Tetrahedron. Vol. 31, pp. 1245 to 1250 Pergamon Press 1975 Printed in Great Britain

PHOTOINDUCED REACTIONS—LXXIX
PHOTOCHEMISTRY OF 2-THIAZOLINES†

T. MATSUURA* and Y. ITO
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

(*Received in Japan* 24 *September* 1974; *Received in the UK for publication* 1 *January* 1975)

Abstract—Upon irradiation with light at 2537 Å 2-alkyl-2-thiazolines (**1**) underwent rearrangement to N-alkenylthioamides (**2** and **3**) as the major pathway and fragmentation to a nitrile and an episulphide as the minor one. Evidence is provided for the intermediary formation of a valence bond isomer, N-thioacylaziridine, followed by its photochemical transformation into N-alkenylthioamides.

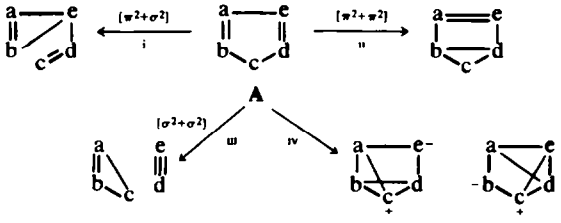
The photochemical reactions of 5-membered heteroaromatics have attracted attention of many workers.[3] Among them, the photochemical rearrangement and fragmentation reactions of type A compounds (c=O, S, or NR) have been interpreted mostly in terms of one of three types of valence bond tautomerization formally regarded as [2 + 2] reactions (i, ii, and iii in Scheme 1),[3,4] although in particular cases (c=S) some evidence has been provided for the occurrence of type iv valence tautomerization.[3,5]

However, there have been fewer reports on the photochemical reactions of partially hydrogenated 5-membered heteroaromatics of type B (c=O, S, or NR). By analogy with the photochemical [2 + 2] reactions of Scheme 1, type B compounds would be expected to undergo five types of photochemical [2 + 2] reactions (i–v in Scheme 2). It has already been known that reaction i occurs with 4,5-dihydrofurans,[6] 2-pyrazolines,[7] and 2-thiazolines,[2] reaction iii with 2-thiazolines,[2] 1,2,3-triazolines,[8] and 2-isoxazolines,[9a] reaction iv with 2-isoxazolines,[9] and reaction v with 2-isoxazolines.[9a] ‡ However, three-membered cyclic compounds resulting from such reactions cannot always be isolated, but in many cases they undergo further photochemical or thermal transformation into the final products. An exceptional case is found in the photochemical rearrangement of 4,5-dihydrofurans which give acylcyclopropanes.[6] In the present paper we describe studies of the photochemical reactions of 2-thiazolines involving reactions i and iii in full detail, and the photochemistry of 2-isoxazolines will be presented in the subsequent paper.[11] (Hereafter the designation, reaction i, ii, etc. will be used for the pathways in Scheme 2.)

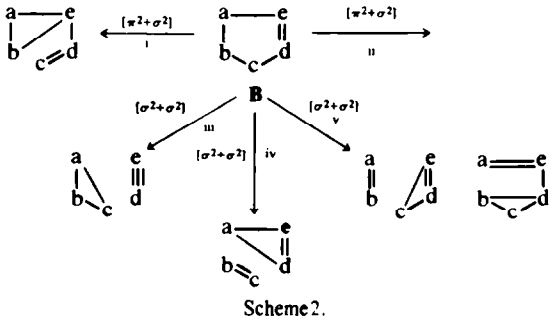
Photolysis products of substituted 2-thiazolines. Several 2-alkyl-2-thiazolines **1a**–**1g** were irradiated in acetonitrile with a low-pressure mercury lamp with Vycor housing (mainly 2537 Å). In most runs, after evaporation of the solvent the residue was found by NMR analysis to consist mainly of the starting material and its rearranged products, N-alkenylthioamides **2** or/and **3**. In the case of **1c** it contained additionally benzyl cyanide. These products were isolated by silica gel chromatography and their structures determined on the basis of chemical and spectral evidence or by direct comparison with authentic samples. Among these products, N-vinylthioacetamide **2a** was unstable to heat (above 80°), but considerably stable under irradiation conditions giving only a small amount of polymeric product. The conditions and results of the photolysis experiments are presented in Table 1.

In some cases, attempts were made to detect products other than **2** and **3**. Thus, ethylene sulphide was obtained from 2-methyl-2-thiazoline **1a**, propionitrile from 2-ethyl-2-thiazoline **1b**, and benzyl cyanide from 2-benzyl-2-thiazoline **1c**. The results indicate that 2-alkyl-2-thiazolines **1** undergo two types of photoreactions, rearrangement to N-alkenylthioamides, **2** and **3** and $[\sigma 2 + \sigma 2]$ cyclo-reversion to an episulphide and a nitrile (reaction iii), as shown in a general scheme below. Longer wavelength light from a high-pressure mercury lamp through Pyrex was ineffective to both types of reactions, thus **1a** was recovered unchanged under these conditions.

