Synthesis of Unsaturated Aldehydes by Sequential Claisen and Cope Rearrangements

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Condensation of hexa-1,5-dien-3-ol (Ia) with 1,1,3-triethoxy-2-methylbutane, catalysed by *o*-nitrobenzoic acid, proceeds with elimination of three moles of ethanol to form an intermediate dienol ether that undergoes Claisen rearrangement to 2-methyl-2-vinylocta-4,7-dienal (Va). At higher temperatures (*ca.* 160°) this aldehyde (Va) rearranges to 2-methyl-5-vinylocta-2,7-dienal (VIa), which at still higher temperatures (*ca.* 190°) equilibrates through a second Cope rearrangement with the more stable 2-methyldeca-2,5,9-trienal (VIIa). The same sequence of reactions was carried through with two methyl derivatives of the hexadienol (Ia).

Reduction of the aldehyde (VIa) formed the allyl alcohol (X), which rearranged to the same dimethylated straight-chain alcohol (XI) as was produced by reduction of the isomer (VIIa). Condensation with 1,1,3-triethoxy-2-methylbutane converted (X) through Claisen rearrangement and two successive Cope rearrangements into the ' linear ' 2,6-dimethyltetradeca-2,6,9,13-tetraenal (XV), also formed in the same way from the rearranged isomer (XI) through Claisen rearrangement and one Cope rearrangement.

THE succession of a Claisen rearrangement by a Cope rearrangement, known for many years in the isomerisation[1] of 2,6-disubstituted phenyl allyl ethers to 4-allylphenols, has been applied with great effect by Thomas to the synthesis of terpenes.[2] The overall reaction amounts to a simple γ-allylation of an $\alpha\beta$-unsaturated carbonyl compound. We now describe in detail a system that allows a Claisen rearrangement to be followed by two Cope rearrangements.[3]

In principle any dienol ether of a 1,5,8, . . . n — 3,n-polyen-3-ol can undergo successive [3,3] sigmatropic shifts to form a straight-chain aldehyde or ketone in which each allyl unit has been inverted with respect to the following one. In practice only the first members of the series are likely to be of value in synthesis; the reactions of three different hexa-1,5-dien-3-ols, easily made by the addition of an allylic Grignard reagent to an unsaturated carbonyl compound,[4] are described here.

The first reactions investigated were those of hexa-1,5-dien-3-ol (Ia) with 1,1,3-trimethoxybutane and with

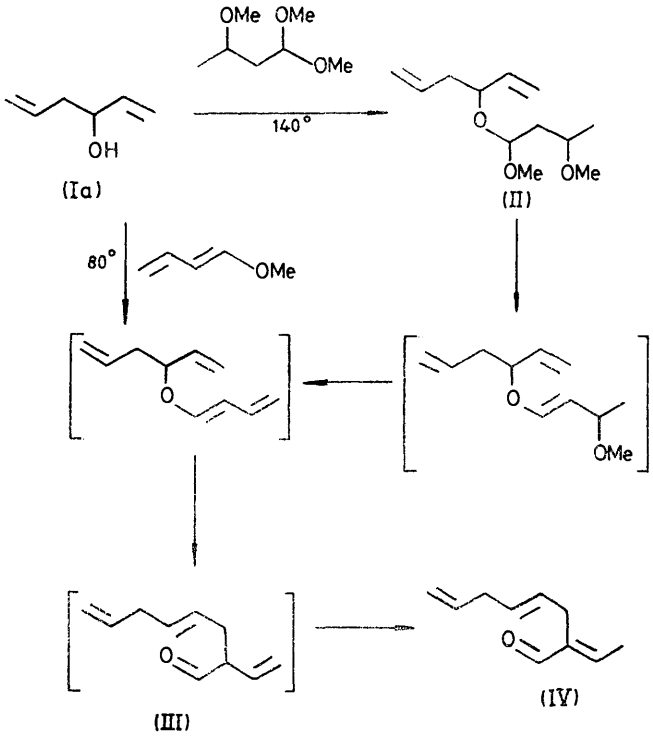
[1] D. S. Tarbell, *Org. Reactions*, 1944, **2**, 1.

[2] A. F. Thomas, *J. Amer. Chem. Soc.*, 1969, **91**, 3280; A. F. Thomas and G. Ohloff, *Helv. Chim. Acta*, 1970, **53**, 1145; A. F. Thomas and M. Ozainne, *J. Chem. Soc.* (*C*), 1970, 220.

[3] Preliminary note: R. C. Cookson and N. R. Rogers, *J.C.S. Chem. Comm.*, 1972, 248.

[4] A. Viola, E. J. Iorio, K. K. Cher, G. M. Glover, U. Nayak, and P. J. Kocierski, *J. Amer. Chem. Soc.*, 1967, **89**, 3462 and references therein.

1-methoxybutadiene (Scheme 1). Analogous allyl butadienyl ethers had already been shown to undergo a Claisen rearrangement, followed by a 1,3-hydrogen shift,

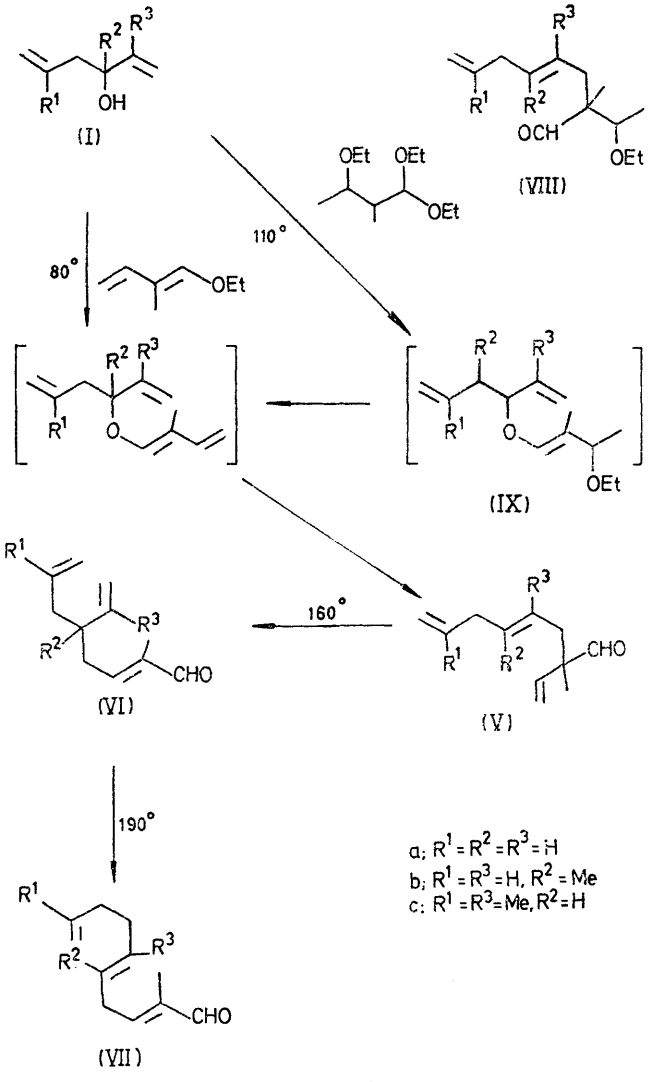


SCHEME 1

to give a stable αβ-unsaturated aldehyde rather than the desired product from Claisen–Cope rearrangement.[2,5] This was so in our system and the major product was the conjugated aldehyde (IV), which was stable to further rearrangement.*

The best conditions of many tried for production of the aldehyde (IV) formed the basis for those used for the other Claisen reactions. 2,4-Dinitrophenol [6] and orthophosphoric acid [7] have been reported to catalyse the reactions of allyl alcohols with acetals to give aldehydes, the reaction proceeding by initial formation of the mixed acetal followed by equilibration to the allyl vinyl ether and Claisen rearrangement.[6,7] These two compounds, together with sulphanilic acid and oxalic acid, did catalyse the reactions of hexa-1,5-dien-3-ol with 1,1,3-trimethoxybutane but yields (<40%) † were unsatisfactory. The best catalyst was *o*-nitrobenzoic acid (pK_a 2·16) although to obtain consistently good yields (60—70%) methanol formed during the reaction had to be removed by distillation.‡

1-Methoxybutadiene, instead of 1,1,3-trimethoxybutane, can also be used as a starting material and good yields were obtained with *o*-nitrobenzoic acid as catalyst as long as the butadiene was present in excess. Mercury(II) acetate, which has been shown [2,9,10] to catalyse the reaction of several allyl alcohols with enol or dienol ethers, gave unreliable and often rather low yields (<15%). There was no advantage in using the alkoxybutadiene, especially as it tended to polymerise. The



SCHEME 2

reactions were carried out in refluxing benzene (reactions with alkoxybutadienes), toluene, or xylene.

