

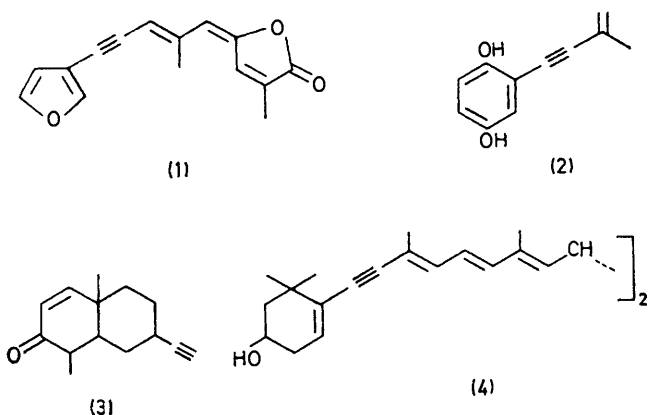
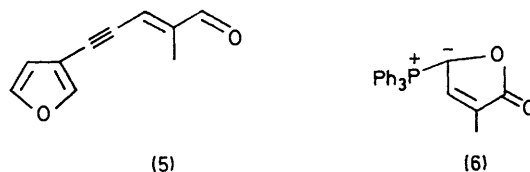
Synthesis of Freelingyne, an Acetylenic Sesquiterpene from *Eremophila freelingii*

By David W. Knight and Gerald Pattenden,* Department of Chemistry, The University, Nottingham NG7 2RD

The application of the 2-methyl-4-triphenylphosphoranylidenebut-2-en-4-olide (6) in the total synthesis of natural freelingyne (19) and its geometrical isomer (1) [(4*Z*)- and (4*E*)-isomers of (6*E*)-9-(3-furyl)-2,6-dimethylnona-2,4,6-trien-8-yn-4-olide] is described. A coupling reaction between 3-furylcopper (16) and the iodoacetylene (15) provided the (3-furyl)-enyne (17b), hydrolysis of which, followed by oxidation, led to the aldehyde (5). Condensation between the ylide (6) and the aldehyde (5) produced a mixture of isomers of freelingyne, one of which, assigned the structure (19) from *X*-ray measurements, was identical with the naturally derived material.

THE sesquiterpene freelingyne (1), from *Eremophila freelingii*, was the first natural acetylenic terpenoid to be isolated.¹ The occurrence of the acetylenic grouping in terpenoids is rare: up to now the only other examples are the hydroquinone derivative (2) from the fungus *Helminthosporium siccans* g 207,² compounds of the chamaecynone (3) type from *Chamaecyparis formosensis* Matsum,³ and some carotenoids, e.g. alloxanthin (4), from algae and marine organisms.⁴ In addition to having an acetylenic bond, freelingyne contains the unusual 4-ylidenebutenolide end grouping. In the preceding

shown in structure (1) were suggested from ¹H n.m.r. data.¹ Our approach to (1) had the attraction that it could permit the synthesis of all four possible isomers of freelingyne.



Almost without exception, syntheses of natural sesquiterpenoids containing a 3-substituted furan ring, such as torreyal, dendrolasin, etc., have been approached from a 3-furoate and have proceeded *via* stepwise chain extension.⁷ The presence of the 3-furylacetylene unit in freelingyne suggested a route to the key intermediate (5) based on a Stephens-Castro-type coupling⁸ between 3-iodofuran and a suitable copper(I) acetylide or a coupling between 3-furylcopper and an iodoacetylene.⁹ The feasibility of this approach was explored in the 2-furyl series, by using the easily available acetylenic alcohol (7a).¹⁰

The alcohol (7a) was protected by formation of the tetrahydropyranyl ether and the latter was then metalated with *n*-butyl-lithium. Reaction with powdered iodine produced the iodoacetylene (8), which was not isolated but was added immediately to 2-furylcopper (9) in tetrahydrofuran at -45° ; compound (9) was previously prepared from 2-furyl-lithium¹¹ and copper(I) bromide at -70° . After work-up, chromatography separated the expected 2-furyl-enyne (10) in ca. 30% yield [based on (7b)]. This product was accompanied by the dienediynes (11) (ca. 1%) and by 2,2'-bifuran (12) (ca. 5%), both compounds resulting from self coupling of reagents, presumably as a result of metal-halide exchange

paper,⁵ a method was described for the synthesis of this unit. We now report the development of this approach in the total synthesis of natural freelingyne and of one of its geometrical isomers.⁶