Although the synthesis of several N-alkenylthioamides has been reported by Smith and Sullivan,[12] the present photoreaction of 2-alkyl-2-thiazolines provides a new synthetic method for them, especially for N-vinylthioamides which are unknown to date. However, 2-thiazolines having a substituent allowing resonance interaction with the thiazoline chromophore, such as 2-phenyl-, 2-styryl-, 2-(β-pyridyl)-, and 2-mercapto-2-thiazolines, were inert to photolysis under similar conditions. 2-Thiazoline itself underwent complex photo-



Scheme 1.



Scheme 2.

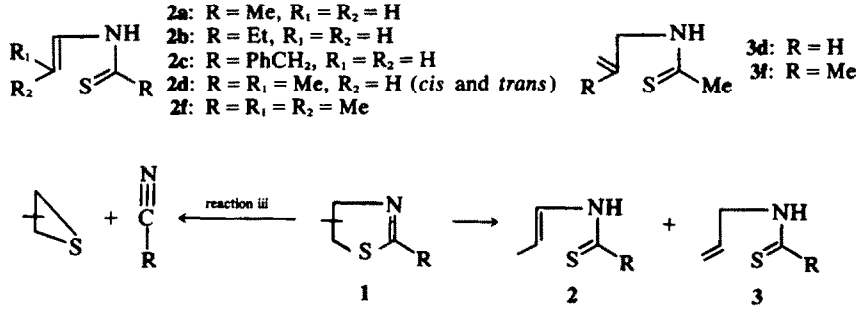
†Part LXXVIII, Ref. 1. Part of this work was presented in the preliminary form.[2]

‡The photochemical valence tautomerization of dihydroheteroaromatics of type B(b = hetero atom) has also been known.[10]

Table 1. Photolysis of 2-thiazolines

2-Thiazoline	Irrad. conditions Concn. (M/l)[a]	Time (hr)	Thioamide	Products (% yield)[b] Others	% Recovered
1a 2-Me	0·25	87	**2a** (25)	nd[c]	nd
	0·31	61	**2a** (17)	 (2)	65
1b 2-Et	0·15	74	**2b** (25)	nd	25[d]
	0·29†	66	**2b** (14)	EtCN(9)	68
1c 2-$PhCH_2$	0·15	62	**2c** (17)	$PhCH_2CN$(13)	68
1d 2,4-Me_2	0·18	68	*trans*-**2d** (10) *cis*-**2d** (10) **3d** (1)	nd	21[d]
1e 2,5-Me_2	0·25	72	*trans*-**2d** (8) *cis*-**2d** (8) **3d** (3)	nd	20[d]
1f 2,4,4-Me_3	0·22	67	**2f** (10) **3f** (12)	nd	23[d]
1g 2,5,5-Me_3	0·18	70	**2f** (16) **3f** (17)	nd	20[d]

[a]MeCN was used as solvent except † (Et_2O). [b]Yields are based on the starting 2-thiazolines. [c]Not determined. [d]A considerable amount of the recovered 2-thiazoline was lost during evaporation of the solvent, because a special care was not taken.



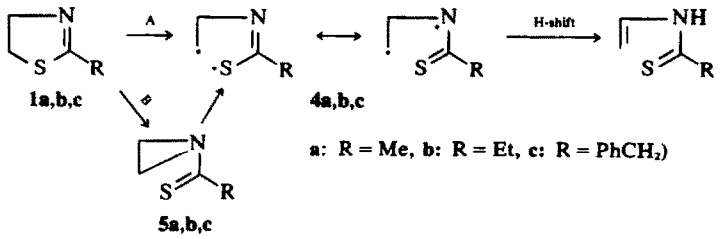
reaction to yield an unexpected product in low yield which is believed to be N-thioformylthiazolidine.

Mechanism. The transformation of 2-alkyl-2-thiazolines **1a**, **b**, and **c** into **2a**, **b**, and **c** respectively may proceed through a biradical **4** formed by C-5–S bond fission* followed by hydrogen shift from C-4 to N (path A, Scheme 3). However, by analogy with the photochemical valence tautomerization of 4,5-dihydrofuran (reaction i, Scheme 2),[6] a mechanism involving a thioacylaziridine intermediate **5**, which can be formed directly from **1a**, **b**, and **c** (path B, Scheme 3), is also attractive.

