Photochemical Reactions of Aromatic Compounds. XI[1] The Photochemical Cycloaddition of Vinyl Ethers to α-Naphthonitrile

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The photochemical reactions of α-naphthonitrile with vinyl ethers gave two stereo-isomeric (2+2) cycloadducts, *trans*-1-cyano-8-alkoxy-2,3-benzobicyclo[4.2.0]octa-2,4-diene **1** and the *cis* isomer, **2**, in 80—90% yields. From the results of fluorescence measurements and kinetic analysis, the photocycloaddition was established to occur from the lowest excited singlet state of α-naphthonitrile.

Recently much attention has been paid to the photocycloaddition of unsaturated bonds to aromatic rings. Although the photocycloaddition to the benzene ring has been well investigated,[2] the cycloaddition to the naphthalene ring has been less investigated; only a few examples have been studied, the (2+2) addition of acrylonitrile[3] or diarylacetylenes[4] to naphthalene, the (2+2+2) addition of dimethyl acetylenedicarboxylate to naphthalene,[5] the (4+4) addition of acyclic dienes to naphthalene,[6] and the (4+4) addition of furan to α-naphthonitrile.[7]

The present paper will describe the photochemical (2+2) cycloaddition of alkyl vinyl ethers to α-naphthonitrile (α-NN) and will suggest that the photocycloaddition takes place *via* an exciplex generated from the lowest excited singlet state of α-NN.

Results

Irradiation-results and Structural Assignment of Products. The irradiation of a mixture of α-NN and a large excess of methyl vinyl ether in methanol or benzene with a high-pressure mercury arc at room temperature through a Pyrex glass (>300 nm) and under a nitrogen atmosphere gave two isomeric 1 : 1-adducts, **1a** and **2a**, in 80—90% yields when 90—95% of α-NN was consumed. The formation-ratio of **1a** to **2a** was dependent on the solvent used; it was *ca.* 1 for a benzene solution and 2—3 for methanolic and acetonitrile solutions, though the total yields of the products did not change with the solvents used.

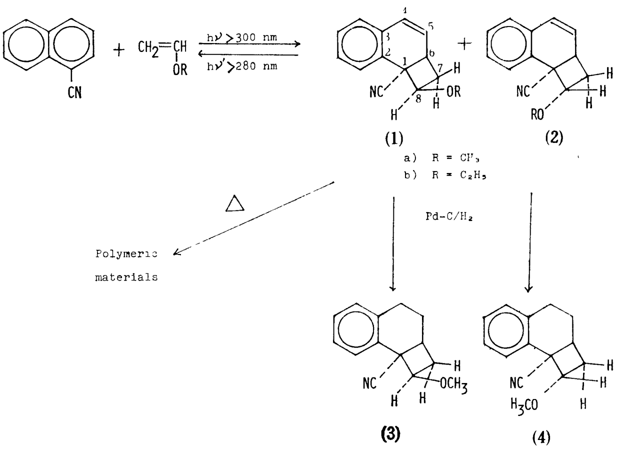

Chart 1.

The **1a** adduct, mp 86—87°C, was separated from **2a** by chromatography on the silica gel of the photolysate. On the other hand, **2a** could not be obtained in a pure form, since the chromatographic separation of **2a** from **1a** was incomplete and preparative vpc was not suitable because of the thermal instability of the adducts. Since **2a** was found to be thermally more stable than **1a** (*vide infra*), the photolysate from a benzene solution was subjected to thermolysis at 180—200°C; we thus obtained a mixture enriched with **2a**. The repeated chromatography of that mixture afforded **2a** containing only a small amount of **1a**.

The structure of the adducts was determined by IR, UV, and NMR analyses and by studying the mass spectroscopic data. The mass spectra of both adducts exhibit a weak parent peak at *m/e* 211, a strong peak at *m/e* 153 (α-NN), and a moderate peak at *m/e* 58 (C_3H_6O), along with other, far less important peaks. This fragmentation pattern strongly suggests the structure of 1 : 1-cycloadduct for the adducts. The two adducts have similar IR spectra, which show bands at 3040, 3020 (aromatic and olefinic C–H), 2990, 2930 (aliphatic C–H), 2210 (C≡N), 1640 (C=C), and 1140 cm^{-1} (C–O–C). The UV spectra, $\lambda_{\max}^{\text{MeOH}}$ (ε) 265 (7.6×10^3) and 300 nm (1.17×10^3) for **1a** and 265 (5.2×10^3) and 300 nm (sh) for **2a**, show that both adducts have a

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[1] Part X, C. Pac, T. Sugioka, and H. Sakurai, *Chem. Lett.*, **1972**, 39.

