phenacyl bromide (**2**), and 30 mL of chloroform were heated at reflux with stirring for 21 h. A white solid began to precipitate within 10 min; the solution gradually turned yellow then orange. After cooling the solid was filtered, washed three times with chloroform, and dried; yield was 1.1 g, mp 215–220 °C (chloroform filtrate contained pentafluorophenacyl bromide adduct of **17a**, see below). This solid was slurried with 25 mL of ethanol, cooled in an ice bath, treated with 1 g of potassium carbonate in 5 mL of water, diluted with 20 mL of water, and extracted three times with methylene chloride. From the latter solution, 0.8 g of free bases were recovered; TLC on silica gel indicated only two compounds, a yellow fluorescent material and starting bromotriazaadamantane. Chromatography on 20 g of silica gel using chloroform furnished 0.33 g of the fluorescent component; recrystallization from *n*-hexane gave bright yellow, feathery needles and blades, mp 198–200 °C. NMR (see Table I). Analysis of CI mass spectrum revealed M/I + 1 = 406. High-resolution EI spectrum reveals a match for parent minus Br, $C_{15}H_{12}N_3O_1F_4$, which is within 6.1 ppm of the calculated mass. Anal. Calcd for $C_{15}H_{12}BrF_4N_3O$: C, 44.35; H, 2.98; Br, 19.67; F, 18.71; N, 10.35. Found: C, 44.60; H, 3.20; Br, 19.54; F, 18.67; N, 10.35.

Pentafluorphenacyl Bromide Adduct of 17a (19). The original chloroform mother liquors and washings from the preparation of **17a** were combined and evaporated giving 1.9 g of a viscous orange oil. This was extracted three times with 20-mL portions of *n*-hexane as follows: heat to boiling, cool to ambient, decant the supernatant (the hexane-insoluble residue contained additional quantities of **17a** and **19**, see below). Evaporation of the combined extracts gave 0.7 g of an oil mixed with solid; slurrying with 10 mL of *n*-hexane and chilling to 5 °C yielded a yellow solid. Recrystallization from chloroform/*n*-hexane gave a pale yellow powder, mp 213–214 °C dec. Analysis of CI mass spectrum indicate M/I + 1 = 614. High-resolution analysis reveals a match for parent minus bromine $C_{23}H_{13}N_3O_2F_9$, which is within 7.3 ppm of the calculated mass. ^1H and ^{13}C NMR results are consistent with a C_9N_3 cage molecule and two inequivalent carbonyl units. Anal. Calcd for $C_{23}H_{13}BrF_9N_3O_2$: C, 44.97; H, 2.13; Br, 13.01; F, 27.84; N, 6.84. Found: C, 45.30; H, 2.27; Br, 13.10; F, 27.44; N, 6.90.

Recovery of Additional 17a and 19. The 1.2 g of hexane-insoluble residue (from isolation of **19** above) was converted to free bases; 0.88 g, mp 189–195 °C. An additional 0.12 g of the adduct **19** was isolated by dissolving this mixture in 6 mL of chloroform, chilling to 5 °C, filtering through a cold frit, and washing once with chloroform chilled in a dry ice–acetone bath. Recrystallization from 30 mL of 1:1 acetonitrile–absolute ethanol furnished pale-yellow, small, flat needles, mp 212–213 °C dec. Chromatography of the mother liquors on 15 g of silica gel with chloroform as eluent gave an additional 0.15 g of **19** followed by 0.23 g of **17a**.

3-Aminotetrafluorobenzo[*b*]-1,5,7-triazatetracyclo-[$7.3.1^{3,7}.1^{5,9}.0^{4,9}$]tetradecan-10-one (17b). This compound was made similarly from 7-amino-1,3,5-triazaadamantane and pentafluorophenacyl bromide; bright yellow pills after recrystallization from 8:5 cyclohexane–*n*-hexane; mp 194–196 dec. NMR (see Table I). Anal. Calcd for $C_{15}H_{14}F_4N_4O$: F, 22.20; N, 16.37. Found: F, 21.91; N, 16.46.

