REACTION OF PHOTOGENERATED VINYL CATIONS WITH AMBIDENT ANIONS

Tsugio KITAMURA, Shinjiro KOBAYASHI, and Hiroshi TANIGUCHI[*]

Department of Applied Chemistry, Faculty of Engineering,

Kyushu University 36, Hakozaki, Fukuoka 812

Photolysis of vinyl bromides with cyanate anion in a two-phase
system gave only isoquinolinones as the N-site attacked products.
However, the photolysis with thiocyanate anion gave both the N-site
attacked products, isothioquinolinones or vinyl isothiocyanates,
and the S-site attacked products, vinyl thiocyanates.

Although solvolytic reactions of vinyl halides have been investigated exten-
sively, the reactions of the solvolytically generated vinyl cations with various
nucleophiles, except for solvents, are little known.[1] Recently we found that
photogenerated vinyl cations react with azide anion in nonnucleophilic solvents.[2]
It is suggested that this photochemical technique is useful for the investigation
on nucleophilic substitution of vinyl halides. This paper describes the behavior
of photogenerated vinyl cations toward ambident anions which has not been
reported so far and provides a useful synthesis of isoquinolinone derivatives
from vinyl halides.

We carried out the reaction of vinyl cations with ambident anions using a
photochemical method under phase transfer conditions.[2] A two-phase solution was
prepared by mixing vinyl bromide 1 (1 mmol) in methylene chloride (90 ml), potas-
sium cyanate or thiocyanate (10 mmol) in water (10 ml), and tetrabutylammonium
bromide (2 mmol) in an immersion-type photoreactor. Irradiation of this solution
was performed with stirring by use of a Pyrex-filtered high-pressure Hg lamp (100
W) under N_2 atmosphere at 10 °C. After workup of the organic layer the crude
reaction mixture was submitted to column chromatography on silica gel. The
products were assigned by the spectral data[3] and elemental analyses.

In the case of cyanate anion, as shown in Table 1, triarylvinyl bromides 1a-
1d afforded the only isoquinolinones 4a-4d which should be formed by photo-

cyclization of vinyl isocyanates $\underline{3a}$-$\underline{3d}$.[4] No products derived from the O-site

attack of cyanate anion were detected. These results mean that cyanate anion

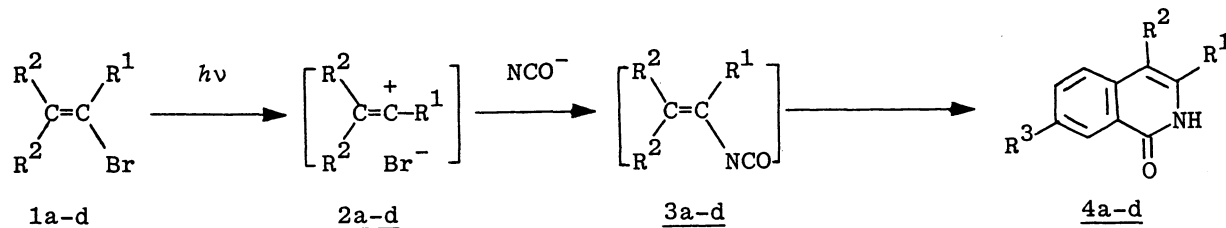reacts with vinyl cations regiospecifically and are parallel to those of alkyl

halides.[5]

$\underline{1a-d}$ $\qquad$ $\underline{2a-d}$ $\qquad$ $\underline{3a-d}$ $\qquad$ $\underline{4a-d}$

Table 1. Isoquinolinones $\underline{4}$ from the photolysis of vinyl bromides $\underline{1}$ in the
presence of cyanate anion

Vinyl bromide $\underline{1}$[a]		Irr. time	Conv.	Yield of $\underline{4}$[b]
R^1	R^2	h	%	%
a: p-An	p-An	2	75	93 (R^3 = OMe)
b: p-An	Ph	3	89	91 (R^3 = H)
c: p-Tol	Ph	8	83	77 (R^3 = H)
d: Ph	Ph	24	100	46[c] (R^3 = H)

a) An = $MeOC_6H_4$; Tol = MeC_6H_4. b) Isolated yield. Based on the consumed vinyl
bromide $\underline{1}$. c) Reduced products (triphenylethylene and 9-phenylphenanthrene)
were also obtained in ca. 40% yield.

