Rhodium(I)-catalysed Reactions of Enynes. Linear Coupling *vs.* Cycloaddition

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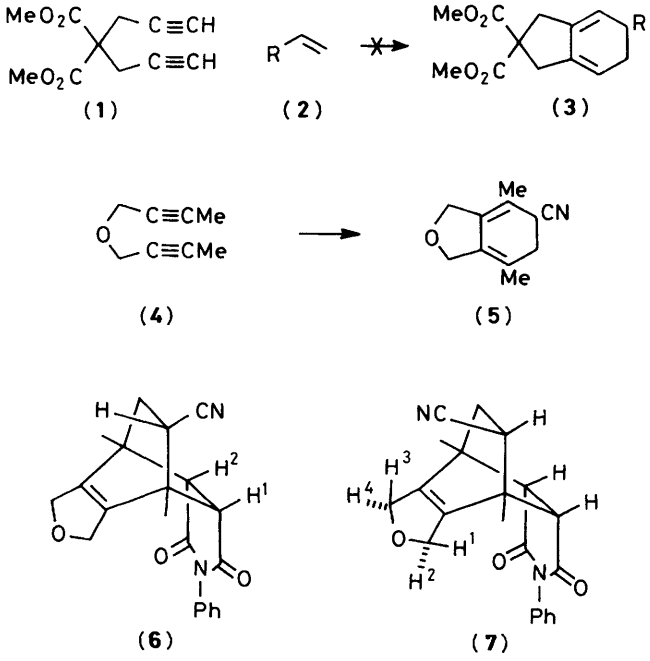
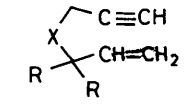
The Rh^{I}-catalysed [2 + 2 + 2]-cycloaddition of dibut-2-ynyl ether (a 2,7-diyne) and acrylonitrile gives the corresponding bicyclic cyclohexadiene. Terminally unsubstituted 1,6-diynes fail to give an analogous reaction. Allyl propargyl ethers undergo a related Rh^{I} catalysed [2 + 2 + 2]-cyclodimerisation but substitution of the terminal alkene diverts the reaction to linear dimerisation involving the terminal alkyne. 4,9-Dioxadodec-1-ene-6,11-diyne gives a novel bicyclic triene by an unusual intramolecular Rh^{I}-catalysed [2 + 2 + 2]-reaction. The mechanisms of these various processes are discussed.

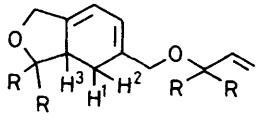
In the preceding paper[1] we described the rhodium(I)-catalysed chemospecific [2 + 2 + 2]-cycloaddition of hepta-1,6-diynes with monoynes in polar solvents, particularly alcohols, to give polysubstituted benzene derivatives. We now report studies showing how, in appropriate cases, alkenes can be incorporated into the cycloaddition process. The cobalt complex $CpCo(CO)_2$ is known to promote such reactions stoichiometrically[2] and Vollhardt has reported a number of interesting applications of this reaction,[3] including steroid syntheses.[4] We now describe our attempts to use Wilkinson's catalyst [$(Ph_3P)_3RhCl$] to achieve related co-trimerisations catalytically.

Initially we surveyed the reactions of the diyne (**1**) with a series of electronically different alkenes (**2**; R = CH_2OH, Bu, OEt, Ph, Ac, CN, and H) in ethanol or t-butanol in the presence of $(Ph_3P)_3RhCl$. No cyclohexadiene (**3**) could be detected. However, we had previously found[1] that terminal disubstitution of a 1,6-diyne supresses dimerisation and other side reactions and facilitates intermolecular cycloadditions. This prompted a study of the reaction of (**4**) with an excess of acrylonitrile (Bu^tOH, 82 °C, 6 h) in the presence of 2 mol% of Wilkinson's catalyst. The desired [2 + 2 + 2]-cycloaddition occurred to give (**5**) in 59% yield. The n.m.r. spectrum of (**5**) showed the presence of traces of double bond isomers. However, (**5**) reacted with *N*-phenylmaleimide in boiling benzene to give a 2:3 mixture of the Diels–Alder adducts (**6**) and (**7**) in 46% combined yield. The n.m.r. spectrum of (**6**) shows significantly different chemical shifts for 1-H and 2-H (δ 1.92 and 2.72) due to the anisotropy of the cyano group. A similar effect manifests itself in the ^1H n.m.r. spectrum of (**7**) where the 1-H to 4-H, in contrast to (**6**), exhibit different chemical shifts. In this latter cycloadduct *endo*-stereochemistry is assumed.

