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SINGLET-PHOTOSENSITIZED RING-SPLITTING AND ISOMERIZATION REACTIONS OF 1,2-DIPHENYLCYCLOBUTANE BY AROMATIC NITRILES. A POSSIBLE PROBE FOR RELATIONSHIPS BETWEEN REACTIVITIES AND ELECTRONIC NATURE OF EXCIPLEX INTERMEDIATES[1)]

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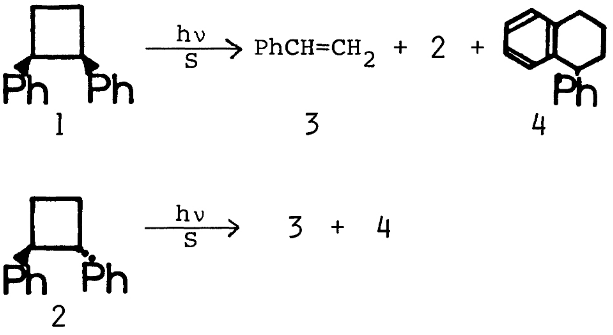
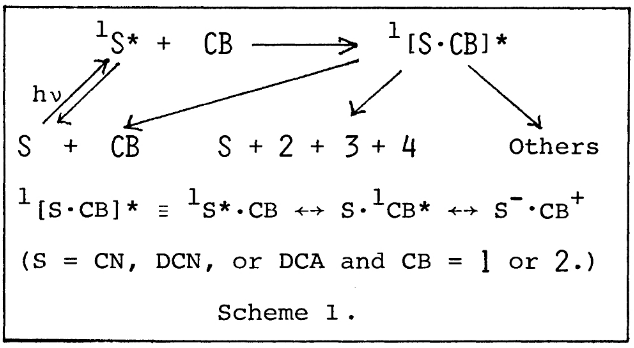
The photosensitized reactions of cis-1,2-diphenylcyclobutane by 1,4-dicyanonaphthalene and 9,10-dicyanoanthracene gave styrene, the trans isomer, and 1-phenyltetralin whereas the photosensitization by 1-cyanonaphthalene effected the ring-splitting and cis,trans-isomerization reactions without the formation of 1-phenyltetralin. Similar reactions of the trans isomer were photosensitized by the aromatic nitriles though the trans,cis isomerization did not occur. Features of the reactions were discussed in terms of exciplex intermediates of different charge-transfer and excitation-resonance contributions.

Bond-cleavage reactions of cyclobutane compounds can provide excellent probes to explore mechanistic details as well as to manifest steric and electronic factors operating in reaction courses.[2-4)] Recently a novel type of photosensitization which is induced by electron transfer has been successfully utilized to investigate mechanistic aspects of ring-cleavage reactions involving ion-radical species.[4-6)] On the other hand, only a few papers [7,8)] on singlet-photosensitized reactions of cyclobutanes by way of exciplexes have appeared since the first pulication[9)] on the photosensitized isomerization of quadricyclane to norbornadiene by aromatic hydrocarbons. In this photosensitized isomerization, controversy still remains on relative importance of charge-transfer (CT) and excitation-resonance (ER) contributions of hypothetical exciplex intermediates.[9-11)] The present paper deals with the photosensitized reactions of cis- and trans-1,2-diphenylcyclobutane (CB = **1** and **2**) by 1-cyanonaphthalene (CN), 1,4-dicyanonaphthalene (DCN), or 9,10-dicyanoanthracene (DCA), which reveal the dependency of product distribution on both the excitation energies (*E) and the reduction potentials (*E_{red}) of the sensitizers (S) in the excited singlet state as well as on solvent polarity.

The ring cleavage of 1 or 2 to styrene (3) and the isomerization of 1 to 2 commonly occurred upon photosensitization by each S, whereas the isomerization of 1 or 2 to 1-phenyltetralin (4) was photosensitized by either DCN or DCA but not at all by CN. On the other hand, the isomerization of 2 to 1 did not occur by photosensitization using any S. It was confirmed that the disappearance of S is much slower than the formation of the products in each case. Table 1 lists quantum yields for the formation of each product together with *E and *E_{red} of S.





