

Synthesis and Characterization of Representative Octa-1,3,5,7-tetraenes and Deca-1,3,5,7,9-pentaenes

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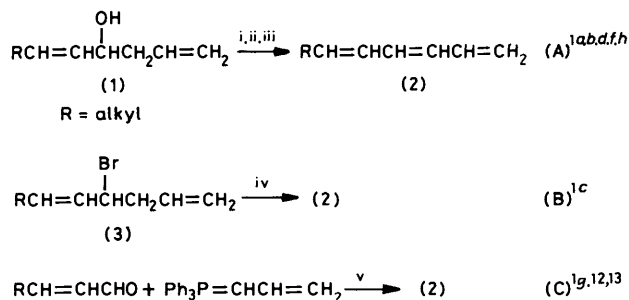
Several representative conjugated linear tetraenes and pentaenes were prepared by a variety of synthetic methods including Wittig condensation, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-induced dehydrobromination, and Hofmann elimination. For the preparation of (*E,E*)- and (*Z,E*)-octa-1,3,5,7-tetraene, the Hofmann elimination sequence is by far the most convenient method of synthesis, while DBU-induced dehydrobromination of (*E,E*)-4-bromonona-1,5,7-triene produces excellent yields of (*E,E,E*)- and (*3Z,5E,7E*)-nona-1,3,5,7-tetraene. Deca-1,3,5,7,9-pentaene can be produced by several methods, but not in high yield. Undeca-1,3,5,7,9-pentaene and trideca-1,3,5,7,9,11-hexaene can also be prepared in low yield by the Wittig reaction. All the polyenes produced in this study polymerize rapidly in the crystalline state.

THE synthesis, isolation, and characterization of pure conjugated polyenes has been a problem of continuing interest not only for the synthetic organic chemist, but also for physical chemists interested in comparing actual physical and spectral properties with theoretical or calculated values. We have reported several studies of synthetic methods aimed at producing pure conjugated hexa-1,3,5-trienes and cyclohexa-1,3-dienes,¹ and now report an extension of these studies towards the synthesis, isolation, and characterization of octa-1,3,5,7-tetraenes and deca-1,3,5,7,9-pentaenes.

The parent octa-1,3,5,7-tetraene was first prepared by Woods and Schwartzman² who catalytically dehydrated octa-1,5,7-trien-4-ol over alumina at 250–280 °C, and later by Evans,³ *via* a similar dehydration of octa-2,4,6-trien-1-ol at 290 °C. Only one isomer was isolated in modest yield (40–58%), and was assigned the *E,E*-configuration (5a). (*Z,E*)-Octa-1,3,5,7-tetraene (6a) has been obtained by Ziegenbein⁴ *via* partial reduction of octa-1,7-dien-3,5-diyne, and more recently by Granville *et al.*⁵ *via* photoisomerization of the (*E,E*)-isomer (5a).

Deca-1,3,5,7,9-pentaene was first prepared by Mebane⁶ *via* the coupling of 5-chloropenta-1,3-diene in liquid ammonia, and has more recently been prepared by D'Amico *et al.*⁷ *via* catalytic dehydration of deca-1,4,6,8-tetraen-3-ol; both methods gave very low yields (5–10%). Both octa-1,3,5,7-tetraene and deca-1,3,5,7,9-pentaene can be purified by low-temperature recrystallization from hydrocarbons, and both compounds polymerize rapidly in the crystalline state.^{2,6} All literature reports of the synthesis of deca-1,3,5,7,9-pentaenes indicate that only the (*E,E,E*)-isomer (13) was isolated. This is not unexpected since the isomers with one or more *Z*-configurations would undergo further reactions, such as electrocyclization, under the severe reaction conditions. This has been recognized previously both in our laboratory for hexa-1,3,5-trienes,^{1,8,9} and by Huisgen *et al.*,¹⁰ Ziegenbein,^{4b} and Roth and Peltzer¹¹ for octa-1,3,5,7-tetraenes. Thus, in the present work, we were primarily interested in exploring synthetic routes to octa-1,3,5,7-tetraenes and deca-1,3,5,7,9-pentaenes which might allow the isolation of more than one of the possible geometric isomers.

Three possible synthetic routes (A)–(C) are useful in the preparation of pure hexa-1,3,5-trienes uncontaminated by electrocyclization by-products (Scheme 1).

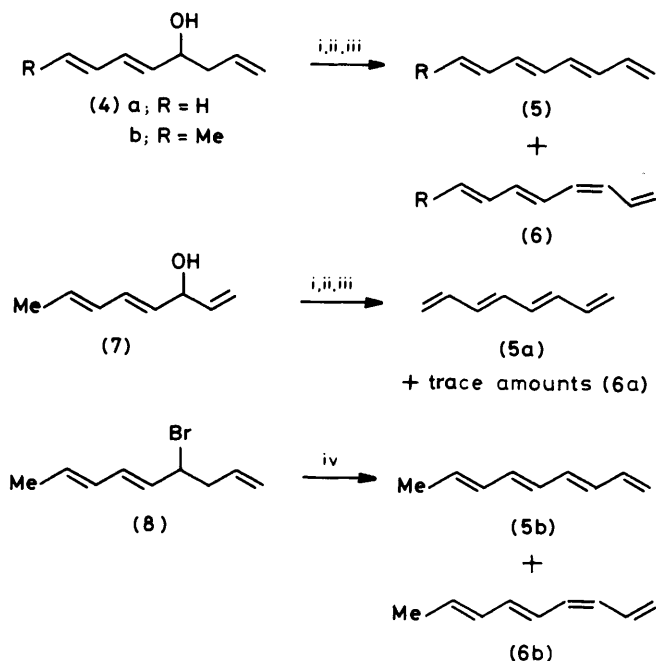


SCHEME 1 Reagents and conditions: i, PBr₃; ii, PhCH₂NMe₂; iii, aq. NaOH, 100 °C; iv, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-Me₂SO or other aprotic solvent; v, HCONMe₂, Me₂SO, or hexane

