CHEMISTRY LETTERS, pp. 1909 - 1912, 1984.

PHOTO-INDUCED HIGHLY SELECTIVE OLEFIN-MIGRATION OF *N*-(2- OR 3-PHENYLALLYL) AROMATIC IMIDES

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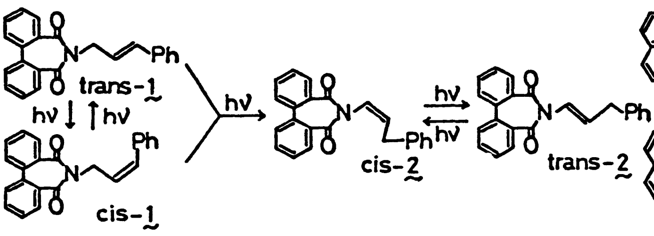
A Highly selective migration of double bond was observed on irradiation of *N*-(2- or 3-phenylallyl) aromatic imides in acetonitrile to afford *N*-(2- or 3-phenyl-1-propenyl) aromatic imides. The reaction seems to proceed via photochemical intramolecular one electron transfer from the double bond to the imide moiety.

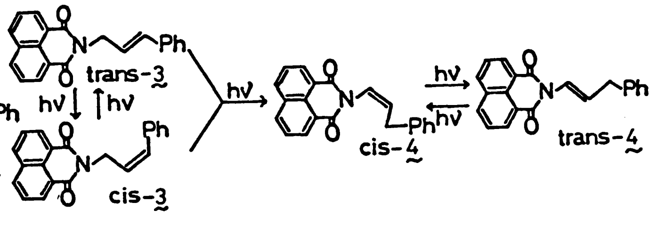
Recently, photoreactions involving electron-transfer process have received much attention from synthetic and mechanistic aspects in organic photochemistry.$^{1)}$ Numerous intermolecular photoreactions of A (electron acceptor) - D (electron donor: olefins) pairs in polar solvent have been studied in view of ion radical intermediate, A-D adduct formation,$^{2)}$ effect of addition of nucleophiles to the olefins,$^{3)}$ A-D adduct formation incorporating the nucleophiles.$^{4)}$ Other examples are homo-$^{5)}$ and hetero-dimerization,$^{6)}$ *cis*-*trans* isomerization,$^{7)}$ and oxidation of olefins.$^{8)}$ However, little is known about the intramolecular photoreactions of A-D pairs (where olefins as D), except for cyclization reactions associated with incorporation of certain nucleophiles.$^{4b,9)}$ Here we report on a highly selective photo-migration of the double bond in *N*-(2- or 3-phenylallyl) aromatic imides, which occurs probably via electron transfer within the intramolecular A-D systems.

Typically, irradiation of an acetonitrile solution of *trans*-*N*-(3-phenylallyl)diphenimide (*trans*-**1**) (10 mM, 1 mM = 1×10^{-3} mol dm^{-3}) under N_2 with a high pressure Hg-lamp through a Pyrex wall gave a mixture of two pairs of compounds, i.e., *trans*-**1**, *cis*-**1** and an isomeric pair of *trans*- and *cis*-*N*-(3-phenyl-1-propenyl)diphenimides (*trans*-**2** and *cis*-**2**, respectively).$^{10)}$ Time dependence of amounts of the four compounds in the reaction mixture examined by ^{1}H-NMR is shown in Fig. 1. Clearly, at the initial stage of irradiation of *trans*-**1** there occurs *trans*-*cis* isomerization of **1** together with selective photo-migration of the olefinic moiety into *cis*-**2**. During a prolonged irradiation *trans*-**2** increases only slowly. These results are summarized in Scheme 1.

The photochemical interconversion between *trans*-**2** and *cis*-**2** was confirmed by separate experiments, e.g., upon irradiation in an acetonitrile solution *trans*-**2** or *cis*-**2** was converted into an equilibrium mixture having a molar ratio of *trans*-**2** : *cis*-**2** = 0.95 : 1. Absorption spectra of the four compounds indicate that the absorbance of *trans*-**2** in >300 nm region is somewhat greater than those of other isomers.$^{11)}$ Hence, accumuration of *trans*-**2** in the reaction mixture with time appears to prevent further photo-migration of *trans*-**1** or *cis*-**1** into *cis*-**2** or



Scheme 1.



Scheme 2.

