

Photochemical Reactions of Pyridine-4-thiones and Acridine-9-thiones with Alkenes

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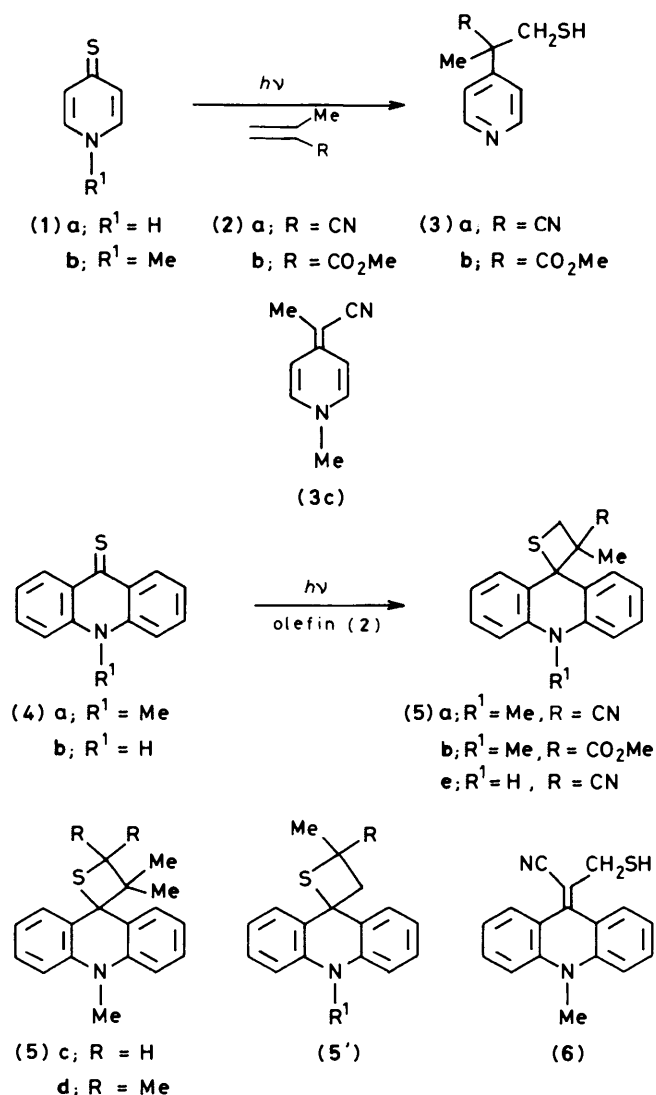
The photochemical reactions of thiones with alkenes have been examined. Irradiation of pyridine-4-thione (**1a**) in the presence of electron-poor alkenes (**2a,b**) gave 4-substituted pyridines (**3a,b**) via ring cleavage and aromatization of a thietane intermediate. The photocycloaddition reaction of acridine-9-thiones (**4**) to alkenes (**2**) proceeds regiospecifically to form the spirothietanes (**5**). Irradiation of semi-cyclic enamino thiones (**9**) in the presence of an alkene affords the 3-substituted cyclohex-2-en-1-one (**10**).

The photochemical reactions of thiocarbonyl compounds have received much attention, the majority of those reported involving thioketones which undergo cycloaddition with alkenes, allenes, imines, or alkynes, intramolecular or intermolecular hydrogen abstraction, and photo-oxidation.¹⁻⁵ However, few reports have dealt with the photochemical reactions involving the C=S group of thioamides⁶ and thioimides.⁷ Das and his co-workers have shown that indoline-2-thione undergoes photoaddition to methyl acrylate and vinyl ketones to give 2-substituted indoles.^{6c,d} Recently, we reported a synthetically useful method of carbon-carbon bond formation with quinoxaline-2-thiones,^{8a} pyridine-2-thiones,^{8b} and quinoxaline-2-thiones^{8b} through a photoinduced addition reaction. We now report the photochemical reactions of pyridine-4-thiones (**1**), acridine-9-thiones (**4**), and related compounds (**9**) and (**11**) with alkenes (**2**).

