Allenes. Part XIV.* The Synthesis of Allenynols and Allenenols by the Reduction of 4,6-Diyn-2-en-1-ols and Diynediols with Lithium Aluminium Hydride

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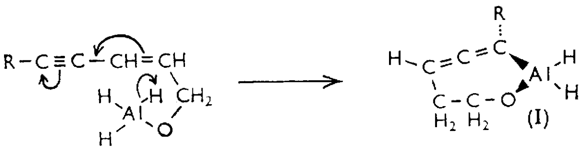
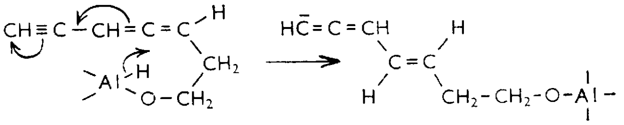
The reduction of 4,6-diyn-2-en-ols with an excess of lithium aluminium hydride gives allenenes (3,5,6-trien-1-ols) as the main product and allenynes as the minor product. DL-Marasin, claimed to be the product from the reduction of non-2-en-4,6,8-triyn-1-ol, was shown to be a minor component only. Reduction with dialkoxylithium aluminium hydride gave improved yields of allenynes together with allenenes whereas the lithium aluminium hydride–butane-2,3-diol complex gave allenynes only.

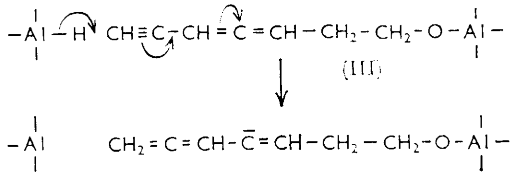
An investigation of the reduction of diynenols with lithium aluminium hydride[1] as a potential route to naturally occurring allenynols was initiated in 1960. It soon became apparent that whereas simple alkyl- and aryl-penta-3,4-dienols of a molecular weight similar to that of the naturally occurring allenes could be prepared both in a pure form and in excellent yield, alkynylpenta-3,4-dienols (allenynols) underwent further reduction with an excess of lithium aluminium hydride to give, in the main, allenenols. The use of equivalent quantities of lithium aluminium hydride gave unchanged starting material, allenyne, and allenene, indicating that further reduction had not been prevented. Since allenynes were difficult to separate from the corresponding allenenes, even by careful chromatography, it was essential to reduce the amount of allenene formed to a minimum. A consideration of the mechanism of the two-stage reduction led to the following conclusion. The mechanism of the first stage of the reduction is now well established by deuteration experiments[2] and the formation of a seven-membered allenynoxyaluminium hydride complex (I) has been suggested.[3] Since further hydride transfer from aluminium hydride to (I) would produce a double negatively charged intermediate, it seems preferable to postulate that (I) picks up a proton first (possibly from a hydroxylated aluminium hydride complex formed from traces of moisture present).



It was reasoned that if the second-stage transfer is also intramolecular, as shown in (II), then removal of two hydrogen atoms on the aluminium hydride by methanol or ethanol should prevent further reductions even if a large excess of reducing agent is used (this was essential if recovery of much of the starting material was to be avoided). Reduction of alkynylpenta-2-en-4-yn-1-ols with dimethoxy- and diethoxy-lithium aluminium hydride (see Experimental section) certainly gave less allenene but did not suppress its formation completely. This suggests attack by a second molecule of lithium aluminium hydride as in (III). A large substituent on the acetylene such as a t-butyl group also tends to suppress allenene formation as would be expected from mechanism (III). Both mechanisms should give a *trans*-disubstituted double bond as is found in practice. Careful chromatographic separation finally gave pure allenynes, but only in poor yield, since much material was lost due to incomplete separation from the corresponding allenenes. The best results were obtained with



(II)



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* Part XIII, P. D. Landor, S. R. Landor, and E. S. Pepper, preceding Paper.

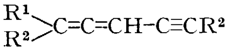
[1] E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1954, 1854.

[2] F. Bohlmann, R. Enkelmann, and W. Plettner, *Ber.*, 1964, **97**, 2118.

[3] R. J. D. Evans, S. R. Landor, and J. P. Regan, *Chem. Comm.*, 1965, 397.

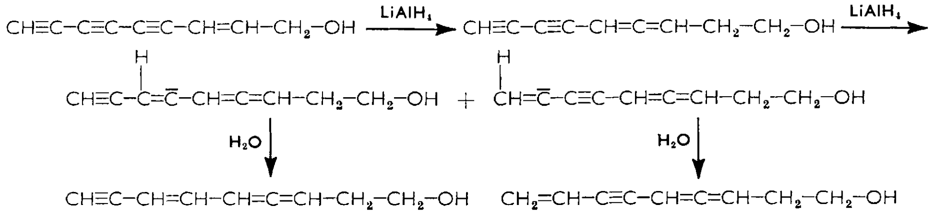
the lithium aluminium hydride–butane-2,3-diol cyclic complex which prevented further reduction and gave allenynes together with starting material only.

