Rhodium-catalysed [2 + 2 + 2]-Cycloadditions of Acetylenes

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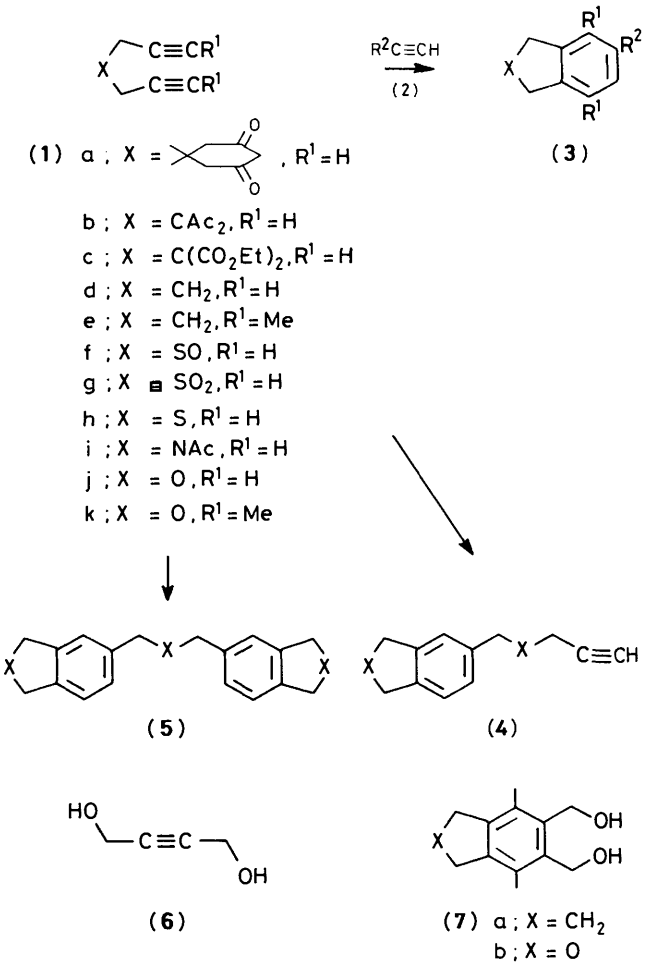
Wilkinson's catalyst [$(PPh_3)_3RhCl$] (0.5—2 mol%) catalyses the chemospecific [2 + 2 + 2]-cycloaddition of hepta-1,6-diynes with monoynes to give polysubstituted benzene derivatives in moderate to good yield. The reaction is favoured by polar solvents such as ethanol and occurs at 0—78 °C. Several examples of intramolecular [2 + 2 + 2]-cycloadditions of triynes are described and a mechanism that accounts for the chemospecificity and observed variations in rates of reaction is discussed.

Regio- and stereo-specific C–C bond formation and chemo-specific processes are essential prerequisites of modern synthetic organic chemistry. Reactions in which two or more C–C bonds are formed regio- and stereo-specifically are especially valuable in this context because of the greater increase in molecular complexity that results.[2] The wide synthetic application of the [4 + 2]-Diels–Alder[3] and [3 + 2]-1,3-dipolar cycloaddition[4] reactions attests to this, particularly in their intramolecular variants. In principle still greater versatility resides in symmetry-allowed thermal [2 + 2 + 2]-cycloadditions[5] but entropic factors mitigate against such processes and literature examples are rare. However, use of a transition metal as a catalyst or as a stoichiometric reagent enables the entropic constraints to be circumvented by co-ordination to the metal ion. Thus metal-catalysed trimerisation of acetylenes to benzene derivatives, though devoid of stereochemistry, is well known and can be achieved with many transition metals (*e.g.* Ni, Pd, Co, Cr, Fe) as well as Ziegler-type catalysts.[6] This trimerisation has been modified to incorporate nitriles.[7] Vollhardt has recently reviewed his elegant contribution to $CpCo(CO)_2$-mediated [2 + 2 + 2]-cycloadditions[8] which have proved especially valuable in the synthesis of steroids and alkaloids.

In contrast to cobalt, rhodium complexes generally react with acetylenes to give linear dimers,[9] although Muller[10] reported stoichiometric two-step trimerisations proceeding through isolable rhodacyclopentadiene intermediates, and diphenylacetylene is reported to be cyclotrimerised by CpRhCOD.[11] We now report the facile rhodium(I)-catalysed [2 + 2 + 2]-cycloaddition of hepta-1,6-diynes (**1a**—**i**) to monoynes (**2**) to give benzene derivatives (**3**).

The reaction (**1**) + (**2**) ⟶ (**3**) shows good chemoselectivity with no detectable cyclotrimerisation of the monoacetylene (**2**) and usually none, or only minor amounts, of the dimer (**4**) and/or trimer (**5**) arising from the diyne (**1**). These side reactions are often effectively suppressed by adding an excess of the monoyne. No linear dimers of (**2**) are observed in these reactions except in the case where R^2 = Ph where small amounts of linear dimer are formed. The cyclotrimerisation of the monoyne (**2**) is a major shortcoming of other catalyst systems.[12] The formation of (**3**) is catalysed by 0.5—2 mol% of Wilkinson's catalyst [$(Ph_3P)_3RhCl$] and occurs in a range of solvents (Bu^{t}OH, THF, EtOH, EtOH–$CHCl_3$) at 0—78 °C. The reaction can be used to synthesise both substituted indanes (Table 1) from (**1**; X = CR_2), and the heterocyclic analogues (Table 2) from (**1**; X = O, S, SO, SO_2, or NR). Thus hepta-1,6-diyne (**1d**) and propargyl alcohol react in ethanol at room temperature over 1.5 h in the presence of 1 mol% of $(Ph_3P)_3RhCl$ to give (**3d**; R^2 = CH_2OH) in 87% yield (Table 1). The reaction tolerates wide variation in X (Tables 1 and 2) and in R^2 in the monoyne (**2**) (Tables 1 and 2). Solutions of acetylene gas, propargyl alcohol, and pent-1-yne give good yields of benzene derivatives (**3**) whilst phenyl



acetylene, trimethylsilyl acetylene, and isopropylacetylene are poor substrates. Yields of (**3**) with phenyl acetylene as the precursor monoyne can be increased by employing a 7-mol excess of the monoyne (Table 1). The low yields in the aforementioned cases arises because of competing dimerisation and trimerisation of the 1,6-diyne to (**4**) and (**5**), respectively. The reaction of the disubstituted acetylene (**6**) with the 1,6-diynes (**1**; R^1 = H) was unsuccessful, the only products were (**4**) and (**5**). The diyne (**1a**) gives rise to an interesting range of spirocyclic products usually in good to excellent yield (Table 1). The 1,5-diyne [**2**; R^2 = $(CH_2)_2C{\equiv}CH$] participates moderately well as a monoyne component in cycloadditions with (**1a**) and (**1d**) (Table 1), and (**1d**) gives a 1:3 mixture of dimer (**4**; X =

Table 1. Reaction of 1,6-diynes (**1a**—**e**) with (**2**) in ethanol to give indanes (**3**)

Diyne	Monoyne R^2 (mol)	Catalyst (mol%)	Temp. (°C)	Time (h)	Product (%)
(**1a**)	H (s)	2	40	1	79
(**1a**)	CH_2OH (4)	1	70	5	64
(**1a**)	CH_2OMe (4)	2	78	24	61
(**1a**)	CH_2OAc (4)	0.5	70	6	70
(**1a**)	CH_2CH_2OH (4)	1	70	1	73
(**1a**)	Pr (4)	1	40	4	65
(**1a**)	$(CH_2)_2C{\equiv}CH$ (2)	1	40	2	59
(**1a**)	Ph (8)	1	60	6	55
(**1a**)	Me_3Si (4)	1	80	20	3
(**1b**)	H (s)	0.5	40	1	60
(**1b**)	CH_2OH (1.3)	0.5	78	1	36
(**1b**)	Pr (4)	1	25	3	75
(**1b**)	Ph (3)	0.5	78	1	15
(**1c**)	CH_2OH (2)	2	25	1.5	64
(**1d**)	CH_2OH (2)	1	25	1.5	87
(**1d**)	Bu (2)	1	60	2	57
(**1d**)	Ph (2)	1	40	1.5	20
(**1d**)	$(CH_2)_2C{\equiv}CH$ (4)	1	78	8	40
(**1d**)	$(CH_2)_3C{\equiv}CH$	1	50	0.75	23[a] and 75[b]
(**1e**)	CH_2OH (2)	2	78	20	56
(**1e**)	[c] (5)	5	78	17	99

[a] Yield of dimer (**4**; X = CH_2). [b] Yield of trimer (**5**; X = CH_2). [c] Monoyne (**6**), product (**7a**). (s) = saturated solution.