The previous studies⁵ suggested that the reaction between the 4-phosphoranylidenebutenolide (6) and the substituted enynal (5) would lead to the freelingyne structure. At the outset of our investigation, the configurations about the double bonds in natural freelingyne were not known with certainty; the assignments

¹ R. A. Massy-Westropp, G. D. Reynolds, and T. M. Spotswood, *Tetrahedron Letters*, 1966, 1939.

² K. Ishibashi, K. Nose, T. Shindo, M. Arai, and H. Mishina, *Ann. Reports Sankyo Res. Lab.*, 1966, 1939.

³ T. Nozoe, Y. S. Cheng, and T. Toda, *Tetrahedron Letters*, 1966, 3663; T. Asao, S. Ibe, K. Takase, Y. S. Cheng, and T. Nozoe, *ibid.*, 1968, 3639; K. Takase, S. Ibe, T. Asao, T. Nozoe, H. Shimanouchi, and Y. Sasada, *Chem. and Ind.*, 1968, 1638.

⁴ For review see B. C. L. Weedon in 'Carotenoids,' ed. O. Isler, Birkhäuser, Basel, 1971.

⁵ D. W. Knight and G. Pattenden, preceding paper.

⁶ Preliminary communication, D. W. Knight and G. Pattenden, *J.C.S. Chem. Comm.*, 1974, 188.

⁷ Cf. A. F. Thomas, *Chem. Comm.*, 1968, 1657; K. A. Parker and W. S. Johnson, *Tetrahedron Letters*, 1969, 1329; see also D. L. Dare, I. D. Entwistle, and R. A. W. Johnstone, *J.C.S. Perkin I*, 1973, 1130.

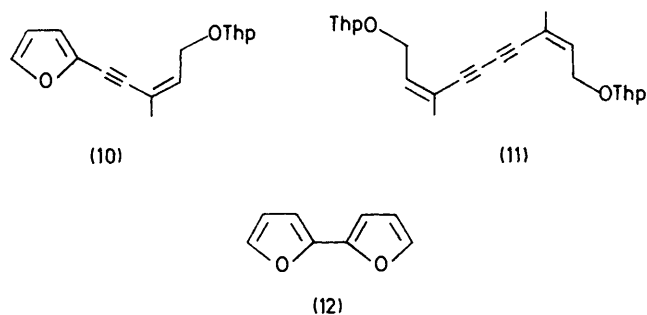
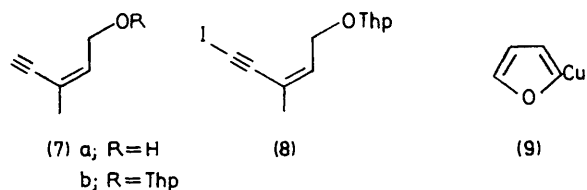
⁸ R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 1963, **28**, 3313; C. E. Castro, R. Havlin, V. K. Honwad, A. Malte, and S. Mojé, *J. Amer. Chem. Soc.*, 1969, **91**, 6464.

⁹ Cf. R. Oliver and D. R. M. Walton, *Tetrahedron Letters*, 1972, 5209.

¹⁰ J. Cymerman, I. M. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 1945, 90.

¹¹ V. Ramanathan and R. Levine, *J. Org. Chem.*, 1962, **27**, 1216.

in compounds (8) and (9). In model studies of the Stephens-Castro-type coupling between 3-iodofuran and