[2] K. Okumura, S. Takamuku, and H. Sakurai, *Kogyo Kagaku Zasshi*, **72**, 200 (1969); J. G. Atkinson, D. E. Ayer, G. Buchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963); B. E. Joband and J. D. Little-hailes, *J. Chem. Soc. C*, **1968**, 886; R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **87**, 4653 (1965); R. Srinivasan, *ibid.*, **93**, 3555 (1971); N. C. Perrins and J. P. Simons, *Chem. Comm.*, **1967**, 999; H. Morrison and W. I. Ferree, *ibid.*, **1969**, 268; G. Koltzenburg and K. Kraft, *Tetrahedron Lett.*, **1966**, 389; K. Kraft and G. Koltzenburg, *ibid.*, **1967**, 4357; K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2067 (1966); **93**, 2073 (1971); D. Brce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968); W. M. Hardham and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3200 (1967); J. D. Bradshaw, *Tetrahedron Lett.*, **1966**, 2033; D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Chem. Commun.*, **1970**, 498; H.-D. Scharf and R. Klar, *Chem. Ber.*, **105** 575 (1972).

[3] J. J. McCullough, *Chem. Commun.*, **1970**, 948; R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, **92**, 4106 (1970).

[4] T. Teitei, P. J. Collin, and W. H. F. Sasse, *Aust. J. Chem.*, **25**, 171 (1972) and references cited therein.

[5] E. Grovenstein, Jr., T. C. Campbell, and T. Shibata, *J. Org. Chem.*, **34**, 2418 (1969).

[6] K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, **1967**, 4723.

[7] Ref. 1.

Table 1. NMR data of **1a** and **2a**

Compounds	δ (Multiplicity)/Coupling constants (Hz)						
	C_4–H	C_5–H	C_6–H	$C_{7'}$–H	C_7–H	C_8–H	OCH_3
1a	6.32	5.86	3.02	1.95	2.51	4.40	3.35
	(d)	(q)	(oct)	(complex)		(q)	(s)
	$J_{4,5}=10$,	$J_{5,6}=6$,	$J_{6,7}=10$,	$J_{6,7'}=9$,	$J_{7,8}=8.5$,	$J_{7',8}=8$,	and $J_{7,7'}=10$
2a	6.33	5.75	3.14—3.5	234.	2.71	4.09	3.30
	(d)	(q)	(m)	(complex)		(t)	(s)
	$J_{4,5}=9$,	$J_{5,6}=4$,	$J_{6,7}=11$,	$J_{6,7'}=3$,	$J_{7,8}=J_{7',8}=8$, and $J_{7,7'}=11$		

a) NMR spectra were taken for CCl_4 solutions using TMS as an internal standard and aromatic protons showed the signals at δ 6.9—7.5 as multiplets.

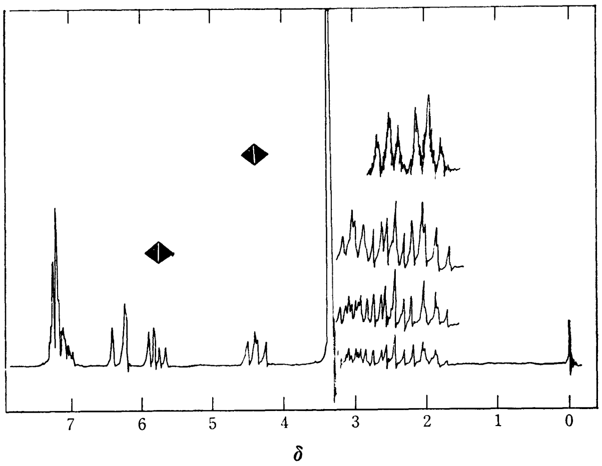

Fig. 1. NMR spectrum of **1a** in CCl_4.

1,2-dihydronaphthalene-chromophore.[8] From these spectral data, the structures of substituted napthhalene and the (2+4) cycloadduct can be safely eliminated.

