *cis* and *trans* isomers; $\lambda_{max.}$(ethanol) 262 nm; $\nu_{max.}$(liq. film) 2 998, 1 730, 1 680, 1 595, and 1 150b cm^{-1}; δ 1.14 (s, 9 H), 1.20 (s, 9 H), 1.65 and 1.72 (pair of singlets, 3 H), 3.64 and 3.72 (pair of singlets, 3 H), and 5.0—6.5 (m, 4 H); *m/z* 296.199 ($M^{+\bullet}$; Calc. for $C_{17}H_{28}O_4$: *m/z* 296.198), 239 (*M* − 57, 5), 211 (6), 195 (6), and 155 (100). The formation of the furanone, described below, was also observed.

An excess of sodium borohydride was added to a sample of the enol ether in ethanol. After 10 min the solution exhibited no u.v. light absorption maximum above 210 nm.

5-*Ethoxy*-2,2,6-*trimethyl*-6-*pivaloyloxyocta*-4,7-*dien*-3-*one* (**38**).—Substitution of ethanol for methanol in the previous reaction gave the following.

(i) The enol ether (1.6 g); $\lambda_{max.}$(ethanol) 262 nm; $\nu_{max.}$(liq. film) 2 964, 2 863, 1 735, 1 638, 1 595, and 1 160 cm^{-1}; δ 1.16 (s, 9 H), 1.23 (m, 12 H), 1.66 (s, 3 H), 4.00 (q, *J* 7 Hz, 2 H), 5.40 (m, 2 H), 5.92 (s, 1 H), and 6.10 (dd, J_1 17 Hz, J_2 11 Hz, 1 H); *m/z* 310 ($M^{+\bullet}$; Calc. for $C_{18}H_{30}O_4$: *m/z* 310). Its behaviour on borohydride reduction paralleled that of the methyl ether.

(ii) 2-*Methyl*-5-*t*-*butyl*-2-*vinylfuran*-3(2H)-*one* (**41**) (330 mg); $\lambda_{max.}$(ethanol) 262 nm; $\nu_{max.}$(liq. film) 2 995, 1 700, and 1 683 cm^{-1}; δ 1.28 (s, 9 H), 1.35 (s, 3 H), 5.10 (d, *J* 11 Hz, 1 H), 5.30 (s, 1 H), 5.32 (d, *J* 17 Hz, 1 H), and 5.80 (dd, J_1 11 Hz, J_2 17 Hz, 1 H); *m/z* 180 ($M^{+\bullet}$; Calc. for $C_{11}H_{16}O_2$: *m/z* 180). The formation of the furanone was favoured by prolonging the reaction time. An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution exhibited no u.v. light absorption maximum above 210 nm.

(4-*Ethoxy*-3,7,7-*trimethyl*-6-*oxo*-*octa*-2,4-*dien*-1-*yl*)*triphenylphosphonium Bromide* (**40**).—Reaction of the preceding enol ether (**38**) with triphenylphosphonium bromide in chloroform in the usual way gave the Wittig salt (22%), and the furanone (40%) described above. Attempts to condense the Wittig salt with 12′-apo-β-carotenal in propan-2-ol containing potassium hydroxide were unsuccessful.

5-*Hydroxy*-2,2-*dimethylhept*-4-*en*-3-*one* (**14**) *and* 5-*Hydroxy*-6,6-*dimethylhept*-4-*en*-3-*one*.—A drop of sulphuric acid was added to 2,2-dimethylhept-4-yn-3-one (1.4 g) in ethanol (15 ml), and the reaction was monitored by u.v. light absorption spectroscopy and t.l.c. After 3 h water (20 ml) was added and the product was isolated with ether. Preparative t.l.c. (2% acetone in light petroleum) then gave the β-*diketone* (1.3 g) which existed mainly as a mixture of the two enols; $\lambda_{max.}$(ethanol) 275 nm; $\lambda_{max.}$(ethanolic NaOH) 290 nm; $\nu_{max.}$(liq. film) 2 925, 1 600b, and 1 123 cm^{-1}; δ 1.18 (s, 9 H), 1.21 (m, 3 H), 2.16 (q, *J* 7 Hz, 2 H), 5.58 (s, 1 H), and 15.80 (br s, 1 H; lost on deuteriation); *m/z* 156 ($M^{+\bullet}$; Calc. for $C_9H_{16}O_2$: *m/z* 156).

