

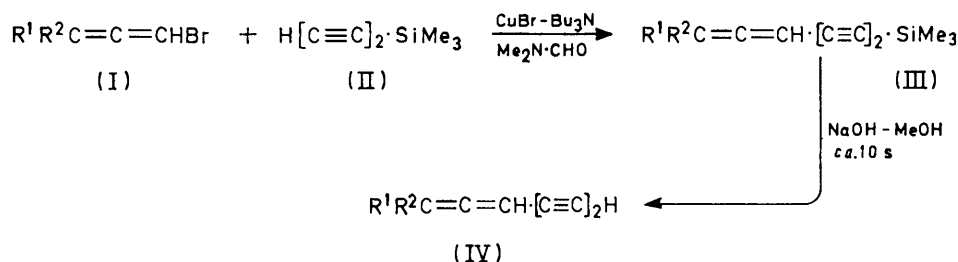
Allenes. Part XXXII.¹ A General Synthesis of Allenediynes from Allenic Bromides and Butadiynyl(trimethyl)silane and the Synthesis of Two Natural Allenes, (±)-Octa-2,3-diene-5,7-diyn-1-ol and (±)-Undeca-5,6-diene-8,10-diyn-1-ol

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Allenediynes have been synthesised by reactions of 1-bromoallenes with butadiynyl(trimethyl)- or butadiynyl(triethyl)-silane, followed by desilylation with methanolic sodium hydroxide. Application of this method to the first synthesis of two natural allenes, (±)-octa-2,3-diene-5,7-diyn-1-ol and (±)-undeca-5,6-diene-8,10-diyn-1-ol, is described.

A NUMBER of natural allenes produced by micro-organisms² contain the allenediynes system $\text{-C=C-CH-C}\equiv\text{C-C}\equiv\text{C-}$, which has been synthesised previously by reduction of alkenediynols with lithium aluminium hydride complexes,³ or by coupling of allenic halides with buta-1,3-diyne.⁴

We now report a much improved coupling reaction⁵ whereby an allenic bromide (I) reacts with butadiynyl(trimethyl)silane (II) to give a product (III) with the terminal acetylene group of the allenediynes protected by a stabilising trimethylsilyl group⁶ (Scheme 1).



SCHEME 1

Model compounds (III; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Et}$ or Pr) were synthesised in about 70% yield (crude) and purified by dry column chromatography.⁷ Yields of pure compounds were 45–50% and satisfactory microanalyses were obtained. I.r. spectra had bands at 2 110 ($\text{C}\equiv\text{C}\cdot\text{SiMe}_3$), 1 950 ($\text{C}=\text{C}$), and 1 250 and 850 cm^{-1} (SiMe_3), and u.v. spectra showed a typical shift to higher wavelengths for all absorption bands in comparison with the unsilylated compounds. N.m.r. spectra showed the allenic proton signal at τ 4.66. Compound (III; $\text{R}^1 = \text{R}^2 = \text{Me}$; SiEt_3 for SiMe_3) was prepared

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¹ Part XXXI, P. M. Greaves, P. D. Landor, S. R. Landor, and O. Odyek, *Tetrahedron*, 1974, **30**, 1427.

² Sir Ewart Jones, *Chem. in Brit.*, 1966, 6.

³ S. R. Landor, B. J. Miller, J. P. Regan, and A. R. Tatchell, *J.C.S. Perkin I*, 1974, 557; R. J. D. Evans, S. R. Landor, and J. P. Regan, *ibid.*, p. 552.

⁴ C. S. L. Baker, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 1965, 4659.

⁵ Presented at the International Symposium on Acetylenes and Allenes, Nottingham, July 1971. Preliminary account, P. D. Landor, S. R. Landor, and J. P. Leighton, *Tetrahedron Letters*, 1973, 1019.

similarly by using butadiynyl(triethyl)silane. Desilylation to the allenediynes (IV) was carried out by shaking with aqueous methanolic sodium hydroxide for 10 s and immediately pouring the mixture into dilute hydrochloric acid; complete removal of the trimethylsilyl group was effected with virtually no isomerisation of the allenediynes system. For example compound (IV; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Et}$) was obtained, after chromatography, in 84% yield.

For the synthesis of the naturally occurring octa-2,3-diene-5,7-diyn-1-ol (IV; $\text{R}^1 = \text{HO}\cdot\text{CH}_2$, $\text{R}^2 = \text{H}$),⁸ the required allenic bromide (VI)⁹ was synthesised by

bromination of vinylacetylene¹⁰ (Scheme 2); then, by utilising the fast replacement of bromine by acetoxy in the allylic position in comparison with the vinylic position, the acetoxy-allenic bromide (V) was obtained. Hydrolysis then gave the hydroxy-compound (VI).