Since the product of method (A) is isolated by straight-lead steam distillation from the alkaline solution as it is formed, this method becomes less useful as the product volatility decreases. Methods (B) and (C) can be used at room temperature or below, and the product can be isolated quickly without the need for heating.

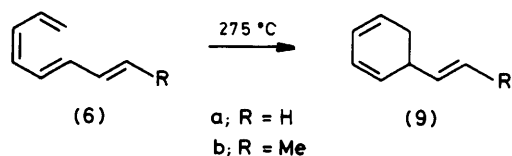
Octa-1,3,5,7-tetraenes (5a) and (6a) and nona-1,3,5,7-tetraenes (5b) and (6b) can be prepared by method (A). In both cases a mixture of (*E,E*)- and (*Z,E*)-isomers can be obtained (Scheme 2). Nona-1,3,5,7-tetraene can also be obtained in excellent yield by DBU-induced dehydrobromination of the intermediate trienyl bromide (8). The (*Z,E*)-isomers (6a,b) could be identified by flash-vacuum thermolysis at 275 °C, wherein they formed the appropriate 5-substituted cyclohexa-1,3-dienes (9). The corresponding (*E,E*)-isomers (5a,b) are unaffected under these conditions.

We were particularly interested in the synthesis and possible thermal reactions of (*E,Z,E*)-deca-1,3,5,7,9-pentaene (10), since there are three possible modes of electrocyclization (6π, 8π, or 10π). In keeping with the hexa-1,3,5-triene and octa-1,3,5,7-tetraene preparations, it would be desirable to prepare deca-1,3,7,9-tetraen-5-ol as a starting point for the decapentaene synthesis *via* either method (A) or (B). However, alcohols of this

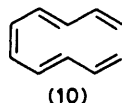


SCHEME 2 Reagents and conditions: i, ii, iii as for Scheme 1; iv, DBU-Et₂O

type are generally prepared by an appropriate Grignard procedure, similar to that used for the preparation of octa-1,5,7-trien-4-ol and nona-1,5,7-trien-4-ol (Scheme 3). Reaction of the (*E*)-penta-2,4-dienyl Grignard



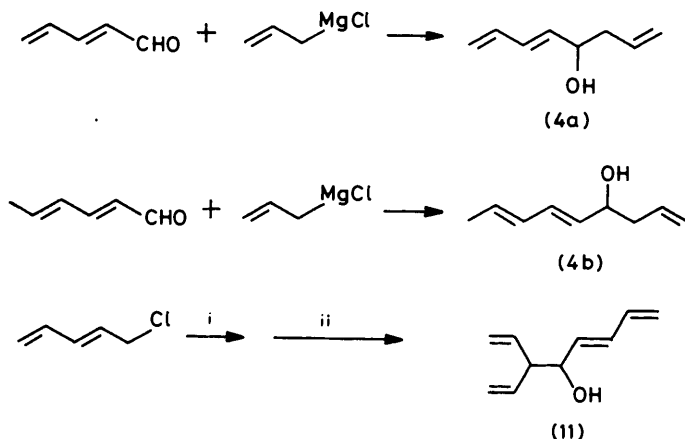
reagent with penta-2,4-dienal does not yield the desired decatetraenol, as had previously been reported by Woods and Schwartzman,² but instead gave (*E*)-3-vinylocta-1,5,7-trien-4-ol (11). This alcohol, when converted into a decapentaene by method (A), yielded 3-vinylocta-1,3,5,7-tetraene.



An alternate approach would be *via* (*E,E,E*)-deca-1,4,6,8-tetraen-3-ol (12), although it might be expected to produce only (*E,E,E*)-deca-1,3,5,7,9-pentaene (13) in a manner similar to the corresponding octatetraene synthesis described above. This indeed was the case; when the alcohol, prepared from (*E,E,E*)-octa-2,4,6-trienal and vinylmagnesium bromide, was converted into the decapentaene *via* method (A), only the (*E,E,E*)-isomer was obtained (in low yield).

Another possible approach was to synthesize the intermediate (*E,E*)-5-bromodeca-1,3,7,9-tetraene directly

from (*E,E*)-deca-1,3,7,9-tetraene (14) *via* allylic bromination, followed by DBU-induced dehydrobromination to the decapentaene. The allylic bromination, however, could only be carried out in poor yield, and the



SCHEME 3 Reagents: i, Mg-tetrahydrofuran; ii, (*E*)-penta-2,4-dienal

resulting bromodecatetraene yielded only the (*E,E,E*)-decapentaene when treated with DBU.