* Heating with acid catalysts might have equilibrated it with the βγ-isomer (III), capable of Cope rearrangement to analogues of (VI) and (VII) (Scheme 2); this rearrangement could not be achieved.

† Glycine, mercury(II) acetate, mercury(II) oxide, boron trifluoride, and ammonium dihydrogen phosphate did not catalyse the reaction. Faulkner has recently noted [8] that the weakest acid catalyst usually gave the highest yield.

‡ A similar procedure has been used previously in the reaction of 2-methylbut-3-en-2-ol with high-boiling acetals.[7]

[5] S. Julia and M. Julia, *Bull. Soc. chim. France*, 1962, 1960.
[6] W. S. Johnson, T. J. Brockson, P. L. Loew, D. H. Rich, L. Werthemann, R. A. Arnold, T. Li, and D. J. Faulkner, *J. Amer. Chem. Soc.*, 1970, **92**, 4463; W. S. Johnson and P. L. Loew, *ibid.*, 1971, **93**, 3765; D. J. Faulkner and M. R. Peterson, *ibid.*, p. 3766.
[7] G. Saucy and R. Marbet, *Helv. Chim. Acta*, 1967, **50**, 2095.
[8] D. J. Faulkner and M. R. Peterson, *J. Amer. Chem. Soc.*, 1973, **95**, 553.
[9] R. F. Church, R. E. Ireland, and J. A. Marshall, *J. Org. Chem.*, 1966, **31**, 2526.
[10] D. J. Faulkner and M. R. Peterson, *Tetrahedron Letters*, 1969, 3243.

The isomerisation of the aldehyde (III) to the conjugated isomer (IV) can be readily blocked by a methyl group (Scheme 2).[2] The Claisen product (V) can then undergo two sequential Cope rearrangements to give (VII). The suggested reaction schemes (Schemes 1 and 2) were supported by the isolation of the mixed acetal (II) (Scheme 1) and the aldehyde (VIIIb) (Scheme 2). The mixed acetal was the major product of the reaction of hexa-1,5-diene-3-ol with 1,1,3-trimethoxybutane in the presence of a small amount of 2,4-dinitrophenol as catalyst, though at higher concentrations, provided that the methanol formed was removed by distillation, the reaction proceeded smoothly to the aldehyde (IV). The aldehydes of type (VIII) [(VIIIb) isolated; (VIIIa and c) indicated from spectral evidence] arising from the

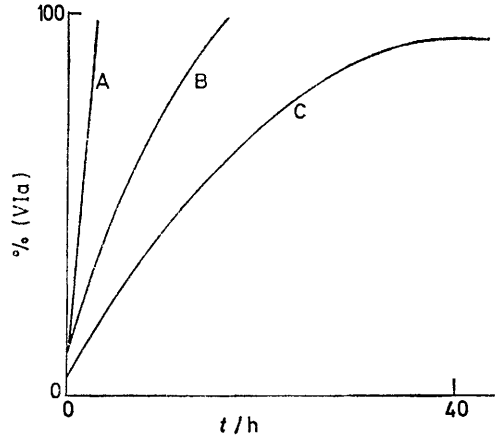


FIGURE 1 Formation of (VIa) from (Va) in various solvents [A, decalin (b.p. 192°); B, bis-(2-methoxyethyl) ether (b.p. 164°); C, xylene (b.p. 140°)]: plot of % (VIa) against time (in hours)

Claisen rearrangement of (IX) fortunately were only minor products [<7% (VIIIb) and <2% (VIIIa and c)].

The reactions of hexa-1,5-dien-3-ols (Ia—c) with 2-methyl-1,1,3-triethoxybutane in the presence of *o*-nitrobenzoic acid gave good yields of (Va), (Vb) (toluene as solvent), and (Vc) (xylene as solvent). As expected from the reactions of 1-methoxybutadiene, the reaction of 2-methyl-1-ethoxybutadiene (in excess) with hexa-1,5-dien-3-ol (Ia) in the presence of *o*-nitrobenzoic acid gave good yields of (Va). Use of mercury(II) acetate again gave low yields (<16%).

It was initially hoped to prepare the aldehydes (VIIa—c) directly by these reactions. Unfortunately the final Cope rearrangement proceeds slowly below 190° and at this temperature polymerisation, enhanced by the acidic conditions, was extensive. Compound (Ia) gave only a very low yield (<8%) of (VIIa) under these conditions. It was possible, because the first Cope rearrangement occurred at a much lower temperature, to prepare (VIa—c) directly by using xylene as solvent. Generally, however, the best route to either aldehydes (VI) or (VII) was to isolate the product of the Claisen rearrangement (V) and then to rearrange this under neutral conditions at the appropriate temperature.

The Cope rearrangements (Va) ⟶ (VIa) and (VIa) ⟶ (VIIa) were studied in detail, by using g.l.c. to determine the percentage of product at a particular time.

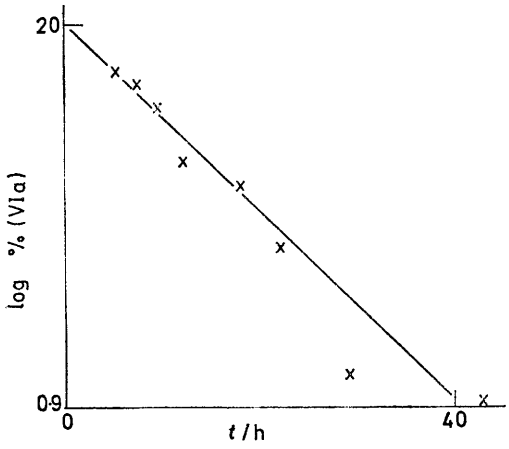


FIGURE 2 Formation of (VIa) from (Va) in xylene (log plot)

The formation of a small amount (<2%) of (VIa) in the reaction of hexa-1,5-dien-3-ol with 1-ethoxy-2-methylbutadiene in benzene after 80 h showed that the first Cope rearrangement did proceed, albeit slowly, at 80°. The formation of (VIa) from (Va) in various other refluxing solvents is shown in Figures 1 and 2. The rearrangement in xylene (b.p. 140°) roughly obeyed overall first-order kinetics (Figure 2) with a rate constant of *ca.* $1{\cdot}5 \times 10^{-5}$ s^{-1}. The final Cope rearrangement proceeded slowly at 160° [in refluxing bis-(2-methoxyethyl) ether] but rapidly at 190° (in refluxing decalin) (see Figures 3 and 4). This rearrangement also roughly obeyed overall

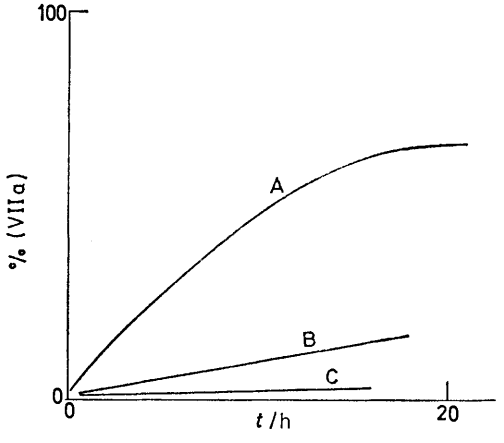


FIGURE 3 Formation of (VIIa) from (VIa) in various solvents [A, decalin (b.p. 192°); B, *o*-dichlorobenzene (b.p. 180°); C, bis-(2-methoxyethyl) ether (b.p. 164°)]

first-order kinetics with the same rate constant (*ca.* $1{\cdot}5 \times 10^{-5}$ s^{-1}). The lower temperatures required for Cope rearrangements which lead to an increase in conjugation [*e.g.* (V) ⟶ (VI)] have been noted previously.[11]

[11] (*a*) A. C. Cope, C. M. Hoffman, and E. M. Hardy, *J. Amer. Chem. Soc.*, 1941, **63**, 1853; (*b*) J. M. Conia and M. Bortolussi, *Bull. Soc. chim. France*, 1972, 3402 and references therein.