5-*Hydroxy*-2,2-*dimethylnon*-4-*en*-3-*one* (**16**) *and* 3-*Hydroxy*-2,2-*dimethylnon*-3-*en*-5-*one*.—Hydration of 2,2-dimethylnon-4-yn-3-one (1.6 g), as for the lower homologue above, gave the β-*diketone* (1.3 g) which existed mainly as a mixture of the two enols; $\lambda_{max.}$(ethanol) 275 nm; $\lambda_{max.}$(ethanolic NaOH) 292 nm; $\nu_{max.}$(liq. film) 2 985, 1 600br s, and 1 125 cm^{-1}; δ 0.96 (t, *J* 7 Hz, 3 H), 1.16 (s, 9 H), 1.4—1.7 (m, 4 H), 2.3 (t, *J* 7 Hz, 2 H), 5.57 (s, 1 H), and 15.82 (s, 1 H; lost on deuteriation); *m/z* 184 ($M^{+\bullet}$; Calc. for $C_{11}H_{20}O_2$: *m/z* 184).

trans-5-*Hydroxy*-2,2,6-*trimethyl*-8-*pivaloyloxyocta*-4,6-*dien*-3-*one* (**43**).—Attempts to hydrate (**30**), under the conditions described below for its isomer (**34**), were unsuccessful.

The acetylenic ketone (**30**) (1.0 g) in methanol (5 ml) was added to boron trifluoride–diethyl ether (3 ml) in methanol (5 ml) at 0 °C. The mixture was stirred at 20 °C for 3 h, and the reaction was monitored by u.v. light absorption spectroscopy. Water (20 ml) was added and the product was isolated with ether. Preparative t.l.c. (4% acetone in light petroleum) gave the *boron complex* (**42**) (520 mg), m.p. 77—78 °C; $\lambda_{max.}$(ethanol) 324 nm; $\nu_{max.}$(KBr) 1 722, 1 540, and 1 170 cm^{-1}; δ 1.26 (s, 9 H), 1.32 (s, 9 H), 2.00 (m, 3 H), 4.80 (dm, J_1 6 Hz, 1 H), 6.26 (s, 1 H), and 6.88 (tm, J_1 6 Hz, 1 H); *m/z* 330 ($M^{+\cdot}$; Calc. for $C_{16}H_{25}BF_2O_2$: *m/z* 330), 310 (*M* − HF, 16; *m** 291, $310^2/330$ = 291.2), 295 (3), 282 (14), 226 (46), 215 (26), 156 (29), 127 (37), 123 (26), 85 (40), and 57 (100).

The boron complex (200 mg) was stirred with an excess of aqueous sodium acetate at 50 °C until reaction was complete. Isolation of the product with ether, and preparative t.l.c. [4% acetone in light petroleum, (b.p. 60—80 °C)] gave the β-*diketone* (160 mg) as a pale yellow liquid; $\lambda_{max.}$(ethanol) 305; $\lambda_{max.}$(ethanolic NaOH) 315 nm; $\nu_{max.}$(liq. film) 2 980, 1 595br, and 1 152 cm^{-1}; δ 1.18 (s, 9 H), 1.22 (s, 9 H), 1.9 (m, 3 H), 5.76 (dm, J_1 6 Hz, 2 H), 5.88 (s, 1 H), 6.58 (tm, J_1 6 Hz, 1 H), and 15.94 (s, 1 H; disappears on deuteriation); *m/z* 282 ($M^{+\cdot}$).

5-*Hydroxy*-2,2,6-*trimethyl*-6-*pivaloyloxyocta*-5,7-*dien*-3-*one* (**36**).—A drop of concentrated sulphuric acid (or a few crystals of toluene-*p*-sulphonic acid monohydrate) was added to a solution of the acetylenic ketone (**34**) (2.6 g) in ethanol (15 ml). The mixture was stirred at 20 °C and the reaction was monitored by the change in $\lambda_{max.}$ from 224 to 275 nm. After 3 h water was added and the product was isolated with ether. Preparative t.l.c. (2% acetone in light petroleum) gave the β-*diketone* (2.2 g) as a colourless liquid; $\lambda_{max.}$(ethanol) 275 nm; $\lambda_{max.}$(ethanolic NaOH) 298 nm; $\nu_{max.}$(liq. film) 2 980, 1 730, 1 595, 1 150, 925, and 978 cm^{-1}; δ 1.14 (s, 9 H), 1.24 (s, 9 H), 1.62 (s, 3 H), 5.2 (d, *J* 10 Hz, 1 H), 5.30 (d, *J* 15 Hz, 1 H), 5.62 (s, 1 H), 6.12 (dd, J_1 10 Hz, J_2 17 Hz, 1 H), and 15.00 (br s, 1 H; disappears on deuteriation); *m/z* 282.184 ($M^{+\cdot}$; Calc. for $C_{16}H_{26}O_4$: *m/z* 282.184, 3), 267 (*M* − 15, 2), 173 (100), and 120 (100).