Preliminary coupling reactions were carried out with the allenic bromide (V) or (VI) and hex-1-yne. 4-Bromobuta-2,3-dien-1-ol coupled normally, to give the expected allenynol but in rather low yield (22%), whereas 4-acetoxy-1-bromobuta-1,2-diene gave a mixture of allenyne acetate (VIII) and dec-1-ene-3,5-diyne (IX) with elimination of the acetoxy-group (Scheme 3).

The reaction of 4-acetoxy-1-bromoallene with buta-1,3-

⁶ R. Eastmond and D. R. M. Walton, *Chem. Comm.*, 1968, 204; D. R. M. Walton and F. Waugh, *J. Organometallic Chem.*, 1972, **37**, 45; R. Eastmond, T. R. Johnson, and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 4601.

⁷ B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

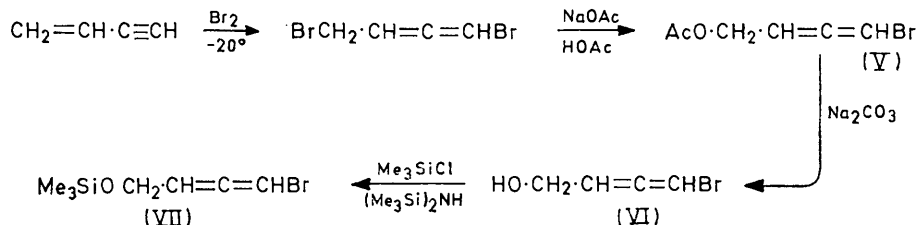
⁸ R. E. Bew, J. R. Chapman, E. R. H. Jones, B. E. Lowe, and G. Lowe, *J. Chem. Soc. (C)*, 1966, 129.

⁹ During this work a slightly different procedure was reported: M. V. Mavrov, E. S. Voskanyan, and V. P. Kucherov, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1967, 2774.

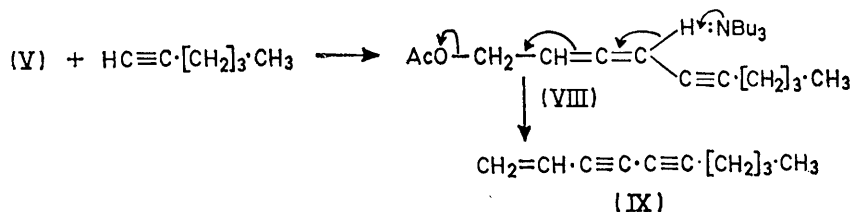
¹⁰ A. A. Petrov, G. I. Semenov, and N. P. Sopov, *Zhur. obshchei Khim.*, 1950, **20**, 708.

diyne similarly resulted in elimination of the 4-acetoxy-group and was further complicated by the formation of a mixture of octa-1,3,5,7-tetrayne and 2-ethynyl-oct-1-ene-3,5-diyne, produced by self-coupling of butadiyne.

scopic data in agreement with those of the natural product.⁸ These two examples of the synthesis of natural allenediynols in racemic form illustrate the general utility of the coupling reaction with allenic



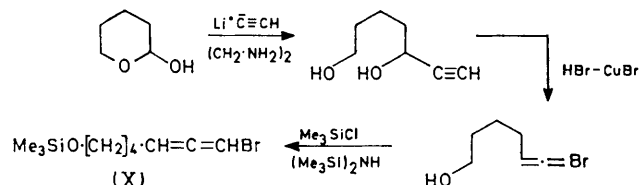
SCHEME 2



SCHEME 3

However, a trace of the natural allene (IV; $\text{R}^1 = \text{HO}\cdot\text{CH}_2$, $\text{R}^2 = \text{H}$) was isolated by chromatography of the crude product obtained from the reaction of the hydroxy-bromoallene (VI) and butadiyne. These difficulties were overcome by protecting the hydroxy-group of the allenic bromide (VI) with a trimethylsilyl group and then coupling compound (VII) with butadiynyl-(trimethyl)silane (II). The *O*-trimethylsilyl group was lost during the work-up with hydrochloric acid, and desilylation of the terminal alkyne was achieved by rapid treatment with methanolic sodium hydroxide, as with the model compounds. (\pm)-Octa-2,3-diene-5,7-diyn-1-ol was purified by dry column chromatography and had i.r. and u.v. spectra which agreed closely with those of the natural material.⁸ Removal of the trimethylsilyl group from the terminal acetylene effected the expected hypsochromic shift of the u.v. absorption bands.

