Base-catalysed Intramolecular Cycloadditions of Allyl 3-Phenylprop-2-ynyl Ethers and 4-Methylpent-4-en-2-ynyl Prop-2-ynyl Ethers [1]

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The base-catalysed intramolecular cycloadditions of allyl 3-phenylprop-2-ynyl ethers (VIa and b) leading to tetrahydronaphtho[2,3-*c*]furans [(X) and (XI)] is rationalised in terms of (*a*) a base-catalysed isomerisation of the acetylenic group to an allene, (*b*) $[_{\pi}4 + _{\pi}2]$ cycloaddition of the allyl group to the phenylallene, and (*c*) hydrogen shifts (Scheme 2). The base-catalysed intramolecular cycloaddition of 4-methylpent-4-en-2-ynyl prop-2-ynyl ether (VIIa) proceeds in an analogous manner *via* either mono- or bis-allenic intermediates (Scheme 3).

THE base-catalysed intramolecular cycloadditions of allyl-3-phenylprop-2-ynylammonium ions [*e.g.* (I)] have been recently investigated.[2] These reactions take place under mild conditions and involve the following sequence: (i) base-catalysed isomerisation of the acetylenic to an allenic grouping[3] [(I) $\longrightarrow$ (II)], (ii) intramolecular Diels–Alder $[_{\pi}4 + _{\pi}2]$ cycloaddition of the allyl group to the phenylallene [(II) $\longrightarrow$ (III)], and (iii) aromatisation by hydrogen shift giving the salt (IV). A competing pathway in protic solvents is a [3,3] sigmatropic rearrangement of the intermediate allene[4] (II) leading after hydrolysis of the intermediate iminium salt to the aldehyde (V). We now report on the base-catalysed isomerisation of allyl 3-phenylprop-2-ynyl ethers (VIa—d) and 4-methylpent-4-en-2-ynyl prop-2-ynyl ethers (VIIa and b). The results provide good evidence for the intermediacy of allenes in these reactions and lead to novel synthetic routes to isobenzofuran and naphthofuran systems under relatively mild conditions from readily available starting materials.

The ethers (VIa—d), (VIIa and b), (VIIIa and b), and (XIXa—d) were prepared from the sodium salt of 3-phenylprop-2-yn-1-ol or 4-methylpent-4-en-2-yn-1-ol by alkylation with the appropriate allyl or propynyl halide in tetrahydrofuran solution. The ethers were characterised by their n.m.r. and mass spectra.

The ethers were isomerised by using an excess of potassium t-butoxide in t-butyl alcohol at temperatures up to 60°. Thus, the bis-acetylenic ether (VIIIa) at room temperature was transformed into the dihydronaphthofuran (IXb) (77%). The base-catalysed isomerisation of the ether (VIa) proceeded at 55° giving the tetrahydronaphthofurans (Xa) (55%) and (XI) (28%). The structural relationship between these two compounds was established by catalytic hydrogenation: uptake of 1 mol. equiv. of hydrogen in each case yielded the same ether (XII), presumably containing a *cis*-fused ring junction. The constitution of the product (XI) was deduced from its simple n.m.r. spectrum, which showed three singlets at τ 2·77, 5·30, and 6·59 in the ratio 1 : 1 : 1 as expected for the symmetrical structure (XI). The n.m.r. spectrum of isomer (Xa) was much more complex and the coupling constants were determined after addition of the lanthanide shift reagent Eu(fod)$_3$.[5] The complex overlapping ABX and ABMXY systems could then be analysed in a

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[1] Preliminary communication, A. J. Bartlett, T. Laird, and W. D. Ollis, *J.C.S. Chem. Comm.*, 1974, 496.

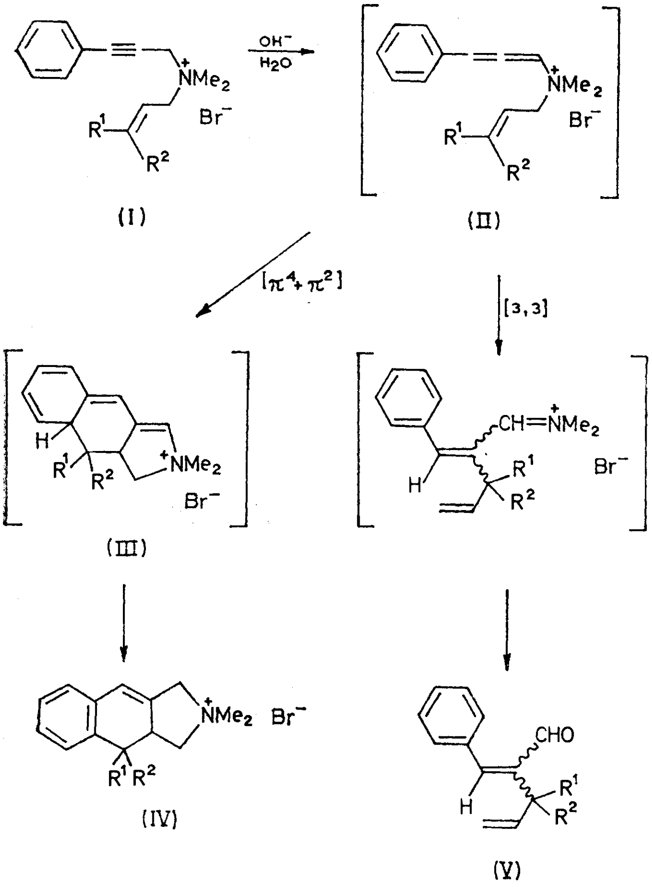
[2] T. Laird and W. D. Ollis, *J.C.S. Chem. Comm.*, 1972, 557.

