Allenes. Part XXIV.[1] Preparation of α-Allenic Alcohols from the Mono-O-tetrahydropyran-2-yl Derivatives of Butyne-1,4-diols

By James S. Cowie, Phyllis D. Landor, and Stephen R. Landor,*† Woolwich Polytechnic, London SE18 and Makerere University, Kampala, Uganda
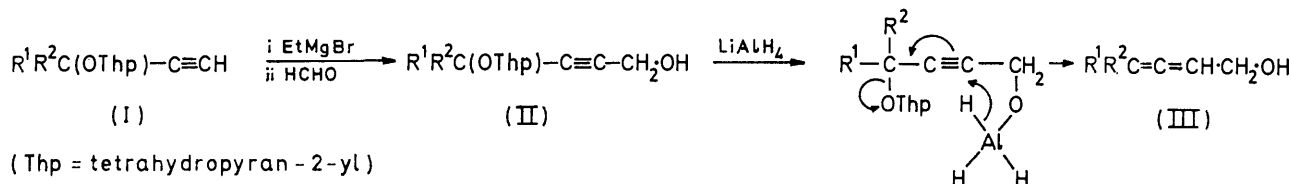
α-Allenic alcohols are obtained in high yield by the ready reductive elimination of the tetrahydropyranyloxy-group from the mono-O-tetrahydropyran-2-yl derivatives of butyne-1,4-diols with lithium aluminium hydride. Attempted reduction of the mono-O-tetrahydropyranyl derivative of an enynediol gave an isomeric mixture of an allenic and an acetylenic alcohol. O-Tetrahydropyranyl groups on secondary or tertiary alcohol functions have been shown to migrate to primary systems.

METHODS hitherto reported for the preparation of α-allenic alcohols include the reaction of allenic organo-metallic reagents with carbonyl compounds,[2] the reaction of alkyl-lithium compounds with alk-4-en-2-yn-1-ols,[3] the replacement of bromine in 2-bromoallenes by acetate and then hydroxy,[4] and addition of dibromocarbene to an olefinic alcohol followed by treatment with butyl-lithium.[5] These methods give low yields of allenic alcohols, mixtures with acetylenic alcohols, or branched-chain compounds.

The new method described here [6] overcomes these disadvantages: an α-allenic alcohol (III) can easily be prepared by the reaction of a prop-1-yn-3-ol with di-hydropyran, followed by treatment with ethylmagnesium bromide and gaseous formaldehyde to give the mono-O-tetrahydropyranyl derivative of a butyne-1,4-diol (II). Reduction of this with lithium aluminium hydride gives the allenic alcohol (III) as the sole product in high yield (Scheme 1). The method has been applied to both straight-chain (III; $R^1 = Pr$, $R^2 = H$) and branched-chain (III; $R^1 = Me$, $R^2 = Et$; $R^1 = Pr^i$, $R^2 = H$) allenic alcohols and used to prepare dodeca-2,3-dienol (III; $R^1 = $ n-octyl, $R^2 = H$), the key allenic alcohol in the synthesis of (±)-methyl tetradeca-*trans*-2,4,5-trienoate, the allenic sex pheromone produced by the male dried bean beetle.[7] Yields of allenic alcohols from the monoprotected diols (II) were 73—94%. The mechanism of the reductive elimination step is seen as an intramolecular hydride transfer to C-2 with concerted elimination of the tetrahydropyranyloxy-group. This was supported by the observation of C-2 deuteriation (as

shown by i.r. and n.m.r. spectra) on reduction with lithium aluminium deuteride.

Mono-O-tetrahydropyranyl derivatives of butyne-1,4-diols (II) should be dried over potassium carbonate-magnesium sulphate and must be distilled at low temperature and pressure (e.g. 10^{-4} mmHg) in order to avoid migration of the tetrahydropyranyl group from a secondary or tertiary to a primary alcoholic function. Thus in an early experiment, when these precautions were not taken (4-tetrahydropyran-2-yloxyhept-2-yn-1-ol was distilled at 124° and 1·3 mmHg), a mixture of allenic alcohols (IV) and (V) was produced on reduction

SCHEME 1

(Scheme 2). Further investigation showed that this is a general reaction: when an equimolar mixture of 3-methyl-3-tetrahydropyran-2-yloxypent-1-yne and prop-2-yn-1-ol is heated at 170° under reflux, 75% exchange
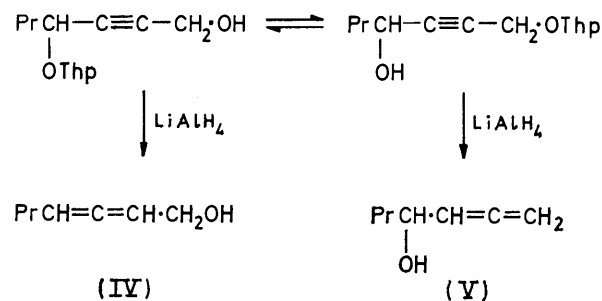
SCHEME 2

has occurred after 35 h; on addition of a trace of hydro-chloric acid at room temperature exchange takes place

† Present address: Makerere University, P.O. Box 16020, Kampala, Uganda.