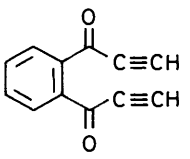
Table 2. Reaction of 1,6-diynes (**1f**—**k**) with monoynes (**2**) in ethanol to give heterocycles (**3f**—**k**)

Diyne	Monoyne R^2 (mol)	Catalyst (mol%)	Temp. (°C)	Time (h)	Product (%)
(**1f**)	CH_2OH (4)	1	50	6	52
(**1f**)	Ph (10)	1	25	5.5	58
(**1g**)	CH_2OH (4)	2	78	0.16	66
(**1g**)	H (s)	2	25	1	66
(**1g**)	Ph (8)	1	55	1.5	41
(**1g**)	Pr (8)	1	55	6	42
(**1g**)	Me_3Si (5)	1	25	48	5
(**1g**)	$CMe{=}CH_2$ (10)	1	25	1.5	30
(**1h**)	H (s)	1	25	11	5
(**1i**)	CH_2OH (4)	1	78	3.5	76
(**1j**)	H (s)	0.5	25	2	42
(**1j**)	CH_2OH (5)	0.5	0	5	44
(**1j**)	Pr (3)	0.5	0	4	58
(**1j**)	Ph (2)	0.5	0	2	11
(**1j**)	$CH_2OCH_2C{\equiv}CH$	0.5	25	0.16	66[a]
(**1k**)	CH_2OH (1.1)	2	83[b]	2	72
(**1k**)	Pr (1.5)	2	83[b]	2	47
(**1k**)	[c] (4)	2	83[b]	0.75	56

[a] Product (**4**; X = 0). [b] Solvent Bu^{t}OH. [c] Monoyne (**6**), product (**7b**). (s) = saturated solution.

CH_2) and trimer (**5**; X = CH_2) in the absence of monoyne. 1,6-Diynes (**1**) in which the central atom X is a heteroatom also undergo Rh^I-catalysed cycloaddition to monoynes (Table 2). Although dipropargyl sulphide (**1h**) gives a very poor yield (5%) of (**3h**; R^2 = H) with acetylene as the monoyne the corresponding sulphoxide (**1f**) and sulphone (**1g**) proved to be better substrates and give reasonable yields of (**3**; X = SO or SO_2). The low yield in the case of (**1h**) may result from catalyst poisoning by the sulphur atom since only 40% of the diyne reacted. Dipropargylamine (**1**; X = NH) did not undergo cyclotrimerisation with (**2**): under a range of conditions only polymeric material was obtained. However, the *N*-acetyl derivative (**1i**) reacts with propargyl alcohol to give a good yield (76%) of (**3i**; R^2 = CH_2OH) (Table 2). Dipropargyl ether (**1j**) proved to be the most reactive, 1,6-diyne studied. Its cycloaddition reactions to monoynes (**2**) were typically carried out at 0 °C using 0.5 mol% $(Rh_3P)_3RhCl$ (Table 2). However, (**1j**) showed a strong tendency to dimerise and trimerise to (**4**; X = 0) and (**5**; X = 0) and yields of (**3**; X = 0) were thus only moderate (Table 2). Indeed, in the absence of the monoyne (**2**), (**1j**) gives (**4**; X = 0) in 66% yield after 10 min at room temperature using 0.5 mol% of $(Ph_3P)_3RhCl$.

Attempted cycloaddition of (**1c**) with either acetonitrile or benzonitrile failed to yield any pyridine derivatives (**8**) and the nitrile (**9**) also failed to react with propargyl alcohol in the presence of Wilkinson's catalyst. A range of other 1,ω-diynes in place of (**1**) was surveyed to ascertain the potential of the reaction for formation of other ring systems. Reactions of (**10a**, **b**), (**11**), and (**12**) with propargyl alcohol gave either starting material or tarry products. No cyclic products were detected. The origin of the chemospecificity of the reaction thus stems from the fact that only 1,6-diynes can function as the diyne precursor and the key reactive intermediate involves rhodium and the 1,6-diyne since monoynes are not catalytically trimerised by Wilkinson's catalyst, at least under our conditions.



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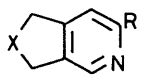

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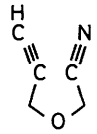

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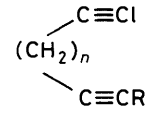
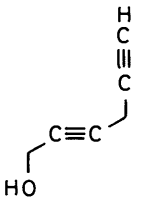


(10) a; $n = 2$, R = H
b; $n = 4$, R = H
c; $n = 4$, R = Me

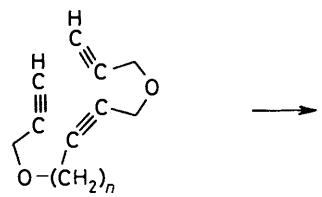


(12)

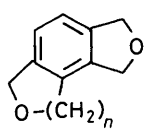
The terminally disubstituted 1,6-diynes (**1e**) and (**1k**) participate in the cycloaddition reaction with monoynes (**2**) and (**6**) (Table 1, last two entries) (Table 2, last three entries). Dibut-2-ynyl ether (**1k**) is much more reactive than (**1e**) but both react with but-2-yne-1,4-diol (**6**) to give (**7b**) and (**7a**), respectively. One interesting aspect of these reactions is that (**1k**) reacts faster with but-2-yne-1,4-diol than with propargyl alcohol.

Two intramolecular examples of the [2 + 2 + 2]-cycloaddition have been studied. Thus (**13a**) cyclises to (**14a**) (74%) when allowed to stand at room temperature for 3 h in the presence of 2 mol% of $(Ph_3P)_3RhCl$ whilst (**13b**) requires heating in boiling ethanol for 3 days to effect cyclisation to (**14b**) (38%).

Mechanism.—Rhodacyclopentadienes are believed to be the key intermediates in the rhodium(I)-catalysed cycloaddition of 1,6-diynes to monoynes. The suggested intervention of such an intermediate is based on Muller's isolation of (**16**) from the reaction of (**15**) with $(Ph_3P)_3RhCl$[10] in a non-polar solvent (benzene). He further showed that (**16**) reacted stoichiometrically with a further molecule of diphenylacetylene to give (**17**). Related cobaltocyclopentadiene complexes are well known.[13–15] These observations and the specificity of the catalytic cyclisation for 1,6-diynes lead us to suggest the mechanism shown in the Scheme.