[3] R. J. Bushby, *Quart. Rev.*, 1970, **24**, 585.

[4] For other examples of [3,3] rearrangements involving allenes, see L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, 1965, **87**, 4506; H. M. Frey and D. M. Lister, *J. Chem. Soc.* (*A*), 1967, 26; H. M. Frey and A. M. Lamont, *ibid.*, 1969, 1592; P. Gilgen, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 681; J. A. Deyrup and M. Betkouski, *Tetrahedron Letters*, 1973, 1131.

[5] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.

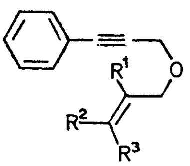
first-order approximation (see Experimental section). Of particular interest is the high vicinal coupling constant (J_{MY} 15 Hz) of H_M and H_Y of the dihydronaphthalene ring. This is easily understood by examination of a Dreiding model of the molecule, which shows that a *trans*-diaxial relation exists between H_M and H_Y (see Figure). The u.v. spectra of isomers (Xa) and (XI) are in agreement with the assigned constitutions. These isomers are stable under the reaction conditions and no interconversion was detected.



Scheme 1

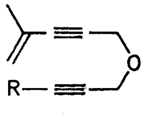
Similarly, the ether (VIb) was transformed into the tetrahydronaphthofuran (Xb) (52%) and the dihydronaphthofuran (IXa) (30%). The major product was identified as the isomer (Xb) rather than the alternative (Xc) on the basis of its n.m.r. spectrum, which, when expanded after addition of $Eu(fod)_3$,[5] showed an ABMXY system having similar coupling constants and chemical shifts to the isomer (Xa). This required that the phenyl substituent was present in a styrenoid residue. The dihydronaphthofuran (IXa) was identified by comparison with an authentic sample, prepared by base-catalysed isomerisation of the ether (VIIIb);[6] it presumably arises by atmospheric oxidation of the tetrahydronaphthofuran (Xb).

Base-catalysed isomerisations of the ethers (VIc and d) were also examined but the products were complex mixtures which we could not separate.

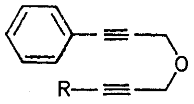


(VI)

a; $R^1=H$, $R^2=H$, $R^3=H$
b; $R^1=H$, $R^2=Ph$, $R^3=H$
c; $R^1=Me$, $R^2=H$, $R^3=H$
d; $R^1=H$, $R^2=Me$, $R^3=Me$



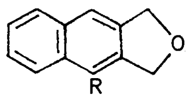
(VII)



(VIII)

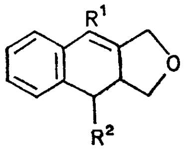
a; R = H
b; R = Ph

The reactions (VIa) → (Xa) + (XI) and (VIb) → (Xb) + (IXa) are best rationalised (see Scheme 2) by a mechanism involving base-catalysed isomerisation of the acetylenic ethers (VIa and b) to allenes, followed by



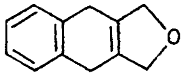
(IX)

a; R = Ph
b; R = H
c; R = CH_2:CMe

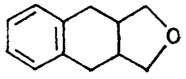


(X)

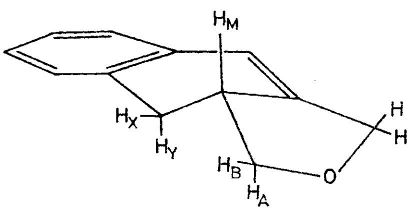
a; $R^1=R^2=H$
b; $R^1=Ph$, $R^2=H$
c; $R^1=H$, $R^2=Ph$



(XI)



(XII)



Figure

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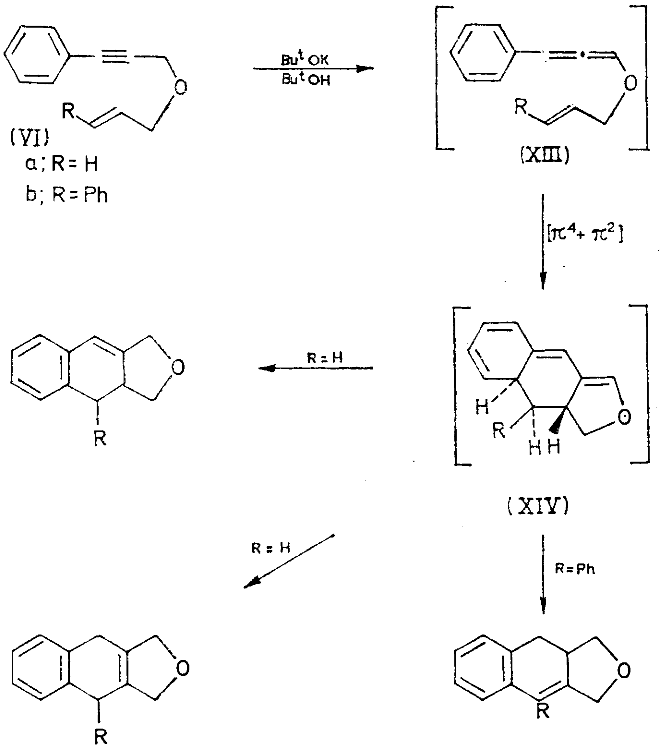
[6] I. Iwai and J. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 1094.