The last attempted preparation of (*E,Z,E*)-deca-1,3,5,7,9-pentaene (10) utilized a Wittig synthesis in which the 5,6-double bond was formed last. This approach has been used previously to obtain modest



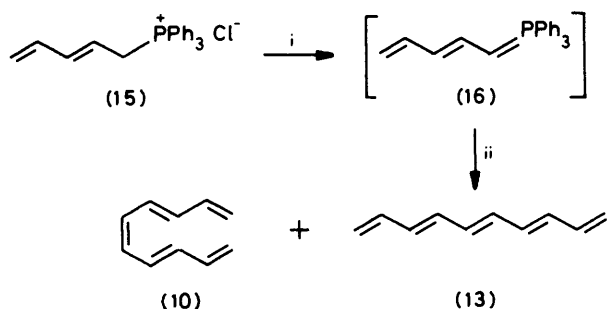
(only isomer)
Reagents and conditions: i, PBr₃; ii, PhCH₂NMe₂; iii, aq. NaOH, 100 °C

yields of substituted hexa-1,3,5-trienes^{10,12,13} with approximately 1 : 1 mixtures of *Z*- and *E*-configurations for the 3,4-double bond formed in the Wittig condensation process. Thus, the decapentaene was prepared (Scheme 4) from (*E*)-penta-2,4-dienal and (*E*)-penta-2,4-dienyltriphenylphosphonium chloride (15) using (i) *n*-butyl-lithium in hexane at -5 °C or (ii) potassium *t*-



(only isomer)
Reagents: i, *N*-Bromosuccinimide-CCl₄; ii, DBU-Me₂SO

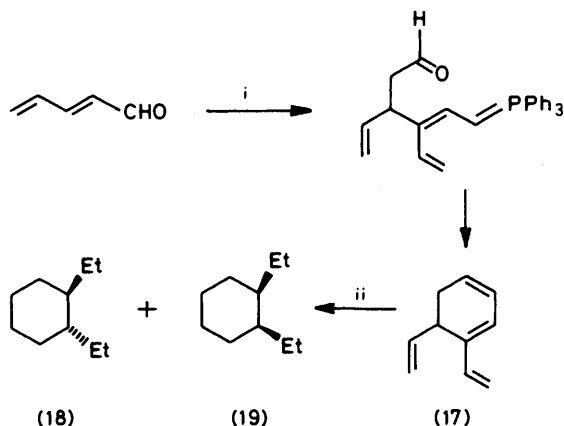
butoxide in dimethylformamide (DMF), both bases having been used for previous hexatriene Wittig synthesis. Under both sets of conditions, (*E,E,E*)-deca-1,3,5,7,9-pentaene (13) was formed, as well as several other products. None of these by-products had a u.v. absorption spectrum which was characteristic of a conjugated pentaene. Catalytic hydrogenation of the reaction mixture produced decane and *cis*- and *trans*-1,2-



SCHEME 4 Reagents: i, Bu^nLi -hexane or Bu^tOK -DMF; ii, (*E*)-penta-2,4-dienal

diethylcyclohexane (19) and (18) (major products) (Scheme 5), as well as decalin and tetralin as minor products, and several additional minor products which could not be identified. Neither cyclodecane nor 2-ethylcyclo-octane were formed.

If (*E,Z,E*)-deca-1,3,5,7,9-pentaene (10) had been formed in the initial Wittig condensation, only *cis*-1,2-diethylcyclohexane (19) should be found in the hydrogenation mixture. An alternative explanation would involve a condensation producing a divinylcyclohexa-1,3-diene, a process previously described by Bohlman¹⁴ and Dauben *et al.*¹⁵ 1,6-Divinylcyclohexa-1,3-diene (17)

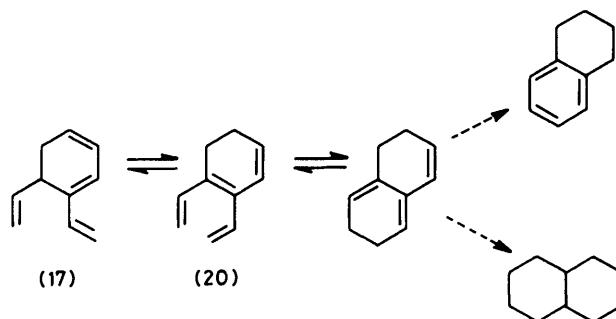


SCHEME 5 Reagents: i, Compound (16) *in situ*; ii, H_2 -Pd

would produce a mixture of *cis*- and *trans*-1,2-diethylcyclohexane upon hydrogenation. In addition, electrocyclic ring-closure of (*E,Z,E*)-decapentaene (10), followed by sigmatropic hydrogen migration to afford 1,6-divinylhexa-1,3-diene, could produce compound (17). In either case, further electrocyclization would yield intermediates leading to decalin or tetralin upon hydrogenation (Scheme 6).

At the present time we are not able to distinguish between the two possible mechanisms, nor have we been able to isolate pure reaction products other than the (*E,E,E*)-decapentaene (13) which crystallizes from the reaction mixture in the cold. The u.v. spectra of the other products were obtained by passing the g.l.c. effluent directly into spectro-grade solvent and analysing immediately; however, these products tend to polymerize upon preparatory liquid chromatography or when

trapped as neat liquids after g.l.c. Attempted independent syntheses of 1,6-divinylcyclohexa-1,3-diene (17) and the other possible intermediate, 1,2-divinylcyclohexa-1,3-diene (20), while desirable, have proved to be unsuccessful since the instability of vinylcyclohexadienes is well documented.^{17,16}



SCHEME 6

Condensation of (*E,E*)-hexa-2,4-dienal with the pentadienylphosphonium salt (15) yields one isomer of undeca-1,3,5,7,9-pentaene, while condensation of dodeca-2,4,6,8,10-pentaenal with methyltriphenylphosphonium iodide yields one isomer of trideca-1,3,5,7,9,11-hexaene. Both of these polyenes are unstable solids which polymerize rapidly. Neither compound was characterized apart from its u.v. and ^1H n.m.r. spectra.

