Photo-induced Ring-opening Reactions of 1-(2-Naphthoyl)aziridine in Various Solvents

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Photoreactions of 1-(2-naphthoyl)aziridine (NAz) have been investigated in various solvents under the deaerated conditions at room temperature. The photo-irradiation of NAz in halogenated hydrocarbons afforded halogen substituted secondary amides such as *N*-(2-chloroethyl)-2-naphthamide (CENA) or *N*-(2-bromoethyl)-2-naphthamide (BENA), a ring-expanded isomer of 2-(2-naphthyl)-2-oxazoline (NOz) and the NAz oligomer containing a chlorine atom. Secondary amides such as *N*-(2-methoxyethyl)-2-naphthamide (MENA) and *N*-ethyl-2-naphthamide (ENA) were obtained together with NAz oligomer in methanol and 2-propanol, respectively. The formation of *N*-(2-phenoxyethyl)-2-naphthamide (PENA), phenyl-2-naphthoate (PN) and NAz oligomer was observed in phenol (72 vol%)-acetonitrile mixture.

Extensive studies have been accomplished on the photochemical reactions of three-membered ring compounds such as cyclopropanes[1)] and cyclopropenes.[2)] The photochemistry of three-membered heterocycles has also received considerable attention.[3,4)] A common feature of these photoreactions is ring-opening in the initial step, leading to cis-trans isomerization, acyclic compound formation, or rearrangement to ring-expanded products.

Although three-membered aziridines have been well characterized with respect to the thermal reactivities,[5)] the photoreactions of these compounds have been little reported.[4)] In this paper, the photochemical behavior of 1-(2-naphthoyl)aziridine (NAz) in various solvents was studied. Particular attention has been paid to the role of solvent molecules on the photochemical ring-opening of the aziridinyl group.

Experimental

General Methods. Melting points of all the products obtained are uncorrected. IR spectra were recorded on a JASCO DS-403 spectrophotometer, UV spectra on a Shimadzu UV-200S spectrophotometer, and ^{1}H NMR spectra on a JOEL PMX-60 spectrometer using tetramethylsilane as an internal standard. High speed liquid phase chromatography (HLPC) was carried out with a TOYO SODA HLC-802UR apparatus (gel permeation type column: TSK-GEL GMH6 and G2000H, 600 mm × 7.5 mm × 2, eluted with tetrahydrofuran at a flow rate of 1 cm^3 min^{-1} at 40 °C), using benzene as an internal standard.

Materials. Aziridine supplied from Nippon Shokubai Kagaku Kogyo Co. Ltd. was used after distillation. 2-Naphthoyl chloride (Tokyo Kasei Kogyo) was used without further purification. Acetonitrile was dried with calcium carbonate and distilled from phosphorus pentaoxide before use. Dibromomethane was dried with calcium chloride and distilled before use. Gaseous hydrogen chloride was prepared by the reaction of concentrated sulfuric acid (75 cm^3) with concentrated hydrochloric acid (40 cm^3).[6)] The other solvents obtained commercially were used without further purification.

Preparation of 1-(2-Naphthoyl)aziridine (NAz). A solution of 2-naphthoyl chloride (53 mmol) in acetone (70 cm^3) was added to the equimolar (53 mmol) mixture of aziridine and triethylamine in acetone (200 cm^3) cooled in an ice bath. Triethylamine hydrochloride formed was removed as powder by filtration from the reaction mixture. The residue obtained by the evaporation of acetone was washed with methanol, followed by recrystallization three times from carbon tetrachloride to afford NAz (46% in yield), mp 82—83 °C. Found: C, 79.24; H, 5.56; N, 7.22; O, 7.90%. Calcd for $C_{13}H_{11}NO$: C, 79.19; H, 5.58; N, 7.11; O, 8.12%.