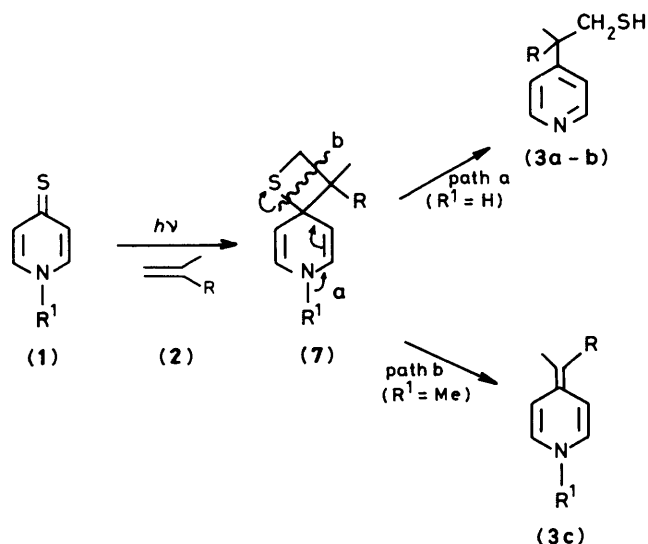
Results and Discussion

Irradiation of a solution of pyrimidine-4-thione (**1a**) in 1,2-dimethoxyethane (DME) in the presence of methacrylonitrile (**2a**) for 12 h with a high-pressure mercury lamp under an argon atmosphere at room temperature gave the 4-substituted pyridine (**3a**) (67%), the structure of which was elucidated on the basis of spectral data and elemental analysis. The microanalysis of (**3a**) indicated the product to be a 1:1 adduct of pyridine-4-thione (**1a**) and the alkene (**2a**) whilst its i.r. spectrum showed absorption characteristic of thiol and nitrile groups. The ¹H n.m.r. spectrum of (**3a**) indicated the presence of a mercapto-methyl group, a methyl group, and a pyridine ring. The ¹³C n.m.r. spectrum of (**3a**) showed peaks due to methyl, methylene, quaternary, and nitrile carbons in addition to pyridine ring signals. Irradiation of pyridine-4-thione (**1a**) in the presence of methyl methacrylate (**2b**) gave the 4-(2-mercaptoalkyl)pyridine (**3b**) (63%). The formation of the 4-substituted pyridines (**3a,b**) can be best explained through the intermediacy of an unstable spirothietane (**7**), which is formed initially by the photochemical [2 + 2] cycloaddition of thiocarbonyl to alkenes, and then undergoes ring cleavage with aromatization of the pyridine ring to yield the final products (**3a,b**) (path a in Scheme 1). On the other hand, irradiation of *N*-methylpyridine-4-thione (**1b**) with methacrylonitrile in DME under the same conditions as described above yielded *N*-methyl-4-(1-cyanoethylidene)pyridine (**3c**) (56%) probably by elimination of thioformaldehyde from the thietane intermediate (path b in Scheme 1). The intermediacy of the spirothietane could not be confirmed even by spectroscopic methods probably because of its fast cleavage to the final products.

Irradiation of a solution of *N*-methylacridine-9-thione (**4a**) in DME in the presence of methacrylonitrile (**2a**) for 4 h under the



same conditions as described above gave, as the sole product in almost quantitative yield, the spirothietane (**5a**), the structure of which was confirmed by spectroscopic properties and elemental analysis. The mass spectrum (chemical ionization) of the spirothietane (**5a**) showed a molecular ion peak at *m/z* 293 (*M*⁺ + 1) and displayed two characteristic fragments at *m/z* 247 (*M*⁺ + 1 - CH₂S) and 226 (*M*⁺ + 1 - C₄H₅N): this



cleavage pattern points to the orientation of addition as shown, rather than that of the alternative mode (**5'**; R = CN). The spirothietane (**5a**) when heated in benzene or toluene under reflux yielded *N*-methyl-9-(1-cyanoethylidene)acridine (**8**) and

Table 1. Yield of photoproducts (3), (5), (6), and (9)

Compd.	Solvent	Alkene (2)	Irr. time (h)	Yield (%) ^a	
				Product	Recovered
(1a)	DME ^b	(2a)	12	(3a) 67	15
(1a)	DME	(2b)	12	(3b) 63	10
(1b)	DME	(2a)	4	(3c) 56	38
(4a)	DME	(2a)	4	(5a) 99	~0
(4a)	CH ₂ Cl ₂	(2a)	4	(5a) 96	~0
(4a)	CH ₂ Cl ₂	(2b)	5	(5b) 81	trace
(4a)	CH ₂ Cl ₂	Isobutene (2c)	3	(5c) 67	25
(4a)	CH ₂ Cl ₂	Tetramethylethylene (2d)	10	(5d) 49	40
(4a)	CH ₂ Cl ₂	Acrylonitrile	4	(6) 99	~0
(4b)	DME	(2a)	2	(5e) 84	trace
(9a)	DME	(2b)	15	(10) 23	~0
(9b)	CH ₂ Cl ₂	(2b)	15	(10) 10	~0

^a Isolated yield. ^b 1,2-Dimethoxyethane.