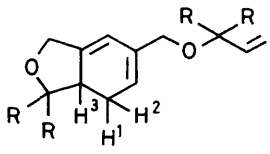




(**8**) a; X = O, R = H
b; X = O, R = Me
c; X = CH_2, R = H
d; X = NAc, R = H
e; X = S, R = H
f; X = $C(CO_2Et)_2$, R = H



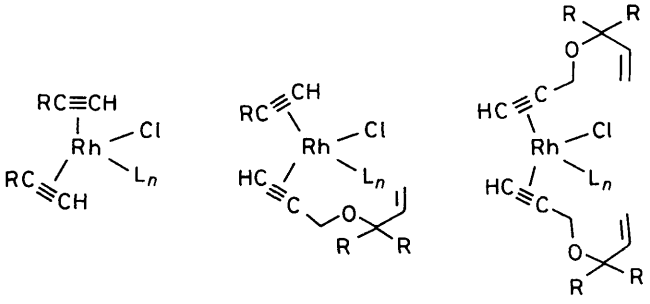
(**9**) a; R = H
b; R = Me



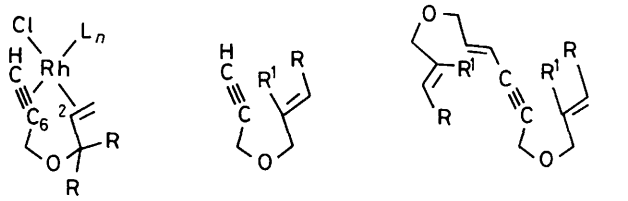
(**10**) a; R = H

It is known that rhodium exhibits metallacyclopentene as well as metallacyclopentadiene chemistry[5] and attempts were therefore made to co-trimerise (**8a**) with methyl propargyl ether, propargyl alcohol, phenyl acetylene, and pent-1-yne. In all cases no cyclohexadiene products were obtained and only 5—10% of (**8a**) was consumed even after prolonged reaction times in boiling ethanol. These observations reflect the greater stability and preponderance of diyne Rh^{I} complexes (**11**)—(**13**) (only one regioisomer is shown in each case for brevity) compared to the crucial ene-yne complex (**14**) (see later). However, when the 1,6-enyne ether (**8a**) was treated with 2 mol% $(Ph_3P)_3RhCl$ in boiling ethanol for 1 h the cyclic dimer (**9a**) was formed in 60% yield. The enyne ether (**8b**) reacted under analogous conditions, but substantially faster (20 min), to give (**9b**) (89%). This rate enhancement is a manifestation of the Thorpe–Ingold effect.[6] Two regioisomeric dimers (**9**) and (**10**) are possible from this [2 + 2 + 2]-cycloaddition process. It was clear from the

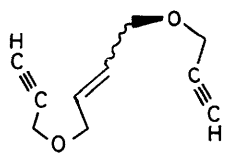
n.m.r. spectra of the products, particularly the ^{13}C n.m.r. spectra, that a small amount of another isomer (*ca.* 15%) was present in the reaction mixture. The structure of the major isomer was established by an analysis of the ^{1}H n.m.r. spectra. In particular the protons 1-, 2-, and 3-H in (**9a**) give rise to an ABX splitting pattern, whilst in (**10a**) protons 1-H and 2-H would be expected to show further coupling to 4-H. Decoupling experiments involving irradiation of 3-H result in the simplification of the signals due to 1-H and 2-H in (**9a**) to a simple AB pattern.