The NMR spectra of the two adducts are similar (Table 1). The chemical shifts and the coupling constants are determined by first-order analysis of the spectra and a spin-decoupling method. The integral of signals shows that both **1a** and **2a** have four aromatic protons, two vinyl protons, two methine protons, two methylene protons, and three methoxy protons. Figure 1 shows the NMR spectrum of **1a** and the results of the spin-decoupling experiment. Irradiation at δ 5.77 changes the octet at δ 2.84—3.22 (C_6–H) into a quartet with the coupling constants of 9 and 10 Hz. Thus, it is confirmed that the two vinyl protons (C_4– and C_5–H) and the C_6-methine proton form an ABX-spin system (J_{AX}~0 Hz) and that the X-part couples further with the adjacent unequivalent methylene protons (C_7– and $C_{7'}$–H). The quartet at δ 4.40 are clearly due to the C_8-proton. On irradiation at this position, the complex signal in the methylene region collapses into two triplets at δ 1.95 and 2.51, with a coupling constant of *ca.* 10 Hz. This result unambiguously shows, that the C_8-methine proton couples with the $C_{7,7'}$-methylene protons in an ABX type of coupling. Thus, these data establish the ring skeleton of **1a** to be 1-cyano-8-methoxy-2,3-benzobicyclo[4.2.0]octa-2,4-diene.

The similarity of the IR, UV, and NMR spectra between **1a** and **2a** strongly suggests that **2a** has the same ring skeleton as **1a**. Especially, the NMR data support the structure. The triplet at δ 4.09 and the ABX-type of signal pattern in the olefinic region cannot be resonably interpreted by the other possible structures of (2+2) cycloadducts. On irradiation at δ 4.09, the multiplet due to methylene protons collapses into a triplet with a coupling constant of 11 Hz at δ 2.71 and a quartet with coupling constants of 3 and 11 Hz at δ 2.34. These results unambiguously show that **2a** has the same spin system as **1a**, though the signal pattern of C_6–H of **2a** cannot be firmly established on account of the overlapping of the signal with that of the methoxy protons.

Therefore, the structural difference between **1a** and **2a** occurs from the stereochemical difference, the *cis* or *trans* configuration of the methoxy group to the cyano group, *i.e.*, the *endo*- or *exo*-location of the C_8-proton in relation to the benzene ring. In the case of benzo-polycyclic compounds, it is well known that an *endo*-proton is more shielded than an *exo*-proton.[9,10] Therefore, it is important to note that the signal of the C_8-proton of **2a** appears 0.31 ppm higher in field than that of the proton of **1a**. This fact requires the *endo*-location of the proton of **2a**. In the case of the dihydro isomers, **3** and **4** obtained by the catalytic hydrogenation of **1a** and **2a**, this type of anisotropic effect can be expected to be more evident for the C_8-proton, since the molecular models indicate that the C_8-proton of **4** is more closely located over the benzene ring than that of any other isomer. For the same reason, the methoxy protons of **3** must be most shielded. In fact, **4** shows the signal of the C_8-proton at a higher field (δ 3.67) than any other isomer, while the methoxy protons of **3** have the signal at the highest field (δ 3.21)

Table 2. Comparison of chemical shifts of C_8-proton and methoxy protons between **1a**, **2a**, **3**, and **4**

Protons	Compounds Chemical shift (δ)			
	1a	**2a**	**3**	**4**
C_8–H	4.40	4.09	4.27	3.67
OCH_3	3.35	3.30	3.21	3.35

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[8] W. Hückel, E. Ververa, and U. Wörfel, *Chem. Ber.*, **90**, 901 (1957); J. J. McCullough, *Can. J. Chem.*, **1969**, 757.

[9] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, **1966**, 9.

[10] H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961).

TABLE 3. NMR DATA OF **1b** AND **2b**[a)]

Compounds	δ(Multiplicity)/Coupling constants (Hz)					
	C_4–H	C_5–H	C_6–H	$C_{7'}$–H	C_7–H	C_8–H
1b	6.28	5.75	2.99	1.92	2.50	4.45
	(d)	(q)	(oct)	(complex)		(q)
	$J_{4,5}=10$,	$J_{5,6}=6$,	$J_{6,7}=10$,	$J_{6,7'}=8$,	$J_{7,8}=9$,	$J_{7',8}=8$, and $J_{7,7'}=10$
2b	6.3	5.75	3.1—3.3	2.32	2.55	4.16
	(d)	(q)	(m)	(complex)		(t)
	$J_{4,5}=10$,	$J_{5,6}=4$,	$J_{6,7}=9$,	$J_{6,7'}=3$,	$J_{7,8}=J_{7',8}=8$, and $J_{7,7'}=11$	

a) The adduct **1b** exhibited the signal of ethoxy group at δ 1.1 (t, CH_3, J=7 Hz) and 3.55 (q, OCH_2) and aromatic protons at δ 6.8—7.4 (m), and **2b** showed the signals at δ 1.18 (t, CH_3, J=8 Hz), 3.43 (q, OCH_2), and 6.8—7.5 (m, aromatic protons).

among the four isomers (see Table 2). Thus, these NMR data clearly establish that **1a** and **3** require the *exo*-location of the C_8-proton, *i.e.*, the *trans*-configuration between the cyano and methoxy groups, whlie **2a** and **4** have the *cis*-configuration.