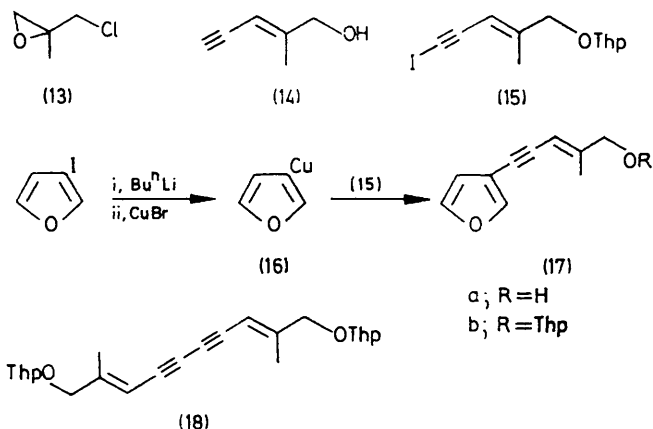


the copper reagent from phenylacetylene, significant amounts of diyne and bisfurans accompanied the required (3-furyl)phenylacetylene, and we concluded that the coupling reaction was a less practical route to 3-furylacetylenes than the alternative *via* 3-furylcopper.

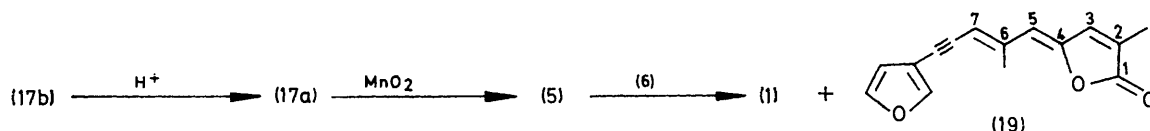
We next turned to the application of 3-furylcopper and the isomeric acetylenic compound (15) towards the synthesis of the precursor (17b) to freelingyne. The acetylenic alcohol (14) was first prepared by Ahmad and Weedon¹² from the chloro-epoxide (13) and sodium acetylide. Although the configuration about the double bond in (14) was not discussed in their paper, the authors no doubt presumed it to be *E* on the basis of its subsequent application in all-*E*-bixin synthesis. More recently Macomber¹³ reported the preparation of (14) by the same route, and presented evidence implying that the double bond had the *Z*-configuration. We prepared compound (14) by the literature procedure and found it to be a single isomer. ¹H N.m.r. data did not lead to an unambiguous stereochemical assignment, and we sought a

from (14) led to the iodo-compound (15) which, in a coupling reaction with 3-furylcopper (16), gave the furfuryl-ene (17b). The dienediynes (18) and a mixed fraction (<1% of total product) containing bifurans were also separated; the latter compounds presumably result from a series of reversible reactions between 3-iodofuran and base, similar to those reported for 3-bromothiophen.¹⁵

The tetrahydropyranyl ether (17b) was smoothly converted into the key intermediate (5) by removal of the protecting group with acid to produce (17a), and oxidation of the latter with manganese dioxide. The reaction between the enynal (5) and phosphorus ylide (6) was carried out as described in the preceding paper, and led to the desired product as a 3 : 2 mixture of (4*Z*)- and (4*E*)-isomers, in a total yield of 65%. The isomers were separated by chromatography, and the less polar one, m.p. 157–159°, was identical (mixed m.p., n.m.r., i.r., visible, and mass spectra, and t.l.c. behaviour) with natural freelingyne. The more polar isomer, which was the major product, showed a closely similar m.p. (158–159°), which was depressed to 135–140° on admixture with natural material; its spectral data were distinct from those of the less polar isomer, and consistent with



the 4,5-double bond isomer of freelingyne. The remaining problem, of assigning structure (1) or (19) to natural freelingyne, could not be solved from comparative ¹H n.m.r. data alone because of the dearth of suitable model compounds. Massy-Westropp and his colleagues¹



solution to the problem from *X*-ray measurements on the α -naphthylurethane derivative. These clearly established the *E*-configuration for the derivative, and by inference for (14).¹⁴

Iodination of the tetrahydropyranyl ether derived

¹² R. Ahmad and B. C. L. Weedon, *J. Chem. Soc.*, 1953, 3286.

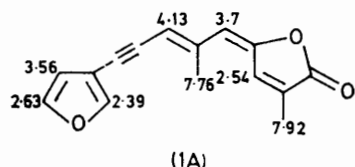
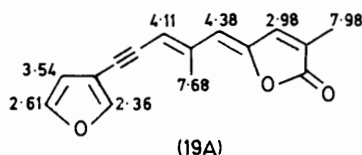
¹³ R. S. Macomber, *J. Amer. Chem. Soc.*, 1970, **92**, 7101.