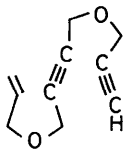
(**11**) (**12**) (**13**)



(**14**) (**15**) **a**; R = Me, R^1 = H **b**; R = H, R^1 = Me (**16**) **a**; R = Me, R^1 = H **b**; R = H, R^1 = Me



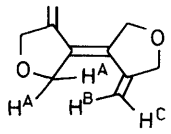
(**17**) **a**; *cis* **b**; *trans*



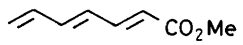
(**18**)

Attempts to extend this [2 + 2 + 2]-cyclodimerisation to (**8c**—**e**) were unsuccessful. Thus (**8c**) gave a complex mixture of products including dimers (mass spectroscopy) whilst (**8d**) gave tars and (**8c**) failed to react. Furthermore, the [2 + 2 + 2]-cyclodimerisation is suppressed by substitution on the alkene moiety. Thus (**15a**) and (**15b**) react with Wilkinson's catalyst in boiling ethanol to give the linear dimers (**16a**) and (**16b**) in 85 and 35% yield, respectively. In the latter case, the reaction is slow and the yield is based on 40% consumption of (**15b**).

Intramolecular versions of the [2 + 2 + 2]-enyne cycloaddition process were also investigated. The enediynes (**17a**) and (**17b**) failed to cyclise or to give linear dimers and were recovered unchanged from reactions in boiling ethanol. Attempts to carry out the reaction at elevated temperatures in ethylene glycol at 180 °C resulted in decomposition of the enediynes. In contrast, the enediyne (**18**) reacted in ethanol at 25 °C in the presence of 2 mol% $(Ph_3P)_3RhCl$ to give the unusual bicyclic triene (**19**) in 56% yield. Triene (**19**) is unstable and readily decomposes in chloroform solution at room temperature. The stereochemistry about the central double bond in



(**19**)



(**20**)

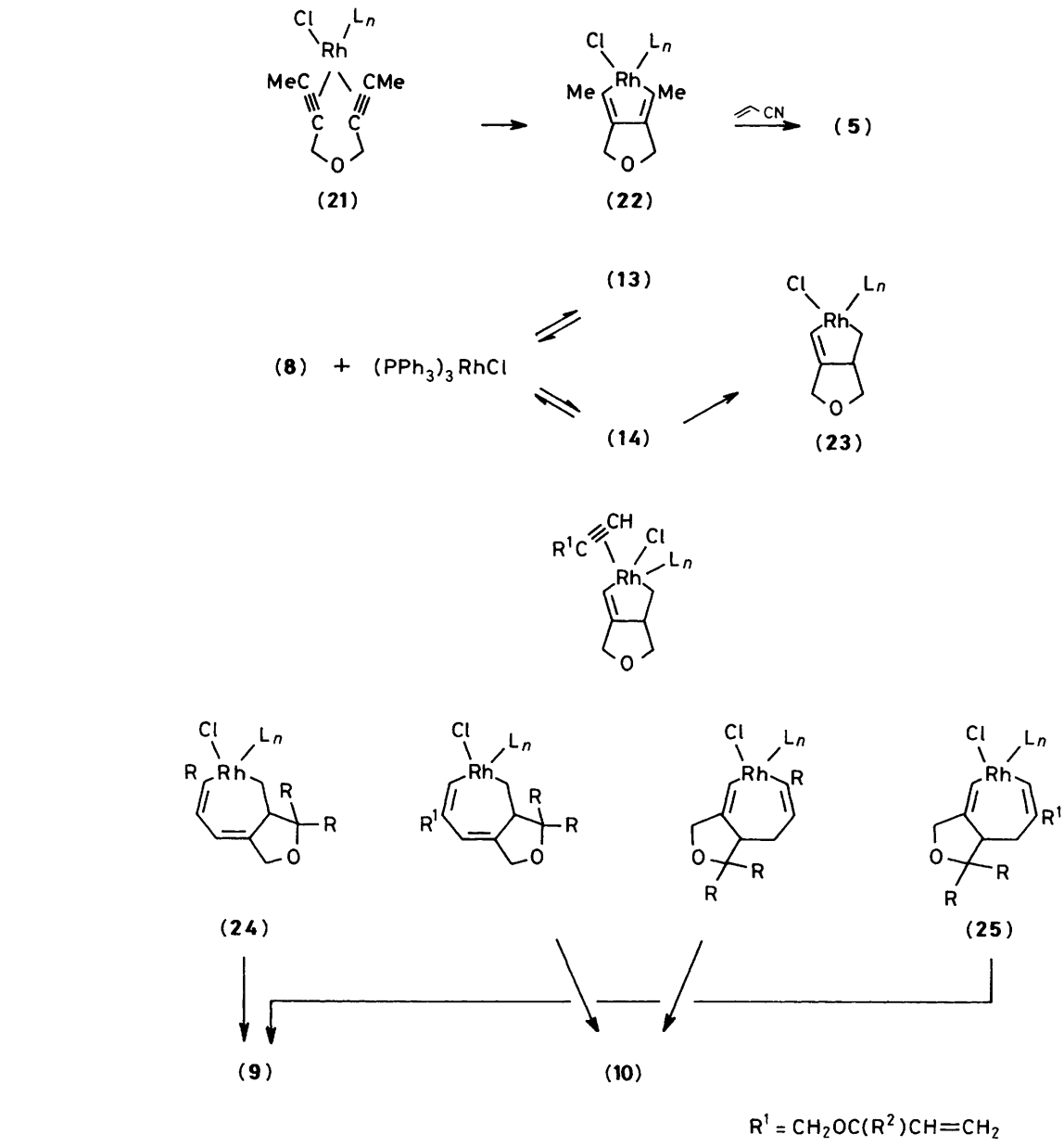
(**19**) was established by n.O.e. difference spectroscopy. Thus irradiation of the signal for H^A at δ 4.74 gives a 6.5% enhancement of the signals for H^B at δ 4.88 and no enhancement of the signal for H^C at δ 5.20. There appears to be only one report of a related reaction in which a triene is produced from two moles of an alkyne and one mole of an alkene. Thus Reppe[7] reported the reaction of acetylene with ethyl acrylate in the presence of $Ni(CO)_2(PPh_3)_2$ to give (**20**) (stereochemistry undefined).