[1] Part XXIII, S. R. Landor, B. Demetriou, R. J. Evans, R. Grzesowiak, and D. Pavey, J.C.S. Perkin II, 1972, 1995.
[2] J. L. Moreau and M. Gaudemar, Bull. Soc. chim. France, 1970, 2171.
[3] L. N. Cherkasov, Kh. V. Bal'yan, and V. A. Kormer, Zhur. org. Khim., 1966, 2, 1934.

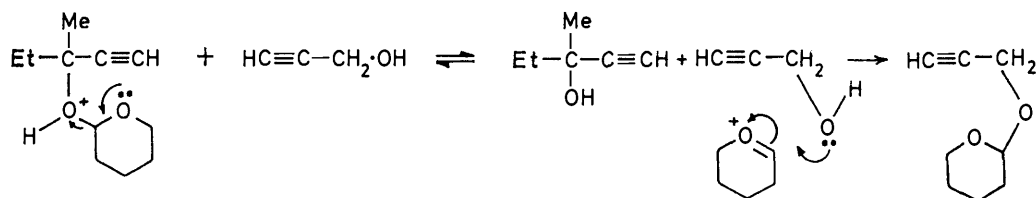[4] F. Michael and C. Troyanowsky, Compt. rend., 1966, 262C, 1705.
[5] M. Bertrand and R. Maurin, Bull. Soc. chim. France, 1967, 2779; T. L. Jacobs and R. S. Macomber, J. Amer. Chem. Soc., 1969, 91, 4824.
[6] Preliminary communication, J. S. Cowie, P. D. Landor, and S. R. Landor, Chem. Comm., 1969, 541.
[7] P. D. Landor, S. R. Landor, and S. Mukasa, Chem. Comm., 1971, 1638.

and equilibrium (4 : 96) is reached very rapidly (Scheme 3).

The exchange reaction was used to prepare the O-tetrahydropyranyl derivatives of 3-chloropropan-1-ol and 3-bromopropan-1-ol, by use of the tetrahydropyranyl derivative of t-butyl alcohol; this could be the method
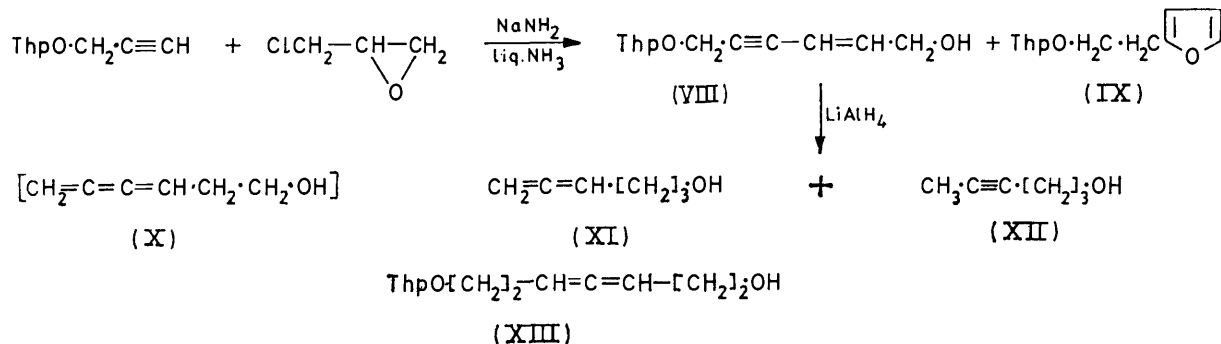
of an enynediol should give a cumulenic alcohol. To test this, 6-tetrahydropyran-2-yloxyhex-2-en-4-yn-1-ol (VIII) was required. This was prepared from 1-tetrahydropyran-2-yloxyprop-2-yne and 2-chloromethyl-oxiran. A low boiling by-product was shown to be 1-(2-furyl)-2-tetrahydropyran-2-yloxyethane (IX) by

SCHEME 3

of choice in cases where the direct reaction with dihydro-pyran is difficult.