Scheme 1.

Table 1. Quantum Yields and Product Ratios in the Photosensitized Reactions of 1,2-Diphenylcyclobutane by Aromatic Nitriles[a)]

CB[b)]	S	*E[c)] eV	$-E_{red}$[d)] V	*E_{red}[e)] V	Solvent	ϕ_3 (x 10^3)	ϕ_2 (x 10^3)	ϕ_4 (x 10^3)	$\phi_3 : \phi_2 : \phi_4$
1 (1.29)	CN	4.13	2.33	1.80	PhH	11	3.8	0.0	2.9: 1 :0.00
	DCN	3.69	1.05	2.64	C_6H_{12}	210	30	14	7 : 1 :0.47
					AcOEt	190	41	31	4.6: 1 :0.76
	DCA	2.91	1.12	1.79	PhH	54	9.8	1.2	5.5: 1 :0.13
					AcOEt	44	8.8	2.0	5 : 1 :0.23
2 (1.33)	CN				PhH	0.1		0.0	
	DCN				C_6H_{12}	19		2.8	6.8: - :1
	DCA				PhH	0.35		f	

a) [1] or [2] = 2 x 10^{-2} mol dm^{-3}; irradiation at 313 nm for the CN and DCN runs and at 436 nm for the DCA runs. b) In parentheses are the half-peak oxidation potentials vs. Ag/Ag^+ in acetonitrile. c) The lowest excited singlet-state energies of S estimated from the 0-0 bands of fluorescence. d) The reversible half-wave reduction potneitals vs. Ag/Ag^+ in acetonitrile. e) *E + E_{red}. f) Not determined.

Figure 1 shows the appearance of a new longer-wavelength emission following quenching of the fluorescence of CN by 2 , thus demonstrating the intervention of an exciplex in the fluorescence quenching. In line with this exciplex mechanism, the rate constant for quenching of the DCN fluorescence by 2 (8.1×10^9 $dm^3 mol^{-1} s^{-1}$ in cyclohexane) is greater than that of CN (5.1×10^8 $dm^3 mol^{-1} s^{-1}$ in benzene), apparently arising from greater $*E_{red}$ of DCN. Consequently, it is reasonable to assume that the photosensitized reactions proceed via exciplexes formed between CB and excited-singlet S ($^1S*$),[12)] as is shown in Scheme 1.

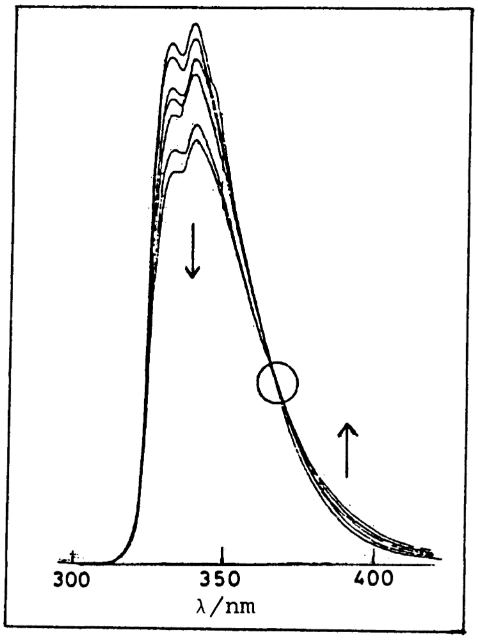


Fig. 1. Fluorescence spectra of CN in aerated benzene taken at different concentrations of 2; an isoemissive point is shown in the circle. The fluorescence quenching follows a linear Stern-Volmer plot with a slope of 4.5 dm^3 mol^{-1}.

