Sulfurization of Azines; Part IX. (1-Chloroalkylthio)-azines[1]

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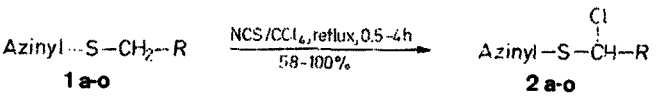
Chlorination of 2-, 3-, or 4-alkylthioquinolines (or -pyridines) with *N*-chlorosuccinimide or sulfuryl chloride affords 2-, 3-, or 4-(1-chloroalkylthio)-quinolines (or -pyridines), respectively, which in the case of ethyl or propyl compounds can be dehydrochlorinated to 1-alkenylthio derivatives. 4-Chloro-3-(1-chloroalkylthio)-quinolines react with thiourea to give 2-alkyl-1,3-dithiolo[4,5-*c*]quinolines.

Several papers deal with the halogenation of alkylthioazines, e.g., the preparation of 5-bromo-8-alkylthioquinolines via bromination of 8-alkylthioquinolines[2], or the formation of 4-chloroquinolines by "wet" chlorination of 4-benzylthio-quinolines[3,4]. However, there are no reports concerning preparation and properties of (1-chloroalkylthio)-azines.

(1-Chloroalkylthio)-quinolines (**2**) can be obtained by chlorination of the previously prepared 2-,3-, and 4-methylthioquinolines[5] and 4-chloro-3-alkylthioquinolines[6] (Schemes **A** and **B**). Taking into account the well estabilished reactivity of 1-chloroalkylthio compounds[7], an extension of the synthetic applicability of quinoline sulfurization products (converted into *S*-alkyl derivatives) is thus apparent.

In order to obtain (1-chloroalkylthio)-azines **2**, *N*-chlorosuccinimide, *N*-bromosuccinimide, sulfuryl chloride, and



1 a-o **2 a-o**

Azinyl = 2-, 3-, 4-pyridinyl
2-, 3-, 4-quinolinyl
4-chloro-3-quinolinyl
1-isoquinolinyl
R = H, CH_3, C_2H_5

Scheme A

Table 1. α-Chlorination of (Alkylthio)-azines **1** and of Methyl Phenyl Sulfide, and Attempted Bromination

Substrate **1**			Halogenating Agent (Method)	Reaction Time [h]	Product	Conversion of **1** [%][a]	Yield of **2** [%]	m.p. [°C]	Molecular Formula[b]
Azinyl Group		R							
1a	2-pyridinyl	H	NCS (A)	0.75	**2a**	96	90[d]	oil	C_6H_6ClNS (159.6)
1b	3-pyridinyl	H	NCS (A)	1	**2b**	58	50[d]	oil	C_6H_6ClNS (159.6)
1c	4-pyridinyl	H	NCS (A)	1	**2c**	17	7	oil	C_6H_6ClNS (159.6)
1d	4-pyridinyl	CH_3	NCS (A)	1	**2d**	85	72[d]	oil	C_7H_8ClNS (173.6)
1e	2-quinolinyl	H	NCS (A)	1	**2e**	94	89[d]	52–55	$C_{10}H_8ClNS$ (209.7)
			SO_2Cl_2 (B)	3	**2e**	25	18[c]		
			NBS (A)	5	[e]	6	6[c]		
1f	2-quinolinyl	CH_3	NCS (A)	1	**2f**	100	100	oil	$C_{11}H_{10}ClNS$ (223.7)
			SO_2Cl_2 (B)	3	**2f**	29	22[c]		
			SO_2Cl_2 (B)	24	**2f**	100	91[c]		
			SO_2Cl_2 (B)[g]	2.5	**2f**[f]	100	80[c]		
			$SOCl_2$[g]	10	[h]	70	31[c]		
1g	3-quinolinyl	H	NCS (A)	1	**2g**	65	58[d]	oil	$C_{10}H_8ClNS$ (209.7)
1h	3-quinolinyl	CH_3	NCS (A)	1	**2h**	100	100	oil	$C_{11}H_{10}ClNS$ (223.7)
1i	4-quinolinyl	H	NCS (A)	0.5	**2i**	14	6	oil	$C_{10}H_8ClNS$ (209.7)
1j	4-quinolinyl	CH_3	NCS (A)	1	**2j**	90	80[d]	oil	$C_{11}H_{10}ClNS$ (223.7)
1k	4-chloro-3-quinolinyl	H	NCS (A)	1	**2k**	82	75[d]	82–85	$C_{10}H_7Cl_2NS$ (244.1)
			NBS (A)	3	[e]	~3	~3[c]		
			SO_2Cl_2 (B)	48	**2k**[f]	100	92[c]		
1l	4-chloro-3-quinolinyl	CH_3	NCS (A)	0.5	**2l**	100	100	oil	$C_{11}H_9Cl_2NS$ (258.2)
			SO_2Cl_2 (B)	24	**2l**[f]	56	49[c]		
			SO_2Cl_2 (B)	48	**2l**[f]	100	89[c]		
			$SOCl_2$[g]	18		0	0		
1m	4-chloro-3-quinolinyl	C_2H_5	NCS (A)	1	**2m**	100	100	oil	$C_{12}H_{11}Cl_2NS$ (272.2)
1n	8-quinolinyl	H	NCS (A)	0.5	**2n**	30	24[c]		
1o	1-isoquinolinyl	H	NCS (A)	1	**2o**	96	91[d]	oil	$C_{10}H_8ClNS$ (209.7)
	methoxybenzene (anisole)		NCS (A)	1	–	0			
	methyl phenyl sulfide (methylthiobenzene)		NCS (A)	1	[i]	87	74	b.p. 103–104°C/ 12 torr	Ref. 14. b.p. 98°C/12 torr