EXPERIMENTAL

Gas-liquid chromatography (g.l.c.) was performed with a Hewlett-Packard 5480A dual-column instrument equipped with $\frac{1}{8}$ in \times 20 ft 15% Carbowax 20 M on Chromosorb W SS columns. U.v. spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer in 95% ethanol solutions. ^1H N.m.r. spectra were determined as solutions in CDCl_3 (SiMe_4 as internal reference) using Varian A-60A, JEOL PFT-100, and IBM NR 80 spectrometers. ^{13}C N.m.r. spectra were obtained at 20.1 MHz with an IBM NR 80 spectrometer. N.m.r. spectra were recorded for pure isomers, unless otherwise noted.

(*E,E*)- and (*Z,E*)-Octa-1,3,5,7-tetraene (5a) and (6a).—(a) A solution of (*E*)-octa-1,5,7-trien-4-ol² (4a) (10.2 g, 0.082 mol) in anhydrous diethyl ether (50 ml) was added dropwise to ice-cooled phosphorus tribromide (10 g, 0.037 mol) during 1 h. After the addition was complete the mixture was allowed to warm slowly to room temperature and was kept overnight. The mixture was then hydrolysed with ice-water, and the resulting mixture was neutralized by the careful addition of sodium carbonate. The crude bromide was extracted with diethyl ether (2×200 ml), and the extract was washed with water (2×200 ml) and dried (MgSO_4). After filtration, the solvent was removed under reduced pressure and the crude 5-bromo-octa-1,3,7-triene (11.6 g, 76%) was obtained as an unstable yellow lachrymatory liquid ($>95\%$ pure by g.l.c.).

The crude bromide was immediately dissolved in anhydrous diethyl ether (100 ml) and *N,N*-dimethylbenzylamine (20 g, 0.15 mol) was added to the solution which became cloudy and the crude ammonium salt precipitated as a brown, glassy deposit. The mixture was kept for 10 d at room temperature, after which time the liquid was decanted

and the residue was dissolved in water (20 ml). The resulting aqueous solution was extracted with diethyl ether to remove a small amount of suspended organic material, and was then heated to remove dissolved diethyl ether. The resulting clear amber solution was then added dropwise to a refluxing solution of sodium hydroxide (30 g) in water (50 ml) in a distillation apparatus. The distillate was collected in an ice-cooled flask containing pentane (100 ml) and, after the addition was complete, distillation was continued until no organic product was present in the distillate. A small quantity of the product condensed as a solid in the water condenser and was collected by dissolution in pentane. The pentane and aqueous phases were separated and the aqueous phase was extracted with pentane (100 ml). The combined pentane phases were washed in turn with 3*N* HCl (2 × 200 ml) and water (2 × 200 ml) and were then dried (MgSO₄). After filtration, the solvent was removed under reduced pressure to yield (*E,E*)- or (*Z,E*)-octa-1,3,5,7-tetraene (6.6 g, 94% based on crude bromide). Recrystallization from pentane yielded needles, m.p. 88–90 °C; $\lambda_{\max.}$ ($\epsilon_{\max.}$) 303 (53 000), 289 (54 300), 276 (37 000), 264 (19 900), and 252sh nm [lit.,² 303, 290, 277, and 268 nm]. G.l.c. analysis of the mother liquor, when compared with a pentane solution of the aforementioned isomer, revealed the presence of a second isomer, a small sample of which was trapped from the g.l.c. effluent in 95% EtOH and subjected to u.v. analysis: $\lambda_{\max.}$ 302, 289, 277, 265, and 255sh nm [lit.,^{4b} 302, 288.5, 276.5, 266, and 256sh nm]. When a small sample of the pentane solution containing ca. 10% of the two isomers was subjected to flash-vacuum thermolysis over Pyrex helices at 275 °C and the products analysed by g.l.c., one of the octatetraene peaks had disappeared while the other remained unchanged. One new product appeared, with $\lambda_{\max.}$ 259 nm, characteristic of a cyclic conjugated diene [lit.,¹⁷ 260 nm for 5-vinylcyclohexa-1,3-diene (9a) prepared from (*Z,E*)-octatetraene (6a)]. On the basis of the above results, we assign the structures of the two isomers as *E,E* and *Z,E*. In the original product, the isomer distribution is 59% *E,E* and 41% *Z,E*. The freshly recrystallized (*E,E*)-isomer (5a) has the following n.m.r. spectra: δ_{H} 4.9–5.5 (4 H, m, CH₂=) and 6.3 (6 H, s, CH=); δ_{C} 117.5, 133.2, 134.1, and 137.2 p.p.m.

