3-Alkoxypropenals as Precursors in the Synthesis of Conjugated and Semiconjugated Polyenes: Methyl-Substituted Octa- and Nona-tetraenes[1]

Charles W. Spangler,* Ray K. McCoy, and Alexa A. Karavakis
The Michael Faraday Laboratories, Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.

Vinylic and allylic Grignard reagents react cleanly and rapidly with 3-ethoxypropenal and 2-methyl-3-ethoxypropenal to produce excellent yields of conjugated and semiconjugated dienals useful in the subsequent preparation of substituted octa- and nona-trienols. Variations in the substitution pattern allow the preparation and isolation of 2-, 3-, and 4-methylocta-1,3,5,7-tetraenes, nona-1,3,5,8-tetraene, and 5-methylnona-1,3,5,8-tetraene in good yield from the octa- and nona-trienols. Thus oxopropenylation of unsaturated Grignard reagents allows the straightforward preparation of numerous previously unknown and uncharacterized polyenes.

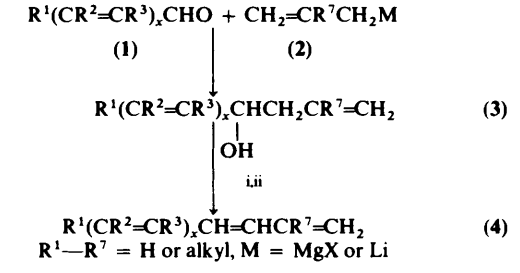
The synthesis of both parent and substituted conjugated and semiconjugated polyenes has become increasingly important during the past decade due to a continuing interest in pericyclic reaction processes,[2] theoretical interpretation of polyene electronic spectra,[3] further examples of polyene pheromone activity,[4] polyenylic moieties in compounds with mutagenic properties,[5] and most recently the proposal of the crystal structure of *E,E*-octa-1,3,5,7-tetraene as a model structure for semicrystalline polyacetylene.[6] However, this increased interest has been focused primarily on unsubstituted polyenes containing, at most, three or four double bonds. Very few substituted octa- or nona-tetraenes, either fully conjugated or partially conjugated, have been fully characterized. We now report a synthetic sequence which will allow the preparation of a wide variety of conjugated and partially conjugated polyenes with four or more double bonds.

In general, recently reported polyene syntheses have utilized either a Wittig approach[2d,g,4,7] or mild elimination reactions.[2] The success of both approaches requires the availability of appropriately substituted polyenals. With the exception of sorbaldehyde (hexa-2,4-dienal), however, very few aliphatic polyenals are generally available, and most literature preparations report disappointingly low if not dismal yields. Spangler and Little[2g] recently reported that attempted syntheses of deca-1,3,5,7,9-pentane *via* Wittig reactions yield an extremely complex set of reaction products whose diversity can best be explained by conjugate as well as normal addition. For this reason Wittig approaches to aliphatic polyene synthesis are increasingly limited as the number of ene units increases. Thus, it would appear that polyenols still represent the best precursors to both substituted and higher polyenes (Scheme 1).

We have recently reported[8] a general, convenient synthesis of both conjugated and semiconjugated alkadienals from readily available 3-ethoxypropenals (Scheme 2).

Rustemeier and Breitmaier[9] had first proposed the possibility of oxopropenylation of alkyl Grignard reagents, but only obtained modest yields (28—56%) of α,β-unsaturated aldehydes. After extensive revision of their procedure, however, we were able to obtain both fully conjugated and semiconjugated alkadienals from allylic and vinylic Grignard reagents in excellent yield (Table).

In all cases the reaction proceeds *via* 1,2-carbonyl addition followed by elimination of EtOH from the intermediary ethoxy alcohols in acid media. If the hydrolysis of the original Grignard complex is carried out under cold neutral conditions (ice–water), the intermediary alcohols can be isolated (distilled) in



Scheme 1. *Reagents and conditions:* i, PBr_3, 0 °C; ii, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), hexane, 50—60 °C

reasonable yield (Scheme 3): however, they are extremely acid labile. Treatment of the intermediary alcohols at 25 °C with a catalytic quantity of PTSA for 15 min was usually sufficient to convert the ethoxy alcohols into the alkadienals without rearrangement in the case of the semiconjugated examples.