The ultraviolet spectra (see Table) show that there is a 5 mμ bathochromic shift for each alkyl substituent added to the allenyne system. However, two alkyl substituents on the allene end of the molecule in 1,1,5-trialkylallenynes give rise to no further increase in the bathochromic shift.[5] The allenene, hepta-3,4,6-trien-1-ol was synthesised in 73% yield from *trans*-hept-2-en-4,6-diyn-1-ol by reduction with a tenfold excess of lithium aluminium hydride. During the course of this work Bohlman, Herbst, and Gleinig [6] described the reduction of non-2-en-4,6-8-tri-yn-ol with a large excess of lithium aluminium hydride and claimed to have obtained DL-marasin in 83% yield. Their product was described as showing a 968 cm.$^{-1}$ band, typical of the *trans*-double bond in the allenene system, and absent in natural marasin.[7] Repetition of this work in our laboratories under the conditions described by the previous workers gave a product which consisted largely of the allenenes, nona-3,4,8-trien-6-yn-ol (V) and nona-3,4,6-trien-8-yn-1-ol (IV). A bathochromic shift of 2—3 mμ for the 263 mμ band in the ultraviolet spectrum of marasin (see Figure) shown by the new compound is typical for the allenene system as is a band at 965 cm.$^{-1}$ in the infrared; bands at 930 and 990 cm.$^{-1}$ may be ascribed to a vinyl group. The proposed mechanism for allenene formation from marasin is as follows:



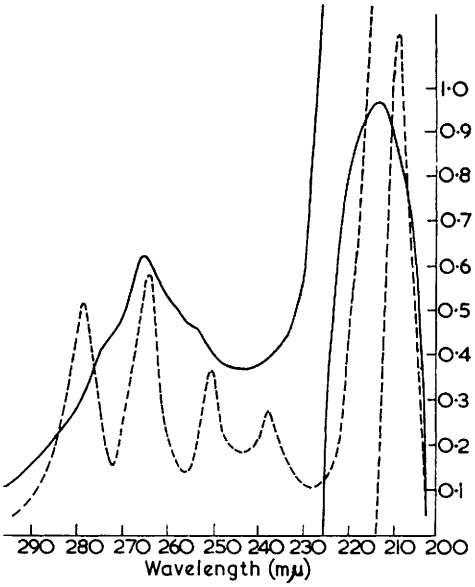
$$\begin{matrix}R^1\\R^2\end{matrix}\!\!>\!C{=}C{=}CH{-}C{\equiv}CR^2$$

R^1	R^2	R^3	λ_{max} (mμ)	ε
H	H	H	211·5 [4]	11,000
H	CH_2CH_2OH	H	216	11,700
H	CH_2CH_2OH	Et	221	14,600
H	CH_2CH_2OH	Bu^t	222	10,606
H	CH_2CH_2OH	CH_2OH	221	8200
H	Et	CH_2OH	220 [5]	12,800
H	Bu^t	CH_2OH	221 [5]	10,100
Me	Et	CH_2OH	220 [5]	14,400
Me	Bu^t	CH_2OH	221 [5]	16,800



(IV) (V)

A small quantity (0·6%) of DL-marasin could be separated from the mixture by careful chromatography. Using diethoxylithium aluminium hydride the yield of DL-marasin was increased to 6%. The synthesis and determination of the absolute configuration of optically active marasin using a cyclic complex of lithium aluminium hydride has recently been outlined.[8]



The ultraviolet spectra of DL-marasin (- - - -) and dihydromarasin (IV) and (V) (——)

Reduction of two diynendiols (VI; R = H, n = 1 or 2) with lithium aluminium hydride gave mixtures of allenynes (VII) and allenenes (VIII) in varying proportions according to the conditions employed.

$HO{-}CH_2{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_n{\cdot}OR$ (VI)

$HO{-}CH_2{-}CH_2{-}CH{=}C{=}CH{-}C{\equiv}C{-}(CH_2)_n{\cdot}OR$ (VII)

$HO{-}CH_2{-}CH_2{-}HC{=}C{=}CH{-}CH{=}CH_2{-}(CH_2)_n{\cdot}OR$ (VIII)

An excess of lithium aluminium hydride reacts with the diol (VI) (R = H; n = 1) to give 95% pure allenene (VII); however, substituting a bulky tetrahydropyranyl group for one hydrogen in (VI) (R = C_6H_4O, n = 1) protects the allenyne (VII) from further reduction and pure allenyne was obtained after 12 hr. heating with a large excess of lithium aluminium hydride. The tetrahydropyranyl group was finally lost, presumably by hydrogenolysis, and this appears to be the first recorded instance of removal of a tetrahydropyranyl group by reduction under basic conditions. The diol (VI) (R =

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[4] E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 1960, 341.

[5] C. S. L. Baker, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 1965, 4659.

[6] F. Bohlmann, P. Herbst, and H. Gleinig, *Ber.*, 1961, **94**, 948.

[7] G. Benz, *Arkiv Kemi*, 1959, **14**, 305; R. C. Cambie, H. Hirschberg, E. R. H. Jones, and G. Lowe, *J. Chem. Soc.*, 1963, 4120.

[8] S. R. Landor, B. J. Miller, J. P. Regan, and A. R. Tatchell, *Chem. Comm.*, 1966, 585.

H, $n = 2$) although less prone to reduction to allenene still gave mixtures with an excess of the reagent.