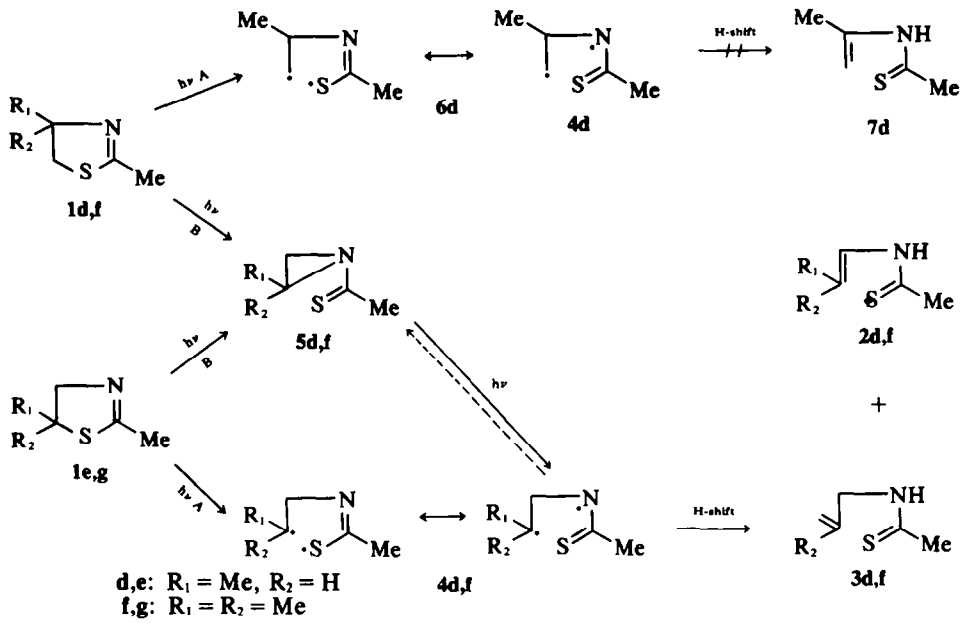
The occurrence of the latter pathway (B) is evidently demonstrated by the photorearrangement of two sets of isomeric 2-thiazolines, **1d** and **1e** or **1f** and **1g**. Scheme 4 summarizes possible pathways for the photorearrangement of these 2-thiazolines. Both **1d** and **1e** gave the same products, trans-**2d**, cis-**2d**, and **3d**, in a similar ratio. Similarly, either **1f** or **1g** gave the same products, **2f** and **3f**, in nearly the same ratio. The results indicate that **1d** and **1e** (or **1f** or **1g**) should rearrange to the final products through a common thioacetylaziridine **5d** (or **5f**) followed by cleavage to a biradical species **4d** (or **4f**) and by subsequent intramolecular hydrogen shift. It was also confirmed by NMR analysis of the photolyzate that no interconversion between **1d** and **1e** and between **1f** and **1g** takes place during photolysis. This suggests that the thioacetylaziridine formation must be an irreversible process.

There are two possible routes to the aziridine intermediate **5**, namely concerted [$\pi 2 + \sigma 2$] cycloaddition (path B, Scheme 4) and stepwise pathway via a a biradical species such as **1** → **6** → **5** or **1** → **4** → **5**. The concerted process is more probable, since in the photolysis products from **1d** N-isopropenylthioacetamide **7d** could not be detected, which is the expected product if the biradical **6d** is formed. It

*The C-5–S bond is supposed to be the weakest bond in the ring. A zwitterionic species (· = +, − in **4**) may also be a candidate for the intermediate.



Scheme 3.



Scheme 4.

has been reported that the photochemical transformation of 4,5-dihydrofuran into formylcyclopropane involves in part a concerted process.[6f]

In order to obtain further evidence for the intermediary formation of the N-thioacylaziridine **5**, we synthesized N-thioacetylaziridine **5a** from carboxymethyl dithioacetate and ethylene imine by the procedure employed for the synthesis of N-thioarylaziridine,[13] and its chemical properties were examined. The aziridine **5a** was considerably unstable, so that it could not be obtained in a pure state. However, NMR analysis of the carbon tetrachloride extract from the reaction mixture showed signals at τ 7·42 (s, 3H, Me) and 7·49 (s, 4H, CH_2–CH_2)[13] besides signals of impurities, indicating that it contained 40–65% of **5a**. Although **5a** decomposed gradually even at −20° to give a complex mixture of products, the production of **2a** was not observed in the temperature range −20° to 50°. Reaction of **5a** with picric acid and thiophenol gave expectedly[13] the picrate of **1a** (nearly quantitatively) and N-(β-phenylthioethyl)thioacetamide (**8a**, 65% yield), respectively.

Irradiation of an ethereal solution of crude **5a** at 2537 Å under cooling with ice-water gave **2a** in 63% yield, while under similar conditions without irradiation it showed no significant change. A control irradiation experiemnt with **1a** under similar conditions showed that the conversion of **1a** into **2a** was very slow compared with the phototransformation of **5a** into **2a**. Therefore, a pathway, by which **5a** rearranges to **2a** via **1a** can be ruled out.

In order to obtain more direct evidence for the formation of the N-thioacylaziridine **5** during the photolysis of 2-thiazolines **1**, attempts were made to trap **5a** during irradiation of **1a**. After a solution of **1a** in acetonitrile had been photolyzed below 5° for a short time, the NMR spectrum of aliquots was measured. Three sharp singlets attributable to the methyl and methylene protons of **5a** and to the methyl protons of **2a** were observed between τ 7·51 and 7·62. On further irradiation the intensity of the methyl signal of **2a** increased, while that of the methyl and methylene signals of **5a** remained constant. Addition of thiophenol, which reacted with neither **1a** nor **2a**, to the photolysate resulted in the formation of the adduct **8a**. Similarly the adduct **8b** was obtained by treatment of the photolysate of **1e** with thiophenol, indicating the formation of **5d**.