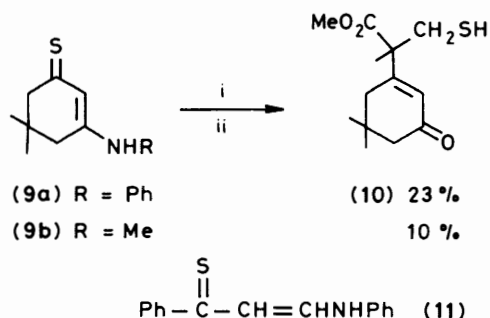
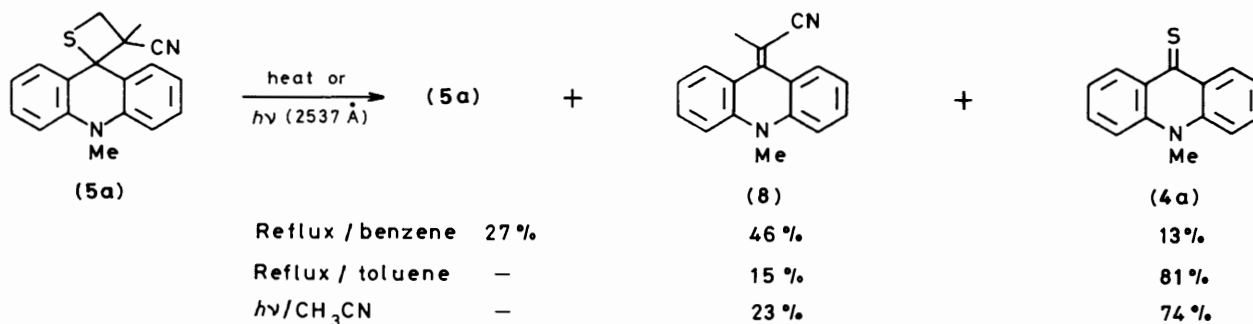
Table 2. Photoreaction of *N*-methylacridine-9-thione (4a) in the presence of methacrylonitrile (2a) under various conditions

Run	Solvent	(h)	Conditions	Yield (%) ^a	
				Thietane (5b)	Recovered
1	DME ^b	4	Ar, ^c > 300 nm	99	~0
2	CH ₂ Cl ₂	4	Ar, > 300 nm	96	~0
3	CH ₂ Cl ₂	4	Ar, 366 nm ^d	91	Trace
4	CH ₂ Cl ₂	4	Ar, > 400 nm ^e	90	Trace
5	CH ₂ Cl ₂	4	Ar, 366 nm thioxanthen-9-one ^f	ND ^g	ND
6	CH ₂ Cl ₂	4	Ar, 366 nm cyclo-octatetraene ^h	78	Trace
7	CH ₂ Cl ₂	4	Ar, 366 nm <i>trans</i> -stilbene ^h	88	Trace

^a Isolated yield. ^b 1,2-Dimethoxyethane. ^c Under an argon atmosphere. ^d A Pyrex glass filter and a methanol solution of naphthalene (5 g/l) were used to isolate the 366 nm region. ^e Halogen lamp was used. ^f A sensitizer absorbed more than 95% light. ^g Not detected. ^h 2 Molar equiv. quencher was used.