The reductive elimination has also been applied to the synthesis of terminal allenic alcohols (VII). The intermediate tetrahydropyranyl derivative (VI) can readily

$$R^1R^2C(OH)-C{\equiv}C-CH_2{\cdot}OThp \qquad R^1R^2C(OH)-CH{=}C{=}CH_2$$
$$(VI) \qquad\qquad\qquad (VII)$$
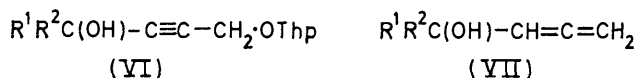
be prepared from the reaction of an aldehyde or ketone with 3-tetrahydropyran-2-yloxyprop-1-yne,[8] followed by reductive elimination of the tetrahydropyranyloxy-group by lithium aluminium hydride. The allenic alcohols (VII; R^1 = Pr, R^2 = H; R^1 = Et, R^2 = Me)

analysis, i.r. and u.v. spectra, and hydrolysis to the known 2-(2-furyl)ethanol,[10] and was presumably formed by cyclisation of 6-tetrahydropyran-2-yloxyhex-cis-2-en-4-yn-1-ol.[11] The desired alcohol (VIII) was reduced with lithium aluminium hydride but did not give the cumulenic alcohol (X); instead further reduction gave a mixture of hexa-4,5-dien-1-ol (XI) and hex-4-yn-1-ol (XII) (63 : 37 by g.l.c.). Hydrogenation of the mixture gave only n-hexanol, showing that the two components were isomeric. Separation was achieved by g.l.c. and identification by i.r. and n.m.r. spectra and analysis.

The interpolation of a further methylene group between the tetrahydropyranyloxy- and acetylene groups of compound (VIII) prevents concerted elimination

$$[CH_2{=}C{=}C{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH] \qquad CH_2{=}C{=}CH{\cdot}[CH_2]_3OH \qquad + \qquad CH_3{\cdot}C{\equiv}C{\cdot}[CH_2]_3OH$$
$$(X) \qquad\qquad\qquad (XI) \qquad\qquad\qquad\qquad (XII)$$

$$ThpO[CH_2]_2{-}CH{=}C{=}CH{-}[CH_2]_3OH$$
$$(XIII)$$

have been prepared in 78—87% yield. The tetra-hydropyranyloxy-group is much more easily displaced than a hydroxy-group, as is shown by the reduction with lithium aluminium hydride of but-2-yne-1,4-diol under comparable conditions. Only 2% of buta-2,3-dien-1-ol was obtained; the major product was but-2-ene-1,4-diol (98%). However, when the displaced hydroxy-group was in a tertiary position, as in 2,5-dimethylhex-3-yne-2,5-diol, the allenic alcohol was obtained in 6% yield, and with a large excess of lithium aluminium hydride this was increased to 51%, with concomitant formation of trans-2,5-dimethylhex-3-ene-2,5-diol.[9]

Finally, it was reasoned that the application of this reaction to the mono-O-tetrahydropyranyl derivative

of the tetrahydropyranyloxy-group, and the expected allenic product (XIII) is formed.

EXPERIMENTAL

I.r. spectra were determined for liquid films (0·025 mm cell) and for 5% solutions in chloroform with Perkin-Elmer 237 and 337 spectrophotometers. U.v. spectra were obtained for ethanolic solutions with a Bausch and Lomb Spectronic 505 spectrometer. N.m.r. spectra were determined with Perkin-Elmer R10 and Varian A60 spectrometers for solutions in deuteriochloroform with tetramethylsilane as internal standard. G.l.c. was carried out with a Pye 104 instrument on glass columns (5 ft), with nitrogen as carrier gas at a flow rate of 2·5 l h⁻¹.

[8] P. D. Landor, S. R. Landor, and E. S. Pepper, J. Chem. Soc. (C), 1967, 185.
[9] A. C. Day and M. C. Whiting, J. Chem. Soc. (B), 1967, 991.
[10] E. D. Amstutz and J. Plucker, J. Amer. Chem. Soc., 1941, 63, 206.
[11] S. R. Landor and E. S. Pepper, J. Chem. Soc., 1966, 2283.

