

Polar and Stereochemical Aspects of 1,2-Photoaddition of Ethylenes to Benzene

By DEREK BRYCE-SMITH,* ANDREW GILBERT, BRIAN ORGER, and HILARY TYRRELL

(Department of Chemistry, The University, Whiteknights Park, Reading)

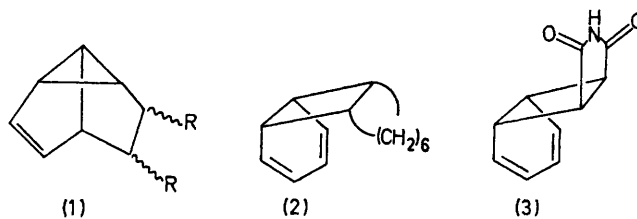
Summary Two observations concerning photochemical 1,2-cycloadditions of mono-olefins to benzene may be of wider significance: the 1,2-process tends to occur most readily with olefins having either marked donor or acceptor properties, otherwise 1,3-addition tends to be

preferred; and 1,2-additions of the donor olefins *cis*-cyclo-octene and *cis*-but-2-ene are stereospecifically *endo*, whereas 1,2-addition of the acceptor maleimide is stereospecifically *exo*.

SOME ethylenes *e.g.* cyclopentene undergo only 1,3-photochemical cycloaddition to benzene, others, *e.g.* maleimide and maleic anhydride,¹ undergo only 1,2-addition and some *e.g.* but-2-enes undergo both processes concurrently.² It appears that S_1 benzene is involved in all cases except that of maleic anhydride, and orbital symmetry considerations indicate that only the 1,3-adducts (1) can be formed by a concerted homopolar process.³

Additions of the C_5 - C_8 cyclic mono-olefins are qualitatively and quantitatively dependent on the olefin (Table). The high quantum yields, especially with cyclo-octenes, are noteworthy in view of the tendency to discuss the gas-phase photochemistry of benzene largely in terms of photo-physical processes. Although 1,3-addition always occurs, 1,2-adducts were only detected in the cases of *cis*- and

is not known, but in the cases of ethyl vinyl ether and tetramethylethylene we have observed a marked effect of polar



solvents (MeOH, MeCN) in promoting the 1,2-process: $\Phi_{1,2}$ is increased 20–50%. In contrast, $\Phi_{1,3}$ is unaffected by

TABLE

Olefin	Ionisation potential	$\Phi_{1,3}$	$\Phi_{1,2}$	$\Phi_{1,2}/\Phi_{1,3}$	Φ_{other}	Total Φ^c
<i>cis</i> -dimethoxyethylene ^a	7.97 ^b	No adducts observed				
<i>trans</i> -dimethoxyethylene ^a	8.04 ^b	0.04	0.03 (total)	1.3		
tetramethylethylene ^a	8.3	0.25	0.03	8	0.03 (ene product) ⁷	0.31
ethyl vinyl ether ^a	8.6	0.2	0.06 (total)	3.3		
<i>trans</i> -cyclo-octene ^a	8.51 ^b	0.37	0.14, 0.14	1.3 ^h		0.65
<i>cis</i> -di- <i>t</i> -butylethylene ^a	8.71 ^b	No adducts observed ^g				
<i>cis</i> -cyclo-octene ^a	8.75 ^b	0.09	{ 0.31 (<i>cis endo</i>) 0.07 (<i>cis exo</i>) }	0.24 ^h		0.47
<i>cis</i> -cyclononene ^a	8.78 ^b	—	0.13 <i>cis endo</i> + <i>cis exo</i>		0.02, 0.02 ^f	0.17
cycloheptene ^a	8.86 ^b	—	{ 0.16 (<i>cis endo</i>) 0.11 (<i>cis exo</i>) }		0.01, 0.01 ^f	0.29
cyclohexene ^e	8.94 ^b	—			0.06 (olefin dimer)	0.25
cyclopentene ^a	9.02 ^b	—	{ 0.17 (<i>cis endo</i>) 0.02 (<i>cis exo</i>) }			
<i>trans</i> -but-2-ene ²	9.13	0.1 ^d	0.33 ^d	0.3 ^h	0.01–0.02 } 1, 4-	0.44–0.45
<i>cis</i> -but-2-ene ²	9.13	0.06 ^d	0.40 ^d	0.15 ^h	0.01–0.02 } addition	0.47–0.48
benzene	9.24 ^b					
methyl vinyl ketone ^a	9.61 ^b	0.02				0.02
maleimide	10.28 ^b	} <i>ca.</i> 0.1				
maleic anhydride	11.11 ^b					
acrylonitrile ^a	10.88 ^b		0.09			