(b) A solution of (*E,E*)-octa-1,4,6-trien-3-ol (7) (37.3 g, 0.30 mol) in anhydrous diethyl ether (100 ml) was added dropwise during 2 h to phosphorus tribromide (39 g, 0.144 mol) cooled in an ice-bath. The crude bromide was obtained in essentially quantitative yield in a manner identical to that described above with octa-1,5,7-trien-4-ol. The crude bromide, an unstable yellow lachrymatory oil, was immediately dissolved in anhydrous diethyl ether (400 ml) to which was then added *N,N*-dimethylbenzylamine (50 g, 0.37 mol). A precipitate of the ammonium salt began to form almost immediately and the mixture was kept for 2 d at room temperature. The glassy salt was dissolved in water (300 ml) as described previously and the resulting solution was added to aqueous sodium hydroxide (50 g in 1 l) under reflux in a distillation apparatus. Octa-1,3,5,7-tetraene was isolated in a manner similar to that described in (a) above (5.6 g, 18%). G.l.c. analysis showed essentially pure (*E,E*)-isomer (5a), with only a trace of the (*Z,E*)-isomer (6a).

(*E,E*)-Nona-1,5,7-trien-4-ol (4b).—A solution of (*E,E*)-hexa-2,4-dienal (67 g, 0.70 mol) in anhydrous diethyl ether (150 ml) was added to an ice-cooled solution of allyl-

magnesium bromide prepared from allyl bromide (1 mol) in the usual manner. When the addition was complete the product was stirred at room temperature for 1 h. The mixture was then hydrolysed with a mixture of ice-water and ammonium chloride. The ethereal phase containing the product was separated, the aqueous phase was extracted with diethyl ether (2 × 250 ml), and the combined ethereal phases were washed with water (500 ml). After being dried (MgSO₄), the extract was filtered and evaporated to dryness under reduced pressure to afford (*E,E*)-nona-1,5,7-trien-4-ol (88 g, 92%) as an oil, b.p. 64–65 °C at 0.5 mmHg; n_{D}^{22} 1.4998, δ_{H} 1.70 (3 H, d, *J* 7 Hz, CH₃), 2.30 (2 H, t, *J* 7 Hz, CH₂), 3.0 (1 H, s, OH), 4.1 (1 H, q, CHOH), 4.6–5.2 (2 H, m, CH₂=), and 5.2–6.7 (5 H, m, CH=C) (Found: C, 77.9; H, 10.65. Calc. for C₉H₁₄O: C, 78.21; H, 10.31%).

(*E,E,E*)- and (3*Z*,5*E*,7*E*)-Nona-1,3,5,7-tetraene (5b) and (6b).—(a). A solution of (*E,E*)-nona-1,5,7-trien-4-ol (4b) (69.1 g, 0.50 mol) in anhydrous diethyl ether (100 ml) was added dropwise to ice-cooled phosphorus tribromide (69 g, 0.25 mol) during 2 h. The crude bromide was obtained in the same way as described for the octatetraenes (94.5 g, 95%), and was immediately dissolved in anhydrous diethyl ether (600 ml) and treated with *N,N*-dimethylbenzylamine (100 g, 0.74 mol). The mixture was kept at room temperature for 2 d, and the glassy product was then dissolved in water (500 ml) in the manner described for octatetraene. The resulting solution was added to refluxing aqueous sodium hydroxide (50 g in 1 l) as above. Nona-1,3,5,7-tetraene (4.1 g, 7% over two steps) was obtained as a crystalline solid, $\lambda_{\max.}$ ($\epsilon_{\max.}$) 305 (43 400), 291 (45 800), 278 (31 400), 267 (17 700), and 255sh nm; δ_{H} 1.80 (3 H, d, *J* 7 Hz, CH₃), 4.9–6.0 (2 H, m, CH₂=), and 6.0–6.5 (7 H, s, CH=). The crystalline solid softens at 130 °C and decomposes at 140–147 °C.

(b). A solution of (*E,E*)-nona-1,5,7-trien-4-ol (4b) (15.3 g, 0.11 mol) in anhydrous diethyl ether (50 ml) was added to phosphorus tribromide (15.0 g, 0.055 mol) as described above, but the crude bromide was not isolated. The ethereal solution of the bromide was reduced to 50 ml volume under reduced pressure and was added dropwise to a solution of DBU (22.8 g, 0.15 mol) in anhydrous diethyl ether (100 ml). A precipitate began to form immediately, and after the addition was complete the mixture was refluxed (water-bath) during 1 h. The product was poured into ice-water and the ether layer was separated. After further ethereal extraction of the aqueous phase, the combined ethereal phases were washed in turn with 3*N* HCl (2 × 100 ml) and water (2 × 100 ml) and were then dried (MgSO₄). The solvent was removed under reduced pressure to yield crystalline nona-1,3,5,7-tetraene (9.9 g, 75%). G.l.c. analysis showed the presence of two isomers. Flash-vacuum pyrolysis at 275 °C of a small sample dissolved in pentane, followed by g.l.c. analysis, showed the disappearance of one of the isomers while the other remained unchanged. One new product appears, $\lambda_{\max.}$ 259 nm. On this basis the thermally unstable isomer is assigned a *Z,E,E* configuration. The other isomer obtained in this preparation and in part (a) above is assigned the *E,E,E* configuration. G.l.c. analysis of the original product indicated 68% (*E,E,E*)- and 32% (*Z,E,E*)-isomer distribution; δ_{C} 18.332, 116.7, 130.3, 130.4, 132.1, 132.7, 133.7, 133.9, and 137.4 p.p.m. [(*E,E,E*)-isomer]; $\lambda_{\max.}$ ($\epsilon_{\max.}$) 305 (43 400), 291 (45 800), 278 (31 400), 267 (17 700), and 255sh nm (mixture of 68% *E,E,E*, 32% *Z,E,E*). Each isomer was trapped separately from the g.l.c. effluent in 95% EtOH: (*E,E,E*)-

(5b) λ_{max} 305, 291, 278, 267, and 255sh nm; (*Z,E,E*)-(6b) λ_{max} 307, 293, 280, and 268 nm.