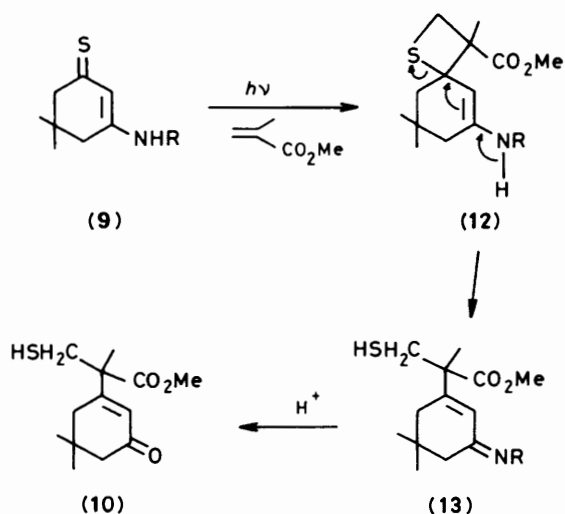
N-methylacridine-9-thione (**4a**), the thietane ring of (**5a**) being cleaved in two possible modes with loss of thioformaldehyde and methacrylonitrile respectively, the latter were not, however, identified. Irradiation of the spirothietane (**5a**) at 2 537 Å also gave both products, (**8**) and (**4a**). *N*-Methylacridine-9-thione (**4a**) reacted photochemically with alkenes such as methyl methacrylate (**2b**), isobutene (**2c**), and tetramethylethylene (**2d**) in an analogous fashion yielding the corresponding spirothietanes (**5b,d**) (49–81%) together with a second regioisomer which could not be identified. Since in the mass spectra of photoproducts (**5b,c**) the main fragmentations derived from the molecular ion led to peaks at masses corresponding to $M^+ + 1 - \text{CH}_2\text{S}$ and $M^+ + 1 - \text{C}_5\text{H}_8\text{O}_2$ (or $M^+ + 1 - \text{C}_4\text{H}_8$), the alternate structure (**5'**) must be ruled out. Thus the reaction of acridine-9-thione (**4a**) with alkenes (**2**) is regioselective, as seen in the reactions of thioamide with alkenes,^{6a} to give the spirothietanes (**5**) and in the photoaddition of analogous thioketones such as xanthen-9-thione and thioxanthen-9-thione with alkenes to give thietanes.⁹ The spirothietane (**5a**) was not detected when a solution of (**4a**) and methacrylonitrile (**2a**) in methylene dichloride was irradiated in the presence of thioxanthen-9-one as a triplet sensitizer, although many unidentified products were produced (Table 2, run 5). The formation of the spirothietane (**5a**) was not quenched by the triplet quenchers, cyclo-octatetraene¹⁰ or *trans*-stilbene (run 6 and 7). The spirothietane (**5a**) was also obtained when a mixture of (**4a**) and (**2a**) was irradiated with light of longer wavelength (> 400 nm) (run 4). These results suggest that the photoreaction of (**4a**) with alkenes proceeds from the $n-\pi^*$ singlet state of acridine-9-thione (**4a**). Irradiation of (**4a**) in the presence of an electron-rich alkene, eg. vinyl ethyl ether, or an electron-neutral alkene, eg. styrene, gave small amounts of several unseparable mixtures and the corresponding spirothietane could not be isolated. *N*-Methyl-9-(2-mercapto-1-cyanoethylidene)acridine (**6**) was obtained when a solution of (**4a**) in methylene dichloride was irradiated in a similar way in the presence of acrylonitrile. The formation of the product (**6**) can be rationalized by the ring cleavage of the thietane, which was formed by photochemical [2 + 2]cycloaddition of the C=S bond of (**4a**) and the alkene.

Acridine-9-thione (**4b**) also reacted photochemically with methacrylonitrile (**2a**) to yield the spirothietane (**5e**). As pyridine-4-thiones (**1**) and acridine-9-thiones (**4**) have a cyclic enamino thione chromophore, we investigated the photochemical reactions of semi-cyclic (**9**) and acyclic enamino thiones (**11**) with alkenes. Irradiation of a mixture of semi-cyclic enamino thione (**9**) and methyl methacrylate (**2b**) under the same conditions gave a complex mixture of products from which the 3-substituted cyclohex-2-en-1-one (**10**) was isolated in



Reagents: i, $h\nu/\text{CH}_2=\text{C}(\text{Me})\text{CO}_2\text{Me}$; ii, silica gel

low yield when the reaction mixture was purified through a silica gel column chromatography. The structure of (10) was elucidated on the basis of usual spectral and microanalytical data. The formation of (10) may be explained according to the mechanism shown in Scheme 2, which takes into account the



Scheme 2.

specific properties of the thiocarbonyl entity. The acyclic enamino thione (11), however, did not react with alkenes such as methyl methacrylate and methacrylonitrile on irradiation and the starting enaminothione (11) was recovered quantitatively. The photoreactions reported here represent an efficient and novel method for preparing 4-substituted pyridines (3) and the spirothietanes of acridines (5).

