Photochemistry of Conjugated Nitrogen–Thiocarbonyl Systems. VII.[1a] Photoaddition of Quinoline-, Isoquinoline- and Phthalazine-Thione Systems to Olefins[1b]

Eisuke SATO,* Yoshiya IKEDA, and Yuichi KANAOKA*

Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-12, Nishi-6, Kita-ku, Sapporo 060, Japan. *Received October 19, 1989*

Photolyses of quinoline-2-thiones (1A, B), isoquinoline-1-thione (14A), and phthalazine-1-thiones (14B—D) in the presence of olefins (2) afforded photoaddition products such as substituted quinolines, isoquinolines, phthalazines, and novel tricyclic products, probably by way of thietanes formed by photoaddition of olefins to the C$=$S bond.

Keywords photoaddition; olefin; thietane; quinoline-2-thione; isoquinoline-1-thione; phthalazine-1-thione

Although the photochemistry of nitrogen–carbonyl systems has been studied extensively,[2] that of nitrogen–thiocarbonyl systems has received little attention except for thioparabanic acid,[3] indole-2-thione,[4] thioanilide[5] and 4-thiouracil.[6] During the course of the development of the photochemistry of nitrogen–thiocarbonyl systems (*e.g.*, thioamide and thioimide[7]), it became apparent that the major photoreaction of 2-thiopyridone and 2-thiopyrimidone, the simplest members of the family, with olefins is a [2+2]addition reaction which is predominantly localized at the C$=$S bond.[8]

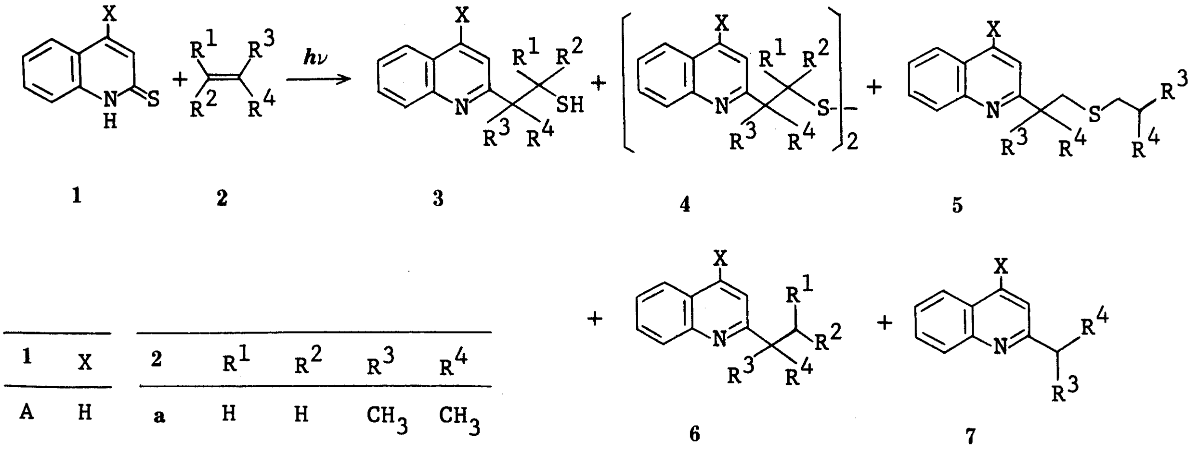
Our preliminary reports[1a,9a] on the photoaddition of olefins to bicyclic nitrogen–thione systems alluded briefly to their interesting photochemical properties. We present here a full account of the photochemical behavior of the bicyclic homologues of such heteroaromatic thione systems as quinoline-2-thiones (**1**), isoquinoline-1-thione (**14A**) and phthalazine-1-thiones (**14B**—**D**).

Irradiation of quinoline-2-thiones (**1**) (1.0 mmol) in acetonitrile in the presence of excess olefins (**2**) (10 mmol) through a Pyrex filter with a 500 W high-pressure mercury lamp for 0.75—3 h under an argon atmosphere gave a series of 2-substituted quinolines (**3**—**7**), whose structures were determined to be as shown in Chart 1 based on their spectral and analytical data. The results are listed in Table I. It was observed that oily products with a β-mercaptoethyl group (**3Aa**, **3Ac** and **3Ba**: $R^1=R^2=H$) were gradually oxidized to corresponding disulfides (**4**) on standing in air. Among olefins, a less substituted olefin such as isobutene (**2a**) gave a "two-fold addition" product (**5**) probably *via* the sterically less hindered intermediate biradical **9**, similarly to the case of photoaddition of 2-thiopyridone to **2a**.[8] It was newly observed that a more substituted olefin, 2,3-dimethyl-2-butene (**2b**) gave desulfurized 2-substituted products (**6** and **7**) in addition to the thiol (**3**) and the disulfide (**4**).

A plausible pathway for the formation of all the photoproducts may involve initial [2+2]cycloaddition of the thione to the olefin to give the common thietane intermediate **8** (Chart 2). Subsequent photolysis of **8** gives the thiyl biradical **9**, but heterolytic cleavage of **8** to form a mercaptide **10** would also be possible. Hydrogen abstraction by the thiyl radical **9** (path A) and/or proton transfer from nitrogen to sulfur in **10** (path B) may give sulfides **3**. Air oxidation of **3** may afford disulfides **4**, though a direct

TABLE I. Yields of Photoproducts (3—7)

Thione (mmol)	Olefin (mmol)	Time (h)	Product yield (%)				
			3	4	5	6	7
1A (1)	2a (10)	2	9	14	5	—	—
1A (1)	2b (10)	3	27	7	—	8	8
1A (1)	2c (5)	3/4	20	24	—	—	—
1B (1)	2a (10)	2	15	24	10	—	—
1B (1)	2b (10)	3	33	7	—	7	Trace