¹⁴ M. J. Begley, D. W. Knight, and G. Pattenden, unpublished work.

assigned the (4*E*)-configuration to natural freelingyne largely on the basis of chemical shift data for the 6-methyl protons and the magnitude of the coupling between H-3 and -5. However, even with the two pure (4*Z*,6*E*)- and (4*E*,6*E*)-isomers (1) and (19) the stereochemistries cannot be defined unequivocally from

¹⁵ See J. A. Joule and G. F. Smith, 'Heterocyclic Chemistry,' Van Nostrand-Reinhold, New York, 1972, p. 230.

n.m.r. data, since it is not clear whether the butenolide oxygen atom or the butenolide olefinic bond would exercise the greatest deshielding effect on neighbouring protons. We ultimately solved the problem by X-ray measurements on the synthetic material, which was identical with natural freelingyne. These measurements established that the configurations of the double bonds in this isomer, and hence in natural freelingyne, are as depicted in formula (19), *viz.* 4*Z*,6*E*. The interpretation of the n.m.r. data follows; see formulae (1A) and (19A). The butenolide oxygen atom is more deshielding than the butenolide olefinic bond, and hence H-5 in isomer (1) and the 6-methyl protons in natural freelingyne (19) resonate at lower field than the corresponding protons in the other isomer [τ 3.7 and 4.38, and τ 7.68 and 7.76]. The H-3 in isomer (1) resonates at lower field than the same proton in natural freelingyne because of its *cis*-relationship to the 6,7-olefinic bond (τ 2.54 and 2.98); the other resonances of the isomers (1) and (19) are closely similar.



EXPERIMENTAL

For general experimental details see preceding paper.¹

(*Z*)-3-Methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (7b).—The ether, prepared from the corresponding alcohol and dihydropyran in the presence of hydrochloric acid in the usual way, showed b.p. 68–70° at 2 mmHg, n_D^{22} 1.4832, ν_{\max} (film) 2110, 1263, and 1202 cm^{-1} , τ 4.18 (dt, S 2 and 7, :CH), 5.45br (O·CH·O), 5.7–5.9 (m, :CH·CH₂·O), 5.9–6.7 (m, OCH₂), 6.9 (:CH), 81.3 (d, S 2, :CMe), and 8.2–8.6 (6H, m) (Found: M^+ , 180.1158. C₁₁H₁₆O₂ requires M , 180.1150).

(*Z*)-5-(2-Furyl)-3-methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (10).—The ether (7b) (3.6 g) was added during 5 min to a stirred solution of 2.2*M*-*n*-butyl-lithium (11 ml; in hexane) in dry tetrahydrofuran (35 ml) maintained at –30° under nitrogen. The solution was stirred at –30° for 5 min and then powdered iodine (6.6 g) was introduced. The mixture was stirred at –20° for 0.5 h, then diluted with iced water (50 ml) and extracted with ether. The extracts were washed successively with aqueous potassium thio-sulphate and saturated aqueous sodium chloride, then dried and concentrated to 20 ml, to leave a solution of (*Z*)-5-iodo-3-methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne in ether which was used immediately in the next stage.

A solution of furan (1.63 g) and 2.2*M*-*n*-butyl-lithium (12 ml; in hexane) in tetrahydrofuran (40 ml) was boiled under

