

SOLVENT POLARITY EFFECTS ON THE REGIOSELECTIVITY OF PHOTOADDITION

REACTIONS OF ARENE-ETHENE SYSTEMS

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**Abstract:** Use of polar solvents in the ortho photocycloaddition of ethenes to anisole greatly increases the regioselectivity of the process and the major adducts reflect 1,2-attack onto the arene.

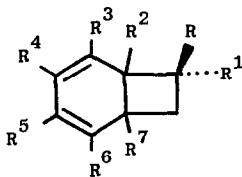
The photoreactions of arene-ethene systems in which the arene may formally be considered as either an electron donor or acceptor partner in any ground or excited state complex, have received considerable attention in recent years.<sup>1-7</sup> Investigations of these systems which have involved solvent studies have been largely concerned with the effects of polar aprotic and protic solvents on the ratio of (2+2) photocycloaddition and arene substitution reactions,<sup>4-6</sup> and of solvent polarity on the relative efficiencies of the ortho and meta cycloadditions of ethenes to benzene.<sup>7</sup> We now report that the regioselectivity, with respect to the arene, of the ortho (2+2) photocycloaddition of electron donor-acceptor arene-ethene pairs can be markedly influenced by solvent polarity.

Irradiation (254 nm, 20°C, sealed quartz tubes) of the arene (toluene, anisole, 1.1M) and ethene (methyl acrylate, methyl methacrylate, acrylonitrile, 3.5M) in solvents of differing polarity produced solely the ortho 1:1 photocycloadducts (1). The regio- and stereo-isomers were resolved analytically by WCOT gas chromatography (OV101) and individual 1:1 adduct isomers were isolated by flash chromatography or as their 1:1:1 N-phenylmaleimide adducts.<sup>8</sup> In some cases the more minor components could not in practise be obtained wholly free from their isomers and the position of the substituent was assigned by spectroscopic analysis of simple mixtures of the 1:1 adducts or their 1:1:1 Diels-Alder derivatives.

It was apparent that for reactions with anisole, the complexity of the adduct mixture was markedly affected by polarity of the solvent. In particular the selectivity of the orientation of the addition with respect to the arene was greatly increased with increase in solvent polarity whereas change of this reaction parameter had no significant effect on the stereochemistry of the process nor on the ethene addition regioselectivity. The results are summarised in the Table for the extreme cases of cyclohexane and acetonitrile as solvent. It is noteworthy that for the weaker electron donor toluene, changes in solvent polarity had little effect on the regio-selectivity of its photoadditions to the ethenes presently under study.

**Table:** Relative Rates of Formation of ortho Photocycloadducts of Ethenes and Anisole.  
\* Ratios comparable between solvents and systems.

Ethene	Cyclohexane *			Acetonitrile *		
	1,2-	2,3-	3,4-	1,2-	2,3-	3,4-
Methyl acrylate	55	2.5	12	60	2.5	5
Methyl methacrylate	100	-	33	200	-	25
Acrylonitrile	20	-	13	20	-	1
Methacrylonitrile	300	-	150	300	-	50



- (1) where  $R = H$  or  $Me$  and  $R^1 = CN$  or  $CO_2Me$   
 or  $R = CN$  or  $CO_2Me$  and  $R^1 = H$  or  $Me$   
 and one of  $R^2-R^7 = OMe$

Inspection of the data in the Table shows that the increase of regioselectivity of the ortho cycloadditions of the acrylates to anisole with increase in solvent polarity is a result of a combination of enhancement of formation of the 1,2-isomer and suppression of the 3,4-product whereas for the reactions with the acrylonitriles it is essentially the decrease in rate of formation of the latter mode of addition which is responsible for the remarkable solvent effect. All ortho cycloadducts of ethenes and arenes are photolabile to some extent,<sup>7</sup> and in the present systems the photostationary concentrations of some isomers were solvent dependent thus reflecting a variability of photodecomposition efficiencies with media polarity, a feature demonstrable with the isolated adducts. Such considerations do not, however, account for the present results which were observed at very low reactant conversions (<5%) while rates of production of all isomers were linear. Attempts to correlate orientations of loose ground-state complexes of arene-ethene systems with the stereochemistry of their ortho photocycloadducts had only limited success.<sup>10</sup> It is, however, feasible that the present observations are a result of the stabilisation by the polar solvent of a particular addend orientation (1,2- with respect to the arene) in a ground or excited state complex whereas other orientations which occur in cyclohexane are much less favoured.

#### References and Notes

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