The rearrangements of (VIa—c) ⟶ (VIIa—c) led to mixtures of (VI) and (VII) [generally >70% (VII)] which could be enriched in (VII) by column chromatography.

The stereospecificity of Claisen and Cope rearrangements has been widely reported [7,10,12] and the rearrangements often lead to only one isomer with retention of

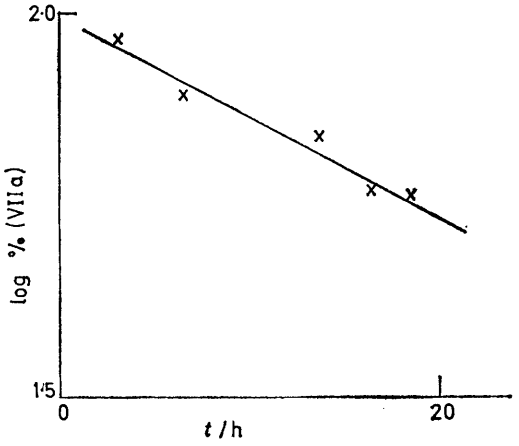


FIGURE 4 Formation of (VIIa) from (VIa) in decalin (log plot)

optical activity (if present in the migrating group). Claisen followed by Cope rearrangements too have been shown to occur stereospecifically with retention of optical activity.[2] Recently the stereospecific double Cope rearrangement of *trans*-3,4-dimethylcyclo-octa-*cis*-1,*trans*-5-diene to *cis*-3,4-dimethylcyclo-octa-*cis*-1,-*cis*-5-diene has been reported.[13]

The stereochemistry of the compounds (V)—(VII), summarised in the Table, was consistent either with the

Aldehyde	(V)	(VI)	(VII)
a	*trans*-4	*trans*-2	*trans*-2,*trans*-5
b	*trans*-4 *cis*-4	*trans*-2	*trans*-2,*trans*-5 *trans*-2,*cis*-5
c	*trans*-4	*trans*-2	*trans*-2,*trans*-5

generally preferred ' chair-like ' transition states, or with the ' cyclohexane-like ' transition state proposed by Faulkner for both Claisen and Cope rearrangements, where the bulky groups occupy pseudoequatorial or equatorial positions.[8,12] The assignment of stereochemistry is dealt with in a separate section (see later).

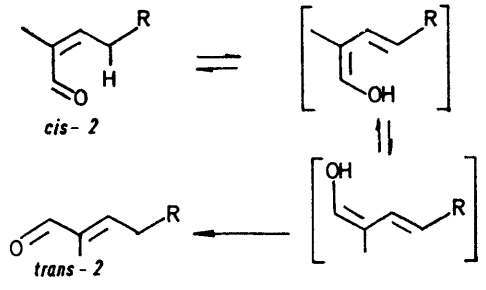
The Claisen rearrangements to (Va) and (Vc) gave predominantly (>80%) the *trans*-4 (*E*) isomers whereas a mixture (50 : 50) of the *trans*-4 (*E*) and *cis*-4 (*Z*) isomers of (Vb) was obtained. In the same way the allyl vinyl ethers derived from secondary alcohols gave one product whereas the ethers derived from tertiary alcohols gave a mixture. The major isomer of (IV) was the *trans*-2,-*trans*-4, and though some *cis*-2 * was formed none of the *cis*-4 isomer was detected. The available spectral evidence also indicated that the by-product (VIIIb) was a mixture of *cis*-4 and *trans*-4 isomers.

* Exact percentage dependent on reaction conditions; analogous reactions of geraniol or nerol gave 2-*cis*-ethylidene-3,7-dimethyl-3-vinyloct-6-enal as major product.[2]

† Major fraction after chromatography contains <2% *cis*-2-isomer.

The first Cope rearrangement of (V) to (VI) in refluxing bis-(2-methoxyethyl) ether (b.p. 160°) appeared to give predominantly the *trans*-2 isomer of (VI) [87% *trans*-2 (VIa) indicated before chromatography †]. Closer examination of the rearrangement of (Va) to (VIa) in xylene showed that after 1·5 h the *trans*-2 isomer of (VIa) was indeed the major isomer (67%) but that a significant amount of the *cis*-2 form was also present. As the reaction proceeded the percentage of the *cis*-2 isomer decreased and only 14% remained after 40 h. The isomerisation of the *cis*-2 to the *trans*-2 isomer of (VIa) was then shown experimentally (chromatography gave a mixture rich in the *cis*-2 isomer which readily changed to a mixture rich in the *trans*-2 isomer after refluxing in xylene).

The formation of *trans*-2 (VI) as the major product of the Cope rearrangement requires the formyl group to occupy a pseudoequatorial position and this preference has been previously noted.[2] The further *cis–trans* isomerisation can be rationalised in terms of formation of an intermediate enol which is readily produced by the *cis*- but not by the *trans*-isomer (Scheme 3). Similar mechanisms have been postulated to explain the isomerisation of several other unsaturated aldehydes and ketones.[11b,14] Reduction of the aldehyde group to an



SCHEME 3

alcohol gave a product which, as expected, no longer underwent *cis–trans* isomerisation (even at 190°).