Similarly, a higher homologue, (\pm)-undeca-5,6-diene-8,10-diyn-1-ol (IV; $\text{R}^1 = \text{HO}\cdot[\text{CH}_2]_4$, $\text{R}^2 = \text{H}$), was synthesised from 1-bromo-7-trimethylsilyloxyhepta-1,2-diene (X), prepared by the new method outlined in



SCHEME 4

Scheme 4, and butadiynyl(trimethyl)silane (II). Desilylation gave the racemic allenediynol, showing spectro-

halides, but the problem remains as to whether it can be adapted to the synthesis of optical enantiomers. Studies on this aspect are in progress.

EXPERIMENTAL

I.r. spectra were determined for liquid films 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 a Varian A60 spectrometer for *ca.* 20% solutions in deuteriochloroform except where otherwise stated, with tetramethylsilane as internal standard. G.l.c. was carried out with a Pye 104 instrument (5 ft glass columns with nitrogen at 2.5 l h⁻¹). Columns were packed with 10% silicone oil SE 30 or 20% Carbowax 20M on Chromosorb W. Column chromatography was carried out with either Spence type H alumina deactivated by treatment with 10% by weight of 10% acetic acid or Woelm (acid) alumina deactivated by treatment with 3% by weight of water. All experiments with allenediynes were carried out under oxygen-free nitrogen and light was excluded from chromatography columns. Solvents designated as dry were dried over sodium wire (ether and tetrahydrofuran) or potassium hydroxide (pyridine), or by azeotropic distillation with benzene (*NN*-dimethylformamide). Etheral solutions were dried over MgSO_4 .

Butadiynyl(trimethyl)- and butadiynyl(triethyl)-silane were prepared by literature methods⁶ from butadiyne and chlorotrimethylsilane or bromotriethylsilane. The 3,3-dialkyl-1-bromoallenes were prepared from the appropriate prop-2-yn-1-ols and hydrobromic acid.¹¹

7-Methyl-1-trimethylsilylnona-5,6-diene-1,3-diyne (III; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Et}$).—Copper(I) bromide (0.97 g, 0.0068 mol), hydroxylamine hydrochloride (0.1 g), and tri-*n*-butylamine (1.2 g, 0.0068 mol) were stirred in dry *NN*-dimethylformamide (20 ml) for 2 min at room temperature. Butadiynyl(trimethyl)silane (1.2 g, 0.01 mol) was added, followed

¹¹ S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc. (C)*, 1966, 1223.

after 2 min by a solution of 1-bromo-3-methylpenta-1,2-diene (1.1 g, 0.0068 mol) in *NN*-dimethylformamide (5 ml). The mixture was heated and stirred at 40–50 °C for 1.5 h, and after cooling the complex was decomposed by addition of saturated aqueous potassium cyanide (25 ml). The product was extracted into ether (4 × 50 ml), washed with water, dilute hydrochloric acid, and water, and dried. Ether was removed under reduced pressure (finally at 40 °C and 0.5 mmHg for 2 h) to give a crude product (ca. 70%). Purification was effected on a dry column⁷ of type H alumina by eluting with pentane to give 7-methyl-1-trimethylsilylnona-5,6-diene-1,3-diyne (0.63 g, 46%) (Found: C, 76.9; H, 8.7; Si, 13.7. C₁₃H₁₈Si requires C, 77.1; H, 9.0; Si, 13.9%), ν_{\max} 2 210 (C=C), 2 110 (C=C-Si), 1 950 (C=C-C), and 1 250 and 850 cm⁻¹ (SiMe₃), λ_{\max} 211 (ϵ 54 500), 220 (65 200), 234sh (5 000), 246 (6 500), 259.5 (12 200), 274 (17 300), and 291 nm (13 700), τ 9.82 (9H, s, SiMe₃), 8.98 (3H, t, CH₂·CH₃), 8.26 (3H, d, CH₃·C=), 7.98 (2H, dq, CH₂Me), and 4.66 (1H, m, =CH); g.l.c. gave one peak, t_R 7.5 min (silicone oil; 170 °C).

