

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

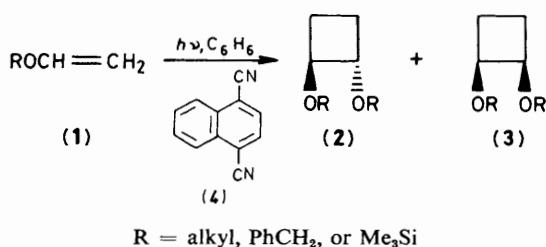
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Irradiation of alkyl, benzyl, and trimethylsilyl vinyl ethers in the presence of 1,4-dicyanonaphthalene in benzene affords *trans*- and *cis*-head-to-head cyclodimers in a 1 : 1 ratio.

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.

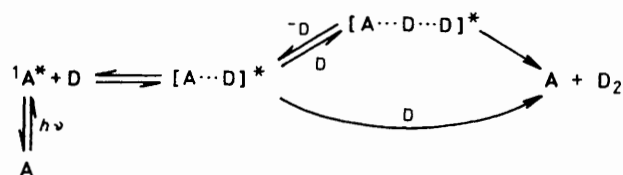
Irradiation of a benzene solution (100 ml) containing ethyl vinyl ether (**1b**) (100 mmol) and 1,4-dicyanonaphthalene (**4**) (5 mmol) through Pyrex with a 300 W high-pressure mercury arc gave *trans*- and *cis*-1,2-diethoxycyclobutane (**2b**) and (**3b**) (2.8 g, 39%) in a 1 : 1 ratio,[†] which were 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).



The cycloadducts were isolated by column chromatography on silica gel or preparative g.l.c., and their structures were assigned from their ¹H 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**); D₂, (**2a-g**) and (**3a-g**).

[†] 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 ₆ H 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 C₆D₆. 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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