Photoreactions. Solutions of NAz in various solvents were deaerated by several freeze-pump-thawing cycles under vacuum in a Vycor or Pyrex glass tube (6 mmϕ) and sealed off. The photo-irradiation was carried out at room temperature, using a merry-go-round apparatus equipped with a high-pressure mercury lamp (EIKOSHA 500 W). After the irradiation, solvent was removed with a rotary evaporator under reduced pressure. The residual reaction mixture was subjected to the spectroscopic analyses. The conversion of NAz and the product yields were determined by the simultaneous use of ^{1}H NMR and HLPC measurements.

The photo-irradiation of a large amount of NAz solution was also carried out in order to identify the reaction products, using an immersion-type irradiation apparatus. The resulting reaction mixture was concentrated with a rotary evaporator and chromatographed on a silica gel column. The crude reaction mixture was also separated by repeated liquid phase chromatographies using the same column as mentioned above. The structures of the products were confirmed by the following data.

N-*Ethyl-2-naphthamide (ENA).* Mp 129.5—130 °C; IR (CHCl$_3$): 3420 (NH), 1510 and 1500 (NH), 1430, 1280, and 1230 (C–N) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 1.29 (3H, t, J=7.2 Hz), 3.60 (2H, q, J=6.6 Hz), 6.78 (1H, br), 7.68 (2H, m), 8.00 (4H, m), and 8.36 (1H, s). Found: C, 78.44; H, 6.70; N, 6.99; O, 7.89%. Calcd for $C_{13}H_{13}NO$: C, 78.39; H, 6.53; N, 7.04; O, 8.04%.

An identical product was obtained by the following procedures. 2-Naphthoyl chloride (14 mmol) dissolved in a minimum amount of acetone was added dropwise to a cooled aqueous solution (100 cm^3) containing ethylamine (14 mmol) and sodium hydroxide (31 mmol) under vigorous stirring. The white precipitate was purified from methanol (28% in yield).

N-*(2-Chloroethyl)-2-naphthamide (CENA).* Mp 135—136 °C; IR (CHCl$_3$): 3440 (NH), 1660 (C=O), 1519 and 1508 (NH), and 1285 (C–N) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 3.73 (4H, s), 6.83 (1H, br), 7.60 (2H, m), 7.83 (4H, m), and 8.27 (1H, s). Found: C, 66.70; H, 5.19; N, 5.84; O, 6.89; Cl, 15.11%. Calcd for $C_{13}H_{12}NOCl$: C, 66.81; H, 5.14; N, 6.00; O, 6.85; Cl, 15.20%.

An identical product was obtained when gaseous hydrogen chloride was bubbled through a solution of NAz (90 mmol)

TABLE 1. PHOTOCHEMICAL REACTIONS OF NAz IN VARIOUS SOLVENTS[a)]

Run	Solvent	Glass tube	$[NAz]_0$	Conversion	Products (Yield[b)]/%)			
			mmol dm^{-3}	%	Secondary amide	Esters	NOz	Oligomer
1	Hexane	V	26	9	4 (ENA)		0	5
2	Benzene	V	156	7	2 (ENA)		0	5
3	Diethyl ether	V	105	6	1 (ENA)		0	5
4	Acetone	V	100	10	3 (ENA)		0	7
5	CH_3CN	V	91	10	3 (ENA)		0	7
6	CCl_4	V	91	84	57 (CENA)		2	25
7	CCl_4	P	91	13	10 (CENA)		0	3
8	$CHCl_3$	V	91	62	55 (CENA)		5	2
9	$CHCl_3$	P	91	4	4 (CENA)		0	0
10	CH_2Br_2	V	90	89	84 (BENA)		0	5
11	CH_2Br_2	P	90	70	17 (BENA)		52	1
12	CH_3OH	V	47	49	31 (MENA)	0	0	18
13	CH_3OH	P	47	31	18 (MENA)	0	0	11
14	$(CH_3)_2CHOH$	V	47	29	20 (ENA)	0	0	7
15	$(CH_3)_2CHOH$	P	47	13	10 (ENA)	0	0	3
16	Phenol/CH_3CN[c)]	V	91	100	38 (PENA)	19 (PN)	0	42
17	Phenol/CH_3CN[c)]	P	91	100	42 (PENA)	23 (PN)	0	35

a) Under the photo-irradiation in a Vycor (V) or Pyrex (P) glass tube for 200 min. b) Yields based on NAz were determined by ^1H NMR and HLPC. c) 72 vol% of phenol.

in chloroform (1 cm^3) at 0 °C (quantitative yield).