The above results led us to conclude that the photorearrangement of 2-thiazolines **1** proceeds via N-thioacylaziridines **5** which are photochemically transformed into N-alkenylthioamides **2** and **3**.

EXPERIMENTAL

M.ps were uncorrected. NMR spectra were recorded on a NEVA EM-360 or T-60 spectrometer with TMS as an internal standard. IR, UV and mass spectra were recorded on a JASCO IRS spectrometer, a JASCO ORD/UV-5 spectrometer, and a Hitachi RMS-4 spectrometer, respectively. Vapour phase chromatography (VPC) was carried out with a Shimadzu GC-2C using helium as carrier gas. Column chromatography (CC) was carried out on Mallinckrodt silica gel (100 mesh) and thin layer chromatography (TLC) on Merck Kieselgel GF_{254} using UV light and iodine vapour for detection.

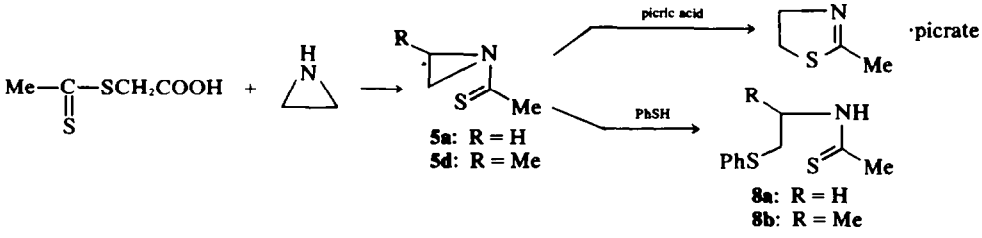
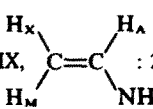


Table 2. Spectral data of thioamides 2 and 3

Thioamides	CH_3CS- (3H, s)	τ, [Solvent], J(Hz)[a] NH (1H, br)	=CH–NH– (1H)	Others		ν_{max}^{Nest} (cm^{-1}) NH	C=C	CS–N	m/e (Rel int)[b]	λ_{max}^{EtOH} (ε) nm
2a	7·40	0·20	2·30–2·86 (dq,[b] J = 10)	4·80–5·34 (2H, q, –CH=CH_2)[c]	[CCl_4]	3200	1630, 975 880	1510 1130	101(100, M^+), 100(97) 59(80), 43(52), 42(46)	300(15700)
2b	7·27(2H, q, J = 7, –CH_2CH$_3$)	0·88	2·21–2·80 (dq, J = 10)	4·83–5·29 (2H, q, –CH=CH_2)[c] 8·67 (3H, t, J = 7, –CH_3CH_3)	[$CDCl_3$]	3250	1645, 960 865	1515 1120	115(100, M^+), 114(95) 73(81, EtC=S$^+$), 45(81)	300(19100)
2c	5·87 (2H, s, CH_2Ph)	1·47	2·20–2·81 (6H, m[d])	5·04–5·34 (2H, m, –CH=CH_2)[c]	[$CDCl_3$]	3250	1635, 970 890	1520 1110	177(66, M^+), 176(60) 134(62), 91(100, $C_7H_7^+$) 59(60)	303(18000)
cis-**2d**	7·40	0·90	2·65–3·05 (tm,[e] J = 9·5)	4·91 (1H, br, quintet, $J_{-CH=CH-}^{cis}$ = 9 J_{-CHCH_3} = 8, –CH=CHCH$_3$), 8·23(3H, dd, $J_{-CH-CCH_3}$ = 1·5, –CH=CHCH_3)	[CCl_4]	3260	1670, 725	1510 1105	115(86, M^+), 100(100) 59(87), 56(70), 42(62)	300(21600)
trans-**2d**	7·47	0·08	2·55–3·03 (tm,[e] J = 9·5)	4·36 (1H, sextet, $J_{-CH=CH-}^{trans}$ = 14, J_{-CHCH_3} = 7, –CH=CHCH$_3$), 8·24 (3H, dd, $J_{-CH-CCH_3}$ = 1·5, –CH=CHCH_3)	[CCl_4]	3250	1675, 940	1530 1115	115(46, M^+), 100(100) 59(85), 56(57)	300(24500)
2f	7·39	1·07	3·01 (dm,[f] J = 9)	8·21 (6H, d, J = 1·5, –CH=C(CH_3)$_2$)	[$CDCl_3$]	3250	1645, 825	1515 1130	129(17, M^+), 114(80) 59(78)	300(17300)
3d	7·48	1·93	—	3·81–4·35 (1H, m, –CH=CH_2), 4·55–4·93 (2H, m, –CH=CH_2), 5·76 (2H, tm,[e] J_{-CH_2NH-} = 6, J_{-CH_2-CH-} = 6), –NHCH_2–	[CCl_4]	3300	1645, 940	1535 1170	—	—
3f	7·36	1·96	—	5·06 (2H, m, CH_3C=CH_2), 5·70 (2H, br d,[e] J_{-CH_2NH-} = 6, –CH_2NH–), 8·19 (3H, br s, CH_2=CCH_3)	[$CDCl_3$]	3250	1655, 930	1530 1170	129(13, M^+), 114(88) 59(50), 42(68)	267(16700)

[a]s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [b]Became q by adding D_2O. [c]Interpreted as an AMX,  : 2·58(H_A), 4·94(H_M), 5·27(H_X); J_{AM} = 16Hz, J_{AX} = 9Hz, J_{MX} = OHz for **2a**.