[a] The reaction mixture contained product **2** and unconverted substrate **1**. Conversion of **1** estimated by ^{1}H-NMR spectrometry.
[b] The microanalyses were in good agreement with the calculated values: C ±0.21, H ±0.12, N ±0.18, S ±0.20, Cl ±0.23.
[c] Yield of **2** formed in the chlorination reaction, estimated by ^{1}H-NMR spectrometry.
[d] Yield of isolated product **2** (preparative TLC on silica gel using 5:2 cyclohexane/ethyl acetate as eluant) based on amount of **1** reacted.
[e] This product was a bromo analog of compound **2e** or compound **2k**, respectively.
[f] The reaction mixture contained also 5–7% undefined compounds.
[g] The reaction was performed in boiling chloroform.
[h] The reaction mixture contained about equal amounts of substrate **1f**, product **2f**, vinyl derivative **3**, and some amounts of undefined compounds.
[i] Chloromethyl phenyl sulfide (chloromethylthiobenzene).

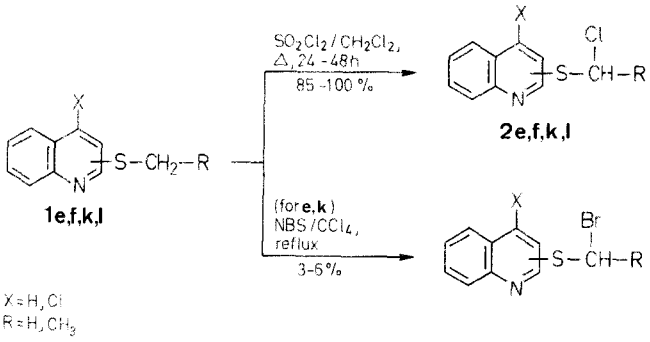
thionyl chloride were examined as halogenating agents for alkylthioazines. We found that the reaction of alkylthioazines (**1**) with a 5–10% molar excess of *N*-chlorosuccinimide (Scheme **A**) gives high yields of (1-chloroalkylthio)-azines **2**; it appears to be the most convenient method.

The reactions of 2-methylthio-, 2-ethylthio-, 4-chloro-3-methylthio-, and 4-chloro-3-ethylthioquinolines (**1e, f, k, l**) with sulfuryl chloride (Scheme **B**) are slower than those with *N*-chlorosuccinimide. The reaction products **2e, f, k, l** are sometimes accompanied by small amounts of undefined compounds.

