Reactions of Thionyl Chloride with *C*-Methyl Heterocycles. Part 2.[1] The Formation of [1,2]Dithiolo[3,4-*c*]quinolin-1-ones and Bis[dichloro(4-quinolyl)methyl]trisulphanes from 4-Methylquinolines

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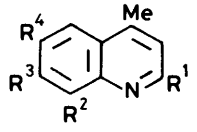
4-Methylquinolines (**1**) react with hot thionyl chloride to give either 4-chloro[1,2]dithiolo[3,4-*c*]-quinolin-1-ones (**2**) or bis[dichloro(4-quinolyl)methyl]trisulphanes (**18**). The mode of formation of these products is discussed and their reactions with various reagents are described.

In the preceding paper we described the transformation of $HetCH_3 \rightarrow HetCCl_2SCl$ for 2-methylquinolines using thionyl chloride.[1] We now describe products of reactions of 4-methylquinolines (**1**) with thionyl chloride and show that these have structures which are novel and different to those obtained from the isomers.

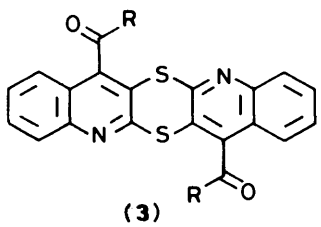
Reaction of 4-methylquinoline (**1a**) with an excess of hot thionyl chloride gave an amorphous solid which was purified by chromatography giving 4-chloro[1,2]dithiolo[3,4-*c*]quinolin-1-one (**2**; R = H) as a yellow crystalline solid (10%). No other product was isolated from the reaction mixture. Using 4,8-dimethylquinoline (**1b**) an analogous product (**2**; R = Me) was obtained. The structure of the novel heterocyclic system (**2**; R = H) is supported by spectroscopic and chemical evidence. A carbonyl absorption at 1 640 cm^{-1} in the i.r. spectrum is consistent with the presence of a 1,2-dithiol-3-one fragment. The ^1H n.m.r. spectrum is associated with four aromatic protons. Particularly significant is the chemical shift of the proton at the 9-position (δ 9.12—9.18) which may be attributed to the negative anisotropic shielding effect of the neighbouring carbonyl group. A molecular ion (*m/z* 253) is clearly observed in the mass spectrum.



(**1**)

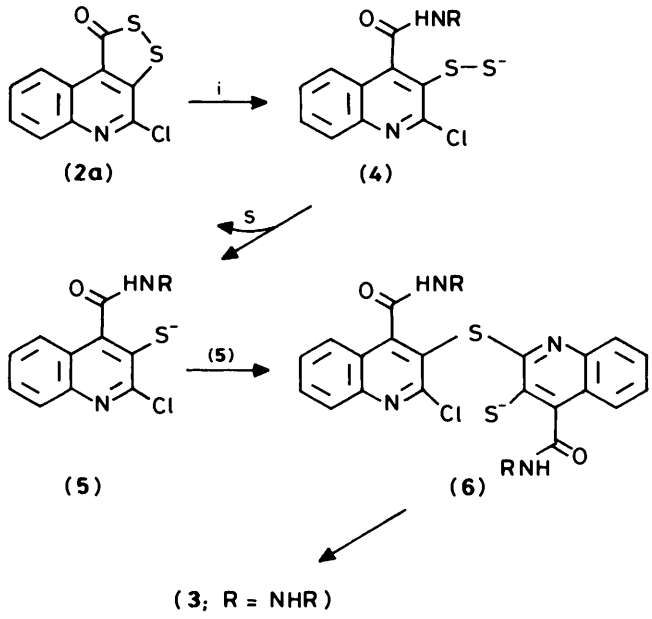
(**2**)

	R^1	R^2	R^3	R^4
a;	H	H	H	H
b;	H	Me	H	H
c,	Cl	H	H	H
d;	Cl	H	Me	H
e;	H	NO_2	H	H
f;	H	H	H	OMe



(**3**)