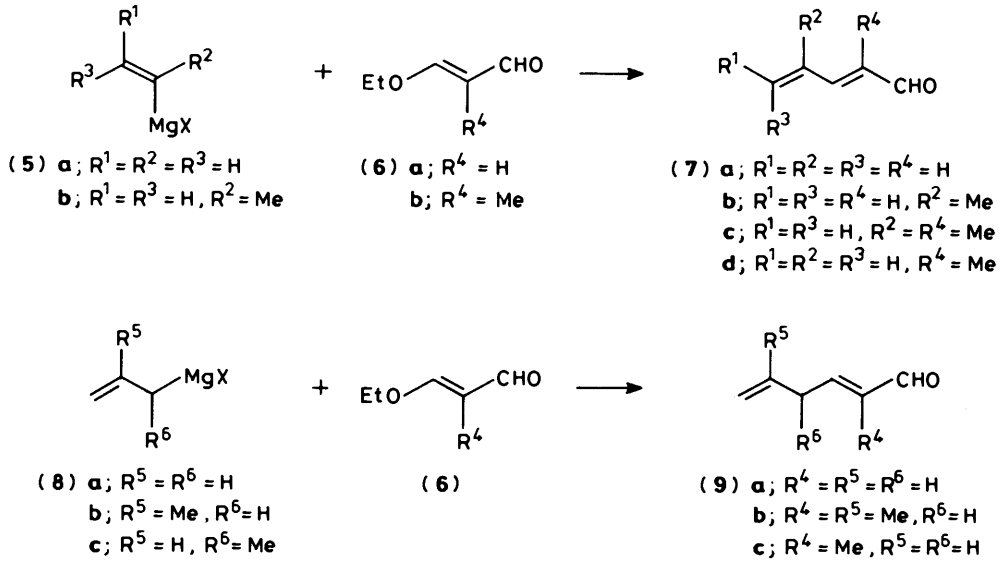
Control of substitution in the ethoxypropenal–Grignard addition and in the subsequent conversion of the intermediary alkadienals into alkatrienols allows preparation of any given series of substituted polyenes. We had previously reported[2g] the preparation of nona-1,3,5,7-tetraene. The 2-Me, 3-Me, and 4-Me positional isomers were prepared as shown in Scheme 4.

In a similar fashion, partially conjugated tetraenes may also be prepared, *e.g.* nona-1,3,5,8-tetraene (**15**) and 5-methylnona-1,3,5,8-tetraene (**17**), as shown in Scheme 5.

In the above two sequences there was very little tendency for isomerization to the fully conjugated tetraene, < 2% in the case of tetraene (**15**), while there was no detectable rearrangement in the preparation of compound (**17**). Should this prove to be a general phenomenon, then this route shows great promise for preparation of interrupted conjugation isomers. In general, we believe that the above schemes have shown the generality of using ethoxyalkenals as precursors for conjugated polyene synthesis, and future polyene synthesis should be a much easier task, particularly when a family of related isomers is desired.

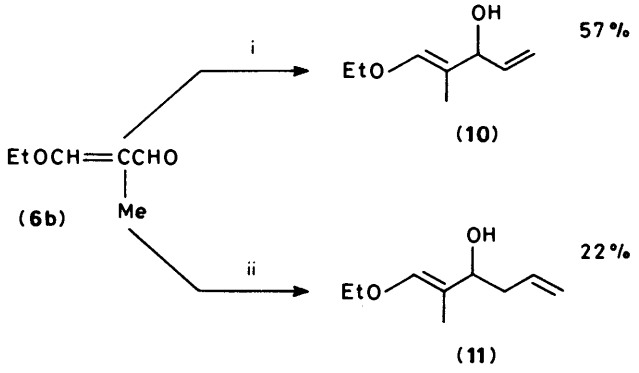
Experimental

Gas-liquid chromatography (g.l.c.) was performed with a Hewlett Packard 5480A dual-column instrument equipped with $\frac{1}{8}$ in × 6 or 20 ft 15% Carbowax 20M on Chromosorb W SS columns. U.v. spectra were recorded with a Varian 2290



Scheme 2.

spectrophotometer, for 95% ethanol solutions. ^1H and ^{13}C N.m.r. spectra were determined as solutions in $CDCl_3$ ($SiMe_4$ as internal reference) using an IBM 200 spectrometer. N.m.r. spectra were recorded for pure isomers unless otherwise noted. C, H, N analyses were carried out in our laboratories with a Perkin-Elmer Model 240 Analyzer by Paulanne Rider.



Scheme 3. *Reagents and conditions:* i, (**5a**; X = Br), then water, 0 °C; ii, (**8a**; X = Br), then water, 0 °C