(4-*Hydroxy*-3,7,7-*trimethyl*-6-*oxo*-*octa*-2,4-*dien*-1-*yl*)*triphenylphosphonium Bromide* (**39**).—A solution of 2,2,6-trimethyl-6-pivaloyloxyoct-7-en-5-yn-3-one (2.6 g) and triphenylphosphonium bromide (3.42 g) in methanol (20 ml) containing 1 drop of concentrated hydrochloric acid was stirred at 20 °C for 24 h. The solvent was evaporated under reduced pressure, and the residue was triturated with ether to give the Wittig salt as a pale yellow solid which was used without further purification.

The same salt was obtained by reaction of (**36**) and (**43**) with triphenylphosphonium bromide in chloroform.

8-*Hydroxy*-5-*methyl*-6-*oxo*-5,6-*dihydro*-4,12′-*diapo*-*caroten*-12′-*al* (**45**).—Potassium hydroxide (200 mg) in water (2 ml) and propan-2-ol (10 ml), and the preceding Wittig salt (200 mg), were added separately in small portions over 30 min to a solution of 2,7-dimethylocta-2,4,6-triene-1,8-dial[17] (50 mg) in isopropyl alcohol (10 ml) at 0 °C. The mixture was stirred at 20 °C for 2 h, and water was then added. Isolation of the product with ether, and preparative t.l.c. (10% acetone in light petroleum) gave the β-*diketone* (22 mg) as red needles; $\lambda_{max.}$(ethanol) 436infl and 421 nm; $\lambda_{max.}$(ethanolic NaOH) 420 nm; δ 1.20 (s, 9 H), 1.88 (s, 3 H), 2.00 (s, 3 H), 2.04 (s, 3 H), 5.92 (s, 1 H), 6.3—7.2 (m, 7 H), 9.46 (s, 1 H) and 16.10 (s, 1 H; lost on deuteriation); *m/z* 328 ($M^{+\cdot}$; Calc. for $C_{21}H_{28}O_3$: *m/z* 328). The bis-β-diketone (**46**) (5 mg) was also isolated, and was identical with the sample prepared by a Claisen condensation described below.

8′-*Hydroxy*-5′-*methyl*-15,15′-*didehydro*-5′,6′-*dihydro*-4′-*apo*-β-*caroten*-6′-*one* (**49**).—Lithamide (20 mmol) was added in small portions to a well stirred solution of methyl 15,15′-didehydro-8′-apo-β-carotenoate (1 mmol) and 3,3-dimethylbutan-2-one (2 mmol) in tetrahydrofuran (15 ml), and the mixture was then boiled under reflux. When the reaction was complete, as judged by t.l.c. monitoring, the mixture was cooled and water (10 ml) was added cautiously. Isolation of the product with ether, preparative t.l.c. on silica gel (2% acetone in light petroleum), and crystallisation from ether–light petroleum, gave the β-*diketone* (92%) as orange needles, m.p. 138—139 °C; $\lambda_{max.}$(ethanol) 440 nm; $\lambda_{max.}$(ethanolic NaOH) 425 nm; $\nu_{max.}$(KBr) 2 980, 2 920, 2 860, 1 590, 1 548, 965, and 794 cm^{-1}; δ, see Table; *m/z* 512.364 ($M^{+\cdot}$; Calc. for $C_{36}H_{48}O_2$: *m/z* 512.364, 100), 497 (*M* − 15, 3), 486 (3), 468 (3), 427 (*M* − 85, 5), 421 (*M* − 92, 18), 406 (*M* − 106, 2), 385 (*M* − 127, fission of 8′,9′ bond, 70), 127 (100), 91 (100), 85 (fission of 6′,7′ bond, 18), and 69 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 15 min the solution had $\lambda_{max.}$ 432 and 409 nm.