3-Nitrotetrafluorobenzo[*b*]-1,5,7-triazatetracyclo-[$7.3.1^{3,7}.1^{5,9}.0^{1,9}$]tetradecan-10-one (17c). A solution of 1.46 g of 7-nitro-1,3,5-triazaadamantane[9] in 75 mL of chloroform was treated with 2.4 g of 70% pentafluorophenacyl bromide. A turbidity and fluorescence developed within 15 min; after standing for 4 days at ambient temperature much yellow solid had crystallized. After 18 days the solid (hydrobromide salt of 7-nitro-1,3,5-triazaadamantane) was removed by filtration and washed with chloroform. The combined chloroform washes and mother liquors were stirred with 20 mL of ethanol plus 40 mL of water and made basic with solid potassium carbonate. The organic phase was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were dried before evaporating to leave 2.25 g of a yellow semisolid. Slurrying with 30 mL of chloroform and chilling to 5 °C gave 0.38 g of yellow solid, mp 265–270 °C dec; recrystallization from benzene furnished pale yellow plates, mp 277–278 °C dec. An additional 1.05 g of product was obtained by chromatography of the chloroform solution on 70 g of silica gel, using chloroform as eluent. Recrystallization from benzene gave pale yellow needles, mp 278–279 °C dec. NMR (see Table I). Anal. Calcd for $C_{15}H_{12}F_4N_4O_3$: C, 48.39; H, 3.25; F, 20.41; N, 15.05. Found: C, 48.74; H, 3.48; F, 20.57; N, 14.70.

Registry No. 1, 124562-72-7; 1·$HClO_4$, 124581-13-1; 1·HCl, 124562-74-9; 1·HBr, 124562-82-9; **2**, 5122-16-7; **4**, 655-15-2; **5**, 93102-96-6; **7**, 383-53-9; **8**, 124562-75-0; **9**, 124562-76-1; **13**, 99-81-0; 14, 88260-40-6; **15**, 124562-77-2; **16a**, 51706-46-8; **16b**, 14707-75-6; **16c**, 14612-28-3; **16c**·HBr, 66570-68-1; **17a**, 124562-78-3; **17b**, 124562-79-4; **17c**, 124562-81-8; **19**, 124562-80-7; *o*-FC_6H_4Ac, 450-95-3; pentafluoroacetophenone, 652-29-9; pentafluorophenacyl dibromide, 124562-73-8; hexamine, 100-97-0; isonicotinyl chloride, 14254-57-0.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Photolysis of Vinyl Halides. Reaction of Photogenerated Vinyl Cations with Cyanate and Thiocyanate Ions

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The title reaction was conducted in a two-phase system of dichloromethane and water using a tetrabutylammonium halide as a phase-transfer catalyst. The reaction of the photogenerated arylvinyl cations with cyanate ion gave only isoquinolone derivatives, whereas the reaction with thiocyanate ion afforded products derived from S attack, vinyl thiocyanates, and products derived from N attack, vinyl isothiocyanates or thioisoquinolones. The ambident nature of thiocyanate ion is compared with the reaction of benzyl bromides.

Most early studies on vinyl cations[1] have dealt with mechanistic aspects of their generation and behavior. Recently there has been an increasing number of synthetic applications of reactions involving vinyl cations.[1a] Al-

Scheme I

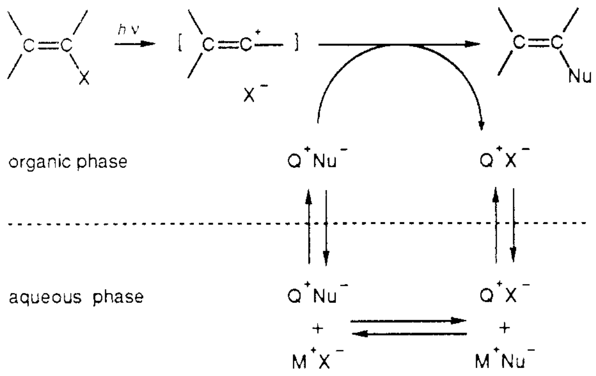

Table I. Isoquinolones 4a–d from Photolysis of Vinyl Bromides 1a–d with Cyanate Ion

vinyl bromide 1					
	R^1	R^2	irrdtn time, h	convn, %	yield,[a,b] %
1a	MeO	MeO	2	75	93
1b	MeO	H	3	89	91
1c	Me	H	8	83	77
1d	H	H	24	100	46[c]

[a] Isolated yield. Based on the consumed vinyl bromide 1. [b] Small amounts of triarylethene and 9-arylphenanthrene were detected (<10%) in each case as a radical-derived product. [c] Triphenylethene and 9-phenylphenanthrene were formed in 40% yield.

though vinyl cations are synthetically important reactive intermediates, there are some restrictions for their generation.[1] Especially, the strong C–X bond of vinyl derivatives (vinyl halides, for example) requires a high temperature and a protic, polar solvent for the solvolytic reaction.