7-Methyl-1-trimethylsilylnona-5,6-diene-1,3-diyne (IV; R¹ = Me, R² = Et).—The above trimethylsilyl derivative (0.5 g, 0.0025 mol) was dissolved in methanol (20 ml) and dilute aqueous sodium hydroxide (5 ml; 2.5N) was added with vigorous shaking for about 10 s. The mixture was poured immediately into a separating funnel containing dilute hydrochloric acid (100 ml; 2.5N) and ether (25 ml). The water layer was further extracted with ether (3 × 20 ml), and the combined ether layers were dried, and then repeatedly evaporated, with the addition of pentane, to obtain the crude product in pentane (ca. 5 ml). Dry column chromatography on alumina (type H), with pentane as eluant, gave the *allenediyne* (0.27 g, 84%), ν_{\max} 3 300 (C≡CH), 2 200 (C=C), and 1 955 cm⁻¹ (C=C=C), λ_{\max} 212 (ϵ 19 000), 225 (3 800), 236 (6 600), 248 (11 400), 262 (15 400), and 277 nm (12 600).

7-Methyl-1-trimethylsilyldeca-5,6-diene-1,3-diyne (III; R¹ = Me, R² = Pr).—Copper(I) bromide, tri-*n*-butylamine, and butadiynyl(trimethyl)silane in *NN*-dimethylformamide were treated as above with 1-bromo-3-methylhexa-1,2-diene (1.75 g, 0.01 mol) to give, after chromatography, 7-methyl-1-trimethylsilyldeca-5,6-diene-1,3-diyne (1.04 g, 48%) (Found: C, 77.8; H, 9.3; Si, 13.1. C₁₄H₂₀Si requires C, 77.7; H, 9.3; Si, 13.0%), ν_{\max} 2 200 (C=C), 2 100 (C=C-Si), 1 950 (C=C=C), and 1 250 and 840 cm⁻¹ (SiMe₃), λ_{\max} 211 (ϵ 36 000), 220 (26 000), 233.5 (4 900), 246 (6 900), 260 (14 380), 274 (19 500), and 291 nm (15 500), τ 9.81 (9H, s, Me₃Si), 9.06 (3H, t, CH₃·CH₂), 7.82–8.85 (4H, m, CH₂·CH₂), 8.28 (3H, d, CH₃·C=), and 4.78 (1H, m, =CH).

7-Methyldeca-5,6-diene-1,3-diyne (IV; R¹ = Me, R² = Pr).—The above trimethylsilyl derivative (0.4 g, 0.002 mol) was desilylated as before to give the *allenediyne* (0.25 g, 79%), ν_{\max} 3 300 (C≡CH), 2 210 (C=C), and 1 955 cm⁻¹ (C=C=C), λ_{\max} 211 (ϵ 24 000), 224 (1 800), 236 (4 500), 248 (9 000), 262 (13 500), and 277 nm (10 800).

7-Methyl-1-triethylsilylocta-5,6-diene-1,3-diyne (III; R¹ = R² = Me; SiEt₃ for SiMe₃).—Copper(I) bromide (1.44 g, 0.01 mol), tri-*n*-butylamine (1.8 g, 0.01 mol), and hydroxylamine hydrochloride (0.25 g) were shaken together for 30 s and added to stirred butadiynyl(triethyl)silane (1.64 g, 0.01 mol) in *NN*-dimethylformamide (20 ml). After 1 min, 1-bromo-3-methylbuta-1,2-diene (1.4 g, 0.0095 mol) in *NN*-dimethylformamide (5 ml) was added and the mixture heated to 40–50 °C for 2 h. The product was worked up as above to give 7-methyl-1-triethylsilylocta-5,6-diene-1,3-diyne

(1.19 g, 55%) (Found: C, 78.0; H, 9.5; Si, 12.3. C₁₅H₂₂Si requires C, 78.2; H, 9.6; Si, 12.2%), ν_{\max} 2 205 (C≡C), 2 105 (C≡CSi), 1 956 (C=C=C), and 1 235 and 820 cm⁻¹ (SiEt₃), λ_{\max} 213 (ϵ 50 400), 221 (51 400), 234sh, 246 (5 800), 260^{max} (10 000), 275 (14 300), and 292 nm (11 550), τ 9.7–8.6 (15H, m, Et₃Si), 8.28 (6H, d, Me₂C=), and 4.8 (1H, m, CH=); g.l.c. gave one peak, t_R 18 min (silicone oil; 170 °C).