3-*Tetrahydropyran*-2-*yloxyhex*-1-*yne* (I; R^1 = Pr, R^2 = H).—Hex-1-yn-3-ol (32·7 g, 0·33 mol) was mixed with 2,3-dihydropyran (30·7 g, 0·36 mol) and concentrated hydrochloric acid (2 drops) was added. The mixture was shaken, allowed to cool to room temperature, dried (K_2CO_3–$MgSO_4$), filtered, and distilled to give 3-*tetrahydropyran*-2-*yloxyhex*-1-*yne* (49·2 g, 81%), b.p. 103° at 15 mmHg (Found: C, 72·7; H, 9·9. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%), $\nu_{max.}$ 3253 (≡CH) and 2100 (C≡CH) cm⁻¹, g.l.c., t_R 5·6 (60%) and 6·2 min (40%) (10% silicone oil on Chromosorb W; 120°) due to diastereoisomers.

3-*Methyl*-3-*tetrahydropyran*-2-*yloxypent*-1-*yne* (I; R^1 = Me, R^2 = Et).[12]—3-Methylpent-1-yn-3-ol (32·7 g) was treated similarly with dihydropyran to give 3-methyl-3-tetrahydropyran-2-yloxypent-1-yne (51·3 g, 85%), b.p. 82—83° at 6 mmHg, $\nu_{max.}$ 3250 (≡CH) and 2100 (C≡CH). G.l.c. showed an unresolved doublet (diastereoisomers), t_R 4·3 min (10% silicone oil on Chromosorb W; 120°).

4-*Tetrahydropyran*-2-*yloxyhept*-2-*yn*-1-*ol* (II; R^1 = Pr, R^2 = H).—3-Tetrahydropyran-2-yloxyhex-1-yne (22·4 g, 0·125 mol) dissolved in dry tetrahydrofuran (40 ml) was added dropwise with stirring to ethylmagnesium bromide [from ethyl bromide (26·4 g, 0·25 mol) and magnesium (6 g, 0·25 g atom) in tetrahydrofuran (100 ml)]. Gaseous formaldehyde, generated from paraformaldehyde (6 g), was passed through a heated tube onto the surface of the stirred mixture. After 2 h the mixture was poured on aqueous ammonium chloride (10%; 60 ml). The organic phase and ether extracts of the aqueous phase were dried (K_2CO_3–$MgSO_4$) and distilled at 5×10^{-5} mmHg to give 4-*tetrahydropyran*-2-*yloxyhept*-2-*yn*-1-*ol* (20 g, 80%) (Found: C, 67·7; H, 9·4. $C_{12}H_{20}O_3$ requires C, 67·7; H, 9·5%), $\nu_{max.}$ 3400 (OH) and 2200 (C≡C) cm⁻¹, g.l.c. t_R 27 min (10% silicone oil on Chromosorb W; 150°). Heating a sample at 160° for several h and monitoring by g.l.c. showed the gradual appearance of the isomeric 1-tetrahydropyran-2-yloxyhept-2-yn-4-ol, t_R 30·6 min. 4-Tetrahydropyran-2-yloxyhept-2-yn-1-ol similarly prepared but distilled at 1·3 mmHg (b.p. 124—126°) gave a mixture containing 1-tetrahydropyran-2-yloxyhept-2-yn-4-ol (37%).

4-*Methyl*-4-*tetrahydropyran*-2-*yloxyhex*-2-*yn*-1-*ol* (II; R^1 = Me, R^2 = Et).—3-Methyl-3-tetrahydropyran-2-yloxypent-1-yne (17·5 g) was similarly treated with ethylmagnesium bromide then gaseous formaldehyde to give 4-*methyl*-4-*tetrahydropyran*-2-*yloxyhex*-2-*yn*-1-*ol* (19·2 g, 76%), b.p. 104—106° at 0·5 mmHg (Found: C, 67·4; H, 9·4. $C_{12}H_{20}O_3$ requires C, 67·8; H, 9·5%), $\nu_{max.}$ 3400 (OH) and 2200 (C≡C) cm⁻¹, g.l.c. t_R 14·7 min (10% silicone oil on Chromosorb W; 150°).

Migration of the Tetrahydropyran-2-*yl Group.*—(a) An equimolar mixture of 3-methyl-3-tetrahydropyran-2-yloxy-pent-1-yne (6·0 g, 0·033 mol) and prop-2-yn-1-ol (1·9 g, 0·033 mol) was refluxed (bath temp. 170°) and the reaction was monitored by g.l.c. Migration of the tetrahydropyran-2-yl group took place from tertiary to primary OH and equilibrium was reached in 35 h, when 75% 3-tetrahydro-pyran-2-yloxyprop-1-yne was present.