1 2 3 4 5 6 7

1	X
A	H
B	CH_3

2	R^1	R^2	R^3	R^4
a	H	H	CH_3	CH_3
b	CH_3	CH_3	CH_3	CH_3
c	H	H	CH_3	Ph

Chart 1

pathway (C) from **9** can not be ruled out. Addition of a second molecule of isobutene to **9a** ($R^1 = R^2 = H$), in which the thiyl radical center is less hindered, leads to "two-fold addition" products **5**[8] (path D). In contrast, the biradical **9b** from 2,3-dimethyl-2-butene (**2b**), which is a sterically hindered olefin, gave desulfurized alkylated products (**6** and **7**), whereas similar products were not formed in the case of the monocyclic pyridinethiones and pyrimidinethiones.[8] These products probably arose from unimolecular collapse of **9b** either by desulfurization by way of the more stable tertiary carbon radical (**12**) (path E to **6**) or elimination of thioacetone (path F to **7**) (Chart 2). It appears that extended conjugation of the bicyclic moiety of the radical intermediate **9** favors these E and F courses. The facile C–C bond formation described here would provide a convenient route to 2-substituted quinoline derivatives. It was reported that the photoaddition of quinoline-2-thione to olefins bearing electron-withdrawing substituents such as methyl methacrylate or methacrylonitrile afforded only 2-(2-mercaptoalkyl)quinolines.[9b,c] It is therefore worth noting that photolysis of **1** in the presence of olefins with an electron-donating group such as a methyl group gave not only 2-(2-mercaptoalkyl)quinoline but also the two-fold addition products (**5**) and desulfurized products (**6** and **7**).

Isoquinoline-1-thione (**14A**) was irradiated with olefins (**2a**—**e**) under similar photolytic conditions to those de-

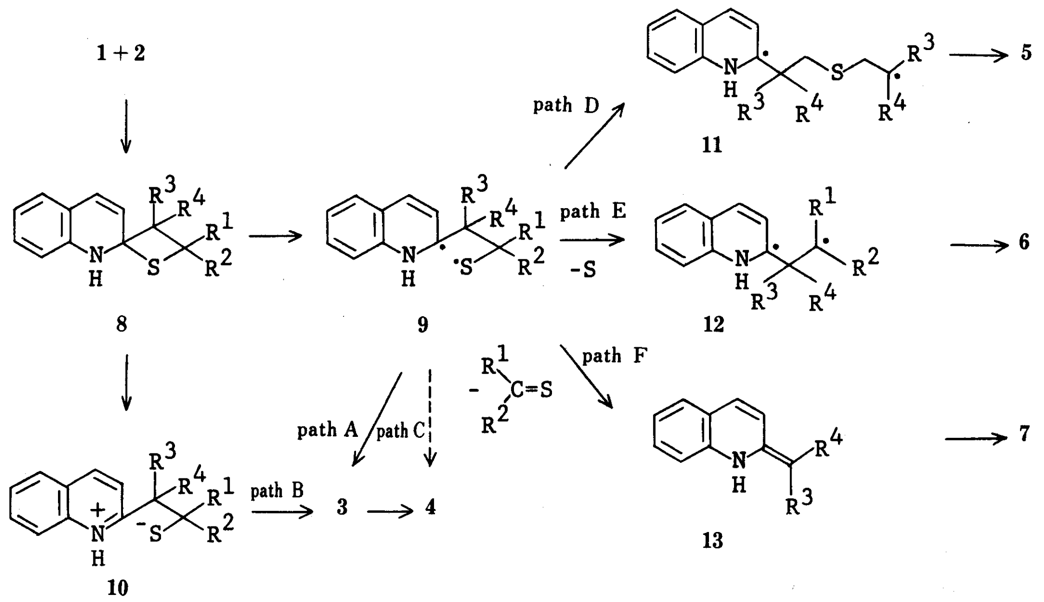
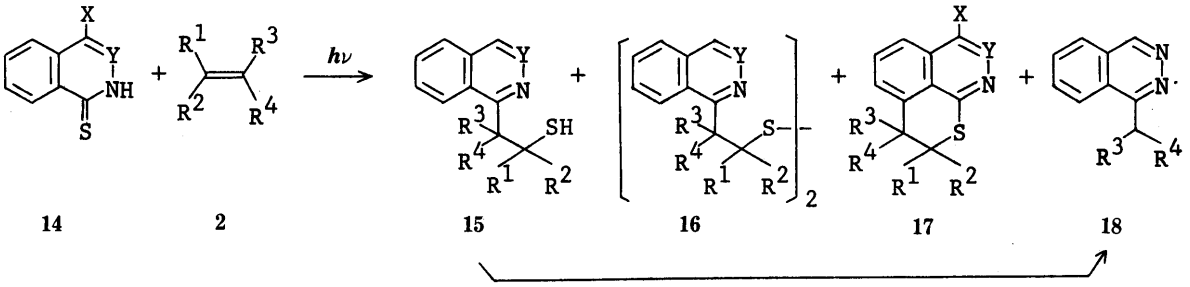


Chart 2



14	X	Y
A	H	CH
B	H	N
C	CH_3	N
D	Ph	N

2	R^1	R^2	R^3	R^4
a	H	H	CH_3	CH_3
b	CH_3	CH_3	CH_3	CH_3
d	H	CH_3	CH_3	CH_3
e	H	H	CH_3	CN
f	H	H	CH_3	CO_2CH_3
g	H	H	CH_3	OCH_3