EXPERIMENTAL

Ether and tetrahydrofuran were dried over sodium wire and then distilled from lithium aluminium hydride. The ethanol used was absolute, and the light petroleum had b. p. 40—60°. Infrared spectra were determined with a Perkin-Elmer Infracord and ultraviolet spectra on absolute ethanolic solutions with a Bausch and Lomb Spectronic 505 spectrometer. G.l.c. was carried out on a Griffin and George Instrument with 6 ft. glass columns, and nitrogen as a carrier gas, at a flow rate of 2 l./hr.

Undec-3,4-*diene*-1-*ol*.—*trans*-Undec-2-en-4-yn-1-ol [9] (3·3 g., 0·02 mole) in ether (20 ml.) was added dropwise to lithium aluminium hydride (1·2 g., 0·03 mole) in ether (60 ml.) and the mixture was heated under reflux for 3 hr. After the addition of water (10 ml.), the mixture was filtered to remove the solid suspension, dried ($MgSO_4$), and distilled to give *undec*-3,4-*dien*-1-*ol* (2·4 g., 73%), b. p. 58°/5 × 10^{-3} mm. (Found: C, 79·3; H, 12·1. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%); $\nu_{\text{max.}}$ 3400—3250vs (OH), 1950m (C=C=C), 1040vs (C–O), 872m (C=C=CH) and 720m. cm.$^{-1}$.

5-*Phenylpenta*-3,4-*dien*-1-*ol*.— *trans*-5-Phenylpent-2-en-4-yn-1-ol [10] (4·7 g., 0·030 mole) in ether (30 ml.) was added dropwise to lithium aluminium hydride (1·7 g., 0·045 mole) in ether (100 ml.) and the mixture was heated under reflux for 3 hr. The complex was decomposed with water, and the solid suspension removed by filtration; the filtrate was dried ($MgSO_4$) and distilled, to give 5-*phenylpenta*-3,4-*dien*-1-*ol* (2·6 g., 55%), b. p. 98—100°/5 × 10^{-3} mm. (Found: C, 82·0; H, 8·0. $C_{11}H_{12}O$ requires C, 82·5; H, 7·55%); $\lambda_{\text{max.}}$ 289·5 (ε 1100), 281 (ε 1500), 250·5 (ε 18,600), and 204 mμ (ε 27,800); $\nu_{\text{max.}}$ 3450—3250vs (OH), 3005m (=C–H), 1950s (C=C=C), 1600s, 1490s (aromatic C=C), 1045vs (C–O), 912m, 875ms (C=C=CH–), 775s and 690s cm.$^{-1}$ (monosubstituted phenyl).

Hepta-3,4-*dien*-6-*yn*-1-*ol*.—(a) Ethanol (9·2 g., 0·20 mole) in ether (50 ml.) was added dropwise with stirring, to a solution of lithium aluminium hydride (3·8 g., 0·10 mole) in ether (250 ml.). After 30 min., *trans*-hept-2-en-4,6-diyn-1-ol,[9] m. p. 48—49° (5·3 g., 0·05 mole) in ether (50 ml.) was added dropwise, the reaction mixture was heated under reflux for 4 hr. after which water (10 ml.) was added slowly. The solid suspension was removed by filtration, the filtrate dried ($MgSO_4$), and the solvent removed (the last traces *in vacuo*). The crude product (4·0 g.) [$\nu_{\text{max.}}$ 3450—3200vs (OH), 2200mw (C≡C), 2090w (C≡CH), 945s (*trans*-CH=CH), and 865s (C=C=CH–), 1950m (C=C=C), 1630w (C=C), and 1040s cm.$^{-1}$; ν_{infl} 1930 cm.$^{-1}$ (C=C=C)] was chromatographed on alumina (type H, 250 g.) deactivated with 10% aqueous acetic acid (12·5 ml.). Elution with light petroleum–ether (17 : 3) gave trans-*hepta*-3,5,6-*trien*-1-*ol* (0·1 g. 0·2%); $\lambda_{\text{max.}}$ 218 and 224 mμ, followed by a mixture of *trans*-hepta-3,5,6-trien-1-ol, trans-*hept*-2-*en*-4,6-*diyn*-1-*ol*, and *hepta*-3,4-*dien*-6-*yn*-1-*ol* (2·5 g., 46%), and finally pure *hepta*-3,4,*dien*-6-*yn*-1-*ol* (0·50 g., 9%) (Found: C, 78·3; H, 7·55. C_7H_8O requires C, 77·8; H, 7·45%); $\lambda_{\text{max.}}$ 216 mμ (ε 11,700); $\nu_{\text{max.}}$ 3450—3250vs (OH), 3250s (C≡C–H), 2090w (C=CH), 1950m (C=C=C), 1045vs (C–O), and 868m cm.$^{-1}$ (C=C=CH–).