Mechanism.—The formation of the cyclohexadiene (**5**) proceeds *via* an intermediate metallacyclopentadiene (**21**) ⟶ (**22**). This process has been fully discussed in the preceding paper. Co-ordination of acrylonitrile to the rhodium in (**22**) followed by insertion then leads to (**5**) in an analogous manner to that discussed previously.[1] On the other hand, formation of the cyclic dimers (**9a**) and (**9b**) is believed to involve rhodacyclopentene formation (**14**) ⟶ (**23**) (Scheme 1). The formation of both rhodacyclopentadienes[1,8] and rhodacyclopentenes[5] has been previously reported. Thus, as discussed previously,[1] only (**14**) is capable of conversion to a rhodacycle due to the proximity of C-2 and C-6 in the complex (**14**). Co-ordination of a further alkyne moiety to the rhodacyclopentene is then followed by insertion to give a rhodacycloheptadiene. This insertion step can involve the alkyl–rhodium bond or the vinyl–rhodium bond and in each case can occur with two different orientations of R^1 (Scheme 1) leading to four possible rhodacycloheptadienes. Reductive elimination of Rh^I then furnishes (**9**) and (**10**). The major product (**9**) thus arises either by insertion of the alkyne into the vinyl–rhodium bond with the R^1 group adjacent to rhodium (**24**) or by insertion of alkyne into the alkyl–rhodium bond with R^1 oriented away from rhodium (**25**). Reductive elimination of Rh^I from (**24**) or (**25**) then generates the product (**9**).

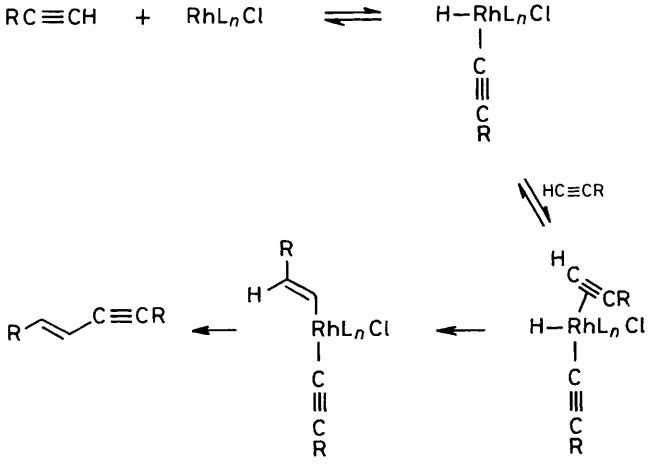
Previous work with cobaltacyclopentene complexes[9] suggests regiospecific insertion into the vinyl–rhodium σ-bond to give (**24**) is the most likely route to (**9**).