Table 2. (1-Alkenylthio)-azines (**3**) and 1,3-Dithiolo[4,5-*c*]quinolines (**4**) Prepared

Substrate **2**			Product	Yield [%][a]	m.p. [°C] or b.p. [°C]/torr	Molecular Formula[b]	MS (15 eV)[c] *m/e* (M^+)
	Azinyl Group in **2** and **3**	R					
2d	4-pyridinyl	H	**3d**	80	oil	C_7H_7NS (137.2)	137 (100%)
2f	2-quinolinyl	H	**3f**	61	oil	$C_{11}H_9NS$ (187.3)	187 (41.2%)
2h	3-quinolinyl	H	**3h**	81	oil	$C_{11}H_9NS$ (187.3)	187 (100%)
2j	4-quinolinyl	H	**3j**	80	oil	$C_{11}H_9NS$ (187.3)	187 (100%)
2l	4-chloro-3-quinolinyl	H	**3l**	87	m.p. 70–72 b.p. 140–143/1	$C_{11}H_8ClNS$ (221.7)	221 (100%)
2m	4-chloro-3-quinolinyl	CH_3	**3m**	77	m.p. 65–67 b.p. 176–178/0.8	$C_{12}H_{10}ClNS$ (235.7)	235 (100%)
	Azinyl Group in **2**	R					
2k	3-quinolyl	H	**4a**	82	m.p. 101–102	$C_{10}H_7NS_2$ (205.1)	205 (100%)
2l	3-quinolyl	CH_3	**4b**	71	m.p. 81–83 b.p. 188–189/1	$C_{11}H_9NS_2$ (219.3)	219 (100%)
2m	3-quinolyl	C_2H_5	**4c**	64	b.p. 185–186/1	$C_{12}H_{11}NS_2$ (233.2)	233 (59%)

[a] Yield of isolated pure product.
[b] The microanalyses were in good agreement with the calculated values: C ±0.15, H ±0.13, N ±0.17, S ±0.17, Cl ±0.18.
[c] Recorded on a LKB 9000 mass spectrometer.
[d] The structure of compound **3f** was confirmed by its reaction with bromine[13].



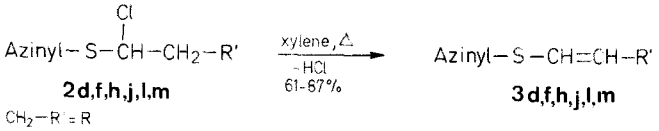
Scheme **B**

The chlorination of ethylthio and propylthio compounds **1f, h, l, m** with *N*-chlorosuccinimide (and in the case of compound **1f** also with sulfuryl chloride) proceeds cleanly without formation of any alkenylthioquinolines **3**; i.e., the HCl-elimination products of compounds **2**)[8].

4-Methylthiopyridine (**1c**) and 4-methylthioquinoline (**1i**) exhibited low reactivity toward *N*-chlorosuccinimide as compared to the 4-ethylthio compounds **1d** and **1j** and also to the 2- and 3-methylthio- and ethylthio derivatives **1a, b, e, f, g**.