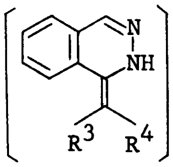
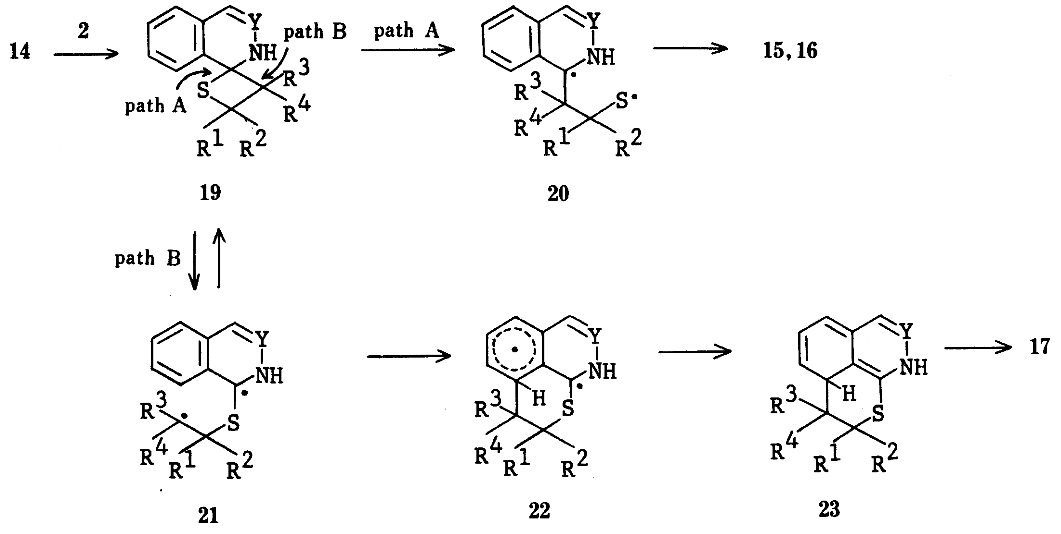

24

Chart 3



A : Y = CH

B : Y = N

Chart 4

Table II. Yields of Photoproducts (**15**—**18**)

Thione (1 mmol)	Olefin (10 mmol)	Time (h)	Product yield (%)			
			15	**16**	**17**	**18**
14A	**2a**	2	64	—	9	
14A	**2b**	2	—	17	26	
14A	**2d**	2	—	—	37	
14A	**2e**	2	68	—	—	
14B	**2b**	2	71[a]	—	—	31[b]
14B	**2e**	2	77[a]	—	—	70[b]
14B	**2f**	2	90[a]	—	—	52[b]
14B	**2g**	2	35	—	—	
14B	**2a**	2	—	—	51	
14B	**2d**	2	—	—	25	
14C	**2a**	2	—	—	53	
14C	**2d**	2	—	—	30	
14D	**2a**	2	—	—	39	
14D	**2d**	2	—	—	26	

a) Crude yield before distillation. *b*) Yield after distillation.

scribed above. The products thus obtained were identified as the unexpected tricyclic products **17**, in addition to the thiol **15** and the sulfide **16** (Chart 3 and Table II). The tricyclic structure of **17** was confirmed by spectral data. The nuclear magnetic resonance (NMR) spectra of **17** characteristically showed loss of one aromatic proton, and the mass spectra (MS) gave molecular ion peaks (215, 229 and 243 for **17Aa**, **17Ab** and **17Ad**, respectively), indicative of loss of two hydrogen atoms from the sum of the starting materials. Although intramolecular aromatic substitution of a sulfur-containing biradical on an *ortho*-position of a benzene ring is known on photoaddition of thiobenzophenone to multiple bonds,[10)] the present result is the first example of the formation of a 6-membered ring by ring closure at the *ortho*- or *peri*-position of a nitrogen–thiocarbonyl system.[11)]

As a mechanism for this reaction, the intermediacy of a thietane **19** is again postulated: a normal photolysis of the thietane C–S bond (A) then forms a thiyl radical **20** ultimately leading to **15** and **16** (Chart 4). The formation of 8,9-dihydrothiopyrano[4,3,2-*ij*]isoquinoline **17** is interesting from a synthetic viewpoint, and may be explained by an alternative photolysis (B) to form a "non-thiyl" biradical **21**, whose side chain radical end attacks the neighboring *peri*-position of the benzene ring (**22**) forming a new C–C bond, followed by oxidative aromatization (**23**→**17**).

In order to evaluate fruther the applicability of this new photoaddition–cyclization, phthalazine-1-thiones (**14B**—D) were irradiated in the presence of olefins (**2a** and **2d**). As expected, 8,8-dimethyl- and 8,8,9-trimethyl-8,9-dihydrothiopyrano[4,3,2-*ij*]phthalazines (**17**) were obtained, respectively, as sole products. The phthalazine biradical (**21B**) would be somewhat stabilized by the second nitrogen atom compared with the similar type radical (**21A**) from isoquinoline-1-thione, so that the phthalazine ring would be more susceptible to radical attack on the *peri*-position. In fact, the intramolecular *peri*-ring closure takes place predominantly, giving the tricyclic products. Similar photolyses of phthalazine-1-thione (**14B**) with substituted olefins **2b**,**e**—**g** afforded sulfides (**15**) in good yields. Distillation of **15Bb**,**Be**,**Bf** under reduced pressure in an attempt at purification afforded the corresponding 1-alkylphthalazines (**18**) with a concomitant elimination of thioacetone or thioformaldehyde (Chart 3 and Table II). This facile thermal elimination would be due to the stabilizing effect in the putative intermediate (**24**) by conjugation of the π-electron system with the nitrile or ester substituent. These olefins **2b**,**e**—**g** have bulky or multiple substituents, and the steric interference probably accounts for the absence of subsequent attack of the biradical end on the *peri*-position. From the above results, it may be concluded that olefins which afford *peri*-cyclization products, such as isobutene (**2a**) and 2-methyl-2-butene (**2d**), commonly have low steric hindrance in the vicinity of the intermediate biradical (**21**) generated from thietane, and two geminal methyl groups stabilize the side chain of the biradical (**21**) as a tertiary carbon radical.