The incorporation of substituents into the alkene moiety of (**8a**) to give (**15a**) and (**15b**) results in less effective co-ordination of the terminal alkene, *i.e.* rhodacyclopentene formation is retarded or suppressed and this allows linear dimerisation to (**16**) to compete effectively. The linear dimerisation involves a rhodium hydride intermediate (Scheme 2).[10]

Finally, the formation of the triene (**19**) from the enediyne (**18**) is believed to involve a rhodacyclopentadiene intermediate (**26**) (Scheme 3). In this particular case both a rhodacyclopentene and rhodacyclopentadiene could conceivably form (Scheme 3) and both could give rise to product (**19**). However, the studies reported in this and the preceding paper clearly show the much greater reactivity of dipropargyl ether compared to allyl propargyl ether with $(Ph_3P)_3RhCl$. Insertion of the terminal alkene into the rhodacyclopentadiene (**26**) gives rise to (**27**). Note that the alternative regiochemistry for this insertion would give rise to an energetically unfavourable anti-Bredt's rule intermediate.[11] A molecular model of (**27**) shows it to be puckered with a perfect alignment between H^A and the rhodium atom for a *cis*-β-hydride elimination. This is apparently energetically preferable to reductive elimination of Rh^I from (**27**) to give the cyclohexadiene (**28**). The final reductive elimination of Rh^I



Scheme 1.



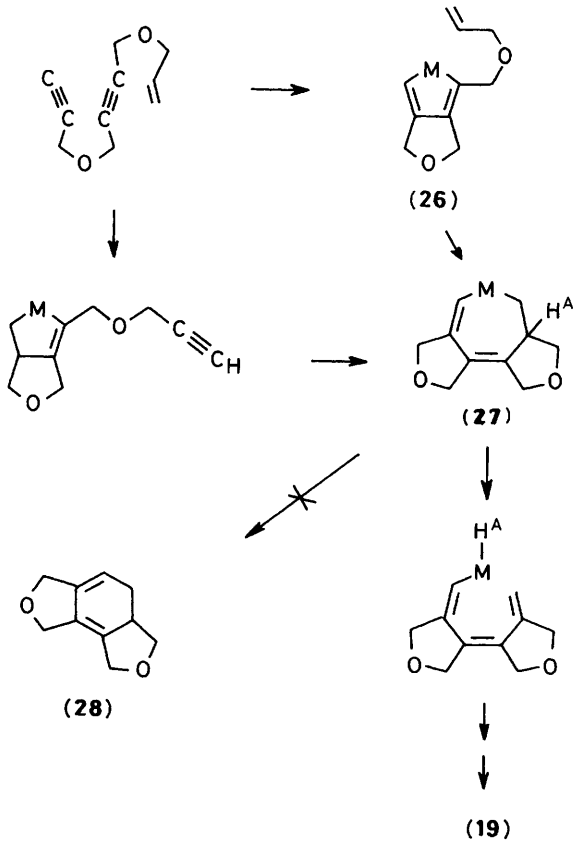
Scheme 2.

generates the *cis*-triene rather than (**19**). Thus an isomerisation step is required.

Experimental

General spectroscopic details are as noted in the preceding paper.

5-*Cyano*-4,7-*dimethyl*-1,3,5,6-*tetrahydroisobenzofuran* (**5**).—A mixture of dibut-2-ynyl ether (2.0 g, 16.4 mmol), acrylonitrile (18.0 g, 321 mmol), and tris(triphenyl phosphine)rhodium(I) chloride (305 mg, 0.33 mmol) in t-butyl alcohol (200 ml) was boiled under reflux for 6 h. Work-up followed by distillation gave the *product* (**5**) (1.7 g, 59%) as a colourless oil, b.p. 70 °C/0.01 mmHg; δ 1.75 (3 H, s, Me), 1.85 (3 H, s, Me), 2.4 (2 H, m, CH_2CH), 3.2 (1 H, m, CHCN), and 4.49 (4 H, s, CH_2O); $\nu_{max.}$ 2 920, 2 835, 2 200, 1 581, 1 050, and 905 cm^{-1}; *m/z* 175 (M^+, 100%), 160 (40), 146 (33), and 130 (29). The compound was further characterized as its Diels–Alder adduct.



Scheme 3.