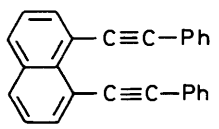


(13) a; $n = 1$
b; $n = 2$



(14)

Rh^I is initially considered to form a series of complexes (**18**)—(**20**) each containing two co-ordinated acetylene moieties. For brevity only single regioisomers of these and subsequent complexes are shown. Only complex (**18**) progresses further to the bicyclic Rh^{III} rhodacyclopentadiene (**21**) by oxidative addition–cyclisation. The failure of (**19**) and (**20**) to produce an analogous rhodacycle and the contrasting high reactivity of dipropargyl ether (**1j**) compared with hepta-1,6-diyne (**1d**) results from the favourable geometry of 1,6-diynes, and (**1j**) in particular, for metallacycle formation. Thus the C–X bond



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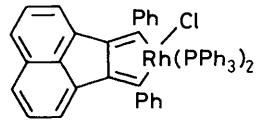

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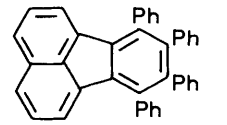


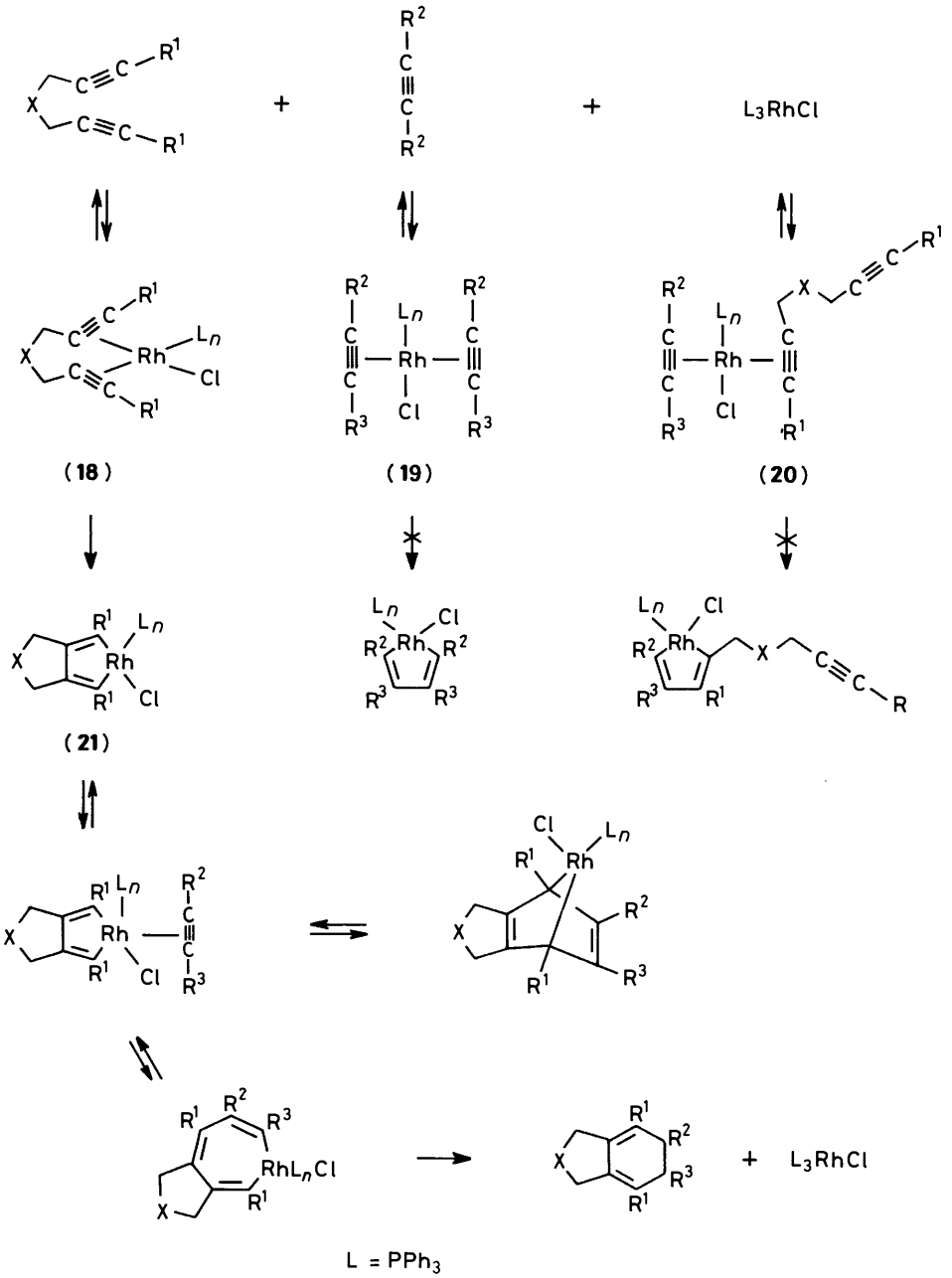
(17)

length (C–O) in (**1j**) is shorter than the C–X bond length (C–C) in (**1d**) and the C–X–C bond angle in (**1j**) is smaller than that in (**1d**). The net result of these geometrical factors is that the two centres, C(2) and C(6) in structure (**22**) involved in C–C bond formation at the rhodacyclopentadiene stage are brought within favourable bonding distance on complexation to Rh(I) in 1,6-diynes but especially so in the case of (**1j**). The failure of (**10a**) and (**12**) to cyclise with monoynes is thus due to the strain inherent in the corresponding intermediate bicyclic rhodacyclopentadienes (3/5 and 4/5 fused rings). Both (**11**) and (**10b**) also have unfavourable geometry for initial rhodacyclopentadiene formation with the two alkyne carbon centres involved in C–C bond formation too far apart. This is due to the sp^2 carbon linking chain in the diyne (**11**) and to the longer bridge in (**10b**), *i.e.* (**23**), compared with (**18**) (Scheme). It is interesting that the smaller cobalt atom in $CpCo(PPh_3)_2$ is capable of cobaltacyclopentadiene formation with (**10c**) to give (**24**).[14]

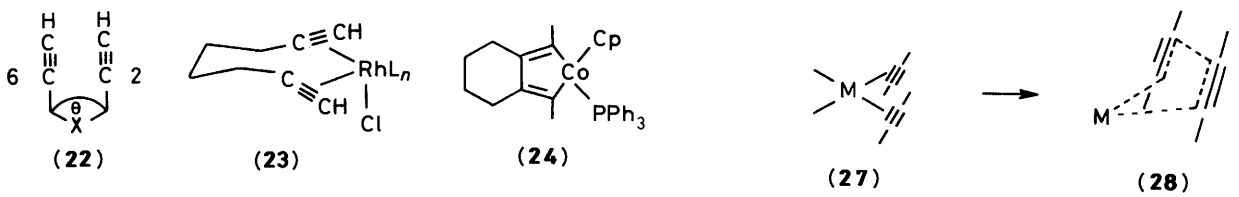
If a terminally disubstituted 1,6-diyne such as (**1e**) or (**1k**) is allowed to react with a monoyne (**2**) then (**2**) is expected to co-ordinate preferentially to Rh^I resulting in concentrations of the intermediate diyne-complexes being in the order (**19**; R^3 = H) ≫ (**18**; R^1 = Me) ≃ (**20**; R^1 = Me, R^3 = H). Only (**18**) can lead to products and if the equilibration of the diyne complexes (**18**)—(**20**) is slow this will result in slow product formation from (**18**; R^1 = Me). However, if a disubstituted monoyne such as (**6**) reacts with a terminally disubstituted 1,6-diyne (**1e**) or (**1k**) then (**18**) will compete much more favourably with (**19**) and (**20**) and will probably be the favoured species (chelate effect). This analysis accounts for the observation that (**1e**) and (**1k**) react faster with (**6**) than with (**2**; $R^2 = CH_2OH$). A similar effect accounts for the much faster and cleaner cyclisation of (**13a**) compared to (**13b**). Thus (**13b**) gives rise to two π-complexes (**25**) and (**26**) but only (**25**) can lead on to product (**14b**). If the equilibration of (**25**) and (**26**) is slow compared to the rhodacyclopentadiene forming step then formation of (**14b**) will be retarded as observed.

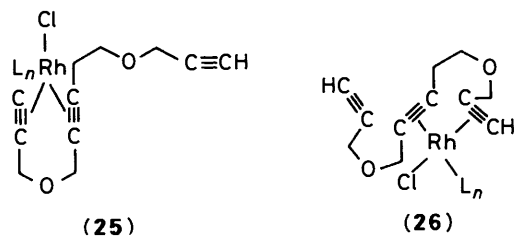
The later stages of the [2 + 2 + 2]-cycloaddition involve addition of the monoyne to (**21**) and might involve either a 'Diels–Alder type' reaction generating a bridged ring intermediate or insertion of the monoyne into the rhodacyclopentadiene. We have no evidence pertaining to the later stages but literature precedent favours a rhodacycloheptatriene intermediate. Finally, reductive elimination of Rh^I completes the catalytic cycle.