The reactive sites of the excited states of aza-aromatic

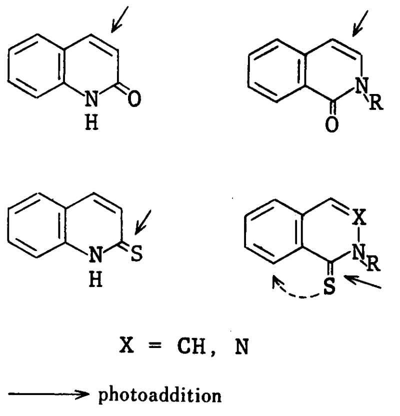


Chart 5

carbonyl systems such as 2-quinolone and 1-quinolone, including those for dimerization[12] and olefin-addition,[13] are well known to be the 3,4-double bond of the aza-aromatics as shown in Chart 5. In contrast, photoaddition of olefins to the bicyclic aza-aromatic thione systems occurs predominantly at the $C=S$ group, leading to various aza-aromatics with substituents introduced at the thiocarbonyl-carbon (Chart 5). Bicyclic structures may impart more resonance stabilization to the relevant intermediate biradical (**9**) than in the monocyclic counterparts,[8] and one interesting variation is the novel addition–cyclization reaction involving the *peri*-position of the azanaphthalenes **14** leading to the new tricyclic aza-thio system **17**.

Experimental

All melting points are uncorrected. Vacuum distillation was carried out by using a Büchi Kugelrohr apparatus and boiling points are uncorrected bath temperature. NMR spectra were taken on a JEOL JNM-FX 100 FT-NMR spectrometer with tetramethylsilane as an internal standard. MS were obtained with a JMS-D 300 mass spectrometer. Infrared spectra (IR) were recorded with a JASCO IRA-1 infrared spectrometer. The light source was a Type EHBW1 (Eikoh-sha) 500 W high-pressure mercury lamp.

General Procedure for the Photolyses A solution of **1A**—**B** or **14A**—**D** (1.0 mmol) in 100 ml of solvent **1A**—**B**, **14A** in acetonitrile, **14B**—**D** in methanol) with olefin (10 mmol, but 5 mmol for **2c**) was irradiated with a 500 W high-pressure mercury lamp through a Pyrex filter for 45 min—3 h (Tables I and II) under an argon atmosphere. After removal of the solvent *in vacuo*, the residue was purified by silica gel or aluminum oxide layer chromatography (PLC). spectral and elemental analysis data are summarized in Tables III—V.

2-(2-Mercapto-1,1-dimethylethyl)quinoline (3Aa), Bis[2,2-dimethyl-2-(2-quinolyl)ethyl]disulfide (4Aa) and 2-(2-Isobutylthio-1,1-dimethylethyl)-quinoline (5Aa) From 161 mg (1.0 mmol) of **1A** and 0.60 g (10 mmol) of **2a**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (15 : 1). **3Aa**: bp 160 °C (bath temp.)/0.7 mmHg, colorless oil, 19 mg (9%). **4Aa**: colorless oil of 30 mg (14%). **5Aa**: bp 185 °C (bath temp.)/0.7 mmHg, colorless oil, 15 mg (5%).

2-(2-Mercapto-1,1,2-trimethylpropyl)quinoline (3Ab), Bis[1,1,2,2-tetramethyl-2-(2-quinolyl)ethyl]disulfide (4Ab), 2-(1,1,2-Trimethylpropyl)quinoline (6Ab) and 2-Isopropylquinoline (7Ab) From 161 mg (1.0 mmol) of **1A** and 842 mg (10 mmol) of **2b**. Irradiated for 3 h. PLC (aluminum): eluted with *n*-hexane–acetone (40 : 1). **3Ab**: bp 200 °C (bath temp.)/0.4 mmHg, colorless solid, 65 mg (27%), mp 113—115 °C. **4Ab**: colorless prisms, 17 mg (7%) from *n*-hexane, mp 46—50 °C. **6Ab**: bp 100 °C (bath temp.)/0.4 mmHg, colorless oil, 18 mg (8%). **7Ab**: bp 100 °C (bath temp.)/0.6 mmHg, colorless oil, 12 mg (8%), picrate: mp 153—155 °C (dec).[14]

2-(2-Mercapto-1-methyl-1-phenylethyl)quinoline (3Ac) and Bis[2-methyl-2-phenyl-2-(2-quinolyl)ethyl]disulfide (4Ac) From 161 mg (1.0 mmol) of **1A** and 590 mg (5.0 mmol) of **2c**. Irradiated for 45 min. PLC (silica gel): eluted with *n*-hexane–acetone (30 : 1). **3Ac**: bp 250 °C (bath temp.)/0.7 mmHg, colorless oil, 57 mg (20%). **4Ac**: colorless oil, 67 mg (24%).