Experimental

M.p.s and b.p.s were measured with a Yanaco micro melting point apparatus (MP-J3) and Buchi Kugelrohr distillation apparatus (KR-3), respectively and are uncorrected. I.r. spectra were recorded on a Hitachi 260-30 photospectrometer. ^1H and ^{13}C N.m.r. spectra were recorded on a JEOL FX 100 spectrometer (100 MHz) using CDCl_3 as solvent and tetramethylsilane as an internal standard. A Halös (Eikosha EHP-300 W) high-pressure mercury lamp was used as the irradiation source.

Starting Materials.—Pyridine-4-thiones (1),¹¹ acridine-9-thiones (4),¹² semi-cyclic (9),¹³ and acyclic enaminothiones (11)¹³ were prepared according to methods previously described in the literature.

General Procedure for the Photochemical Reactions of Pyridine-4-thiones (1), Acridine-9-thiones (4), Semi-cyclic (9), and Acyclic Enaminothiones (11) in the Presence of Alkenes (2).—A solution of the thione (1), (4), (9) or (11) (200 mg) and the alkene (2) (ca. 1 ml) in DME or methylene dichloride (70 ml) was irradiated in a Pyrex vessel under argon with a high-pressure mercury lamp (300 W) for 2–15 h until disappearance of the solution colour at room temperature. After removal of the solvent under reduced pressure, the residual oil was chromatographed on a silica gel column (Wakogel C-300 for flash chromatography) with methylene dichloride–ethyl acetate [4:1 for the thiones (1)] or benzene–ethyl acetate [50:1–9:1 for the thiones (4), (9), and (11)] as eluants to give the photoproducts (3), (5), (6), and (10) respectively.

4-(2-Mercaptoalkyl)pyridine (3a). B.p. 130 °C at 2 mmHg (Found: C, 60.65; H, 5.85; N, 15.65. $\text{C}_9\text{H}_{10}\text{N}_2\text{S}$ requires C, 60.65; H, 5.65; N, 15.7%); ν_{max} (film) 2555 (SH) and 2225 cm^{-1} (CN); δ_{H} 1.64 (1 H, t, J 9.3 Hz, SH), 1.83 (3 H, s, Me), 3.02 (2 H, d, J 9.3 Hz, CH_2), 7.35–7.43 (2 H, m), and 8.64–8.71 (2 H, m) (pyridine ring H); δ_{C} 25.2 (q, Me), 35.3 (t, CH_2), 45.3 (s, quaternary C), 120.9 (s, CN), 120.9 (d), 147.4 (s), and 150.6 (d) (pyridine ring C).

4-(2-Mercaptoalkyl)pyridine (3b). B.p. 125 °C at 2 mmHg (Found: C, 56.85; H, 6.3; N, 6.45. $\text{C}_{10}\text{H}_{13}\text{NO}_2\text{S}$ requires C, 56.85; H, 6.2; N, 6.6%); ν_{max} (film) 2555 (SH), 1720 (CO_2), 1230, and 1195 cm^{-1} (CO_2); δ_{H} 1.42 (1 H, t, J 8.8 Hz, SH), 1.69 (3 H, s, Me), 2.93 (1 H, A of ABX, J 8.8, 13.6 Hz) and 3.20 (1 H, B of ABX, J 8.8, 13.6 Hz) (CH_2), 3.71 (3 H, s, OMe), 7.19–7.26 (2 H, m), and 8.54–8.61 (2 H, m) (pyridine ring H); δ_{C} 21.0 (q, Me), 33.6 (t, CH_2), 52.0 (s, quaternary C), 52.5 (q, OMe), 123.1 (d), 150.0 (d), 150.5 (s) (pyridine ring C), and 173.7 (s, CO_2).

4-(1-Cyanoethylidene)-N-methylpyridine (3c). M.p. 124–125 °C (Found: C, 73.8; H, 6.9; N, 19.1. $\text{C}_9\text{H}_{10}\text{N}_2$ requires C, 73.95; H, 6.9; N, 19.15%); ν_{max} (KBr) 2170 (CN) and 1660 cm^{-1} (C=C); δ_{H} 1.69 (3 H, s, Me), 3.34 (3 H, s, NMe), 5.87 (1 H, dd, J 2.9, 8.4 Hz) and 6.27–6.62 (3 H, m) (pyridine ring H); δ_{C} 13.5 (q,

Me), 42.1 (q, NMe), 70.2 [s, C=C(CN)], 107.5 (d), 112.0 (d), (pyridine ring C) 125.1 (s, CN), 134.0 (d), 135.0 (d) (pyridine ring C), and 145.5 [s, C=C(CN)Me]; m/z 146 (M^+).