The catalytic reactions described in this paper do not proceed in benzene but require a polar solvent (EtOH, THF, Bu^tOH). The need for a polar solvent suggests that loss of chloride ion from one of the intermediates in the catalytic cycle (Scheme)



Scheme.





may promote one of the steps. The chemospecificity observed with Rh^{I} contrasts with Co^{I} which forms cobaltacyclopentadienes with monoynes and (**10c**). These differences are due to the larger ionic radius of Rh^{I} compared to Co^{I} such that the tilting of the termini of the acetylenic ligands[15] in the intermediate diacetylene complex (**27**) ⟶ (**28**) is energetically unfavourable for Rh^{I} presumably due to reduction in M-alkene π-bonding. The steric effects of this tilting motion control the regio-

selectivity in Co processes such that the acetylene carbon atom bearing the more bulky substituent becomes the α-carbon atom in the metallacycle.[15]

Experimental

N.m.r. spectra were recorded on JEOL 60 MHz and Bruker 90 and 250 MHz instruments for deuteriochloroform solutions using tetramethylsilane as an internal standard except where otherwise stated. Mass spectra were recorded on an AEI MS902 machine operating at 70 eV. Infrared spectra were recorded with a Perkin-Elmer 475 spectrometer and refer to potassium bromide discs. Gas liquid chromatography was performed on a Perkin-Elmer F11 machine using 15% Carbowax 20M (4 m), 2.5% SGR (2 m), or 5% SGR (4 m) columns. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected.

The diynes (**1b**), (**1c**), (**1e**)—(**1k**), (**10c**), (**11**), and (**12**) and the nitrile (**9**) were prepared by literature procedures. The diynes (**1d**), (**10a**), and (**10b**) were supplied by Eastman Kodak.

2,2-*Diprop*-2-*ynyldimedone** (**1a**).—A mixture of dimedone (100 g, 0.71 mol), prop-2-ynyl bromide (178 g, 1.50 mol) and anhydrous potassium carbonate (207 g, 1.50 mol) in acetone (2 l) was vigorously stirred and boiled under reflux for 20 h. The mixture was then filtered and the solid was washed with acetone. The combined filtrate and washings were evaporated to leave a thick oil which was dissolved in a little ether and set aside at 0 °C for 3 days during which time colourless prisms of the *product* (100 g, 65%) separated, m.p. 83—84 °C (Found: C, 77.4; H, 7.6; $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.45%); δ 1.06 (6 H, s, Me) 2.66 (4 H, s, CH_2CO), 2.64 (4 H, d, $CH_2C{=}$), and 2.05 (2 H, t, ≡CH); $\nu_{max.}$ 1 722 and 1 692 cm^{-1}; *m/z* 216 (M^+, 8%), 215 (5), 177 (14), 132 (15), 131 (6), 118 (4), 89 (17), 84 (6), 83 (100), and 79 (6).

4,9-*Dioxadodeca*-1,6,11-*triyne* (**13a**).—Potassium hydroxide (20.7 g, 0.37 mol) in water (15 ml) was added to a solution of but-2-yne-1,4-diol (13.3 g, 0.15 mol) in dimethyl sulphoxide (50 ml) and the resulting solution was stirred at room temperature for 15 min and then cooled to 0 °C in an ice bath. Propargyl bromide (45 g, 0.37 mol) in dimethyl sulphoxide (20 ml) was then added dropwise with stirring over 30 min. The mixture was then heated at 70 °C for 4 h. Work-up followed by distillation gave the *product* (13 g, 53%) as a colourless oil, b.p. 78—81 °C/1.0 mmHg (Found: C, 73.75; H, 6.35. $C_{10}H_{10}O_2$ requires C, 74.05; H, 6.20%); δ 2.50 (2 H, t, ≡CH), 4.23 (4 H, d, CH_2O), and 4.3 (4 H, s, CH_2CH_2O); $\nu_{max.}$ 2 112 cm^{-1}; *m/z* 162 (M^+, 3%), 103 (25), 77 (32), and 39 (100).

4,10-*Dioxatrideca*-1,6,12-*triyne* (**13b**).—Pent-2-yne-1,5-diol (6 g, 0.06 mol)[16] was dissolved in dry DMF (50 ml) and a 50% dispersion of sodium hydride in oil (6.91 g, 0.144 mol) added in portions. When evolution of hydrogen had ceased the mixture was cooled in an ice bath to 0 °C and prop-2-ynyl bromide (17.13 g, 0.144 mol) was added dropwise. The mixture was then allowed to warm to room temperature and stirring was continued for a further 12 h when water (100 ml) was added and the mixture extracted with ether (4 × 50 ml). The ether extracts were combined and washed with water (4 × 100 ml), dried ($MgSO_4$), and evaporated. Distillation of the residue afforded the *product* (8.92 g, 84%) as a colourless oil, b.p. 82—84 °C/0.01 mmHg (Found: C, 75.25; H, 7.1. $C_{11}H_{12}O_2$ requires C, 74.95; H, 6.85%); δ 2.55 (2 H, t, ≡CH), 3.80 (2 H, t, 8-H_2), and 4.35 (m, 8 H, CH_2O); $\nu_{max.}$ 2 100 cm^{-1}; *m/z* 176 (M^+, 1%), 117 (22), 115 (44), 109 (10), 108 (17), 107 (63), 103 (11), 91 (70), 90 (15), 81 (23), 79 (71), 78 (30), 77 (64), 69 (49), 67 (16), 66 (12), 65 (24), 55 (14), 53 (29), 52 (35), 51 (24), 50 (10), 41 (37), and 39 (100).

Cyclisation of 1,6-*Diynes with Monoynes.—General Procedure.* A solution of the diyne (**1**) and monoyne (**2**) in absolute ethanol was degassed by bubbling nitrogen through the solution for 10 min. Wilkinson's catalyst was then added and the resulting clear red solution was stirred at the appropriate temperature until all the diyne had been consumed (g.l.c., n.m.r., or t.l.c. monitoring as appropriate). The solvent was then removed and the residue was filtered through a short alumina or silica column eluting with ether or methylene chloride to remove the catalyst. The eluant was then evaporated to dryness and the residue crystallised or distilled as noted below.

Diprop-2-*ynyl dimedone* (**1a**). (*a*) *With acetylene.* A solution of diprop-2-ynyldimedone (1.08 g, 5 mmol) and tristriphenylphosphinerhodium(I) chloride (90 mg, 0.1 mmol) in ethanol (100 ml) was warmed to 40 °C for 1 h with continuous saturation of the solution with bubbling acetylene gas. Work-up and crystallisation from methylene chloride afforded the *product* (**3**; X = 4,4-dimethyl-2,6-cyclohexyl, $R^1 = R^2 = H$) (960 mg, 79%) as colourless rods, m.p. 176—177 °C (Found: C, 79.4; H, 7.55. $C_{16}H_{18}O_2$ requires C, 79.30; H, 7.50%); δ 1.03 (6 H, s, 2 × Me) 2.68 (4 H, s, 2 × CH_2CO), 3.45 (4 H, s, 2 × CH_2), and 7.14 (4 H, s, ArH); $\nu_{max.}$ 1 720 and 1 689 cm^{-1}; *m/z* 242 (M^+, 13%), 224 (7), 214 (8), 159 (12), 158 (100), 116 (25), 115 (42), 55 (10), 41 (10), and 39 (8).