Both **1a** and **2a** are thermally as well as photochemically unstable. When the adducts are subjected to vpc analyses by changing the temperature of the inlet-part, the peaks of **1a** and **2a** decrease over 180 and 230°C respectively. However, the peak of α-NN does not so increase, even upon the complete decomposition of **1a** and **2a**. When **1a** and **2a** are heated at 180°C and over 250°C respectively, brownish polymeric materials are mostly yielded, along with a small amount of α-NN. In contrast to the thermolysis, the irradiation of both adducts by a light longer than 280 nm affords α-NN in a quantitative yield. This result indicates that the photoaddition is competitive with the retro-reaction when both α-NN and the adducts absorb the incident light. However, the retro-reaction may be less important when methyl vinyl ether is present in an excess.

The photocycloaddition of ethyl vinyl ether to α-NN is also efficient in giving **1b** and **2b** in good yields. The relative ratio of **1b** to **2b** is again dependent on the solvent used and is similar to that of **1a** to **2a**. The structural determination of **1b** and **2b** was carried out by means of elemental analyses and spectroscopic data. The NMR data are listed in Table 3. On the other hand, vinyl acetate and isobutylene react only slowly with α-NN, and the products can not be isolated in a pure form. Although the photocycloaddition of acrylonitrile to naphthalene has been reported,[3)] the irradiation of α-NN in the presence of acrylonitrile affords no adducts, but only polymers. Moreover, the photoreaction of naphthalene with vinyl ethers results in the quantitative recovery of naphthalene upon irradiation for a longer time, though vpc analyses indicate the formation of at least four products in trace amounts.

Quantum Yield. On the irradiation of a dilute cyclohexane solution of α-NN containing ethyl vinyl ether at 313 nm, there appear an isosbestic point at 279 nm and new absorption maxima similar to those of **1b** and **2b** (Fig. 2). Therefore, the quantum yields for the disappearance of α-NN can be determined by monitoring the decrease in the absorbance at 307 nm, using a potassium ferroixalate actinometer. The reciprocals of the quantum yields are linearly changed

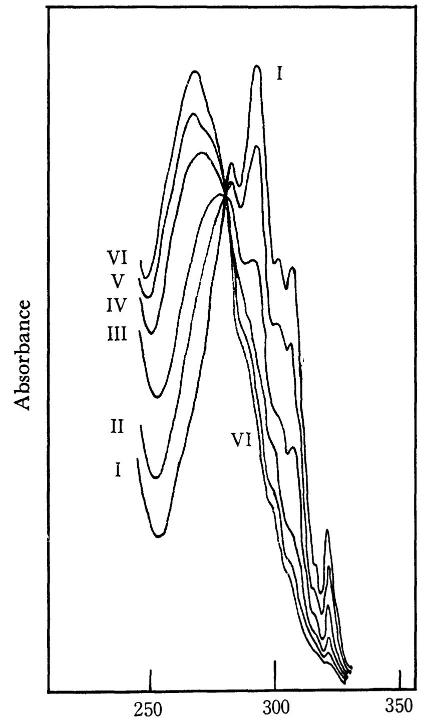

Fig. 2. Spectral change of a cyclohexane solution containing 1.5×10^{-4}M of α-NN and 0.93M of ethyl vinyl ether with time (min); I(0), II(1.5), III(5.0), IV(10.0), V(20.0), and VI(40.0). Absorbance is in an arbitary unit.

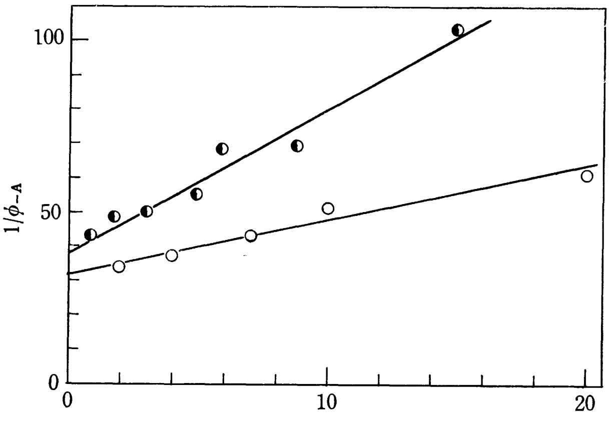

Fig. 3. The plots of $1/\phi_{-A}$ *vs.* 1/[VE] for degassed (–○–) and air saturated (–◐–) cyclohexane solutions, [α-NN]=1.38 $\times10^{-4}$M.