On the other hand, thiocyanate anion behaved in a different way from cyanate

anion. It is well-known that alkyl halides readily react with thiocyanate anion,

where the ratios of S- and N-site displacements both in S_N1 reaction and in S_N2

reaction have been discussed.[6] However, the reaction of vinyl halides with thio-

cyanate anion has not been reported except for the addition-elimination reaction,

where a soft S-site attack only takes place.[7] As shown in Table 2, photolysis

of triarylvinyl bromides $\underline{1a}$-$\underline{1d}$ in the presence of thiocyanate anion afforded vinyl

thiocyanates $\underline{5a}$-$\underline{5d}$ and isothioquinolinones $\underline{7a}$-$\underline{7d}$. The isomerization from $\underline{5}$ to $\underline{7}$

did not occur when vinyl thiocyanate $\underline{5b}$ was irradiated in methylene chloride for

2 h. This indicates $\underline{5}$ and $\underline{7}$ are produced independently. The isothioquinolinone

$\underline{7}$ is considered to be formed by photocyclization of the corresponding vinyl iso-

thiocyanate $\underline{6}$. This is supported by the result that photolysis of α-aryl-β,β-

dimethylvinyl bromides $\underline{1e}$ and $\underline{1f}$ in the presence of thiocyanate anion gives the

vinyl isothiocyanates $\underline{6e}$ and $\underline{6f}$ together with the vinyl thiocyanates $\underline{5e}$ and $\underline{5f}$.
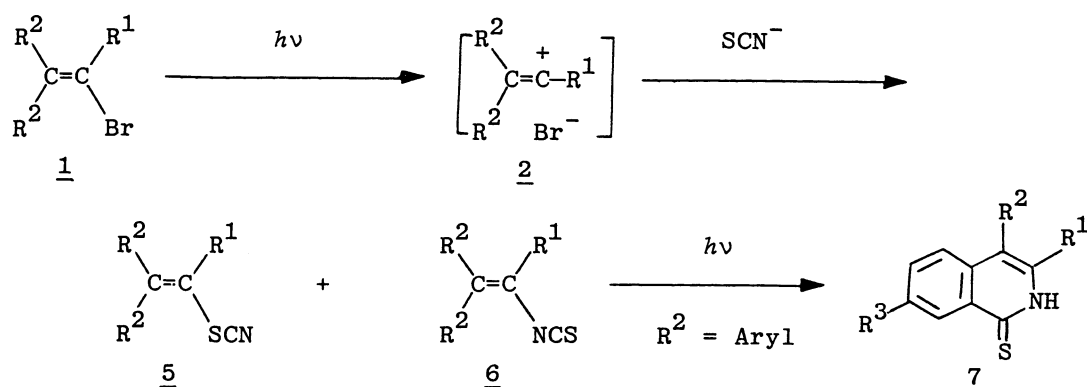
Table 2. Product distributions in the photolysis of vinyl bromide **1** in the presence of thiocyanate anion

| Vinyl bromide **1** | | Irr. time[a] | Conv. | Yield/%[c] | | | [**5**] |
R^1	R^2	h	%	**5**	**6**	**7**	([**6**]+[**7**])
a: p-An	p-An	1	77	77	0	15 (OMe)[d]	5.1
b: p-An	Ph	1.5	85	62	0	26 (H)[d]	2.4
c: p-Tol	Ph	3	60	39	0	31 (H)[d]	1.3
d: Ph	Ph	3	53	48	0	34 (H)[d]	1.4
e: p-An	Me	1.5[b]	46	42	27	–	1.6
f: Ph	Me	3[b]	66	18	29	–	0.62

a) Irradiated through a Pyrex-filter. b) Irradiated without a Pyrex-filter.
c) Isolated yield. Based on the consumed vinyl bromide **1**. d) Substituent R^3.

Thus, thiocyanate anion can react with the photogenerated vinyl cation **2** at either site of sulfur and nitrogen atoms.

The selectivity of the S-product and the N-product, i.e., [**5**]/([**6**]+[**7**]), is given in Table 2. Tris(p-methoxyphenyl)vinyl bromide **1a** gave the highest selectivity among the vinyl bromides used. The selectivity on the substituent is the following order: p-MeOC$_6$H$_4$ > Ph $\geq$ p-MeC$_6$H$_4$.[8] As a whole, low values of selectivity in the photolysis of vinyl bromides are characteristic of S_N1 reactions, since S_N1 reaction of alkyl halides shows also a low selectivity value.[6] The order of the selectivity should be discussed by the hardness and softness of the reaction center. Higher selectivity of p-methoxyphenyl group is attributed to the increasing preference for the reaction with softer sulfur atom of thiocyanate anion.

References

1) P. J. Stang, Z. Rappoport, M. Hanack, and R. L. Subramanian, "Vinyl Cations," Academic Press, New York (1979).

2) T. Kitamura, S. Kobayashi, and H. Taniguchi, Tetrahedron Lett., 1979, 1619; T. Kitamura, S. Kobayashi, and H. Taniguchi, submitted for publication in J. Org. Chem.