(*E*)-3-Vinylocta-1,3,5,7-tetraene.—A solution of (*E*)-3-vinylocta-1,5,7-trien-4-ol¹⁸ (11) (29 g, 0.21 mol) in anhydrous diethyl ether (100 ml) was added to phosphorus tribromide (30 g, 0.11 mol) as described above but the crude bromide was not isolated. The ethereal solution (300 ml) of the product was treated directly with *N,N*-dimethylbenzylamine (50 g, 0.37 mol). Precipitation of the ammonium salt occurred almost immediately, and the mixture was kept at room temperature for 2 d. The liquid was decanted and the glassy brown salt was dissolved in water (200 ml) and suspended impurities were extracted into diethyl ether. The aqueous solution of the salt was then added to refluxing aqueous sodium hydroxide (50 g in 1 l) as before and the distillate was collected. A large quantity of polymer remained in the distillation flask. The product was extracted with pentane, and the extract was washed twice with 3*N* HCl and then twice with water and dried (MgSO₄). The pentane was removed under reduced pressure, and a yellowish waxy product, (*E*)-3-vinylocta-1,3,5,7-tetraene (1.2 g, 4%), was obtained; λ_{max} (ϵ_{max}) 334 (12 500), 317 (21 100), and 305 (20 100) nm; δ_{H} 4.3—5.6 (6 H, m, CH₂=) and 5.7—7.8 (6 H, m, CH=). When purification by g.l.c. was attempted, only one peak was evident in the chromatogram; however, its u.v. spectrum was significantly different from that of the starting pentaene, λ_{max} 309 and 299sh nm, and was characteristic of a divinylcyclohexadiene. We conclude that ring closure occurs during the chromatography to afford 2,5-divinylcyclohexa-1,3-diene. Similar behaviour has been reported¹⁷ for 3-vinylhexa-1,3,5-triene which converts into 2-vinylcyclohexa-1,3-diene upon g.l.c. When a pentane solution of 3-vinylocta-1,3,5,7-tetraene or 2,5-divinylcyclohexa-1,3-diene is subjected to flash-vacuum thermolysis at 375 °C another new product is obtained, whose u.v. spectrum is identical with that of 1,4-divinylcyclohexa-1,3-diene: * λ_{max} 345, 328, 313, 300, and 287sh nm. This appears to confirm our structural assignments of both 3-vinylocta-1,3,5,7-tetraene as the reaction product and 2,5-divinylcyclohexa-1,3-diene as its primary ring-closure product.

(*E,E*)-Deca-1,3,5,9-tetraene (14).—(*E*)-5-Chloropenta-1,3-diene (24.6 g, 0.24 mol) was added to magnesium metal (20 g, 0.83 g-atom) in anhydrous diethyl ether (200 ml) at 0 °C in the manner typical for the preparation of allylic Grignard reagents. After the addition was complete the ice-bath was removed and the solution of the Grignard reagent was decanted from the excess of magnesium under nitrogen. The excess of magnesium remaining was then further rinsed with diethyl ether (2 × 50 ml) and the ethereal solutions were combined. The Grignard solution was cooled to 0 °C and was treated dropwise with a second portion of (*E*)-5-chloropenta-1,3-diene (18 g, 0.18 mol) in diethyl ether (50 ml). After the addition was complete the mixture was stirred at room temperature for 3 h. Water (50 ml) was then added dropwise to decompose any excess of Grignard reagent and then the mixture was poured into ice-water and the ethereal layer was separated. The aqueous layer was extracted with diethyl ether (2 × 100 ml), and the combined ethereal solutions were washed with water and dried (MgSO₄). After filtration, the product was distilled at reduced pressure to afford a clear liquid (20.1 g, 86%).

* Authentic 1,4-divinylcyclohexa-1,3-diene may be prepared from 1,4-divinylcyclohexane-1,4-diol by a variety of procedures which will be reported in a future communication.

G.l.c. analysis showed the presence of two components in a ca. 1:1 ratio. Fractional distillation yielded (*E*)-6-vinylocta-1,3,7-triene, b.p. 52—54 °C at 15 mmHg; n_{D}^{24} 1.5046; δ_{H} 2.0—2.4 (2 H, m, CH₂), 2.5—3.1 (1 H, m, 6-H), 4.8—5.2 (6 H, m, CH₂=), and 5.4—6.7 (5 H, m, CH=) and (*E,E*)-deca-1,3,7,9-tetraene (14), b.p. 68—70 °C at 20 mmHg; n_{D}^{24} 1.5046; δ_{H} 2.0—2.3 (4 H, m, CH₂), 4.8—5.3 (4 H, m, CH₂=), and 5.4—6.6 (6 H, m, CH=) (Found: C, 89.45; H, 10.3. Calc. for C₁₀H₁₄: C, 89.49; H, 10.51%).