N-*(2-Bromoethyl)-2-naphthamide (BENA).* Mp 147.5—149 °C (lit,[7)] mp 152 °C); IR (KBr): 3220 (NH), 1620 (C=O), 1535 (NH), 1310 (C–N), and 480 (C–Br) cm^{-1}; ^1H NMR (CD_2Cl_2): δ 3.71 (4H, q, J=4.8 Hz), 6.70 (1H, br), 7.50 (2H, m), 7.67 (4H, m), and 8.20 (1H, s).

The IR and ^1H NMR spectral data were identical with those of an authentic sample prepared by the reported method.[7)]

Oligomer Obtained in Carbon Tetrachloride. IR (KBr): 1715, 1644, 1520, 1400, 1110, and 620 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.79 (3H, br), 7.56, 7.89, and 8.34 (7H, broad signals corresponding to the naphthyl group). Found: C, 46.52; H, 3.27; N, 3.33; O, 6.14; Cl, 35.00%.

2-(2-Naphthyl)-2-oxazoline (NOz). Mp 85.5—86.5 °C; IR ($CHCl_3$): 1645 (C=N), 1275 (=C–O–C), 1068 (C–O–C), 983, 961, and 943 cm^{-1}; ^1H NMR (CD_2Cl_2): δ 4.29 (4H, quartet, J=7.4 Hz), 7.60 (2H, m), 7.93 (4H, m), and 8.47 (1H, s). Found: C, 79.38; H, 5.59; N, 7.05; O, 8.19%. Calcd for $C_{13}H_{11}NO$: C, 79.19; H, 5.58; N, 7.11; O, 8.12%.

The IR and ^1H NMR spectral data were identical with those of an authentic sample prepared by the reported method.[7)]

N-*(2-Methoxyethyl)-2-naphthamide (MENA).* Mp 86.5—87.5 °C; IR (CCl_4): 3440 (NH), 2975 (CH_3), 2820 (CH_3), 1664 (C=O), 1504 (NH), and 1068 (C–O–C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.42 (3H, s), 3.61 (4H, m), 7.59 (2H, m), 7.89 (4H, m), and 8.29 (1H, s). Found: C, 72.61; H, 6.62; N, 5.94; O, 13.70%. Calcd for $C_{14}H_{15}NO_2$: C, 73.36; H, 6.55; N, 6.11; O, 13.97%.

An identical product was obtained when a solution of NAz (0.24 mmol) in methanol (40 cm^3) was permitted to stand for 30 min at room temperature in the presence of a catalytic amount of boron trifluoride under an argon atmosphere (quantitative yield).

Oligomer Obtained in Methanol. IR ($CHCl_3$): 3420 and 3300 (NH), 1760, 1650 (C=O), 1520 (NH), 1430, 1290 (C–N), and 1150 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.46 (5H, br), 3.73 (0.3H, singlet signal corresponding to the methoxyl group), and 7.53—8.28 (7H, br). Found: C, 52.79; H, 5.48; N, 5.03; O, 12.16%.

N-*(2-Phenoxyethyl)-2-naphthamide (PENA).* Mp 73—74 °C; IR (KBr): 3320 (NH), 1638 and 1625 (C=O), 1545 (NH), and 1081 (C–O–C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.03 (4H, q, J=4.7 Hz), 6.63 (1H, br), 6.88—7.20 (5H, phenyl group), 7.61 (2H, m), 7.87 (4H, m), and 8.30 (1H, s). Found: C, 78.19; H, 6.39; N, 4.27; O, 10.61%. Calcd for $C_{19}H_{17}NO_2$: C, 78.35; H, 5.84; N, 4.81; O, 11.00%.

