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REACTION OF PHOTOGENERATED VINYL CATIONS WITH AMBIDENT ANIONS

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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 extensively, 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), potassium 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 photocyclization of vinyl isocyanates 3a-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]

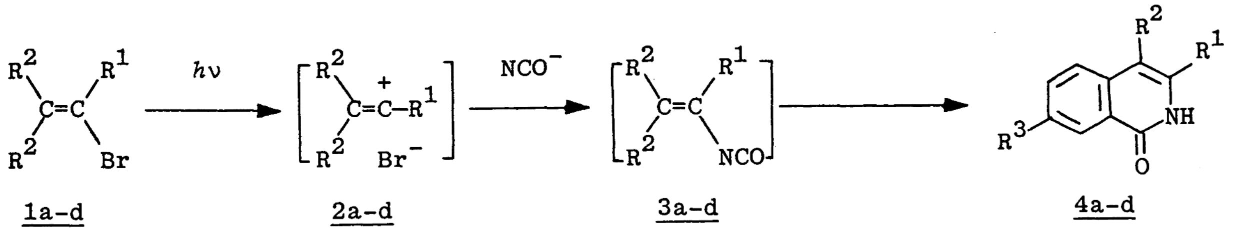

Table 1. Isoquinolinones 4 from the photolysis of vinyl bromides 1 in the presence of cyanate anion

Vinyl bromide 1[a)] R^1	R^2	Irr. time h	Conv. %	Yield of 4[b)] %
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 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 thiocyanate 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 1a-1d in the presence of thiocyanate anion afforded vinyl thiocyanates 5a-5d and isothioquinolinones 7a-7d. The isomerization from 5 to 7 did not occur when vinyl thiocyanate 5b was irradiated in methylene chloride for 2 h. This indicates 5 and 7 are produced independently. The isothioquinolinone 7 is considered to be formed by photocyclization of the corresponding vinyl isothiocyanate 6. This is supported by the result that photolysis of α-aryl-β,β-dimethylvinyl bromides 1e and 1f in the presence of thiocyanate anion gives the vinyl isothiocyanates 6e and 6f together with the vinyl thiocyanates 5e and 5f.

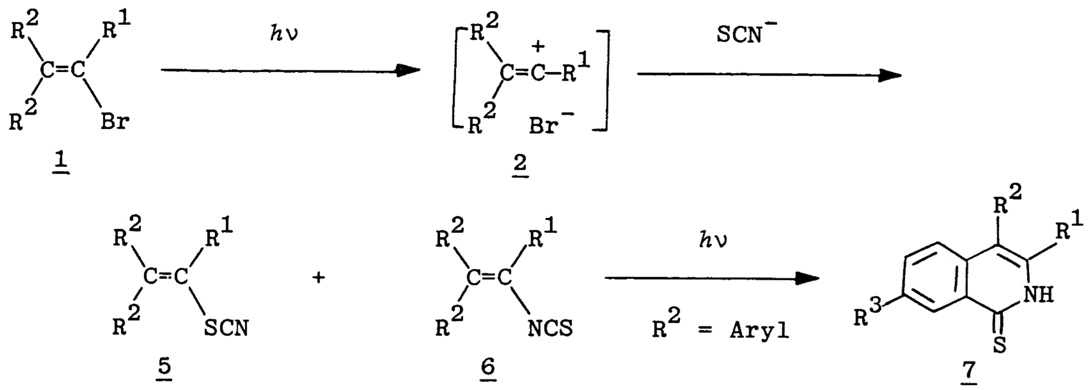

Table 2. Product distributions in the photolysis of vinyl bromide 1 in the presence of thiocyanate anion

Vinyl bromide 1		Irr. time[a)]	Conv.	Yield/%[c)]			[5]/([6]+[7])
R^1	R^2	h	%	5	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-$MeOC_6H_4$ > Ph ≥ p-MeC_6H_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 Derivatives," 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.

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