7-Methylocta-5,6-diene-1,3-diyne (IV; R¹ = R² = Me).—The triethylsilyl derivative (0.7 g, 0.0037 mol) in methanol (20 ml) was desilylated as above to give the *allenediyne* (0.33 g, 76%), ν_{\max} 3 300 (C≡CH), 2 210 (C=C) and 1 958 cm⁻¹ (C=C=C), λ_{\max} 212 (ϵ 21 000), 224 (4 500), 236 (5 500), 248 (10 000), 261 (14 000), and 276 nm (11 500).

But-1-en-3-yne¹² (with D. R. J. LAWS).—Ethylene glycol (500 ml), potassium hydroxide (400 g), and butylcellosolve (100 ml) were heated at 150 °C under nitrogen, and 1,4-dichlorobut-2-ene (125 g, 1.0 ml) was added over 1.5 h. But-1-en-3-yne (28 g, 54%), which distilled off, was dried by passing over CaCl₂ and condensed in a trap at -70 °C.

1,4-Dibromobuta-1,2-diene.¹⁰—This was obtained by brominating but-1-en-3-yne in chloroform at -20 °C. G.l.c. (silicone oil; 100 °C) showed two main components, t_R 5.6 (1,2-dibromobuta-1,3-diene; 30%) and 11.2 min (1,4-dibromobuta-1,2-diene; 52%). Fractionation gave, at best, a sample of allenic bromide with b.p. 62–63° at 6 mmHg (82% pure by g.l.c.) which was used in subsequent experiments; a pure sample obtained by preparative g.l.c. (silicone oil; 150 °C) showed ν_{\max} 1 959 cm⁻¹ (C=C=C), λ_{\max} 206 nm (ϵ 9 150), τ 6.0 (2H, dd, CH₂), 4.33 (1H, dt, CH=), and 3.79 (1H, dt, =CHBr).

4-Bromobuta-2,3-dienyl Acetate (V).—(a) 1,4-Dibromobuta-1,2-diene (7.4 g, 0.035 mol) was added dropwise to fused sodium acetate (6.3 g) in glacial acetic acid (37.5 ml) under reflux. After 2 h the mixture was cooled, diluted with water (100 ml), neutralised with sodium carbonate, and extracted into ether. The ether layer was washed with sodium hydrogen carbonate solution and water, dried, and evaporated to give a crude product (6.3 g, 95%). Chromatography on type H alumina and elution with pentane-ether (3:1) gave the acetate (82%) (Found: C, 37.9; H, 3.8; Br, 49.3. Calc. for C₆H₇BrO₂: C, 37.7; H, 3.7; Br, 48.4%), ν_{\max} 1 965 (C=C=C) and 1 745 cm⁻¹ (C=O), λ_{\max} 214 (ϵ 8 000), 268 (1 100), and 288 nm (1 100), τ 7.93 (3H, s, CH₃), 5.32 (2H, dd, OCH₂), 4.52 (1H, dt, CH=), and 3.92 (1H, dt, =CHBr), g.l.c. t_R 10.9 min (silicone oil; 100 °C).

(b) 1,4-Dibromobuta-1,2-diene (15 g, 0.07 mol) was converted by the Mavrov method⁹ into the acetate (V) (8.6 g, 64%), b.p. 50–52° at 0.5 mmHg (lit.⁹ 78%; b.p. 53° at 3 mmHg). Spectroscopic data agreed with those of the sample described in (a).

4-Bromobuta-2,3-dien-1-ol (VI).—(a) The acetate (V) (0.95 g, 0.005 mol) was added to 2N-sodium carbonate in 3:1 water-methanol (10 ml) and the mixture heated under reflux for 1 h. After cooling, the solution was extracted with ether, dried, and evaporated to give a crude product (0.67 g, 89%). Chromatography on type H alumina and elution with pentane-ether (3:1) gave the alcohol (78%) (Found: C, 33.3; H, 3.5; Br, 53.2. Calc. for C₄H₅BrO: C, 32.2; H, 3.4; Br, 53.6%), ν_{\max} 3 330 (OH) and 1 965 cm⁻¹ (C=C=C), λ_{\max} 205 nm (ϵ 5 500), τ 7.1 (1H, s, OH),

¹² Modified from G. de Vries, and H. G. Peer, *Rec. Trav. chim.*, 1963, **82**, 521.

5.72 (2H, dd, CH₂), 4.43 (1H, q, CH=), and 3.85 (1H, m, =CHBr), g.l.c. t_R 5.7 min (silicone oil; 100 °C).

(b) The acetate (V) (9.5 g, 0.05 mol) was hydrolysed by the Mavrov method⁹ to give the alcohol (VI) (5.26 g, 71%), b.p. 55° at 0.6 mmHg (lit.⁹ 77%; b.p. 42.5–44.5° at 3 mmHg). Spectroscopic data agreed with those reported in (a).