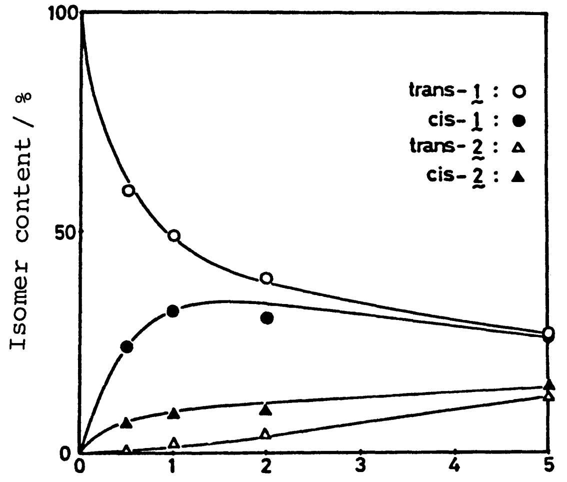


Fig. 1. Conversion of *trans*-1.

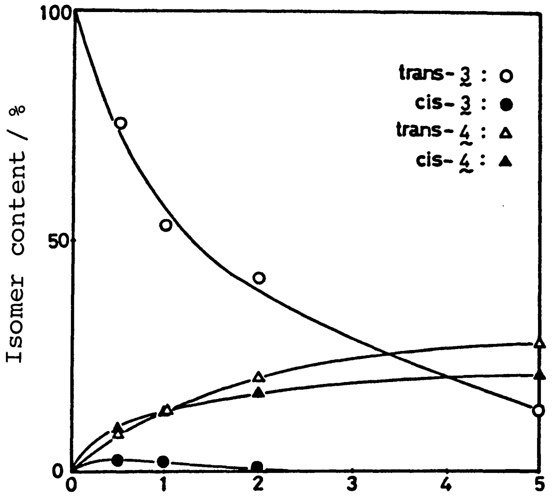
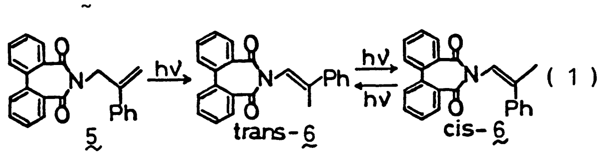


Fig. 2. Conversion of *trans*-3.

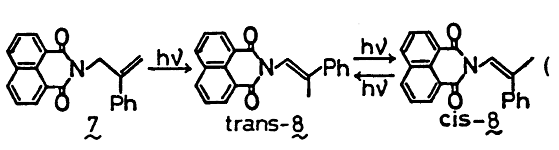
trans-2.

The intramolecular nature of the reactions was suggested from the fact that little concentration dependence on the rate of reaction was observed in a wide concentration range of 0.1-10 mM. The photo-migration of *trans*-1 (β-styryl moiety, Et = 250 kJ mol^{-1})[12] was not sensitized by benzophenone (Et = 290 kJ mol^{-1})[13] as a triplet sensitizer. This type of sensitization resulted only in *trans-cis* isomerization to give an equilibrium mixture of *trans*-1 and *cis*-1 (0.42 : 0.58).

The results of photolysis of *trans-N*-(3-phenylallyl)-1,8-naphthalimide (*trans*-3) are shown in Fig. 2 and Scheme 2. Despite the isomerization of *trans*-3



(1)



(2)

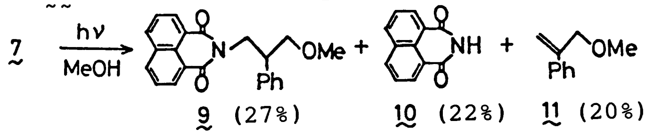
Table 1. Photo-reactions of 5 and 7[a)]

Starting material	Irradiation time / h	Product	Yield[b)] / % *trans*	Yield[b)] / % *cis*	Yield[c)] / % *trans*	Yield[c)] / % *cis*
5	0.5	6	5	1	20	4
	1		6	2	17	6
	5		12	6	17	9
7	0.5	8	5	1	71	14
	1		6	3	60	30
	5		17	14	41	34
	12		35	26	35	26

a) In acetonitrile (10 mM) under N_2 using a Pyrex filter. b) Based on the starting material used. c) Based on the starting material consumed.

into *cis*-3 being extremely slow, the photo-migration into *cis*-*N*-(3-phenyl-1-propenyl)-1,8-naphthalimide (*cis*-4) was likewise observed with lower selectivity than that of *trans*-1, together with photochemical interconversion between *cis*-4 and *trans*-4. Irradiation of *N*-(2-phenylallyl)diphenimide (5) gave *trans*-*N*-(2-phenyl-1-propenyl)diphenimide (*trans*-6) selectively, followed by photochemical interconversion between *trans*-6 and *cis*-6 (Eq. 1, Table 1). Similar results were obtained by irradiation of *N*-(2-phenylallyl)-1,8-naphthalimide (7) (Eq. 2, Table 1).