^a Irradiations carried out on 1.1M benzene and 3.5 M olefin solutions in iso-octane at 20° using an ozone-free, quartz low-pressure-mercury arc (1×10^{-7} E/min) (Primarc Ltd.). ^b Ionisation potentials measured on a Perkin Elmer PS-18 Photoelectron Spectrometer. ^c Limit of adduct detection corresponds to $\Phi < 0.003$ under the conditions outlined in (a). ^d Measurements for 10% benzene–90% olefin solutions. ^e Under conditions (a) employed for determination of the quantum yields, no adducts from cyclohexene could be detected, but irradiation of a 10% v/v solution of benzene in cyclohexene gave 1,3-adduct(s) ($\Phi < 0.01$) and olefin dimers. The anomalous behaviour of cyclohexene will be the subject of a future publication. ^f Values of Φ (other) are based on observed molecular weights and the assumption that one quantum is involved in the formation of each product. ^g Models indicate that both 1,2- and 1,3- adducts would be seriously overcrowded. ^h Ratios invariant with olefin concentration.

trans-cyclo-octenes: these olefins have the lowest ionisation potentials of the group. Although some of the differences in ionisation potentials are numerically small, it seems significant that *cis*- and *trans*-cyclo-octene undergo no detectable 1,2-cycloaddition to the weaker acceptor toluene (I.P. 8.82 eV) and only the 1,3-process occurs, whereas the stronger acceptor benzonitrile (I.P. 9.71 eV) undergoes 1,2-addition of simple olefins including *cis*-cyclo-octene, with no detectable formation of 1,3-adducts.⁴ For additions to benzene, it appears that $\Phi_{1,2} > \Phi_{1,3}$ when $9.6 < \text{I.P. (ethylene)} < 8.65$ eV. If this is correct, it follows that 1,2-addition of ethylenes to S_1 benzene necessarily involves an element of charge transfer to or from the ethylene (ref. 3). The degree of polarity of the transition state for 1,2-addition

changes in solvent polarity in all cases so far examined.

Although 1,3-cycloadditions to benzene preserve the stereochemistry of the ethylene they give both *endo*- and *exo*-adducts.^{1,5} In contrast, ethylenes of donor or acceptor type give a single 1,2-adduct with benzene. The *endo* structure of the adduct (2) from *cis*-cyclo-octene has been established by X-ray crystallographic analysis of its maleimide adduct.⁶ An *endo* structure has previously been suggested for the photoadduct of *cis*-but-2-ene on the basis of n.m.r. evidence.² Where *endo* addition is sterically hindered, as with *cis*-dimethoxyethylene and *cis*-di-*t*-butylethylene, it seems significant that neither this nor the unhindered *exo*-addition occurs. In comparison, the acceptor maleimide gives a single 1,2-adduct having the *exo*-structure (3).

Other acceptors, including acrylonitrile, citraconic anhydride, and methyl vinyl ketone, also give a single 1,2-adduct with benzene which in each case has been provisionally assigned an *exo*-structure on the basis of n.m.r. evidence: it is hoped that more conclusive structural assignments will be provided from crystallographic studies.

It appears that 1,2-photoaddition to benzene differs from the 1,3-process in requiring an ethylene of either donor or acceptor character: the donors add *endo*, and the acceptors add *exo*.

(Received, 20th February 1974; Com. 221.)

¹ D. Bryce-Smith, *Pure Appl. Chem.*, 1973, **34**, 193 and references therein.

² K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073.

³ D. Bryce-Smith, *Chem. Comm.*, 1969, 806.

⁴ M. A. Hems, Ph.D. thesis, Reading 1967, p. 211; see also D. E. Ayer, G. H. Büchi, and E. W. Robb, *J. Amer. Chem. Soc.*, 1963, **85**, 2257.

⁵ B. H. Orger, Ph.D. thesis, Reading 1969; R. Srinivasan, *Tetrahedron Letters*, 1971, 4551; *J. Phys. Chem.*, 1972, **76**, 15.

⁶ Work in collaboration with Dr. M. G. B. Drew and Mr. A. Wolters: details to be published elsewhere.

⁷ D. Bryce-Smith, B. E. Foulger, A. Gilbert, and P. J. Twitchett, *Chem. Comm.*, 1971, 794.