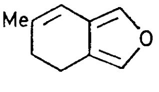
an intramolecular $[_{\pi}4 + _{\pi}2]$ cycloaddition.[7-16] This sequence is analogous to that already postulated [1,2] for the isomerisation of the ammonium ions (Scheme 1). However, under the more vigorous conditions required to isomerise the ethers (VIa and b), further base-catalysed hydrogen shifts of the intermediate (XIV) take place giving the isolated products. No competing [3,3] sigmatropic (Claisen) rearrangement of the intermediate allenes [4] (XIII) was observed, in contrast to the corresponding reactions of the allenic ammonium ions (II). This result is compatible with the observations that sigmatropic rearrangements in cationic systems take place much more readily than in neutral molecules.[17]



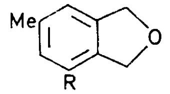
SCHEME 2

The base-catalysed isomerisations of the 4-methylpent-4-en-2-ynyl propynyl ethers, however, gave rather different results. The ether (VIIa) was isomerised by an excess of potassium t-butoxide in t-butyl alcohol at room temperature giving 4,5-dihydro-6-methylisobenzofuran (XV) (45%) and 1,3-dihydro-5-methylisobenzofuran (XVIa) (15%). The formation of the product (XV) provides good evidence for the intermediacy of allenes in these transformations (Scheme 3). The product (XV) can arise by intramolecular cycloaddition of the bis-allene (XVIII), whereas the formation of the minor product (XVIa) is best rationalised as involving intramolecular cycloaddition of the intermediate mono-allene (XVII) followed by hydrogen transfer.

We have also examined the possibility of competition between intramolecular cycloadditions either to phenylallene or to vinylallene systems. Treatment of the ether (VIIb) with base gave the major product (IXc) (55%) which arises by a route involving isomerisation of the phenylacetylene group to phenylallene followed by $[_{\pi}2 + _{\pi}4]$ cycloaddition of the vinyl group ($_{\pi}2$) to the phenylallene residue ($_{\pi}4$) (*cf.* Scheme 2). The minor product, tentatively identified as the dihydrobenzofuran (XVIb) (11%), arises from isomerisation of the vinylacetylene group to vinylallene followed by Diels–Alder addition and hydrogen transfer (Scheme 3). The preferential formation of the isomer (IXc) may be due to the faster base-catalysed isomerisation of the phenylacetylene as compared with the vinylacetylene grouping or faster $[_{\pi}4 + _{\pi}2]$ cycloaddition of the phenylallene ($_{\pi}4$) as compared with the vinylallene ($_{\pi}4$) residue.

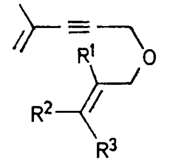


(XV)



(XVI)

a; R = H
b; R = Ph



(XIX)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Me,\ R^2 = R^3 = H$
c; $R^1 = H,\ R^2 = R^3 = Me$
d; $R^1 = R^2 = H,\ R^3 = Ph$

We have been unable to effect base-catalysed cycloadditions of allyl 4-methylpent-4-en-2-ynyl ethers

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[7] H. W. Gschwend, *Helv. Chim. Acta*, 1973, **56**, 1763; H. W. Gschwend and H. P. Meier, *Angew. Chem. Internat. Edn.*, 1972, **11**, 294.

[8] W. Oppolzer and K. Keller, *Tetrahedron Letters*, 1970, 1117, 4313; *J. Amer. Chem. Soc.*, 1971, **93**, 3836; W. Oppolzer, *Tetrahedron Letters*, 1970, 3091; *J. Amer. Chem. Soc.*, 1971, **93**, 3833 and 3834.

[9] O. L. Chapman, M. R. Engel, J. P. Springer, and J. C. Clardy, *J. Amer. Chem. Soc.*, 1971, **93**, 6696.

[10] D. J. Bichan and P. Yates, *J. Amer. Chem. Soc.*, 1972, **94**, 4773.

[11] H. Greuter, Gy. Frater, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 526; H. Greuter and H. Schmid, *ibid.*, p. 2382.

[12] D. Bilovic, *Croat. Chem. Acta*, 1966, **38**, 293; 1968, **40**, 15; D. Bilovic and V. Hahn, *ibid.*, 1967, **39**, 189; D. Bilovic, Z. Stojanac, and V. Hahn, *Tetrahedron Letters*, 1964, 2071.

[13] H. H. Wasserman and A. R. Doumaux, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 4611.

[14] H. O. House and T. H. Cronin, *J. Org. Chem.*, 1965, **30**, 1061.