A recent development of organic photochemistry provides a photochemical generation of vinyl cations[2] and suggests that photolysis of vinyl halides is useful as a synthetic method involving vinyl cations. We reported that photolysis of arylvinyl halides in the presence of azide ion gave heterocycles derived from the reaction of azirines generated in situ.[3] In addition, we found that this method is effective in a two-phase system of dichloromethane and water using a phase-transfer catalyst. This two-phase photochemistry can be easily applied to other water-soluble nucleophiles such as potassium cyanate and thiocyanate (Scheme I).[4] Hence, by means of this technique, we examined photochemical vinylic substitutions by cyanate and thiocyanate ions. Here we wish to report formation of isoquinolones by the reaction with cyanate ion and the ambident character of thiocyanate ion toward the photogenerated vinyl cations.

Table II. Product Distributions in Photolysis of Vinyl Bromides 1a–d with Thiocyanate Ion

vinyl bromide 1			irrdn		yield,[c] %		
	R^1	R^3	time,[a] g	convn, %	**5**	**6**	**7**
1a	MeO	*p*-An[d]	1	77	77	0	15 (R^2 = OMe)
1b	MeO	Ph	1.5	85	62	0	26 (R^2 = H)
1c	Me	Ph	3	60	39	0	31 (R^2 = H)
1d	H	Ph	3	53	48	0	34 (R^2 = H)
1e	MeO	Me	1.5[b]	46	42	27	0
1f	H	Me	3[b]	66	18	29	0

[a] Irradiated through a Pyrex filter. [b] Irradiated without a Pyrex filter. [c] Isolated yield. Based on the consumed vinyl bromide 1.

Results and Discussion

Reaction with Cyanate Ion. A two-phase solution was prepared by dissolving triarylvinyl bromide **1**, potassium cyanate, and tetrabutylammonium chloride in a mixture of dichloromethane and water. Irradiation of the two-phase system gave isoquinolone derivatives **4** as the cyanate ion incorporated product (Scheme II). No vinyl isocyanates **3** were obtained. The results are given in Table I. Except for the reaction of triphenylvinyl bromide (**1d**), high yields of isoquinolones **4** were obtained in the reactions of other triarylvinyl bromides **1a–c**. Small amounts of the corresponding triarylethenes and 9-arylphenanthrenes were also obtained. However, in the case of photolysis of triphenylvinyl bromide (**1d**), triphenylethene and 9-phenylphenanthrene constituted 40% of the total products. Formation of the triarylethenes and 9-arylphenanthrenes is attributable to hydrogen abstraction by the triphenylvinyl radical, which is generated by homolytic cleavage of the carbon–bromine bond in triarylvinyl bromide.[5] The enhanced formation of radical products in the case of **1d** can be explained by substituent effect and recombination of the resulting vinyl cation and bromide ion pair. As discussed earlier,[3] α substituent strongly affects on formation of vinyl cations. Photolysis of **1d** affords less ionic products than that of **1a–c** because the resulting vinyl cation **2d** lacks stability compared with **2a–c**.[3] In addition, since photolysis of triphenylvinyl bromide (**1d**) in methanol[6] gave an 88% yield of methanol-incorporated products, it is suggested that cyanate ion cannot be effectively trapped by triphenylvinyl cation because in this photolysis, there is a significant extent of internal return by the liberated bromide ion.[7] Accordingly, photolysis of **1d** results in increasing amounts of radical products.

No products derived from O-site attack of cyanate ion were detected. Only N-site attack was observed. This result is parallel to the reaction of alkyl halides with cyanate ion with regard to products.[8] Although alkyl halides under S_N1 conditions primarily yield a mixture of O- and N-attacked products, alkyl cyanates rapidly isomerize to thermodynamically stable alkyl isocyanates.[8] Since at the initial stage displacement at the O-site of cyanate ion takes place under S_N1 displacement of alkyl halides, reaction of arylvinyl cations with cyanate ion is regiospecific. This difference may be attributable to charge