(*b*) *With prop*-2-*ynyl alcohol.* A solution of diprop-2-ynyldimedone (2.16 g, 10 mmol), prop-2-ynyl alcohol (2.24 g, 40 mmol), and $(Ph_3P)_3RhCl$ (90 mg, 0.1 mmol) in ethanol (150 ml) was heated at 70 °C for 5 h. Work-up and crystallisation from ether–acetone gave the *product* (**3**; X = 4,4-dimethyl-2,6-dioxocyclohexyl, $R^1 = H$, $R^2 = CH_2OH$) (1.75 g, 64%) as colourless cubes, m.p. 158—159 °C (Found: C, 75.0; H, 7.45. $C_{17}H_{20}O_3$ requires C, 74.95; H, 7.40%); δ 1.00 (6 H, s, 2 × Me), 1.90 (1 H, br s, OH), 2.66 (4 H, s, 2 × CH_2CO), 3.40 (4 H, s, 2 × CH_2), 4.56 (2 H, s, CH_2O), and 7.10 (3 H, s, ArH); $\nu_{max.}$ 3 400, 1 720, and 1 687 cm^{-1}; *m/z* 272 (M^+, 22%), 254 (15), 244 (12), 213 (11), 189 (13), 188 (100), 158 (13), 128 (11), 116 (11), and 115 (18).

(*c*) *With methyl prop*-2-*ynyl ether.* A solution of diprop-2-ynyldimedone (1.08 g, 5 mmol), methyl prop-2-ynyl ether (1.04 g, 20 mmol), and $(Ph_3P)RhCl$ (90 mg, 0.1 mmol) in ethanol (100 ml) was boiled under reflux for 24 h. Work-up and crystallisation from ether gave the *product* (**3**; X = 4,4-dimethyl-2,6-dioxo-cyclohexyl, $R^1 = H$, $R^2 = CH_2OMe$) as colourless plates, m.p. 113—115 °C (Found: C, 75.3; H, 7.75. $C_{18}H_{22}O_3$ requires C, 75.50; H, 7.75%); δ 1.02 (6 H, s, 2 × Me), 2.65 (4 H, s, 2 × CH_2CO), 3.32 (3 H, s, OMe), 3.41 (4 H, s, 2 × CH_2), 4.33 (2 H, s, CH_2O), and 7.03 (3 H, s, ArH); $\nu_{max.}$ 1 720 and 1 688 cm^{-1}; *m/z* 286 (M^+, 19%), 268 (13), 258 (15), 213 (11), 203 (15), 202 (100), 171 (19), 129 (14), 128 (23), and 45 (16).

(*d*) *With prop*-2-*ynyl acetate.* A solution of diprop-2-ynyldimedone (1.08 g, 5 mmol), prop-2-ynyl acetate (1.96 g, 20 mmol), and $(Ph_3P)_3RhCl$ (45 mg, 0.05 mmol) in ethanol (100 ml) was heated at 70 °C for 6 h. Work-up and crystallisation from ether gave the *product* (**3**; X = 4,4-dimethyl-2,6-dioxo-cyclohexyl, $R^1 = H$, $R^2 = CH_2OAc$) (1.10 g, 70%) as colourless cubes, m.p. 123—124 °C (Found: C, 72.5; H, 6.85. $C_{19}H_{22}O_4$ requires C, 72.60; H, 7.05%); δ 1.00 (6 H, s, 2 × Me), 2.05 (3 H, s, Me), 2.65 (4 H, s, 2 × CH_2CO), 3.42 (4 H, s, 2 × CH_2), 5.00 (2 H, s, CH_2O), and 7.08 (3 H, s, ArH); $\nu_{max.}$ 1 722 and 1 685 cm^{-1}; *m/z* 314 (M^+, 2%), 255 (17), 254 (69), 213 (15), 230 (100), 226 (37), 188 (12), 171 (13), 170 (16), 129 (11), 128 (34), 83 (18), and 43 (21).

(*e*) *With but*-3-*yn*-1-*ol.* A solution of diprop-2-ynyldimedone (1.08 g, 5 mmol), but-3-yn-1-ol (1.40 g, 20 mmol), and

* Dimedone = 5,5-dimethylcyclohexane-1,3-dione.

$(Rh_3P)_3RhCl$ (45 mg, 0.05 mmol) in ethanol (100 ml) was heated at 70 °C for 1 h. Work-up and crystallisation from ether gave the *product* (**3**; X = 4,4-dimethyl-2,6-dioxocyclohexyl, R^1 = H, R^2 = CH_2CH_2OH) (1.04 g, 73%) as colourless needles, m.p. 141—142 °C (Found: C, 75.35; H, 7.75. $C_{18}H_{22}O_3$ requires C, 75.5; H, 7.75%); δ 1.00 (6 H, s, 2 × Me), 1.68 (1 H, br s, OH), 2.63 (4 H, s, 2 × CH_2CO), 2.72 (2 H, t, CH_2CH_2OH), 3.35 (4 H, s, 2 × CH_2), 3.72 (2 H, br t, CH_2O), and 6.95 (3 H, s, ArH); $\nu_{max.}$ 3 280, 1 720, and 1 685 cm^{-1}; *m/z* 285 (M^+, 28%), 268 (12), 258 (19), 213 (12), 203 (15), 202 (100), 171 (40), 129 (16), 128 (18), and 83 (11).

(*f*) *With pent-1-yne.* A solution of diprop-2-ynyldimedone (2.16 g, 10 mmol), pent-1-yne (2.72 g, 40 mmol), and $(Ph_3P)_3RhCl$ (90 mg, 0.1 mmol) in ethanol (150 ml) was heated at 40 °C for 4 h. Work up and crystallisation from ether-acetone gave the *product* (**3**; X = 4,4-dimethyl-2,6-dioxocyclohexyl, R^1 = H, R^2 = Pr) as colourless cubes, m.p. 120—122 °C (Found: C, 80.0; H, 8.35. $C_{19}H_{24}O_2$ requires C, 80.25; H, 8.50%); δ_H 1.03 (9 H, m, 3 × Me), 1.69 (2 H, m, CH_2), 2.50 (2 H, t, CH_2), 2.68 (4 H, s, 2 × CH_2CO), 3.41 (4 H, s, 2 × CH_2), and 6.96 (3 H, s, ArH); $\nu_{max.}$ 1 720 and 1 690 cm^{-1}; *m/z* 284 (M^+, 29%), 266 (9), 256 (17), 213 (14), 201 (16), 200 (100), 171 (24), 129 (14), and 128 (13).

(*g*) *With hexa-1,5-diyne.* A solution of diprop-2-ynyldimedone (2.16 g, 10 mmol), hexa-1,5-diyne (1.56 g, 20 mmol), and $(PPh_3)_3RhCl$ (90 mg, 0.1 mmol) in ethanol (150 ml) was heated at 40 °C for 2 h. Work-up and crystallisation from ether–acetone gave the *product* [**3**; X = 4,4-dimethyl-2,6-dioxocyclohexyl, R^1 = H, R^2 = $(CH_2)_2C{\equiv}CH$] (1.74 g, 59%) as colourless rods, m.p. 110—112 °C (Found: C, 81.65; H, 7.55. $C_{20}H_{22}O_2$ requires C, 81.60; H, 7.55%); δ 1.01 (6 H, s, 2 × Me), 1.93 (1 H, t, ≡CH), 2.59 (m, 4 H, $(CH_2)_2C{\equiv}C$), 2.66 (4 H, s, 2 × CH_2CO), 3.40 (4 H, s, 2 × CH_2), and 7.00 (3 H, s, ArH); $\nu_{max.}$ 2 100, 1 720, and 1 686 cm^{-1}; *m/z* 294 (M^+, 41%), 276 (23), 266 (34), 227 (11), 211 (16), 210 (100), 195 (11), 172 (10), 171 (80), 153 (10), 129 (19), 128 (24), 83 (39), and 55 (11).