1-Bromo-4-trimethylsilyloxybuta-1,2-diene (VII).—Hexamethyldisilazane (10 g, 0.06 mol) and chlorotrimethylsilane (0.1 g) were added to 4-bromobuta-2,3-dien-1-ol (15 g, 0.1 mol) in dry tetrahydrofuran (50 ml) and the mixture was left for 12 h. The precipitate was filtered off and the filtrate distilled to give the *silyl ether* (18.0 g, 82%), b.p. 70° at 7 mmHg, ν_{\max} 1 965 (C=C=C) and 1 250 and 840 cm⁻¹ (SiMe₃), g.l.c. t_R 6.5 min (silicone oil; 80 °C).

Hept-6-yne-1,5-diol.—(a) Ethylenediamine-stabilised lithium acetylide (30 g, 0.33 mol) was added to stirred anhydrous tetrahydrofuran (300 ml) previously saturated with acetylene at -30 °C. After 15 min, 2-hydroxypyran (10.2 g, 0.1 mol) in tetrahydrofuran (50 ml) was run in over 30 min and then acetylene was passed for a further 12 h at room temperature. The mixture was decomposed with saturated ammonium chloride, the tetrahydrofuran separated, and the aqueous phase extracted with ether; the combined organic layers were dried and the *product* was purified by dry column chromatography on type H alumina (200 g) and eluted with di-isopropyl ether; yield 4.5 g (35%) (Found: C, 65.3; H, 9.1. C₇H₁₂O₂ requires C, 65.6; H, 9.4%), ν_{\max} 3 350 (OH), 3 300 (C≡CH), and 2 110 cm⁻¹ (C≡C), τ [(CD₃)₂SO] 8.53 (6H, m, [CH₂]₃), 6.95 (1H, d, CH=), 6.59 (2H, m, CH₂O), 5.82 (2H, m, CHOH), and 4.80 (1H, d, CH₂·OH).

(b) A similar reaction, but with ethynylmagnesium bromide, gave the diol (8%), identical with the sample described above.

7-Bromohepta-5,6-dien-1-ol.—Hept-6-yne-1,5-diol (4 g, 0.032 mol) was added to a mixture of copper(I) bromide (2.6 g, 0.18 mol), ammonium bromide (2.3 g, 0.23 mol), copper powder (0.3 g), and 48% hydrobromic acid (25 ml) and stirred at room temperature for 2 h. Solid was filtered off and the filtrate was extracted with chloroform; the extract was dried and evaporated and the *product* purified by dry column chromatography on type H alumina (100 g) and eluted with di-isopropyl ether; yield 3.4 g (56%) (Found: C, 44.1; H, 5.6; Br, 40.8. C₇H₁₁BrO requires C, 44.0; H, 5.8; Br, 41.9%), ν_{\max} 3 350 (OH) and 1 965 cm⁻¹ (C=C=C), λ_{\max} 206 nm (ϵ 6 300), τ 8.45 (4H, m, [CH₂]₂), 7.83 (2H, m, CH₂·CH=), 6.97 (1H, s, OH), 5.41 (2H, m, CH₂·OH), 4.61 (1H, dt, =CH), and 4.08 (1H, dt, =CHBr).

1-Bromo-7-trimethylsilyloxyhepta-1,2-diene (X).—7-Bromohepta-5,6-dien-1-ol was treated with hexamethyldisilazane and chlorotrimethylsilane as described above to give 1-bromo-7-trimethylsilyloxyhepta-1,2-diene (76%), b.p. 92–93° at 10 mmHg, ν_{\max} 1 960 (C=C=C), 1 250 and 830 cm⁻¹ (SiMe₃), g.l.c. t_R 7.3 min (silicone oil; 100 °C).