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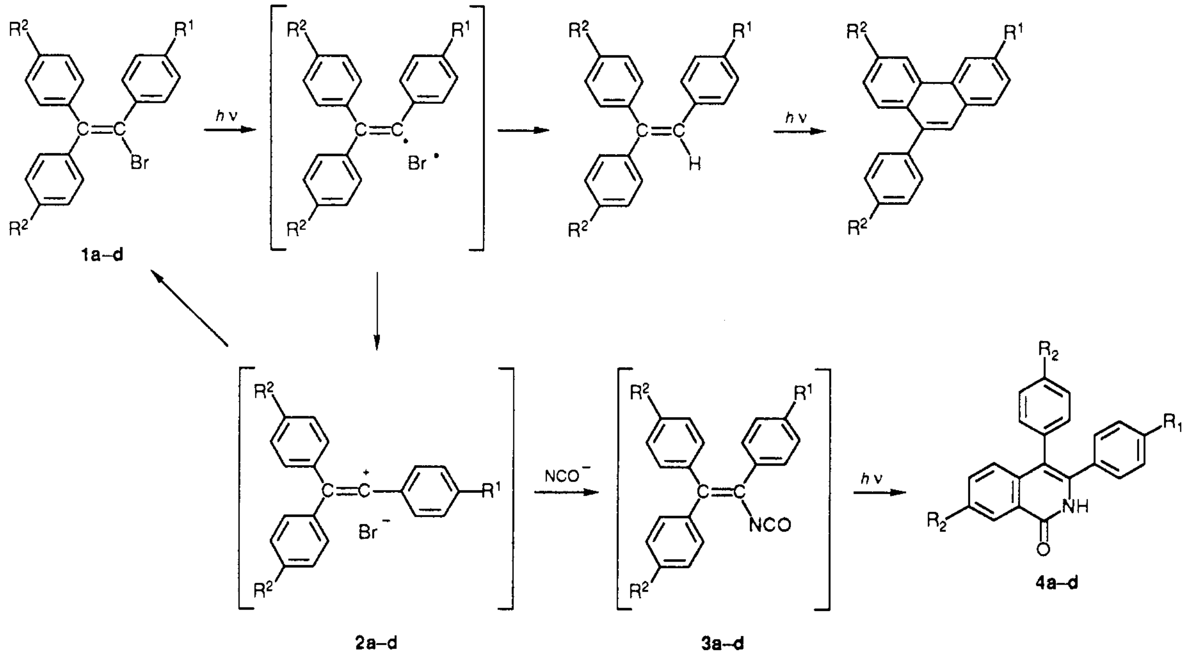
Scheme II^a

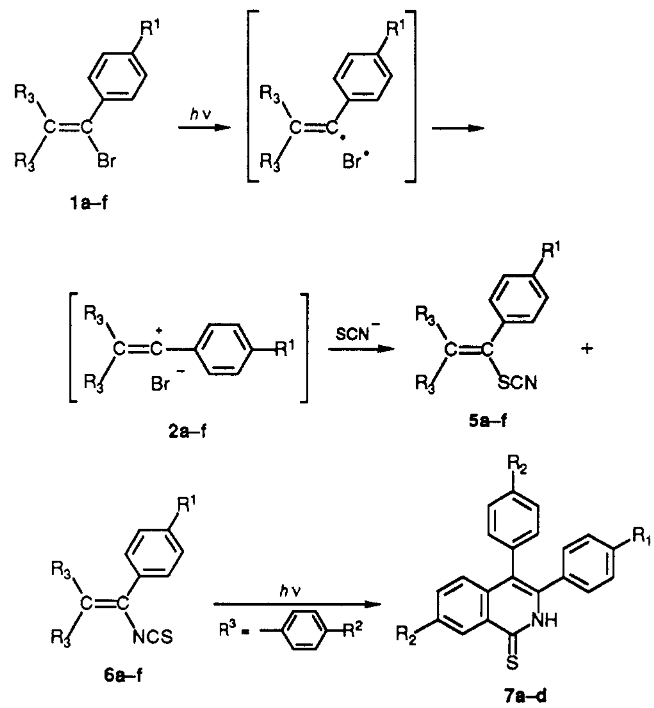


^{a} **a**, R^1 = MeO, R^2 = MeO; **b**, R^1 = MeO, R^2 = H; **c**, R^1 = Me, R^2 = H; **d**, R^1 = R^2 = H.

delocalization of the plus charge into the α aromatic ring, which makes the softness of the reactive cationic center and reacts with the less electronegative N-site of cyanate ion selectively. According to the known photocyclization of β-arylvinyl isocyanates,[9] it is assumed that the cyclization of vinyl isocyanates **3** to isoquinolones **4** occurs photochemically.