Diels–Alder Adducts (**6**) *and* (**7**).—A solution of *N*-phenylmaleimide (1.1 g, 6.4 mmol) and compound (**5**) (1.06 g, 6.1 mmol) in dry benzene (30 ml) was boiled under reflux for 3 h. The solvent was then removed and the residual gum was chromatographed (silica gel) eluting with ether–light petroleum (3:7 v/v) to give (**6**) (160 mg, 7.5%) together with a mixture of (**6**) and (**7**) (805 mg, 38%). The latter mixture was further purified by preparative t.l.c. eluting with ether–light petroleum (3:7 v/v) to give pure (**7**).

Isomer (**6**). Colourless prisms, m.p. 172—175 °C (from ethanol) (Found: C, 72.35; H, 5.75; N, 8.0. $C_{21}H_{20}N_2O_3$ requires C, 72.40; H, 5.80; N, 8.05%); δ(C_6D_6) 0.85 and 1.15 (2 H, 2 × q, CH_2CHCN), 1.16 (3 H, s, Me), 1.40 (1 H, q, CHCN), 1.49 (3 H, s, Me), 1.92 and 2.72 (2 × 1 H, 2 × d, 1- and 2-H), 4.43 (4 H, m, 2 × CH_2O), and 7.14 (5 H, m, ArH); $\nu_{max.}$ 2 215 and 1 700 cm^{-1}; *m/z* 348 (M^+, 64%), 233 (62), 175 (76), and 174 (100).

Isomer (**7**). Colourless prisms, m.p. 178—180 °C (from ethanol) (Found: C, 72.4; H, 5.55; N, 7.85%); δ 1.61 (3 H, s, Me), 1.70 and 2.06 (2 × 1 H, 2 × q, CH_2CHCN), 1.80 (3 H, s, Me), 2.78 (1 H, q, CHCN), 2.81 (2 H, s, ring junction H), 4.68 and 4.86 (2 × 2 H, 2 × q, 2 × CH_2O), and 7.50 (5 H, m, ArH); $\nu_{max.}$ 2 220 and 1 701 cm^{-1}; *m/z* 348 (M^+, 19%), 175 (28), 174 (31), and 43 (100).

1,1-*Dimethylallyl Prop*-2-*ynyl Ether* (**8b**).—Prepared from sodium hydride (7.0 g, 0.15 mol), prop-2-ynyl bromide (20 g, 0.17 mol) and 2-methylbut-1-en-2-ol (13.3 g, 0.15 mol) in DMF (100 ml).[12] The *product* (5.9 g, 32%) distilled as a colourless oil, b.p. 140 °C (Found: C, 76.85; H, 9.4. $C_8H_{12}O$ requires C, 77.40; H, 9.75%); δ 1.30 (6 H, s, 2 × Me), 2.50 (1 H, t, ≡CH), 4.08 (2 H, d, CH_2O), 5.20 and 5.50 (2 × 1 H, 2 × m, C=CH_2) and 5.95 (1 H, q, C*H*=CH_2).

Cyclodimerisation of Allyl Prop-2-*ynyl Ether* (**8a**).—A solution of allyl prop-2-ynyl ether (1.0 g, 10.4 mmol) and Wilkinson's catalyst (200 mg, 0.22 mmol) in ethanol (50 ml) was boiled under reflux for 1 h. Work-up followed by distillation gave the *product* (**9a**) (600 mg, 60%) as a yellow oil, b.p. 63 °C/0.005 mmHg (Found: C, 74.7; H, 8.2. $C_{12}H_{16}O_2$ requires C, 74.95; H, 8.40%); δ(C_6D_6) 1.71 and 2.06 (2 × 1 H, 2 × q, 1- and 2-H), 2.75 (1 H, m, 3-H), 3.24 and 4.95 (2 × 1 H, 2 × q, $CHCH_2O$), 3.85 (4 H, m, 2 × CH_2O), 4.42 (2 H, AB, CH_2O), 5.07 and 5.27 (2 × 1 H, 2 × d, C=CH_2), 5.02 and 5.87 (2 × 1 H, 2 × m, =CH–CH=), 5.85 (m, 1 H, C*H*=CH_2); *m/z* 192 (M^+, 35%), 151 (20), 121 (25), and 91 (100).

