

Base Catalysed Intramolecular Cycloadditions of 3-Phenylprop-2-ynyl Allyl Ethers and 4-Methylpent-4-en-2-ynyl Prop-2-ynyl Ethers

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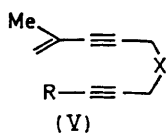
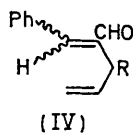
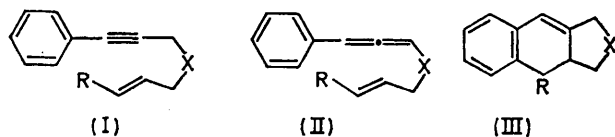
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Summary The base catalysed isomerisations (Ia \rightarrow IIIa + VI), (Ib \rightarrow VIII), (Xa \rightarrow IXa), (Xb \rightarrow IXb), (Va \rightarrow XI + XIIa), and (Vb \rightarrow IXc + XIIb) involve the sequence: acetylene \rightarrow allene isomerisation, intramolecular ($\pi^4 + \pi^2$) cycloaddition, and sigmatropic or prototropic hydrogen shift.

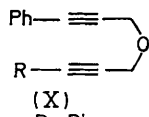
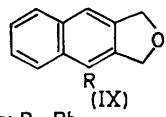
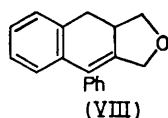
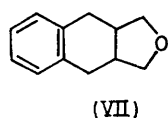
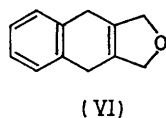
RECENTLY considerable interest has developed¹⁻⁷ in intramolecular cycloaddition of unstable intermediates as a method for the stereospecific synthesis of polycyclic compounds. In this connection, we have described⁶ the base catalysed isomerisation of (3-phenylprop-2-ynyl)allyl-

ammonium cations (I; X = NMe₂), which can lead to two

types of product: the dihydronaphthalenes (III; X = NMe₂),



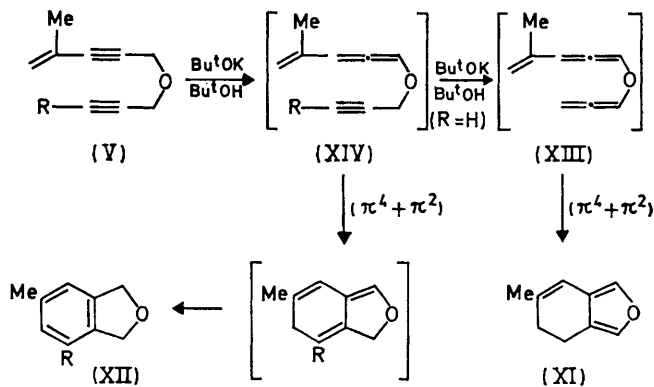
In (I)-(V):
a; R=H, X=O
b; R=Ph, X=O



a; R = Ph
b; R = H
c; R = CH₃-C=CH₂

a; R = Ph
b; R = H

formed by intramolecular Diels-Alder cycloaddition ($\pi^4 + \pi^2$) of the intermediate allene (II; X = NMe₂), and aldehydes (IV) formed by hydrolysis of the immonium salt derived by [3,3] sigmatropic rearrangement of the allenes (II; X = NMe₂). We now report on the corresponding base catalysed reactions of the ethers (I; X = O) and 4-methylpent-4-en-2-ynyl propynyl ethers (V; X = O). Further evidence for the intermediacy of allenes in these reactions has been obtained and the results provide a new method for the synthesis of polycyclic heterocyclic systems.



SCHEME

a; R=H, b; R=Ph

The ether (Ia) was isomerised by excess potassium *t*-butoxide in *t*-butyl alcohol at 55° into the dihydronaphthalenes (IIIa) (55%) and (VI) (28%), whose structures [(IIIa) and (VI)] were supported by spectral data and by their catalytic hydrogenation to the ether (VII). Similarly, the ether (Ib) was transformed into the isomer (VIII) (52%) and the product (IXa) (30%), which presumably arises by atmospheric oxidation of its dihydro-derivative (VIII). The compound (IXa) was identical with that prepared (97%) by base catalysed isomerisation of the ether (Xa).⁸ Similar base catalysed isomerisation of the bis-acetylenic ether (Xb) at room temperature gave the isomer (IXb) (77%). These reactions [(Ia) \rightarrow (IIIa) + (VI)], [(Ib) \rightarrow (VIII)], [(Xa) \rightarrow

