September, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *2937—2941 (1982)* 2937

# Photoinduced Ring-opening Reaction of 1-(2-Naphthoyl)aziridine in Various Halogenated Hydrocarbons

Sei-ichi Nishimoto, Tsukuru Izukawa, and Tsutomu Kagiya*
*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606*

(Received December 5, 1981)

The in-source photoreaction and the postreaction of 1-(2-naphthoyl)aziridine (NAz) in various halogenated hydrocarbons have been investigated at room temperature under deaerated conditions. Secondary amide such as *N*-(2-chloroethyl)-2-naphthamide (CENA) or *N*-(2-bromoethyl)-2-naphthamide (BENA) was obtained along with a rearranged product of 2-(2-naphthyl)-2-oxazoline (NOz). The initial rate of secondary amide formation increased with decreasing dissociation energy of the carbon–halogen bond of halogenated hydrocarbon. The yield of CENA in the postreaction was substantially equal to that of chloride ion formed *via* the photolyses of chlorinated hydrocarbons. The rearranged product of NOz was confirmed to undergo subsequently photochemical ring-opening reaction to afford CENA or BENA.

We previously reported the photoinduced ring-opening reaction of the aziridinyl group of 1-(2-naphthoyl)-aziridine (NAz) in deaerated solution to afford various secondary amides.[1] The structure of secondary amides obtained was dependent on solvent used for the photoreaction. In the case of chlorinated and brominated hydrocarbons, the formations of *N*-(2-chloroethyl)-2-naphthamide (CENA) and *N*-(2-bromoethyl)-2-naphthamide (BENA) were observed, respectively, accompanied by a rearranged product of 2-(2-naphthyl)-2-oxazoline (NOz).

In the present paper, the in-source photoreaction of NAz in a series of chlorinated and brominated hydrocarbons was investigated in further detail at room temperature under deaerated conditions. The dark reaction of NAz in preirradiated solvents was determined to clarify the influence of the photolysis of solvent. The behavior of NOz as an intermediate in the ring-opening of NAz to CENA or BENA is also described.

## Experimental

IR spectra were recorded on a JASCO DS-403 spectrophotometer and $^1$H NMR spectra on a JEOL PMX-60 spectrometer using tetramethylsilane as an internal standard, respectively. High speed liquid phase chromatography (HLPC) was carried out with a TOYO SODA HLC-802UR apparatus under the same column conditions as reported.[1] Colorimetry was performed with a Shimadzu UV-200S spectrophotometer.

*Materials.* 1-(2-Naphthoyl)aziridine (NAz) and 2-(2-naphthyl)-2-oxazoline (NOz) were prepared and purified as reported.[1] Dibromomethane was purified by distillation. *t*-Butyl chloride was passed through a silica-gel column, washed with ice water, dried with calcium chloride, and then fractionally distilled before use. The other halogenated hydrocarbons (spectroscopic or guaranteed grade) were used without further purification. Gaseous $Cl_2$ was prepared by the reaction of manganese dioxide (10 g) with concentrated hydrochloric acid (50 $cm^3$).[2]

*Procedures.* The in-source photoreaction of NAz in various halogenated hydrocarbons was carried out according to the same procedures as reported.[1]