Deca-2,3-dien-5-ynyl Acetate (VIII).—Tri-n-butylamine (2.2 g, 0.012 mol) and hydroxylamine hydrochloride (0.2 g) were added to a slurry of copper(I) bromide (1.7 g, 0.012 mol) in *NN*-dimethylformamide (10 ml) and stirred for 1 min to equilibrate, then hex-1-yne (1.2 g, 0.015 mol) was stirred in for 5 min; an intense yellow copper complex formed. 4-Bromobuta-2,3-dienyl acetate (2.25 g, 0.12 mol) in *NN*-dimethylformamide (5 ml) was then added and the mixture heated at 40–50 °C for 4 h. After cooling, the mixture was treated with saturated aqueous potassium

cyanide, diluted with water, and extracted into ether. The extract was washed with water, dilute hydrochloric acid, water, 10% ammoniacal silver nitrate, and water, dried, and evaporated. The crude product was chromatographed on Woelm acid alumina. Elution with pentane gave *dec-1-ene-3,5-diyne* (0.42 g, 22%), ν_{\max} 2 220 (C≡C), 1 600 (C=C), and 975 and 935 cm⁻¹ (C=CH₂), λ_{\max} 212 (ϵ 25 100), 228 (4 680), 239 (10 700), 251 (21 300), 265 (29 400), and 281 nm (24 200), τ 9.08 (3H, t, CH₃·CH₂), 8.61 (4H, m, CH₂·CH₂), 7.67 (2H, m, ≡C·CH₂), and 4.30 (3H, m, CH₂=CH). Hydrogenation, in *n*-pentane, gave *n*-decane, identical (g.l.c. and spectra) with an authentic sample.

Elution with pentane-ether (3:1) gave the *dienyne acetate* (0.38 g, 17%), ν_{\max} 2 220 (C≡C), 1 952 (C=C=C), and 1 730 cm⁻¹ (C=O), λ_{\max} 210 nm (ϵ 7 710), τ 9.09 (3H, t, CH₃·CH₂), 8.55 (4H, m, CH₂·CH₂), 7.92 (3H, s, CH₃·CO), 7.70 (2H, m, ≡C·CH₂), 5.31 (2H, dd, OCH₂), 4.50 (1H, m, CH₂·CH=), and 3.87 (1H, dt, =CH-C≡).

Deca-2,3-dien-5-yn-1-ol.—Hex-1-yne (1.5 g, 0.018 mol) was coupled with 4-bromobuta-2,3-dien-1-ol (2.2 g, 0.015 mol) as described for the acetate except that heating at 40–50 °C was continued for 6 h. The crude product was purified on Woelm acid alumina (200 g) and elution with pentane-ether (3:1) gave *deca-2,3-dien-5-yn-1-ol* (0.32 g, 22%), ν_{\max} 3 300 (OH), 2 220 (C≡C), and 1 955 cm⁻¹ (C=C=C), λ_{\max} 217 nm (ϵ 5 600), τ 9.09 (3H, t, CH₃), 8.60 (4H, m, CH₂·CH₂), 7.74 (3H, m, OH and ≡C·CH₂), 5.81 (2H, dd, CH₂·OH), and 4.44 (2H, m, CH=C=CH), g.l.c. t_R 8.0 min (silicone oil; 150 °C).

Reaction of 4-Bromobuta-2,3-dienyl Acetate with Butadiyne.—Copper(I) bromide (5.8 g, 0.04 mol), tri-*n*-butylamine (7.4 g, 0.04 mol), and hydroxylamine hydrochloride (0.1 g) in *NN*-dimethylformamide (5 ml) were added to stirred butadiyne (2.8 g, 0.056 mol) in *NN*-dimethylformamide (10 ml) at 0 °C. The mixture was allowed to warm to room temperature, the bromo-acetate diene (1.0 g, 0.005 mol) in *NN*-dimethylformamide (5 ml) was added, and stirring was continued at 40–50 °C for 1.5 h. The product was worked up as before but the silver nitrate washing was omitted, to give after two chromatographic separations, a main fraction eluted with pentane which had ν_{\max} 3 300 (C≡CH), 2 220 (C≡C), and 2 110 (C≡CH) but no band at 1 950 cm⁻¹ (C=C=C), λ_{\max} 217, 227, 252, 266, 281, and 298 nm.

Reaction of 4-Bromobuta-2,3-dien-1-ol with Butadiyne.—The alcohol (2.24 g, 0.015 mol) and butadiyne (7.5 g, 0.15 mol) in a similar manner to the above, gave a crude product which was chromatographed on Woelm acid alumina (200 g). Elution with pentane gave fractions showing λ_{\max} 216.5, 227, 237, 251, 265, 280, and 296 nm, similar to the product obtained from the self coupling of butadiyne (see below). Elution with pentane-ether (4:1) gave fractions showing λ_{\max} 210, 247, 262, and 277 nm which were rechromatographed to give impure octa-2,3-diene-5,7-diyne-1-ol, ν_{\max} 3 400 (OH), 3 300 (C≡CH), 2 220 (C≡C), 2 110 (C≡CH), and 1 962 cm⁻¹ (C=C=C), λ_{\max} 208, 236, 248, 262, and 277 nm, which contained 4-bromobuta-2,3-dien-1-ol (shown by g.l.c. and comparison with an authentic sample).