Combination of an aromatic imide and an aromatic olefin has been known as one of the typical electron transfer systems in photolysis.[9] As the example of relevant intermolecular reaction, photolysis of *N*-ethyl-1,8-naphthalimide with 1,1-diphenylethylene gave 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene in acetonitrile while methyl 2,2-diphenylethyl ether in methanol. These products have been suggested to be derived from 1,1-diphenylethylene radical cation,[5b] and methanol quenches the latter species. Thus, photolysis in methanol generally gives no detectable amounts of olefin-migration products, e.g., photolysis of 7 (10 mM) in methanol gave 9, an anti-Markownikoff addition product of methanol, together with 10 and 11, methanol incorporated elimination products (Eq. 3).[9b]



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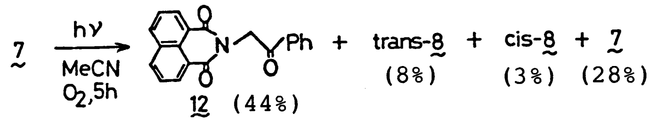
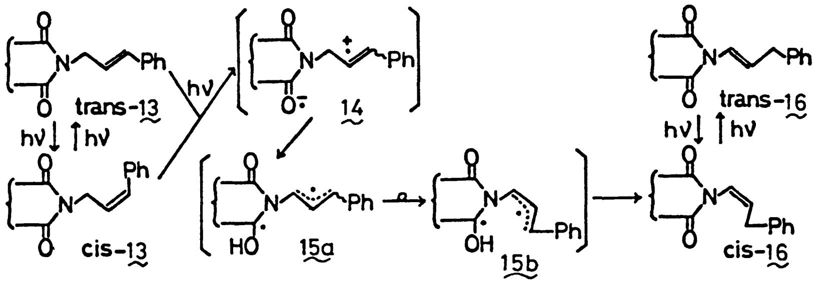


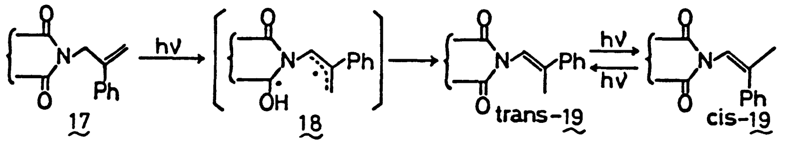
(4)

In acetonitrile the olefin-migration of 7 was quenched by oxygen; instead, *N*-(2-phenyl-2-oxoethyl)-1,8-naphthalimide (12) was formed probably via "electron-transfer photo-oxygenation" process (Eq. 4).[8b]

On the basis of these results, we propose the reaction mechanism for the photochemical olefin-migration of *trans*-1 and *trans*-3 (Scheme 3, where they are denoted as *trans*-13). The first step is photo-induced intramolecular electron transfer from the electron donating aromatic double bond to the excited aromatic imide moiety to form an intermediate 14. The second step is proton transfer from the *α*-position of olefinic radical cation to the carbonyl oxygen of imide radical anion moiety to form a biradical species 15. This step is associated with the



Scheme 3.



(5)

familiar deprotonation reaction from radical cations.[4b,14] The last step is intramolecular hydrogen transfer from the OH-group in the imide moiety to the α-position of phenyl group of 15.[15] The most favorable geometry of this step would be that shown as 15b where both of the reaction sites are in a close proximity. This steric requirement seems to be responsible for selective formation of *cis*-16. The same geometrical requirement of "close proximity of the reactive sites" reasonably leads 17 (terminal double bond) to *trans*-19 selectively (Eq. 5).

Although the reaction mechanism proposed is still tentative, extensive studies on a variety of intramolecular A-D system in this line would open a new stereochemistry of photo-reactions.

We are indebted to Mr. Tetsufumi Misawa for his experimental assistance.

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10) All new compounds obtained here afforded satisfactory spectral data (^{1}H-NMR, IR, UV, and mass) and elemental analyses.

11) Since intramolecular CT-complex formation was not observed, diphenimide moiety of *trans*-1 seemed to be directly excited by the light of >300 nm. Irradiation through a $CuSO_4 \cdot 5H_2O$ solution filter (25 g/100 ml) of 1 cm thickness (>320 nm), resulted in the same effects as shown in Fig. 1.

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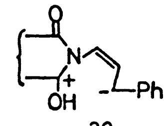
15) We cannot rule out the other possibilities; a proton may be transfered, instead of the hydrogen, via an electron migration through the conjugated system to form a zwitter ion 20.



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(Received August 13, 1984)