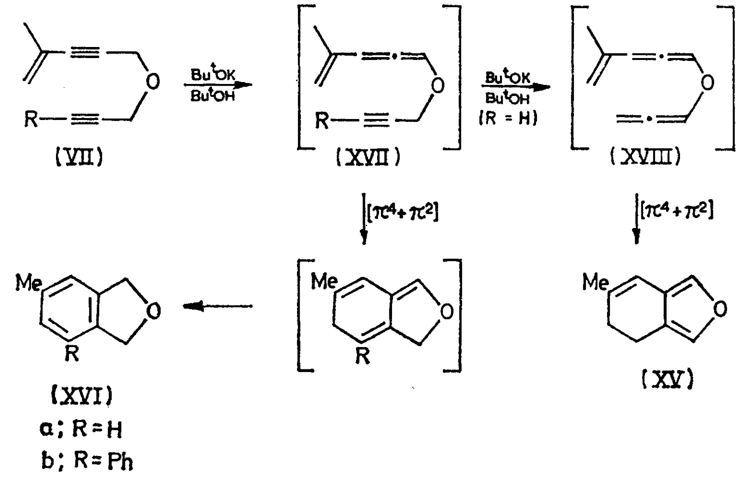
[15] B. A. M. Oude-Alink, A. W. K. Chan, and C. D. Gutsche, *J. Org. Chem.*, 1973, **38**, 1993.

[16] L. H. Klemm, R. A. Klemm, P. S. Santhanam, and D. V. White, *J. Org. Chem.*, 1971, **36**, 2169; E. Block and R. Stevenson, *ibid.*, p. 3453.

[17] J. Borgulya, R. Madeja, P. Fahrni, H.-J. Hansen, H. Schmid, and E. Barner, *Helv. Chim. Acta*, 1973, **56**, 14; U. Widmer, J. Zsindely, H.-J. Hansen, and H. Schmid, *ibid.*, p. 75; U. Widmer, H.-J. Hansen, and H. Schmid, *ibid.*, p. 2644; U. Svanholm and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 645; R. Breslow and J. M. Hoffman, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 2111.

(XIXa—d) under a variety of conditions. In each case starting material was recovered.

During this investigation we encountered a discrepancy between the m.p. recorded (99°) [18] for 1,3-dihydronaphtho[2,3-*c*]furan (IXb) and that (152—154°) which we obtained for this compound. The compound of m.p. 99° was produced by an unusual process,[18] so in order to resolve this difference we synthesised compound (IXb) by an unambiguous route. A previous attempt to obtain the ether (IXb) by dehydration of 2,3-bis-hydroxymethylnaphthalene failed.[18] However, treatment of the monotosylate of 2,3-bis-hydroxymethylnaphthalene with sodium hydride in benzene yielded the ether (IXb), m.p. 152—154°.



SCHEME 3

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for solutions in chloroform, u.v. spectra in ethanol, and 60 and 100 MHz ^{1}H n.m.r. spectra in deuteriochloroform (tetramethylsilane as internal reference). Only significant bands from these spectra are quoted. Mass spectra were determined using A.E.I. MS 9 and MS 12 spectrometers. M.p.s were determined using a Kofler hot-stage apparatus. Extracts were dried with magnesium sulphate. Evaporation refers to evaporation under diminished pressure.

Separations by column chromatography were carried out using Hopkin and Williams MFC grade silica. Merck Kieselgel G and Reeve Angel Silica CT were used for preparative thick- and thin-layer chromatography. Products were located by examination under u.v. illumination or by spraying with 5% cerium(IV) sulphate in 2N-sulphuric acid followed by heating.

When substances are stated to be identical, their identity has been established by comparison of m.p. and by mixed m.p., and where appropriate by comparison of i.r., n.m.r., and mass spectra and t.l.c. behaviour.

Allyl 3-*Phenylprop*-2-*ynyl Ether* (VIa).—3-Phenylprop-2-yn-1-ol (10 g) was added to a stirred suspension of sodium hydride (2 g) in anhydrous tetrahydrofuran (30 ml). After the mixture had been warmed overnight at 50°, allyl bromide (6·4 ml) was added. The mixture was stirred for a further 24 h, poured into water, and extracted with ether. The extracts were washed with water, dried, evaporated, and distilled, giving the *ether* (VIa) (7·3 g, 56%), b.p. 140° at 3 mmHg (Found: M^+, 172·0886. $C_{12}H_{12}O$ requires M, 172·0888); *m/e* 143, 131, and 115; $\nu_{max.}$ 2230, 2100, and 1060 cm^{-1}; τ 2·47—2·86 (m, 5 aromatic H), $ABMX_2$ system, τ_A 4·69, τ_B 4·82, τ_M 3·87—4·32, τ_X 5·90 [J_{AB} 1, J_{AM} 14, J_{BM} 10, J_{MX} 6 Hz, $O{\cdot}C(H_X)_2{\cdot}CH_M{=}CH_AH_B$], and τ 5·66 (s, $\equiv C{\cdot}CH_2{\cdot}O$).