A solution of boron trifluoride in methanol (40%; 2 ml) was added to one of the β-diketones (10 mg) in ether (5 ml). The resulting dark brown solution was stirred for 1 h. Water (10 ml) was added, and the product was isolated with ether. Preparative t.l.c. on silica gel [10% acetone in light petroleum (b.p. 40—60 °C)] gave the *boron complex* (9 mg) as a brick red solid; $\lambda_{max.}$(ethanol) 484 nm; $\lambda_{max.}$(ethanolic NaOH) 460 nm; $\nu_{max.}$ 2 960, 2 930, 2 863, 1 538, 1 498, and 962 cm^{-1}; δ 1.04 (s, 6 H), 1.29 (s, 9 H), 1.4—1.6 (m, 4 H), 1.71 (s, 3 H), 1.98 (s, 3 H), 2.06 (s, 3 H), 2.12 (s, 6 H), 6.22 (s, 7′-proton), 5.8—6.8 (m, 9 H), and 7.6 (d, *J* 10 Hz, 10′-H, 1 H); *m/z* 560.364 ($M^{+\cdot}$; Calc. for $C_{36}H_{47}BF_2O_2$ 560.364, 100), 545 (*M* − 15, 4), 540 (*M* − HF, 2), 468 (*M* − 92, 2), and 57 (100).

An excess of sodium borohydride was added to a sample of the boron complex in ethanol. After 10 min the solution had $\lambda_{max.}$ 430 and 406 nm.

8′-*Hydroxy*-5′-*methyl*-5′,6′-*dihydro*-4′-*apo*-β-*caroten*-6′-*one* (**51**).—Substitution of methyl 8′-apo-β-carotenoate[22] for its acetylenic analogue in the previous Claisen condensation gave (85%) the β-*diketone* which crystallised from chloroform–methanol as red needles, m.p. 169—171 °C; $\lambda_{max.}$(ethanol) 470 nm; $\lambda_{max.}$(ethanolic NaOH) 455 nm; $\nu_{max.}$(KBr) 2 920, 2 860, 1 610, 1 590, 1 567, and 965 cm^{-1}; δ, see Table; *m/z* 514.392 ($M^{+\cdot}$; calc. for $C_{36}H_{50}O_2$ 514.381, 55), 499 (*M* − 15, 1), 457 (*M* − 57, 1), 408 (*M* − 106, 3), 127 (40), 106 (43), 105 (38), 92 (100), 91 (100), and 85 (6).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 15 min the solution had $\lambda_{max.}$ 452, 426, and 406 nm.

8′-*Hydroxy*-5′,6′-*dihydro*-4′-*apo*-β-*caroten*-6-*one* (**52**).—Condensation of methyl 8′-apo-β-carotenoate with 3-methylbutan-2-one, as described in the preceding experiment, gave (90%) the β-*diketone* which crystallised from ether–methanol as dark red needles, m.p. 210—215 °C; $\lambda_{max.}$(ethanol) 472 nm; $\lambda_{max.}$(ethanolic NaOH) 455 nm; $\nu_{max.}$(KBr) 2 960, 2 920, 2 860, 1 580, 1 555, and 965 cm^{-1}; δ, see Table; *m/z* 500.364 ($M^{+\cdot}$; Calc. for $C_{35}H_{48}O_2$: *m/z* 500.365, 47), 408 (*M* − 92, 2), 394 (*M* − 106, 11), 167 (100), 113 (fission of 8′,9′ bond, 36), 109 (10), 71 (fission of 6′,7′ bond, 30), and 43 (fission of 5′,6′ bond, 100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 458, 428, and 406 nm.

8,8′-*Dihydroxy*-5,5′-*dimethyl*-5,6,5′,6′-*tetrahydro*-4,4′-*diapo*-*carotene*-6,6′-*dione* (**46**).—Condensation of dimethyl 8,8′-diapo-

carotenedioate[23] with 3,3-dimethylbutan-2-one in the usual way gave (75%) the *bis*-β-*diketone* which crystallised from methanol–ether as red needles, m.p. 185—187 °C; $\lambda_{max.}$(ethanol) 472 nm; $\lambda_{max.}$(ethanolic NaOH) 452 nm; $\nu_{max.}$(KBr) 2 965, 1 608, 1 570, and 958 cm^{-1}; δ, see Table; *m/z* 492.323 ($M^{+\cdot}$; Calc. for $C_{32}H_{44}O_4$: *m/z* 492.324, 60), 455 (*M* − 57, 2), 407 (*M* − 85, 3), 400 (*M* − 92, 4), 365 (*M* − 127, 5), 127 (60), and 57 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 15 min the solution had $\lambda_{max.}$ 426, 400, and 370 nm.

