Photocyclodimerization of Alkyl, Benzyl, and Trimethylsilyl Vinyl Ethers in the Presence of 1,4-Dicyanonaphthalene

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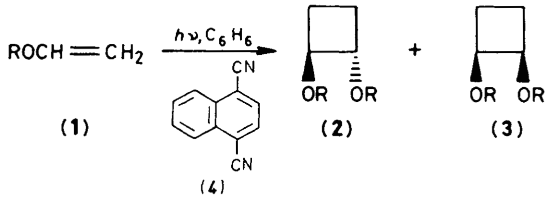
Irradiation of alkyl, benzyl, and trimethylsilyl vinyl ethers in the presence of 1,4-dicyanonaphthalene in benzene affords *trans*- and *cis*-head-to-head cyclodimers in a 1 : 1 ratio.

Aryl vinyl ethers undergo photocyclodimerization *via* their dimer cation radicals in acetonitrile in the presence of an electron acceptor.[1-3] However, in the case of alkyl vinyl ethers, the efficiency of this photoreaction decreases markedly under similar conditions.[1,4] We now report that the photocyclodimerization of alkyl, benzyl, and trimethylsilyl vinyl ethers proceeds efficiently in benzene in the presence of 1,4-dicyanonaphthalene.

Irradiation of a benzene solution (100 ml) containing ethyl vinyl ether (**1b**) (100 mmol) and 1,4-dicyanonaphthalene (**4**) (5 mmol) through Pyrex with a 300 W high-pressure mercury arc gave *trans*- and *cis*-1,2-diethoxycyclobutane (**2b**) and (**3b**) (2.8 g, 39%) in a 1 : 1 ratio,† which were stable under these conditions. Similar irradiation of other vinyl ethers (**1a**) and (**1c**—**g**) in the presence of (**4**) gave respectively the corresponding [2 + 2] cyclodimers (**2a**), (**2c**—**g**) and (**3a**), (**3c**—**g**) in good yields with 50—70% recovery of (**4**); the ratios of (**2**) to (**3**) were about 1 : 1 in each case (Table 1).

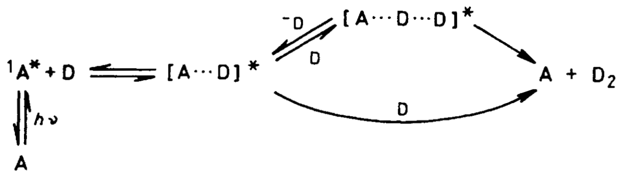


R = alkyl, PhCH$_2$, or Me$_3$Si

The cycloadducts were isolated by column chromatography on silica gel or preparative g.l.c., and their structures were assigned from their ^{1}H n.m.r. and mass spectra. 9,10-Dicyanoanthracene was found to be an effective sensitizer, whereas 1-cyanonaphthalene and 9-cyanophenanthrene were rapidly consumed, giving [2 + 2] photocycloadducts with the vinyl ethers.[5]

No cyclodimers were obtained in the absence of sensitizer. The photocyclodimerization of the vinyl ethers (**1**) in the presence of (**4**) in acetonitrile occurred far less efficiently than in benzene. This is in sharp contrast to the photocyclodimerization of aryl vinyl ethers that proceeds efficiently in acetonitrile *via* their dimer cation radicals.[1-3]

The fluorescence of (**4**) was efficiently quenched by (**1b**—**g**) in both benzene and acetonitrile, giving linear Stern–Volmer plots (Table 1).‡ The photoreactions reported here probably involve a termolecular interaction leading to the triplex [A · · · D · · · D]*, or a bimolecular process



Scheme 1. A, (**4**); D, (**1a**—**g**); D$_2$, (**2a**—**g**) and (**3a**—**g**).

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† The u.v. spectra revealed that the charge-transfer complexes between (**1**) and (**4**) are not formed in the ground state.

‡ The exciplex emission was not observed in both solvents.

Table 1. Photocyclodimerization of vinyl ethers in the presence of (**4**).

Substrate (**1**):R	Irradn. time/h	% Yield[a] (**2**) and (**3**)	B.p., t/°C (p/Torr)	$k_q\tau^b$/mol^{-1} dm^3	
				C_6H_6	MeCN
a; Me	72	55	122—124 (760)		
b; Et	72	70 (39)	80—81 (73)	41	82
c; Bu^n	72	65 (46)	98—100 (10)	34	75
d; Bu^t	72	65 (47)	86—87 (10)	35	78
e; Cyclohexyl	72	70 (54)	120—125 (0.55)	37	60
f; $PhCH_2$	36	45 (34)[c]	150—155 (0.3)	33	85
g; $SiMe_3$	48	50 (34)	77—78 (13)	34	80

[a] Total yields of (**2**) and (**3**) were determined by g.l.c. and 60 MHz ^1H n.m.r. spectroscopic analyses of the reaction mixtures in C_6D_6. Values in parentheses were isolated yields based on the substrates used. [b] The $k_q\tau$ values were obtained from the fluorescence quenching of (**4**) in aerated solutions. [c] The starting vinyl ether (**1f**) was recovered in 52% yield.

between the exciplex [A · · · D]* and D as shown in Scheme 1.[6] An electron transfer mechanism involving ion radicals is unlikely in these photoreactions.

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