(*h*) *With phenylacetylene.* A solution of diprop-2-ynyldimedone (2.16 g, 10 mmol), phenylacetylene (8.16 g, 80 mmol), and $(Ph_3P)_3RhCl$ (90 mg, 0.1 mmol) in ethanol (150 ml) was heated at 60 °C for 6 h. Work-up and crystallization from ether–hexane gave the *product* (**3**; X = 4,4-dimethy-2,6-dioxocyclohexyl, R^1 = H, R^2 = Ph) (1.75 g, 55%) as colourless rods, m.p. 156—157 °C (Found: C, 83.0; H, 6.95. $C_{22}H_{22}O_2$ requires C, 83.0; H, 6.95%); δ 1.01 (6 H, s, 2 × Me), 2.67 (4 H, s, 2 × CH_2CO), 3.48 (4 H, s, 2 × $ArCH_2$), and 7.16—7.63 (8 H, m, ArH); $\nu_{max.}$ 1 720 and 1 688 cm^{-1}; *m/z* 318 (M^+, 38%), 290 (18), 235 (18), 234 (100), 192 (15), and 191 (15).

(*i*) *With trimethylsilylacetylene.* A solution of diprop-2-ynyldimedone (1.08 g, 5 mmol), trimethylsilylacetylene (1.96 g, 20 mmol), and $(Ph_3P)_3RhCl$ (40 mg, 0.05 mmol) in ethanol (100 ml) was heated at 80 °C for 20 h. Work-up and repeated (× 3) crystallisation from ether–acetone gave the *product* (**3**; X = 4,4-dimethyl-2,6-dioxocyclohexyl, R^1 = H, R^2 = $SiMe_3$) (50 mg, 3%) as colourless plates, m.p. 145—147 °C (Found: C, 70.85; H, 8.15. $C_{19}H_{26}O_2Si$ requires C, 72.55; H, 8.35%); δ 0.23 (9 H, s, $SiMe_3$), 1.03 and 1.5 (2 × 3 H, 2 × s, 2 × Me), 2.71 (4 H, s, 2 × CH_2CO), 3.47 (4 H, s, 2 × $ArCH_2$), 7.20 (1 H, d, ArH), 7.30 (1 H, s, ArH), and 7.35 (1 H, d, ArH); $\nu_{max.}$ 1 718 and 1 684 cm^{-1}; *m/z* 324 (M^+, 22%), 300 (12), 299 (45), 296 (16), 286 (21), 231 (21), 230 (100), 216 (11), 215 (49), 213 (16), 173 (11), and 73 (16).

Diprop-2-ynylacetylacetone (**1b**). (*a*) *With acetylene.* The *product* (**3**; X = CAc_2, R^1 = H, R^2 = H) (60%) crystallised from light petroleum (b.p. 40—60 °C) as colourless prisms, m.p. 58—60 °C (Found: C, 77.45; H, 7.15. $C_{13}H_{14}O_2$ requires C, 77.20; H, 7.00%); δ 2.10 (6 H, s, 2 × Me), 3.12 (4 H, s, $ArCH_2$), and 7.1 (4 H, s, ArH); $\nu_{max.}$ 1 690 cm^{-1}; *m/z* 160 (12%), 159 (M^+ − 43, 100), and 43 (57).

(*b*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = CAc_2, R^1 = H, R^2 = CH_2OH) (36%) crystallised from light petroleum (b.p. 40—60 °C as colourless rods, m.p. 54 °C (Found: C, 72.35; H, 7.05. $C_{14}H_{14}O_3$ requires C, 72.40; H, 6.95%); δ 2.23 (6 H, s, 2 × Me), 3.53 (4 H, s, $ArCH_2$), 4.66 (2 H, s, CH_2O), and 7.20 (3 H, s, ArH); $\nu_{max.}$ 3 470 and 1 685 cm^{-1}; *m/z* 232 (M^+, 0.5%), 190 (13), 189 (100), and 43 (37).

(*c*) *With pent-1-yne.* The *product* (**3**; X = CAc_2, R^1 = H, R^2 = Pr) (75%) distilled as a colourless oil, b.p. 90—92 °C/0.1 mmHg (Found: C, 78.7; H, 8.35. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%); δ 0.9 (3 H, t, CH_2Me) 1.62 (2 H, m, CH_2Me), 2.16 (6 H, s, 2 × Me), 2.51 (2 H, t, $ArCH_2Et$), 3.5 (4 H, s, 2 × CH_2), and 6.99 (3 H, m, ArH); *m/z* 244 (M^+, 2%), 202 (70), 201 (100), 158 (55), and 87 (38).

(*d*) *With phenylacetylene.* The *product* (**3**; X = CAc_2, R^1 = H, R^2 = Ph) (15%) crystallised from methanol as colourless plates, m.p. 89—90 °C (Found: C, 82.15; H, 6.6. $C_{19}H_{18}O_2$ requires C, 82.00; H, 6.50%); δ 2.20 (6 H, s, 2 × Me), 3.53 (4 H, s, $ArCH_2$), and 7.3 (8 H, m, ArH); $\nu_{max.}$ 1 687 cm^{-1}; *m/z* 278 (M^+, 2%), 235 (100), 192 (7), and 43 (57).

Cyclisation of diethyl 2,2-diprop-2-ynylmalonate (**1c**) *with propargyl alcohol.* The *product* [**3**; X = $C(CO_2Et)_2$, R^1 = H, R^2 = CH_2OH] (64%) was isolated as a colourless oil by column chromatography (SiO_2) eluting with ether–methylene chloride (Found: C, 65.25; H, 7.0. $C_{16}H_{20}O_5$ requires C, 65.75; H, 6.90%); δ 1.20 (6 H, t, 2 × CH_2Me), 3.25 (1 H, br s, OH), 3.5 (4 H, s, 2 × CH_2), 4.11 (4 H, q, 2 × CH_2Me), 4.46 (2 H, s, CH_2O), and 7.02 (3 H, s, ArH); $\nu_{max.}$ 3 450 and 1 725 cm^{-1}; *m/z* 292 (M^+, 38%), 247 (9), 220 (6), 219 (40), 218 (100), 191 (18), 173 (10), 145 (19), 129 (16), 128 (16), 117 (18), 116 (18), and 115 (23).

Cyclisation of hepta-1,6-diyne. (*a*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = CH_2, R^1 = H, R^2 = CH_2OH) (87%) crystallised [light petroleum (b.p. 40—60 °C)–ether] as colourless needles, m.p. 71—72 °C (Found: C, 81.0; H, 8.15. $C_{10}H_{12}O$ requires C, 81.05; H, 8.15%); δ 1.85 (1 H, br s, OH), 2.13 (2 H, q, CH_2), 2.88 (4 H, t, $ArCH_2$), 4.56 (2 H, s, CH_2O), and 7.08 (3 H, m, ArH); $\nu_{max.}$ 3 320 cm^{-1}; *m/z* 148 (M^+, 100%), 147 (33), 131 (25), 130 (54), 129 (21), 120 (44), 119 (50), 117 (93), 116 (24), 115 (59), 92 (19), 91 (85), and 77 (14).

(*b*) *With hex-1-yne.* The *product* (**3**; X = CH_2, R^1 = H, R^2 = Bu), prepared (57%) by the general procedure, distilled as a colourless oil, b.p. 86—88 °C/2 mmHg (Found: C, 89.55; H, 10.5. $C_{13}H_{18}$ requires C, 89.60; H, 10.40%); δ 0.93 (3 H, t, CH_2Me), 1.65 (4 H, m, CH_2CH_2Me), 2.01 (2 H, q, CH_2), 2.57 (2 H, t, $ArCH_2$), 2.87 (4 H, t, $ArCH_2$), and 7.05 (3 H, m, ArH); *m/z* 174 (M^+, 43%), 132 (36), 131 (100), 124 (9), 128 (8), 117 (18), 115 (13), and 91 (10).

(*c*) *With phenylacetylene.* The *product* (**3**; X = CH_2, R^1 = H, R^2 = Ph) (20%) crystallised from ether as colourless rods, m.p. 75—76 °C (Found: C, 92.95; H, 7.25. $C_{15}H_{14}$ requires C, 92.75; H, 7.25%); δ 2.11 (2 H, q, CH_2), 2.95 (4 H, q, $ArCH_2$), and 7.38 (8 H, m, ArH); *m/z* 194 (M^+, 100%), 193 (30), 179 (13), 178 (31), 165 (18), 117 (19), 115 (12), and 32 (13).