(b) 3-Methyl-3-tetrahydropyran-2-yloxypent-1-yne (12·1 g, 0·066 mol) and prop-2-yn-1-ol (3·7 g, 0·066 mol) were mixed and concentrated hydrochloric acid (2 drops) was added. The mixture was cooled to room temperature, anhydrous K_2CO_3 was added, and the mixture was filtered

[12] D. N. Robertson, *J. Org. Chem.*, 1960, **25**, 931.
[13] W. E. Parham and E. L. Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 4187.

and distilled to give 3-tetrahydropyran-2-yloxyprop-1-yne (7·9 g; 96% pure by g.l.c.), b.p. 42° at 1·5 mmHg, identified by comparison with an authentic sample. 3-Methylpent-1-yn-3-ol was recovered from the cold trap.

1-*Bromo*-3-*tetrahydropyran*-2-*yloxypropane*.[13]— 2-Methyl-2-tetrahydropyran-2-yloxypropane (15·8 g, 0·1 mol) (prepared from t-butyl alcohol and 2,3-dihydropyran), was mixed with 3-bromopropan-1-ol (13·9 g, 0·1 mol) and concentrated hydrochloric acid (2 drops) was added. Work-up in the usual way gave 1-bromo-3-tetrahydropyran-2-yloxy-propane (9·4 g, 42%), b.p. 69° at 1·2 mmHg, g.l.c. t_R 20 min (10% silicone oil on Chromosorb W; 100°), τ (CDCl₃) 8·39br (6H, s, CH·[CH₂]₃·CH₂), 7·88 (2H, m, CH₂·CH₂·CH₂-Br), 5·92—6·7 (6H, m, OCH₂, CH₂·CH₂Br, CH·[CH₂]₃·CH₂), and 5·41 (1H, unresolved t, CH·[CH₂]₃·CH₂).

1-*Chloro*-3-*tetrahydropyran*-2-*yloxypropane*.[13]— 2-Methyl-2-tetrahydropyran-2-yloxypropane (31·6 g) was similarly treated with 3-chloropropan-1-ol to give 1-chloro-3-tetra-hydropyran-2-yloxypropane (30 g, 84%), b.p. 56—57° at 1·0 mmHg, g.l.c. t_R 12 min (10% silicone oil on Chromosorb W; 120°), τ (CDCl₃) 8·37 (6H, s, [CH₂]₃), 8·0 (2H, m, CH₂·CH₂), 6·33 (6H, m, CH₂·O, CH₂Cl, CH·[CH₂]₃·CH₂), and 5·42 (1H, unresolved t, CH·[CH₂]₃·CH₂).

1-*Tetrahydropyran*-2-*yloxyhept*-2-*yn*-4-*ol* (*with* J. P. REGAN).—3-Tetrahydropyran-2-yloxyprop-1-yne (22 g, 0·15 mol) was added to stirred ethylmagnesium bromide [from ethyl bromide (14·5 g, 0·15 mol) and magnesium (3·6 g, 0·15 atom) in dry tetrahydrofuran (60 ml)] and after 1 h n-butyraldehyde (10·8 g, 0·15 mol) was added. The mixture was stirred under reflux for 2 h, poured into aqueous ammonium chloride, and worked up in the usual way. Distillation gave 1-tetrahydropyran-2-yloxyhept-2-yn-4-ol (28·4 g, 89%), b.p. 97—98° at 10⁻⁴ mmHg, $\nu_{max.}$ 3425 (OH) and 2200 (C≡C) cm⁻¹. G.l.c. showed one major peak (97%), t_R 25·8 min (10% silicone oil on Chromosorb W; 150°).

3-*Methyl*-6-*tetrahydropyran*-2-*yloxyhex*-4-*yn*-3-*ol*.— 3-Tetrahydropyran-2-yloxyprop-1-yne (22 g) was treated similarly with butan-2-one (10·8 g) to give 3-*methyl*-6-*tetra-hydropyran*-2-*yloxyhex*-4-*yn*-3-*ol* (28·7 g, 90%), b.p. 104° at 0·2 mmHg (Found: C, 67·8; H, 9·2. $C_{12}H_{20}O_3$ requires C, 67·8; H, 9·5%), $\nu_{max.}$ 3425 (OH) and 2200 (C≡C) cm⁻¹. G.l.c. gave a single peak, t_R 14·5 min (10% silicone oil on Chromosorb W; 150°).