TABLE III. Spectral Data for the Photoproducts

Product	MS m/z [IR ν_{max} (cm^{-1})]	^1H-NMR ($CDCl_3$) δ (ppm) J (Hz)
3Aa	217 (M^+) 216 184 (base)	1.31 (1H, t, $J=9$, –SH), 1.52 (6H, s), 3.08 (2H, d, $J=9$), 7.4—7.8 (4H, m), 7.9—8.2 (2H, m)
4Aa	432 (M^+, base)	1.44 (12H, s), 3.28 (4H, s), 7.3—7.8 (8H, m), 8.02 (4H, d, $J=9$)
5Aa	273 (M^+) 216 184 (base)	0.85 (6H, d, $J=7$), 1.54 (6H, s), 1.5—1.8 (1H, m), 2.22 (2H, d, $J=7$), 3.08 (2H, s), 7.38—7.83 (4H, m), 8.01—8.13 (2H, m)
3Ab	245 (M^+) 244, 212 171	1.44 (3H, s), 1.67 (3H, s), 1.80 (1H, s, –SH), 7.41—7.83 (4H, m), 8.06 (2H, d, $J=9$)
4Ab	489 ($M^+ + 1$) 244	1.24 (12H, s), 1.60 (12H, s), 7.44—8.07 (12H, m)
6Ab	213 (M^+) 198 171 (base) 169	0.80 (6H, d, $J=7$), 1.38 (6H, s), 2.28 (1H, sep, $J=7$), 7.42—7.71 (4H, m), 8.04 (2H, d, $J=8$)
7Ab	171 (M^+) 156	1.40 (6H, d, $J=7$), 3.27 (1H, sep, $J=7$), 7.30—7.80 (4H, m), 8.07 (2H, dd, $J=8$, 3)
3Ac	279 (M^+) 278 246 (base)	1.37 (1H, dd, $J=9$, 8, –SH), 1.90 (3H, s), 3.35 (1H, dd, $J=14$, 8), 3.73 (1H, dd, $J=14$, 9), 7.00—8.16 (11H, m)
4Ac	556 (M^+) 278	1.88 (6H, s), 3.45 (2H, d, $J=13$), 3.96 (2H, d, $J=13$), 6.94—8.15 (22H, m)
3Ba	231 198 (base) 185	1.32 (1H, t, $J=9$, –SH), 1.51 (6H, s), 2.65 (3H, d, $J=1$), 3.07 (2H, d, $J=9$), 7.29—8.08 (5H, m)
4Ba	460 (M^+) 230 (base)	1.44 (12H, s), 2.64 (6H, s), 3.28 (4H, s), 7.42—8.05 (10H, m)
5Ba	287 (M^+) 230 198 (base)	0.85 (6H, d, $J=6$), 1.51 (6H, s), 1.50—1.84 (1H, m), 2.23 (2H, d, $J=7$), 2.68 (3H, d, $J=1$), 3.06 (2H, s), 7.32—7.73 (3H, m), 7.89—8.08 (2H, m)
3Bb	259 (M^+) 226, 185	1.43 (6H, s), 1.65 (6H, s), 1.86 (1H, s, –SH), 2.69 (3H, s), 7.4—7.7 (3H, m), 7.9—8.1 (2H, m)
4Bb	516 (M^+) 258 (base)	1.24 (12H, s), 1.61 (12H, s), 2.66 (6H, s), 7.39—7.70 (6H, m), 7.88—8.06 (4H, m)
6Bb	227 (M^+) 212 185 (base) 184	0.79 (6H, d, $J=7$), 1.36 (6H, s), 2.27 (1H, sep, $J=7$), 2.67 (3H, d, $J=1$), 7.28—7.72 (3H, m), 7.88—8.09 (2H, m)
15Aa	217 (M^+) 184	1.49 (1H, t, $J=8$, –SH), 1.73 (6H, s), 3.24 (2H, d, $J=8$), 7.4—7.8 (4H, m), 8.3—8.5 (2H, m)
17Aa	215 (M^+) 200 (base)	1.56 (6H, s), 3.10 (2H, s), 7.42—7.54 (4H, m), 8.45 (1H, d, $J=6$)
16Ab	488 (M^+) 244 (base)	1.33 (12H, s), 1.85 (12H, s), 7.44—7.82 (8H, m), 8.44—8.64 (4H, m)
17Ab	243 (M^+) 228, 213	1.37 (6H, s), 1.51 (3H, s), 1.63 (3H, s), 7.33—7.54 (4H, m), 8.45 (1H, d, $J=6$)
17Ad	229 (M^+) 214 200 (base)	1.40 (3H, d, $J=7$), 1.47 (3H, s), 1.59 (3H, s), 3.33 (1H, q, $J=7$), 7.35—7.57 (4H, m), 8.46 (1H, d, $J=6$)
15Ae	228 (M^+) 213, 195 [2240 ($C\equiv N$)]	1.91 (1H, dd, $J=10$, 8, –SH), 2.00 (3H, s), 3.16 (1H, dd, $J=14$, 10), 3.77 (1H, dd, $J=14$, 8), 7.62—7.96 (4H, m), 8.48 (1H, d, $J=6$), 8.64—8.74 (1H, m)
15Bb	246 (M^+) 245, 213	1.55 (6H, s), 1.73 (1H, s, –SH), 1.93 (6H, s), 7.70—8.01 (3H, m), 8.67—8.77 (1H, m), 9.43 (1H, d, $J=1$)
18Bb	172, 171 157 (base)	1.55 (6H, d, $J=7$), 3.91 (1H, sep, $J=7$), 7.79—7.97 (3H, m), 8.03—8.23 (1H, m), 9.40 (1H, d, $J=1$)
15Be	229 (M^+) 214, 196 [2240 ($C\equiv N$)]	2.07 (3H, s), 2.11 (1H, dd, $J=10$, 8, –SH), 3.26 (1H, dd, $J=14$, 10), 3.90 (1H, dd, $J=14$, 8), 7.95—8.15 (3H, m), 8.66—8.76 (1H, m), 9.51 (1H, d, $J=1$)

TABLE III. (continued)