(*b*) Similarly *trans*-hept-2-en-4,6-diyn-1-ol (1·06 g., 0·01 mole) with lithium aluminium hydride [standardised solution, (1·5 g., 0·04 mole) in dry ether (69 ml.)] and butane-2,3-diol (3·6 g., 0·04 mole) gave, after chromatography, hepta-3,4-dien-6-yn-1-ol (0·1 g., 9%) and recovered *trans*-hept-2-en-4,6-diyn-1-ol (0·8 g.).

trans-*Hepta*-3,5,6-*trien*-1-*ol*.—A solution of *trans*-hept-2-en-4,6-diyn-1-ol [9] (1·06 g., 0·01 mole) in ether (20 ml.) was added dropwise with stirring to lithium aluminium hydride (1·9 g., 0·05 mole) in ether (100 ml.) and the mixture was heated under reflux for 1 hr. Water (10 ml.) was added, the mixture filtered, and the filtrate dried ($MgSO_4$). Removal of solvent gave *trans*-hepta-3,5,6-trien-1-ol (0·80 g., 73%); $\lambda_{\text{max.}}$ 224 (ε 10,000) and 218 mμ (ε 10,000); $\nu_{\text{max.}}$ 3400—3200vs (OH), 1920m (C=C=C), 1640w (C=C), 1040vs (C–O), 965s (*trans*–CH=CH–), 850s (C=C=CH_2), and 865w cm.$^{-1}$ (C=C=CH–). Very weak bands at 2210 (C≡C) and 2100 cm.$^{-1}$ (C≡CH) showed that the product contained a little hepta-3,4-dien-6-yn-1-ol and *trans*-hept-2-en-4,6-diyn-1-ol.

Nona-3,4-*dien*-6-*yn*-1-*ol*.—Methanol (3·73 g., 0·117 mole) in ether (50 ml.) was added dropwise with vigorous stirring to lithium aluminium hydride (2·21 g., 0·058 mole) followed by *trans*-non-2-en-4,6-diyn-1-ol [9] (3·90 g., 0·029 mole) in ether (50 ml.) and the mixture was heated under reflux for 4·5 hr. Water (15 ml.) was added dropwise, the solid suspension filtered off, and the filtrate dried ($MgSO_4$). Distillation gave a colourless liquid (2·0 g.), b. p. 55—60°/5 × 10^{-3} mm.; $\lambda_{\text{max.}}$ 220 mμ (ε 1100); $\nu_{\text{max.}}$ 3450—3250vs (OH), 2200w (C=C), 1940m (C=C=C), 1350ms, 1040vs (C–O) 965ms (*trans*-CH=CH), and 867ms cm.$^{-1}$ (C=C=CH–). Chromatography on alumina (type H, 220 g.), deactivated with 10% aqueous acetic acid (11 ml.) and elution with light petroleum–ether (17 : 3) gave pure *nona*-3,4-*dien*-6-*yn*-1-*ol* (0·8 g., 21%) (Found: C, 79·9; H, 8·65. $C_9H_{12}O$ requires C, 79·4; H, 8·65%); $\lambda_{\text{max.}}$ 221 mμ (ε 14,600); $\nu_{\text{max.}}$ 3450—3260vs (OH), 2200w (C≡C), 1940m (C=C=C), 1305ms, 1040vs (C–O), and 867ms cm.$^{-1}$ (C=C=CH–).

trans-8,8-*Dimethylnon*-2-*en*-4,6-*diyn*-1-*ol*.— 3,3-Dimethylbut-1-yne (11·9 g., 0·145 mole) was added dropwise, with stirring to 70% aqueous ethylamine (20·5 c.c.), cuprous chloride (0·22 g.), and methanol (40 c.c.). The mixture was stirred for 5 min. after which crude *trans*-5-bromopent-2-en-4-yn-1-ol (23·3 g., 0·145 mole), in methanol (25 c.c.) was added dropwise during 30 min., at 20°; hydroxylaminium chloride (0·5 g.) was added during the addition. After stirring for 1 hr., potassium cyanide (1·5 g.) was added and the mixture was stirred for a further 10 min. The product was extracted with ether (3 × 70 ml.) and the combined extracts were washed with dilute hydrochloric acid, water, and sodium hydrogen carbonate solution. After drying ($MgSO_4$) and removal of solvent, the product was chromatographed on alumina (type H, 600 g.), deactivated with 10% aqueous acetic acid (30 ml.). Fractions eluted with light petroleum–ether (4 : 1) gave trans-8,8-*dimethylnon*-2-*en*-4,6-*diyn*-1-*ol* (7·0 g., 30%), a pale yellow liquid; $\lambda_{\text{max.}}$ 282·5 (ε 9500), 266·5 (ε 12,200), 252·5 (ε 9300), 240 (ε 8500), 230 (ε 6900), 213 (ε 31,700), and 206·5 mμ (ε 23,800); $\nu_{\text{max.}}$ 3450—3250vs (OH), 2220mw, 2170mw (C≡C), 1630w (C=C), 1360s (C–Me), 1090s, 1010s (C–O), 950s, (*trans*-CH=CH–) and 905w cm.$^{-1}$.

8,8-*Dimethylnona*-3,4-*dien*-6-*yn*-1-*ol*.—(*a*) Methanol (2·76 g., 0·086 mole) in ether (20 ml.) was added dropwise with

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[9] S. R. Landor and E. S. Pepper, *J. Chem. Soc.* (*C*), 1966, 2283.