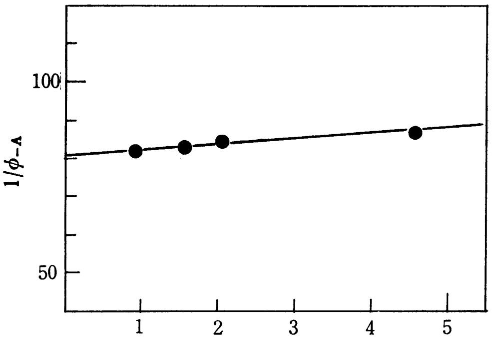

Fig. 4. The plots of $1/\phi_{-\mathrm{A}}$ *vs.* 1/[VE] for air saturated methanolic solution, [α-NN]$=1.38\times10^{-4}$M.

with the reciprocals of the concentrations of ethyl viny ether; thus, the slopes and intercepts are determined to be 1.6M and 32 for degassed cyclohexane solutions, 4.1M and 39 for air-saturated cyclohexane solutions, and 1.5M and 82 for air-saturated methanolic solutions (Figs. 3 and 4).

Quenching of Fluorescence. A dilute cyclohexane or methanolic solution of α-NN emits a fluorescence with the maxima at 320—340 nm. The fluorescence is quenched by ethyl vinyl ether without any change in the shape of the spectra, and linear Stern-Volmer plots are obtained (Fig. 5). The slopes of the Stern-Volmer plots are determined to be 19M^{-1} for degassed cyclohexane solutions, 10.3M^{-1} for air-saturated cyclohexane solutions, and 51M^{-1} for air-saturated methanolic solutions.

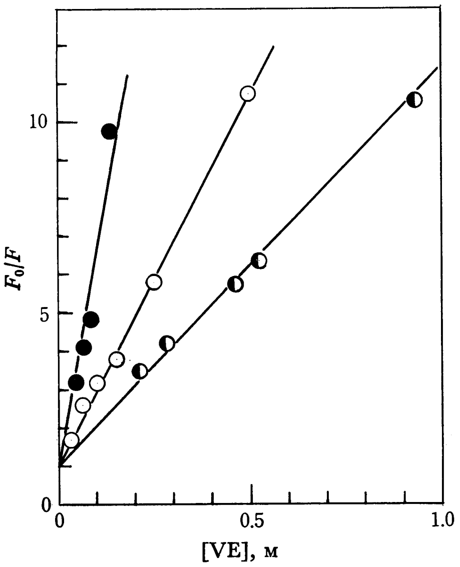

Fig. 5. The Stern-Volmer plots for the quenching of α-NN fluorescence with ethyl vinyl ether; degassed cyclohexane solutions (-○-), air saturated cyclohexane solutions (-◐-), and air saturated methanolic solutions (-●-). [α-NN]$=1.38\times10^{-4}$M.

On the other hand, acrylonitrile does not appreciably quench the fluorescence of α-NN. The fluorescence quenching with vinyl acetate is quite ineffective, as 0.8M of vinyl acetate causes only a *ca.* 10% decrease in the fluorescence.

Discussion

The effective fluorescence-quenching by ethyl vinyl ether indicates that the photochemical cycloaddition of ethyl vinyl ether to α-NN takes place from the lowest excited singlet state of α-NN (^{1}A). Moreover, benzophenone does not sensitize the photocycloaddition, though the photoreduction of benzophenone with benzhydrol is effectively quenched by α-NN. Therefore, a triplet mechanism can be safely eliminated.

$$\mathrm{A} \xrightarrow{h\nu} {}^1\mathrm{A} \tag{1}$$

$$^1\mathrm{A} \xrightarrow{k_d} \mathrm{A} \tag{2}$$

$$^1\mathrm{A} + \mathrm{O}_2 \xrightarrow{k_o} \mathrm{A} + \mathrm{O}_2 \tag{3}$$

$$^1\mathrm{A} + \mathrm{VE} \xrightarrow{k_r} \text{(intermediate)} \tag{4}$$

$$\text{(intermediate)} - \begin{array}{ll} \xrightarrow{k_c} \mathbf{1} \text{ and } \mathbf{2} & (5) \\ \xrightarrow{k_n} \alpha\text{-NN} + \mathrm{VE} & (6) \end{array}$$

$$F_0/F = (1+k_r[\mathrm{VE}])/(k_d+k_o[\mathrm{O}_2]) \tag{7}$$

$$1/\phi_{-\mathrm{A}} = \left(1+\frac{k_d+k_o[\mathrm{O}_2]}{k_r[\mathrm{VE}]}\right)\left(1+\frac{k_n}{k_c}\right) \tag{8}$$

Scheme 1.