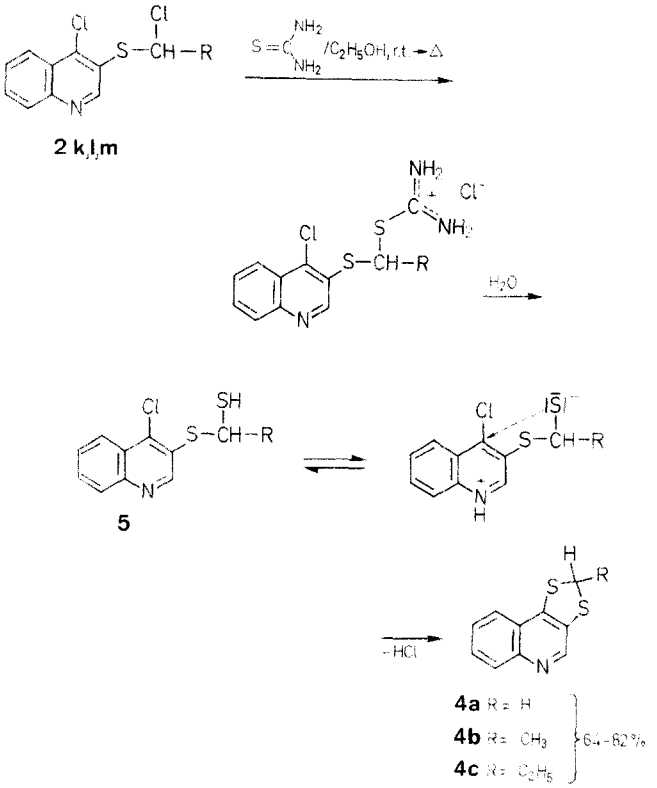
In contrast to the reactions with sulfuryl chloride and *N*-chlorosuccinimide, the reactions of alkylthioquinolines **1e** and **1k** with *N*-bromosuccinimide (Scheme **B**) or of compound **1e** with thionyl chloride are ineffective.

The (1-chloroalkylthio)-azines **2** can be thermally transformed into the 1-alkenylthio derivatives **3**:



Scheme **C**

The reaction of 4-chloro-3-(1-chloroalkylthio)-quinolines (**2k, l, m**) with thiourea produces 2-alkyl-1,3-dithiolo[4,5-*c*]quinolines (**4a, b, c**; Scheme **D**). These products are probably formed *via* chloro-monoisothiouronium salts which are hydrolyzed to give intermediate chloro-thiols (**5**). The transformation of chloro-thiols **5** into dithiols **4** corresponds to the well-known reaction of 4-chloroquinolines with mercaptans applied to the preparation of alkyl[9] or aryl[10,11] 4-quinolinyl sulfides. To explain the results of the reactions o 4-chloroquinolines with mercaptans, a process



Scheme **D**

Table 3. ^{1}H-NMR ($CDCl_3$) Data of Compounds **2**, **3**, **4**[a]

