Solvent Effects in 1,3-Photocycloaddition of Vinyl Ethers to Monosubstituted Benzenes

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Summary The photocycloadditions of vinyl ethers to benzonitrile, benzene, toluene, and anisole are described; the 1,3-cycloaddition of ethyl vinyl ether to anisole is unexpectedly promoted by polar solvents.

Factors which affect the mode and efficiency of photocycloaddition of olefins to simple arenes are currently of considerable interest.[1–5] While it was to be expected that irradiation of acrylonitrile and anisole would yield a 1,2-cycloadduct of type (**1**),[4] it is surprising in view of the well documented results with benzene–olefin systems[1] that anisole and hydrocarbon olefins such as cyclopentene apparently only yield the 1,3-product of type (**2**).[2,3] In order to assess further the involvement of ground-[1,6] and excited-[3,7] state complexes and polar intermediates[1] in these intriguing addition reactions, and to examine the usefulness and scope of the proposal made from studies with benzene–olefin systems that the preferred course of the reaction (*i.e.* 1,2- *vs.* 1,3-cycloaddition) may be predicted from the ionisation potential differences† of the addends,[1] we have investigated the photoadditions of the electron-rich olefins ethyl vinyl ether and dihydropyran with anisole, toluene, and benzonitrile and compared these results with those for benzene as arene.

Irradiation (254 nm) of the arene (1·1 M) and olefin (3·5 M) in cyclohexane solution led to a variety of products which were separated by preparative g.l.c. and identified by comparison of their spectroscopic properties with those of similar adducts of proven structure. The results along with those from the corresponding benzene system are summarised in the Table.

Table

Arene	I.P./eV	Cycloadduct type with ethyl vinyl ether (I.P. 8·6 eV)
Anisole	8·54[a]	1,3 only
Toluene	8·82	1,3 + trace of 1,2
Benzene	9·24	1,2 and 1,3[b]
Benzonitrile	10·02	1,2

[a] I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley–Interscience, New York, 1976, p. 59. [b] Φ ratio of 1,2 to 1,3 cycloadducts 4:1.

Essentially similar results were observed with 2,3-dihydropyran (I.P. 8·34 eV) as olefin although the trace amounts of the 1:1 adduct from benzonitrile made its identification as the 1,2-cycloadduct only tentative (*cf.* the anisole–acrylonitrile system[4]).

The above results are in broad agreement with the empirical observation made from studies with benzene that as the donor or acceptor properties of the olefin increase relative to the arene, as judged by ionisation potential differences, the preference for 1,2-cycloaddition as against the 1,3-process increases.[1] The 1,2-reaction is thus considered to involve an element of charge-transfer to or from the arene in the transition state and consistent

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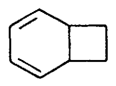
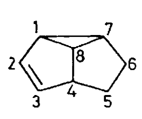
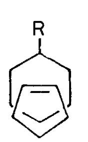
† There is no correlation between ionisation potential of the olefin and efficiency of cycloaddition (see the Table in ref. 1): a recent report (ref. 3) erroneously states that this had been postulated in ref. 1.

with this such processes are promoted in polar solvents (*e.g.* MeCN) whereas the homopolar 1,3-cycloaddition remains unaffected.[1,3,5] The effect of change in solvent polarity on the present systems, however, differs markedly from those previously reported for although essentially it is only the 1,2-process with ethyl vinyl ether and benzene which is promoted on change of solvent from cyclohexane to acetonitrile, with this olefin and toluene or anisole the formation of the 1,3-adducts is favoured in the more polar solvent; further the effect is more pronounced with the latter arene. Thus the total quantum yield (0·2 in cyclohexane) for formation of the vinyl ether–anisole 1,3-cycloadducts is doubled in methyl cyanide whereas that for the toluene addition is increased by only *ca.* 15%. Change of solvent in the present systems did not result in the formation of products other than those described. In particular no evidence was obtained to suggest that in the more polar solvent the chemistry of an intermediate exciplex is changed to give other products (*e.g.* olefin dimers) instead of enhancement or formation of the 1,2-cycloadduct. In contrast, corresponding cycloadditions of hydrocarbon olefins to anisole are reported to be independent of solvent polarity,[3] but it is very significant that these, the similar toluene additions,[7] and the 1,3-cycloadditions of ethyl vinyl ether reported here all yield adducts in which the arene substituent selectively resides on the 8-position in (**2**).‡ It has been previously suggested that such selectivity of attack at the 2,6-positions of the arene is a result of the preferred orientation (**3**) in the exciplex.[7] The vinyl ethers quenched the arene fluorescence in solution only weakly (kq_T values in the range 1—15 l mol^{-1}) and the efficiency decreased in the order benzene > toluene > anisole. There was no evidence for exciplex emission nor charge-transfer absorption of a complex of the addends.


(1)



(2)



(3)

The solvent effects described above are puzzling but require comment. Neither the increasing effect of solvent polarity on the 1,3-cycloaddition of ethyl vinyl ether in the series benzene, toluene, and anisole nor the preferred 2,6-positions of attack of olefins on to monosubstituted benzenes can be rationalised on the basis of overall charge distribution of the excited arene; indeed it is only for the S_2 state of anisole, inaccessible in the present experiments, that the 2- and 6-positions are relatively the most electron deficient in any particular state.[8] Stabilisation of a ground-state complex which has a degree of polarity is unlikely as the promotional effects are most pronounced where the differences in electron donor–acceptor properties of the addends are least, *i.e.* with ethyl vinyl ether and anisole. The difficulty in explaining the preferred 1,3-positions of olefin attack on the arenes is very similar to that currently experienced in understanding light-induced nucleophilic substitutions at the *ortho* positions of anisole.[9]

It does appear, however, that the polarity of an important intermediate is greatly increased by increase in the nucleophilicity of the olefin (*i.e.* changing from hydrocarbon olefins to vinyl ethers) but, from the present results, this must be an effect of combination with some feature of the arene as the 1,3-cycloadditions of vinyl ethers to benzene are solvent independent. Although at present this is not understood, for the first time evidence has been obtained which clearly shows that the 1,3-cycloaddition reaction can be susceptible to polar factors and is not the general homopolar process as considered previously.

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‡ Formation of the present 1,3-cycloadducts showed no regio- or stereo-selectivity with respect to the OEt group.

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