Intramolecular Photocycloaddition of Phenethyl Vinyl Ether

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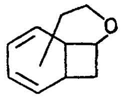
Summary Phenethyl vinyl ether has been shown to undergo photoisomerisation to the 1,3- and 1,4-intramolecular cycloadducts (**3**) and (**4**) in relative yields of 1:15 respectively.

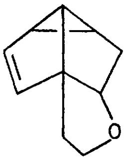
The electron donor and acceptor properties of ethylenes with respect to benzene are known to influence markedly the relative efficiency of formation of their 1,2- and 1,3-photocycloadducts with this arene.[1,2] Corresponding intramolecular systems have received little attention, but consistent with intermolecular analogues, *cis*- and *trans*-6-phenylhex-2-enes yield only 1,3-intramolecular adducts[3] while the product from irradiation of the corresponding acetylene is 8-methylbicyclo[6.3.0]undeca-1,3,5,7-tetraene and/or the -2,4,6,8-isomer formed no doubt *via* the 1,2-tricyclic triene adducts.[4]

$PhCH_2CH_2OCH{=}CH_2$

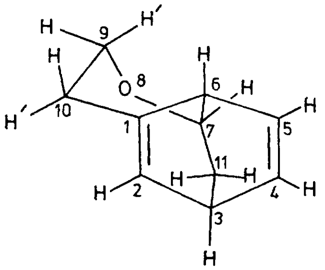
(1)



(2)



(3)



(4)

We now report that irradiation (254 nm, 20 °C, air, 10% solution in cyclohexane) of phenethyl vinyl ether (**1**) surprisingly yields no detectable amounts of the expected 1,2-intramolecular adducts (**2**), but 1,4-cycloaddition, a normally very minor process,[5] is the major reaction pathway. Two photoisomers (M^+ 148 a.m.u.) of (**1**) were formed during the reaction in an initial ratio of *ca.* 1 : 15† (g.l.c. retention times relative to starting material of 1·33 and 1·64 respectively; 9% Apiezon L/2% KOH) and these are deduced from chemical and spectroscopic properties to be respectively the 1,3- and 1,4-cycloadducts (**3**) and (**4**) arising from 1,3- and 2,5-intramolecular attack of the vinyl group on to the arene. Both isomers were inert to *N*-phenylmaleimide under conditions which readily yield the Diels–Alder adduct of this dienophile and the 1,2-cycloadduct of benzene and ethyl vinyl ether thus demonstrating the absence of a *cis*-1,3-diene unit as in (**2**). Consistent with the assignment, the minor adduct was essentially thermally stable at temperatures up to 240 °C while the major isomer reverted to phenethyl vinyl ether. The assignments of (**3**) and (**4**) to the minor and major reaction components respectively were confirmed by their spectral properties, in particular n.m.r. spectra, of the separated adducts. The n.m.r. spectrum (C_6D_6) of the minor isomer had resonances at δ 5·1—5·7 (2H, ABq, $J = 6$ Hz, olefinic H), 4·2—3·4 (4H, m), and 2·2—1·6 (6H, m), which is analogous to one of the products for the irradiation of *cis*-6-phenylhex-2-ene.[3] The n.m.r. spectrum (C_6D_6) of the major isomer had resonances at δ 5·6 (3H, m, 2-, 4- and 5-H, $J_{4,5} = 5{\cdot}5$ Hz), 4·6 (1H, br s, 7-H), 3·7 (2H, m, 9-H, $J_{9,10'} = J_{9,10} = 5$ Hz, $J_{9,10} = 0$ Hz, $J_{9',10'} = J_{9,9'} = J_{10,10'} = 12$ Hz), and 2·4—1·3 (6H, complex m, 3-, 6-, 10-, and 11-H, $J_{3,11} = 8$ Hz, $J_{5,6} = 1$ Hz). The assignments were confirmed by the use of a europium shift reagent which also allowed the above coupling constants to be determined.

Exciplexes have frequently been postulated as intermediates in arene–olefin cycloaddition reactions.[6] We have observed that with phenethyl vinyl ether the arene fluorescence is quenched approximately ten-fold in comparison with that of phenethyl ethyl ether but no long wavelength emission attributable to an exciplex was observed at temperatures down to −50 °C.

Factors which dictate the selectivity of reaction towards the normally disfavoured 1,4-cycloaddition are not obvious in the present case. By analogy with the intermolecular systems,[1,2] the major product from phenethyl vinyl ether would have been expected to be the 1,2-cycloadduct (**2**) with minor amounts of (**3**) and its isomers also being formed. Molecular models of phenethyl vinyl ether suggest that whereas a planar approach of the vinyl and arene chromophores appears to be reasonably favourable for both 1,2- and 2,3-attack leading to (**2**), and 1,3- and 2,6-attack which would result in the formation of (**3**) and an isomer of (**3**) respectively, the 2,5-mode of approach which gives (**4**) is comparatively unfavourable.

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† Neither the yield nor ratio of products was significantly affected by change of solvent from cyclohexane to ethyl acetate, acetonitrile, or methanol but under the conditions of its formation the major isomer undergoes slow reversion to the starting material and this leads to a ratio of minor to major product of *ca.* 1 : 5 on prolonged irradiation. As expected variable amounts of 2-phenylethanol and 1-methoxy-1-(2-phenethoxy)ethane were produced thermally from (**1**) in the presence of methanol.

[1] D. Bryce-Smith, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *J.C.S. Chem. Comm.*, 1974, 334.

[2] D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1977, 2459.

[3] W. Ferree, J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 5502.

[4] W. Lippke, W. Ferree, and H. Morrison, *J. Amer. Chem. Soc.*, 1974, **96**, 2134.

[5] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073.

[6] See for example J. A. Ors and R. Srinivasan, *J. Org. Chem.*, 1977, **42**, 1321, and references therein.