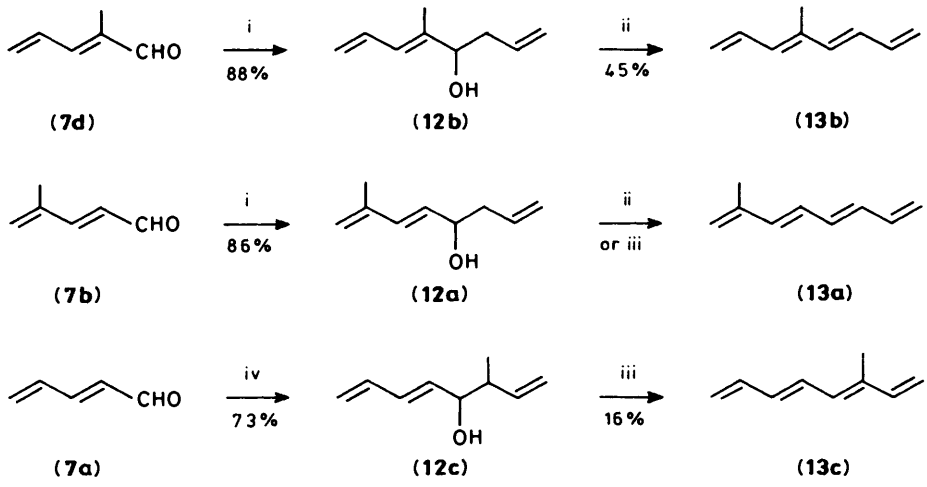
2-Methylpenta-2,4-dienal (**7d**).—A solution of 3-ethoxy-2-methylpropenal (**6b**)* (52.8 g, 0.46 mol) in anhydrous diethyl ether (100 ml) was added dropwise to a solution of vinylmagnesium bromide (**5a**; X = Br) [prepared from vinyl bromide (0.6 mol)] at 0 °C. The resulting mixture was stirred for an additional 0.5 h at room temperature, after which it was hydrolysed by being poured into a mixture of ice–saturated aqueous ammonium chloride. 3M-HCl (200 ml) was then added, and the product mixture was stirred for several minutes before finally being extracted with ether (3 × 200 ml). The combined extracts were washed with brine (2 × 200 ml) and dried ($MgSO_4$). Distillation at reduced pressure yielded essentially pure (*E*)-2-methylpenta-2,4-dienal (**7d**) [< 5% (*Z*)], b.p. 47—49 °C (20 mmHg) (31 g, 70%); n_D^{25} 1.5153 [< 5% (*Z*)]; δ_H 1.8 (3 H, s, Me), 5.0—7.0 (4 H, m, CH=), and 9.5 (1 H, s, CHO); 2,4-dinitrophenylhydrazone, m.p. 165—166 °C (lit.,[10] 170—172 °C) (Found: C, 52.0; H, 4.7; N, 20.5. Calc. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.29%).

4-Methylpenta-2,4-dienal (**7b**).—A solution of 3-ethoxypropenal (**6a**)[11] (15 g, 0.15 mol) in anhydrous ether (100 ml) was added dropwise to a solution of isopropenylmagnesium bromide (**5b**; X = Br) [prepared from 2-bromopropene (0.2 mol)] in anhydrous tetrahydrofuran (THF) (200 ml). The work-up and isolation procedure was similar to that described for 2-methylpenta-2,4-dienal. Distillation at reduced pressure yielded (*E*)-4-methylpenta-2,4-dienal (**7b**) (11.3 g, 78%), b.p. 28—30 °C (1 mmHg); n_D^{20} 1.5085; δ_H 2.0 (3 H, s, Me), 5.5 (2 H, d, *J* 1 Hz, CH_2=), 6.1 (1 H, dd, *J* 16 and 9 Hz, =C*H*CHO), 7.2 (1 H, d, *J* 16 Hz, C*H*=CHCHO), and 9.6 (1 H, d, *J* 9 Hz, CHO); 2,4-dinitrophenylhydrazone, m.p. 133—135 °C (lit.,[10] 132—133 °C) (Found: C, 51.9; H, 4.6; N, 19.95. Calc. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.29%).

2-Methylhexa-2,5-dienal (**9c**).—A solution of 3-ethoxy-2-methylpropenal (**6b**) (91 g, 0.80 mol) in anhydrous ether (100 ml) was added dropwise to a solution of allylmagnesium bromide (**8a**; X = Br) [prepared from allyl bromide (1 mol)] in anhydrous ether (500 ml). The work-up and isolation procedure was similar to that described above for 2-methylpenta-2,4-dienal. Distillation at reduced pressure yielded (*E*)-2-methylhexa-2,5-dienal (**9c**) (74 g, 84%), b.p. 28—30 °C (0.5 mmHg); n_D^{29} 1.4674; δ_H 1.8 (1 H, s, Me), 3.0—3.4 (2 H, m, CH_2), 5.0—5.4 (2 H, m, CH_2=), 5.6—6.2 (1 H, m, CH_2=C*H*), 6.4—6.7 (1 H, m, 3-H), and 9.4 (1 H, s, CHO); 2,4-dinitrophenylhydrazone, m.p. 148—150 °C (Found: C, 53.65; H, 5.0; N, 19.3. Calc. for $C_{13}H_{14}N_4O_4$: C, 53.78; H, 4.86; N, 19.30%).

2,5-Dimethylhexa-2,5-dienal (**9b**).—A solution of 3-ethoxy-2-methylpropenal (**6b**) (22.8 g, 0.20 mol) in anhydrous ether (100 ml) was added dropwise to a solution of 2-methylprop-2-enylmagnesium chloride (**8b**; X = Cl) [prepared from 3-chloro-2-methylpropene (0.3 mol)] at 0 °C. The work-up and isolation were similar to those described above for 2-methylpenta-2,4-dienal. Distillation at reduced pressure yielded (*E*)-2,5-dimethylhexa-2,5-dienal (**9b**) [< 5% (*Z*) isomer], b.p. 32 °C (1 mmHg). The first fraction (16.7 g) contained pure aldehyde. The distillation residue was stirred at room temperature for 3 h with a catalytic amount (0.1 g) of PTSA and redistilled to yield

* Aldrich Chemical Co.