Similar interpretations were done for **2b** and **2c**. [d]Overlapped with Ph protons. [e]Became br d by adding D_2O. [f]Became m by adding D_2O. [g]Became br s by adding D_2O. [h]A peak at m/e 59 is assigned for CH_3–$\dot{C}$=S.

Preparation of 2-thiazolines. 2-Methyl-**1a**, 2-ethyl-**1b**, 2,5-dimethyl-**1e**, 2,4,4-trimethyl-**1f**, 2,5,5-trimethyl-**1g**, 2-phenyl-, and unsubstituted 2-thiazolines were prepared according to the Wenker's method,[14] 2,4-dimethyl-2-thiazoline **1d** according to the method of Lowell and Helmkamp,[15] and 2-benzyl-**1c**, 2-(β-pyridyl)-, and 2-styryl-2-thiazolines according to the method of Kuhn and Drawert.[16] The purity of the prepared 2-thiazolines was over 98% by NMR, except **1d** (96%). 2-Mercapto-2-thiazoline was commercially available.

General procedure for irradiation and product isolation. Irradiations were performed with an acetonitrile solution of **1** with a 10 W low-pressure mercury lamp (Vycor housing) under nitrogen with external water cooling, unless otherwise specified. After removing the solvent under reduced pressure, products were isolated by CC and preparative TLC using benzene as eluent. For volatile products special procedures were taken. In attempts to recover the unreacted 2-thiazolines, it was found that they were mostly hydrolyzed on silica gel during elution with chloroform-acetone, reflecting their instability under acidic conditions.[17] Spectral properties of **2** and **3**, which are new compounds, except **3d** and **3f**,[12] are summarized in Table 2.

N-Vinylthioacetamide **2a**. From the photolysate of **1a** (5·64 g, 220 ml, 87 hr), 1·39 g of **2a** was isolated by CC (100 g silica gel, 1·9 l benzene) and purified by TLC, b.p. 70° (bath temp.)/2 mm Hg (Found: C, 47·56; H, 7·26; N, 13·93; S, 31·40. C_4H_7NS requires: C, 47·52; H, 6·98; N, 13·86; S, 31·65%).

A mixture of 360 mg of **2a**, 50 ml 0·1N HCl, and a few drops of MeOH was maintained at 56–60° for 4 hr. After cooling, the mixture was extracted with 50 ml ether and the ethereal layer dried over anhydrous Na_2SO_4. Evaporation of ether gave 115 mg (43%) of thioacetamide, m.p. 112–114° ($CHCl_3$-petroleum ether) [lit.[18] 113–114°], identical with an authentic sample (NMR and IR). Acetaldehyde concurrently evolved was reacted with 2,4-dinitrophenylhydrazine - H_2SO_4 reagent to give its 2,4-dinitrophenylhydrazone in 45% yield, m.p. 154–161° (EtOH) [lit.[19] 162°], identical with an authentic sample (IR). The above result indicates that **2a** has an enamine moiety.[20]

Ethylene sulphide. The photolysate of **1a** (8·10 g, 220 ml; 61 hr at ca 10°) was distilled through a Widmer fractionating column. From the distillate (3·5 ml) up to 80°, ethylene sulphide was separated by VPC (PEG 20M, 20%, 40–60 mesh, 0·5 atm cm^{-2} gauge, 50°) in 2% yield, which was identified by VPC retention time and IR. The yield of **2a** and the recovered **1a** were determined by UV analysis of the photolysate.

N-Vinylthiopropionamide **2b**. From the photolysate of **1b** (3·70 g, 220 ml, 74 hr), 900 mg of **2b** was isolated by CC (80 g silica gel, 1·3 l benzene) and purified by TLC, b.p. 90° (bath temp.)/4 mmHg (Found: C, 51·87; H, 7·84; N, 11·90; S, 27·50. C_5H_9NS requires: C, 52·16; H, 7·88; N, 12·17; S, 27·79%).

Propionitrile. The photolysate of 7·31 g of **1b** in 220 ml ether (66 hr) was evaporated through a Vigroux column to remove most of the solvent. Distillation of a part of the residue afforded propionitrile, identified by VPC retention time (Silicone DC 550; 0·4 atm/cm^2 gauge; at 60°) and IR. The yield (9%) was determined by VPC. From the rest of the residue, ether was carefully removed under reduced pressure, and the yields of **2b** and the recovered **1b** were determined by NMR, using 2-methyl-imidazole as an internal standard.

N-Vinylthiophenylacetamide **2c**. From the photolysate of **1c** (6·01 g, 220 ml, 62 hr), 1·01 g of **2c** and 0·75 g of benzyl cyanide were successively isolated by CC (110 g silica gel, 1·3 l benzene). Benzyl cyanide was identical with an authentic sample (IR). Recrystallisation of **2c** from ligroin gave colourless crystals, m.p. 91·5–92·5° (Found: C, 67·17; H, 6·00; N, 8·09; S, 18·30. $C_{10}H_{10}NS$ requires: C, 67·78; H, 6·28; N, 7·91; S, 18·06%).