(*E,E,E*)- and (*E,Z,E*)-Deca-1,3,5,7,9-pentaene (13) and (10).—(a) Authentic (*E,E,E*)-deca-1,3,5,7,9-pentaene (13) was obtained by catalytic dehydration of (*E,E,E*)-deca-1,4,6,8-tetraen-3-ol (12) over alumina (Houdry HA-100A) at 300 °C and 15 min, essentially by the method of D'Amico *et al.*⁷ The product was recrystallized from pentane to give needles which polymerized rapidly; λ_{max} 334, 318, 303, 291, and 279 nm (lit.^{6,7,19} 334, 318, 304, 291, and 280 nm); δ_{H} 5.0—5.3 (4 H, m, CH₂=) and 6.3 (8 H, s, CH=).

(b) (*E,E*)-Deca-1,3,7,9-tetraene (14) (2.3 g, 0.017 mol) was dissolved in CCl₄ (50 ml) and *N*-bromosuccinimide (NBS) (3.0 g, 0.017 mol) and benzoyl peroxide (0.1 g) were added in turn to the solution. The mixture was then refluxed for 14 h. The crude product was filtered to remove succinimide and residual NBS and the filtrate was evaporated under reduced pressure. The crude bromide was then treated with DBU (0.026 mol, 1.5 equiv.) in dimethyl sulphoxide (DMSO) (100 ml) at 60 °C for 2 h, after which time the solution was extracted with pentane (2 × 200 ml). The combined extracts were washed in turn with 3*N* HCl (2 × 100 ml) and water (2 × 100 ml) and then dried (MgSO₄) and reduced in volume to ca. 50 ml whence deca-1,3,5,7,9-pentaene could be crystallized from the mixture by cooling in solid CO₂-acetone. A u.v. spectrum (λ_{max} 334, 318, 303, 291, and 279 nm) and g.l.c. analysis revealed only the (*E,E,E*)-isomer (13) in low yield (0.2 g), together with some starting material. No other products were found.

(c) (*E*)-Penta-2,4-dienyltriphenylphosphonium chloride (15) (36.5 g, 0.1 mol) was slurried with pentane (300 ml) under nitrogen. A solution of *n*-butyl-lithium (0.1 mol) in hexane was then added dropwise to the slurry and the mixture was stirred for 0.5 h at room temperature. A solution of (*E*)-penta-2,4-dienal (8.2 g, 0.1 mol) in pentane (100 ml) was then added dropwise to the deep red solution which was cooled in a salt-ice-water-bath at -5 °C, and a white solid precipitated immediately. After the addition was complete, an aliquot was taken which indicated no residual aldehyde (u.v.). After being stirred for another 0.5 h the mixture was filtered and the pale yellow filtrate was stored at -78 °C in the presence of hydroquinone (0.1 g) under nitrogen for 36 h, and was then refiltered. The solution was allowed to warm to 0 °C, and was then evaporated under reduced pressure to ca. 15 ml volume; it was then again filtered. G.l.c. analysis of the filtrate showed ten product peaks, four major and six minor. Of the major products, one had a triene absorption in the u.v. (λ_{max} 273, 262, and 253 nm), the second corresponded to (*E,E,E*)-deca-1,3,5,7,9-pentaene (13) (λ_{max} 334, 318, 303, 289, and 278 nm), the third had λ_{max} 273, 262, and 253 nm with a secondary absorption at 232, 224, and 218 nm, and the final major product showed λ_{max} 308, 295, 283, and 273 nm. [Relative proportions (g.l.c.) 2.1:1.7:1:1.2.]

The first product was identified as nona-1,3,5-triene (2; R = Prⁿ), presumably formed by addition of *n*-butyllithium to the pentadienal, followed by dehydration under

the reaction conditions or during work-up; λ_{\max} 273, 262, and 253 nm; δ_{H} 0.83–0.97 (3 H, t, J 7 Hz, CH_3), 0.98–1.46 (2 H, m, CH_2CH_3), 1.53–2.1 (2 H, m, $\text{CH}_2\text{CH}=\text{}$), and 5.1–6.4 (7 H, m, $\text{CH}=\text{}$).

Hydrogenation of the mixture in hexane solution with 5% Pd-C catalyst produced an extremely complex mixture of over twenty compounds. Several major compounds could be identified: *n*-decane, *cis*- and *trans*-1,2-diethylcyclohexane (19) and (18), respectively, decalin, and tetralin. No ethylcyclo-octane or cyclodecane was present.

(d) The phosphonium salt (15) (36.5 g, 0.1 mol) was slurried in (DMF) (250 ml), after which potassium *t*-butoxide (13.4 g, 0.12 mol) was added and the mixture was purged with nitrogen. After being stirred during 1 h the deep-red mixture was cooled to -5°C and a solution of (*E*)-penta-2,4-dienal (8.2 g, 0.1 mol) in DMF (50 ml) was added dropwise. After the addition was complete, the mixture was stirred for 1.5 h at -5°C and extracted with pentane (3×50 ml). The combined extracts were concentrated to 3 ml, any DMF which separated being discarded. G.l.c. analysis showed the presence of ten products. (*E,E,E*)-Deca-1,3,5,7,9-pentaene (13), and a product identical with one of the products from the Bu^nLi reaction (λ_{\max} 308, 295, 283, and 273 nm), were the main condensation products.