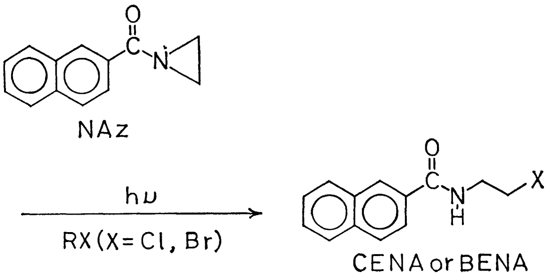
In the postreaction of NAz, each halogenated hydrocarbon (2 $cm^3$) was irradiated in advance at room temperature under deaerated conditions in a Vycor or Pyrex glass tube, using a merry-go-round apparatus equipped with a high-pressure mercury lamp (EIKOSHA 400 W). NAz was dissolved in the resulting halogenated hydrocarbon and permitted to stand for a specified time at room temperature in the dark. The photolytic product such as HCl or $Cl_2$ was extracted with water (10 $cm^3$) from 1 $cm^3$ aliquots of chlorinated hydrocarbons after preirradiation. Chloride ion derived from HCl and $Cl_2$ in aqueous solution was determined by Volhard titration using silver nitrate.[3] Similarly, both HBr and $Br_2$ was extracted with water (100 $cm^3$) from 0.1 $cm^3$ aliquots of brominated hydrocarbons after preirradiation. From 5 $cm^3$ aliquots of the aqueous solution thus obtained $Br_2$ was extracted with $CCl_4$ (45 $cm^3$) and was determined colorimetrically with diphenylcarbazone.[4] Bromide ion due to HBr in aqueous solution was determined by Volhard titration and colorimetry with diphenylcarbazone.[5]

The structures of CENA, BENA, and NOz were identified by comparing their spectral data with those of the authentic sample.[1] The product afforded by the reaction of NOz with HCl in $CHCl_3$ was assigned to 2-(2-naphthyl)-2-oxazolinium hydrochloride from the IR spectral data; IR ($CHCl_3$): 2450 ($=\overset{+}{N}H$), 1947 ($C=\overset{+}{N}H$), 1640 ($C=\overset{+}{N}$), 1239 (C–O), and 895 (ring) $cm^{-1}$.[6]

The conversion of NAz and the product yield were determined by the same method as reported.[1]

## Results and Discussion

*In-source Photoreaction of NAz in Various Halogenated Hydrocarbons.* Solutions of NAz in various halogenated hydrocarbons (see Table 1) were irradiated with the UV light through a Vycor (>215 nm) or a Pyrex (>286 nm) glass tube under deaerated conditions. Inspection of Table 1 provides a general feature that *N*-(2-chloroethyl)-2-naphthamide (CENA) is a common photoproduct in chlorinated hydrocarbons and *N*-(2-bromoethyl)-2-naphthamide (BENA) in brominated hydrocarbons, respectively, irrespective of the irradiation wavelength.



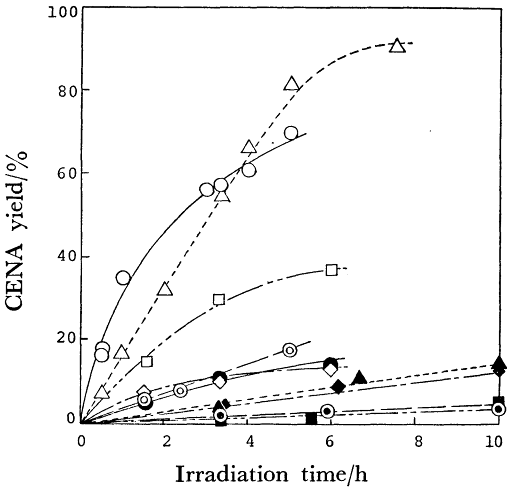


Fig. 1. Variation in CENA yield as a function of irradiation time in the in-source photoreaction of NAz. ——: $CCl_4$ (V:○, P:●), ----: $CHCl_3$ (V:△, P:▲), — —: $CH_2Cl_2$ (V:◎, P:⊙), ——: *t*-BuCl (V:◇, P:◆), ———: PhCl (V:□, P:■).