Product	MS m/z [IR ν_{max} (cm^{-1})]	^{1}H-NMR (CDCl$_3$) δ (ppm) J (Hz)
18Be	183 (M$^+$) [2240 (C≡N)]	1.98 (3H, d, $J=7$), 4.83 (1H, q, $J=7$), 7.94—8.09 (3H, m), 8.21—8.31 (1H, m), 9.52 (1H, d, $J=1$)
15Bf	262 (M$^+$) 261, 229 [1725 (C=O)]	1.53 (1H, dd, $J=10$, 10, –SH), 1.88 (3H, s), 3.58 (1H, d, $J=10$), 3.61 (1H, d, $J=10$), 3.64 (3H, s), 7.71—8.04 (4H, m), 9.43 (1H, d, $J=1$)
18Bf	216 (M$^+$) 157 (base) [1730 (C=O)]	1.81 (3H, d, $J=7$), 3.69 (3H, s), 4.71 (1H, q, $J=7$), 7.86—8.16 (4H, m), 9.46 (1H, d, $J=1$)
15Bg	234 (M$^+$) 233, 203 201, 187	1.55 (1H, d, $J=10$, 7, –SH), 1.91 (3H, s), 3.11 (3H, s), 3.39 (1H, dd, $J=14$, 10), 3.56 (1H, dd, $J=14$, 7), 7.85—8.05 (3H, m), 8.91—8.99 (1H, m), 9.44 (1H, d, $J=1$)
17Ba	216 (M$^+$) 201 (base)	1.64 (6H, s), 3.13 (2H, s), 7.57—7.76 (3H, m), 9.37 (1H, s)
17Bd	230 (M$^+$) 215 201 (base)	1.42 (3H, d, $J=7$), 1.56 (3H, s), 1.67 (3H, s), 3.36 (1H, q, $J=7$), 7.56—7.75 (3H, m), 9.39 (1H, s)
17Ca	230 (M$^+$) 215 (base)	1.62 (6H, s), 2.94 (3H, s), 3.11 (2H, s), 7.65—7.80 (3H, m)
17Cd	244 (M$^+$) 229 215 (base)	1.40 (3H, d, $J=7$), 1.53 (3H, s), 1.64 (3H, s), 2.95 (3H, s), 3.41 (1H, q, $J=7$), 7.64—7.78 (3H, m)
17Da	292 (M$^+$) 277 (base)	1.69 (6H, s), 3.16 (2H, s), 7.50—7.61 (3H, m), 7.67—7.84 (5H, m)
17Dd	306 (M$^+$) 291 277 (base)	1.46 (3H, d, $J=7$), 1.60 (3H, s), 1.72 (3H, s), 3.40 (1H, q, $J=7$), 7.51—7.61 (3H, m), 7.66—7.84 (5H, m)

TABLE IV. Elemental Analysis Data for the Photoproducts

Product	Formula	Calcd (Found)			
		C	H	N	S
3Ab	$C_{15}H_{19}NS$	73.44	7.81	5.71	13.07
		(73.61	7.84	5.76	12.97)
4Ab	$C_{30}H_{36}N_2S_2$	73.72	7.42	5.73	13.12
		(73.66	7.18	5.66	13.14)
3Bb	$C_{16}H_{21}NS$	74.08	8.16	5.40	12.36
		(74.31	8.16	5.49	12.31)
17Aa	$C_{13}H_{13}NS$	72.51	6.09	6.51	14.89
		(72.60	6.06	6.41	15.01)
18Be	$C_{11}H_9N_3$	72.11	4.95	22.94	
		(72.13	4.82	22.82)	
15Bg	$C_{12}H_{14}N_2OS$	61.51	6.02	11.96	13.68
		(61.26	6.05	11.90	13.44)
17Ba	$C_{12}H_{12}N_2S$	66.63	5.59	12.95	14.83
		(66.64	5.62	12.92	14.63)
17Bd	$C_{13}H_{14}N_2S$	67.79	6.13	12.16	13.92
		(67.87	6.15	11.94	13.83)
17Ca	$C_{13}H_{14}N_2S$	67.79	6.13	12.16	13.92
		(67.95	6.15	12.14	13.80)
17Cd	$C_{14}H_{16}N_2S$	68.81	6.80	11.47	13.12
		(68.99	6.63	11.61	12.96)
17Da	$C_{18}H_{16}N_2S$	73.95	5.52	9.58	10.95
		(73.81	5.57	9.53	10.79)
17Dd	$C_{19}H_{18}N_2S$	74.47	5.92	9.14	10.46
		(74.40	5.86	9.06	10.55)

2-(2-Mercapto-1,1-dimethylethyl)-4-methylquinoline (3Ba), Bis[2,2-dimethyl-2-(4-methyl-2-quinolyl)ethyl]disulfide (4Ba) and 2-(2-Isobutylthio-1,1-dimethylethyl)-4-methylquinoline (5Ba) From 175 mg of **1B** and 0.60 g (10 mmol) of **2a**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (15 : 1). **3Ba**: bp 160 °C (bath temp.)/0.7 mmHg, colorless oil, 34 mg (15%). **4Ba**: colorless oil, 55 mg (24%). **5Ba**: bp 185 °C (bath temp.)/0.7 mmHg, colorless oil, 28 mg (10%).

TABLE V. High-Resolution Mass Spectral Data for the Photoproducts

Product	Formula	Calcd	Found
3Aa	$C_{13}H_{15}NS$	217.09265	217.09223
4Aa	$C_{26}H_{28}N_2S_2$	432.16964	432.16620
5Aa	$C_{17}H_{23}NS$	273.15529	273.15570
6Ab	$C_{15}H_{19}N$	213.15187	213.15151
3Ac	$C_{18}H_{17}NS$	279.10831	279.10670
3Ba	$C_{14}H_{17}NS$	231.10831	231.10855
5Ba	$C_{18}H_{25}NS$	287.17095	287.16856
6Bb	$C_{16}H_{21}N$	227.16753	227.16690
15Aa	$C_{13}H_{15}NS$	217.09265	217.09270
17Ab	$C_{15}H_{17}NS$	243.10831	243.10809
17Ad	$C_{14}H_{15}NS$	229.09265	229.09327
15Ae	$C_{13}H_{12}N_2S$	228.07226	228.07246
15Bb	$C_{14}H_{18}N_2S$	246.11924	246.11699
18Bb	$C_{11}H_{12}N_2$	172.10076	172.10632
15Be	$C_{12}H_{11}N_3S$	229.06753	229.06829
15Bf	$C_{13}H_{14}N_2O_2S$	262.07772	262.07539
18Bf	$C_{12}H_{12}N_2O_2$	216.08996	216.09036

Measurements were unsuccessful in the cases of **4Ac**, **4Ba**, **4Bb** and **16Ab** owing to a lack of parent peaks.