Cinnamyl 3-*Phenylprop*-2-*ynyl Ether* (VIb).—The ether (VIb) was prepared by the above method from 3-phenylprop-2-yn-1-ol (5·0 g) and cinnamyl bromide (7·5 g) and purified by chromatography on neutral alumina (200 g), with benzene–light petroleum as eluant, giving an *oil* (VIb) (7·8 g, 83%) (Found: M^+, 248·1178. $C_{18}H_{16}O$ requires M, 248·1201); *m/e* 115; $\nu_{max.}$ 2250, 2200, 1700, 1660, and 1080 cm^{-1}; τ 2·4—2·83 (m, 10 aromatic H), ABX_2 system, τ_A 3·30, τ_B 3·68, τ_X 5·68 [J_{AB} 16, J_{BX} 6 Hz, $CH_A{=}CH_B{\cdot}C(H_X)_2{\cdot}O$], and τ 5·58 (s, $\equiv C{\cdot}CH_2{\cdot}O$).

2-*Methylallyl* 3-*Phenylprop*-2-*ynyl Ether* (VIc).—The ether (VIc) was prepared similarly from 3-phenylprop-2-yn-1-ol (5·0 g), and 2-methylallyl bromide (3·4 g), giving an *oil* (53%), b.p. 120—122° at 0·9 mmHg (Found: M^+, 186·1026. $C_{13}H_{14}O$ requires M, 186·1046); *m/e* 115; $\nu_{max.}$ 2160, 2100, 1660, and 1070 cm^{-1}; τ 2·3—2·8 (m, 5 aromatic H), AB system, τ_A 4·92, τ_B 5·00 (J_{AB} 1 Hz, $=CH_AH_B$), τ 5·62 (s, $\equiv C{\cdot}CH_2{\cdot}O$), 5·92 (s, $=C{\cdot}CH_2{\cdot}O$), and 8·22 (s, vinylic Me).

3-*Methylbut*-2-*enyl* 3-*Phenylprop*-2-*ynyl Ether* (VId).—The *ether* (VId) was similarly prepared (68% yield) from 3-phenylprop-2-yn-1-ol (5·0 g) and 3-methylbut-2-enyl bromide (5·6 g); b.p. 124—132° at 0·6 mmHg (Found: M^+, 200·1194. $C_{14}H_{16}O$ requires M, 200·1201); *m/e* 185, 171, 157, 131, and 115; $\nu_{max.}$ 2250, 1675, and 1060 cm^{-1}; τ 2·4—2·85 (m, 5 aromatic H), AX_2 system, τ_A 4·57, τ_X 5·87 [J_{AX} 7 Hz, $=CH_A{\cdot}C(H_X)_2$], τ 5·65 (s, $\equiv C{\cdot}CH_2{\cdot}O$), and 8·27 (s, $Me_2C{=}$).

4-*Methylpent*-4-*en*-2-*ynyl Prop*-2-*ynyl Ether* (VIIa).—4-Methylpent-4-en-2-yn-1-ol [18] (7·5 g) and prop-2-ynyl bromide (9·3 g) gave, by the above method, the *ether* (VIIa) (8·0 g, 76%), b.p. 44—46° at 0·1 mmHg (Found: M^+, 134·0719. $C_9H_{10}O$ requires M, 134·0732); $\nu_{max.}$ 3300, 2240, 2130, and 1090 cm^{-1}; τ 4·65—4·7 (m, $=CH_2$), τ 5·60 (s, $CH_2{=}CMe{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}O$), AX_2 system, τ_X 5·72, τ_A 7.55 [J_{AX} 3 Hz, $H_AC{\equiv}C{\cdot}C(H_X)_2{\cdot}O$], and τ 8·10 (t, J 2 Hz, vinylic Me).

4-*Methylpent*-4-*en*-2-*ynyl* 3-*Phenylprop*-2-*ynyl Ether*

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[18] J. Altman and D. Ginsburg, *Tetrahedron*, 1971, **27**, 93.

(VIIb).—4-Methylpent-4-en-2-yn-1-ol[19] (3·0 g) and 3-phenylprop-2-ynyl bromide (6·1 g) similarly gave after chromatography on neutral alumina (170 g), the *ether* (VIIb) (4·9 g, 73%) (Found: M^+, 210·1015. $C_{15}H_{14}O$ requires M, 210·1044), *m*/*e* 115; $\nu_{max.}$ 2220 and 1080 cm^{-1}; τ 2·4—2·82 (m, 5 aromatic H); AB system, τ_A 4·68, τ_B 4·77 (J_{AB} 1 Hz, $CH_AH_B{=}$), τ 5·56 (s, $C{\equiv}C{\cdot}CH_2{\cdot}O$), 5·60 (s, ${\equiv}C{\cdot}CH_2{\cdot}O$), and 8·12 (s, vinylic Me).

3-*Phenylprop*-2-*ynyl Prop*-2-*ynyl Ether* (VIIIa).—The ether (VIIIa) was prepared as above from 3-phenylprop-2-yn-1-ol (7·5 g) and prop-2-ynyl bromide (6·8 g), giving an *oil* (7·8 g, 80%) (Found: M^+, 170·0732. $C_{12}H_{10}O$ requires M, 170·0731); *m*/*e* 115; $\nu_{max.}$ 3300, 2230, and 1070 cm^{-1}; τ 2·4—2·8 (m, 5 aromatic H), 5·54 (s, $PhC{\equiv}C{\cdot}CH_2{\cdot}O$), and an AX_2 system, τ_X 5·7, τ_A 7·58 [J_{AX} 2 Hz, $H_AC{\equiv}C{\cdot}C(H_X)_2$].