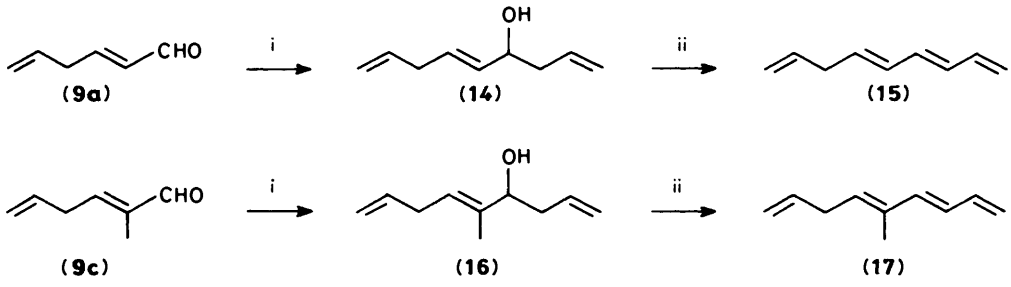
Scheme 4. *Reagents and conditions:* i, (**8a**; X = Br); ii, PBr_3, Et_2O, 0 °C, then DBU, hexane, 50 °C; iii, PBr_3, Et_2O, 0 °C; then $C_6H_5CH_2NMe_2$; then aq. NaOH, distil; iv, (**8a**; X = Cl)

Table. Preparation of alkadienals from 3-ethoxypropenals

$$R^1MgX + EtOCH{=}CR^2CHO \longrightarrow R^1CH{=}CR^2CHO$$

R^1	Grignard	R^2	Propenal	Aldehyde	(%) yield[a,b]
$CH_2{=}CHCH_2$	(**8a**)	Me	(**6b**)	(**9c**)	84
$CH_2{=}CH$	(**5a**)	Me	(**6b**)	(**7d**)	70
$CH_2{=}C(Me)$	(**5b**)	Me	(**6b**)	(**7c**)	73
$CH_2{=}C(Me)CH_2$	(**8b**)	Me	(**6b**)	(**9b**)	65[c]
$CH_2{=}CH$	(**5a**)	H	(**6a**)	(**7a**)	79
$CH_2{=}CHCH_2$	(**8a**)	H	(**6a**)	(**9a**)	78
$CH_2{=}C(Me)$	(**5b**)	H	(**6a**)	(**7b**)	73

[a] Distilled yield of pure *E* aldehydes. [b] All products were identified by ^1H n.m.r. and C, H, N analysis of 2,4-dinitrophenylhydrazone derivatives. [c] After treatment with catalytic toluene-*p*-sulphonic acid (PTSA).



Scheme 5. *Reagents and conditions:* i, (**8a**; X = Br); ii, PBr_3, Et_2O, 0 °C; then DBU, hexane, 50 °C

an additional crop (1.3 g) of aldehyde (total yield 18 g, 73%), n_D^{20} 1.4715; δ_H 1.8 (6 H, s, 2 × Me), 3.1 (2 H, d, *J* 7 Hz, CH_2), 4.6—5.0 (2 H, m, CH_2=), 6.4—6.8 (1 H, m, CH=), and 9.5 (1 H, s, CHO); 2,4-dinitrophenylhydrazone, m.p. 143—144 °C (Found: C, 55.1; H, 5.7; N, 18.8. Calc. for $C_{14}H_{16}N_4O_4$: C, 55.26; H, 5.30; N, 18.42%).

5-*Methylnona*-1,5,8-*trien*-4-*ol* (**16**).—A solution of 2-methylhexa-2,5-dienal (**9c**) (38.5 g, 0.35 mol) in anhydrous ether (100 ml) was added dropwise to a solution of allylmagnesium bromide (**8a**; X = Br) [prepared from allyl bromide (0.5 mol)]. After the addition was complete the product was hydrolysed with NH_4Cl–ice–water and isolated in the usual manner. Distillation at reduced pressure yielded 5-methylnona-1,5,8-trien-4-ol (**16**) (46.5 g, 93%), b.p. 52—54 °C (1 mmHg); n_D^{23} 1.4738; δ_H 1.7 (3 H, s, Me), 2.2—2.5 (2 H, m, CH_2), 2.6—3.0 (3 H, m, CH_2 and OH), 3.9—4.2 (1 H, m, 4-H), and 4.8—6.1 (7 H, m, olefinic H) (Found: C, 79.0; H, 10.6. Calc. for $C_{10}H_{16}O$: C, 78.89; H, 10.60%).