Compound	δ[ppm]
2a	5.18 (s, 2H, S—C$\underline{H}_2$Cl); 6.75–7.53 (m, 3H, 3-$\underline{H}$, 4-$\underline{H}$, 5-$\underline{H}$); 8.35–8.43 (m, 1H, 6-$\underline{H}$)
2b	4.78 (s, 2H, S—C$\underline{H}_2$Cl); 7.0–7.86 (m, 2H, 4-$\underline{H}$, 5-$\underline{H}$); 8.38–8.68 (m, 2H, 2-$\underline{H}$, 6-$\underline{H}$)
2c	4.78 (s, 2H, S—C$\underline{H}_2$Cl); 7.08–7.15 (m, 2H, 3-$\underline{H}$, 4-$\underline{H}$); 8.33–8.43 (m, 2H, 2-$\underline{H}$, 6-$\underline{H}$)
2d	1.77 (d, J = 7 Hz, 3H, CH—C$\underline{H}_3$); 5.83 [q, J = 7 Hz, 1H, S—C$\underline{H}$(Cl)—CH$_3$]; 6.78–6.91 (m, 2H, 3-$\underline{H}$, 5-$\underline{H}$); 8.11–8.23 (m, 2H, 2-$\underline{H}$, 6-$\underline{H}$)
2e	5.38 (s, 2H, S—C$\underline{H}_2$Cl); 7.03–8.0 (m, 6H$_{arom}$)
2f	1.75 (d, J = 7 Hz, 3H, CH—C$\underline{H}_3$); 6.37 [q, J = 7 Hz, 1H, S—C$\underline{H}$(Cl)—CH$_3$]; 7.0–8.02 (m, 6H$_{arom}$)
2g	4.77 (s, 2H, S—C$\underline{H}_2$Cl); 7.35–8.27 (m, 5H$_{arom}$); 8.85 (d, J = 1.8 Hz, 1H, 2-$\underline{H}$)
2h	1.78 (d, J = 7 Hz, 3H, CH—C$\underline{H}_3$); 5.37 [q, J = 7 Hz, 1H, S—C$\underline{H}$(Cl)—CH$_3$]; 7.3–8.32 (m, 5H$_{arom}$); 8.9 (d, J = 1.8 Hz, 1H, 2-$\underline{H}$)
2i	4.98 (s, 2H, S—C$\underline{H}_2$Cl); 7.08 (d, J = 4.2 Hz, 1H, 3-$\underline{H}$); 7.35–7.6 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 7.87–8.23 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 8.62 (d, J = 4.2 Hz, 1H, 2-$\underline{H}$)
2j	1.73 (d, J = 7 Hz, 3H, CH—C$\underline{H}_3$); 5.67 [q, J = 7 Hz, 1H, S—C$\underline{H}$(Cl)—CH$_3$]; 7.06 (d, J = 4.2 Hz, 1H, 3-$\underline{H}$); 7.32–7.57 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 7.84–8.21 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 8.6 (d, J = 4.2 Hz, 1H, 2-$\underline{H}$)
2k	4.92 (s, 2H, S—C$\underline{H}_2$Cl); 7.43–7.82 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 8.02–8.25 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 9.02 (s, 1H, 2-$\underline{H}$)
2l	1.77 (d, J = 7 Hz, 3H, CH—C$\underline{H}_3$); 5.45 [q, J = 7 Hz, 1H, S—C$\underline{H}$(Cl)—CH$_3$]; 7.43–7.87 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 8.0–8.28 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 9.03 (s, 1H, 2-$\underline{H}$)
2m	0.94 (t, J = 7 Hz, 3H), CH$_2$—C$\underline{H}_3$); 1.9 (m, 2H, CH—C$\underline{H}_2$—CH$_3$); 5.17 [t, J = 7 Hz, 1H, S—C$\underline{H}$(Cl)—CH$_2$CH$_3$]; 7.33–7.77 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 7.92–8.2 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 8.95 (s, 1H, 2-$\underline{H}$)
2n	5.24 (s, 2H, S—C$\underline{H}_2$Cl); 7.26–7.48 (m, 4H$_{arom}$); 8.04 (dd, J = 8 Hz, J = 1.7 Hz, 1H, 4-$\underline{H}$); 8.95 (dd, J = 4 Hz, J = 1.7 Hz, 1H, 2-$\underline{H}$)
2o	5.38 (s, 2H), S—C$\underline{H}_2$Cl); 7.27–7.72 (m, 4H$_{arom}$); 7.85–8.07 (m, 1H$_{arom}$); 8.27 (d, J = 6 Hz, 1H, 3-$\underline{H}$)
3d	5.11–5.4 (m, 2H, CH—C$\underline{H}_2$); 6.0–6.43 (m, 1H, S—C$\underline{H}$=CH$_2$); 6.67–6.8 (m, 2H, 3-$\underline{H}$, 5-$\underline{H}$); 8.0–8.12 (m, 2H, 2-$\underline{H}$, 6-$\underline{H}$)
3f	5.2–5.5 (m, 2H, CH=C$\underline{H}_2$); 6.76–7.9 (m, 7H, rest of protons)
3h	4.92–5.33 (m, 2H, CH=C$\underline{H}_2$); 6.05–6.5 (m, 1H, S—C$\underline{H}$=CH$_2$); 7.03–7.93 (m, 5H$_{arom}$); 8.7 (d, J = 1.8 Hz, 1H, 2-$\underline{H}$)
3j	5.3–5.6 (m, 2H, CH=C$\underline{H}_2$); 6.2–6.6 (m, 1H, S—C$\underline{H}$=CH$_2$); 7.03 (d, J = 4.2 Hz, 1H, 3-$\underline{H}$); 7.27–7.52 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 7.8–8.17 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 8.56 (d, J = 4.2 Hz, 1H, 2-$\underline{H}$)
3l	5.35–5.67 (m, 2H, CH=C$\underline{H}_2$); 6.32–6.75 (m, 1H), S—C$\underline{H}$=CH); 7.4–7.75 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 7.9–8.2 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 8.58 (s, 1H, 2-$\underline{H}$)
3m	1.64 (d, J = 5 Hz, 3H, =CH—C$\underline{H}_3$); 5.87–6.17 (m, 2H, C$\underline{H}$=C$\underline{H}$); 7.4–7.73 (m, 2H, 6-$\underline{H}$, 7-$\underline{H}$); 7.85–8.15 (m, 2H, 5-$\underline{H}$, 8-$\underline{H}$); 8.57 (s, 1H, 2-$\underline{H}$)
4a	4.7 (s, 2H, S—C$\underline{H}_2$—S); 7.45–7.7 (m, 3H, 7-$\underline{H}$, 8-$\underline{H}$, 9-$\underline{H}$); 7.96–8.08 (m, 1H, 6-$\underline{H}$); 8.63 (s, 1H, 4-$\underline{H}$)
4b	1.4 (d, J = 7 Hz, 3H, CH—C$\underline{H}_3$); 4.83 (q, J = 7 Hz, 1H, C$\underline{H}$—CH$_3$); 7.4–7.68 (m, 3H, 7-$\underline{H}$, 8-$\underline{H}$, 9-$\underline{H}$); 7.9–8.04 (m, 1H, 6-$\underline{H}$); 8.61 (s, 1H, 4-$\underline{H}$)
4c	0.9 (t, J = 7 Hz, 3H, CH$_2$—C$\underline{H}_3$); 1.69 (m, 2H, CH—C$\underline{H}_2$—CH$_3$); 4.79 (t, J = 7 Hz, 1H, S—C$\underline{H}$—CH$_2$CH$_3$); 7.41–7.7 (m, 3H, 7-$\underline{H}$, 8-$\underline{H}$, 9-$\underline{H}$); 7.9–8.06 (m, 1H, 6-$\underline{H}$); 8.61 (s, 1H, 4-$\underline{H}$)