Cyclodimerisation of 1,1-*Dimethylallyl Prop*-2-*ynyl Ether* (**8b**).— Prepared in an analogous manner to the above example but with a reaction time of 20 min. The *product* (**9b**) (89%) distilled as a yellow oil, b.p. 90 °C/0.001 mmHg (Found: C, 77.25; H, 9.85. $C_{16}H_{24}O_2$ requires C, 77.35; H, 9.75%); δ 1.30 (3 H, s, Me), 1.31 (6 H, s, 2 × Me), 1.35 (3 H, s, Me), 2.05 (2 H, m, CH_2C=C), 1.61 (1 H, m, 3-H), 3.38 (2 H, s, CH_2O), 4.45 (2 H, AB, CH_2O), 5.15 (2 H, m, C=CH_2), 5.71 and 5.94 (2 × 1 H, 2 × m, =CH–CH=), and 5.85 (1 H, m, C*H*=CH_2); *m/z* 248 (M^+, 11%), 121 (11), 104 (31), and 69 (100).

But-2-*enyl Prop*-2-*ynyl Ether* (**15a**).—Aqueous potassium hydroxide (4M; 126 ml) was added dropwise over 15 min to a well stirred ice-cooled mixture of prop-2-ynyl alcohol (22.4 g, 0.4 mol) and crotyl bromide (67.5 g, 0.5 mol). When the addition was complete the mixture was heated at 80 °C for 4 h, cooled, and the aqueous layer separated. The organic layer was washed with water (× 2), dried ($MgSO_4$), and distilled to afford the *product* (26.84 g, 61%) as a colourless oil, b.p. 136—138 °C (Found; C, 76.1; H, 9.25. $C_7H_{10}O$ requires C, 76.3; H, 9.15%); δ 1.70 (3 H, d, Me), 2.38 (2 H, t, CH_2O), 4.08 (2 H, d, =CCH_2O), and 5.63 (2 H, m, CH=CH); *m/z* 110 (M^+, 1%), 95 (20), 82 (20), 81 (57), 79 (20), 67 (46), 57 (19), 55 (73), and 39 (100).

Prop-2-*ynyl Methylallyl Ether* (**15b**).—Prepared in an analogous manner to the preceding experiment except that the aqueous potassium hydroxide was added in one lot at 25 °C followed by heating at 70 °C for 6 h. The *product* (40%) distilled as a colourless oil, b.p. 24—29 °C/16 mmHg (Found: C, 76.6; H, 9.5. $C_7H_{10}O$ requires C, 76.30; H, 9.15%); δ 1.77 (3 H, s, Me), 2.40 (1 H, t, ≡CH), 3.97 (2 H, s, CH_2O), 4.10 (2 H, d, CH_2O), and 4.93 (2 H, m, C=CH_2); *m/z* 109 (9%), 79 (56), and 71 (100).

5,12-*Dioxahexadeca*-2,7,14-*trien*-9-*yne* (**16a**).—A solution of but-2-enyl prop-2-ynyl ether (5.5 g, 50 mmol) and Wilkinson's catalyst (920 mg, 1 mmol) in ethanol (50 ml) was boiled under reflux for 8 h. Work-up followed by distillation gave the *product* (4.67 g, 85%) as a colourless oil, b.p. 82—84 °C/0.005 mmHg (Found: C, 76.2; H, 9.4. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%); δ 1.72 (6 H, d, 2 × Me), 3.97 (6 H, m, 3 × CH_2O), 4.25 (2 H, s, =CCH_2O), and 5.52—5.81 (6 H, m, 6 × CH=C); *m/z* 220 (M^+, 1%), 135 (14), 105 (16), 91 (19), 76 (16), 77 (14), 55 (100), 43 (10), 41 (13), and 39 (14).