Phenyl-2-naphthoate (PN). Mp 90—90.5 °C (lit,[8)] 96 °C); IR (KBr): 1732 (C=O), 1280 and 1228 (C–O–C) cm^{-1}. The IR spectrum was identical with that of an authentic sample prepared by the reported method.[8)]

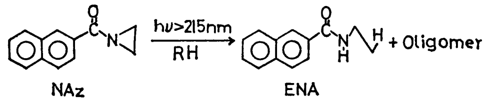
N-*(2-Acetoxyethyl)-2-naphthamide (AENA).* Mp 78—79 °C; IR ($CHCl_3$): 3420 (NH), 1725 (C=O), 1648 (C=O), and 1500 (NH) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.09 (3H, s), 3.83 (2H, t, J=5.0 Hz), 4.36 (2H, t, J=5.0 Hz), 7.63 (2H, m), 7.87 (4H, m), and 8.32 (1H, s). Found: C, 69.10; H, 5.78; N, 5.54; O, 18.72%. Calcd for $C_{15}H_{15}NO_3$: C, 70.03; H, 5.84; N, 5.45; O, 18.68%.

Results and Discussion

UV Absorption Characteristics of NAz. The solution of NAz in hexane exhibited ultraviolet absorption maxima at 337 nm (ε; 1310), 282 nm (ε; 8320), and 245 nm (ε; 51800). These absorption bands may be attributed to the π-π^* transitions of naphthyl group of NAz in view of the similarity to those of naphthalene.[9)] No absorption bands were observed in the wavelength region longer than these principal absorption bands. It thus seems that the carbonyl n-π^* band lies behind the intense π-π^* bands of the naphthyl group.[10)]

Photoreactions of NAz in Non-halogenated Aprotic Solvents. The photo-irradiations of NAz in various solvents were carried out for 200 min at room temperature under deaerated conditions, using Vycor and Pyrex glass tubes which transmit the light with wavelength longer than 215 and 286 nm, respectively. The results are summarized in Table 1.

It is apparent from Table 1 that NAz exhibits less photoreactivity in non-halogenated aprotic solvents such as hexane, benzene, diethyl ether, acetone and acetonitrile, in which the overall conversion of NAz did not exceed 10% (Runs 1—5). *N*-Ethyl-2-naphthamide (ENA) was afforded in low yield as a common ring-opened product in these solvents, accompanied by NAz oligomer.

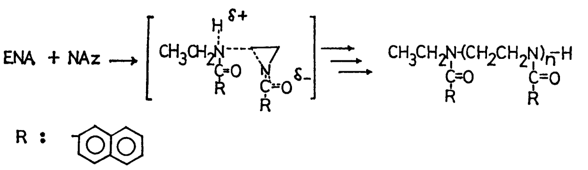


(1)

This photochemical ENA formation suggests that the hydrogen abstraction by NAz in the electronically excited state from a solvent molecule occurs to bring about α-cleavage of the aziridine ring. In this regard, it was confirmed that acetone is afforded along with the photochemical ENA formation in $(CH_3)_2CHOH$, as shown below (Eq. 10). Accordingly, the ENA formation in these solvents is expected to proceed by a radical mechanism in a similar manner to that in $(CH_3)_2CHOH$.