[a] The spectra were recorded on a Varian Anaspect EM 360 spectrometer at 60 MHz.

involving the formation of a 4-chloroquinolinium cation and a thiolate anion followed by nucleophilic displacement of the Cl-substituent by thiolate ion, has been proposed[11].

4-Chloro-3-alkylthioquinolines are purified as follows: a hot solution of the crude compound[6] in tetrachloromethane is filtered; the filtrate is concentrated, and distilled under reduced pressure: **1k**, b.p. 158–9°C/0.6 torr, m.p. 105–6°C (ethanol); **1l**, b.p. 160–2°C/0.6 torr, m.p. 59–61°C (methanol); **1m**, b.p. 169–170°C/1 torr, m.p. 42–44°C (methanol).

3-Alkylthioquinolines (1g, h)[12]:

Tin (1.79 g, 0.015 g-atom) and 20% hydrochloric acid (50 ml) are added to the 4-chloro-3-alkylthioquinoline (**1k** or **1l**; 10 mmol) and the mixture is stirred at 85–90°C for 24 h. After cooling to room temperature, tin chloride complex of 3-alkylthioquinoline is filtered off and alkalized with an excess of 10% sodium hydroxide solution. 3-Alkylthioquinoline is extracted with ether (3 × 15 ml). The extract is dried with sodium sulfate, and distilled under reduced pressure to give the product **1g, h**.

3-Methylthioquinoline (**1g**); yield: 1.3 g (74%); b.p. 131–133°C/0.8 torr; m.p. 30–32°C (pentane).

MS (15 eV): m/e = 175 (M^+, 100%).

^{1}H-NMR data in agreement with Ref.[5].

3-Ethylthioquinoline (**1h**); yield: 1.4 g (74%); b.p. 137–138°C/0.8 torr.

MS (15 eV): m/e = 189 (M^+, 100%).

^{1}H-NMR ($CDCl_3$): δ = 1.03 (t, 3H, J = 7 Hz, S—CH$_2$—C$\underline{H}_3$); 2.60 (q, 2H, J = 7 Hz, S—C$\underline{H}_2$—CH$_3$); 7.38–7.88 (m, 3H, 5-$\underline{H}$, 6-$\underline{H}$, 7-$\underline{H}$); 7.94–8.33 (m, 2H, 4-$\underline{H}$, 8-$\underline{H}$); 8.86 ppm (d, 1H, J = 1.7 Hz, 2-$\underline{H}$).