Reaction of the [1,2]dithiolo[3,4-*c*]quinolin-1-one (**2**; R = H) with butylamine in hot ethanol gave [1,4]dithiino[2,3-*b*:5,6-*b'*]diquinoline (**3**; R = NHBu) (28%). The corresponding diamide (**3**; R = $NHCH_2Ph$) was obtained using benzylamine but diethylamine in ethanol solution gave only the diester (**3**; R = OEt). The formation of these products (**3**) can be rationalised by initial nucleophilic attack on the carbonyl group followed by ring opening to a dithiane anion (**4**) (Scheme 1). Loss of sulphur and condensation of two molecules of the

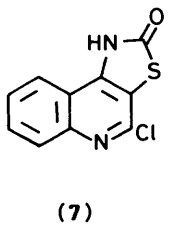


(**2a**) (**4**) (**5**) (**6**) (**3**; R = NHR)

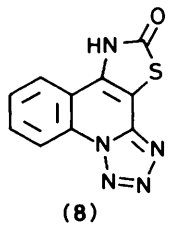
Scheme 1. *Reagents:* i, RNH_2

resulting thiolate (**5**) gives the sulphide (**6**) which subsequently cyclises to the product (**3**) (Scheme 1).

When compound (**2**; R = H) was treated with sodium azide two products were obtained which were identified as the thiazolo[5,4-*c*]quinolin-2(1*H*)ones (**7**) (9%) and (**8**) (25%). The formation of the minor product (**7**) can be rationalised in terms



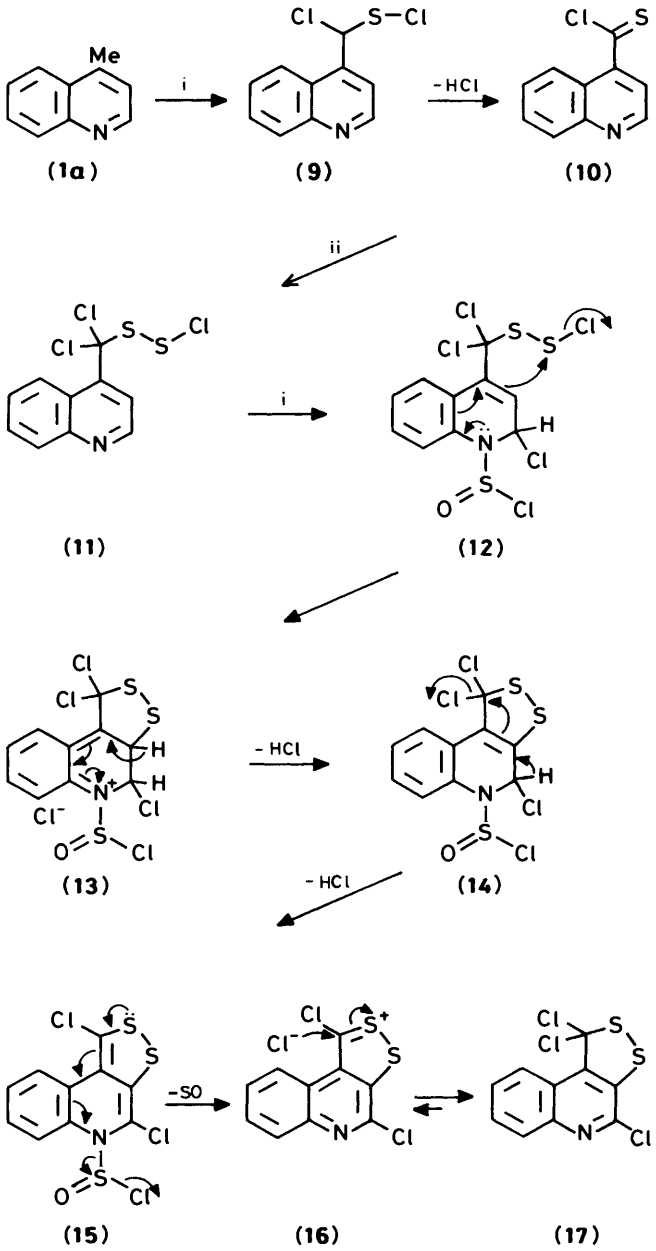
(**7**)



(**8**)

of initial ring opening and loss of sulphur (*cf.* Scheme 1) giving an acyl azide which undergoes a Curtius rearrangement to the isocyanate and subsequent cyclisation to compound (**7**). Displacement of the 4-chloro substituent by azide anion followed by cyclisation then leads to the major product (**8**).