(*d*) *With hex-1,5-diyne.* The *product* [**3**; X = CH_2, R^1 = H, R^2 = $(CH_2)_2C{\equiv}CH$] (40%) distilled as a colourless oil, b.p. 56—58 °C/0.01 mmHg (Found: C, 91.7; H, 8.2. $C_{13}H_{14}$ requires C, 91.70; H, 8.30%); δ 1.97 (1 H, t, ≡CH), 2.05 (2 H, q, CH_2), 2.45 (2 H, m, $CH_2C{=}$), 2.87 (6 H, m, $ArCH_2$), 6.89 (1 H, d, ArH), 7.09 (1 H, s, ArH) and 7.15 (1 H, d, ArH); $\nu_{max.}$ 2 102 cm^{-1}; *m/z* 170 (M^+, 18), 132 (12), 131 (100), 129 (8), 128 (8), 116 (10), 115 (13), and 91 (12).

(*e*) *With hepta-1,6-diyne.* The *product* (**4**; X = CH_2) (23%) distilled as a colourless oil, b.p. 58—59 °C/0.01 mmHg (Found: C, 91.35; H, 8.80. $C_{14}H_{16}$ requires C, 91.25; H, 8.75%); δ 1.82 (2 H, q, CH_2), 1.97 (1 H, t, ≡CH), 2.50 (2 H, q, CH_2), 2.19 (2 H, m, $CH_2C{\equiv}$), 2.69 (2 H, t, $ArCH_2$), 2.87 (4 H, t, $ArCH_2$), 6.96 (1 H, d, ArH), 7.06 (1 H, s, ArH), and 7.13 (1 H, d, ArH); $\nu_{max.}$ 2 120 cm^{-1}; *m/z* 184 (M^+, 74%), 183 (28), 169 (47), 156 (40), 155 (32), 145 (16), 144 (57), 143 (24), 141 (45), 132 (23), 131 (100), 129 (50), 128 (42), 117 (54), 116 (38), 115 (46), 91 (38), and 77 (25).

The residue from the first distillation was transferred to a molecular distillation apparatus and afforded a fraction b.p. 160—165 °C/0.001 mmHg which solidified to give colourless needles of the trimer (**5**; X = CH_2), m.p. 39—41 °C (lit.,[17] m.p. 41—43 °C).

Cyclisation of diprop-2-ynyl sulphoxide. (*a*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = SO, R^1 = H, R^2 = CH_2OH) (52%) crystallised from chloroform as colourless cubes, m.p. 112—113 °C (Found: C, 59.25; H, 5.6; S, 17.5. $C_9H_{10}SO_2$ requires C, 59.30; H, 5.55; S, 17.60%); δ 3.30 (1 H, br s, OH), 4.12 (4 H, br s, 2 × CH_2SO), 4.50 (2 H, s, CH_2O), and 7.20 (3 H, s, ArH); *m/z* 182 (M^+, 81%), 135 (19), 134 (100), 133 (15), 105 (52), 103 (10), 91 (34), and 77 (15).

(*b*) *With phenylacetylene.* The *product* (**3**; X = SO, R^1 = H, R^2 = Ph) (58%) crystallised from methylene chloride as pale yellow rods. Further purification by sublimation gave colourless rods, m.p. 136—138 °C (Found: C, 73.75; H, 5.4; S, 14.2. $C_{14}H_{12}SO$ requires C, 73.65; H, 5.30; S, 14.05%); δ 4.12 (4 H, br s, 2 × CH_2SO) and 7.15—7.55 (8 H, m, ArH); *m/z* 228 (M^+, 39%), 211 (10), 210 (10), 181 (15), 180 (100), 179 (14), 178 (15), 165 (15), and 89 (10).

Cyclisation of diprop-2-ynyl sulphone. (*a*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = SO_2, R^1 = H, R^2 = CH_2OH) (66%) crystallised from water as colourless needles, m.p. 97—98 °C (Found C, 54.25; H, 5.15; S, 16.0. $C_9H_{10}SO_3$ requires C, 54.55; H, 5.10; S, 16.15%); δ (CD_3CN) 3.16 (1 H, br s, OH), 4.10 (4 H, s, 2 × CH_2SO_2), 4.35 (2 H, s, CH_2), and 7.06 (3 H, s, ArH); *m/z* 198 (M^+, 11), 135 (11), 134 (100), 105 (32), 91 (16), and 77 (9).

(*b*) *With acetylene.* The *product* (**3**; X = SO_2, R^1 = R^2 = H) (66%) crystallised from methylene chloride as colourless needles, m.p. 152—153 °C (lit.,[18] m.p. 150—151 °C).

(*c*) *With phenylacetylene.* A solid which precipitated during the reaction was removed by filtration and appeared (i.r. and m.s.) to be the trimer (**5**; X = SO_2). The filtrate was evaporated to dryness and triturated with benzene to remove the insoluble dimer (**4**; X = SO_2). The benzene solution was chromatographed (SiO_2) eluting with benzene. The first fraction afforded the linear dimer of phenylacetylene, m.p. 95—97 °C, followed by the *product* (**3**; X = SO_2, R^1 = H, R^2 = Ph) (41%) which crystallised from methylene chloride as colourless needles, m.p. 193—194 °C (Found: C, 68.95; H, 4.95; S, 13.1. $C_{14}H_{12}SO_2$ requires C, 68.85; H, 4.95; S, 13.10%); δ 4.38 (4 H, s, CH_2) and 7.42 (8 H, m, ArH); *m/z* 244 (M^+, 24%), 181 (16), 180 (100), 179 (13), 178 (16), 165 (14), 152 (5), 89 (7), and 76 (6).

(*d*) *With pent-1-yne.* The *product* (**3**; X = SO_2, R^1 = H, R^2 = Pr) (42%) crystallised from ether as colourless needles, m.p. 78—79 °C (Found: C, 62.6; H, 6.6; S, 15.35. $C_{11}H_{14}SO_2$ requires C, 62.85; H, 6.70; S, 15.25%); δ 0.90 (3 H, t, CH_2Me), 1.56 (2 H, m, CH_2Me), 2.57 (2 H, t, $ArCH_2$), 4.25 (4 H, s, 2 × CH_2SO_2) and 7.10 (3 H, s, ArH); *m/z* 210 (M^+, 14), 147 (13), 146 (100), 117 (47), 115 (19), and 91 (15).

(*e*) *With trimethylsilylacetylene.* The *product* (**3**; X = SO_2, R^1 = H, R^2 = $SiMe_3$) (5%) was obtained by sublimation at 120—130 °C/0.001 mmHg as a colourless solid, m.p. 94—96 °C (Found: C, 55.15; H, 6.75; S, 13.05. $C_{11}H_{16}O_2SSi$ requires C, 54.95; H, 6.70: S, 13.35%); δ 0.27 (9 H, s, $SiMe_3$), 4.38 (4 H, s, 2 × CH_2SO_2), 7.33 (1 H, d, ArH), 7.48 (1 H, s, ArH), and 7.55 (1 H, d, ArH); *m/z* 240 (M^+, 22%), 226 (26), 225 (81), 177 (17), 176 (90), 162 (16), 161 (100), and 80 (14).

(*f*) *With isopropenylacetylene.* The *product* (**3**; X = SO_2, R^1 = H, R^2 = CMe=CH_2) (30%) crystallised from methylene chloride as colourless needles, m.p. 130—132 °C (Found: C, 63.7; H, 6.0; S. 15.55. $C_{11}H_{12}SO_2$ requires C, 63.45; H, 5.80; S, 15.4%); δ 2.14 (3 H, s, Me), 4.34 (4 H, s, 2 × CH_2SO_2), 5.14 and 5.36 (2 × 1 H, 2 × br s, C=CH_2), and 7.30 (3 H, m, ArH); *m/z* 208 (M^+, 18%), 145 (13), 144 (100), 129 (25), 128 (22), 115 (13), 104 (7), and 77 (9).