Hepta-2,3-*dien*-1-*ol* (III; R^1 = Pr, R^2 = H).—4-Tetra-hydropyran-2-yloxyhept-2-yn-1-ol (11·5 g, 0·05 mol) in dry ether (20 ml) was added to a slurry of lithium aluminium hydride (2·3 g, 0·054 mol) in dry ether (100 ml). The mixture was refluxed for 4 h, decomposed with the minimum amount of cold water (added dropwise until the grey slurry just turned white), and filtered; the solid was washed with ether (3 × 10 ml) and the combined extracts were dried ($MgSO_4$). Distillation gave *hepta*-2,3-*dien*-1-*ol* (5·7 g, 95%), b.p. 82° at 15 mmHg, n_D^{21} 1·4750 (Found: C, 74·8; H, 11·1. $C_7H_{12}O$ requires C, 74·9; H, 10·8%), $\nu_{max.}$ 3330 (OH), 1965 (C=C=C), and 875 (C=C=CH) cm⁻¹, g.l.c. t_R 17·4 min (20% Carbowax 20M on Chromosorb W; 100°), τ (CDCl₃) 9·1 (3H, t, CH₃), 8·58 (2H, m, CH₃·CH₂·CH₂), 8·08 (2H, m, =CH·CH₂), 7·36 (1H, s, OH, disappears on deuteriation), 5·9 (2H, dd, CH₂·OH), and 4·72—4·66 (2H, m, CH=C=CH).

2-*Deuteriohepta*-2,3-*dien*-1-*ol*.— 4-Tetrahydropyran-2-yl-

oxyhept-2-yn-1-ol (2·12 g, 0·01 mol) in dry ether (10 ml) was added dropwise with stirring to lithium aluminium deuteride (0·42 g, 0·01 mol) in dry ether (20 ml). The mixture was refluxed for 6 h and worked up as before. Distillation gave 2-deuteriohepta-2,3-dien-1-ol (1·1 g, 99%), b.p. 73° at 12 mmHg. G.l.c. showed two peaks, t_R 12 (7%) and 22·5 min (93%) (20% Carbowax 20M on Chromosorb W; 100°) and these compounds were separated by g.l.c. (6 ft Carbowax columns at 150°) to give (a) 3-deuteriohepta-1,2-dien-4-ol, $v_{max.}$ 3350 (OH), 1950 (C=C=C), and 840 cm^{-1} ($>$C=C=CH$_2$), g.l.c. t_R 12 min (20% Carbowax 20M on Chromosorb W; 100°), and (b) 2-deuteriohepta-2,3-dien-1-ol, $v_{max.}$ 3350 (OH), 1960 (C=C=C), and 865 (HC=C=CD) cm^{-1}, g.l.c. t_R 22·0 min (20% Carbowax 20M on Chromosorb W; 100°), τ (CDCl$_3$) 9·08 (3H, t, $J_{6,7}$ 6·5 Hz, CH$_3$), 8·58 (2H, m, $J_{5,6}$ 6·5 Hz, CH$_3$·CH$_2$·CH$_2$), 8·01 (2H, m, $J_{5,6}$ 6·5 Hz, CH$_2$–CH=), 7·78 (1H, s, OH), 5·92 (2H, d, $J_{4,1}$ 3, $J_{1,5}$ 0·75 Hz, CH$_2$OH), and 4·76 (1H, m, $J_{4,5}$ 6, $J_{1,4}$ 3 Hz, CH$_2$–CH=C=CD).

4-Methylhexa-2,3-dien-1-ol (III; R^1 = Me, R^2 = Et).— 4-Methyl-4-tetrahydropyran-2-yloxyhex-2-yn-1-ol (14·2 g) was similarly treated with lithium aluminium hydride to give *4-methylhexa-2,3-dien-1-ol* (5·5 g, 73%), b.p. 56° at 7 mmHg (Found: C, 75·2; H, 10·8. C$_7$H$_{12}$O requires C, 74·9; H, 10·8%), $v_{max.}$ 3325 (OH), 1970 (C=C=C), and 875 (HC=C=CH) cm^{-1} n_D^{21} 1·4779, g.l.c. t_R 4·5 min (20% Carbowax 20M on Chromosorb W; 100°), τ (CDCl$_3$) 9·05 (3H, m, CH$_3$·CH$_2$), 8·32 [3H, dt, CH$_3$C(Et)], 8·26br (1H, s, OH, disappears on deuteriation), 8·16 (2H, qd, CH$_3$·CH$_2$), 5·95 (2H, d, CH$_2$·OH), and 4·71 (1H, m, =CH).