(1R)-1-*Acetyl*-1,2,2-*trimethylcyclopentane* (**60**).—A solution of (1*R*)-1,2,2-Trimethylcyclopent-3-ene-1-carboxylic acid[21,35] (10.0 g) in ethanol (100 ml) was shaken with palladised charcoal (0.8 g, 5% Pd) in an atmosphere of hydrogen until absorption was complete. Removal of catalyst and solvent, and crystallisation from acetonitrile, gave (1*R*)-1,2,2-trimethylcyclopentane-1-carboxylic acid (8.0 g) as colourless needles, m.p. 190—192 °C (Goldman *et al.*,[35] give m.p. 192—193 °C); $\nu_{max.}$(Nujol) 1 700, 1 220, and 1 138 cm^{-1}; δ 0.98 (s, 3 H), 1.06 (s, 3 H), 1.18 (s, 3 H), 1.5—1.7 (m, 5 H), 2.4 (m, 1 H), and 11.4 (br s, 1 H; lost on deuteriation).

A solution of methyl-lithium in ether (0.5M; 100 ml) was added over 30 min to a stirred solution of the preceding acid (8.0 g) in ether (20 ml). The mixture was stirred at 20 °C for 3 h, and then under reflux for 14 h. The mixture was cooled and water (20 ml) was added cautiously. Isolation of the product in the usual way, and preparative t.l.c. on silica gel [1% acetone in light petroleum (b.p. 60—80 °C)]; gave the methyl ketone (8.0 g), m.p. 10—12 °C; $\nu_{max.}$(liq. film) 2 980 and 1 700 cm^{-1}; δ 0.81 (s, 3 H), 1.01 (s, 3 H), 1.04 (s, 3 H), 1.25—1.75 (m, 5 H), 2.01 (s, 3 H), and 2.01—2.45 (m, 1 H). For a sample of the racemate, prepared by a different route. Barber *et al.*[26] give m.p. 50 °C.

(1R,3R)-3-*Acetyl*-2,2,3-*trimethylcyclopentanol* (**62**).—A solution of methyl-lithium in ether (1M; 100 ml) was added over 30 min to (1*R*,3*R*)-3-hydroxy-1,2,2-trimethylcyclopentane-1-carboxylic acid (1.2 g) (prepared by alkaline hydrolysis of the corresponding methyl ester[7,21]) in ether (20 ml). The mixture was stirred at 20 °C for 3 h, and then under reflux for 4 h. The mixture was cooled and water (20 ml) was added cautiously. Isolation of the product in the usual way, and preparative t.l.c. on silica gel [6% acetone in light petroleum (b.p. 60—80 °C)], gave the hydroxy ketone (600 mg) as a colourless liquid; $\nu_{max.}$(liq. film) 3 450, 2 950, and 1 690 cm^{-1}; δ 0.86 (s, 3 H), 1.00 (s, 3 H), 1.27 (s, 3 H), 1.2—2.2 (m, 5 H), 2.10 (s, 3 H), and 3.85 (m, 1 H). The n.m.r. properties were in good agreement with those reported for a sample prepared from the acetylcyclopentene (**61**).[21]

(1R,3R)-1-*Acetyl*-1,2,2-*trimethyl*-3-*trimethylsilyloxycyclopentane* (**63**).—The preceding hydroxy ketone was added to a solution of hexamethyldisilazane (2 ml) and trimethylchlorosilane (1 ml) in pyridine (10 ml). After 20 min the solvent was evaporated and the product was isolated with ether giving (100%) the trimethylsilyl ether; $\nu_{max.}$(liq. film) 2 950, 1 705, 1 460, 1 115, 1 015, 990, and 878 cm^{-1}.

(1R,3S)-1-*Acetyl*-1,5,5-*trimethyl*-3-*trimethylsilyloxycyclopentane* (**65**).—A sample of (1*R*,3*S*)-3-hydroxy-1,5,5-trimethylcyclopentane-1-carboxylic acid was prepared by hydroboration of methyl (1*R*)-1,2,2-trimethylcyclopent-3-ene-1-carboxylate[35] as described by Chopra *et al.*[7] and Rüttimann *et al.*[21] Hydrolysis, and treatment of the resulting acid with an excess of methyl-lithium, gave[21] the hydroxy ketone (**64**) which had properties in good agreement with those reported previously for samples prepared by different routes also based on (+)-camphor.[21,21] Trimethylsilylation, as described for the isomeric hydroxy ketone, gave (100%) the required trimethylsilyl ether; $\nu_{max.}$(liq. film) 2 950, 1 700, 1 440, 1 380, 1 240, 1 040, and 850 cm^{-1}.