Allyl 4-*Methylpent*-4-*en*-2-*ynyl Ether* (XIXa).—4-Methylpent-4-en-2-yn-1-ol[19] (5 g) was added dropwise to a suspension of sodium hydride (1·5 g) in anhydrous tetrahydrofuran (100 ml); the mixture was stirred overnight, and then allyl bromide (6·3 g) was added. The mixture was stirred for 24 h, poured into water, and extracted with ether. The extracts were washed with water, dried, and evaporated giving the *ether* (XIXa) as an oil (6·3 g, 89%) (Found: M^+, 136·0883. $C_9H_{12}O$ requires M, 136·0882); $\nu_{max.}$ 2220 and 1610 cm^{-1}; τ 3·9—4·34 (m, $CH{=}CH_2$), 4·58—4·92 (m, two $CH_2{=}$), 5·76 (s, ${\equiv}C{\cdot}CH_2{\cdot}O$), 5·96 (d, J 6 Hz, ${=}CH{\cdot}CH_2{\cdot}O$), and 8·12 (s, vinylic Me).

2-*Methylallyl* 4-*Methylpent*-4-*en*-2-*ynyl Ether* (XIXb).—The ether (XIXb) was similarly prepared from 4-methylpent-4-en-2-yn-1-ol[19] (5·0 g) and 2-methylallyl chloride (4·7 g) giving an *oil* (4·7 g, 60%), b.p. 46—54° at 0·4 mmHg (Found: M^+, 150·1018. $C_{10}H_{14}O$ requires M, 150·1045); *m*/*e* 135, 121, 107, 95, and 80; $\nu_{max.}$ 2200, 1650, 1610, and 1085 cm^{-1}; AB system, τ_A 4·73, τ_B 4·80 (J_{AB} 1 Hz, $CH_AH_B{=}C{-}C{\equiv}C$), AB system, τ_A 5·03, τ_B 5·10 (J_{AB} 1 Hz, $CH_AH_B{=}C{\cdot}CH_2$), τ 5·78 (s, ${\equiv}C{\cdot}CH_2{\cdot}O$), 6·04 (s, $CH_2{=}CMe{\cdot}CH_2{\cdot}O$), and 8·12 (s) and 8·26 (s) (two vinylic Me).

3-*Methylbut*-2-*enyl* 4-*Methylpent*-4-*en*-2-*ynyl Ether* (XIXc).—4-Methylpent-4-en-2-yn-1-ol[19] (5·0 g) and 3-methylbut-2-enyl bromide (7·75 g) gave, after purification by distillation followed by chromatography on alumina, the *ether* (XIXc) (4 g, 47%), b.p. 60—70° at 0·2 mmHg (Found: M^+, 164·1194. $C_{11}H_{16}O$ requires M, 164·1201); $\nu_{max.}$ 2220, 1680, 1620, and 1080 cm^{-1}; τ 4·4—4·85 (m, ${=}CH_2$ and ${=}CH{\cdot}CH_2$), 5·75 (s, ${\equiv}C{\cdot}CH_2{\cdot}O$), 5·93 (d, J 7 Hz, ${=}CH{\cdot}CH_2{\cdot}O$), 8·12 (t, J 1 Hz, $CH_2{=}C{\cdot}CH_3$), and 8·25 (s) and 8·30 (s) (two vinylic *Me*).

Cinnamyl 4-*Methylpent*-4-*en*-2-*ynyl Ether* (XIXd).—The ether (XIXd) was prepared from 4-methylpent-4-en-2-yn-1-ol[19] (5·0 g) and cinnamyl bromide (10·3 g) giving an *oil* (10·7 g, 97%) (Found: M^+, 212·0830. $C_{15}H_{18}O$ requires M, 212·0837); $\nu_{max.}$ 2220 and 1050 cm^{-1}; τ 2·4—2·96 (m, 5 aromatic H), ABX_2 system, τ_A 3·38, τ_B 3·71, τ_X 5·79 [J_{AB} 16, J_{AX} 6 Hz, $CH_A{=}CH_B{\cdot}C(H_X)_2{\cdot}O$], τ 4·72br (s) and 4·80 (m) (J 1·5 Hz, ${=}CH_AH_B$), 5·72 (s, ${\equiv}C{\cdot}CH_2{\cdot}O$), and 8·12 (d, J 1·5 Hz, vinylic Me).

Base-catalysed Intramolecular Cycloaddition of 3-*Phenylprop*-2-*ynyl Prop*-2-*ynyl Ether* (VIIIa).—The ether (VIIIa) (3·0 g) was stirred (12 h) with a solution of potassium t-butoxide [from potassium (6·9 g)] in t-butyl alcohol. The solvent was evaporated off and the residual solid was dissolved in ether; the solution was washed with water, dried, and evaporated giving a solid (2·6 g) which was purified by preparative t.l.c. giving 1,3-dihydronaphtho[2,3-*c*]furan (IXb) (77%), m.p. 152—154° (lit.,[18] 99°); $\nu_{max.}$ 1050, 905, and 870 cm^{-1}; τ 2·18—2·74 (m, 6 aromatic H) and 4·86 (s, two $CH_2{\cdot}O$); $\lambda_{max.}$ 224 (ε 60,150), 261 (3500), 269 (4725), 279 (5240), 289 (3575), 305·5 (965), and 319 nm (1228). Mixed m.p. with an authentic specimen (see below) showed no depression.