3) 4a: Mp 232-235 °C(benzene-ethanol); NMR(CDCl$_3$) δ=3.72(s,3H,OMe), 3.77(s,3H,OMe), 3.90(s,3H,OMe), 6.61-7.82(m,11H,ArH), and 9.41(bs,1H,NH); IR(Nujol) 1630 cm^{-1}. 4b: Mp 250-252 °C(benzene-ethanol); NMR(CDCl$_3$) δ=3.68(s,3H,OMe), 6.57-7.61(m, 12H,ArH), 8.28-8.43(m,1H,ArH), and 9.51(bs,1H,NH); IR(Nujol) 1640 cm^{-1}. 4c: Mp 226-227 °C(benzene-ethanol); NMR(CDCl$_3$) δ=2.37(s,3H,Me), 6.90-7.71(m,12H, ArH), 8.39-8.60(m,1H,ArH), and 9.10(bs,1H,NH); IR(Nujol) 1650 cm^{-1}. 4d: Mp 251-252 °C(benzene-ethanol); NMR(CDCl$_3$) δ=7.00-7.46(m,13H,ArH), 8.28-8.54(m,1H, ArH), and 9.44(bs,1H,NH); IR(Nujol) 1640 cm^{-1}. 5a: Mp 101-103 °C(ethanol); NMR(CDCl$_3$) δ=3.63(s,3H,OMe), 3.71(s,3H,OMe), 3.77(s,3H,OMe), and 6.39-7.14(m, 12H,ArH); IR(Nujol) 2150 cm^{-1}. 7a: Mp 222-226 °C(benzene-CH$_2$Cl$_2$); NMR(CDCl$_3$) δ=3.72(s,3H,OMe), 3.76(s,3H,OMe), 3.92(s,3H,OMe),6.30-7.40(m,10H,ArH), 8.10- 8.40(m,1H,ArH), and 10.60(bs,1H,NH). 5b: Mp 132-134 °C(benzene-hexane); NMR (CDCl$_3$) δ=3.68(s,3H,OMe) and 6.59-7.26(m,14H,ArH); IR(Nujol) 2140 cm^{-1}. 7b: Mp 252-256 °C(benzene-CH$_2$Cl$_2$); NMR(CDCl$_3$) δ=3.76(s,3H,OMe), 6.67-7.69(m,12H, ArH), 8.94-9.10(m,1H,ArH), and 10.67(bs,1H,NH). 5c: oil; NMR(CDCl$_3$) δ=2.26(s, 3H,Me) and 6.70-7.50(m,14H,ArH); IR(neat) 2130 cm^{-1}. 7c: Mp 249-254 °C (benzene-CH$_2$Cl$_2$); NMR(CDCl$_3$) δ=2.27(s,3H,Me), 6.30-7.60(m,12H,ArH), 8.32-9.02 (m,1H,ArH), and 10.62(bs,1H,NH). 5d: oil; NMR(CCl$_4$) δ=6.65-7.40(m,ArH); IR (neat) 2140 cm^{-1}. 7d: Mp 264-269 °C(benzene-CH$_2$Cl$_2$); NMR(CDCl$_3$) 6.75-7.60(m, 13H,ArH), 8.75-8.96(m,1H,ArH), and 10.40(bs,1H,NH). 5e: oil; NMR(CCl$_4$) δ= 1.75(s,3H,Me), 2.10(s,3H,Me), 3.74(s,3H,OMe), and 6.65-7.13(m,4H,ArH); IR(neat) 2140(s) and 2050 cm^{-1}(m,br). 6e: oil; NMR(CCl$_4$) δ=1.75(s,3H,Me), 1.99(s,3H, Me), 3.73(s,3H,OMe), and 6.67-7.20(m,4H,ArH); IR(neat) 2060 cm^{-1}(s,br). 5f: oil; NMR(CCl$_4$) δ=1.75(s,3H,Me), 2.11(s,3H,Me), and 7.16(bs,5H,ArH); IR(neat) 2140(s) and 2000 cm^{-1}(s,br). 6f: oil; NMR(CCl$_4$) δ=1.74(s,3H,Me), 1.98(s,3H,Me), and 7.13(bs,5H,ArH); IR(neat) 2060 cm^{-1}(s,br).

4) F. Eloy and A. Deryckere, J. Heterocycle Chem., 7, 1191 (1970); R. L. Williams and M. G. ElFayoumy, ibid., 9, 1021 (1972); J. H. Boyer and G. J. Mikol, ibid., 9, 1325 (1972).

5) R. Richter and H. Ulrich, "The Chemistry of Cyanates and Their Thio Deriva- tives," ed by S. Patai, John Wiley & Sons, New York (1977), Chap. 17; J. March, "Advanced Organic Chemistry," 2nd ed, McGraw-Hill, Inc. (1977), p. 336.

6) R. G. Guy, "The Chemistry of Cyanates and Their Thio Derivatives," ed by S. Patai, John Wiley & Sons, New York (1977), Chap. 18.

7) M. Koremura and K. Tomita, Nippon Nogei Kagaku Kaishi, 36, 479 (1962); Z. Rappoport and A. Topol, J. Am. Chem. Soc., 102, 406 (1980).

8) The similar order, p-MeOC$_6$H$_4$ > Ph > p-MeC$_6$H$_4$, was observed in the reaction of p-substituted benzyl bromides with mercury thiocyanate in hexane.