In Scheme 1, therefore, a simplified singlet mechanism is described, from which the Stern-Volmer expression for fluorescence-quenching (7) and the rate equation (8) are derived. In the equations, let $\phi_{-\mathrm{A}}$, F_0, and F denote the quantum yield for the disappearance of α-NN and the fluorescence intensities in the absence and in the presence of ethyl vinyl ether (VE) respectively. The (2) process indicates all the unimolecular decay of ^{1}A involving radiative and nonradiative processes. In the case of air-saturated runs, the oxygen-quenching process (3) should be taken into account, whereas it can be neglected for degassed runs.

From the intercepts and the slopes in Figs. 3 and 4, the intercept-to-slope ratios can be calculated to be 20M^{-1} for degassed cyclohexane solutions, 9.5M^{-1} for air-saturated cyclohexane solutions, and 54.7M^{-1} for air-saturated methanolic solutions; these ratios are in good agreement with the slopes of the Stern-Volmer plots for the respective solutions in Fig. 5. This agreement, especially for the air-saturated runs, clearly shows that the photocycloaddition takes place in the lowest excited singlet state of α-NN, since both the intercept-to-slope ratio and the slope of the Stern-Volmer plots represent the same rate term, k_r/k_d for degassed runs or $k_r/(k_d+k_o[\mathrm{O}_2])$ for air-saturated runs.

The fluorescence decay life of a degassed cyclohexane solution of α-NN was determined to be 17 nsec by the use of a TRW nsec flashspectrophotometer. The oxygen-quenching method,11) using an L_0/L value $(=1+k_o[\mathrm{O}_2]/k_d=1.77)$, gave a similar decay life. From this value of the decay life, k_r can be calculated to be $1.1\times10^9\mathrm{M}^{-1}\mathrm{sec}^{-1}$, very close to the diffusion rate in-

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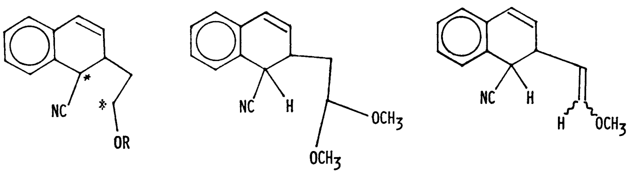
11) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York and London (1965), p. 36.

cyclohexane (*ca.* 5×10^9 M^{-1}sec^{-1}). Unfortunately, not many kinetic studies of the cycloaddition of π,π^*-singlet species to olefins have been reported,[3,12] and the rate constant, k_r, has not yet been given.

On the other hand, kinetic investigations of electronically-excited carbonyl compounds have been intensively carried out. In the n,π^*-triplet state, the oxetane-formation takes place through 1,4-biradicals, with rate constants of 5×10^7—10^8 M^{-1}sec^{-1}.[13] In the present case, therefore, it is not suitable to suggest that a 1,4-biradical or 1,4-dipolar intermediate, **5**, is directly generated by the attack of ^{1}A on VE in a near diffusion rate, since ^{1}A might be considered to be less electrophilic than the n,π^*-triplet carbonyl compounds, which have been well established to have a high electrophilic character.

On the other hand, it has been reported that the photocycloaddition of acetone to dicyanoethylene[14] and that of propionaldehyde to cyclohexadiene[15] afford oxetanes by way of the exciplexes generated from the excited singlet state of the carbonyl compounds in a diffusion-controlled rate.[16] In many cases, the exciplex formation is well established to occur in a diffusion-controlled rate from the excited singlet state.[17] In the present case, therefore, the large value of k_r can be reasonably interpreted by assuming an exciplex intermediate. The inefficiency of acrylonitrile and the less effective nature of vinyl acetate in the fluorescence-quenching and the photoreaction may also suggest an exciplex intermediate with a charge-transfer character; ethyl vinyl ether is known to be an electron-rich olefin, whereas vinyl acetate has less of a donor-ability and acrylonitrile is an acceptor rather than a donor.