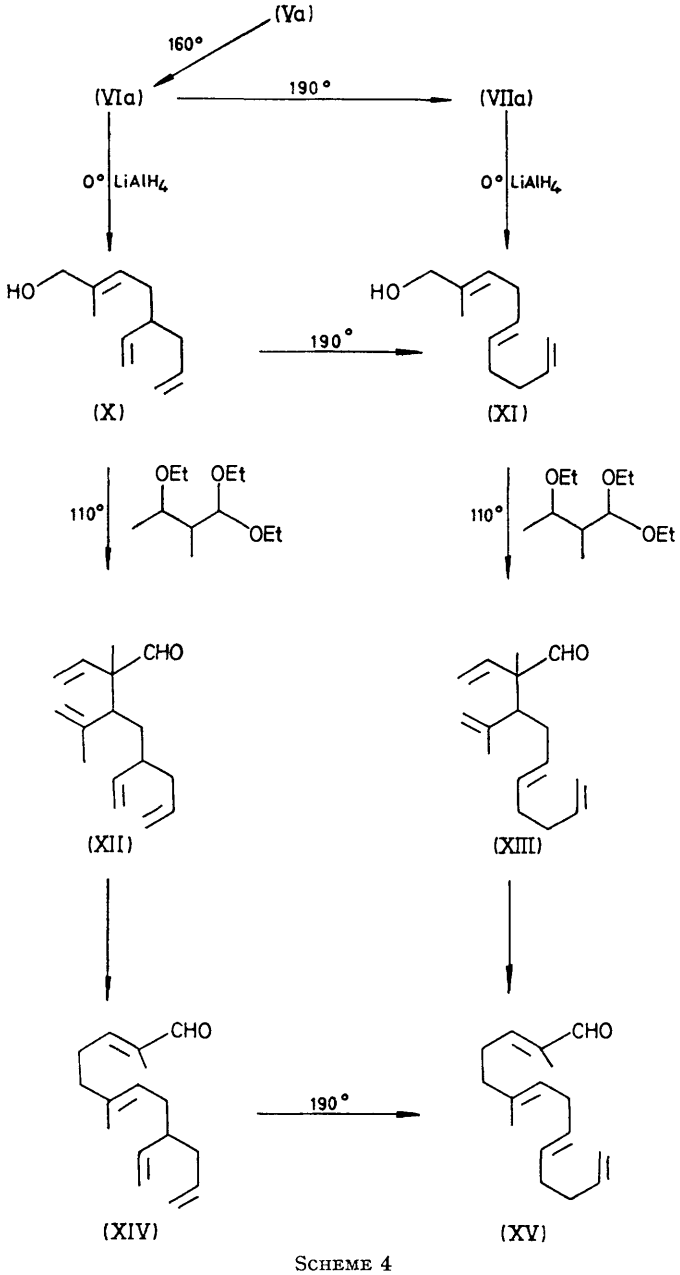
The products from the second Cope rearrangement of (Va) and (Vc) were again formed with high stereospecificity and predominantly the *trans*-2,*trans*-5 isomers were isolated after chromatography. None of the *cis*-2 or *cis*-5 isomers of (VIIa) were detected. Similarly none of the *cis*-2 and less than 10% of the *cis*-5 isomer of (VIIc) were detected. The Cope rearrangement of (VIb) to (VIIb), however, gave a mixture of isomers, *trans*-2,*trans*-5 (56%) and *trans*-2,*cis*-5 (44%) (up to

[12] R. K. Hill and A. G. Edwards, *Tetrahedron Letters*, 1964, 3239; A. W. Burgstahler, *J. Amer. Chem. Soc.*, 1960, **82**, 4681; D. J. Faulkner and C. L. Perrin, *Tetrahedron Letters*, 1969, 2783; J. Corbier and P. Cresson, *Compt. rend.*, 1971, **272C**, 695; W. von E. Doering and W. Roth, *Tetrahedron*, 1962, **18**, 67; R. K. Hill and N. W. Gillman, *Chem. Comm.*, 1967, 619; W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, 1971, **27**, 5299; R. K. Hill, R. Soman, and S. Sawade, *J. Org. Chem.*, 1972, **37**, 3737.

[13] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, 1972, **94**. 7597; J. A. Berson, P. B. Dervan, and J. A. Jenkins, *ibid.*, p. 7598.

[14] G. Ohloff, *Tetrahedron Letters*, 1960, **11**, 10.

4% overall of *cis*-2 isomers were detected). It can be seen that the stereochemistry of the final products is determined by the final Cope rearrangement, which is in turn determined by the nature of the hexa-1,5-dien-3-ol used. These results indicate that with secondary hexa-1,5-dien-3-ols the major if not exclusive isomer of the



SCHEME 4

final product will be the *trans*-2,*trans*-5 system, whereas with tertiary hexa-1,5-dien-3-ols a mixture of isomers can be expected.

A preliminary study of the reactions of the allyl alcohols (X) and (XI) (prepared by reduction of the corresponding aldehydes) with 1,1,3-triethoxy-2-methylbutane (*o*-nitrobenzoic acid as catalyst) showed the feasibility * of this reaction sequence to give long-chain unsaturated aldehydes (Scheme 4). It was possible to effect the ' final ' Cope rearrangement at three different stages [(VIa) ⟶ VIIa); (X) ⟶ (XI); (XIV) ⟶ (XV)]; the products (XIV) and (XV) result from Claisen–Cope rearrangements analogous to those described by Thomas. The stereochemistry of final products was consistent with ' chair-like ' transition states from an equilibrating mixture of the allyl butadienyl ethers and the major isomers isolated were the *trans*-2,*trans*-6 of (XIV) and the *trans*-2,*trans*-6,*trans*-9 of (XV). Compound (XIV) also contained 6% of *cis*-2 and 12% of *cis*-6 isomers; (XV) did not appear to contain any of the *cis*-2 or *cis*-9 isomers.

Assignment of Stereochemistry.—The assignment of configuration of a disubstituted double bond [in (IV), (Va), (VIIa), and (XV)] was based on the i.r. spectra, which showed a strong *trans*-disubstituted olefinic C–H bending vibration at 980—990 cm^{-1} and only a weak (or non-existent) *cis*-disubstituted olefinic band at 690 cm^{-1}. The n.m.r. spectra for these compounds in the olefinic region were complicated and could not be used for assignment.

Assignment of stereochemistry of a trisubstituted double bond was based on the n.m.r. data. The work of Bates [15] on the *cis*- and *trans*-isomers of farnesol, together with subsequent studies,[2,16] showed that the signal from a methyl group on a *cis* (*Z*) double bond consistently appeared at lower field than that from one on a *trans* (*E*) double bond. The ratio of intensities of the methyl signals in the region δ 1·5—1·75 was used as a quantitative measure of the *cis–trans* ratios. The stereochemistry of the conjugated double bonds was determined from the n.m.r. signal of the aldehydic proton, at δ 10—11 for the *cis*-2 configuration and at about δ 9·3 for the *trans*-2.[2,17]

Further support for the structural assignments came from g.l.c. retention times: those of the *trans*-isomers (conjugated and non-conjugated) were generally found to be longer than those of the corresponding *cis*-isomers. Thomas [2] also found that *trans*-isomers of unsaturated aldehydes had longer retention times than *cis*-isomers.

EXPERIMENTAL

The hexa-1,5-dien-3-ols were prepared as described.[4] A commercial sample (Aldrich) of 1,1,3-trimethoxybutane was used. 1,1,3-Triethoxy-2-methylbutane was prepared by the reaction of acetaldehyde diethyl acetal with 1-ethoxypropene in the presence of boron trifluoride–ether complex.[18] 1-Ethoxy-2-methylbutadiene and 1-methoxybutadiene were prepared from the respective trialkoxybutanes, with

* No attempts were made to optimise reaction conditions; trial runs gave rather low (30%) yields of (XIV) from (X).

[15] R. B. Bates, D. M. Gales, and B. J. Gruner, *J. Org. Chem.*, 1963, **28**, 1086.

[16] B. M. Trost, *Accounts Chem. Res.*, 1970, **3**, 120; J. W. K. Burrel, L. M. Jackman, R. F. Garwood, E. Oskay, and B. C. L. Weedon, *J. Chem. Soc.* (*C*), 1966, 2144.

[17] K. C. Chan, W. H. Nutting, R. A. Jewell, and H. Rapoport, *J. Org. Chem.*, 1968, **33**, 3382.

[18] K. C. Brannock, *J. Amer. Chem. Soc.*, 1959, **81**, 3379.

ammonium dihydrogen phosphate or orthophosphoric acid as catalyst.[2,19] All catalysts and solvents used were commercial products and were not further purified.

The reaction products were separated and purified by fractional distillation and/or column chromatography on silica gel (100—200 mesh; 100 × wt. of material). The columns were eluted initially with petroleum, which removed remaining solvent (*e.g.* benzene, toluene, xylene, or decalin). Elution with petroleum–ether (50 : 1 v/v) removed unchanged acetals and non-polar by-products. The percentage of ether was gradually increased and the aldehydic products were eluted with petroleum–ether (50 : 3 to 50 : 4 v/v); the $\beta\gamma$-unsaturated aldehydes were generally the first to come off the column. Small amounts of unidentified material (many peaks by g.l.c.) remained on the column unless eluted with ether or ether containing a low percentage of methanol. All chromatographic separations were followed by g.l.c. on a 10 ft. 15% polypropylene glycol adipate (PPGA) glass column (Pye series 104 chromatograph). Various flow rates were used according to requirements (usually 30—50 ml min^{-1}) and the temperature was kept below that of the reaction (to prevent further thermal isomerisation on the column) to which the products corresponded. Only the optimum reaction conditions, or the only ones tried, are given.