Methyl 12-*Oxo*-2,6,11-*trimethyldodeca*-2,4,6,8,10-*pentaenoate* (**55**).—3-Methoxycarbonyl-3-methylprop-2-enyltriphenylphosphonium bromide[24] (1.5 g) was added slowly to a solution of 2,7-dimethylocta-2,4,6-triene-1,8-dial[17] (500 mg) and potassium hydroxide (0.1 g) in water (1 ml) and propan-2-ol (35 ml). During the addition, a solution of potassium hydroxide (0.5 g) in water (2 ml) and propan-2-ol (70 ml) was added dropwise. The mixture was stirred at 20 °C for 3 h, and then diluted with water (30 ml). Isolation of the product with ether, preparative t.l.c. [silica gel, 10% acetone in light petroleum (b.p. 60—80 °C)], and crystallisation from ether–light petroleum (b.p. 40—60 °C), gave the *aldehydo ester* (320 mg) as yellow needles, m.p. 158—160 °C; $\lambda_{max.}$(ethanol) 406 and 388 nm; $\nu_{max.}$(KBr) 2 945m, 1 700s, 1 660s, 1 605s, and 965m cm^{-1}; δ 1.88 (s, 3 H), 2.06 (s, 3 H), 2.08 (s, 3 H), 3.70 (s, 3 H), 3.7 (br s, 1 H), 6.3—7.1 (m, 5 H), 8.00 (d, *J* 16 Hz, 1 H), and 9.46 (s, 1 H); *m/z* 260.140 ($M^{+\cdot}$; Calc. for $C_{16}H_{20}O_3$: *m/z* 260.141, 22), 239 (*M* − 31, 4), 76 (100), 44 (100), and 42 (100). Crocetin dimethyl ester (200 mg) was also isolated and had m.p. 219—222 °C (Isler *et al.*[23] give m.p. 225—227 °C).

An excess of sodium borohydride was added to a sample of the aldehydoester in ethanol. After 10 min the solution had $\lambda_{max.}$ 386, 369 and 345infl nm.

3-*Methyl*-5-(2,3,4-*trimethylphenyl*)*pent*-1,4-*dien*-3-*ol* (**57**).—A solution of 4-(2,3,4-trimethylphenyl)but-3-en-2-one[25] (2.0 g) in tetrahydrofuran (10 ml) was added slowly at 0 °C to vinylmagnesium bromide (from 250 mg of Mg) in tetrahydrofuran (30 ml). After the mixture had been stirred overnight at 20 °C, saturated aqueous ammonium chloride (20 ml) was added and the product was isolated with ether. Preparative t.l.c. on silica gel [8% acetone in light petroleum (b.p. 60—80 °C)] gave the *vinyl alcohol* (1.7 g) as a pale yellow oil; $\lambda_{max.}$(ethanol) 260 and 215 nm; $\nu_{max.}$(liq. film) 3 450, 2 980, 2 950, 1 460, 978, and 925 cm^{-1}; δ 1.58 (s, 3 H), 1.76 (br s, 1 H; lost on deuteriation), 2.19 (s, 3 H), 2.27 (s, 3 H), 2.25 (s, 3 H), 5.1 (d, *J* 10 Hz, 1 H), 5.3 (d, *J* 16 Hz, 1 H), 6.08 (d, *J* 16 Hz, 1 H), 6.0 (dd, J_1 16 Hz, J_2 10 Hz, 1 H), 6.9 (d, *J* 16 Hz, 1 H), 6.94 (d, *J* 8 Hz, 1 H), and 7.14 (d, *J* 8 Hz, 1 H); *m/z* 216 ($M^{+\cdot}$; Calc. for $C_{15}H_{20}O$: *m/z* 216, 52), 201 (*M* − 15, 15), 149 (30), and 133 (100).

3-*Methyl*-5-(2,3,4-*trimethylphenyl*)*penta*-2,4-*dien*-1-*yltriphenylphosphonium Bromide* (**58**).—A solution of the preceding vinyl alcohol (2.2 g) and triphenylphosphonium bromide (3.4 g) in dichloromethane (20 ml) was stirred at 20 °C for 14 h. The solvent was evaporated under reduced pressure and the residue was triturated with ether, giving the phosphonium salt (5 g) as a pale yellow gum which was used without further purification.