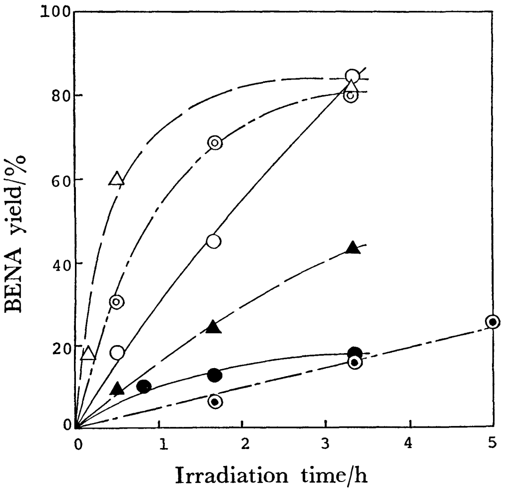


Fig. 2. Variation in BENA yield as a function of irradiation time in the in-source photoreaction of NAz. ——: $CH_2Br_2$ (V:○, P:●), — —: *n*-PrBr (V:△, P:▲), ----: PhBr (V:◎, P:⊙).

Variations in the CENA and BENA yields as a function of irradiation time are shown in Figs. 1 and 2, respectively. Table 1 summarizes the initial rate of the formation of halogen substituted secondary amide which was estimated from Figs. 1 and 2 by extrapolation. The initial rate in the Vycor system is larger than that in the Pyrex system by a factor of 3—76 in chlorinated hydrocarbons and 3—14 in brominated hydrocarbons, depending on the solvent structure. It can also be seen from Table 1 that the initial rate of CENA formation observed in a series of chloromethanes increases with increasing the number of substituted chlorine atom; $CCl_4 > CHCl_3 > CH_2Cl_2$. Comparing the initial rate of BENA formation with that of CENA formation observed in a couple of brominated and chlorinated hydrocarbons having mutually analogous structure, *e.g.*, $CH_2Br_2/CH_2Cl_2$ and PhBr/PhCl, the former was 6—33 times larger than the latter.

Table 1. In-source photoreaction of NAz in various halogenated hydrocarbons[a)]

| Run | Solvent | Glass tube | $[NAz]_0$ / mmol $dm^{-3}$ | Initial rate × $10^7$ / mol $min^{-1}$ | |
|---|---|---|---|---|---|
| | | | | CENA (BENA)[b)] | NOz |
| 1 | $CCl_4$ | V | 91 | 5.8 | 0.041 |
| 2 | $CCl_4$ | P | 91 | 0.52 | 0 |
| 3 | $CHCl_3$ | V | 91 | 2.5 | 0.38 |
| 4 | $CHCl_3$ | P | 91 | 0.23 | 0 |
| 5 | $CH_2Cl_2$ | V | 90 | 0.52 | 0 |
| 6 | $CH_2Cl_2$ | P | 90 | 0.056 | 0 |
| 7 | *t*-BuCl | V | 65 | 0.48 | 0 |
| 8 | *t*-BuCl | P | 65 | 0.15 | 0 |
| 9 | PhCl | V | 90 | 1.6 | 0 |
| 10 | PhCl | P | 90 | 0.021 | 0 |
| 11 | $CH_2Br_2$ | V | 90 | (4.9) | 0 |
| 12 | $CH_2Br_2$ | P | 90 | (1.6) | 3.8 |
| 13 | *n*-PrBr | V | 17 | (4.6) | 0 |
| 14 | *n*-PrBr | P | 17 | (1.1) | 0.27 |
| 15 | PhBr | V | 90 | (9.3) | 0 |
| 16 | PhBr | P | 90 | (0.69) | 0.75 |

a) Under the photoirradiation through a Vycor (V) or a Pyrex (P) glass tube at room temperature for 200 min. b) The value in parenthesis denotes the initial rate of BENA formation.