nitrogen for 4 h then cooled to 25° and added to a vigorously stirred suspension of copper(I) bromide¹⁶ (3.74 g) in tetrahydrofuran (30 ml) at –30°. The mixture was stirred at –30° for 5 min, then treated with a solution of the (*Z*)-iodoacetylene (above) in ether (20 ml), and stirred at –30° for 3 h and at 25° for 14 h. The mixture was poured into water (200 ml) and then extracted with ether. Evaporation of the dried extracts left an oil which was dissolved in *n*-pentane; the solution was filtered and evaporated to give an oil which was chromatographed on silica gel (4 : 1 chloroform–benzene as eluant) to give (a) the 2-furyl-enyne ether (*ca.* 1.4 g) (eluted second), λ_{\max} (EtOH) 299 and 283 nm, ν_{\max} (film) 2215, 1635, 1572, 1460, 1445, and 760 cm^{-1} , τ 2.64 (d, S 2, ·O·CH·CH·), 3.45 [d, S 4, ·CH·C(O)·C_i], 3.68 (dd, S *ca.* 2, ·O·CH·CH), 4.1 (t, S 6.5, :CH·CH₂), 5.36 (m, O·CH·O), 5.5–5.78 (m, :CH·CH₂·O), 5.9–6.6 (m, OCH₂), 8.04br (Me), and 8.2–8.5 (6H, m) (Found: M^+ , 246.1251. C₁₅H₁₈O₃ requires M , 246.1256); (b) 2,2'-bifuran (12) (0.3 g) (eluted first), τ 2.6 (2H) and 3.4–3.7 (4H), *me* 134, 105, 95, 78, 51, and 39, closely similar to the data reported;¹⁷ and (c) 3,8-dimethyl-1,10-(bistetrahydropyran-2-yloxy)deca-2,8-diene-4,6-diyne (11) (0.03 g) (eluted last), λ_{\max} 263, 276, 293, and 312 nm, ν_{\max} (KBr) 2220 cm^{-1} , τ 4.02 (tq, S 7 and 1, 2 × :CH), 5.4br (2 × O·CH·O), 5.6–6.6 (m, 4 × OCH₂), 8.1 (d, S 1, 2 × :CMe), and 8.2–8.5 (12H, m) (Found: M^+ , 358.2147. C₂₂H₃₀O₄ requires M , 358.2144).

1-Chloro-2,3-epoxy-2-methylpropane (13).—The chloroepoxide was prepared either directly from 3-chloro-2-methylpropene and *m*-chloroperbenzoic acid¹³ or by elimination of hydrogen bromide from the bromohydrin obtained from 3-chloro-2-methylpropene;¹² it showed b.p. 121–124° (lit.,¹² 123–124°), ν_{\max} (film) 1296, 1258, 820, 740, and 702 cm^{-1} , τ 6.5 (CH₂Cl), 7.28 (2H), and 8.57 (Me).

(*E*)-2-Methylpent-2-en-4-yn-1-ol (14).—The alcohol, prepared as described previously,¹² showed b.p. 75–78° at 14 mmHg (lit.,¹² 85–87° at 20 mmHg), ν_{\max} (film) 3350, 2105, 1636, and 822 cm^{-1} , τ 4.49br (:CH), 6.0 (CH₂·OH), 6.3br (OH), 6.88 (d, S 2, :CH), and 8.14 (Me).

The α -naphthylurethane crystallised from light petroleum (b.p. 80–90°) as needles, m.p. 103–104° (lit.,¹² 104°), λ_{\max} (CHCl₃) 204 nm, ν_{\max} (KBr) 3450, 3312, 1700, 1645, 1544, 1235, 789, and 766 cm^{-1} , τ 2.1–2.7 (7H, m), 2.95br (NH), 4.45br (:CH), 5.37 (OCH₂), 6.89 (d, S 2, :CH), and 8.07br (Me) (Found: C, 76.7; H, 5.9; N, 5.15. Calc. for C₁₇H₁₅NO₂: C, 77.0; H, 5.65; N, 5.3%).

(*E*)-2-Methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne [O-Thp-(14)].—Hydrochloric acid (0.5 ml) was added during 5 min to a cooled (0 ± 2°) mixture of (*E*)-2-methylpent-2-en-4-yn-1-ol (12.5 g) and dihydropyran (10 g) and the solution was then left at 25° for 18 h. The mixture was diluted with ether and the ethereal extract was then washed with *n*-potassium hydroxide and saturated sodium chloride solution, dried, and evaporated. Distillation of the residue gave the ether (13.2 g), b.p. 68–70° at 0.7 mmHg (lit.,¹² 68–69° at 0.1 mmHg), ν_{\max} 2105, 1262, 1202, and 825 cm^{-1} , τ 4.46br (:CH), 5.43br (O·CH·O), 5.9–6.7 (m, 2 × CH₂O), 6.92 (d, S 2, :CH), 8.14 (Me), and 8.2–8.6 (m, 3 × CH₂).