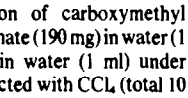
*N-(cis-1-Propenyl)- and N-(trans-1-propenyl)thioacetamides (cis- and trans-***2d***) and N-allylthioacetamide* **3d**. From the photolysate of **1d** (4·17 g, 200 ml, 68 hr), 420 mg of cis-**2d**, 420 mg of trans-**2d**, and 40 mg of **3d** were successively isolated by CC (80 g silica gel, 4·1 l benzene). Careful inspections of NMR spectra of the photolysate and the CC fractions showed no signals attributed to **1e** and expected for **7d**. **3d** was identical with an authentic sample obtained by an independent synthesis.[12] Distillation of cis-**2d** gave an oil, b.p. 80–90° (bath temp.)/3 mmHg, which crystallised on standing, m.p. 40–42° (Found: C, 52·33; H, 8·01; N, 12·26; S, 27·92. C_5H_9NS requires: C, 52·16; H, 7·88; N, 12·17; S, 27·79%). Distillation of trans-**2d** gave an oil, b.p. 90–95° (bath temp.)/3 mmHg. (Found: C, 51·86; H, 8·02; N, 11·99; S, 27·53. C_5H_9NS requires: C, 52·16; H, 7·88; N, 12·17; S, 27·79%).

The photolysis of **1e** (6·50 g, 220 ml, 72 hr) gave a similar result (Table 1).

N-2-Methyl-1-propenylthioacetamide **2f** *and N-2-methyl-allylthioacetamide* **3f**. NMR analysis of the photolysate of **1f** (6·17 g, 220 ml, 67 hr) showed no interconversion between **1f** and **1g** during photolysis. From the photolysate 620 mg of **2f** and 740 mg of **3f** were successively obtained by CC (silica gel 140 g, 5·5 l benzene). Distillation of **2f** gave an oil, b.p. 55–65° (bath temp.)/2 mmHg (Found: C, 55·55; H, 8·71; N, 10·64; S, 24·51. $C_6H_{11}NS$ requires: C, 55·79; H, 8·58; N, 10·85; S, 24·78%). Distillation of **3f** gave an oil, b.p. 85–100° (bath temp.)/4 mmHg, which was identical with an authentic sample (IR).[12,†]

The photolysis of **1g** (5·16 g, 220 ml, 70 hr) gave a similar result (Table 1).

N-Thioformylthiazolidine. From the photolysate of 2-thiazoline (5·00 g, 220 ml, 70 hr), 60 mg of the titled compound was obtained by CC (silica gel 100 g, 2·1 l benzene) and TLC (50:1 benzene–AcOH) as an oil, b.p. 125–130° (bath temp.)/3 mmHg. NMR ($CDCl_3$) τ 0·68 (1H, sharp signal with very fine splitting, $-CH{=}S$), 5·19 (2H, sharp signal with very fine splitting, $S-CH_2-N$), 5·74–6·04 (2H, m, $SHC-N-CH_2-CH_2-$), 6·68–6·96 (2H, m, $-S-CH_2-CH_2-$); IR ν_{max}^{Neat} 1480, 1230, 1155, 1110 cm^{-1} ($-CS-N-$);[22] UV λ_{max}^{EtOH} 272 nm (ϵ 15900); *m/e* 133 (rel. int. 100, M^+), 54 (57), 45 (70), 28 (77). The spectral data are consistent with the following structure.



(Found: C, 36·34; H, 5·45; N, 10·55; S, 47·82. C_4H_7NS requires: C, 36·09; H, 5·30; N, 10·52; S, 48·08%).

N-Thioacetylaziridine **5a**. To a solution of carboxymethyl dithioacetate[23] (300 mg) and sodium bicarbonate (190 mg) in water (1 ml) was added ethylene imine (0·16 ml) in water (1 ml) under ice-cooling. The reaction mixture was extracted with CCl_4 (total 10 ml) and the organic layer washed with ice-water, dried over anhydrous Na_2SO_4, and immediately submitted to NMR analysis. It showed two singlets at τ 7·42 (Me protons) and 7·49 (aziridine protons)[13] in addition to many low-intensity signals owing to impurities. For several preparations, the yield of **5a** was estimated to be 20–30% and the purity of **5a** in the CCl_4 extracts to be 40–65% by NMR integration.

Reaction of **5a** *with picric acid.* To 3 ml of the above CCl_4 extract was added picric acid (100 mg) and the mixture refluxed for 3 hr, giving a yellow precipitate which was separated by filtration and recrystallised from benzene–EtOH to give 2-methyl-2-thiazoline picrate (65 mg) in almost quantitative yield, m.p. 155–170° [lit.[14] 171°], identical with an authentic sample (IR).