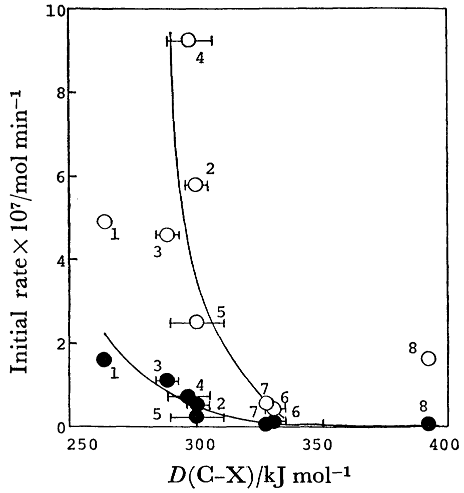


Fig. 3. Relationship between the initial rate of CENA or BENA formation and the carbon-halogen (C–X) bond-dissociation energy of halogenated hydrocarbon solvent for the Vycor (○) and Pyrex (●) systems. 1: $CH_2Br_2$, 2: $CCl_4$, 3: *n*-PrBr, 4: PhBr, 5: $CHCl_3$, 6: *t*-BuCl, 7: $CH_2Cl_2$, 8: PhCl.

As shown in Fig. 3, a fairly good correlation between the initial rate of secondary amide formation and the dissociation energy of the carbon-halogen bond $D$(C–X) of solvent[7)] except for PhCl was obtained in each of the Vycor and Pyrex systems. Apparently, the decrease in the $D$(C–X) value tends to increase the initial rate of CENA or BENA formation. This seems to indicate that the photochemical ring-opening of NAz to CENA or BENA involves the radical decomposition of halogenated hydrocarbon solvent in its car-

TABLE 2. POSTREACTION OF NAz IN VARIOUS HALOGENATED HYDROCARBONS[a)]

| Run | Solvent | Glass tube | $[NAz]_0$ / mmol dm$^{-3}$ | Conversion / % | Product yield[b)]/% |  |
|---|---|---|---|---|---|---|
|  |  |  |  |  | CENA(BENA)[c)] | NOz |
| 1 | $CCl_4$ | V | 91 | 53 | 53 | 0 |
| 2 | $CCl_4$ | P | 91 | 0 | 0 | 0 |
| 3 | $CHCl_3$ | V | 91 | 52 | 52 | 0 |
| 4 | $CHCl_3$ | P | 91 | 0 | 0 | 0 |
| 5 | $CH_2Cl_2$ | V | 90 | 33 | 33 | 0 |
| 6 | $CH_2Cl_2$ | P | 90 | 0 | 0 | 0 |
| 7 | *t*-BuCl | V | 65 | 9 | 9 | 0 |
| 8 | *t*-BuCl | P | 65 | 3 | 3 | 0 |
| 9 | PhCl | V | 90 | 39 | 39 | 0 |
| 10 | PhCl | P | 90 | 12 | 12 | 0 |
| 11 | $CH_2Br_2$ | V | 90 | 49 | (33) | 14 |
| 12 | $CH_2Br_2$ | P | 90 | 30 | (18) | 10 |
| 13 | *n*-PrBr | V | 17 | 17[d)] | (17)[d)] | 0[d)] |
| 14 | *n*-PrBr | P | 17 | 3 | (3) | 0 |
| 15 | PhBr | V | 90 | 54 | (28) | 26 |
| 16 | PhBr | P | 90 | 37 | (11) | 26 |

a) Under the photoirradiation through a Vycor (V) or a Pyrex (P) glass tube at room temperature for 200 min unless otherwise noted. b) Yield based on NAz. c) The value in parenthesis denotes the BENA yield. d) 30 min-irradiation.

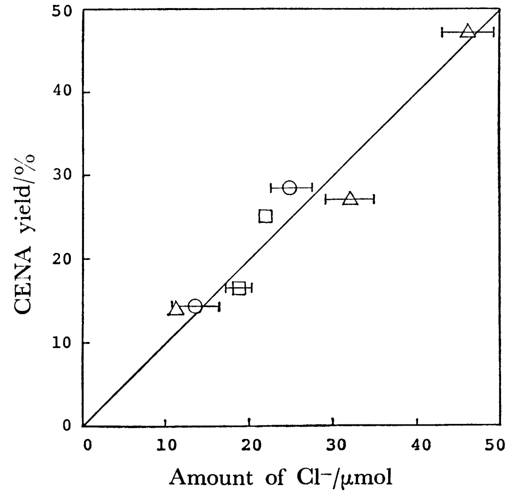


Fig. 4. A plot of CENA yield against the amount of chloride ion ($Cl^-$) in the Vycor postreaction system of NAz.
○: $CCl_4$, △: $CHCl_3$, □: $CH_2Cl_2$.

bon-halogen bond.