7-*Methylocta*-1,5,7-*trien*-4-*ol* (**12a**).—A solution of 4-methylpenta-2,4-dienal (**7b**) (11.3 g, 0.12 mol) in anhydrous ether (50 ml) was added dropwise to a solution of allylmagnesium bromide (**8a**; X = Br) [prepared from allyl bromide (0.2 mol)]. The product was isolated as described for 5-methylnona-1,5,8-trien-4-ol and distilled at reduced pressure to yield 7-methylocta-1,5,7-trien-4-ol (**12a**) (12.3 g, 76%), b.p. 34—36 °C (0.5 mmHg); n_D^{20} 1.4880; δ_H 1.8 (3 H, s, Me), 2.2—2.4 (2 H, m, CH_2), 3.0 (1 H, s, OH), 4.1—4.3 (1 H, m, 4-H), 4.9 (2 H, s, CH_2=), 5.0—5.2 (2 H, m, CH_2=), 5.5—5.9 (2 H, m, 2-H and 5-H), and 6.3 (1 H, d, *J* 6 Hz, 6-H) (Found: C, 78.5; H, 10.6. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%).

3-*Methylocta*-1,5,7-*trien*-4-*ol* (**12c**).—A solution of penta-2,4-dienal (**7a**) (8.3 g, 0.12 mol) in anhydrous ether (50 ml) was added dropwise to a solution of but-3-en-2-ylmagnesium chloride (**8c**; X = Cl) [prepared from 3-chlorobut-1-ene (0.2 mol)]. The product was isolated as described for 5-methylnona-1,5,8-trien-4-ol and distilled at reduced pressure to yield 3-methylocta-1,5,7-trien-4-ol (**12c**) (13.7 g, 86%), b.p. 36 °C (0.5 mmHg); n_D^{21} 1.4730. The ^{1}H n.m.r. spectrum indicated a mixture of diastereoisomers, δ_H 1.0 [3 H, m (2 superimposed t), 2 × Me], 2.2—2.5 (1 H, m, 3-H), 2.9 (1 H, br s, OH), 3.9—4.1 (1 H, m, 4-H), 5.1—5.3 (4 H, m, 2 × CH_2=), 5.6—5.9 (2 H, m, 2 × CH=), and 6.1—6.4 (2 H, m, CH=) (Found: C, 78.1; H, 10.12%).

5-*Methylocta*-1,5,7-*trien*-4-*ol* (**12b**).—A solution of 2-methylpenta-2,4-dienal (**7d**) (27 g, 0.28 mol) in anhydrous ether (100 ml) was added dropwise to a solution of allylmagnesium bromide (**8a**; X = Br) [prepared from allyl bromide (0.5 mol)]. The product was isolated as described for 5-methylnona-1,5,8-trien-4-ol and distilled at reduced pressure to yield 5-methylocta-1,5,7-trien-4-ol (**12b**) (34 g, 88%), b.p. 48—50 °C (1 mmHg); n_D^{24} 1.5014; δ_H 1.8 (3 H, s, Me), 2.2—2.5 (2 H, br t, *J* 7 Hz, CH_2), 3.2 (1 H, s, OH), 3.9—4.2 (1 H, br t, *J* 7 Hz, 4-H), 4.9—5.4 (4 H, m, 2 × CH_2=), and 5.5—6.8 (3 H, m, 3 × CH=) (Found: C, 78.25; H, 10.3%).

Nona-1,5,8-*trien*-4-*ol* (**14**).—A solution of hexa-2,5-dienal (**9a**) (12.4 g, 0.13 mol) in anhydrous ether (50 ml) was added to a solution of allylmagnesium bromide (**8a**; X = Br) [prepared from allyl bromide (0.3 mol)]. The product was isolated as described for 5-methylnona-1,5,8-trien-4-ol and distilled at reduced pressure to yield nona-1,5,8-trien-4-ol (**14**) (13.2 g, 77%), b.p. 39—40 °C (0.5 mmHg); n_D^{20} 1.4698; δ_H 2.2—2.4 (2 H, m, CH_2), 2.7—3.0 (3 H, m, CH_2 and OH), 4.0—4.3 (1 H, m, 4-H), and 5.0—6.0 (8 H, m, olefinic H) (Found: C, 78.2; H, 10.1. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%).