Spiro-thietane (5a). M.p. 132 °C (decomp.) (Found: C, 73.65; H, 5.55; N, 9.9. $C_{18}H_{16}N_2S$ requires C, 73.95; H, 5.5; N, 9.6%); ν_{\max} (KBr) 2 230 cm^{-1} (CN); δ_H 1.08 (3 H, s, Me), 2.68 (1 H, d, J 9.3 Hz), and 3.51 (1 H, d, J 9.3 Hz) (CH_2), 3.42 (3 H, s, NMe), 6.93—7.50 (6 H, m), 7.93 (1 H, dd, J 1.9, 7.3 Hz), and 8.41 (1 H, dd, J 1.9, 7.3 Hz) (ArH); δ_C 22.8 (q, Me), 30.4 (t, CH_2), 33.9 (q, NMe), 49.3 (s) and 59.2 (s) (quaternary C), 121.1 (s, CN), 112.0 (d), 112.8 (d), 120.7 (d), 121.4 (d), 122.5 (s), 124.7 (s), 127.2 (d), 128.6 (d), 128.9 (d), 142.0 (s), and 142.1 (s) (ArC); m/z (chemical ionization) 293 ($M^+ + 1$), 247 ($M^+ + 1 - CH_2S$), and 226 ($M^+ + 1 - C_4H_5N$, 100%).

Spiro-thietane (5b). M.p. 132—133 °C (Found: C, 70.15; H, 5.95; N, 4.3. $C_{19}H_{19}NO_2S$ requires C, 70.1; H, 5.9; N, 4.3%); ν_{\max} (KBr) 1 730 (CO_2), 1 210 and 1 185 cm^{-1} (CO_2); δ_H 0.94 (3 H, s, Me), 2.53 (1 H, d, J 9.3 Hz) and 3.81 (1 H, d, J 9.3 Hz) (CH_2), 3.03 (3 H, s, NMe), 3.36 (3 H, s, OMe), 6.81—7.39 (6 H, m), and 8.19—8.39 (2 H, m), (ArH); δ_C 22.1 (q, Me), 27.5 (t, CH_2), 33.5 (q, NMe), 51.4 (q, OMe), 58.9 (s) and 62.4 (s) (quaternary C), 111.6 (d), 112.0 (d), 120.3 (d), 128.1 (d), 128.2 (d), 128.8 (d), 130.3 (d), 141.7 (s), 142.0 (s) (ArC), and 173.2 (CO_2); m/z (chemical ionization) 326 ($M^+ + 1$), 280 ($M^+ + 1 - CH_2S$), and 226 ($M^+ + 1 - C_3H_8O_2$, 100%).

Spiro-thietane (5c). M.p. 128—130 °C (Found: C, 76.85; H, 6.85; N, 4.9. $C_{18}H_{19}NS$ requires C, 76.8; H, 6.8; N, 4.95%); ν_{\max} (KBr) 1 590, 1 460, and 755 cm^{-1} ; δ_H 0.66 (6 H, s, Me), 2.69 (2 H, s, CH_2), 3.35 (3 H, s, NMe), 6.86—7.38 (6 H, m), and 8.23 (2 H, dd, J 2.0, 7.8 Hz), (ArH); δ_C 26.9 (q, Me), 33.1 (q, NMe), 33.3 (t, CH_2), 52.2 (s) and 60.9 (s) (quaternary C), 111.6 (d), 120.6 (d), 126.8 (s), 127.3 (d), 128.6 (d), and 142.3 (s) (ArC); m/z (chemical ionization) 282 ($M^+ + 1$), 235 ($M^+ + 1 - CH_2S$), and 225 ($M^+ + 1 - C_4H_8$, 100%).

Spiro-thietane (5d). M.p. 186—188 °C (Found: C, 77.4; H, 7.45; N, 4.45. $C_{20}H_{23}NS$ requires C, 77.6; H, 7.5; N, 4.5%); ν_{\max} (KBr) 1 590, 1 460, and 755 cm^{-1} ; δ_H 0.58 (6 H, s, Me), 1.41 (6 H, s, Me), 3.35 (3 H, s, NMe), 6.86—7.35 (6 H, m), and 8.23 (1 H, dd, J 2.0, 7.3 Hz), (ArH); δ_C 24.0 (q, Me), 29.0 (q, Me), 33.0 (q, NMe), 46.4 (s), 54.6 (s), and 56.7 (s) (quaternary C), 111.3 (d), 120.4 (d), 126.9 (d), 127.9 (s), 128.7 (d), and 143.3 (s) (ArC).