2,13-*Dimethyl*-4,11-*dioxatetradeca*-1,6,13-*trien*-8-*yne* (**16b**).— A solution of 2-methylallyl prop-2-ynyl ether (5 g, 45.5 mmol) and Wilkinson's catalyst (840 mg, 0.91 mmol) in ethanol (200 ml) was boiled under reflux for 3 days at which time g.l.c. monitoring showed 60% of the starting material still remained. Work-up involved column chromatography (silica) eluting with ether–light petroleum (1:6 v/v). The *product* (700 mg, 35%) was a colourless oil for which a satisfactory microanalysis could not be obtained; δ 1.77 (6 H, s, 2 × Me), 3.86 (6 H, m, 3 × CH_2O), 4.16 (2 H, s, CH_2O), 4.93 (4 H, m, 2 × C=CH_2), and 5.46 (2 H, m, CH_2); *m/z* 219 (0.5%), 203 (1), 175 (3), 135 (13), and 55 (100).

cis-4,9-*Dioxadodeca*-6-*ene*-1,11-*diyne* (**17a**).—Using the procedure described above for but-2-enyl prop-2-ynyl ether, *cis*-but-2-ene-1,4-diol (22 g, 0.25 mol) was treated with prop-2-ynyl bromide (71. 4 g, 0.6 mol) and aqueous potassium hydroxide (4M; 128 ml). The reaction was heated at 50 °C for 20 h, when work-up and distillation afforded the *product* (19.27 g, 47%) as a colourless oil, b.p. 58—60 °C/0.2 mmHg (Found: C, 73.05; H, 7.45. $C_{10}H_{11}O_2$ requires C, 73.15; H, 7.35%); δ 2.48 (2 × 1 H, t, 2 × ≡CH), 4.10 (8 H, m, 4 × CH_2O), and 5.66 (2 H, m, CH=CH); *m/z* 164 (M^+, 0.5%), 123 (7), 108 (9), 95 (37), 91 (11), 79 (22), and 39 (100).

trans-4,9-*Dioxadodeca*-6-*ene*-1,11-*diyne* (**17b**).—This was prepared from sodium hydride (18.4 g, 0.4 mol), prop-2-ynyl alcohol (23.0 g, 0.41 mol) and *trans*-1,4-dibromobut-2-ene (40.0 g, 0.19 mol) in DMF (300 ml).[12] Work-up followed by distillation gave the *product* (16.4 g, 54%) as a colourless oil, b.p. 80—82 °C/0.3 mmHg (Found: C, 72.9; H, 7.45. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.35%); δ 4.10 (4 H, t, 2 × CH_2O), 4.20 (4 H, t, CH_2O), and 5.83 (2 H, m, CH=CH); *m/z* 164 (M^+, 0.2), 123 (4), 108 (10), 79 (46), and 39 (100).

4,9-*Dioxadodeca*-1-*ene*-6,11-*diyne* (**18**).—This was prepared from sodium hydride (3.9 g, 81 mmol), 4-oxaocta-7-en-2-yn-1-ol (10 g, 80 mmol), and prop-2-ynyl bromide (11 g, 92 mmol) in DMF (130 ml).[12] Work-up and distillation afforded the *product* (11.3 g, 86%), as a colourless oil, b.p. 68—71 °C/0.1 mmHg (Found: C, 72.8; H, 7.55. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.35%); δ 2.46 (1 H, s, ≡CH), 4.06 (2 H, d, CH_2O), 4.26 and 4.32 (2 × 2 H, 2 × s, 2 × CH_2O), and 5.22, 5.31, and 5.92 (3 × 1 H, 3 × m, CH=CH_2); *m/z* 164 (M^+, 0.3), 123 (1), 99 (22), 78 (25), and 39 (100).

Cyclisation of 4,9-*Dioxadodeca*-1-*ene*-6,11-*diyne* (**18**).—A solution of 4,9-dioxadodeca-1-ene-6,11-diyne (3.0 g, 18.3 mmol) and Wilkinson's catalyst (300 mg, 0.3 mmol) in ethanol (200 ml) was stirred at room temperature for 3 h. The solution was then concentrated under reduced pressure without the application of heat causing the *product* (1.68 g, 56%) to crystallise as colourless needles, m.p. 90 °C (decomp.). The product is unstable and decomposes on attempted recrystallisation (Found: C, 73.35; H, 7.4. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.35%); δ 4.50 (4 H, t, *J* 2.2 Hz, 2 × CH_2O), 4.74 (4 H, s, 2 × CH_2O), 4.88 (2 H, t, *J* 2.2 Hz, 2 × C=CH), and 5.20 (2 H, t, *J* 1.8 Hz, 2 × C=CH); *m/z* 164 (M^+, 100%), 149 (13), 136 (36), 105 (41), 91 (72), and 77 (39).

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