The purity of all samples was checked by g.l.c. and the products were characterised by their i.r. (Unicam SP 200), n.m.r. (Perkin-Elmer R12 and/or Varian HA 100) and mass (A.E.I. MS12) spectra. The i.r. spectra were all recorded for liquid films and the n.m.r. spectra for solutions in carbon tetrachloride with tetramethylsilane as internal reference. The mass spectra were recorded of pure samples and the molecular ion and principal fragments are noted. Fragments related to the molecular ion by observed metastable peaks are marked with an asterisk. The products obtained were unstable with respect to polymerisation, and samples were not considered of sufficient stability or in some cases of sufficient purity (*ca.* 90%) to warrant elemental analysis.

Reaction of Hexa-1,5-dien-3-ol (Ia) *with 1,1,3-Trimethoxybutane.*—A solution of hexa-1,5-dien-3-ol (1·9 g, 20 mmol), 1,1,3-trimethoxybutane (5·96 g, 40 mmol), and *o*-nitrobenzoic acid (0·668 g, 4 mmol) in xylene (30 ml) was refluxed for 17 h. A low b.p. fraction (<80°) was then distilled from the mixture. The reduction in volume after shaking the distillate with water gave the amount of methanol present (4·5 ml distilled; 3·0 ml water-soluble). The mixture was then refluxed for 2 h and allowed to cool. The xylene solution was diluted with ether and washed with aqueous sodium hydrogen carbonate and distilled water. The aqueous layers were further extracted with ether; the extracts were combined with the principal xylene fraction and dried ($MgSO_4$). Distillation gave 2-ethylideneocta-4,7-dienal (IV) (1·92 g, 65%; 90% pure by g.l.c.), b.p. 115° at 14 Torr. Chromatography gave pure (>95%) *trans*-2 (*E*) isomer, $\nu_{max.}$ 940, 990, 1010, 1650, and 1690 cm^{-1}; τ 0·7 (1H, s), 3·45 (1H, q, *J* 7·0 Hz), 4·0—5·2 (5H, m), 7·0—7·1 (2H, m), 7·3—7·4 (2H, m), and 8·05 (3H, d, *J* 7·0 Hz); *m/e* 150 (M^+), 135*, 121, and 109.

The g.l.c. trace of crude (IV) contained a shoulder (*ca.* 7%) to the major peak and the n.m.r. spectrum likewise contained two aldehydic signals, at τ −0·1 (7%) and +0·7 (93%). The minor compound was assigned as the *cis*-2 (*Z*) isomer of (IV).

Compound (IV) was isolated unchanged after refluxing in decalin (under nitrogen), or refluxing in bis-(2-methoxyethyl) ether (containing a trace of toluene-*p*-sulphonic acid), or passing through a hot tube at 260°.

The reaction of hexa-1,5-dien-3-ol with 1,1,3-trimethoxybutane with 2,4-dinitrophenol as catalyst, toluene as solvent, and with no attempt at methanol removal gave one principal product in low yield. After work-up (as previously described), distillation, and chromatography a small amount of this product was isolated. The spectral data strongly indicated it possessed structure (II), $\nu_{max.}$ 920, 1000—1100, and 1640 cm^{-1}; τ 4·0—5·3 (6H, m), 4·45 (1H, t), 6·0 (1H, m), 6·8 (7H, m), 7·75 (2H, m), 8·4 (2H, m), and 8·95 (3H, d).

A trial reaction of 1,1,3-trimethoxybutane and hexa-1,5-dien-3-ol in heptane with 2,4-dinitrophenol as catalyst and a Dean–Stark apparatus to remove methanol was unsuccessful owing to extensive polymerisation. It was desirable to allow the reaction to proceed gradually so as to minimise the concentration of mixed allyl butadienyl ether at any one time.

Reaction of Hexa-1,5-dien-3-ol (Ia) *with 1-Methoxybutadiene.*—A solution of hexa-1,5-dien-3-ol (0·95 gm, 9·5 mmol), 1-methoxybutadiene (1·59 g, 18·9 mmol), and *o*-nitrobenzoic acid (67 mg, 0·4 mmol) in benzene (50 ml) was refluxed for 24 h. More *o*-nitrobenzoic acid (134 mg) was added and the solution was refluxed for a further 20 h. A final amount of catalyst (67 mg) was then added and refluxing was continued for 30 h, after which g.l.c. indicated one principal product. Work-up gave 2-ethylideneocta-4,7-dienal (0·8 g, 55%). The optimum conditions for these particular reactions were not investigated. Experience with 1-ethoxy-2-methylbutadiene and 1,1,3-triethoxy-2-methylbutane suggested that high yields for the reactions with the hexa-1,5-dien-3-ols were obtained by stepwise addition of catalyst. A high initial catalyst concentration enhanced polymerisation of the alkoxybutadiene or intermediate mixed butadienyl ether.

A low yield (*ca.* 16%) of (X) was obtained by the reaction of hexa-1,5-dien-3-ol (7·7 mmol) and 1-methoxybutadiene (15 mmol), under nitrogen, with mercuric acetate (1·5 mmol) as catalyst at 100°.

Reaction of Hexa-1,5-dien-3-ol (Ia) *with 1,1,3-Triethoxy-2-methylbutane.*—A solution of hexa-1,5-dien-3-ol (9·51 g, 97 mmol), 1,1-3-triethoxy-2-methylbutane (20·4 g, 0·1 mol), and *o*-nitrobenzoic acid (0·234 g, 2 mmol) in toluene (100 ml) was refluxed for 12 h. A low b.p. fraction (<80°) was then fractionally distilled from the mixture and the distillate (2·5 ml) was shaken with water to determine the amount of ethanol present. More *o*-nitrobenzoic acid (0·234 g) was added to the mixture, the solution was refluxed for 12 h, and the ethanol was removed as before. This process was repeated for two more 12 h periods; the final amount of *o*-nitrobenzoic acid was 0·936 g (8 mmol), and 8·5 ml of ethanol were separated (virtually no more ethanol distilled over after 48 h, indicating the reaction was complete). Work-up as described for (IV) gave 2-methyl-2-vinylocta-4,7-dienal (Va) (11·6 g, 76%; 95% pure by g.l.c.). b.p. 60—62° at 0·2 Torr, $\nu_{max.}$ 690w, 930, 980, 1000, 1640, and 1720 cm^{-1}; τ 0·7 (1H, s), 3·4—5·3 (8H, m), 7·3 (2H. m), 7·75 (2H, m), and 8·92 (3H, s); *m/e* 164 (M^+), 163, 149*, 135*, and 123.

The reaction in toluene normally gave (Va) as the major product but if the reaction was prolonged or if xylene was used as solvent further rearrangement to (VIa) (see later) occurred. The attempted reaction in decalin to give (VIIa)

[19] H. Normant and G. Martin, *Bull. Soc. chim. France*, 1963, 1646.

directly was unsuccessful owing to polymerisation [<8% (VIIa) isolated]. It was again found desirable to allow the reaction to proceed gradually with stepwise addition of catalyst.

Ammonium dihydrogen phosphate, mercuric acetate, sulphanilic acid, oxalic acid, and salicylic acid were unsatisfactory as catalysts.

Reaction of Hexa-1,5-dien-3-ol (Ia) *with 1-Ethoxy-2-methylbutadiene*.—A solution of hexa-1,5-dien-3-ol (1·96 g, 20 mmol), 1-ethoxy-2-methylbutadiene (4·58 g, 41 mmol) and *o*-nitrobenzoic acid (66 mg, 0·4 mmol) in benzene (50 ml) was refluxed for 14 h. The catalyst concentration was then gradually increased; the subsequent acid concentrations (mmol) and overall reflux times (h) were as follows 3·2, 40; 4·0, 60; 4·8, 80. Work-up gave essentially pure (>95% by g.l.c.) 2-methyl-3-vinylocta-4,7-dienal (Va) [2·1 g, 64% yield based on (Ia)].