3-Iodofuran.—The iodide was prepared, starting from 2-furoic acid, essentially as outlined by Bell *et al.*,¹⁸ except that in the final isolation step it was separated by extraction with ether rather than by steam distillation; τ 2.62 (m, O·CH·

¹⁷ R. Grigg, J. A. Knight, and M. V. Sargent, *J. Chem. Soc. (C)*, 1966, 976.

¹⁸ R. A. Bell, M. B. Gravestock, and V. Y. Taguchi, *Canad. J. Chem.*, 1972, 50, 3749.

¹⁶ A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1951, p. 187.

CH), 2.7 (m, O·CH·Cl), and 3.55m (O·CH·CH). It was estimated from n.m.r. data that <3% of the 2-isomer was present.

(E)-5-(3-Furyl)-2-methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (17b).—(E)-2-Methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (3.6 g) was converted into the 5-iodo-compound as described for the (Z)-3-methyl analogue; the iodo-compound was used immediately in the next stage.

3-Iodofuran (4.65 ml) was added to 2.2M-n-butyl-lithium (11.5 ml; in hexane) in dry tetrahydrofuran (30 ml) under nitrogen at -70° , and the solution was stirred at -70° for 5 min, and then quickly added to a vigorously stirred suspension of copper(I) bromide¹⁶ (3.8 g) in tetrahydrofuran (50 ml) at -45° . The mixture was stirred at -45° for 5 min, then treated with a solution of (E)-5-iodo-2-methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (above) in ether (20 ml), and stirred at -30° for 3 h and at 25° for 18 h. The mixture was poured into water (100 ml) and then extracted with ether. Evaporation of the dried extracts left an oil which was dissolved in n-pentane; the solution was filtered and evaporated to give an orange oil which was chromatographed on silica gel (4 : 1 chloroform–benzene as eluant) to give (a) the (3-furyl)-enyne ether (ca. 1 g) (eluted second), λ_{max} (EtOH) 279, 265, and 245 nm, ν_{max} (film) 2200, 1638, 1504, 1120, and 876 cm^{-1} , τ 2.42 (CH·CH·O·CH·), 2.65 (CH·CH·O·CH·), 3.59 (CH·CH·O·CH·), 4.14 (:C·CH·), 5.4br (O·CH·O), 5.8–6.6 (m, $2 \times \text{CH}_2\text{O}$), 8.08 (:CMe), and 8.2–8.6 (6H, m) (Found: M^+ , 246.1253. $\text{C}_{15}\text{H}_{18}\text{O}_3$ requires M , 246.1256); and (b) 2,9-dimethyl-1,10-(bistetrahydropyran-2-yloxy)deca-2,8-diene-4,6-diyne (ca. 1 g) (eluted last), λ_{max} (CHCl_3) 323, 303.5, 285, and 269 nm, ν_{max} (KBr) 2145, 1629, 1206, 1135, and 821 cm^{-1} , τ 4.35br ($2 \times \text{:CH}$), 5.44br ($2 \times \text{O·CH·O}$), 5.86–6.72 (m, $4 \times \text{OCH}_2$), 8.11 ($2 \times \text{:CMe}$), and 8.2–8.58 (12H, m) (Found: M^+ , 358.2156. $\text{C}_{22}\text{H}_{30}\text{O}_4$ requires M , 358.2144).

(E)-5-(3-Furyl)-2-methylpent-2-en-4-yn-1-ol (17a).—A solution of (E)-5-(3-furyl)-2-methyl-1-(tetrahydropyran-2-yloxy)pent-2-en-4-yne (0.6 g) in 10% hydrochloric acid (20 ml) and tetrahydrofuran (35 ml) was shaken vigorously at 25° for 5 days (t.l.c. monitoring) and then extracted with ether. The combined extracts were washed with saturated sodium chloride solution and then evaporated to give a yellow oil. Chromatography on silica gel (chloroform as eluant) gave the alcohol (0.24 g, 75%), as a viscous oil, λ_{max} (EtOH) 280 and 265 nm, ν_{max} (CHCl_3) 3580, 2205, 1504, 1160, and 878 cm^{-1} , τ 2.42 (:CH·CH·O·CH·), 2.66 (:CH·CH·O·CH·), 3.59 (:CH·CH·O·CH·), 4.27 (:C·CH), 5.91br (CH_2O), 6.82 (OH), and 8.09 (:CMe) (Found: M^+ , 162.0693. $\text{C}_{10}\text{H}_{10}\text{O}_2$ requires M , 162.0681).