The previous paper suggested that both the CENA and BENA formations are due to the dark reaction of NAz with the photolytic product of a halogenated hydrocarbon.[1)] Supposing that the $D$(C–X) value of a given halogenated hydrocarbon provides a measure of the reactivity for photodecomposition, the previous account may be consistent with a correlation observed in Fig. 3. Nevertheless, in view of a fact that most of the incident light (not less than 90%) is absorbed by NAz under the present conditions except for the cases in PhCl and PhBr, it seems likely that the reaction of NAz in the electronically excited state with halogenated hydrocarbon solvents also affords CENA or BENA.

*Postreaction of NAz in Various Halogenated Hydrocarbons.* In order to estimate the contribution from the ring-opening of NAz arising from the photolysis of halogenated hydrocarbon, the dark reaction of NAz was carried out in various halogenated hydrocarbons pre-irradiated through a Vycor or Pyrex glass tube under deaerated conditions. The product yields are summarized in Table 2.

It can be seen from Table 2 that the postreaction of NAz in chlorinated hydrocarbons affords CENA as a sole product. Analogous to gaseous HCl,[1)] $Cl_2$ was confirmed to afford CENA exclusively when bubbled into a solution of NAz in $CCl_4$. Furthermore, as shown in Fig. 4, the CENA yield in the Vycor systems is in fair agreement with the amount of chloride ions produced *via* photolyses of chlorinated hydrocarbons. These results indicate that the photolytic products of both HCl and $Cl_2$ are responsible for the ionic ring-opening of NAz to afford CENA.

In the postreactions in $CH_2Br_2$ and PhBr, the yield of NOz is comparable to that of BENA (Table 2). This is in contrast to the postreaction in *n*-PrBr in which only BENA is obtained. On irradiation through a Pyrex glass for 1 h, both bromide ion (53.3 mmol dm$^{-3}$) and $Br_2$ (5.6 mmol dm$^{-3}$) were detected in $CH_2Br_2$, whereas only bromide ion (55.4 mmol dm$^{-3}$) was produced in *n*-PrBr. A separate experiment indicated that NAz is converted almost quantitatively to BENA (94%) in the presence of an equimolar amount of aqueous HBr in $CH_2Br_2$, accompanied by a minor product of NOz (6%). On the other hand, although the overall conversion decreased considerably, the yield of NOz (5%) was comparable to that of BENA (6%) in the presence of aqueous $Br_2$ in $CH_2Br_2$. It seems therefore that a photolytic product of $Br_2$ is a possible species being responsible for the rearrangement of NAz to NOz.

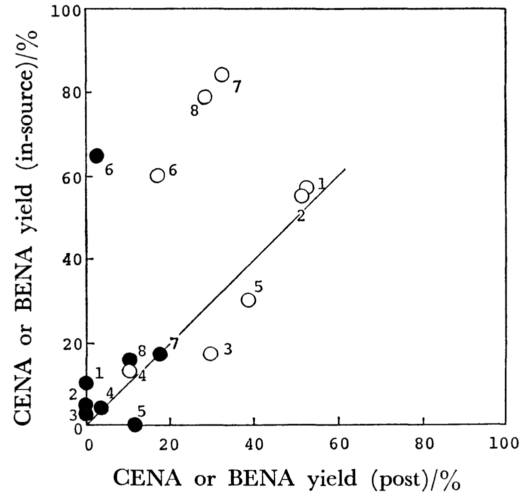


Fig. 5. Relationship between the CENA or BENA yield in the in-source photoreaction and that in the postreaction; (○) Vycor and (●) Pyrex systems. 1: $CCl_4$, 2: $CHCl_3$, 3: $CH_2Cl_2$, 4: *t*-BuCl, 5: PhCl, 6: *n*-PrBr, 7: $CH_2Br_2$, 8: PhBr.