1-*Ethoxy*-2-*methylhexa*-1,5-*dien*-3-*ol* (**11**).—A solution of 3-ethoxy-2-methylpropenal (**6b**) (45.6 g, 0.4 mol) in anhydrous ether (100 ml) was added dropwise to a solution of allylmagnesium bromide (**8a**; X = Br) [prepared from allyl bromide (0.5 mol)] at 0 °C. After the addition was complete, the ice-bath was removed and the mixture was stirred for an additional 0.25 h, and then poured into ice–water and stirred vigorously. The ether layer was separated and the aqueous layer was filtered to remove undissolved magnesium salts and excess of magnesium. The aqueous solution was then extracted with ether, and the combined ether phases were washed with brine and dried ($MgSO_4$). Fast distillation at reduced pressure gave a product (40 g) which was shown to be a mixture of hexa-2,5-dienal (**9a**) and the desired alcohol (**11**) by g.l.c. and ^{1}H n.m.r. analysis. Careful fractional distillation yielded pure 1-ethoxy-2-methylhexa-1,5-dien-3-ol (**11**) (14.2 g, 23%), n_D^{17} 1.4680; δ_H 1.2 (3 H, t, *J* 7 Hz, CH_2*Me*), 1.7—1.9 (6 H, m, 4-H_2, 2-Me, and OH), 2.8 (1 H, m, 3-H), 3.3—3.7 (2 H, m, CH_2O), 4.9—5.2 (3 H, m, CH=CH_2), and 9.2 (1 H, s, 1-H) (Found: C, 69.2; H, 10.2. Calc. for $C_9H_{16}O_2$: C, 69.19; H, 10.32%).

Attempted Preparation of 1-*Ethoxy*-2-*methylpenta*-1,4-*dien*-3-*ol* (**10**).—A solution of 3-ethoxy-2-methylpropenal (**6b**) (45.6 g, 0.4 mol) in anhydrous ether (100) was added dropwise to a solution of vinylmagnesium bromide (**5a**; X = Br) [prepared from vinyl bromide (0.55 mol)] at 0 °C. The product was isolated in a similar manner to 1-ethoxy-2-methylhexa-1,5-dien-3-ol, to yield a crude product (32 g) which proved to be a mixture of the desired product (**10**) and 2-methylpenta-2,4-dienal (**7d**). Repeated attempts to separate the two compounds by fractional distillation failed to provide an analytically pure sample of the ethoxy alcohol, which proved to be very labile with respect to ethanol elimination. No further attempts were made to isolate a pure sample as enrichment beyond 90% by g.l.c. (^{1}H n.m.r. analysis) could not be achieved.

4-*Methylocta*-1,3,5,7-*tetraene* (**13b**).—A solution of 5-methylocta-1,5,7-trien-4-ol (**12b**) (26.5 g, 0.19 mol) in anhydrous ether (100 ml) was added dropwise to phosphorus tribromide (27 g, excess) at 0 °C. After the addition was complete, the solution was allowed to warm to room temperature slowly and was then kept overnight. The mixture was then poured into ice–water and the resulting mixture was neutralized by addition of saturated aqueous sodium carbonate and stirred. The ether layer was separated and the aqueous portion was extracted with ether (2 × 100 ml). The combined ether solutions were then washed with brine (100 ml) and dried ($MgSO_4$). After filtration the crude bromide (35 g, 90%) was obtained as an unstable yellow lachrymatory liquid by removal of the ether under reduced pressure, and was used directly in the next step without further purification.

The bromide was dissolved in hexane (50 ml) and the resulting solution was added dropwise to a solution fo DBU (39.5, 0.26 mol) in hexane (100 ml). After the rapid (15 min) addition was complete, the reaction mixture was heated at 50—60 °C for 2 h, after which time it was diluted with water (200 ml). The hexane layer was separated and the aqueous layer was extracted with hexane (100 ml). The combined hexane fractions were washed first with 3M-HCl (2 × 100 ml), then with brine (2 × 100 ml), and were finally dried ($MgSO_4$). Vacuum distillation yielded 4-methylocta-1,3,5,7-tetraene (**13b**), (9.4 g, 45%) as a pale yellow liquid, b.p. 20—22 °C (1 mmHg); n_D^{23} 1.6002; δ_H 1.9 (3 H, s, Me), 4.9—5.5 (4 H, m, 2 × CH_2=), and 5.9—7.0 (5 H, m, olefinic H); δ_C 12.2, 116.6, 117.5, 129.1, 132.3, 133.0, 135.3, 137.4, and 137.6; $\lambda_{max.}$ ($\varepsilon_{max.}$ × 10^{-4}) 306 (4.56), 292 (4.90), 280 (3.28), 270 (1.68), and 258 nm (sh) (Found: C, 89.9; H, 10.1. Calc. for C_9H_{12}: C, 89.93; H, 10.07%). The g.l.c. and ^{13}C n.m.r. data indicated that only one geometric isomer was obtained, to which we have assigned an *E,E* configuration.