It is well-known that relative contributions of ER and CT of exciplexes can be qualitatively estimated by $*E$ and $*E_{red}$. The large $*E_{red}$ of DCN indicates dominant CT contributions of the DCN exciplexes, while ER contributions should be important for the CN exciplexes because of the large $*E$. Since $*E$ of DCA is too low to allow significant ER, the binding origin of the DCA exciplexes exclusively comes from CT contributions. It can therefore be speculated that 4 is a specific product from higher CT contributions whereas ER contributions are operative, but not specific, for the formation of 2 and 3. In accord with this speculation, the direct or triplet-sensitized photoexcitation of 1 mainly gives 2 and 3[13)] while 4 is the exclusive product in the redox-photosensitized reactions of 1 and 2 [14)] occurring by interactions with the photogenerated cation radical of aromatic hydrocarbons.[4)] Moreover, the $\phi_4/(\phi_2 + \phi_3)$ values in the DCA- and DCN-photosensitized reactions of 1 in ethyl acetate are twice or greater as large as those in the nonpolar solvents; the formation of 4 is certainly more ionic in nature than those of 2 and 3.

Although stereospecificity of the ring cleavage has not been established yet, the isomerization reactions should involve the C_1-C_2 bond being broken or elongated in transition states. However, the decay pathways from the exciplexes to 2 or 4 might differ from each other since electronic requirements for each isomerization are different. Moreover, it should be noted that the ϕ_2/ϕ_3 values vary from system to system, implying different decay pathways for each reaction. In other words, chemistry of the exciplexes may have diverse channels, each of which is affected by CT and ER contributions.

References

1) Photochemical Reactions of Aromatic Compounds. Part 39. Part 38: C. Pac, K. Mizuno, and H. Sakurai, Nippon Kagaku Kaishi, 1984, 110; Part 37: C. Pac, M. Yasuda, K. Shima, and H. Sakurai, Bull. Chem. Soc. Jpn., 55, 1605 (1982).

2) H. Sakurai, S. Takamuku, and S. Toki, Mem. Inst. Sci. Ind. Res., Osaka Univ., 39, 55 (1982).

3) E. Schauman and R. Ketcham, Angew. Chem., Int. Ed. Engl., 21, 225 (1982).

4) C. Pac, J. Kubo, T. Majima, and H. Sakurai, Photochem. Photobiol., 36, 273 (1982); T. Majima, C. Pac, and H. Sakurai, J. Am. Chem. Soc., 102, 5265 (1980); J. Chem. Soc., Perkin Trans. 1, 1980, 2705.

5) G. Jones II, W. Schwarz, and V. Melva, J. Phys. Chem., 86, 2286 (1982); H. D. Roth and M. L. M. Schilling, J. Am. Chem. Soc., 103, 7210 (1981).

6) T. Mukai, K. Sato, and Y. Yamashita, J. Am. Chem. Soc., 103, 670 (1981); H. D. Roth, M. L. M. Schilling, T. Mukai, and T. Miyashi, Tetrahedron Lett., 24, 5815 (1983).

7) S. Takamuku, T. Kuroda, and H. Sakurai, Chem. Lett., 1982, 377.

8) E. Hasegawa, K. Okada, and T. Mukai, Abstracts of Symposium on Photochemistry (Tsukuba, Japan), IIA 124, pp. 199 - 200 (1983).

9) L. M. Stephenson and G. S. Hammond, Pure Appl. Chem., 16, 125 (1968).

10) D. A. Labianca, G. N. Taylor, and G. S. Hammond, J. Am. Chem. Soc., 94, 3679 (1972); G. N. Taylor and G. S. Hammond, ibid., 94, 3684 and 3687 (1972).

11) B. S. Solomon, C. Steel, and A. Weller, Chem. Commun., 1972, 927.

12) The participation of triplet mechanisms can be eliminated since the reactions of **1** and **2** were not photosensitized at all by acetophenone or benzophenone in either the presence or absence of the aromatic nitriles.

13) G. Jones, II and V. L. Chow, J. Org. Chem., 39, 1447 (1974).

14) T. Gotoh, M. Kato, M. Yamamoto, and Y. Nishijima, J. Chem. Soc., Chem. Commun., 1981, 90.

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