Cyclisation of diprop-2-ynyl sulphide. With acetylene. The *product* (**3**; X = S, R^1 = R^2 = H) (5%) was obtained as a colourless oil, b.p. 50—55 °C/1 mmHg (lit.,[18] b.p. 62—72 °/2 mmHg).

Cyclisation of N,N-*diprop-2-ynylacetamide. With prop-2-ynyl alcohol.* The *product* (**3**; X = NCOMe, R^1 = H, R^2 = CH_2OH) (76%) crystallised from methylene chloride as colourless rods, m.p. 136—137 °C (Found: C, 68.55; H, 6.55; N, 7.15. $C_{11}H_{13}NO_2$ requires C, 69.10; H, 6.85 N, 7.35%); δ 2.13 (3 H, s, Me), 2.75 (1 H, br s, OH), 4.68 (6 H, s, 2 × CH_2N and CH_2O), and 7.25 (3 H, s, ArH); $\nu_{max.}$ 3 370 cm^{-1}; *m/z* 191 (M^+, 100%) 176 (20), 174 (42), 149 (41), 148 (81), 130 (29), 118 (64), 117 (34), 91 (34), and 43 (56).

Cyclisation of diprop-2-ynyl ether. (*a*) *With acetylene.* The *product* (**3**; X = O, R^1 = R^2 = H) (42%) distilled as a colourless oil, b.p. 56 °C/16 mmHg (lit.,[19] b.p. 105 °C/50 mmHg).

(*b*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = O, R^1 = H, R^2 = CH_2OH) (44%) crystallised as colourless needles from light petroleum (b.p. 40—60 °C)–ether, m.p. 70—71 °C (Found: C, 71.8; H, 6.65. $C_9H_{10}O_2$ requires C, 72.0; H, 6.70%); δ 2.40 (1 H, br s, OH), 4.67 (2 H, s, CH_2OH), 5.07 (4 H, s, 2 × CH_2O), and 7.20 (3 H, s, ArH); $\nu_{max.}$ 3 400 cm^{-1}; *m/z* 150 (M^+, 35%), 149 (24), 121 (17), 104 (40), and 91 (47).

(*c*) *With pent-1-yne.* The *product* (**3**; X = O, R^1 = H, R^2 = Pr) (58%) was isolated as a colourless oil by chromatography (SiO_2) eluting with 4:1 v/v light petroleum (b.p. 40—60 °C)–ether (Found: C, 80.45; H, 9.35. $C_{11}H_{14}O$ requires C, 81.45; H, 8.70%); δ 0.94 (3 H, t, CH_2Me), 1.62 (2 H, m, CH_2Me), 2.61 (2 H, t, $ArCH_2$), 5.08 (4 H, s, 2 × $ArCH_2O$), and 7.10 (3 H, s, ArH); *m/z* 162 (M^+, 100%), 134 (40), 133 (72), 105 (71), and 91 (87).

(*d*) *With phenylacetylene.* The *product* (**3**; X = O, R^1 = H, R^2 = Ph) (11%) crystallised from light petroleum (b.p. 40—60 °C)–ether as colourless rods, m.p. 82—83 °C (Found: C, 85.7; H, 6.2. $C_{14}H_{12}O$ requires C, 85.65; H, 6.15%); δ 5.17 (4 H, s, 2 × CH_2), and 7.50 (8 H, m, ArH); *m/z* 196 (M^+, 44%), 195 (18), 168 (21), 167 (31), and 104 (100).

(*e*) *Dimerisation.* The *product* (66%) was isolated as a colourless oil, b.p. 80—83 °C/0.1 mmHg, which solidified on standing, m.p. 60—61 °C (Found: C, 76.45; H, 6.3. $C_{12}H_{12}O_2$ requires C, 76.55; H, 6.45%); δ 2.53 (1 H, t, ≡CH), 4.20 (2 H, d, CH_2C≡), 4.63 (2 H, s, CH_2O), 5.17 (4 H, s, CH_2O), and 7.21 (3 H, s, ArH); *m/z* 188 (M^+, 44%), 187 (31), 158 (36), 150 (29), 149 (30), 47 (24), 119 (36), 105 (36), 104 (100), and 91 (83).

Cyclisation of nona-2,7-diyne. (*a*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = CH_2, R^1 = Me, R^2 = CH_2OH) (56%; 76% based on recovered diyne) crystallised from ether as colourless rods m.p. 85—86 °C (Found: C, 81.75; H, 9.1. $C_{12}H_{16}O$ requires C, 81.75; H, 9.15%); δ 1.59 (1 H, br s, OH), 2.08 (2 H, q, CH_2), 2.23 and 2.26 (2 × 3 H, 2 × s, ArMe), 2.86 (4 H, q, $ArCH_2$), 4.66 (2 H, s, CH_2O), and 6.97 (1 H, s, ArH); $\nu_{max.}$ 3 350 cm^{-1}; *m/z* 176 (M^+, 83%), 161 (37), 159 (25), 158 (100), 147 (22), 145 (42), 143 (18), 133 (22), and 91 (11).

(*b*) *With but-2-yne-1,4-diol.* The *product* (**7a**) (99%) crystallised from chloroform as colourless needles, m.p. 151—152 °C (Found: C, 75.75; H, 8.8. $C_{13}H_{18}O_2$ requires C, 75.70; H, 8.80%); δ 2.07 (2 H, q, CH_2), 2.50 (2 H, br s, OH), 2.32 (6 H, s, ArMe), 2.91 (4 H, t, $ArCH_2$), and 4.82 (4 H, s, CH_2O); *m/z* 206 (M^+, 40), 189 (16), 188 (100), 187 (86), 173 (14), 160 (19), 159 (74), 147 (12), 145 (48), 144 (13), 129 (22), 128 (21), 119 (16), and 115 (18).

Cyclisation of dibut-2-ynyl ether. (*a*) *With prop-2-ynyl alcohol.* The *product* (**3**; X = O, R^1 = Me, R^2 = CH_2OH) (72%) crystallised from benzene as colourless rods, m.p. 70—71 °C (Found: C, 73.6; H, 8.1. $C_{11}H_{14}O_2$ requires C, 74.15; H, 7.90%); δ 1.9 (1 H, br s, OH), 2.1 (6 H, s, ArMe), 4.6 (2 H, s, CH_2OH), 5.0 (4 H, s, CH_2O), and 7.0 (1 H, s, ArH); *m/z* 178 (M^+, 77%), 177 (52), 163 (26), 132 (62), 131 (36), and 119 (100).

(*b*) *With pent-1-yne.* The *product* (**3**; X = O, R^1 = Me, R^2 = Pr) (47%) distilled as a colourless liquid, b.p. 64—66 °C/0.5 mmHg (Found: C, 82.05; H, 9.6. $C_{13}H_{18}O$ requires C, 82.05; H, 9.55%); δ 0.98 (3 H, t, CH_2Me), 1.59 (2 H, m, CH_2Me), 2.10 (6 H, s, ArMe), 2.55 (2 H, t, $ArCH_2$), 5.09 (4 H, s, CH_2O), and 6.85 (1 H, s, ArH); *m/z* 190 (M^+, 94%), 189 (74), 175 (30), 162 (68), 133 (99), 119 (100), and 91 (40).

(*c*) *With but-2-ynl-1,4-diol.* The *product* (**7b**) (56%) crystallised from chloroform as colourless prisms, m.p. 158—160 °C (Found: C, 69.35; H, 7.9. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.75%); δ [$(CD_3)_2SO$] 2.18 (6 H, s, ArMe), 4.56 (4 H, d, ArC*H*OH), 4.74 (2 H, t, OH), and 5.01 (4 H, s, CH_2O); *m/z* 208 (M^+, 35%), 207 (13), 190 (97), 175 (25), 161 (70), and 133 (100).

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