(E)-5-(3-Furyl)-2-methylpent-2-en-4-ynal (5).—A solution

of 5-(3-furyl)-2-methylpent-2-en-4-yn-1-ol (0.24 g) in dry methylene chloride (35 ml) was shaken with manganese dioxide (2.3 g) at 25° for 23 h. The manganese dioxide was filtered off and washed with methylene chloride. Evaporation of the methylene chloride solution and chromatography of the residue in chloroform on silica gel gave the aldehyde (0.16 g) as a yellow oil which slowly crystallised; m.p. $30-31^\circ$, λ_{max} (CHCl_3) 319, 280, and 272 nm, ν_{max} (CHCl_3) 2230, 1680, 1617, and 872 cm^{-1} , τ 0.5 (CHO), 2.28 (:CH·CH·O·CH·), 2.57 (:CH·CH·O·CH·), 3.50 (m, CH·CH·O·CH· and :C·CH), and 8.02 (d, S 1.5, :CMe), m/e 160 (M^+ , $\text{C}_{10}\text{H}_8\text{O}_2$).

(4Z)- and (4E)-Isomers of (6E)-9-(3-Furyl)-2,6-dimethylnona-2,4,6-trien-8-yn-4-olide [(19) and (1)].—Powdered 2,5-dihydro-4-methyl-5-oxofuran-2-yl(triphenyl)phosphonium bromide (0.53 g)⁵ was added to a solution of dimethyl sulphoxide (DMSO) anion (1 equiv.) in DMSO (15 ml) and the red solution was stirred for 5 min then treated with a solution of 5-(3-furyl)-2-methylpent-2-en-4-ynal (0.16 g) in DMSO (2 ml). The mixture was stirred at 25° for 18 h then poured into water and extracted with ether. Evaporation of the dried extracts left a residue which was chromatographed in benzene on silica gel to give (a) the (Z)-isomer (72 mg), (eluted first), which crystallised from benzene as needles, m.p. $157-159^\circ$, λ_{max} (CHCl_3) 368 and 269 nm, ν_{max} (CHCl_3) 2205, 1755, 1632, 1581, 1557, 1509, 1450, 1348, 1300, 1262, 1162, 1096, 1062, 992, 958, 897, and 877 cm^{-1} , τ see formula (19A) (Found: M^+ , 240.0772. $\text{C}_{15}\text{H}_{12}\text{O}_3$ requires M , 240.0786); and (b) the (E)-isomer (91 mg) (eluted second), which crystallised from benzene as needles, m.p. $158-159^\circ$ depressed to $135-140^\circ$ on admixture with the (Z)-isomer, λ_{max} (CHCl_3) 369.5 nm, ν_{max} (CHCl_3) 2205, 1760, 1611, 1585, 1558, 1510, 1453, 1396, 1354, 1323, 1260, 1170, 1098, 1075, 1000, 956, 894, and 874 cm^{-1} , τ see formula (1A) (Found: M^+ , 240.0768).

The (Z)-isomer was identical (m.p., mixed m.p., n.m.r. and mass spectra, and t.l.c. behaviour) with naturally derived freelingyne.*

We thank Dr. R. A. Massy-Westropp (University of Adelaide) for a sample of natural freelingyne, and Professor B. C. L. Weedon (Queen Mary College, London) for a gift of the alcohol (7a). We also thank Dr. M. J. Begley for the X-ray data, which will be published separately, and the S.R.C. for a studentship (to D. W. K.).

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* An alternative synthesis of freelingyne has been published recently (C. F. Ingram, R. A. Massy-Westropp, and G. D. Reynolds, *Austral. J. Chem.*, 1974, **27**, 1477).