N-2-Phenylthioethylthioacetamide **8a**. To 5 ml of the above CCl_4 extract was added thiophenol (0·1 ml) and the mixture stirred for 2 hr at room temperature and for an additional 2 hr at 50–60°. Evaporation of the solvent gave a yellow oil (220 mg), from which 36 mg (65%) of **8a** was isolated by preparative TLC (silica gel/$CHCl_3$) followed by distillation as an oil, b.p. 110–140° (bath temp.)/10^{-4} mmHg. NMR (CCl_4) τ 1·97 (1H, broad, NH), 2·53–2·95 (5H, m, aromatic protons), 6·22 (2H, slightly split q, became slightly split t by adding D_2O, J_{CH-CH} = 6Hz, J_{CH-NH} = 6Hz, $-NH-CH_2-CH_2-$), 6·87 (2H, slightly split t, J_{CH-CH} = 6Hz, $-S-CH_2-CH_2-$), 7·58 (3H, s, CH_3-CS-); IR ν_{max}^{Neat} 3300 (NH), 1535, 1150 ($-CS-NH-$), 740, 695 (Ph–) cm^{-1} (Found: C, 56·67; H, 6·26; N, 6·46. $C_{10}H_{13}NS_2$ requires: C, 56·86; H, 6·20; N, 6·63%).

Photolysis of N-thioacetylaziridine **5a**. One-sixth of the reaction mixture of carboxymethyl dithioacetate (325 mg), ethylene imine (0·17 ml), sodium bicarbonate (210 mg), and water (2·5 ml) as above was extracted with 0·4 ml CCl_4. NMR analysis of the extract showed that it contained **5a** in 40% purity. The rest of the reaction mixture was extracted with 5 ml ether, in which the content of **5a** was found to be almost the same as in CCl_4. Three-fifth of the ether extract was transferred into a quartz tube, sealed under nitrogen and irradiated

†The authors wish to thank Professor P. A. S. Smith for sending the IR chart for **3f**.

externally (2537 Å) under cooling with ice-water for 2 hr. NMR spectra of the photolysate and the rest of the ether extract kept in the dark were measured after evaporating ether at low temperature *in vacuo* followed by dissolving the residues in $CDCl_3$. Comparison of the spectra indicated that on irradiation 46% of **5a** (τ 7·43 and 7·48) was recovered and 67% of the reacted **5a** was converted into **2a** (τ 7·48, 5·01–5·47). The NMR signals corresponding to 2-methyl-2-thiazoline were not observed. **2a** was isolated by preparative TLC (silica gel, 50:1 $CHCl_3$-acetone), which was identical with an authentic sample (IR). The yield (63%) was in good agreement with that estimated from NMR analysis.

A control experiment with **1a** (0·1 ml in 10 ml ether) was carried out under the same irradiation conditions. After evaporating the photolysate at low temperature *in vacuo*, NMR analysis (CCl_4) of the residue showed that it consisted of a large amount of the recovered **1a** (ca. 97%), **2a** (ca. 2%), and **5a** (ca. 1%), demonstrating that the photoreaction of **1a** is very slow compared with that of **5a**.

Trapping of **5a** *from the photolysate of* **1a**. A solution of **1a** (6·13 g) in 220 ml acetonitrile was irradiated internally at 1–5°. Aliquots of the photolysate were withdrawn at time intervals 4, 13, and 23 hr. After removing most of the solvent at room temperature *in vacuo*, each residue was analyzed by NMR (CCl_4), which showed the signals of **5a** at τ 7·51 and 7·57 and of **2a** at 7·62. These signals appeared at somewhat higher field than those measured in pure CCl_4, probably due to the solute–solute interactions. To the photolysate after 23 hr irradiation was added thiophenol (2 ml) and the mixture stirred for 2 hr at room temperature, then 2 hr at 55–66°. The solvent was removed and the residue separated by preparative TLC (silica gel, $CHCl_3$) to give **8a** (100 mg) which was identical with an authentic sample (IR). As a control experiment a mixture of **1a** (28 μl) and **2a** (28 mg) was treated with thiophenol (28 μl) in 1 ml acetonitrile as above, to give the starting materials but no **8a** (TLC and NMR).

Trapping of **5d** *from the photolysate of* **1e**. Similar treatment of the photolysate of **1e** (5·35 g) in 220 ml acetonitrile after 18 hr irradiation with thiophenol (2 ml) yielded **8b** (50 mg) as an oil, b.p. 150–165° (bath temp.)/10^{-4} mmHg; NMR (CCl_4) τ 2·16 (1H, broad d, J_{NH-CH} = 7Hz, -NH-CH-), 2·45–3·02 (5H, m, C_6H_5-), 5·27 (1H, broad septet, became broad sextet on adding D_2O. J_{CH-NH} = 7Hz, J_{CH-CH_3} = 6·5Hz, J_{CH-CH_2} = 5·5Hz. -NH-CH(CH_3)-CH_2-, 6·87 (2H, d, J_{CH_2-CH} = 5·5Hz, -CH_2-CH-), 7·74 (3H, s, CH_3-CS-), 8·72 (3H, d, J_{CH_3-CH} = 6·5Hz, CH_3-CH-); IR ν_{max}^{Neat} 3230 (NH), 1535, 1115 (CS-N), 740, 685 (Ph) cm^{-1} (Found: C, 58·93; H, 6·94; N, 6·49. $C_{11}H_{15}NS_2$ requires: C, 58·65; H, 6·71; N, 6·22%).