Base-catalysed Intramolecular Cycloaddition of Allyl 3-*Phenylprop*-2-*ynyl Ether* (VIa).—The ether (VIa) (4 g) was warmed with a solution of potassium t-butoxide [from potassium (9·1 g)] in t-butyl alcohol at 55° for 22 h. The solvent was evaporated off and the residue was partitioned between water and ether and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated giving a solid (3·7 g) which was separated by preparative t.l.c. (silica gel; 3 : 1 benzene–light petroleum) into (a) 1,3,3a,4-*tetrahydronaphtho*[2,3-c]*furan* (Xa) (51%), m.p. 137—139° (Found: M^+, 172·0886. $C_{12}H_{12}O$ requires M, 172·0888); $\lambda_{max.}$ 264·5 (ε 10,200), 271 (10,050), and 319 nm (374); $\nu_{max.}$ 1035, 907, 865, and 843 cm^{-1}; τ 2·5—3·22 (m, 4 aromatic H), ABX system, τ_A 5·39, τ_B 5·60, τ_X 3·72 (J_{AB} 14, $J_{AX} = J_{BX} = 2$ Hz, $CH_X{=}C{\cdot}CH_AH_B{\cdot}O$), and ABMXY system, τ_A 5·66, τ_B 6·52, τ_M 6·8—7·3, τ_X 7·13, τ_Y 7·45 [the coupling constants were determined after the addition of the shift reagent $Eu(fod)_3$: J_{AB} 8, $J_{AM} = J_{BM} = 8$, J_{XY} 15, J_{MX} 7·5, J_{MY} 15 Hz, $ArCH_XH_Y{\cdot}CH_M{\cdot}CH_AH_B{\cdot}O$]; and (b) 1,3,4,9-*tetrahydronaphtho*[2,3-c]*furan* (XI) (28%), m.p. 71—75° (Found: M^+, 172·0893. $C_{12}H_{12}O$ requires M, 172·0888); $\lambda_{max.}$ 266 (ε 1215), 273 (1210), and 320 nm (45); $\nu_{max.}$ 1035 and 905 cm^{-1}; τ 2·77 (s, 4 aromatic H), 5·3 (s, two $CH_2{\cdot}O$), and 6·59 (s, two $ArCH_2$).

Catalytic Hydrogenation of 1,3,3a,4-*Tetrahydronaphtho*[2,3-c]*furan* (Xa).—The naphthofuran (Xa) (90 mg) in ethanol (25 ml) was hydrogenated over 10% Pd–C (25 mg) until 1 mol. equiv. of hydrogen had been absorbed. The catalyst was collected and the filtrate was evaporated giving 1,3,3a,4,9,9a-*hexahydronaphtho*[2,3-c]*furan* (XII) as an oil (80 mg, 88%) (Found: M^+, 174·1045. $C_{12}H_{14}O$ requires M, 174·1045); $\nu_{max.}$ 1045 and 920 cm^{-1}; τ 2·90 (s, 4 aromatic H), 5·92—6·13 (2H, m) and 6·56—6·75 (2H, m) (two CH_2O), and 7·04—7·65 (m, two $ArCH_2{\cdot}CH$).

Catalytic Hydrogenation of 1,3,4,9-*Tetrahydronaphtho*[2,3-c]*furan* (XI).—The naphthofuran (XI) (180 mg) in ethanol (25 ml) was hydrogenated over 10% Pd–C (25 mg) until 1 mol. equiv. of hydrogen had been absorbed. The catalyst was collected and the filtrate evaporated giving 1,3,3a,4,9,9a-hexahydronaphtho[2,3-c]furan (XII) (153 mg, 85%), identical with the product obtained in the preceding experiment.

Base-catalysed Intramolecular Cycloaddition of Cinnamyl 3-*Phenylprop*-2-*ynyl Ether* (VIb).—The ether (VIb) (3·0 g) was warmed to 55° with a solution of potassium t-butoxide [from potassium (4·7 g)] in t-butyl alcohol for 16 h. The solvent was evaporated off and the residual solid was partitioned between ether and water, and extracted with ether. The extracts were dried and evaporated giving a solid (2·7 g) which was separated by preparative t.l.c. (silica gel; 3 : 1 benzene–light petroleum) into (a) 1,3,9,9a-*tetrahydro*-4-*phenylnaphtho*[2,3-c]*furan* (Xb) (52%), m.p. 112—114° (Found: C, 86·9; H, 6·35. $C_{18}H_{16}O$ requires C, 87·1; H, 6·45%); $\lambda_{max.}$ 230·5 (ε 27,900) and 275 nm (9950); $\nu_{max.}$ 1040 cm^{-1}; τ 2·43—3·22 (m, 9 aromatic H), AB system, τ_A 5·30, τ_B 5·80 (J_{AB} 15 Hz, ${=}C{\cdot}CH_AH_B{\cdot}O$), and ABMXY system, τ_A 5·61, τ_B 6·44, τ_M 6·6—7·1, τ_X 7·06, τ_Y 7·31 [coupling constants were determined after addition of shift reagent

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[19] V. M. Vlasov, A. A. Vasil'eva, and E. F. Semenova, *Zhur. org. Khim.*, 1966, **2**, 595; V. M. Vlasov, T. S. Kuznetsova, and N. M. Demglazov, *ibid.*, 1967, **3**, 277.