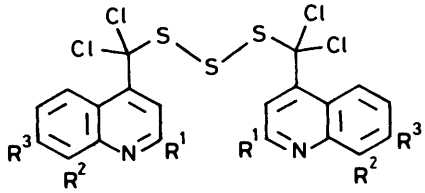
These chemical and spectroscopic properties support the assignment of the [1,2]dithiolo[3,4-*c*]quinolin-1-one structures (**2**). We believe that the actual product of reaction of 4-methylquinoline (**1a**) with thionyl chloride is the dichloro derivative (**17**) which is then hydrolysed to the observed product (**2**; R = H) during chromatographic work-up. A mechanism of formation of the product (**17**) is proposed in Scheme 2. The



Scheme 2. *Reagents:* i, $SOCl_2$; ii, SCl_2

reaction of the methyl substituent with thionyl chloride giving an intermediate chloromethanesulphenyl chloride (**9**) is well established [2] and the mechanism is analogous to that proposed for 2-methyl derivatives in the preceding paper.[1] Thermal decomposition of thionyl chloride gives chlorine, sulphur dioxide, and sulphur monochloride which appears to be derived by disproportionation of initially formed sulphur dichloride ($4SOCl_2 \longrightarrow 2Cl_2 + 2SO_2 + 2SCl_2 \longrightarrow 3Cl_2 + 2SO_2 + S_2Cl_2$).[3] Sulphur dichloride (SCl_2) is therefore a significant component of hot thionyl chloride. We propose that the intermediate (**9**) gives the thioacyl chloride (**10**) which is rapidly trapped by SCl_2 giving the dithiane (**11**). Addition of thionyl chloride to the quinoline 1,2-bond generates the intermediate (**12**) which cyclises forming the dithiole ring (**12**) ⟶ (**13**). The intermediate (**13**) may then undergo loss of two molecules of HCl (**13**) ⟶ (**14**) ⟶ (**15**) followed by formal loss of sulphur monoxide (SO) to give the product (**17**), possibly via the ionic isomer (**16**).

An important feature of the formation of the products (**2**) is chlorination of the 2-position of the quinoline ring. When a chlorine atom was introduced into the 2-position of the starting material then a different type of product was obtained. Thus treatment of 2-chloro-4-methylquinoline (**1c**) with hot thionyl chloride gave the bis[dichloro(4-quinolyl)methyl]trisulphane



	R^1	R^2	R^3
(**18**) **a**;	Cl	H	H
b;	Cl	H	Me
c;	H	NO_2	H

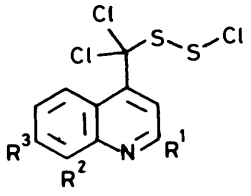
(**18a**) (yield 46%). This structure (**18a**) was firmly supported by elemental analysis ($C_{20}H_{10}Cl_6N_2S_3$) and by ^1H n.m.r. spectroscopy which showed a singlet at δ 8.0, associated with the protons at positions 3 and 3′, together with multiplets characteristic of the remainder of the aromatic protons. The mass spectrum showed a molecular ion, *m/z* 587.

Similar products (**18b**) and (**18c**) were obtained using 2-chloro-4,7-dimethylquinoline (**1d**) and 4-methyl-8-nitroquinoline (**1e**). In neither case was there any evidence of formation of dithiolo[3,4-*c*]quinolin-1-ones. No reaction was observed with 6-methoxy-4-methylquinoline (**1f**). The mechanism of formation of the trisulphanes (**18**) probably follows the same initial pathway as that proposed for dithiolo[3,4-*c*]quinolin-1-one (**2**) formation (Scheme 2). Instead of intramolecular cyclisation (**12**) ⟶ (**13**) (Scheme 2), the chlorodithianes (**20**) then add to a molecule of the thioacyl presursor (**19**) giving the observed trisulphane (**19**) + (**20**) ⟶ (**18**). With data available on only a limited number of 4-methylquinolines (**1**) it is not possible to recognise the structural features which control the preferred formation of products (**2**) or (**18**). The observed substituent effects of compounds (**1d**) and (**1e**) are, however, consistent with the proposed mechanism of formation of derivatives (**2**) (Scheme 2).