(IXa)], and [(Xb) \rightarrow (IXb)] are believed to involve the following sequence: (i) base catalysed isomerisation of the phenylacetylene to a phenylallene, (ii) intramolecular ($\pi^4 + \pi^2$) cycloaddition, and (iii) sigmatropic or prototropic shift of hydrogen. Two differences between the base catalysed reactions of the ethers (I; X=O) and the corresponding

ammonium cations (I; X = NMe₂) may be noted: (a) the range of products formed in the ether rearrangements indicate that the stronger basic conditions which are required cause further hydrogen shifts, and (b) no [3,3] sigmatropic rearrangement of the allenes (IIa and b) could be detected. This accords with the general observation⁹ that sigmatropic rearrangements in cationic systems proceed much more readily than in neutral molecules.

The base catalysed isomerisations of the 4-methylpent-4-en-2-ynyl propynyl ethers (V) take a somewhat different course (Scheme). The ether (Va) was isomerised at room temperature to 6-methyl-4,5-dihydroisobenzofuran (XI) (45%) and 5-methyl-1,3-dihydroisobenzofuran (XIIa) (15%). The formation of the isobenzofuran (XI) provides good evidence for the intermediacy of allenes in these reactions.

The dihydroisobenzofuran (XI) presumably arises by intramolecular cycloaddition ($\pi^4 + \pi^2$) of the bis-allene (XIII), whereas the minor product (XIIa) is presumably formed by cycloaddition ($\pi^4 + \pi^2$) of the mono-allene (XIV) (Scheme).

We have also examined the competition possible between intramolecular ($\pi^4 + \pi^2$) cycloadditions either to phenylallene or to vinylallene groupings as the π^4 component. Treatment of the ether (Vb) with potassium t-butoxide-t-butylalcohol at room temperature gave as the major product the isomer (IXc) (55%) by a route involving phenylacetylene to phenylallene isomerisation, ($\pi^4 + \pi^2$) intramolecular cycloaddition, and hydrogen transfer, analogous to the transformations [(Xa) \rightarrow (IXa)] and [(Xb) \rightarrow (IXb)]. The minor product (XIIb) (11%) could be formed by an alternative equivalent sequence [(Vb) \rightarrow (XIVb) \rightarrow (XIIb)]; see Scheme]. The preference for the transformation [(Vb) \rightarrow (IXc)] rather than [(Vb) \rightarrow (XIIb)] may be due to a faster base catalysed isomerisation of the phenylacetylene as compared with the vinylacetylene grouping or faster ($\pi^4 + \pi^2$) cycloaddition of the phenylallene (π^4) as compared with the vinylallene (π^4).

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- ¹ H. W. Gschwend, *Helv. Chim. Acta*, 1973, **56**, 1763; H. W. Gschwend and H. P. Meier, *Angew. Chem. Internat. Edn.*, 1972, **11**, 294.
² W. Oppolzer and K. Keller, *Tetrahedron Letters*, 1970, 1117 and 4313; *J. Amer. Chem. Soc.*, 1971, **93**, 3836; W. Oppolzer, *Tetrahedron Letters*, 1970, 3091; *J. Amer. Chem. Soc.*, 1971, **93**, 3833 and 3834.
³ O. L. Chapman, M. R. Engel, J. P. Springer, and J. C. Clardy, *J. Amer. Chem. Soc.*, 1971, **93**, 6696.
⁴ D. J. Bichan and P. Yates, *J. Amer. Chem. Soc.*, 1972, **94**, 4773.
⁵ H. Greuter, Gy. Frater, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 526; H. Greuter and H. Schmid, *ibid.*, 1972, **55**, 2382.
⁶ T. Laird and W. D. Ollis, *J.C.S. Chem. Comm.*, 1972, 557.
⁷ C. M. Bowes, D. F. Montecalvo, and F. Sondheimer, *Tetrahedron Letters*, 1973, 3181.
⁸ I. Iwai and J. Ide, *Chem. and Pharm. Bull. (Japan)*, 1964, **12**, 1094.
⁹ J. Borgulya, R. Madeja, P. Fahrni, H.-J. Hansen, H. Schmid, and R. Barner, *Helv. Chim. Acta*, 1973, **56**, 14; U. Widmer, J. Zsindely, H.-J. Hansen, and H. Schmid, *ibid.*, 1973, **56**, 75; U. Widmer, H.-J. Hansen, and H. Schmid, *ibid.*, 1973, **56**, 2644; U. Svanholm and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 645.