[10] T. L. Jacobs, D. Dankner, and A. R. Dankner, *J. Amer. Chem. Soc.*, 1958, **80**, 864.

vigorous stirring to lithium aluminium hydride (1·64 g., 0·043 mole) and ether (100 ml.) over 1 hr.; *trans*-8,8-dimethylnon-2-en-4,6-diyn-1-ol (3·5 g., 0·022 mole) in ether (60 ml.) was then also added and the mixture heated under reflux for 4·5 hr. Water (10 ml.) was added, the solid suspension filtered off, and the filtrate dried ($MgSO_4$), Distillation gave 8,8-*dimethylnona*-3,4-*dien*-6-*yn*-1-*ol*, b. p. 70—75°/5 × 10^{-3} mm. (1·9 g., 54%); $\lambda_{\text{max.}}$ 222 mμ (ε 10,600), λ_{sh} 235 mμ; $\nu_{\text{max.}}$ 3400—3250vs (OH), 2220w (C≡C), 1950m (C=C=C), 1360m (Bu^t), 1040vs (C–O), 955w, and 867w (C=C=CH–). The weak band at 955 cm.$^{-1}$ indicated the presence of some allenene.

(*b*) Similarly, *trans*-8,8-dimethylnon-2-en-4,6-diyn-1-ol (1·62 g., 0·01 mole) with lithium aluminium hydride [standardised solution, (1·52 g., 0·04 mole) in ether (100 ml.)] and butane-2,3-diol (3·6 g., 0·04 mole) gave 8,8-dimethylnona-3,4-dien-6-yn-1-ol (0·23 g., 14%); infrared bands as in (*a*) except the absence of a band at 955 cm.$^{-1}$.

trans-*Oct*-2-*en*-4,6-*diyn*-1,8-*diol*.—*trans*-Pent-2-en-4-yn-1-ol (8·2 g., 0·10 mole) was added to a stirred solution of cuprous chloride (0·15 g.) in 35% aqueous ethylamine (28 ml.). 1-Bromoprop-1-yn-3-ol [11] (13·5 g., 0·10 mole) in methanol (15 ml.) was added dropwise under nitrogen to the mixture at 25—30° during 10 min. together with a little hydroxylaminium chloride. Potassium cyanide (1·0 g.) was added 10 min. after the addition had been completed to give an orange-coloured solution, which was extracted with ether (4 × 50 ml.). The combined extracts were washed with dilute, hydrochloric acid, water, and finally dried ($MgSO_4$). Removal of solvent gave a white solid which, on recrystallisation from chloroform, gave trans-*oct*-2-*en*-4,6-*diyn*-1,8-*diol* (9·7 g., 71%), m. p. 91·5—92·5° (Found: C, 70·5; H, 6·15. $C_8H_8O_2$ requires C, 70·6; H, 6·15%); $\lambda_{\text{max.}}$ 283 (ε 12,700), 267·5 (ε 16,700), 253 (ε 11,600), 241 (ε 4200), 229 (ε 2900), 213·5 (ε 50,600), and 207 mμ (ε 38,700); $\nu_{\text{max.}}$ (Nujol) 3350—3050vs (OH), 2200w (C≡C), 1630w (C=C), 1075s, 1025s (C–O), 955m, 940s (*trans*-CH=CH), 900m, and 735m cm.$^{-1}$.

trans-*Octa*-2,4,5-*trien*-1,8-*diol*.— *trans*-Oct-2-en-4,6-diyn-1,8-diol (3·0 g., 0·022 mole) in dry tetrahydrofuran (50 ml.) was added dropwise to a solution of lithium aluminium hydride (2·5 g., 0·066 mole) in dry tetrahydrofuran (150 ml.). The mixture was heated under reflux for 4 hr., decomposed with water (10 ml.), and filtered. The filtrate was dried ($MgSO_4$) and the solvent was evaporated, to leave a pale yellow liquid (2·5 g., 83%) consisting of trans-*octa*-2,4,5-*trien*-1,8-*diol*, $\lambda_{\text{max.}}$ 226 mμ (ε 12,700) containing *ca.* 5% of trans,trans-*octa*-2,6-*dien*-4-*yn*-1,8-*diol*, as shown by two small maxima at $\lambda_{\text{max.}}$ 273 and 262 mμ; $\nu_{\text{max.}}$ 3450—3150vs (OH), 2210w (C≡C), and 1930m (C=C=C). The product absorbed 3·1 mole of hydrogen (PtO_2).

The product (1·0 g.), on reaction with an ice-cold mixture of acetic anhydride (2·9 g.) and pyridine (2·3 g.), for 24 hr., gave trans-*octa*-2,4,5-*trienyl*-1,8-*diacetate* (1·2 g., 75%) on work-up; g.l.c. on silicone at 167° showed two peaks (95% *t* 14 min., 5% *t* 10 min.); $\lambda_{\text{max.}}$ 226 mμ (ε 14,500); $\nu_{\text{max.}}$ 1930w (C=C=C), 1740s (C=O acetate), 1365s (C–Me), 1230vs (C–O acetate), 1040vs (C–O), and 965m cm.$^{-1}$ (*trans*-CH=CH–), there was no band at 3400—3200 cm.$^{-1}$ (OH).