Acknowledgement—The authors wish to thank Dr. I. Saito for his helpful discussion.

REFERENCES

[1] I. Saito, M. Yamane, H. Shimazu, T. Matsuura and H. J. Cahnmann, to be published.
[2] T. Matsuura and Y. Ito, *Chem. Comm.* 896 (1972); *Symposium on Photochemistry*, Osaka (1972).
[3a] A. Lablache-Combier and M.-A. Remy, *Bull. Soc. Chim. Fr.* 679 (1971); [b] A. Couture and A. Lablache-Combier, *Tetrahedron* **27**, 1059 (1971); *Chem. Comm.* 891 (1971); and references cited therein.
[4] E. E. van Tamelen and T. H. Whitesides, *J. Am. Chem. Soc.* **93**, 6129 (1971); and references cited therein.
[5a] H. Wynberg, R. M. Kellogg, H. van Driel and G. E. Beekhuis, *J. Am. Chem. Soc.* **89**, 3501 (1967); [b] M. Ohashi, A. Iio and T. Yonezawa, *Chem. Comm.* 1148 (1970); [c] M. Kojima and M. Maeda, *Ibid.* 386 (1970); [d] M. Maeda and M. Kojima, *Tetrahedron Letters* 3523 (1973) See also Ref. 3a.
[6a] D. W. Boykin, Jr. and R. E. Lutz, *J. Am. Chem. Soc.* **86**, 5046 (1964); [b] J. Wiemann, N. Thoai and F. Weisbuch, *Tetrahedron Letters*, 2983 (1965); *Bull. Soc. Chim. Fr.* 575 (1966); [c] D. E. McGreer, M. G. Vinje and R. S. McDaniel, *Can. J. Chem.* **43**, 1417 (1965); [d] H. Hiraoka and R. Srinivasan, *J. Am. Chem. Soc.* **90**, 2720 (1968; [e] A. G. Anastassiou and R. P. Cellura, *Chem. Comm.* 1522 (1969); [f] P. Scribe, D. Hourdin and J. Wiemann, *Compt Rend Acad. Sci.* **268C**, 178 (1969); [g] P. Scribe, D. Hourdin and J. Wiemann, *Tetrahedron Letters* 4375 (1970); [h] H. Wamhoff, *Chem. Ber.* **105**, 748 (1972); [i] P. Scribe, M. R. Monot and J. Wiemann, *Tetrahedron Letters* 5157 (1967); [j] S. J. Rhoads and C. F. Brandenburg, *J. Am. Chem. Soc.* **93**, 5805 (1971); [k] W. G. Dauben and G. W. Shaffer, *J. Org. Chem.* **34**, 2301 (1969).
[7] H. J. Rosenkrunz and H. Schmid, *Helv. Chim. Acta* **51**, 1628 (1968).
[8a] P. Scheiner, *J. Am. Chem. Soc.* **90**, 988 (1968); *Tetrahedron*, **24**, 2757 (1968); [b] B. Halton and A. D. Woolhouse, *Tetrahedron Letters* 4877 (1971); and references cited therein.
[9a] T. Matsuura and Y. Ito, *Tetrahedron Letters* 2283 (1973); [b] H. Giezendanner, M. Märky, B. Jackson, H.-J. Hansen and H. Schmid, *Helv. Chim. Acta* **55**, 745 (1972); [c] T. Mukai and H. Sukawa, *Tetrahedron Letters* 1835 (1973).
[10] For a review see T. Matsuura and Y. Ito, *Heterocycles*, to be published.
[11] T. Matsuura and Y. Ito, *Tetrahedron*, a subsequent paper.
[12] P. A. S. Smith and J. M. Sullivan, *J. Org. Chem.* **26**, 1132 (1961).
[13] Y. Iwakura, A. Nabeya and T. Nishiguchi, *Ibid.* **32**, 2362 (1967).
[14] H. Wenker, *J. Am. Chem. Soc.* **57**, 1079 (1935).
[15] J. R. Lowell and G. K. Helmkamp, *Ibid.* **88**, 768 (1966).
[16] R. Kuhn and F. Drawert, *Ann.* **590**, 55 (1954).
[17] For example, K. Linderstrøm-Lang and C. F. Jacobson, *J. Biol. Chem.* **137**, 443 (1941).
[18] *The Merck Index*, 18th Ed. p. 1014 (1968).
[19] O. L. Brady and G. V. Elsmil, *Analyst* **51**, 77 (1926).
[20] E. J. Stamhuis and W. Mass, *J. Org. Chem.* **30**, 2156 (1965).
[21] W. Walter and R. F. Becker, *Tetrahedron* **28**, 1705 (1972).
[22] K. Nakanishi, *Infrared Absorption Spectroscopy—Practical—*, Nankodo, Tokyo, p. 54 (1962).
[23] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.* **15**, 1087 (1961).