(e) The phosphonium salt (15) (20.2 g, 0.055 mol) was dissolved in DMSO (200 ml). Potassium *t*-butoxide (6.1 g, 0.055 mol) was then added and the system was purged with nitrogen and stirred for 2 h. A solution of (*E*)-penta-2,4-dienal (4.1 g, 0.05 mol) in DMSO (20 ml) was then added and the mixture was stirred for a further 2 h at room temperature. The mixture was then extracted with pentane (2×200 ml). The combined yellow extracts were washed with water and dried (MgSO_4). After filtration the extract was reduced to 30 ml volume under a nitrogen stream at 0°C . Triphenylphosphine oxide precipitated from solution at this point, and the yellow pentane solution was decanted. U.v. analysis of the solution showed no decapentaene present. However, a product was present which showed λ_{\max} 308, 295, 283, and 273 nm, identical with the spectrum of one of the major products in the Bu^nLi -hexane and KO^tBu -DMF reactions. Attempts at further isolation and identification of this product by a variety of techniques yielded only polymeric material. Since this spectrum is very similar to that of 1-vinylcyclohexa-1,3-diene, it is possible that this labile product is either 1,6-divinylcyclohexa-1,3-diene (17) or 1,2-divinylcyclohexa-1,3-diene (20), neither of which has been characterized before.

(f) A solution of (*E,E,E*)-deca-1,4,6,8-tetraen-3-ol⁷ (12) (20.0 g, 0.13 mol) in anhydrous diethyl ether (200 ml) was added dropwise to stirred phosphorus tribromide (70 g, 0.26 mol) at 0°C . The mixture was stirred for 3 h at room temperature, then the mixture was poured into ice-water and the bromide was isolated by the method described previously. The ethereal solution of the crude bromide was treated with *N,N*-dimethylbenzylamine (35 g, 0.26 mol). A milky solution formed which deposited a glassy ammonium salt after being kept for 24 h. This mixture was cooled in ice and the liquid was decanted. The solid was dried in a nitrogen stream to afford the crude ammonium salt (2.9 g, 62%) which was then dissolved in water (400 ml). Suspended organic impurities were extracted into diethyl ether and the aqueous phase was heated to remove dissolved diethyl ether. The aqueous solution was added dropwise to

refluxing aqueous sodium hydroxide (40 g in 800 ml) in a distillation apparatus as before. The distillate was collected in pentane (50 ml) cooled to 0°C . The pentane layer was separated and was washed in turn with 3*N* HCl (2×50 ml) and water (2×50 ml), then dried (MgSO_4). The pentane solution was reduced in volume to 5 ml and g.l.c. analysis revealed the presence of the (*E,E,E*)-deca-pentaene (13) (λ_{\max} 334, 318, 303, 289, and 278sh nm) and a product previously found in the Wittig reactions (λ_{\max} 308, 295, 283, and 273sh nm). Two additional products were also present (λ_{\max} 253nm; λ_{\max} 278, 267, and 258sh nm). All these products were formed in very low overall yield from the ammonium salt. A large quantity of polymeric material remained in the distillation pot.

Undeca-1,3,5,7,9-pentaene.—(a) The phosphonium salt (15) (3.64 g, 0.01 mol) was slurried in DMF (70 ml), and potassium *t*-butoxide (1.68 g, 0.011 mol) was added to the slurry, and the mixture was purged with nitrogen. After being stirred for 2 h at room temperature, the red mixture was cooled to -10°C and (*E,E*)-hexa-2,4-dienal (0.96 g, 0.01 mol) was added. A white precipitate immediately formed. U.v. analysis of aliquots of the solution showed that the aldehyde was totally consumed in 1.5 h. The mixture was extracted with pentane (3×50 ml) and the combined extracts were immediately cooled to -78°C and concentrated to 75 ml under reduced pressure. The solution was maintained at -78°C for several minutes during which time a solid slowly crystallized out and was filtered off and dried; λ_{\max} 339, 323, 308, 295, and 280sh nm; δ_{H} 1.7–1.9 (3 H, d, J 6 Hz, CH_3), 5.0–5.5 (2 H, m, $\text{CH}_2=\text{}$), and 5.5–6.8 (9 H, m, $\text{CH}=\text{}$); these data suggest the product is the title undecapentaene. The solid oxidized quickly in air, and after a few minutes would no longer dissolve in pentane. No further attempts were made to characterize this product.

(b) This reaction was repeated on the same scale in pentane but with *n*-butyl-lithium (0.01 mol) as the base to yield the desired ylide. After the addition of (*E,E*)-hexa-2,4-dienal (0.96 g, 0.1 mol) at -10°C , u.v. analysis indicated that undeca-1,3,5,7,9-pentaene was the only product.

Trideca-1,3,5,7,9,11-hexaene.—Methyltriphenylphosphonium iodide (1.2 g, 0.003 mol) was slurried in DMF (100 ml) and potassium *t*-butoxide (0.5 g, 0.0045 mol) was then added. The system was purged with nitrogen and stirred during 0.5 h to yield a pale-yellow solution. Dodeca-2,4,6,8,10-pentaenal^{20,21} (0.5 g, 0.003 mol) in DMF (25 ml) was added dropwise to the solution at 0°C . The mixture was then stirred for 1 h, then was extracted with pentane (3×25 ml). U.v. analysis of the extracts revealed a characteristic polyene spectrum: λ_{\max} 345, 327, 312, and 297sh nm. The combined extracts were reduced to ca. 20 ml volume under nitrogen and were then cooled to -78°C . A crystalline product which slowly formed was filtered off and gave the same u.v. spectrum as did the extract, suggesting the product to be the title tridecahexaene. The solid polymerized very rapidly and could not be characterized further.

[2/206 Received, 5th February, 1982]

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