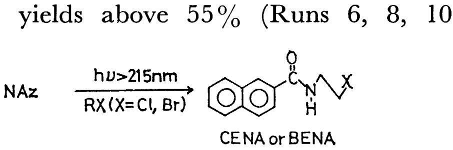
The low yield of ENA in these solvents may be attributed to the requirement of high activation energy for the hydrogen abstraction from solvent molecule. In the present systems, the hydrogen abstraction from either aziridinyl or naphthyl groups of NAz seems minor for the ENA formation because of the low reactivities of hydrogen atoms on these groups.[11]

On the other hand, ENA as a photoproduct was found to initiate oligomerization of NAz slowly in a similar manner to the ring-opening polymerization of most 1-acylaziridines by various amides.[12]



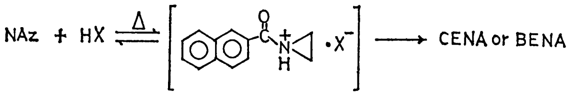
(2)

Photoreactions of NAz in Halogenated Hydrocarbons. The photo-irradiation of NAz in halogenated hydrocarbons through a Vycor glass tube (>215 nm) resulted in α-cleavage of the aziridine ring to afford halogen substituted secondary amide, *N*-(2-chloroethyl)-2-naphthamide (CENA) in CCl_4 and $CHCl_3$ or *N*-(2-bromoethyl)-2-naphthamide (BENA) in CH_2Br_2 with high yields above 55% (Runs 6, 8, 10).



(3)

It was confirmed by a separate experiment that the photolysis of $CHCl_3$ occurs in a Vycor glass tube to afford HCl. Moreover, NAz was converted quantitatively into CENA without oligomerization by bubbling gaseous HCl through a solution of NAz in $CHCl_3$ in the dark. Such a ring-opening reaction by hydrogen halide would proceed *via* the following reactive intermediate of aziridinium salt:[13]



(4)

Under the conditions of the irradiation with light of wavelength longer than 215 nm, it is likely that a halogen atom such as Cl or Br is formed as a primary intermediate by the photolyses of halogenated hydrocarbon solvents and subsequently abstracts a hydrogen atom from a solvent molecule to afford a hydrogen halide, HCl or HBr. The hydrogen abstraction from NAz would be minor because of the low reactivities of hydrogen atoms on NAz, in a similar manner to the ENA formation in non-halogenated aprotic solvents.

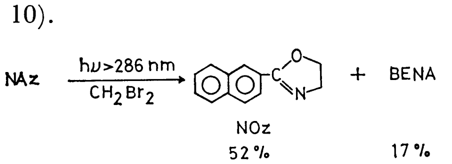
It should be noted that, although CCl_4 does not contain any hydrogen atoms, CENA was obtained in the dark by the addition of NAz (90 mmol dm^{-3}) to a pre-irradiated CCl_4 under the same conditions as in the Vycor system. Furthermore, the yield of CENA (53%) in this post-reaction agreed closely with that (57%) in the in-source photoreaction (Run 6). It has been well known that Cl_2 is formed by the photolysis of CCl_4 at wavelengths shorter than 253.7 nm.[14] Therefore, the reaction of NAz with Cl_2 is presumed to afford HCl in the CCl_4 system.

The oligomer of NAz with a high content of chlorine atoms (35%) was also obtained along with CENA in CCl_4. The yield of this oligomer (25% based on NAz) was much higher than those (less than 5%) in hydrogen-containing $CHCl_3$ and CH_2Br_2. This would also be associated with the reaction between NAz and Cl_2.

On the other hand, the photo-irradiation of NAz in CCl_4 or $CHCl_3$ through a Pyrex glass tube (>286 nm) led to the same product, CENA, as afforded in the Vycor system (Runs 7, 9). Here the yields were reduced to one-sixth in CCl_4 and one-tenth in $CHCl_3$, respectively, and very little oligomerization of NAz occurred (<1%).

$$\text{NAz} \xrightarrow[\text{CCl}_4 \text{ or CHCl}_3]{h\nu>286\text{ nm}} \text{CENA} \qquad (5)$$

On the contrary, the product distribution in CH_2Br_2 was affected remarkably by the wavelength of irradiation. The photo-irradiation of NAz in CH_2Br_2 through a Pyrex glass tube resulted in a ring-expanded isomer of 2-(2-naphthyl)-2-oxazoline (NOz) as a major product, along with BENA (Run 11), in contrast to the exclusive BENA formation in the Vycor system (Run 10).