Hepta-1,2-dien-4-ol (V).—1-Tetrahydropyran-2-yloxy-hept-2-yn-4-ol (9·55 g) on similar reductive elimination gave *hepta-1,2-dien-4-ol* (3·95, 78%), b.p. 56° at 10 mmHg (Found: C, 75·5; H, 10·9. C$_7$H$_{12}$O requires C, 74·9; H, 10·8%), $v_{max.}$ 3350 (OH), 1960 (C=C=C), and 845 (C=C=CH$_2$) cm^{-1}, n_D^{21} 1·4670, g.l.c. t_R 8·4 min (20% Carbowax 20M on Chromosorb W; 100°), τ (CDCl$_3$) 9·05 (3H, m, CH$_3$·CH$_2$), 8·5 (4H, m, CH$_2$·CH$_2$), 7·5 (1H, s, OH, disappears on deuteriation), 5·75 (1H, m, CH·OH), 5·12 (2H, m, =CH$_2$), and 4·72 (1H, m, –CH=).

3-Methylhexa-4,5-dien-3-ol (VIII; R^1 = Me, R^2 = Et).— 3-Methyl-6-tetrahydropyran-2-yloxyhex-4-yn-3-ol (9·5 g) on reductive elimination gave *3-methylhexa-4,5-dien-3-ol* (4·5 g, 87%), b.p. 46—47° at 10 mmHg (Found: C, 74·6; H, 11·0. C$_7$H$_{12}$O requires C, 74·9; H, 10·8%), $v_{max.}$ 3390 (OH), 1965 (C=C=C), and 845 (C=C=CH$_2$) cm^{-1}, g.l.c. t_R 2·5 min (20% Carbowax 20M on Chromosorb W; 120°), n_D^{21} 1·4679, τ (CDCl$_3$) 9·1 (3H, t, CH$_3$·CH$_2$), 8·7 (3H, s, CH$_3$·C), 8·45 (2H, m, CH$_3$·CH$_2$), 8·0 (1H, s, OH, disappears on deuteriation), 5·12 (2H, dd, =CH$_2$), and 4·77 (1H, dd, CH=).

Reduction of But-2-yne-1,4-diol.—But-2-yne-1,4-diol (8·6 g, 0·1 mol) in dry tetrahydrofuran (20 ml) was added dropwise with stirring to a slurry of lithium aluminium hydride (5·7 g, 0·15 mol) in dry ether (200 ml). The mixture was refluxed for 4 h and worked up as before and gave (i) buta-2,3-dien-1-ol (0·14 g, 2%), b.p. 48—50° at 20 mmHg. A pure sample was prepared by g.l.c. (Carbowax 20M on chromosorb W; 120°), $v_{max.}$ 3300 (OH), 1960 (C=C=C), and 840 (C=C=CH$_2$) cm^{-1}, g.l.c. t_R 3 min (Carbowax; 100°), τ (CDCl$_3$) 7·5 (1H, s, OH), 5·87 (2H, m, CH$_2$·OH), 5·15 (2H, m, C=C=CH$_2$), and 4·7 (1H, m, CH=C=CH$_2$); data as for an authentic sample.[14] The other product (ii), but-2-ene-1,4-diol (8·6 g, 98%), had b.p. 84° at 0·2 mmHg, $v_{max.}$ 3350 (OH), 1660vw (C=C), and 980 (C=C, *trans*) cm^{-1}. The di-acetate gave a single peak on g.l.c., t_R 8·1 min; the diacetate of but-2-yne-1,4-diol t_R 13·2 min.

Reduction of 2,5-*Dimethylhex*-3-*yne*-2,5-*diol.*—(i) 2,5-Di-methylhex-3-yne-2,5-diol (14·2 g, 0·1 mol) in dry ether (20 ml) was added to lithium aluminium hydride (3·8 g, 0·1 mol) in ether (150 ml) and the mixture was refluxed for 4 h. Work-up in the usual way and distillation gave (a) 2,5-di-methylhexa-3,4-dien-2-ol (0·8 g, 6%), b.p. 95° at 50 mmHg, $v_{max.}$ 3350 (OH), 1960 (C=C=C), and 900 cm^{-1} (HC=C=CH), g.l.c. t_R 33 min (93%) (Carbowax 20M on Chromosorb W) with minor impurities, and (b) a mixture of 2,5-dimethylhex-3-yne-2,5-diol and 2,5-dimethylhex-3-ene-2,5-diol (11·5 g, 80%), m.p. 101—102°. Preparation and g.l.c. of the di-acetates of this mixture showed two peaks, t_R 6 (56%) (2,5-dimethylhex-3-ene-2,5-diyl diacetate) and 10 min (44%) (2,5-dimethylhex-3-yne-2,5-diyl diacetate).