trans-*Octa*-2,4,5-*trien*-1,8-*diol and* trans,trans-*octa*-2,6-*dien*-4-*yn*-1,8-*diol*.—*trans*-Oct-2-en-4,6-diyn-1,8-diol [11] (5·0 g., 0·037 mole) in ether (100 ml.) was added dropwise with stirring to a solution of lithium aluminium hydride (5·6 g., 0·15 mole) in ether (250 ml.); a white complex precipitated. The mixture was heated under reflux for 12 hr. after which time water (25 ml.) was added dropwise. Filtration, drying ($MgSO_4$), and removal of solvent left a pale yellow liquid (4·3 g., 86%) consisting of a mixture of trans-*octa*-2,4,5-*trien*-1,8-*diol* (approximately 70%) and *trans,trans*-octa-2,6-dien-4-yn-1,8-diol (approximately 30%); $\lambda_{\text{max.}}$ 264 (ε 5900), 253·5 (ε 5500), and 215 mμ (ε 13,300), λ_{infl} 275 (ε 4200) and 225 mμ (ε 11,100); $\nu_{\text{max.}}$ 3450—3150vs (OH), 2210w (C≡C), 1930m (C=C=C), 1640w (C=C), 1050vs (C–O), 965s (*trans*-–CH=CH–), and 890m cm.$^{-1}$ (C=C=CH–). The product (2·0 g.) on alumina (200 g.) deactivated with 10% aqueous acetic acid (20 ml.) and elution with light petroleum–ether (3 : 2) gave partial separation, first *trans*-octa-2,4,5-trien-1,8-diol (0·7 g.); $\lambda_{\text{max.}}$ 274 (ε 3000), 262 (ε 3800), 228 (ε 11,500), and 217 mμ (ε 4400), followed by trans,trans-*octa*-2,6-*dien*-4-*yn*-1-*ol* (0·3 g.); $\lambda_{\text{max.}}$ 274 (ε 6200), 262 (ε 7800), and 217 mμ (ε 8700).

trans-8-*Tetrahydropyran*-2′-*yloxyoct*-2-*en*-4,6-*diyn*-1-*ol*.— A mixture of 1-bromoprop-1-yn-3-ol [11] (15·0 g., 0·11 mole) and 2,3-dihydropyran (14·0 g., 0·17 mole) cooled to 0° was treated with concentrated hydrochloric acid (0·1 c.c.); the mixture became warm and was left to stand for 24 hr. After the addition of potassium carbonate (5 g.), the product was filtered off and distilled, to give 1-*bromo*-3-*tetrahydropyran*-2′-*yloxyprop*-1-*yne* (19·4 g., 80%); $\nu_{\text{max.}}$ 2200m (C≡C) and characteristic tetrahydropyranyl ether fingerprint bands at 1195ms, 1180m, 1120s, 873ms, and 817m cm.$^{-1}$. G.l.c. on silicone oil at 154° gave one peak, (*t* 22 min.).

trans-Pent-2-en-4-yn-1-ol (4·1 g., 0·05 mole) was added dropwise under nitrogen to a stirred solution of cuprous chloride (75 mg.) in 35% aqueous ethylamine (28 ml.). 1-Bromo-3-tetrahydropyran-2′-yloxyprop-1-yne (11·0 g., 0·05 mole) in methanol (8 ml.) was added dropwise to the mixture at 25—30°, and hydroxylaminium chloride as required; potassium cyanide (0·5 g.) was added 30 min. after addition had been completed. The mixture was worked-up and chromatographed on alumina (type H, 750 g.), deactivated with 10% aqueous acetic acid (75 ml.), to give, on elution with light petroleum–ether (3 : 2), a light yellow liquid which was identified as trans-8-*tetrahydropyran*-2′-*yloxyoct*-2-*en*-4,6-*diyn*-1-*ol* (10 g., 90%); $\lambda_{\text{max.}}$ 283·5 (ε 9000), 268 (ε 16,500), 254 (ε 13,500), 241·5 (ε 11,500), and 214·5 mμ (ε 52,500); $\nu_{\text{max.}}$ 3450—3200vs (OH), 2210mw (C≡C), 1630mw (C=C), 950s (*trans*-CH=CH) and characteristic tetrahydropyranyl ether fingerprint bands at 1195ms, 1175m 1120vs, 1015vs, 870m, and 815m cm.$^{-1}$.

Octa-4,5-*dien*-2-*yn*-1,8-*diol* (VII, $n = 1$, $R = 1$).— (*a*) 8-Tetrahydropyran-2′-yloxyoct-*trans*-2-en-4,6-diyn-1-ol (4·4 g., 0·02 mole) in ether (50 ml.) and lithium aluminium hydride (3·1 g., 0·08 mole) in dry ether (250 ml.) were heated under reflux for 12 hr. Work-up gave a pale yellow liquid product (2·4 g., 87%) identified as *octa*-4,5-*dien*-2-*yn*-1,8-*diol*; $\lambda_{\text{max.}}$ 221 mμ (ε 8200); $\nu_{\text{max.}}$ 3400—3200vs (OH), 2210vw (C≡C), 1930m (C=C=C), 1630w (C=C), 1040vs (C–O), and 850m cm.$^{-1}$ (C=C=CH–). The characteristic tetrahydropyranyl ether bands were no longer present in the fingerprint region. Hydrogenation (PtO_2) resulted in the absorption of 3·0 mole of hydrogen.