The rate constant for fluorescence-quenching, $k_r/(k_d+k_o[O_2])$, is about five times greater in methanol than in cyclohexane. This reflects the solvent-dependence of k_r, since the fluorescence intensity of α-NN was found to be similar both in air-saturated methanolic and cyclohexane solutions. In the exciplex-formation, polar solvents have been known to enhance the rate of fluorescence-quenching[7,18,19] and the reaction rate,[7,18] at least in some cases. Moreover, since an exciplex is a special case of well-known charge-transfer complexes, the solvation of exciplexes can occur and, in polar solvents, leads to species with configurations different from those of the exciplexes in non-polar solvents.[20] If this is the case, the solvent-dependent results of k_n/k_c and the product ratio are consistent with the exciplex mechanism. However, the solvent-dependence can possibly be explained as being caused by the solvation of the 1,4-biradical, **5**, generated from an exciplex, since solvent effects have been observed in the Norrish-type II photoelimination, which has been well established to proceed *via* a 1,4-biradical.[21] However, a discrete 1,4-dipolar intermediate is not a likely reaction intermediate, since the photoreaction in methanol gave neither a solvolytic nor an inserted product such as **6** or **7**, even under acidic and basic conditions.



(5) (6) (7)

* = •or −

※= •or +

Chart 2

Experimental

General. The spectroscopic analyses of the products were carried out as follows; the NMR spectra using a Hitachi Perkin-Elmer R-20 spectrophotometer, the IR spectra using a Hitachi EPI-S2 spectrophotometer, the UV spectra using Hitachi 124 spectrophotometer, the fluorescence spectra using a Hitachi MPF-2A spectrofluorometer, and the mass spectra using a Hitachi RMU-6E spectrometer. The yields and the product ratios were determined by vpc with a Shimadzu GC-3AF using a column of SE-30 (5% on Shimalite W, 1m) at 160°C. The thermal behavior of **1** and **2** was checked by vpc with a Shimadzu GC-2C equipped with a flame-ionization detector, by changing the temperature of the inlet-part. The solvents were purified as usual. The ethyl vinyl ether, vinyl acetate, and acrylonitrile were distilled over calcium chloride under a nitrogen stream before use. The methyl vinyl ether was distilled from a gas cylinder before use. The α-NN was purified by vacuum distillation.

Quantum Yields. The solutions were prepared by dissolving α-NN (1.38×10^{-4} M) and ethyl vinyl ether into cyclohexane or methanol. Monochromatic light at 313 nm was isolated through a Toshiba UV-D25 glass filter and a filter solution (0.2 g potassium chromate made up to 1 *l* with distilled water), with a path length of 10 mm from resonance lines of a high-pressure mercury arc. The light intensity (I^0) was determined by potassium ferrioxalate actinometry[22] to be 1.42×10^{-6} mol/cm^{2}min. Sample solutions placed in cuvettes (10 mm × 10 mm × 45 mm) were irradiated by the 313 nm light, and the decrease in the absorbance at 307 nm (κcd) was monitored in order to determine the quantum yields for the disappearance of α-NN (ϕ_{-A}). When natural logarithms of ($e^{\kappa cd}-1$) were plotted against the time (t, min), straight lines were obtained. The quantum yields (ϕ_{-A}) were obtained from the slopes of the lines by applying

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[12] O. L. Chapman and R. D. Lura, *J. Amer. Chem. Soc.*, **92**, 6352 (1970); J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *ibid.*, **93**, 2805 (1971).

[13] For examples, see, H. Sakurai, K. Shima, and S. Toki, *Nippon Kagaku Zasshi*, **89**, 537 (1968).

[14] J. C. Dalton, D. M. Pond, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2173 (1970); J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.* **92**, 1318 (1970).

[15] T. Kubota, K. Shima, S. Toki, qnd H. Sakurai, *Chem. Commun.*, **1969**, 1462.

[16] R. R. Hautala and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 5595 (1971).

[17] For examples, see, A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

[18] C. Pac, T. Tosa, and H. Sakurai, This Bulletin, **45**, 1169 (1972).

[19] K. Kaneta and M. Koizumi, *ibid.*, **40**, 2254 (1967).

[20] N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967); H. Yamashita and M. Koizumi, This Bulletin, **41**, 2313 (1968).

