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REGIO- AND STEREOSELECTIVE INTRAMOLECULAR PHOTOCYCLOADDITION: SYNTHESIS OF MACROCYCLIC 2,ω-DIOXABICYCLO[n.2.0] RING SYSTEM

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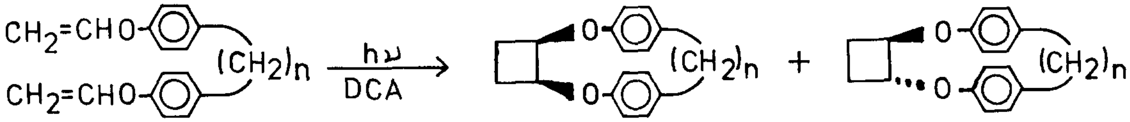
Summary: The intramolecular photocycloaddition of 1,ω-bis(4-vinyloxyphenyl)alkanes (n=4-7,12,20) in the presence of 9,10-dicyanoanthracene in benzene and acetonitrile affords the corresponding cis- and trans-cycloadducts in good yields.

Intramolecular photoaddition between two chromophores which are situated in remote positions in a molecule has been actively investigated in recent years.[1] Recently, we have demonstrated that phenyl vinyl ether undergoes a highly stereoselective photocyclodimerization upon irradiation in the presence of an electron acceptor under certain conditions.[2,3] As an extension of this reaction, we studied the photochemistry of the molecules bearing two vinyloxy groups which are connected by various length of methylene chain. The photoreaction occurred efficiently to give a macrocyclic 2,ω-dioxabicyclo[n.2.0] ring system, and the results are described in this paper.

Irradiation of acetonitrile solutions of **1a-f**(3×10^{-3} mol/dm^3) containing 9,10-dicyanoanthracene(DCA, 1×10^{-4} mol/dm^3) for 30-120 min with a high-pressure mercury lamp through Pyrex filter gave cis- and trans-cycloadducts, **2a-f** and **3a-f**, in good yields.[4] However, irradiations of **1b-d** in benzene in the presence of DCA for 30-50 h afforded **2b-d** and **3b-d** in ratios different from those obtained in the photoreaction in acetonitrile. No intramolecular cycloaddition occurred upon a direct excitation of **1a-f**.



1a~f n=4~7,12,20 **2a~f** **3a~f**

The photocycloadducts were isolated as crystalline materials by column chromatography on silica gel. The structures were assigned from the spectral (^{1}H NMR, IR, and mass) properties and elemental analyses.[5] The results are summarized in Table I.

The stereoselectivity in the intramolecular photocycloaddition depended strongly on the solvent employed(Table I). For **1a-b,e**, the cis isomers **2a-b,e**, were obtained as predominant products in acetonitrile, but in benzene the

Table I. Intramolecular Photocycloaddition of 1a-f.

1	Solvent	Conv %	Yield[a] 2+3, %	Ratio [2] : [3]	Mp, °C 2	Mp, °C 3	Ring size	Relative[b] efficiency
1a(n=4)	CH_3CN	65	25	96 : (4)[c]	147-150		16	0.58
1b(n=5)	CH_3CN	64	63	80 : 20	125-127	132-133	17	1.00
1b(n=5)	C_6H_6	62	85	10 : 90				
1c(n=6)	CH_3CN	40	66	36 : 64	128-130	118-120	18	0.72
1c(n=6)	C_6H_6	58	59	5 : 95				
1d(n=7)	CH_3CN	62	39	46 : 54	84-87	103-106	19	0.57
1d(n=7)	C_6H_6	45	80	≤ 5 ≥ 95				
1e(n=12)	CH_3CN	93	54	69 : 31	67-68	61-63	24	d
1f(n=20)	CH_3CN	89	66	42 : 58	54-56	55-57	32	0.63

[a] Based on 1 consumed. [b] Formation of 2b and 3b as a standard. Using a Pyrex filter on a merry-go-round. [c] Not isolated. [d] Not determined.

formation of the trans isomers generally predominated. Such a solvent effect on the stereoselectivity has also been observed in the intermolecular photocycloaddition of phenyl vinyl ether.[2b]

In the case of 1c-d, the cis isomers 2c-d were rather the minor products even in the photoreaction in acetonitrile. The molecular model suggests that the conformations of the intermediates leading to 2c-d are less favorable than those leading to the trans isomers 3c-d by a steric reason.

Striking features of this photoreaction are that the macrocyclic compounds are efficiently formed from the flexible open chain compounds and the efficiency of the cyclization is substantially independent of the sizes of macrocycles to be constructed(Table I). Therefore, this type of the photoreaction can be utilized as a key reaction of the synthesis of macrocyclic molecules.

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2. (a) K. Mizuno, H. Kagano, T. Kasuga, and Y. Otsuji, Chem. Lett., 133(1983). (b) K. Mizuno and Y. Otsuji, to be published.
3. S. Kuwata, Y. Shigemitsu, and Y. Odaira, J. Org. Chem., 38, 3803(1973).
4. Compounds 1a-f were synthesized by dehydrochlorination of the corresponding 1,ω-bis(β-chloroethoxyphenyl)alkane: K. Mizuno, Y. Kimura, and Y. Otsuji, Synthesis, 688(1979).
5. All new compounds obtained here afforded satisfactory spectral data and elemental analyses.

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