3-*Methylocta*-1,3,5,7-*tetraene* (**13c**).—A solution of 3-methylocta-1,5,7-trien-4-ol (**12a**) (17.8 g, 0.13 mol) in anhydrous ether (100 ml) was treated with phosphorus tribromide (18 g, excess) as described above for 4-methylocta-1,3,5,7-tetraene. The crude bromide was treated with *NN*-dimethylbenzylamine (21 g, 0.16 mol) in a 1:1 toluene–ether solvent mixture for 5 days to allow the crude ammonium salt to separate out (as a yellow glass). The mixture was chilled in an ice-bath and the toluene–ether mixture was decanted and discarded. The glassy salt was dissolved in water (100 ml), and the resulting solution was added dropwise to boiling aqueous sodium hydroxide undergoing straight-lead steam distillation [NaOH (20 g)–water (500 ml)]. The product was collected in pentane (100 ml) in an ice-bath. After the distillate no longer contained organic material, the pentane solution was separated and washed successively with 3M-HCl (2 × 100 ml) and brine (2 × 100 ml), and was dried ($MgSO_4$). After filtration, 3-methylocta-1,3,5,7-tetraene (**13c**) (2.5 g, 12%) was obtained by vacuum distillation, b.p. 20—22 °C (1 mmHg); n_D^{20} 1.6074; δ_H 1.9 (3 H, s, Me), 5.0—5.3 (4 H, m, 2 × CH_2=), and 5.9—6.7 (5 H, m, olefinic H); δ_C 12.0, 112.8, 117.2, 129.6, 131.3, 134.2, 136.3, 137.4, and 141.3; $\lambda_{max.}$ ($\varepsilon_{max.}$ × 10^{-4}) 310 (4.59), 296 (4.96), 284 (3.16), 272 (1.80), and 260 nm (sh) (Found: C, 89.9; H, 10.0%). The g.l.c. and ^{13}C n.m.r. data again indicate that only the *E,E* isomer was obtained.

2-*Methylocta*-1,3,5,7-*tetraene* (**13a**).—A solution of 7-methylocta-1,5,7-trien-4-ol (**12a**) (12.3 g, 0.09 mol) in anhydrous ether (50 ml) was treated with phosphorus tribromide (13 g, excess) as described above for 4-methylocta-1,3,5,7-tetraene. An ether

solution of the crude bromide was added to a solution of DBU (15 g, 0.1 mol) in hexane (100 ml) and the resulting mixture was heated for 2 h at 50—60 °C. 2-Methylocta-1,3,5,7-tetraene (**13a**) was obtained as described for the 4-Me isomer, b.p. 20—22 °C (1 mmHg); n_D^{21} 1.5532. G.l.c. showed the presence of one main isomer (presumably the *E,E*), and two minor isomers. These three isomers could be clearly distinguished in their ^{1}H n.m.r. spectra, showing three overlapping methyl singlets in the proportions 1:2.5:0.6 in order of appearance from $SiMe_4$: δ_H 1.8—2.0 (3 H, 3 s, 3 × Me), 5.0—5.3 (4 H, m, 2 × CH_2=), and 5.8—6.9 (5 H, m, olefinic H); δ_C (main isomer) 18.5, 117.1, 129.0, 130.2, 133.5, 134.8, 136.1, 137.2, and 142.0; $\lambda_{max.}$ 302, 288, 277, 265, and 255 nm (sh). This tetraene was by far the least stable prepared in this study, and began to polymerize upon contact with air within 15 min. In contrast, the 4-Me tetraene (**13b**) was relatively stable in contact with air and a sample was kept for several months at −40 °C without apparent decomposition. Both the 2-Me and 3-Me isomers (**13a** and **c**) completely polymerized at −40 °C within 72 h.

5-*Methylnona*-1,3,5,8-*tetraene* (**17**).—A solution of 5-methylnona-1,5,8-trien-4-ol (**16**) (14 g, 0.09 mol) anhydrous ether (50 ml) was treated with phosphorus tribromide (14 g, excess) as described above for 4-methylocta-1,3,5,7-tetraene. An ether solution of the crude bromide was added to a solution of DBU (17 g, 0.11 mol) in ether (50 ml). The mixture was refluxed for 16 h, then cooled to room temperature. Water (400 ml) was added to dissolve the DBU·HBr salt and the layers were separated. The ether layer was washed successively with 3M-HCl (2 × 100 ml) and brine (2 × 200 ml), and dried ($MgSO_4$). After filtration, 5-methylnona-1,3,5,8-tetraene (**17**) was obtained by vacuum distillation (8.6 g, 70%), b.p. 80—82 °C (20 mmHg); n_D^{28} 1.5406. G.l.c. showed the presence of two geometric isomers (8:1), and the u.v. spectrum was consistent with the assigned structure: $\lambda_{max.}$ ($\varepsilon_{max.}$ × 10^{-4}) 275 (3.47), 264 (4.27), 255 (3.27), and 246 nm (sh). The major isomer has tentatively been assigned an *E,E* configuration, and the minor isomer a *Z,E* structure based primarily on the mode of synthesis. The n.m.r. spectrum showed δ_H 1.8 and 1.9 in the ratio 8:1 (3 H, s, 2 × Me), 2.8—3.0 (2 H, m, CH_2), 4.9—5.3 (4 H, m, 2 × CH_2=), 5.5—5.6 (1 H, t, *J* 6 Hz, CH_2=C*H*), 5.7—5.9 (1 H, m, olefinic H), and 6.1—6.6 (3 H, m, olefinic H); δ_C (main isomer) 12.2, 32.7, 114.9, 116.0, 127.4, 130.3, 134.8, 136.3, 137.6, and 137.9 (Found: C, 89.5; H, 10.6. Calc. for $C_{10}H_{14}$: C, 89.49; H, 10.51%).