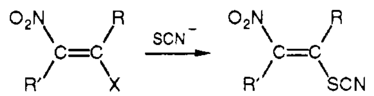
Reaction with Thiocyanate Ion. In a similar manner to the reaction with cyanate ion, a two-phase system of vinyl bromide **1**, potassium thiocyanate, and tetrabutylammonium bromide in dichloromethane and water was irradiated. As shown in Table II, photolysis of triarylvinyl bromides **1a–d** in the presence of thiocyanate ion afforded vinyl thiocyanates **5a–d** and thioisoquinolones **7a–d** (Scheme III). No isomerization was observed when vinyl thiocyanate **5b** was irradiated in dichloromethane for 2 h. Accordingly the photolysis with thiocyanate ion produces vinyl thiocyanates **5** and thioisoquinolones **7** independently. Apparently thioisoquinolones **7** are formed by photocyclization of the corresponding vinyl isothiocyanates **6** similarly to the reaction with cyanate ion. This is supported by the formation of vinyl isothiocyanates **6** together with vinyl thiocyanates **5** in the photolysis of the 1-aryl-2,2-dimethylvinyl bromides **1e** and **1f**. Thus, thiocyanate ion behaves as an ambident anion to the photogenerated vinyl cations **2**.

Scheme III^a



^{a} **a**, R^1 = MeO, R^3 = p-MeOC$_6$H$_4$ (R^2 = MeO); **b**, R^1 = MeO, R^3 = Ph (R^2 = H); **c**, R^1 = Me, R^3 = Ph (R^2 = H); **d**, R^1 = H, R^3 = Ph (R^2 = H); **e**, R^1 = MeO, R^3 = Me; **f**, R^1 = H, R^3 = Me.

It is well-known that alkyl halides readily react with thiocyanate ion[10] where the ratios of S-attack and N-attack have been discussed both in S$_N$1 and in S$_N$2 reactions. However, the reaction of vinyl halides with thiocyanate ion has been limited because no S$_N$2 reaction takes place and severe reaction conditions are required for the S$_N$1 reaction.[1] The only observed reaction with thiocyanate ion involved β-activated vinyl halides.[11] Such activated vinyl halides, i.e., β-nitrovinyl halides, give only β-nitrovinyl thiocyanates derived from the reaction at the S-site of thiocyanate ion. However, these reactions proceed via addition–elimination rather than an S$_N$1 or S$_N$2 mechanism.



On the other hand, photolysis of vinyl halides **1** resulted in the competitive S- and N-attacks of thiocyanate ion.

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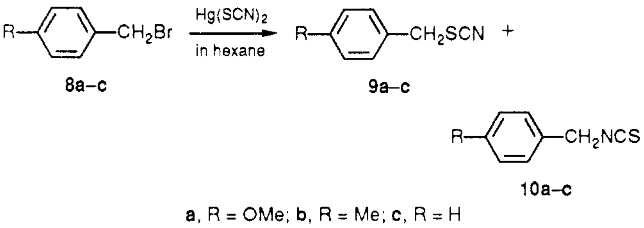
Table III. Mercury-Assisted Reaction of Benzyl Bromides 8 with Thiocyanate Ion

R	temp, °C	rel yield,[a] %	
		9	**10**
OMe	20	82	18
Me	65–70	74	26
H	60–65	66	34

[a] Determined by ^{1}H NMR.

This means that the reaction of arylvinyl bromides **1** under photolytic conditions is different from that of the β-nitrovinyl halides. According to the HSAB principle,[12] the hard nitrogen atom of thiocyanate ion prefers a hard reaction center, as in the trapping of an ionic intermediate. In addition, the low values of the selectivity in the photolysis of vinyl halides **1** are similar to those of the S_N1 reaction of alkyl halides[10] and suggest the involvement of vinyl cations. The variation of the selectivity depends on the electronic demand of the resulting vinyl cation **2** toward the para substituent as shown in a higher selectivity of the methoxy group, which leads to an increasing preference for the reaction with the soft sulfur atom of thiocyanate ion.

It is interesting to compare the observed substituent effect on the arylvinylic system with that of the corresponding alkyl system, a benzylic system. The reported mercury-assisted reaction of alkyl halides with thiocyanate ion[13] is suitable for this purpose because it can be done in an aprotic solvent. The reaction of para-substituted benzyl bromides **8a–c** with mercury(II) thiocyanate in hexane gave para-substituted benzyl thiocyanates **9a–c** and isothiocyanates **10a–c** as shown in Table III. In analogy with the photolysis of vinyl bromides **1**, the methoxy derivative gave the highest degree of trapping through the sulfur atom of the thiocyanate ion. Therefore, a similar substituent effect is operating in both the vinylic and alkyl systems.



a, R = OMe; b, R = Me; c, R = H

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were taken on a HITACHI R-24B spectrometer. Mass spectra were obtained with a JEOL JMS-07 spectrometer. IR spectra were obtained with a Shimadzu IR-400 spectrometer.