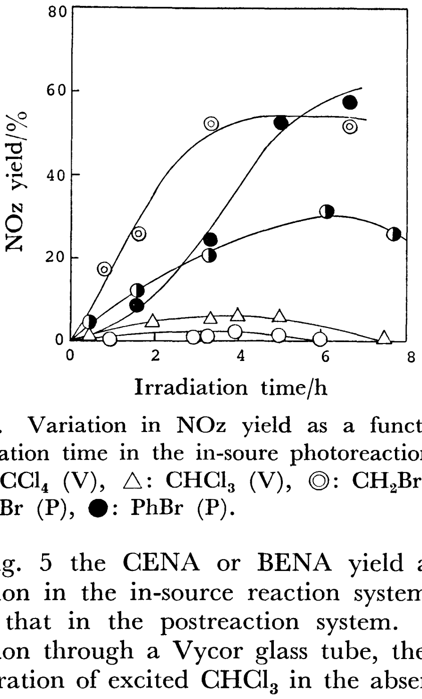


Fig. 6. Variation in NOz yield as a function of irradiation time in the in-soure photoreaction of NAz. ○: $CCl_4$ (V), △: $CHCl_3$ (V), ◎: $CH_2Br_2$ (P), ◑: *n*-PrBr (P), ●: PhBr (P).

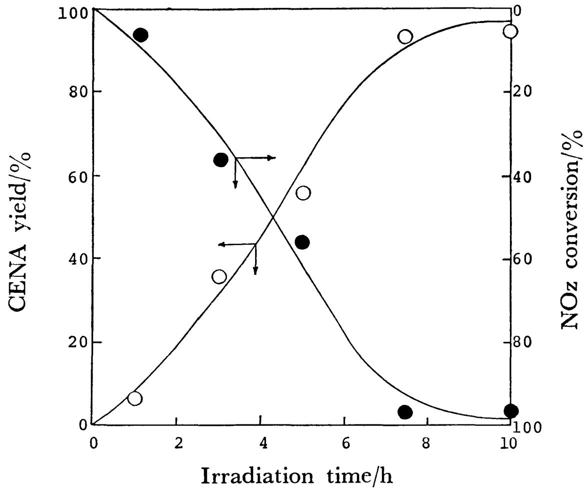


Fig. 7. Variation in NOz conversion (●) and CENA yield (○) as a function of irradiation time in the $CHCl_3$-Vycor in-source photoreaction system; $[NOz]_0 = 91$ mmol $dm^{-3}$.

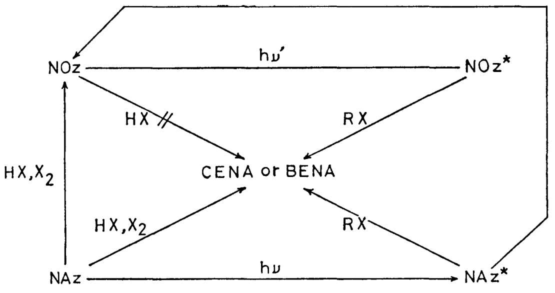
In Fig. 5 the CENA or BENA yield at 200 min-irradiation in the in-source reaction system is plotted against that in the postreaction system. Under the irradiation through a Vycor glass tube, the stationary concentration of excited $CHCl_3$ in the absence of NAz (91 mmol $dm^{-3}$) was estimated to be at least 600-fold larger than that in the in-source photoreaction system because of the intense UV absorption by NAz. It follows that the apparent CENA yield in the postreaction system would provide a roughly 600-fold overestimation for the contribution from the photolysis of $CHCl_3$ to the CENA formation in the in-source photoreaction system. Taking into account such a circumstance, the apparent agreement between the CENA yields in the in-source photoreaction and postreaction in a series of chlorinated hydrocarbon solvents indicates that the photochemical CENA formation in source can be attributed almost exclusively to the reaction of excited NAz with solvent molecules. More explicitly, the BENA yield in the in-source photoreactions is seen to exceed considerably that in the postreactions (Fig. 5).