Methyl 8′-*Apo*-χ-*carotenoate* (**59**).—Propan-2-ol (10 ml) was added to potassium hydroxide (500 mg) in water (1 ml). A portion (2 ml) of the resulting solution was added to the preceding aldehydo ester (100 mg) in propan-2-ol (20 ml). A solution of the preceding phosphonium salt (400 mg) in propan-2-ol (10 ml) was added over 30 min. The mixture was stirred at 20 °C for 3 h, and then diluted with water. Isolation of the product with ether, and chromatography on silica gel [5% acetone in light petroleum (b.p. 60—80 °C)] gave the *methyl ester* (95 mg) as a red solid; $\lambda_{max.}$(ethanol) 452 nm; δ, see Table; *m/z* 442.286 ($M^{+\cdot}$; Calc. for $C_{31}H_{38}O_2$: *m/z* 442.287, 36), 427 (*M* − 15, 3), 417 (3), 403 (3), 358 (43), 350 (*M* − 92, 8), 336 (*M* − 106, 26), 106 (95), 105 (65), 92 (51), 91 (100; ***m**** 78.1, $91^2/106$ = 78.1), 76 (30), and 52 (25).

(5R)-8-*Hydroxy*-κ,χ-*caroten*-6-*one* (**66**).—Condensation of the preceding ester with (1*R*)-1-acetyl-1,2,2-trimethylcyclopentane, as described below for the synthesis of trikentriorhodin derivative (**71**), and crystallisation of the product from light petroleum (b.p. 60—80 °C)–methanol, gave (85%) the β-*diketone*, m.p.(evac. capillary) 255—258 °C; $\lambda_{max.}$(ethanol) 478 nm; $\lambda_{max.}$(ethanolic NaOH) 462 nm; $\nu_{max.}$(KBr) 2 920 2 860, 1 660, 1 555, 965, and 955 cm^{-1}; δ, see Table; *m/z* 564,397 ($M^{+\bullet}$; Calc. for $C_{40}H_{52}O_2$; *m/z* 564.397, 62), 472 (*M* − 92, 10), 458 (*M* − 106, 38), 299 (13), 209 (16), 181 (36), 173 (22), 133 (45), 111 (92), 106 (100), 105 (100), 92 (100), and 91 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 465, 441, and 418infl nm.

(5R)-8-*Hydroxy*-2,3-*didehydro*-κ,χ-*caroten*-6-*one* (**67**).—Substitution of (1*R*)-1-acetyl-1,2,2-trimethylcyclopent-3-ene for its saturated analogue in the previous experiment gave the β-*diketone*; $\lambda_{max.}$(ethanol) 478 nm; $\lambda_{max.}$(ethanolic NaOH) 462 nm; δ, see Table; *m/z* 562.380 ($M^{+\bullet}$; Calc. for $C_{40}H_{50}O_2$: *m/z* 562.381, 25), 470 (*M* − 92, 3), 456 (*M* − 106, 9), 106 (85), 91 (100; *m** 78.1, $91^2/106$ = 78.12), 44 (100), and 43 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 458, 438, and 418infl nm.

(2R,5R)-8-*Hydroxy*-2-*trimethylsilyloxy*-κ,χ-*caroten*-6-*one* (**69**).—Condensation of methyl 8′-apo-χ-carotenoate with (1*R*,3*R*)-1-acetyl-1,2,2-trimethyl-3-trimethylsilyloxycyclopentane gave the β-*diketone*; $\lambda_{max.}$(ethanol) 478; $\lambda_{max.}$(ethanolic NaOH) 462 nm; δ, see Table; *m/z* 652.430 ($M^{+\bullet}$; Calc. for $C_{43}H_{60}O_3Si$: *m/z* 652.431, 12), 637 (*M* − 15, 4), 560 (*M* − 92, 6), 546 (*M* − 106, 36), 199 (98), 158 (97), 143 (158 − 15, 60; *m** 129.3, $143^2/158$ = 129.4), 106 (96), 91 (90); *m** 78.1, $91^2/106$ = 78.1), and 43 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 468, 441, and 416 nm.