Vinyl bromides **1a–f** were prepared by bromination of the corresponding ethenes in CH_2Cl_2 according to the procedures described in the literature: 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (**1a**),[14] 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**1b**),[15] 1-bromo-1-(*p*-methylphenyl)-2,2-diphenylethene (**1c**),[16] 1-bromo-1,2,2-triphenylethene (**1d**),[17] 1-bromo-1-(*p*-methoxyphenyl)-2-methyl-1-propene (**1e**),[18] 1-bromo-2-methyl-1-phenyl-1-propene (**1f**).[19]

Photolysis of Vinyl Bromides 1a–d with Cyanate Ion. In an immersion-type photoreactor was placed a mixture of vinyl bromide **1** (1 mmol), potassium cyanate (10 mmol), tetrabutylammonium chloride (2 mmol), dichloromethane (90 mL), and water (10 mL), which was irradiated through a Pyrex filter by use of a high-pressure Hg lamp (100 W) under an N_2 atmosphere at 10–15 °C. After evaporation of the dichloromethane, the product was extracted with ether. The organic layer was washed with water, followed by saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator. The resulting crystals, isoquinolones **4a–d**, were collected by filtration and the additional crystals were obtained by column chromatography of the mother liquor on silica gel using a hexane–ether eluent. The earlier fraction with a hexane–dichloromethane eluent gave a mixture of triarylethenes and 9-arylphenanthrenes (<10% yield), which were observed also in photolysis of triarylvinyl bromides **1a–d** in the presence of azide ion[3a] or in methanol.[6] However, further work on these products was not done except for the case of vinyl bromide **1d**. In the photolysis of vinyl bromide **1d**, after filtration of the crystals **4d** (70 mg), the mother liquor was submitted to column chromatography on silica gel. Elution with hexane–dichloromethane gave 102 mg of an oil, which was determined to be a mixture of triphenylethene and 9-phenylphenanthrene by comparison with authentic samples[20] (^{1}H NMR and GC, column OV-17). Elution with hexane–ether gave 70 mg of the crystals **4d**.

The physical and spectral data of isoquinolones **4a–d** are as follows.

7-Methoxy-3,4-bis(*p*-methoxyphenyl)-1-isoquinolone (4a): mp 232–235 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 6.61–7.82 (m, 11 H, Ar H), 9.41 (br s, 1 H, NH, exchangeable with D_2O); IR (Nujol) 1630 cm^{-1} (C=O); MS (*m/z*) 387 (M^+). Anal. Calcd for $C_{24}H_{21}O_4N$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.22; H, 5.45; N, 3.59.

3-(*p*-Methoxyphenyl)-4-phenyl-1-isoquinolone (4b): mp 250–252 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3 H, OCH_3), 6.57–7.60 (m, 12 H, ArH), 8.28–8.43 (m, 1 H, Ar H), 9.51 (br s, 1 H, NH, exchangeable with D_2O); IR (Nujol) 1640 cm^{-1} (C=O); MS (*m/z*) 327 (M^+). Anal. Calcd for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.43; H, 5.40; N, 4.07.

3-(*p*-Methylphenyl)-4-phenyl-1-isoquinolone (4c): mp 226–227 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3 H, CH_3), 6.90–7.71 (m, 12 H, Ar H), 8.39–8.60 (m, 1 H, Ar H), 9.10 (br s, 1 H, NH, exchangeable with D_2O); IR (Nujol) 1650 cm^{-1} (C=O); MS (*m/z*) 311 (M^+). Anal. Calcd for $C_{22}H_{17}ON$: C, 84.86; H, 5.50; N, 4.50. Found: C, 85.04; H, 5.67; N, 4.50.

3,4-Diphenyl-1-isoquinolone (4d): mp 251–252 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) δ 7.00–7.46 (m, 13 H, Ar H), 8.28–8.54 (m, 1 H, Ar H), 9.44 (br s, 1 H, NH, exchangeable with D_2O); IR (Nujol) 1640 cm^{-1} (C=O); MS (*m/z*) 297 (M^+). Anal. Calcd for $C_{21}H_{15}ON$: C, 84.82; H, 5.09; N, 4.71. Found: C, 85.22; H, 5.39; N, 4.31.

