Correlation between Selectivity in Photochemical Cross-cycloaddition and Ionization Potential of the Reacting Olefins

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Summary The selectivity (the ratio of crossadducts to homodimers) in the photochemical [2 + 2] cross-cyclo-addition of a 1:1 mixture of several series of (E)-olefins (1) and methyl p-nitro-(E)-cinnamate (2) was found to increase regularly with decreasing ionization potential of (1).

WE describe here the first example where the selectivity in the photochemical [2+2] cross-cycloaddition of several series of (E)-olefins (1) with methyl p-nitro-(E)-cinnamate (2) can be correlated with a physicochemical property (the ionization potential) of (1).

An equimolar mixture of the (E)-olefin (1) and methyl p-nitro-(E)-cinnamate (2) in benzene (0·05 mol dm⁻³ each) was irradiated with a 450 W high pressure mercury lamp for 3 h under argon. T.l.c. of the residue gave cyclobutane
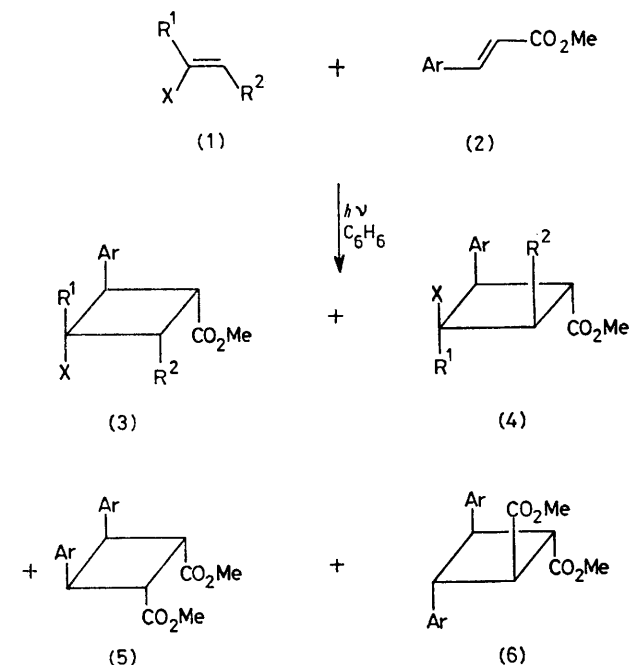
R¹   R²   R¹   R²
a   CH₂=CH   Me   j   p-PrⁱC₆H₄   CO₂Me
b   CH₂=CMe   H   k   p-ClC₆H₄   CO₂Me
c   CH₂=CH   H   l   p-NCC₆H₄   CO₂Me
d   Ph   H   m   MeO₂CCH=CH   Me
e   Ph   H   n   Me[CH₂]₃   H
f   Ph   CO₂Me   o   MeC(:O)O   H
g   Ph   CN   p   H   CO₂Me
h   p-MeOC₆H₄   CO₂Me   q   H   CN
i   p-MeC₆H₄   CO₂Me

X = Me for compound (d) and H for all other compounds.

derivatives generally containing cis-(3) and trans-head-to-head crossadducts (4) together with cis-(5) and trans-head-to-head homodimers (6)[1] of (2). Assignment of the structures of these products is based on their n.m.r. and mass spectra.[1,2]

In the case of the three series of (E)-olefins [1,3-dienes (1a—c),† styrene derivatives (1d—g), and methyl para-substituted (E)-cinnamates (1h—l) and (1f)], irradiation in the presence of (2) led to the formation of cross-cyclo-adducts in 8—90% yields (Table); the ionization potentials of these olefins‡ are shown in the Figure. In contrast, various mono-olefins [hex-1-ene (1n), vinyl acetate (1o), methyl acrylate (1p), and acrylonitrile (1q)], gave no crossadducts with (2), even when used in 7-fold excess. These mono-olefins have ionization potentials§ > ca. 9·7 eV. These findings indicate that in order for the cross-cycloaddition to take place, the ionization potential of the olefin (1) must be lower than that (ca. 9·3 eV) of (2).
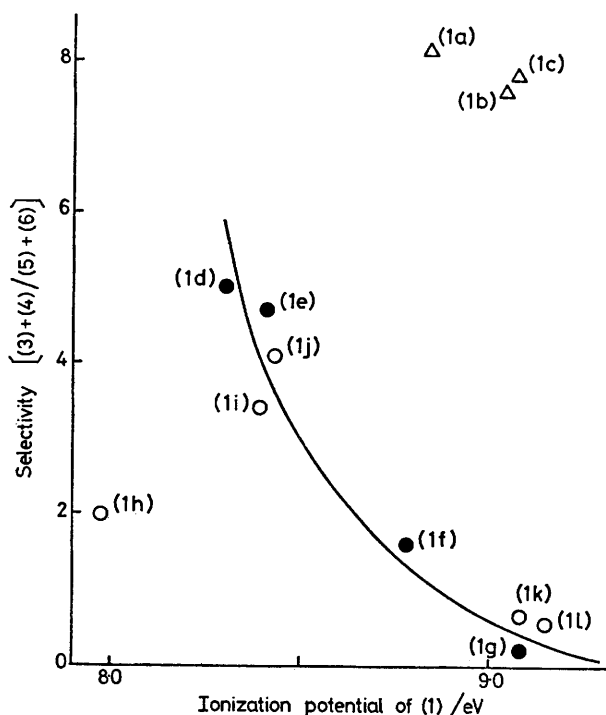