Eu(fod)$_3$: J_{AB} 8, $J_{AM} = J_{BM} = 8$, J_{XY} 15, J_{MX} 5, J_{MY} 15 Hz]; and (b) 1,3-*dihydro*-4-*phenylnaphtho*[2,3-*c*]*furan* (IXa) (30%), m.p. 119—120° (lit.,[19] 121·5—122·5°) (Found: C, 87·8; H, 5·9. Calc. for $C_{17}H_{14}O$: C, 87·8; H, 5·7%); $\nu_{max.}$ 1000, 907, 870, and 850 cm^{-1}; τ 2·1—2·8 (m, 10 aromatic H), 4·74 (s, CH_2·O), and 5·01 (s, CH_2·O).

Base-catalysed Intramolecular Cycloaddition of 4-*Methylpent*-4-*en*-2-*ynyl Prop*-2-*ynyl Ether* (VIIa).—The ether (VIIa) (3·0 g) was stirred for 4 days at room temperature with a solution of potassium t-butoxide [from potassium (8·7 g)] in t-butyl alcohol. The solvent was evaporated off and the residue was partitioned between ether and water and extracted with ether. The extracts were dried and evaporated giving an oil (2·0 g) which was chromatographed on neutral alumina. Eluting with light petroleum–benzene gave (a) 4,5-*dihydro*-6-*methylisobenzofuran* (XV) (1·35 g, 45%) (Found: M^+, 134·0729. $C_9H_{10}O$ requires M, 134·0732); *m/e* 119, 105, and 91; $\nu_{max.}$ 1100, 1025, 887, and 840 cm^{-1}; τ 2·88 (s, 1-H), 2·96 (s, 3-H), 3·86 (s, CH=C), A_2B_2 system, τ_A 7·37, τ_B 7·80 [J_{AB} 7 Hz, $C(H_A)_2{\cdot}C(H_B)_2$] and τ 8·15 (s, vinylic Me); and (b) 1,3-*dihydro*-5-*methylisobenzofuran* (XVIa) (0·45 g, 15%) as a yellow oil (Found: M^+, 134·0729. $C_9H_{10}O$ requires M, 134·0732); *m/e* 119, 105, and 91; $\nu_{max.}$ 1040, 900, and 805 cm^{-1}; τ 2·94 (s, 3 aromatic H), 4·94 (s, two CH_2·O), and 7·65 (s, aromatic Me).

Base-catalysed Intramolecular Cycloaddition of 4-*Methylpent*-4-*en*-2-*ynyl* 3-*Phenylprop*-2-*ynyl Ether* (VIIb).—The ether (VIIb) (2·0 g) was stirred overnight with a solution of potassium t-butoxide [from potassium (3·7 g)] in t-butyl alcohol. After normal work-up, the resultant oil (1·6 g) was separated by preparative t.l.c. (2% ethanol in light petroleum). The first fraction was 1,3-dihydro-4-isopropenylnaphtho[2,3-*c*]furan (IXc) (55%), *m/e* 210 (M^+); τ 2·01—2·71 (m, 5 aromatic H), AB system, τ_A 4·6, τ_B 5·03 (J_{AB} 1 Hz, $=CH_AH_B$), τ 4·80 (s) and 4·89 (s) (two CH_2·O), and 7·93 (s, vinylic Me). The second fraction was tentatively identified as 1,3-dihydro-6-methyl-4-phenylisobenzofuran (XVIb) (11%), although the sample could not be obtained free from impurities; *m/e* 210 (M^+); τ 2·06—3·0 (m, 7 aromatic H), 4·78 (s) and 4·86 (s) (two CH_2·O), and 7·59 (s, aromatic Me).

1,3-*Dihydronaphtho*[2,3-c]*furan* (IXb) (by P. A. CADBY).—Toluene-*p*-sulphonyl chloride (1·0 g) in chloroform (20 ml) was added during 12 h to a solution of 2,3-bis-hydroxymethylnaphthalene (800 mg) in pyridine (20 ml) at 0°. After 48 h, chloroform was added and the mixture was shaken with 2N-sulphuric acid, aqueous sodium hydrogen carbonate, and water. Evaporation gave the intermediate monotosylate which was dissolved in benzene (50 ml), and to the solution sodium hydride (200 mg) was added at room temperature (nitrogen atmosphere; 12 h). Filtration and evaporation gave an oil which was crystallised from light petroleum (b.p. 40—60°), giving 1,3-dihydronaphtho[2,3-*c*]-furan (18%), m.p. 152—154°, identical with the compound described above.

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