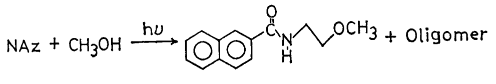
(6)

Although BENA was readily converted into NOz at 70 °C in the presence of potassium hydroxide in CH_3OH (72% in yield), the photocyclization of BENA into NOz did not occur in CH_2Br_2 under the present conditions. Furthermore, BENA was obtained in 18% yield by the addition of NAz (90 mmol dm^{-3}) in the dark to a pre-irradiated CH_2Br_2 under the same conditions as above. The good agreement with the yield of BENA in this post-reaction indicates that the BENA formation in the in-source photoreaction system can be attributed to the reaction of NAz with HBr formed by the photolysis of CH_2Br_2.

It may be presumed for the photo-isomerization that the dipole-dipole interaction of NAz in the electronically excited state with CH_2Br_2 promotes the ionic ring-opening of aziridinyl group, followed by the cyclization into oxazoline due to the stabilization of four center transition state.[5f)]

Photoreactions of NAz in Alcohols and Phenol. The photochemical ring-opening reactions of NAz also occurred in CH_3OH, $(CH_3)_2CHOH$, and phenol (72 vol%)–CH_3CN mixture.

The photo-irradiation of NAz in CH_3OH afforded *N*-(2-methoxyethyl)-2-naphthamide (MENA) accompanied by NAz oligomer, whereas the dark reaction was not observed under the same conditions. As shown in Table 1, the product yields in the Pyrex system decreased compared with those in the Vycor system, but no appreciable difference was observed in the ratio of yields between MENA and oligomer (Runs 12, 13).

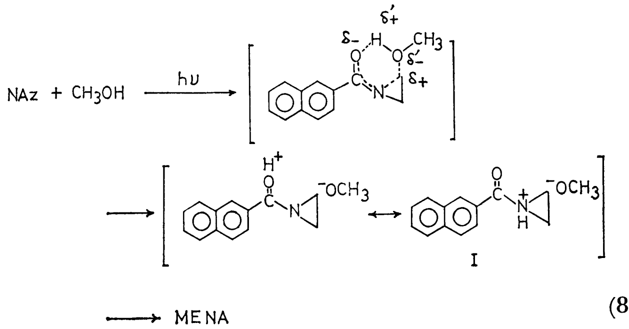


(7)

MENA

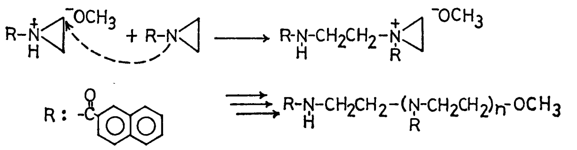
It seems possible that the MENA formation arises from the methanolysis of the aziridine ring of NAz in the electronically excited state in a similar manner to that in the photo-induced alcoholysis of three-membered ring compounds such as cyclopropanes,[1)] oxiranes,[3d)] 1,2,3-triphenylaziridine,[4b)] and 1-(dimethylcarbamoyl)-2,3-diphenylaziridine.[4c)]

Since the O–H bond (418 K J mol^{-1}) is stronger than the C–H bond (386 K J mol^{-1}) in CH_3OH,[15)] radical cleavage of polar O–H bond seems not to be involved in the MENA formation. The addition of CH_3OH to aziridine ring may therefore occur by an ionic mechanism. It is also likely that the hydrogen bonding of CH_3OH to carbonyl oxygen of NAz facilitates the nucleophilic attack of the methoxide ion on the aziridinyl carbon due to the stabilization of a polar transition state.



(8)

It has been well known that protonated aziridines are readily attacked by various nucleophiles on the aziridinium carbon.[5a)] Consequently, the formation of aziridinium ion intermediate (I) would account for the relatively high yield of NAz oligomer in CH_3OH due to the polymerization faster than that initiated by the amide (Eq. 2).[16)] The propagation may proceed by the cationic ring-opening of NAz as a nucleophile *via* aziridinium ion at the growing chain end. This scheme is consistent with the fact that the NAz oligomer contains a methoxyl group.