FIGURE. Dependence of the selectivity [(3) + (4)/(5) + (6)], in the photochemical [2 + 2] cross-cycloaddition of a 1:1 mixture of (1) and (2), upon the ionization potential of (1); △, 1,3-diene series (1a—c); ●, styrene series (1d—g); and ○, methyl para-substituted (E)-cinnamate series (1h—l) and (1f). For the 1,3-diene series, the notation '(3)+(4)' represents all the crossadducts isolated (see footnote d in the Table). The point for methyl sorbate (1m) is not shown, since its ionization potential could not be estimated by the method employed.‡

The Figure shows that there is a close relationship between the selectivity [the ratio of crossadducts (3) and (4) to homodimers (5) and (6)] in this cross-cycloaddition and the ionization potential of (1): the selectivity increases

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† When piperylene (1a) was used, only methyl p-nitro-(E)-cinnamate (2) successfully underwent the cross-cycloaddition among a series of methyl para-substituted (E)-cinnamates examined.

‡ The ionization potentials of (1a—l) were estimated from the charge-transfer spectra in 1,2-dichloroethane with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) as acceptor, by using the well known linear relationship between ionization potential and frequency of the charge-transfer band for a series of complexes of electron donors with a given acceptor; see, for example, E. M. Voigt and C. Reid, J. Amer. Chem. Soc., 1964, 86, 3930.

§ Hex-1-ene (1n), 9·65 eV; vinyl acetate (1o), 9·85 eV; methyl acrylate (1p), 10·72 eV; and acrylonitrile (1q), 10·92 eV; see, for example, J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' U.S. Department of Commerce, National Bureau of Standards, 1969.

TABLE

Yields of products (isolated)[a], %

Olefin Reactants (1) + (2)	Crossadducts[b]		Homodimers[c]		Selectivity $\left(\dfrac{\text{Crossadducts } [(3) + (4)]}{\text{Homodimers } [(5) + (6)]}\right)$
	cis-Isomer (3)	trans-Isomer (4)	cis-Isomer (5)	trans-Isomer (6)	
(1a)	67[d]		2·8	5·4	8·2
(1b)	55[d]		2·1	5·2	7·5
(1c)	90[d]		3·8	7·8	7·8
(1d)	37	16	2·9	7·7	5·0
(1e)	11	42	5·6	5·7	4·7
(1f)	12	31	12	15	1·6
(1g)	2·1	6·2	9·1	27	0·23
(1h)	19	36	13	14	2·0
(1i)	13	39	7·1	8·2	3·4
(1j)	19	40	6·4	7·9	4·1
(1k)	2·0	25	13	28	0·66
(1l)	5·0	13	12	20	0·56
(1m)	26[d]		7·1	13	1·3
(1n)	0		9·0	19	0
(1o)	0		15	34	0
(1p)	0		13	31	0
(1q)	0		16	34	0

[a] In all experiments described here, methyl *para*-substituted (E)-cinnamates (1f) and (1h—l) were recovered in varying amounts, and polymeric substances were formed in small amounts. [b] Crossadducts consisted of the two [cis- (3) and trans- (4)] head-to-head isomers except in the case of the 1,3-diene series [(1a—c) and methyl sorbate (1m)], the amounts of head-to-tail isomers being negligible under the reaction conditions (in benzene). [c] Homodimers of (2) consisted, in all cases, of the two [cis-(5) and trans-(6)] head-to-head isomers, the amounts of head-to-tail isomers being negligible under the reaction conditions. The formation of homodimers of (1d—l) could not be detected, whereas for the 1,3-diene series and mono-olefins it was not confirmed whether their homodimers were formed or not. [d] In the case of the 1,3-diene series, crossadducts consisted of several isomers, whose structures (whether head-to-head or head-to-tail, and whether cis or trans) remain unidentified. The number of isomers involved in crossadducts is 4 for piperylene (1a), 4 for isoprene (1b), at least 2 for 1,3-butadiene (1c), and 3 for methyl sorbate (1m). Therefore, in these cases, the notation '(3) + (4)' represents all the crossadducts isolated.

regularly with decreasing ionization potential of (1), for both the styrene and methyl *para*-substituted (E)-cinnamate series; for the 1,3-diene series this relationship is less obvious. However, the ionization potential of methyl *p*-methoxy-(E)-cinnamate (1h) is lower than would be expected from the selectivity (cf. Figure), and the reason for this remains to be resolved.

[1] D. A. Ben-Efraim and B. S. Green, Tetrahedron, 1974, 30, 2357; B. S. Green and L. Heller, J. Org. Chem., 1974, 39, 196.
[2] T. Ishigami, T. Murata, and T. Endo, Bull. Chem. Soc. Japan, 1976, 49, 3578.