Spiro-thietane (5e). M.p. 195 °C (decomp.) (Found: C, 73.4; H, 5.05; N, 10.1. $C_{17}H_{14}N_2S$ requires C, 73.35; H, 5.05; N, 10.05%); ν_{\max} (KBr) 3 350 (NH) and 2 230 cm^{-1} (CN); δ_H 1.09 (3 H, s, Me), 2.87 (1 H, d, J 9.3 Hz) and 3.53 (1 H, d, J 9.3 Hz) (CH_2), 6.53 (1 H, br s, NH), 6.76—7.35 (6 H, m), 8.03 (1 H, dd, J 1.5, 7.8 Hz), and 8.41 (1 H, dd, J 1.5, 7.8 Hz) (ArH); δ_C 23.0 (q, Me), 30.2 (t, CH_2), 51.5 (s) and 58.1 (s) (quaternary C), 121.1 (s, CN), 113.8 (d), 114.1 (d), 120.9 (d), 121.6 (d), 126.9 (s), 128.5 (d), 128.9 (d), 129.0 (d), 129.9 (d), 130.3 (s), 139.0 (s), and 139.6 (d) (ArC).

N-Methyl-9-(2-mercapto-1-cyanoethylidene)acridine (6). M.p. 154—155 °C (Found: C, 73.4; H, 4.9; N, 9.75. $C_{17}H_{14}N_2S$ requires C, 73.35; H, 5.05; N, 10.05%); ν_{\max} (KBr) 2 540 (SH) and 2 195 cm^{-1} (CN); δ_H 2.17 (1 H, t, J 7.3 Hz, SH), 3.55 (3 H, s, NMe), 3.64 (2 H, d, J 7.3 Hz, CH_2), 7.04—7.67 (7 H, m), and 8.15 (1 H, d, J 1.5, 8.3 Hz) (ArH); δ_C 27.1 (t, CH_2), 33.8 (q, NMe), 103.8 [s, C=C(CN)], 112.6 (d), 113.1 (d) (ArC), 119.8 (s, CN), 120.6 (s), 120.6 (d), 121.1 (d), 121.4 (s), 126.6 (d), 127.3 (d), 130.2 (d), 140.8 (s), 141.7 (s), (ArC), and 144.4 [s, C=C(CN)].

9-(1-Cyanoethylidene)-N-methylacridine (8). M.p. 173.5—174.5 °C (Found: C, 82.55; H, 5.7; N, 11.05. $C_{17}H_{14}N_2$ requires C, 82.9; H, 5.7; N, 11.35%); ν_{\max} (KBr) 2 185 cm^{-1} (CN); δ_H 2.24 (3 H, s, Me), 3.47 (3 H, s, NMe), 6.97—7.48 (7 H, m), and 8.10 (1 H, dd, J 1.5, 7.8 Hz) (ArH); δ_C 19.8 (q, Me), 33.6 (q, NMe), 98.8 [s, C=C(CN)Me], 112.4 (d), 112.7 (d), 119.8 (d), 120.8 (d) (ArC), 122.3 (s, CN), 122.5 (s), 126.6 (d), 129.6 (d), 140.8 (s), 141.9 (s) (ArC), and 144.2 [s, C=C(CN)Me].

3-(2-Mercaptoalkyl)cyclohex-2-enone (10). B.p. 145 °C at 2 mmHg (Found: C, 61.1; H, 7.85. $C_{13}H_{20}O_3S$ requires C, 60.9; H, 7.85%); ν_{\max} (film) 1 725 (CO_2), 1 665 (CO), 1 620 (C=C), 1 230, and 1 100 (CO_2); δ_H 1.00 (3 H, s, Me), 1.03 (3 H, s, Me), 1.39 (1 H, t, J 9.3 Hz, SH), 1.46 (3 H, s, Me), 2.11 (2 H, br s, CH_2), 2.25 (2 H, br s, CH_2), 2.80 (1 H, A of ABX, J 9.3, 13.7 Hz), 3.06 (1 H, B of ABX, J 9.3, 13.7 Hz) (CH_2), 3.27 (3 H, s, OMe), and 5.98 (1 H, br s, C=CH); δ_C 19.8 (q, Me), 27.5 (q, Me), 28.4 (q, Me), 30.7 (t, CH_2), 33.8 (s, quaternary C), 40.9 (t, CH_2), 51.0 (t, CH_2), 52.4 (q, OMe), 53.9 (s, quaternary C), 125.6 (d) and 160.5 (s) (olefinic C), 173.3 (s, CO_2), and 199.4 (CO).