The formation of the heterocyclic trisulphane derivatives (**18**) is analogous to the previously described formation of tetrachlorotrisulphanes when pinacolone or acetophenone are treated with thionyl chloride.[4]

The reactions of the trisulphanes (**18**) with amines and amidines has been studied. Treatment of compound (**18a**) with diethylamine gave the thioamide (**21**; R^1 = H, R^2 = R^3 = Et)


(19)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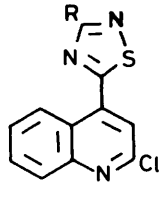
(22)

(52%) and a similar reaction between compound (**18b**) and butylamine gave the thioamide (**21**; R^1 = Me, R^2 = Bu; R^3 = H) (59%). These results are in accord with published accounts of the reaction of tetrachlorotrisulphanes [$(RCCl_2S)_2S$] with amines.[4] Similarly, treatment with amidines gives 1,2,4-thiadiazoles. Typically, compound (**18a**) and acetamidine gave the 3-methyl-1,2,4-thiadiazole (**22**; R = Me) (36%) and the derivatives (**22**; R = SMe) and (**22**; R = Ph) were similarly prepared.

Experimental

General experimental directions are given in the preceding paper.[1]

4-*Chloro*-[1,2]*dithiolo*[3,4-c]*quinolin*-1-*ones* (**2**).—4-Methylquinoline (**1a**) (14.3 g, 0.1 mol) was added slowly, with stirring, to thionyl chloride (119 g, 1 mol) under an argon atmosphere. The dark solution was then slowly heated to boiling point and gentle heating under reflux was maintained (20 h). Evaporation gave a brown amorphous solid (21.3 g) which was purified by m.p.l.c. (chloroform as eluant). The major component (R_F 0.6) was collected and identified as the title compound (**2**; R = H) (2.5 g, 10%), fine yellow needles, m.p. 178—180 °C (Found: C, 47.7; H, 1.45; Cl, 13.9; N, 5.4; S, 25.5. $C_{10}H_4ClNOS_2$ requires C, 47.3; H, 1.59; Cl, 14.0; N, 5.5; S, 25.3%); $\nu_{max.}$ 760, 960, 1 130, 1 160, 1 180, 1 290, and 1 640 cm^{-1}; δ_H 7.74—7.88 (m, 2 ArH), 8.12—8.18 (m, ArH), and 9.12—9.18 (m, ArH); *m/z* 253 ($M^{\cdot+}$ [^{35}Cl]).

The following compound was prepared in a similar manner from 4,8-dimethylquinoline (**1b**): 4-*chloro*-6-*methyl*-[1,2]*dithiolo*[3,4-c]*quinolin*-1-*one* (**2**; R = Me) (0.14 g, 1%), yellow solid m.p. 167—169 °C (Found: C, 49.4; H, 2.07. $C_{11}H_6ClNOS_2$ requires C, 49.3; H, 2.26%); $\nu_{max.}$ 730, 770, 805, 960, 1 160, 1 180, 1 280, 1 380, 1 490, and 1 670 cm^{-1}; δ_H 2.8 (s, Me), 7.5—7.75 (m, 2 ArH), and 8.85—9.05 (m, ArH). The sample contained traces of an impurity according to ^{1}H n.m.r., t.l.c., and chlorine analysis but was used without further purification.