(ii) Use of the Whiting conditions [9] but decomposing the excess of reagent with the minimum amount of cold water to avoid a constant ether extraction, and work-up with ether–chloroform gave (a) 2,5-dimethylhexa-3,4-dien-2-ol (2·7 g, 51%), b.p. 55° at 11 mmHg, $v_{max.}$ 3350 (OH), 1970 (C=C=C), and 880 cm^{-1} (C=C=CH), τ 8·7 [6H, s, (CH$_3$)$_2$C·OH], 8·25 [6H, d, $J_{4,1}$ 3 Hz, (CH$_3$)$_2$C=C=CH], 8·10br (1H, s, OH), and 4·75 [1H, m, $J_{1,4}$ 3 Hz, (CH$_3$)$_2$C=C=CH], and (b) a solid residue, 2,5-dimethylhex-3-ene-2,5-diol, m.p. 87° (from petroleum–benzene).

6-Tetrahydropyran-2-yloxyhex-2-en-4-yn-1-ol (VIII) (*with* N. PUNJA).—1-Tetrahydropyran-2-yloxyprop-2-yne (140 g, 1 mol) was added dropwise with stirring to sodamide [from sodium (23 g, 1 g atom)] in liquid ammonia (3·5 l). After 7 h, 1-chloro-2,3-epoxypropane (46·5 g, 0·5 mol) was added and the mixture was stirred for *ca.* 12 h. Decomposi-tion was effected with ammonium chloride (60 g), excess of ammonia was evaporated off, and the residue was taken up in ether (200 ml). Distillation gave (a) unchanged 1-tetra-hydropyran-2-yloxyprop-2-yne (74 g, 53%), b.p. 65—68° at 9 mmHg, (b) 1-(2-furyl)-2-tetrahydropyran-2-yloxyethane (9 g, 9·2%), b.p. 84—90° at 0·9 mmHg, $v_{max.}$ 1640 (C=C), 1600, 1510, 1440, 800, and 730 cm^{-1} (aromatic C=C), $λ_{max.}$ 216 (ε 5352) and 274 nm (823), g.l.c. t_R 10 min (10% silicone oil on Chromosorb W; 150°), τ (CDCl$_3$) 8·39br (6H, s,

CH·[CH_2]$_3$·CH$_2$), 7·8 (2H, t, furyl-CH_2), 5·8—6·6 (4H, m,

CH·[CH$_2$]$_3$·CH_2 and furyl-CH$_2$·CH_2), 5·59 (1H, unresolved t,

CH·[CH$_2$]$_3$·CH$_2$), 3·92 (1H, dd, furan 3-H); 3·76 (1H, dd, furan 4-H), and 2·62 (1H, dd, furan-5H). Hydrolysis (HCl–MeOH) gave 2-(2-furyl)ethanol, identical with an authentic sample.[10] The third product (c) was 6-tetra-hydropyran-2-yloxyhex-2-en-4-yn-1-ol (27 g, 28%), b.p. 108—110° at 5 × 10^{-4} mmHg (Found: C, 67·1; H, 8·1. C$_{11}$H$_{16}$O$_3$ requires C, 67·3; H, 8·2%), $v_{max.}$ 3400 (OH), 2230 (C=C), and 1640 (C=C) cm^{-1}, $λ_{max.}$ 227 (ε 13,500) and 236 nm (10,830), g.l.c. t_R 16 and 23 min (10% Silicone oil on Chromo-sorb W; 170°) (*cis*- and *trans*-isomers). Treatment of a sample with base resulted in the disappearance of the isomer with t_R 16 min, and more 1-(2-furyl)-2-tetrahydro-pyran-2-yloxyethane was isolated; hence the compound with t_R 23 min must be the *trans*-isomer.

Lithium Aluminium Hydride Reduction of 6-Tetrahydro-pyran-2-yloxhex-2-en-4-yn-1-ol (*with* N. PUNJA).—6-Tetra-hydropyran-2-yloxyhex-2-en-4-yn-1-ol (6·7 g, 0·034 mol) in anhydrous ether (10 ml) was added dropwise with stirring to lithium aluminium hydride (1·3 g, 0·034 mol) in ether

[14] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, 1955, **20**, 95, 1337.