Thermal Reaction of the Spiro-thietane (5a).—A solution of (5a) (200 mg) in benzene or toluene (50 ml) was refluxed under argon for 5 h. After removal of the solvent under reduced pressure, the residual oil was chromatographed on a silica gel column with benzene–ethyl acetate (19:1) to yield (8) and (4a).

Photolysis of the Spiro-thietane (5a).—A solution of (5a) (100 mg) in acetonitrile (50 ml) was irradiated through a quartz filter with a low-pressure mercury lamp under argon at room temperature for 4 h. Work-up as above gave (8) and (4a).

References

- J. D. Coyle, *Chem. Soc. Rev.*, 1975, **4**, 523.
- P. de Mayo, *Acc. Chem. Res.*, 1976, **9**, 52.
- A. Ohno, *Organic Chemistry of Sulfur*, ed. S. Oae, Plenum Press, New York, 1977, p. 189; *Int. J. Sulfur Chem.*, Part B, 1971, **6**, 183.
- N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth, *Chem. Rev.*, 1978, **78**, 125.
- J. D. Coyle, *Tetrahedron*, 1985, **41**, 5395.
- (a) J. L. Fourrey, P. Jouin, and J. Moron, *Tetrahedron Lett.*, 1974, 3005; (b) P. Jouin and J. L. Fourrey, *ibid.*, 1975, 1329 and references cited therein; (c) C. Marazano, J. L. Fourrey, and B. C. Das, *J. Chem. Soc., Chem. Commun.*, 1977, 742; (d) B. C. Das, J. L. Fourrey, C. Marazano, A. Merrien, and J. Polonsky, *J. Chem. Res.*, 1978, (S), 370; (e) R. Paramasivam, R. Palaniappan, and V. T. Pamakrishnan, *J. Chem. Soc., Chem. Commun.*, 1979, 260; (f) P. de Mayo, L. K. Sydnes, and G. Wenska, *J. Org. Chem.*, 1980, **45**, 1549; (g) A. Couture, R. Dubiez, and A. Lablanche-Comber, *ibid.*, 1984, **49**, 714; (h) M. Machida, K. Oda, and Y. Kanaoka, *Tetrahedron Lett.*, 1984, **25**, 409.
- (a) T. Yonezawa, M. Matsumoto, Y. Matsuura, and H. Kato, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2323; (b) H. Gotthardt, S. Nieberl, and J. Donecke, *Liebigs Ann. Chem.*, 1980, 873 and references cited therein; (c) H. Aoyama, M. Sakamoto, and Y. Omote, *Chem. Lett.*, 1983, 1397; (d) J. D. Coyle and P. A. Rapley, *Tetrahedron Lett.*, 1984, **25**, 2247; (e) M. Sakamoto, H. Aoyama, and Y. Omote, *J. Org. Chem.*, 1984, **49**, 1837; (f) J. D. Coyle, P. A. Rapley, J. Kamphus, and H. J. T. Bos, *Tetrahedron Lett.*, 1985, **26**, 2249; (g) M. Machida, K. Oda, E. Yoshioka, and Y. Kanaoka, *J. Org. Chem.*, 1985, **50**, 1681 and references cited therein; (h) J. D. Coyle and P. A. Rapley, *J. Photochem.*, 1985, **31**, 387.
- (a) T. Nishio and Y. Omote, *Heterocycles*, 1985, **23**, 29; (b) *Synthesis*, 1986, 54.
- H. Gotthardt, *Chem. Ber.*, 1972, **105**, 2008; 1974, **107**, 1856; H. Gotthardt and S. Nieberl, *Tetrahedron Lett.*, 1976, 3999; H. Gotthardt and W. Lernz, *ibid.*, 1979, 2879.
- C. C. Liao and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 1971, 1525.
- S. Shiebe, B. S. Pederson, and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 229; R. A. Jones and A. R. Katritzky, *J. Chem. Soc.*, 1958, 3610.
- K. A. Jorgenson, M. T. M. El-Wassimy, and S. O. Lawesson, *Synthesis*, 1983, 373.
- W. Walter and T. Proll, *Synthesis*, 1979, 941.