(*b*) 8-Tetrahydropyran-2′-yloxyoct-*trans*-2-en-4,6-diyn-1-ol (VI; $n = 1$, $R = T_p$) (5·0 g., 0·023 mole) in ether (20 ml.) and lithium aluminium hydride (1·73 g., 0·046 mole) in ether (50 ml.) after heating under reflux for 6 hr. and working up gave a yellow oil (3·0 g.) consisting of a mixture of starting material (∼50%) and 8-*tetrahydropyran*-2′-*yloxyocta*-4,5-*di*-

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[11] W. Chodkiewicz, C. Alhuwalia, P. Cadiot, and A. Willemart, *Compt. rend.*, 1957, **245**, 322.

en-2-*yn*-1-*ol*, $\lambda_{\text{max.}}$ 283 (ε 3800), 268 (ε 5600), 253 (ε 5000), and 215 mμ (ε 26,400), λ_{infl} 226 mμ (ε 8400); $\nu_{\text{max.}}$ 3400—3200vs (OH), 2220w (C=C), 1930m (C=C=C), 1630w (C=C), 950ms (*trans*-CH=CH), 850m cm.$^{-1}$ (C=C=CH–) and characteristic tetrahydropyranylether bands in the fingerprint region.

trans-*Non*-2-*en*-4,6-*diyn*-1,9-*diol*.— *trans*-Pent-2-en-4-yn-1-ol (8·2 g., 0·10 mole) was added dropwise, under nitrogen, with vigorous stirring to a solution of cuprous chloride (150 mg.) in 35% aqueous ethylamine (28 ml.). 1-Bromobut-1-yn-4-ol [11] (14·9 g., 0·10 mole) in methanol (15 ml.) was added dropwise to the mixture during 10 min. and hydroxylaminium chloride as required. Potassium cyanide (1·0 g.) was added 10 min. after the addition had been completed. The dark red solution was extracted with ether (4 × 50 ml.) and the combined extracts washed with dilute hydrochloric acid and dried ($MgSO_4$). Removal of solvent gave a solid, which on recrystallisation from chloroform gave trans-*non*-2-*en*-4,6-*diyn*-1,9-*diol* (10·8 g., 72%), m. p. 56—58° (Found: C, 72·85; H, 6·9. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%); $\lambda_{\text{max.}}$ 282·5 (ε 16,800), 266·5 (ε 21,400), 252 (ε 14,200), 239·5 (ε 6600), 228 (ε 2000), 213 (ε 51,600) and 207 mμ (ε 35,200); $\nu_{\text{max.}}$ (Nujol) 3400—3150vs (OH), 2250w, 2140w (C≡C), 1630w (C=C), 1050s, 1025s, 990s, (C–O), 960s (*trans*-CH=CH), 812w, 762w, and 685m cm.$^{-1}$.

Nona-3,4-*dien*-6-*yn*-1,9-*diol* (VII; $n = 2$, R = H).—(*a*) *trans*-Non-2-en-4,6-diyn-1,9-diol (5·0 g., 0·033 mole) in ether (100 ml.) was added dropwise to lithium aluminium hydride (5·1 g., 0·13 mole) in ether (250 ml.). The suspension was heated under reflux for 12 hr. and water (25 ml.) added. After filtration, drying ($MgSO_4$), and removal of the solvent, a pale yellow liquid (4·2 g., 84%) was obtained consisting of *nona*-3,4-*dien*-6-*yn*-1,9-*diol* (70%) and unreacted *trans*-non-2-en-4,6-diyn-1,9-diol (30%); $\lambda_{\text{max.}}$ 281·5 (ε 3000), 266·5 (ε 4500), 254 (ε 4500), and 214 mμ (ε 15,200); λ_{infl} 223 mμ (ε 1800); $\nu_{\text{max.}}$ 2400—3200vs (OH), 2220w (C≡C), 1940m (C=C=C), 1630w (C=C), 1040vs (C–O), 950 (*trans*-CH=CH–), and 880 cm.$^{-1}$ (C=C=CH–).

(*b*) *trans*-non-2-en-4,6-diyn-1,9-diol (3·0 g., 0·020 mole) in tetrahydrofuran (50 ml.) was added dropwise to lithium aluminium hydride (2·3 g., 0·061 mole) in dry tetrahydrofuran (150 ml.) and heated under reflux for 4 hr. Water (10 ml.) was added, the mixture filtered, the filtrate dried ($MgSO_4$), and solvent evaporated, leaving a pale yellow liquid product (2·4 g., 80%), trans-*nona*-3,4,6-*trien*-1,9-*diol* containing 5% of unreacted trans-*non*-2-*en*-4,6-*diyn*-1,9-*diol*; $\lambda_{\text{max.}}$ 224 mμ (ε 10,400); $\nu_{\text{max.}}$ 3450—3250vs (OH), 1950w (C=C=C), 1630w (C=C), 1050vs (C–O), 968m (*trans*-CH=CH–), and 880m cm.$^{-1}$ (C=C=CH–); 3·05 mole of hydrogen (PtO_2) were observed.