(1-Chloroalkylthio)-azines (2); General Procedures:

Method A, Chlorination of Alkylthioazines **1** with *N*-Chlorosuccinimide: A mixture of the alkylthioazine **1** (10 mmol), *N*-chlorosuccinimide (10.5–11 mmol), and anhydrous tetrachloromethane (50 ml) is irradiated with a 300 W lamp located at a distance of 10 cm. The mixture is boiled for 30–60 min with stirring, then allowed to cool to room temperature. Succinimide is filtered off and the filtrate is evaporated to dryness under reduced pressure. [For isolation of products **2c, i**, see below]. In order to remove the residual succinimides, a solution of the crude product in dichloromethane (80 ml) is filtered through a 3 cm layer of neutral aluminum oxide. The filtrate is concentrated in vacuum. The compounds **2** thus obtained are stable in the refrigerator (4°C) for a period of several days.

In the case of the chlorination of 4-methylthiopyridine (**1c**) and 4-methylthioquinoline (**1i**), the chlorination products **2** are isolated from the semi-solid mixture of succinimides and product **2** (remaining after decantation of the tetrachloromethane solution) by shaking with saturated sodium hydrogen carbonate solution (30 ml) and extraction with tetrachloromethane (2 × 20 ml). The extract is dried with sodium sulfate, filtered and concentrated in vacuum to give compound **2c** or **2i**.

Method B, Chlorination of Alkylthioazines **1** with Sulfuryl Chloride: A mixture of the alkylthioquinoline **1e, f, k, l** (10 mmol), freshly distilled sulfuryl chloride (2.70 g, 20 mmol), and dichloromethane (50 ml) is stirred and gently boiled for 24 h. After cooling to room temperature, the mixture is washed with aqueous 5% sodium hydrogen carbonate (30 ml). The organic layer is dried with sodium sulfate and the solvent is evaporated at water-bath temperature to give the product **2**.

(1-Alkenylthio)-azines (3); General Procedure:

Method A, in the Absence of Base: A solution of the (1-chloroalkylthio)-azine **2** (10 mmol) in xylene (50 ml) is gently boiled for 3 h and then cooled to room temperature and extracted with 5% hydrochloric acid (50 ml). The aqueous layer is neutralized with 5% sodium hydrogen carbonate solution and extracted with tetrachloromethane (2 × 20 ml). The extract is dried with sodium sulfate, filtered, and evaporated under reduced pressure to give the product **3**.

Method B, in the Presence of a Base: A solution of the (1-chloroalkylthio)-azine **2** (10 mmol) in xylene (50 ml) containing *N,N*-dimethylaniline (~ 1.9 ml, 15 mmol) is gently boiled for 3 h, and then cooled to room temperature. The solution is decanted from *N,N*-dimethylaniline hydrochloride, and distilled under reduced pressure; yield of products **3**: 61–87%.

1,3-Dithiolo[4,5-*c*]quinolines (4); General Procedure:
A mixture of the 4-chloro-3-(1-chloroalkylthio)-quinoline **2** (10 mmol), thiourea (0.761 g, 10 mmol), and anhydrous ethanol (50 ml) is stirred at room temperature to give a clear solution (~ 15 min), then kept at 50 °C for 1 h, and refluxed for 15 min. After cooling to room temperature, the mixture is poured into water (200 ml), made alkaline with aqueous 10% sodium hydroxide, and allowed to stand for 1 h. The product is extracted with tetrachloromethane (2 × 20 ml); the extract is dried with sodium sulfate, and concentrated under reduced pressure to give the product **4**.

Received: February 7, 1985
(Revised form: February 6, 1986)

[1] Part VIII: Maślankiewicz, A., Pluta, K., Szmielew, M., Kowalska, A. *Polish J. Chem.* **1984**, *58*, 925.
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