2-(2-Mercapto-1,1,2-trimethylpropyl)-4-methylquinoline (3Bb), Bis[1,1,2,2-tetramethyl-2-(4-methyl-2-quinolyl)ethyl]disulfide (4Bb) and 2-(1,1,2-Trimethylpropyl)-4-methylquinoline (6Bb) From 175 mg (1.0 mmol) of **1B** and 842 mg (10 mmol) of **2b**. Irradiated for 3 h. PLC (aluminum): eluted with *n*-hexane–acetone (40 : 1). **3Bb**: bp 200 °C (bath temp.)/0.4 mmHg, colorless solid, 85 mg (33%), mp 55—59 °C. **4Bb**: colorless oil, 18 mg (7%). **6Bb**: bp 120 °C (bath temp.)/0.6 mmHg, colorless oil, 16 mg (7%).

1-(2-Mercapto-1,1-dimethylethyl)isoquinoline (15Aa) and 3,3-Dimethyl-2,3-dihydrothiopyrano[4,3,2-*ij*]isoquinoline (17Aa) From 161 mg (1.0 mmol) of **14A** and 0.60 g (10 mmol) of **2a**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (10 : 1). **15Aa**: bp 160 °C (bath temp.)/0.7 mmHg, colorless oil, 139 mg (64%). **17Aa**: bp 180 °C (bath temp.)/0.6 mmHg, colorless solid, 20 mg (9%), mp 78—82 °C.

Bis[1,1,2,2-tetramethyl-2-(1-isoquinoline)ethyl]disulfide (16Ab) and 2,2,3,3-Tetramethyl-2,3-dihydrothiopyrano[4,3,2-*ij*]isoquinoline (17Ab) From 161 mg (1.0 mmol) of **14A** and 842 mg (10 mmol) of **2b**. Irradiated for 1 h. PLC (silica gel): eluted with *n*-hexane–acetone (15 : 1). **16Ab**: colorless oil, 41 mg (17%). **17Ab**: bp 200 °C (bath temp.)/0.6 mmHg, colorless oil, 64 mg (26%).

2,3,3-Trimethyl-2,3-dihydrothiopyrano[4,3,2-*ij*]isoquinoline (17Ad) From 161 mg (1.0 mmol) of **14A** and 701 mg (10 mmol) of **2d**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (15 : 1). **17Ad**: bp 160 °C (bath temp.)/0.3 mmHg, colorless oil, 85 mg (37%).

1-(1-Cyano-2-mercapto-1-methylethyl)isoquinoline (15Ae) From 161 mg (1.0 mmol) of **14A** and 671 mg (10 mmol) of **2e**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (3 : 1). **15Ae**: bp 190 °C (bath temp.)/0.65 mmHg, colorless oil, 155 mg (68%).

1-(2-Mercapto-1,1,2-trimethylpropyl)phthalazine (15Bb) and 1-Isopropylphthalazine (18Bb) From 162 mg (1.0 mmol) of **14B** and 842 mg (10 mmol) of **2b**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (5 : 1). Isolated **15Bb** was distilled *in vacuo* at 100 °C for 1 h for purification to give **18Bb**. **15Bb**: pale yellow solid, 174 mg (71%). **18Bb**: bp 165 °C (bath temp.)/0.35 mmHg, colorless oil, 53 mg (31%).

1-(1-Cyano-2-mercapto-1-methylethyl)phthalazine (15Be) and 1-(1-Cyanoethyl)phthalazine (18Be) From 162 mg (1.0 mmol) of **14B** and 671 mg (10 mmol) of **2e**. Irradiated for 2 h. PLC (silica gel): eluted with benzene–ethyl acetate (3 : 1). Isolated **15Be** was distilled *in vacuo* at 220 °C for 1 h for purification to give **18Be**. **15Be**: colorless solid, 176 mg (77%), mp 95—101.5 °C. **18Be**: bp 200 °C (bath temp.)/0.7 mmHg, pale yellow oil, 129 mg (70%), mp 70—73 °C.

1-(2-Mercapto-1-methoxycarbonyl-1-methylethyl)phthalazine (15Bf) and 1-(1-Methoxycarbonylethyl)phthalazine (18Bf) From 162 mg (1.0 mmol) of **14B** and 1.0 g (10 mmol) of **2f**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (1 : 1). Isolated **15Bf** was distilled *in vacuo* at 220 °C for 1 h for purification to give **18Bf**. **15Bf**: colorless solid, 235 mg (90%), mp 113.5—115.5 °C. **18Bf**: bp 240 °C (bath temp.)/0.7 mmHg, colorless oil, 113 mg (52%).

1-(2-Mercapto-1-methoxy-1-methylethyl)phthalazine (15Bg) From 162 mg (1.0 mmol) of **14B** and 721 mg (10 mmol) of **2g**. Irradiated for 2 h.

PLC (silica gel): eluted with *n*-hexane–acetone (3:1). **15Bg**: colorless prisms, 83 mg (35%) from ethyl acetate–*n*-hexane, mp 155—156 °C.

7,7-Dimethyl-7,8-dihydrothiopyrano[4,3,2-*ij*]phthalazine (17Ba) From 162 mg (1.0 mmol) of **14B** and 0.60 g (10 mmol) of **2a**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (3:1). **17Ba**: bp 210 °C (bath temp.)/0.45 mmHg, colorless solid, 111 mg (51%), mp 144.5—146 °C.

7,7,8-Trimethyl-7,8-dihydrothiopyrano[4,3,2-*ij*]phthalazine (17Bd) From 162 mg (1.0 mmol) of **14B** and 701 mg (10 mmol) of **2d**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (4:1). **17Bd**: bp 220 °C (bath temp.)/0.9 mmHg, colorless solid, 58 mg (25%), mp 108—113 °C.