Non-2-*en*-4,6,8-*triyn*-1-*ol*.—(*a*) Repetition of the procedure of Bohlmann, Herbst, and Gleinig [6] with 5-bromopent-2-en-4-yn-ol (1·6 g., 0·01 mole) and buta-1,3-diyne (1·4 g., 0·018 mole) gave the title compound (0·053 g., 4·7%).

(*b*) (With C. S. L. Baker) To buta-1,3-diyne (13·7 g., 0·274 mole) in dimethylformamide (80 ml.) under oxygen-free nitrogen at 0° cuprous chloride (4·95 g., 0·05 mole), hydroxylamine hydrochloride (0·1 g.), dimethylformamide (40 ml.), and ethylamine (70% in water, 8·05 ml. 0·13 mole) were added. 1-Bromopenta-2-en-4-yn-1-ol (8·05 g., 0·05 mole) in dimethylformamide (30 ml.) was then immediately added to the deep red complex; the mixture turned dark brown and was stirred at 0° for 2 hr. The reaction mixture was decomposed with potassium cyanide solution [(30 g.) in water (150 ml.)] extracted into ether (3 × 200 ml.), washed with water (2 × 100 ml.), 2·5N hydrochloric acid (2 × 100 ml.), and water (3 × 200 ml.). The ethereal solution was evaporated to 200 ml. and then methanol (100 ml.) was added; treatment of the solution with ammoniacal silver nitrate [silver nitrate (17 g.) in water (100 ml.) with ammonia (*d*, 0·880) added until the precipitate just dissolved] in a refrigerated centrifuge gave the silver salt of *non*-2-*en*-4,6,8-*triyn*-1-*ol*. (Warning: the silver salt is shock-sensitive and behaves like a detonator giving rise to violent explosions on impact.) This was washed with ether (3 × 200 ml.), decomposed with potassium cyanide solution in the presence of ether, and further extracted into ether (3 × 100 ml.). Evaporation of a 5% portion of the solution showed that the product was *non*-2-*en*-4,6,8-*triynol* (1·52 g., 23·5%); $\lambda_{\text{max.}}$ 229 (ε 61,000), 240 (ε 86,500), 271·5 (ε 7100), 288 (ε 13,200), 306·5 (ε 17,200) 327·5 mμ (ε 12,600); [lit.,[7] gives 229 (ε 60,500), 239·5 (86,500), 271·5 (ε 6500), 288 (ε 13,000), 306 (ε 17,000), and 327·5 mμ (ε 12,500)].

Nona-3,4,6-*trien*-8-*yn*-1-*ol*, *Nona*-3,4,8-*trien*-6-*yn*-1-*ol and Nona*-3,4-*dien*-6,8-*diyn*-1-*ol*.—(*a*) Non-2-en-4,6,8-triyn-1-ol (1·070 g., 0·082 mole) in ether (50 ml.) was added to an 0·4M-lithium aluminium hydride solution (75·5 ml.) and the mixture stirred at room temperature for 2 hr.[6] The mixture was then poured into dilute sulphuric acid (150 ml., 10%), extracted into ether (3 × 200 ml.), washed with water (3 × 100 ml.), and dried ($MgSO_4$). Repeated addition of n-pentane and evaporation, followed by chromatography on Woelm acid alumina (200 g., deactivated with water, 6 ml., 3%) gave, on elution with ether–pentane (1 : 4), *nona*-3,4,8-*trien*-6-*yn*-1-*ol* (V) and *nona*-3,4,6-*trien*-8-*yn*-1-*ol* (IV) [0·36 g., 33·7% (fraction 14)]; $\lambda_{\text{max.}}$ 212 (ε 47,500), 265 mμ (ε 15,200), λ_{sh} 253 (ε 12,400), 272 mμ (ε 12,600); $\nu_{\text{max.}}$ 3500, 3330, 2210, 1950, 1650, 990, 965, and 935 cm.$^{-1}$. The product (0·11 g.) absorbed hydrogen [102·6 ml., 5 mole (PtO_2)]. Fractions 15 (0·19 g.), 16 (0·17 g.), 17 (0·12 g.), and 18 (0·05 g.) consisted mainly of (IV) and (V) with increasing quantities of nona-3,4-dien-6,8-diyn-1-ol; fraction 19 gave nona-3,4-dien-6,8-diyn-1-ol (DL-marasin) (0·006 g., 0·6%); $\lambda_{\text{max.}}$ 208 (ε 51,000), 237 (ε 5000), 239·5 (ε 8900), 263 (ε 14,100), 278m mμ (ε 12,500); $\nu_{\text{max.}}$ 3450, 3320, 2210, and 1960 cm.$^{-1}$.

(*b*) Similarly, 0·4M-ethereal lithium aluminium hydride (75·5 ml., 0·03 mole) with added ethanol (2·76 g., 0·06 mole) and *non*-2-*en*-4,6,8-*triyn*-1-*ol* (0·26 g., 0·002 mole) at room temperature for 2 hr. gave compounds (IV) and (V) (0·17 g., 65·4%), and DL-marasin (0·016 g., 6%).

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