Nona-1,3,5,8-*tetraene* (**15**).—A solution of nona-1,5,8-trien-4-ol (**14**) (8.5 g, 0.06 mol) in anhydrous ether (50 ml) was treated with phosphorus tribromide (13 g, excess) as described above for 4-methylocta-1,3,5,7-tetraene. The crude bromide (11.5 g, 93%) was isolated by evaporation of the solvent under reduced pressure, but was not purified further.

A hexane solution (100 ml) of the crude bromide was added dropwise to a solution of DBU (9 g, 0.065 mol) in hexane (200 ml) and the resulting mixture was refluxed for 2 h and then diluted with water (1 200 ml). Nona-1,3,5,8-tetraene (**15**) was isolated as described above for 4-methylocta-1,3,5,7-tetraene (4.3 g, 62%), b.p. 20—22 °C (0.5 mmHg); n_D^{20} 1.5430. G.l.c. showed one major isomer (90%), presumably the all-*E*, and several whose percentages were each less than 2%. Preliminary u.v. analysis indicated that *ca.* 4% of the mixture was rearranged fully conjugated nona-1,3,5,7-tetraene. For the major isomer, δ_H 2.8—30 (2 H, m, CH_2), 5.0—5.3 (4 H, m, 2 × CH_2=), and 5.6—6.9 (6 H, m, olefinic H); δ_C 36.8, 115.6, 116.5, 131.3, 131.8, 132.6, 133.2, 136.3, and 137.2 (Found: C, 89.8; H, 9.7. Calc. for C_9H_{12}: C, 89.93; H, 10.07%).

References

1 The results of this paper were presented at the 19th Great Lakes Regional Meeting (A.C.S.), Purdue University, June 1985 (R. M.) and at the 36th Undergraduate Research Symposium (Chicago A. C. S.), Amoco Research Center, April, 1985 (A. K.).

2 (*a*) C. Spangler, T. Jondahl, and B. Spangler, *J. Org. Chem.*, 1973, **38**, 2478; (*b*) C. Spangler and T. Hartford, *Synthesis*, 1976, 108; *J. Chem. Soc., Perkin Trans. 1*, 1976, 1792; (*c*) C. Spangler, *Tetrahedron*, 1976, **32**, 2681; (*d*) C. Spangler, B. Keys, and D. Bookbinder, *J. Chem. Soc., Perkin Trans. 2*, 1979, 810; (*e*) C. Spangler, S. Ibrahim, D. Bookbinder, and S. Ahmad, *ibid.*, p. 717; (*f*) C. Spangler, D. Kjell, L. Wellander, and M. Kinsella, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2287; (*g*) C. Spangler and D. Little, *ibid.*, 1982, 2379.

3 M. Granville, B. Kohler, and J. Snow, *J. Chem. Phys.*, 1981, **75**, 3765; L. Heimbrook, J. Kenny, B. Kohler, and G. Scott, *ibid.*, p. 4338; B. Hudson, B. Kohler, and K. Schulten, *Excited States*, 1982, **5**, 1; J. Ackeman, D. Huppert, B. Kohler, and P. Rentzepis, *J. Chem. Phys.*, 1982, **77**, 3967; B. Kohler and P. West, *ibid.*, 1983, **79**, 583; B. Kohler and J. Snow, *ibid.*, p. 2134.

4 L. Jaenicke and K. Seferiadis, *Chem. Ber.*, 1975, **108**, 225; F. Naf, R. Decorzant, W. Thommen, B. Willhalm, and G. Ohloff, *Helv. Chim. Acta*, 1975, **58**, 1016.

5 N. Hirai, D. Kingston, R. Van Tassell, and T. Wilkins, *J. Am. Chem. Soc.*, 1982, **104**, 6149; I. Gupta, K. Suzuki, W. Bruce, J. Krepinsky, and P. Yates, *Science*, 1984, **225**, 521.

6 R. Baughman, B. Kohler, I. Levy, and C. Spangler, *Synth. Met.*, 1985, **11**, 37.

7 F. Edmunds and R. Johnstone, *J. Chem. Soc.*, 1965, 2898.

8 C. Spangler, R. Tan, R. Gibson, and R. McCoy, *Synth. Commun.*, 1985, **15**, 371.

9 K. Rustemeier and E. Breitmaier, *Angew. Chem.. Int. Ed. Engl.*, 1980, **19**, 816.

10 P. Schiess and P. Radimerski, *Helv. Chim. Acta*, 1974, **57**, 2583.

11 S. Tamura and E. Takeda, *Chem. Pharm. Bull.*, 1979, **27**; 403; V. Klinko, T. Protopopova, N. Smirnova, and A. Skoldinov, *Zh. Obsch. Khim.*, 1962, **32**, 2961.

Received 26*th September* 1985; *Paper* 5/1674