In this connection, it can be presumed from Fig. 3 that NAz undergoes radical cleavage of the aziridine ring moiety in the electronically excited state to abstract halogen atom from halogenated hydrocarbon solvents. Such a halogen abstraction would be a rate-determining step in the photochemical CENA and BENA formations in source.

*Photochemical Formation and Decomposition of NOz in Various Halogenated Hydrocarbons.* It is remarkable in Table 1 that although BENA is afforded exclusively on irradiation of NAz in brominated hydrocarbons through a Vycor glass tube, the rearrangement of NAz to NOz occurs simultaneously in the Pyrex system. Such a formation of NOz was also observed in $CCl_4$ and $CHCl_3$ even in the Vycor system.

Figure 6 shows the variation in NOz yield as a function of irradiation time. The yields of NOz exceed 50% in $CH_2Br_2$ and PhBr on irradiation for 200 and 300 min, respectively, and 30% in *n*-PrBr for 360 min. The NOz formation was nevertheless no more observed in these solvents by the prolonged irradiation for over 20 h under the same conditions. During the irradiation for over 300 min in $CCl_4$ and $CHCl_3$, an analogous variation in the NOz yield with its maximum value of <6% was observed.

As can be seen from Fig. 7, NOz undergoes ring-opening reaction to afford CENA as a sole product on irradiation of a deaerated solution in $CHCl_3$ through a Vycor glass tube. Apparently, the photochemical behavior of NOz is very similar to that of NAz. It is however remarkable that the reactivity of NOz toward HCl is quite different from that of NAz. Thus the slow formation of 2-(2-naphthyl)-2-oxazolinium hydrochloride salt[4] was observed when gaseous HCl was bubbled through a solution of NOz in $CHCl_3$, whereas NAz reacts rapidly with HCl to afford CENA under the same conditions.[1] It follows that the photochemical CENA formation shown in Fig. 7 may be attributed to the reaction of excited NOz with $CHCl_3$.



Scheme 1.

In view of the results presented above, the following scheme may be drawn for the photochemical ring-opening reaction of NAz in halogenated hydrocarbons (RX). Although hydrogen halide (HX) and halogen molecule ($X_2$) derived from the solvent photolysis are highly reactive to NAz, the formation of such species in the in-source photoreaction system would be minor under conditions investigated.

## References

1) S. Nishimoto, T. Izukawa, and T. Kagiya, *Bull. Chem. Soc. Jpn.*, **55**, 1484 (1982).

2) M. Schmeisser, "Handbuch der Präparativen Anorganishen Chemie," ed by G. Brauer, Ferdinand Enke Verlag, Stuttgart (1960), p. 249.

3) M. A. Rosanoff and A. E. Hill, *J. Am. Chem. Soc.*, **29**, 269 (1907).

4) T. Okutani, *Nippon Kagaku Zasshi*, **88**, 737 (1967).

5) A. Tomonari, *Nippon Kagaku Zasshi*, **83**, 459 (1962).

6) T. Kagiya and T. Matsuda, *J. Macromol. Sci., Chem.*, **A-5**, 1277 (1971).

7) For $CCl_4$, *t*-BuCl, *n*-PrBr, and PhBr, J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); for $CHCl_3$ and $CH_2Br_2$, J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, **1965**, 3939 and 3950; for PhCl, M. Fox, W. C. Nichols, Jr., and D. M. Lemal, *J. Am. Chem. Soc.*, **95**, 8164 (1973); and for $CH_2Cl_2$, standard bond energy of C–Cl bond is adopted (R. T. Sanderson, "Chemical Bonds and Bond Energy," Academic Press, Inc., New York (1971), p. 153).