Coupling of butadiyne under the above conditions without any added allenic bromide, work-up, and chromatography gave a mixture of octa-1,3,5,7-tetraene and 2-ethynyloct-1-ene-3,5-diyne, ν_{\max} 3 300 (C≡CH), 2 220 (C≡C), 2 100 (C≡CH), and 1 610 cm⁻¹ (C=CH₂), λ_{\max} 207.8 (ϵ 6 500), 217 (11 700), 227 (18 800), 238 (3 500), 252

(5 800), 265 (12 700), 281 (22 800), and 298 nm (23 900). Hydrogenation and g.l.c. gave n-octane (32%) and 8-methylheptane (68%).

8-Trimethylsilylocta-2,3-diene-5,7-diyn-1-ol.— Copper(I) bromide (2.16 g, 0.015 mol), tri-n-butylamine (2.77 g, 0.015 mol), and hydroxylamine hydrochloride (0.25 g) were shaken together for 30 s and added in one portion to stirred butadiynyl(trimethyl)silane (1.83 g, 0.05 mol) in *NN*-dimethylformamide (20 ml). After 2 min, 1-bromo-4-trimethylsilyloxybuta-1,2-diene (3.31 g, 0.015 mol) in *NN*-dimethylformamide (8 ml) was added and the mixture heated to 40–50 °C for 2 h. Work-up was performed as described above, except that low-boiling material was finally removed at 10⁻⁴ mmHg for 4 h, and then the crude product was purified on a dry column of Woelm acid alumina (200 g) and eluted with methylene chloride to give 8-trimethylsilylocta-2,3-diene-5,7-diyn-1-ol (0.5 g, 18%), ν_{\max} 3 300 (OH), 2 200 (C≡C), 2 100 (C≡C-Si), 1 950 (C=C=C), and 1 240 and 850 cm⁻¹ (SiMe₃), λ_{\max} 214 (ϵ 34 000), 220 (40 000), 233sh (3 000), 246 (3 600), 259 (6 800), 274 (12 800), and 291 nm (10 800).

(±)-Octa-2,3-diene-5,7-diyn-1-ol.— 8-Trimethylsilylocta-2,3-diene-5,7-diyn-1-ol (0.5 g, 0.0026 mol) was desilylated as described previously and the product was obtained in pentane solution, with <10% of ether to give a homo-

geneous solution. Purification by dry column chromatography gave (±)-octa-2,3-diene-5,7-diyn-1-ol (0.09 g, 30%), ν_{\max} (CCl₄) 3 400 (OH), 3 320 (C≡CH), 2 220 (C≡C), and 1 940 cm⁻¹ (C=C=C), λ_{\max} (rel. ϵ in parentheses) 211 (3.8), 235 (0.7), 248 (0.9), 261 (1.2), and 276 nm (1.0) in close agreement with lit. values.⁸

11-Trimethylsilylundeca-5,6-diene-8,10-diyn-1-ol.— 7-Trimethylsilyloxyhepta-1,2-diene (1.3 g, 0.005 mol) and butadiynyl(trimethyl)silane (1.2 g, 0.01 mol) gave under the above coupling and chromatography conditions 11-trimethylsilylundeca-5,6-diene-8,10-diyn-1-ol (0.26 g, 22%), ν_{\max} 3 300 (OH), 2 200 (C≡C), 2 100 (C≡C-Si), 1 950 (C=C=C), and 1 250 and 850 cm⁻¹ (SiMe₃), λ_{\max} 214 (ϵ 41 500), 220 (40 800), 233sh (5 800), 246 (7 200), 259 (10 800), 275 (14 200), and 291 nm (11 300).

(±)-Undeca-5,6-diene-8,10-diyn-1-ol.—The above trimethylsilyl derivative (0.1 g) was desilylated and the product worked up as above to give, after chromatography, (±)-undeca-5,6-diene-8,10-diyn-1-ol (0.037 g, 58%), ν_{\max} (CCl₄) 3 400 (OH), 3 295 (C≡CH), 2 210 (C≡CH), and 1 948 cm⁻¹ (C=C=C), λ_{\max} (rel. ϵ in parentheses) 209 (4.2), 236 (0.92), 248 (1.0), 262 (1.3), and 277 nm (1.0), in close agreement with lit. values.⁸

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