Photolysis of Vinyl Bromides 1a–f in the Presence of Thiocyanate Ion. A mixture of the vinyl bromide **1** (1 mmol), potassium thiocyanate (10 mmol), tetrabutylammonium bromide (2 mmol), dichloromethane (90 mL), and water (10 mL) was placed in an immersion-type photoreactor and irradiated through a Pyrex filter, using a high-pressure Hg lamp (100 W) under an N_2 atmosphere at 10 °C. After evaporation of the dichloromethane, the products were extracted with ether–benzene. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated. The products were separated by column chromatography on silica gel using a hexane–ether eluent. The products obtained were vinyl thiocyanates **5a–d** and thioisoquinolones **7a–d**. In the case of vinyl bromides **1e** and **1f**, the photolysis was carried out without a Pyrex filter in a similar manner to the above photolysis. The products were vinyl thio-

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cyanates **5e–f** and vinyl isothiocyanates **6e–f**. The physical and spectral data of the products are as follows.

1,2,2-Tris(*p*-methoxyphenyl)ethenyl thiocyanate (5a): mp 101–103 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 6.39–7.14 (m, 12 H, Ar H); IR (Nujol) 2150 cm^{-1} (SCN); MS (*m/z*, rel intensity) 403 (M^+, 100), 345 (M^+ – SCN, 84). Anal. Calcd for $C_{24}H_{21}O_3NS$: C, 71.44; H, 5.25; N, 3.47. Found: C, 71.11; H, 5.23; N, 3.44.

7-Methoxy-3,4-bis(*p*-methoxyphenyl)-1-thioisoquinolone (7a): mp 222–226 °C (from benzene–dichloromethane); ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 6.30–7.40 (m, 10 H, Ar H), 8.10–8.40 (m, 1 H, Ar H), 10.60 (br s, 1 H, NH, exchangeable with D_2O); MS (*m/z*) 403 (M^+). Anal. Calcd for $C_{24}H_{21}O_3NS$: C, 71.44; H, 5.25; N, 3.47. Found: C, 71.10; H, 5.30; N, 3.28.

1-(*p*-Methoxyphenyl)-2,2-diphenylethenyl thiocyanate (5b): mp 132–134 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3 H, OCH_3), 6.59–7.26 (m, 14 H, Ar H); IR (Nujol) 2140 cm^{-1} (SCN); MS (*m/z*, rel intensity) 343 (M^+, 63), 285 (M^+ – SCN, 100). Anal. Calcd for $C_{22}H_{17}ONS$: C, 76.94; H, 4.99; N, 4.08. Found: C, 76.61; H, 4.96; N, 4.00.

3-(*p*-Methoxyphenyl)-4-phenyl-1-thioisoquinolone (7b): mp 252–256 °C (from benzene–dichloromethane); ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3 H, OCH_3), 6.67–7.69 (m, 12 H, Ar H), 8.94–9.10 (m, 1 H, Ar H), 10.67 (br s, 1 H, NH, exchangeable with D_2O); MS (*m/z*) 343 (M^+). Anal. Calcd for $C_{22}H_{17}ONS$: C, 76.94; H, 4.99; N, 4.08. Found: C, 77.24; H, 5.24; N, 3.84.

1-(*p*-Methylphenyl)-2,2-diphenylethenyl thiocyanate (5c): mp 124–126 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H, CH_3), 6.70–7.50 (m, 14 H, Ar H); IR 2130 cm^{-1} (SCN). Anal. Calcd for $C_{22}H_{17}NS$: C, 80.70; H, 5.23; N, 4.28. Found: C, 80.84; H, 5.11; N, 4.28.

3-(*p*-Methylphenyl)-4-phenyl-1-thioisoquinolone (7c): mp 249–254 °C (from benzene–dichloromethane); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3 H, CH_3), 6.30–7.60 (m, 12 H, Ar H), 8.32–9.02 (m, 1 H, Ar H), 10.62 (br s, 1 H, NH, exchangeable with D_2O); MS (*m/z*) 327 (M^+). Anal. Calcd for $C_{22}H_{17}NS$: C, 80.70; H, 5.23; N, 4.28. Found: C, 80.39; H, 5.39; N, 4.25.

1,2,2-Triphenylethenyl thiocyanate (5d):[21] ^{1}H NMR (CCl_4) δ 6.65–7.40 (m, Ar H); IR 2140 cm^{-1} (lit.[21] 2165 cm^{-1}).