A decreased yield (40%) of (Va) was obtained when a 1 : 1 mixture of hexa-1,5-dien-3-ol and 1-ethoxy-2-methylbutadiene was used. Mercuric acetate was ineffective as a catalyst [*ca.* 15% yield of (Va) obtained].

Rearrangement of 2-Methyl-2-vinylocta-4,7-dienal (Va) *to 2-Methyl-5-vinylocta-2,7-dienal* (VIa).—A solution of 2-methyl-2-vinylocta-4,7-dienal (Va) (1·0 g, 61 mmol), in bis-(2-methoxyethyl) ether (200 ml), containing a small amount of quinol (60 mg), was refluxed under nitrogen for 17 h. Careful removal of the solvent by distillation at 14 Torr followed by fractional distillation of the residue from a Claisen flask gave 2-methyl-5-vinylocta-2,7-dienal (VIa) (5·7 g, 57%), b.p. 60—70° at 0·4 Torr. The crude sample (90% pure by g.l.c.) was purified by column chromatography (98% pure by g.l.c.); $\nu_{max.}$ 920, 1000, 1640, and 1690 cm^{-1}, τ 0·7 (1H, s) (see later), 3·55 (1H, t, *J* 6 Hz, further split into quartets *J* 1·5 Hz), 3·9—5·2 (1H, m), 7·6—8 (5H, m), and 8·45 (3H, s), *m/e* 164 (M^+), 163, 149*, 135*, 123, and 81 [similar pattern to that from (Va) but not identical].

The n.m.r. spectra of both crude and purified samples of (VIa) contained minor signals at τ −0·02 (0·13H crude; 0·02H purified). The minor constituent was also detected by g.l.c. and had a slightly shorter retention time than the major compound. The ratio of peak heights for various samples was identical with the ratio of the aldehydic proton integrals. The minor compound was assigned as the *cis*-2 isomer.

The rearrangement of (Va) (0·5 g, 3 mmol) to (VIa) in xylene (100 ml) was closely followed by g.l.c. and the ratio of (Va) to (VIa) (including *cis–trans* ratio) was measured at intervals (area of peaks measured by triangulation). A graph of % (VIa) *vs.* time is given (Figure 2). The *cis–trans* ratio varied from 1 : 2 after 1·5 h to 1 : 5 after 40 h. The formation of (VIa) in bis-(2-methoxyethyl) ether and in decalin was also followed roughly (Figure 1). A small amount (<3%) of (VIa) was detectable in the reaction of (Ia) with 1-ethoxy-2-methylbutadiene in benzene after 80 h.

Rearrangement of 2-Methyl-2-vinylocta-4,7-dienal (Va) *to 2-Methyldeca-2,5,9-trienal* (VIIa).—A solution of 2-methyl-2-vinylocta-4,7-dienal (Va) (4·2 g, 26 mmol) in decalin (50 ml) containing a small amount of *N*-phenyl-1-naphthylamine (56·5 mg) was flushed with nitrogen for 1 h and then refluxed under nitrogen for 19 h. The solution [contains a mixture of 67% (VIIa) and 33% (VIa) by g.l.c.] was allowed to cool and chromatographed (the decalin is eluted first with petroleum and passes through the column as a translucent layer). Mixtures of 2-methyldeca-2,5,9-trienal (VIIa) (66% overall) and 2-methyl-5-vinylocta-2,7-dienal (VIa) (34% overall) were obtained (2·67 g, 63% yield). The required 2-methyldeca-2,5,9-trienal (VIIa) was eluted first and samples containing >90% (VIIa) could be obtained. Spectral data were recorded for a sample containing >92% (VIIa): $\nu_{max.}$ 930, 980, 1010, 1640, and 1690 cm^{-1} (no 690 cm^{-1} peak), τ 0·68 (1H, s),* 3·65 (1H, t, *J* 6·5 Hz, further split into quartets, *J* 1·2 Hz), 4·0—5·2 (5H, m), 7·0 (2H, m), 7·8—8·0 (4H, m), and 8·3 (3H, s).

The foregoing rearrangement in decalin was closely followed by g.l.c. and the ratios of (VIa) to (VIIa) measured at intervals [the conversion into (VIa) from (Va) is virtually complete (>98%) after 3 h] and a graph of % (VIIa) *vs.* time was drawn (Figure 4). The formation of (VIIIa) from (VIIa) in decalin, in *o*-dichlorobenzene, and in bis-(2-methoxyethyl) ether is shown in Figure 3. Compound (VIIIa) was also formed (*ca.* 10%) by refluxing (Va) in xylene for 43 h. Refluxing (Va) in solvents with higher b.p.s than decalin (*e.g.* quinoline, b.p. 238°) led to extensive polymerisation and decomposition.

Reaction of 3-Methylhexa-1,5-dien-3-ol (Ib) *with 1,1,3-Triethoxy-2-methylbutane*.—A mixture of 3-methylhexa-1,5-dien-3-ol (2·24 g, 20 mmol),† 1,1,3-triethoxy-2-methylbutane (3·06 g, 15 mmol),† and *o*-nitrobenzoic acid (100 mg) in toluene (30 ml) was refluxed for 24 h. Removal of the low-boiling fraction (as previously described) gave 3·5 ml of distillate, of which 1·0 ml was water-soluble (ethanol). A further 100 mg of *o*-nitrobenzoic acid was added, refluxing was continued for a further 20 h, and the ethanol was removed as before. This process was repeated so that the final amount of acid was 0·300 g and a total volume of 1·7 ml ethanol was separated (total reaction time 75 h). Work-up gave 2,5-dimethyl-2-vinylocta-4,7-dienal (Vb) (2·0 g, 76% yield based on acetal), b.p. 80—100° at 0·5 Torr (>90% pure by g.l.c.). Chromatography gave a sample >95% pure by g.l.c., $\nu_{max.}$ 930, 1000, 1640, 1680, and 1720 cm^{-1}, τ 0·68 (1H, s), 3·9—5·3 (7H, m), 7·25 (2H, m), 7·75 (2H, m), 8·33 (1·5H, s), 8·41 (1·5H, m), and 8·88 (3H, s), *m/e* 178 (M^+), 163, 149, 137, and 95.

This reaction when carried out in toluene gave (Vb) as the major product but in xylene rearrangement to 2,5-dimethyl-5-vinylocta-4,7-dienal (VIb) occurred. The crude reaction mixture was shown to contain two minor impurities by g.l.c. (total concentration <7%) in the ratio 4 : 1; on chromatography (Vb) was eluted first, followed by these two compounds. The following data showed them to be the *cis*-4 (*Z*) (20%) and *trans*-4 (*E*) (80%) isomers of 2-(1-ethoxyethyl)-2,5-dimethylocta-4,7-dienal, $\nu_{max.}$ 920, 1000, 1100, 1380, 1640, 1680, and 1720 cm^{-1}, τ 0·55 (1H, s), 4·0—5·2 (4H, m), 6·3—7 (3H, m), 7·2—7·4 (2H, m), 7·6—8·0 (2H, m), 1·58 and 1·66 (3H; see later), and 8·7—9 (9H, m); *m/e* 196 (M^+, weak), 178, 163, 149, 137, 121, 109, and 45. The ratio of the signals due to the methyl groups (τ 1·58 and 1·66) was different in two fractions from the column, one fraction showing predominantly the signal at 1·58 (*trans*-4) and the other predominantly the signal at 1·66 (*cis*-4). The ratio of the integrals was consistent with the ratio of peak areas by g.l.c. (*trans*-4 isomer with longer retention time).