4,8,8-Trimethyl-8,9-dihydrothiopyrano[4,3,2-*ij*]phthalazine (17Ca) From 176 mg (1.0 mmol) of **14C** and 0.60 g (10 mmol) of **2a**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (3:1). **17Ca**: bp 225 °C (bath temp.)/0.7 mmHg, colorless solid, 122 mg (53%), mp 115—117.5 °C.

4,8,8,9-Tetramethyl-8,9-dihydrothiopyrano[4,3,2-*ij*]phthalazine (17Cd) From 176 mg (1.0 mmol) of **14C** and 701 mg (10 mmol) of **2d**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (4:1). **17Cd**: bp 240 °C (bath temp.)/0.5 mmHg, colorless solid, 74 mg (30%), mp 135—140 °C.

8,8-Dimethyl-4-phenyl-8,9-dihydrothiopyrano[4,3,2-*ij*]phthalazine (17Da) From 238 mg (1.0 mmol) of **14D** and 0.60 g (10 mmol) of **2a**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (5:1). **17Da**: colorless prisms, 114 mg (39%) from ethyl acetate–*n*-hexane, mp 139.5—140.5 °C.

8,8,9-Trimethyl-4-phenyl-8,9-dihydrothiopyrano[4,3,2-*ij*]phthalazine (17Dd) From 238 mg (1.0 mmol) of **14D** and 701 mg (10 mmol) of **2d**. Irradiated for 2 h. PLC (silica gel): eluted with *n*-hexane–acetone (5:1). **17Dd**: fine pale yellow needles, 80 mg (26%) from *n*-hexane, mp 172—173.5 °C.

References

1) *a*) Part VII of Photochemistry of Conjugated Nitrogen–Thiocarbonyl Systems: A part of this work has been published in a preliminary communication: E. Sato, Y. Ikeda, and Y. Kanaoka, *Chem. Lett.*, **1987**, 273; Part VI: E. Sato, Y. Ikeda, M. Hasebe, T. Nishio, T. Miura, and Y. Kanaoka, *Chem. Pharm. Bull.*, **36**, 4749 (1988); *b*) Photo-induced Reactions 114. Part 113: K. Ohkura, K. Seki, M. Terashima, and Y. Kanaoka, *Tetrahedron Lett.*, **30**, 3433 (1989).

2) *a*) "Photochemistry of Heterocyclic Compounds," ed. by O. Buchardt, Wiley-Interscience, New York, 1976; *b*) Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978); *c*) S. T. Reid, *Ad. Heterocycl. Chem.*, **30**, 239 (1982); *d*) H. Takechi, M. Machida, and Y. Kanaoka, *Leibigs Ann. Chem.*, **1987**, 859, and references cited therein.

3) *a*) T. Yonezawa, M. Matsumoto, and Y. Matsuura, *Bull. Chem. Soc. Jpn.*, **42**, 2323 (1969); *b*) H. Gottardt and S. Neiberl, *Tetrahedron Lett.*, **1974**, 3397; *c*) *Idem*, *Chem. Ber.*, **109**, 2871 (1976); *d*) *Idem*, *Tetrahedron Lett.*, **1976**, 3563.

4) *a*) C. Marazano, J. L. Fourrey, and B. C. Das, *J. Chem. Soc., Chem. Commun.*, **1977**, 742; *b*) B. C. Das, J. L. Fourrey, C. Marazano, and A. Merrien, *J. Chem. Res.*, **1978**, 370.

5) P. de Mayo, L. K. Sydnes, and G. Wenska, *J. Org. Chem.*, **45**, 1549 (1980).

6) *a*) E. Sato and Y. Kanaoka, *Tetrahedron Lett.*, **1969**, 3547; *b*) D. E. Bergstrom and N. J. Leonard, *Biochemistry*, **11**, 1 (1972); *c*) J. L. Fourrey, P. Jouin, and J. Morton, *Tetrahedron Lett.*, **1973**, 3229; *d*) *Idem*, *ibid.*, **1974**, 3005; *e*) P. Jouin and J. L. Fourrey, *ibid.*, **1975**, 1329.

7) M. Machida, K. Oda, E. Yoshida, and Y. Kanaoka, *J. Org. Chem.*, **50**, 1681 (1985).

8) E. Sato, M. Hasebe, T. Nishio, Y. Ikeda, and Y. Kanaoka, *Leibigs Ann. Chem.*, **1988**, 733.

9) *a*) E. Sato, Y. Ikeda, and Y. Kanaoka, Abstract of Papers, 12th International Conference on Photochemistry, Tokyo, August 1985, p. 349; *b*) T. Nishio and Y. Omote, *ibid.*, p. 350; *c*) *Idem*, *Synthesis*, **1986**, 54.

10) *a*) A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, **1970**, 2025; *b*) A. Ohno, T. Koizumi, and Y. Ohnishi, *Bull. Chem. Soc. Jpn.*, **44**, 2511 (1971); *c*) H. J. T. Bos, H. Schinkel, and Th. C. M. Wijsman, *Tetrahedron Lett.*, **1971**, 3905, and references cited therein; *d*) P. de Mayo and H. Shizuka, *Mol. Photochem.*, **5**, 339 (1973).

11) E. Sato, M. Hasebe, and Y. Kanaoka, *Chem. Pharm. Bull.*, **34**, 3061 (1986).

12) *a*) O. Buchardt, *Acta Chem. Scand.*, **17**, 1461 (1963); *b*) *Idem*, *ibid.*, **18**, 1389 (1964); *c*) G. R. Evenga and D. L. Fabiney, *J. Org. Chem.*, **35**, 1757 (1970).

13) G. R. Evenga and D. L. Fabiney, *Tetrahedron Lett.*, **1971**, 1749.

14) W. Koenigs, *Ber.*, **32**, 226 (1899).