3,4-Diphenyl-1-thioisoquinolone (7d): mp 264–269 °C (from benzene–dichloromethane); ^{1}H NMR ($CDCl_3$) δ 6.75–7.60 (m, 13 H, Ar H), 8.75–8.96 (m, 1 H, Ar H), 10.40 (br s, 1 H, NH, exchangeable with D_2O); MS (*m/z*) 313 (M^+). Anal. Calcd for $C_{21}H_{15}NS$: C, 80.48; H, 4.82; N, 4.47. Found: C, 80.32; H, 4.97; N, 4.42.

1-(*p*-Methoxyphenyl)-2-methyl-1-propenyl thiocyanate (5e): oil; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 6.72–7.22 (m, 4 H, Ar H); IR 2156 cm^{-1} (s); MS (*m/z*) 219 (M^+).

1-(*p*-Methoxyphenyl)-2-methyl-1-propenyl isothiocyanate (6e): oil; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 6.65–7.08 (m, 4 H, Ar H); IR 2080 cm^{-1} (s, Br); MS (*m/z*) 219 (M^+).

2-Methyl-1-phenyl-1-propenyl thiocyanate (5f): oil; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 7.24 (br s, 5 H, Ar H); IR 2156 cm^{-1} (s); MS (*m/z*) 189 (M^+).

2-Methyl-1-phenyl-1-propenyl isothiocyanate (6f):[22] oil; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 7.27 (br s, 5 H, Ar H); IR 2108 cm^{-1} (s, br); MS (*m/z*) 189 (M^+); lit.[22] IR 2120 cm^{-1}.

Reaction of Para-Substituted Benzyl Bromides with Mercury Thiocyanate. A para-substituted benzyl bromide (1 mmol) was added to a stirred suspension of mercury thiocyanate, $Hg(SCN)_2$ (1 mmol), in hexane (10 mL) at the temperature described in Table III and stirring was continued. The reaction mixture was filtered and analyzed by ^{1}H NMR in CCl_4. The ratios were determined by integration of the methylene protons in $ArCH_2XCY$. ^{1}H NMR spectra are as follows. **Benzyl thiocyanate (9c)**:[12] δ (CCl_4) 4.05 (s, CH_2), 7.25 (s, Ar H). **Benzyl isothiocyanate (10c)**:[12] δ (CCl_4) 4.62 (s, CH_2), 7.25 (s, Ar H). ***p*-Methylbenzyl thiocyanate (9b)**:[23] δ (CCl_4) 2.27 (s, CH_3), 3.93 (s, CH_2), 6.96 (s, Ar H). ***p*-Methylbenzyl isothiocyanate (10b)**:[24] δ (CCl_4) 2.27 (s, CH_3), 4.47 (s, CH_2), 6.96 (s, Ar H). ***p*-Methoxybenzyl thiocyanate (9a)**:[25] δ (CCl_4) 3.18 (s, OCH_3), 3.94 (s, CH_2), 6.57–7.11 (m, Ar H). ***p*-Methoxybenzyl isothiocyanate (10a)**:[26] δ (CCl_4) 3.18 (s, OCH_3), 4.46 (s, CH_2), 6.57–7.11 (m, Ar H).

Registry No. **1a**, 25354-46-5; **1b**, 25354-48-7; **1c**, 781-32-8; **1d**, 1607-57-4; **1e**, 40811-05-0; **1f**, 5912-93-6; **4a**, 93119-93-8; **4b**, 93119-94-9; **4c**, 93119-95-0; **4d**, 93119-96-1; **5a**, 93119-50-7; **5b**, 93119-51-8; **5c**, 93119-52-9; **5d**, 61807-34-9; **5e**, 93119-53-0; **5f**, 93119-54-1; **6e**, 93119-55-2; **6f**, 51110-17-9; **7a**, 93119-56-3; **7b**, 93119-57-4; **7c**, 93119-58-5; **7d**, 68883-68-1; 8 (R = OMe), 68883-68-1; 8 (R = Me), 104-81-4; 8 (R = H), 100-39-0; **9a**, 19927-28-7; **9b**, 18991-39-4; **9c**, 3012-37-1; **10a**, 3694-57-3; **10b**, 3694-46-0; **10c**, 622-78-6; HOCN·K, 590-28-3; HSCN·K, 333-20-0; $Ph_2C{=}CHPh$, 57704-78-6; $Hg(SCN)_2$, 53408-91-6; 9-phenylphenanthrene, 844-20-2.

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