(2R,5R)-2,8-*Dihydroxy*-κ,χ-*caroten*-6-*one* (**68**).—2M Hydrochloric acid (0.5 ml) was added to the preceding trimethylsilyloxy derivative (5 mg) in methanol (10 ml). When the reaction was complete (t.l.c. monitoring), water (10 ml) was added, and the product was isolated with ether. Preparative t.l.c. on silica gel [10% acetone in light petroleum (b.p. 60—80 °C)] gave the β-*diketone* as a purple solid (3 mg); $\lambda_{max.}$(ethanol) 478 nm; $\lambda_{max.}$(ethanolic NaOH) 462 nm; $\nu_{max.}$(KBr) 3 400, 3 040, 2 970, 2 930, 1 608, 1 558, and 960 cm^{-1}; δ, see Table; *m/z* 580.391 ($M^{+\bullet}$; Calc. for $C_{40}H_{52}O_3$: *m/z* 580.342, 44), 562 (*M* − 18, 3), 488 (*M* − 92, 12), 474 (*M* − 106, 5), 106 (93), 92 (85), and 91 (100; *m** 78.1, $91^2/106$ = 78.1).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 465, 440, and 420 nm.

(3S,5R)-8-*Hydroxy*-3-*trimethylsilyloxy*-κ,χ-*caroten*-6-*one* (**71**).—Lithamide (46 mg) was added in small portions to a well stirred solution of methyl 8′-apo-χ-carotenoate (50 mg) and (1*R*,3*S*)-1-acetyl-1,5,5-trimethyl-3-trimethylsilyloxycyclopentane (100 mg) in tetrahydrofuran (15 ml). The mixture was heated under reflux until the reaction was complete (t.l.c. monitoring). The mixture was then cooled, and water (10 ml) was added cautiously. Isolation of the product with ether, and preparative t.l.c. on silica gel [2% acetone in light petroleum (b.p. 60—80 °C)], gave the β-*diketone* (20 mg) as a red solid; $\lambda_{max.}$(ethanol) 478 nm; $\lambda_{max.}$(ethanolic NaOH) 462 nm; *m/z* 652.430 (Calc. for $C_{43}H_{60}O_3Si$: *m/z* 652.432, 46), 637 (*M* − 15, 4), 560 (*M* − 92. 10), 542 (*M* − 106, 68), 106 (100), 105 (100), and 92 (100).

An excess of sodium borohydride was added to a sample of the product in ethanol. After 10 min the solution had $\lambda_{max.}$ 466, 441, and 424infl nm.

(3S,5R)-3,8-*Dihydroxy*-κ,χ-*caroten*-6-*one* (*Trikentriorhodin*) (**70**).—2M Hydrochloric acid (1 ml) was added to the preceding trimethylsilyloxy derivative (10 mg) in methanol (10 ml), and the mixture was stirred at 20 °C. When the reaction was complete (t.l.c. monitoring), water (10 ml) was added and the product was isolated with ether. Preparative t.l.c. on silica gel [10% acetone in light petroleum (b.p. 60—80 °C)], and crystallisation from ethanol–ether, gave *trikentriorhodin* (7 mg) as deep red crystals, m.p. (evac. capillary) 255—260 °C; $\lambda_{max.}$(ethanol) 478 nm; $\lambda_{max.}$(ether) 475 nm; $\lambda_{max.}$(acetone) 478 nm; $\lambda_{max.}$(ethanolic NaOH) 462 nm; $\nu_{max.}$(KBr) 3 438, 3 025, 2 922s, 2 856, 1 610s, 1 565s, 965s, and 960s cm^{-1}; δ, see Table; *m/z* 580.393 ($M^{+\bullet}$; Calc. for $C_{40}H_{52}O_3$ 580.392, 37), 562 (*M* − 18, 4), 488 (*M* − 92, 5), 474 (*M* − 106, 34), 109 (33), 106 (100), 105 (65), 92 (64), 91 (100; *m** 78.1, $91^2/106$ = 78.1) and 77 (30); Δε − 0.05 (262 nm), +0.06 (303 nm), and −0.06 (370 nm).

The spectral properties reported by Aguilar-Martinez and Liaaen-Jensen[4] for the natural pigment agree well with those of the synthetic material. The c.d. properties of the latter were qualitatively similar to those reported for trikentriorhodin from *Angelas Schmidtii*,[36] and for the mixture of trikentriorhodin and trikentriophidin from *Microciona prolifera*.[29]

A sample of the natural pigment, extracted from *Trikentrion helium*, did not separate from the synthetic material on mixed t.l.c. on silica gel using either light petroleum (b.p. 60—80 °C)–acetone (10:1), or benzene, ethyl acetate, and ethanol (10:2:1), as eluants. The isomer (**68**) separated readily from trikentriorhodin on mixed t.l.c. on silica gel [10% acetone in light petroleum (b.p. 60—80 °C)].

An excess of sodium borohydride was added to a sample of synthetic trikentriorhodin in ethanol. After 10 min the solution had $\lambda_{max.}$ 466, 441, and 424 nm.

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