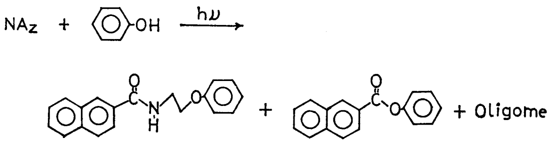

(9)

In $(CH_3)_2CHOH$, on the other hand, the photochemical behavior of NAz was markedly different from that in CH_3OH. The ring-opening reaction due to the addition of alcohol to NAz did not occur in $(CH_3)_2CHOH$, but the formation of an equimolar mixture of ENA and acetone was observed (Runs 14, 15).

$$\text{NAz} + (CH_3)_2CHOH \xrightarrow{h\nu} \text{ENA} + (CH_3)_2C{=}O \qquad (10)$$

It has been well established that $(CH_3)_2CHOH$ readily undergoes oxidation into acetone *via* hydrogen abstraction by various radical species. In view of such a characteristic reactivity of $(CH_3)_2CHOH$, the ring-opening of NAz by a radical mechanism seems to be involved in the photochemical ENA formation. The exclusive formation of ENA without *N*-(2-isopropoxyethyl)-2-naphthamide analogous to MENA may be attributed to the fact that the nucleophilicity of $(CH_3)_2CHOH$ is lower than that of CH_3OH.

In order to clarify the effect of nucleophilicity of alcohol on the photo-induced ring-opening of NAz, the photoreaction of NAz in phenol (72 vol%)–CH_3CN mixture was further examined. Under the irradiation through a Vycor or a Pyrex glass tube, NAz was converted quantitatively to afford *N*-(2-phenoxyethyl)-2-naphthamide (PENA), phenyl-2-naphthoate (PN), and NAz oligomer (Runs 16, 17).

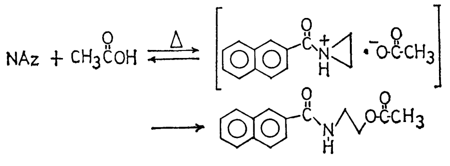


(11)

An identical reaction occurred in the dark to afford PENA and PN with 6% and 2% yields, respectively, but the conversion of NAz was low (8%) relative to the photoreaction. This result shows that the phenolysis of NAz is accelerated by the photo-irradiation.

The formation of PENA accompanied by NAz oligomer is apparently analogous to the photoreaction observed in CH_3OH (Eq. 7). In the phenol system, however, it is characteristic that the phenolysis of the carbonyl-aziridinium nitrogen bond of NAz leading to PN occurs simultaneously with that of the aziridine ring. These results suggest that phenol is capable of nucleophilic attack not only on the aziridinyl carbon but also the carbonyl carbon of NAz in the excited state because the nucleophilicity is higher than that of CH_3OH.

Furthermore, in the relatively strong acidic medium of acetic acid, the quantitative acetolysis of aziridine ring of NAz was observed even in the dark to afford *N*-(2-acetoxyethyl)-2-naphthamide (AENA), which is essentially the same reaction as shown in Eq. 4 for the ring-opening by hydrogen halide. It is likely that the protonation to NAz occurs rapidly in the presence of protonic acids such as hydrogen halide and acetic acid to form an aziridinium ion intermediate, which undergoes nucleophilic addition by halide ion or acetate ion selectively to the aziridinium carbon.



AENA

(12)

These results seem to be consistent with the scheme postulated for the photochemical MENA formation (Eq. 8).

On the basis of the results presented in this paper, it may be concluded that NAz exhibited dual reactivity for the ring-opening reaction in the electronically excited state. In this reaction, solvent molecules play important roles in determining whether radical or ionic reaction occurs. Details of the reactivity of solvent molecule toward NAz in the excited state leading to ring-opening of the aziridinyl group will be reported in a subsequent paper.

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