Rearrangement of 2,5-Dimethyl-2-vinylocta-4,7-dienal (Vb) *to 2,5-Dimethyl-5-vinylocta-2,7-dienal* (VIb).—A solution of 2,5-dimethyl-2-vinylocta-4,7-dienal (VIb) (1·33 g, 7·1 mmol)

* One fraction from chromatography showed very weak n.m.r. signals (<2%) at τ 0·5 (1H, s) and 6·4 (2H, m), assigned to (VIIIa) [*cf.* (VIIIb)].

† Equimolar amounts also gave very good yields.

in bis-(2-methoxyethyl) ether (40 ml) containing a small amount of quinol (80 mg) was flushed with nitrogen for 2 h, and then refluxed under nitrogen for 40 h. Careful removal of the solvent under reduced pressure left a crude residue containing 2,5-dimethyl-2-vinylocta-4,7-dienal (Vb) (30%) and 2,5-dimethyl-5-vinylocta-2,7-dienal (VIb) (70%). Chromatography gave pure (VIb) (0·68 g, 55%; >95% pure by g.l.c.), $\nu_{max.}$ 930, 1020, 1650, and 1690 cm^{-1}; τ 0·7 (1H, s), 3·6 (1H, t, J 7 Hz, further split into quartets, J 1 Hz), 7·6—7·8 (4H, m), 8·72 (3H, d, J 1 Hz), and 8·98 (3H, s).

Rearrangement of 2,5-*Dimethyl*-2-*vinylocta*-4,7-*dienal* (VIb) *to* 2,5-*Dimethyldeca*-2,5,9-*trienal* (VIIb).—2,5-Dimethyl-2-vinylocta-4,7-dienal (Vb) (1·83 g) was converted into 2,5-dimethyl-5-vinylocta-2,7-dienal (VIb) as previously described. Crude (VIb) was dissolved in decalin (50 ml) and *N*-phenyl-1-naphthylamine (22 mg) was added. The solution was flushed with nitrogen for 1 h and then refluxed under nitrogen for 16 h. Chromatography gave 2,5-dimethyldeca-2,5,9-trienal (VIIb) (0·517 g, 31% yield) containing 6% of (VIb); $\nu_{max.}$ 920, 1000, 1360, 1640, and 1690 cm^{-1}, τ −0·24 (0·04H, s), 0·67 and 0·68 (0·96H, two singlets), 3·5—3·8 (1H, two superimposed triplets, J 7 Hz, further split into quartets, J 1 Hz), 4·0—5·2 (4H, m), 7·0 (2H, t, J 6 Hz), 7·8—8 (4H, m), and 8·25—8·4 (6H, m; see later); *m/e* 178 (M^+), 163, 149, 109, and 95 [similar to but not identical with the fragmentation pattern of (VIb)]. The crude decalin solution before chromatography showed two peaks on g.l.c. (56 : 44; major peak with longest retention time). After chromatography two fractions (minor peak by g.l.c. eluted first) containing these peaks in the ratio 56 : 44 (fraction 1) and 66 : 34 (fraction 2) were obtained. The n.m.r. spectra (100 MHz) of these fractions differed only in the region τ 8·25—8·4. This region was composed of three separate peaks (all finely split): τ 8·27 [assigned as methyl group on *cis* (*E*) trisubstituted double bond], 8·3 [assigned as 2-methyl group; *cf.* (Vb)], and 8·48 [d, J 0·75 Hz, assigned as methyl group on *trans* (*E*) trisubstituted double bond]. The ratio of the intensities of the signals at τ 8·27 and 8·48 was greater in fraction 1 than in fraction 2, which indicated that the major isomer with the longest retention time was the *trans*-5 (*E*) form.

Reaction of 2,5-*Dimethylhexa*-1,5-*dien*-3-*ol* (Ic) *with* 1,1,3-*Triethoxy*-2-*methylbutane*.—A mixture of 2,5-dimethylhexa-1,5-dien-3-ol (6·36 g, 50 mmol), 1,1,3-triethoxy-2-methylbutane (15·27 g, 75 mmol), and *o*-nitrobenzoic acid (250 mg, 1·5 mmol) dissolved in xylene (100 ml) was refluxed for 18 h. The ethanol formed during the reaction was removed by distillation as previously described. More catalyst was added and the process repeated. The subsequent acid concentrations (mmol) and overall reaction times (h) were as follows: 3·0, 40; 6·0, 65; 8·0, 85. A total of 8·0 ml of ethanol was separated. Work-up gave a mixture (4·9 g, 51%) of 2,4,7-trimethyl-2-vinylocta-4,7-dienal (Vc) (20%) and 2,7-dimethyl-5-(prop-2-enyl)octa-2,7-dienal (VIc) (80%), b.p. 100—140° at 0·5 Torr. Compounds (Vc) and (VIc) were separated by chromatography.

2,4,7-Trimethyl-2-vinylocta-4,7-dienal (Vc) (>90% pure by g.l.c.) showed $\nu_{max.}$ 900, 930, 1650, and 1720 cm^{-1}, τ 0·65 (1H, s), 3·9—5·4 (6H, m), 7·65 (2H, s), 8·33 and 8·45 (6H, two singlets, see later), and 8·89 (3H, s), *m/e* 192 (M^+), 177, 163, 149, 137, and 109. The ratio of the two n.m.r. signals at τ 8·45 [assigned as methyl group on *trans* (*E*) trisubstituted double bond] and 8·33 [assigned as methyl groups on the disubstituted double bond and on the *cis* (*Z*) trisubstituted double bond] was 1·0 : 1·5, which indicated that (Vc) contained >80% * of the *trans*-4 isomer.

2,7-Dimethyl-5-(prop-2-enyl)octa-2,7-dienal (VIc) [85% pure by g.l.c.; contains 3% (Vc), 12% unknown] showed $\nu_{max.}$ 900, 1640, and 1680 cm^{-1}, τ −0·07 (0·03H, s), 0·65 (0·97H, s), 3·7 (1H, t, J 7·5 Hz, further split into quartets, J 1 Hz), 5·25 (4H, m), 7·5—8 (5H, m), and 8·3 (9H, s).

The crude reaction mixture contained a small amount of an unknown compound, which was shown to be another derived from (Ic); this compound became the major product if high concentrations of catalyst were used.

Rearrangement of 2,4,7-*Trimethyl*-2-*vinylocta*-4,7-*dienal* (Vc) *to* 2,6,9-*Trimethyldeca*-2,5,9-*trienal* (VIIc).—A solution of the crude reaction mixture (1·08 g) of (Vc) (20%) and (VIc) (80%) (prepared as above) in decalin (100 ml), containing *N*-phenyl-1-naphthylamine (25 mg), was flushed with nitrogen for 1 h and then refluxed under nitrogen for 18 h. Chromatography gave a mixture containing (>75%), 2,6,9-trimethyldeca-2,5,9-trienal (VIIc) (0·43 g, 40%). A fraction containing (VIIc) (82%), (VIc) (8%), and unknowns (10%) was obtained; $\nu_{max.}$ 810, 900, 1000, 1650, and 1690 cm^{-1}, τ 0·4 (0·01H, s),† 0·67 (1H, s), 3·6 (1H, t, J 7·4 Hz, further split into quartets, J 1·4 Hz), 4·8 (1H, t, J 7 Hz, further split into quartets, J 1 Hz), 5·3 (2H, s), 6·94 (2H, t, J 7 Hz), 7·84 (4H, s), and 8·2—8·5 (9H, s), *m/e* 192 (M^+), 177, 163, 149, 137, and 109 [fragmentation pattern very similar to that of (Vc)]. Assignment of stereochemistry of the 5-double bond was based on the relative intensities (*ca.* 1 : 1 : 1) of the n.m.r. signals due to the methyl groups which occurred at τ 8·24 [methyl group on the disubstituted double bond (?)], 8·28 [methyl group on 2-trisubstituted double bond], and 8·34 [methyl group on *trans*-5-trisubstituted double bond (?)].