[21] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

[22] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

TABLE 4. ELEMENTAL ANALYSES OF ADUDCTS

Compounds	Bp (°C/mmHg) or Mp[°C]	Formula	Anal					
			Calcd			Found		
			C	H	N	C	H	N
1a	[86—87]	$C_{14}H_{14}NO$	79.59	6.20	6.63	79.83	6.24	6.51
2a	(113/0.01)	$C_{14}H_{13}NO$	79.59	6.20	6.63	79.43	5.94	6.45
1b	[58—58.5]	$C_{15}H_{15}NO$	79.97	6.71	6.22	80.33	6.47	5.84
2b	$(102/10^{-3})$	$C_{15}H_{15}NO$	79.97	6.71	6.22	79.86	6.74	6.11
3	$(102/10^{-3})$	$C_{14}H_{15}NO$	78.84	7.09	6.57	78.60	7.00	6.41
4	[65—65.5]	$C_{14}H_{15}NO$	78.84	7.09	6.57	78.72	7.12	6.54

this equation; $\ln(e^{\kappa cd}-1)=-1000\phi_{-A}I_0t+$ Constant, where κ is the molar extinction coefficient at 307 nm (5.39×10^3 l/mol cm).

Photochemical Reaction in Preparative Scale. a) The photochemical reaction of α-NN with methyl vinyl ether will be described as a typical run, since the procedures were identical in every case. The results of the elemental analyses of the adducts **1**—**4** are listed in Table 4. A methanolic solution (300 ml) containing 1 g of α-NN and 20 ml of methyl vinyl ether in a Pyrex doughnut-type vessel was irradiated for 20 hr with a high-pressure mercury arc at an ambient temperature. The unreacted vinyl ether and methanol were then distilled off *in vacuo*, and the residue was chromatographed on silica gel. After 0.1 g of α-NN had been eluted with a mixture of benzene (30%) in hexane, elution with 300 ml of benzene gave *ca.* 1 g of **1a** containing a small amount of **2a**, which solidified on standing overnight; it was recrystallized from methanol (mp 86—87°C). Further elution with benzene gave a mixture of **1a** and **2a** (0.1 g).

b) In a similar manner, a benzene solution containing 1 g of α-NN and 15 ml of methyl vinyl ether was irradiated for 15 hr. After the unchanged vinyl ether and benzene had been distilled off *in vacuo*, the residue was heated at 180—200°C for 20 min; the subsequent vacuum distillation of the pyrolysate gave an oil (bp 105—113°C/10^{-3}mmHg). The chromatographic treatment of the oil on silica gel gave 0.2 g of α-NN and 0.4 g of a mixture containing **2a** and a small amount of **1a**. The further chromatography of the latter fraction led to a decrease in the content of **1a** to a trace amount. The vacuum distillation of this fraction gave an oil (bp 102°C/10^{-3}mmHg), which did not solidify, even on storage in a refrigerator.

Hydrogenated Adducts, 3 and 4. An ethanolic solution containing 0.2 g of **1a** and **2a** was hydrogenated over Pd-charcoal (5%) at an ambient temperature for 2 hr. The complete hydrogenation was checked by vpc analyses. The filtration of the Pd-charcoal, followed by the evaporation of the ethanol, left an oil, which was then chromatographed on a short column of silica gel. In the case of **4**, it solidified on storage in a refrigerator overnight and was then recrystallized from methanol (mp 65—65.5°C). On the other hand, **3** did not solidify, even on storage in a refrigerator over several weeks.

Pyrolyses of 1a and 2a. The pyrolyses of crystalline **1a** (0.1 g) at 180—200°C for 1 hr gave a brownish glassy material, which was then chromatographed on silica gel. Elution with 500 ml of benzene gave less than 50 mg of α-NN; further elution with a mixture of ether and benzene (1 : 9) afforded brownish glassy materials which could not be identified. Pyrolyses of **2a** at 250—260°C gave similar results, while heating at 180—200°C resulted in no appreciable change in the **2a**.

Photolyses of 1a and 2a. A methanolic or benzene solution of **1a** or **2a** (0.1 g/4 ml) in a Pyrex tube was irradiated with a high-pressure mercury are for 20 hr. During the course of the irradiation, vpc analyses of the photolysate were carried out at 1 hr intervals for the initial 5 hr; it was found that α-NN increased linearly with the disappearance of the adduct. Irradiation for about 10 hr resulted in the complete decomposition of the adduct, and further irradiation for 10 hr gave no additional change. After the irradiation, removal of a solvent left a solid, which was identified as α-NN by studing its IR, and mass spectra, and by a mixed-melting-point determination.

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