2-*Methyl*-5-*vinylocta*-2,7-*dien*-1-*ol* (X).—2-Methyl-5-vinylocta-2,7-dienal (VIa) ‡ (4·98 g, 30 mmol) in dry ether was added dropwise to a stirred solution of lithium aluminium hydride (2·28 g, 60 mmol) in ether at 0°. Stirring was continued for 1 h, the excess of hydride was destroyed by dropwise addition of ethanol, and the mixture was poured into an excess of ice-cold dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether (3 × 20 ml). Combined ethereal fractions were dried ($MgSO_4$). Distillation gave 2-methyl-5-vinylocta-2,7-dien-1-ol (X) (3·96 g, 80%), b.p. 70—80° at 0·2 Torr [<90% pure by g.l.c.; two peaks 87 : 13 (*trans*-2 : *cis*-2)], $\nu_{max.}$ 920, 1000—1040, 1640, and 3400 cm^{-1}, τ 4·05—5·3 (6H, m), 6·25 (2H, d), 6·7 (1H, s), 7·5—8·0 (5H, m), 8·35 (0·39H, s, *cis*-2), and 8·48 (2·61H, s, *trans*-2).

2-*Methyldeca*-2,5,9-*trien*-1-*ol* (XI).—This was prepared from 2-methyldeca-2,5,9-trienal (0·51 g, 3 mmol) (VIIa) by the method described for (X). Distillation gave (XI) (0·4 g, 80%) [>95% pure by g.l.c., contains 5% (X)], $\nu_{max.}$ 920, 980, 1000—1040, 1640, and 3400 cm^{-1} (no 690 cm^{-1} peak), τ 4·0—5·3 (6H, m), 6·0—6·3 (2H, two peaks), 6·65 (1H, s), 7·2—7·5 (2H, m), 7·8—8·0 (4H, m), and 8·44 (3H, s).

Reaction of 2-*Methyl*-5-*vinylocta*-2,7-*dien*-1-*ol* (X) *with* 1,1,3-*Triethoxy*-2-*methylbutane*.—A mixture of 2-methyl-5-vinylocta-2,7-dien-1-ol (2·20 g, 13 mmol), 1,1,3-triethoxy-2-methylbutane (4·08 g, 20 mmol), and *o*-nitrobenzoic acid

* The principal impurity in (Vc) is (VIc) (<5%), which has strong signals in the n.m.r. at τ 8·3. This indicates that >80% of the *trans*-4 isomer is present.

† Assigned as (VIIIc) [*cf.* (VIIIa) and (VIIIb)].

‡ 95% pure by g.l.c.; contains 87% *trans*-2 and 13% *cis*-2 isomer.

(66 mg) dissolved in toluene (30 ml) was refluxed for 24 h. Fractional distillation gave a low-boiling fraction (4 ml) containing ethanol (1 ml). More *o*-nitrobenzoic acid (100 mg) was added and the mixture was refluxed for a further 24 h. Work-up gave a crude residue (3 g) which after chromatography gave a mixture (*ca.* 50 : 50) of 2-methyl-3-(prop-2-enyl)-2,5-divinyloct-7-enal (XII) * and 2,6-dimethyl-9-vinyldodeca-2,6,11-trienal (XIV) (0·9 g, 30% overall). In another reaction with 69 h reaction time the αβ-unsaturated aldehyde (XIV) was the major product (similar yield). Further chromatography of the mixture gave essentially pure (>90% by g.l.c.) 2,6-dimethyl-9-vinyldodeca-2,6,11-trienal (XIV); $\nu_{max.}$ 930, 1000, 1640, and 1690 cm^{-1}, τ −0·05 (0·065H, s), 0·7 (0·935H, s), 3·65 (1H, t, *J* 6 Hz), 4·0—5·3 (7H, m), 7·5—8 (9H, m), and 8·4 and 8·32 (6H, two singlets; see later); *m/e* 232 (M^+), 217, 203, 191, 151, and 149.

The two signals due to methyl groups at τ 8·4 [assigned as methyl group attached to a *trans*-6 trisubstituted double bond] and 8·32 [assigned as methyl groups on *cis*-6 double bond and *trans*/*cis*-2 double bond] were in the ratio 1 : 1·28, which indicated the major isomer was the *trans*-6 (88%). The ratio of signals at τ −0·05 and 0·7 showed that 6·5% *cis*-2 isomer was present.

Rearrangement of 2,6-*Dimethyl*-9-*vinyldodeca*-2,6,11-*trienal* (XIV) *to* 2,6-*Dimethyltetradeca*-2,6,9,13-*tetraenal* (XV).—2,6-Dimethyl-9-vinyldodeca-2,6,11-trienal (XIV) (0·490 g, 21 mmol) † was dissolved in decalin (30 ml), and *N*-phenyl-1-naphthylamine (10 mg) was added. The solution was flushed with nitrogen for 1 h, then refluxed under nitrogen for 24 h to give a mixture (240 mg, 50%) of (XIV) (20%) and (XV) (80%). Chromatography gave 2,6-dimethyltetradeca-2,6,9,13-tetraenal (XV) [*ca.* 75% pure by g.l.c.], $\nu_{max.}$ 930, 980, 1000, 1640, and 1690 cm^{-1} (no 690 cm^{-1} peak), τ 0·68 (1H, s), 3·6 (1H, t, *J* 7 Hz), 4·0—5·3 (7H, m), 7·2—8 (10H, m), and 8·3 and 8·38 (6H, two s; see later), *m/e* 232 (M^+), 217, 203, 191, 151, and 149 [very similar fragmentation pattern to that of (XIV)].

Rearrangement of 2-*Methyl*-5-*vinylocta*-2,7-*dien*-1-*ol* (X) *to* 2-*Methyldeca*-2,5,9-*trien*-1-*ol* (XI).—A solution of 2-methyl-5-vinylocta-2,7-dien-1-ol (X) (581 mg; mixture of 87% *trans*-2 and 13% *cis*-2) in decalin (30 ml) was flushed with nitrogen for 1 h and then refluxed in nitrogen for 15 h. The rearrangement was followed by g.l.c. and two products were formed in the ratio 86 : 14. The major product had a retention time identical with that of a sample of the pure *trans*-2,*trans*-5-isomer of (XI), prepared by reduction of the aldehyde (VIIa). The minor product was assigned as the *cis*-2 isomer (shorter retention time).

Reaction of 2-*Methyldeca*-2,5,9-*trien*-1-*ol* (XI) *with* 1,1,3-*Triethoxy*-2-*methylbutane*.—This reaction was followed by g.l.c. with no attempt at isolation of the products. A mixture of 2-methyldeca-2,5,9-trien-1-ol (285 mg, 1·7 mmol), 1,1,3-triethoxy-2-methylbutane (612 mg, 3 mmol), and *o*-nitrobenzoic acid (10 mg) in toluene (30 ml) was refluxed for 18 h. The mixture contained two products, the major product (90%) with the shorter retention time [(XIII)], and a minor product (XV) (10%). After addition of more *o*-nitrobenzoic acid (15 mg) and refluxing for 17 h the ratio of minor to major product was 40 : 60. The minor compound had a retention time identical with that of 2,6-dimethyltetradeca-2,6,9,13-tetraenal (XV) prepared by rearrangement of (XIV). The major product under these conditions was assigned as 2-methyl-3-(prop-2-enyl)-2-vinyldeca-5,9-dienal (XIII) and this was supported by rearrangement of the 40 : 60 product mixture to a 20 : 80 mixture on refluxing in xylene (20 h).

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* Not isolated; samples containing principally this isomer (g.l.c.) showed strong i.r. absorption at 1700 cm^{-1}. Also mixtures of (XII) and (XIV) were converted predominantly into (XIV) by refluxing in xylene.

† Either pure or a mixture with (XII).