Reactions of 4-*Chloro*-[1,2]*dithiolo*[3,4-c]*quinolin*-1-*one* (**2**; R = H).—(a) *With butylamine.* A mixture of compound (**2**; R = H) (3.2 g, 0.0125 mol), butylamine (1.85 g, 0.025 mol), and ethanol (250 ml) was heated under reflux (1 h). Evaporation gave a brown oil which was triturated with chloroform (10 ml) to give a green solid which was washed. Recrystallisation from 2-ethoxyethanol–water (20:1) gave N,N′-*dibutyl*-[1,4]*dithiino*-[2,3-b:5,6-b′]*diquinoline*-5,12-*dicarboxamide* (**3**; R = NHBu) (0.92 g, 29%), yellow solid, m.p. 333—335 °C (Found: C, 65.5; H, 5.34; N, 10.8; S, 12.6. $C_{28}H_{28}N_4O_2S_2$ requires C, 65.1; H, 5.46; N, 10.8; S, 12.4%); $\nu_{max.}$ 760, 1 130, 1 190, 1 280, 1 290, 1 320, 1 490, 1 540, 1 640, 2 880, 2 940, 2 960, 3 060, and 3 260 cm^{-1}; δ_H([$^2H_6$]DMSO) 1.0 (t, *J* 6 Hz, 6 H), 1.4—1.7 (m, 8 H), 3.46 (q, *J* 6 Hz, 4 H), 7.74—7.86 (m, 6 ArH), 8.04 (d, *J* 8 Hz, 2 ArH), and 9.00 (br t, *J* 5 Hz, 2 exchangeable NH); *m/z* 516 ($M^{\cdot+}$).

(b) *With benzylamine.* Using a procedure similar to that described for butylamine, compound (**2**; R = H) (3.2 g, 0.0125 mol), benzylamine (2.68 g, 0.025 mol), and ethanol (250 ml) gave N,N′-*dibenzyl*([1,4]*dithiino*[2,3-b:5,6-b′]*diquinoline*-5,12-*dicarboxamide* (**3**; R = $NHCH_2Ph$) (0.8 g, 22%), yellow solid, m.p. 308—310 °C (Found: C, 70.0; H, 3.99; N, 9.5; S, 11.2. $C_{34}H_{24}N_4O_2S_2$ requires C, 69.8; H, 4.14; N, 9.6; S, 11.0%); $\nu_{max.}$ 700, 760, 1 120, 1 270, 1 550, 1 640, 3 060, and 3 250 cm^{-1}; δ_H([$^2H_6$]DMSO) 4.70 (d, *J* 6 Hz, 2 × $PhCH_2$), 7.22—7.94 (m, 16 ArH), 8.03 (d, *J* 8 Hz, 2 ArH), and 9.52 (br t, *J* 6 Hz, 2 exchangeable NH); *m/z* 585 (M + H^+ [^{35}Cl]).

(c) *With ethanol.* A mixture of compound (**2**; R = H) (6.40 g, 0.025 mol), diethylamine (7.33 g, 0.1 mol), and ethanol (250 ml) was heated under reflux (1.5 h). Evaporation gave an oil which was purified by m.p.l.c. (chloroform as eluant). The major component (R_F 0.3) was recrystallised from ethyl acetate and identified as *diethyl* [1,4]*dithiino*[2,3-b:5,6-b′]*diquinoline*-5,12-*dicarboxylate* (**3**; R = OEt) (0.35 g, 6%), colourless solid, m.p. 255—257 °C (Found: C, 62.1; H, 3.74; N, 6.1; S, 14.1. $C_{24}H_{18}N_2O_4S_2$ requires C, 62.3; H, 3.92; N, 6.1; S, 13.9%); $\nu_{max.}$ 765, 1 010, 1 030, 1 120, 1 160, 1 180, 1 230, 1 320, 1 540, and 1 760 cm^{-1}; δ_H 1.56 (t, *J* 6 Hz, 2 × CH_2Me), 4.68 (q, *J* 6 Hz, 2 × CH_2Me), 7.52—7.90 (m, 6 ArH), and 8.04 (dd, *J* 1 and 8 Hz, 2 ArH); *m/z* 462 ($M^{\cdot+}$).

(d) *With sodium azide.* A mixture of compound (**2**; R = H) (1.27 g, 0.005 mol), sodium azide (1.30 g, 0.02 mol), and dry DMSO was heated on a steam bath (0.5 h). The dark blue mixture was added to water (200 ml) and the acidity adjusted to pH 1 by cautiously adding concentrated HCl. The yellow solid product was collected, washed, and dried. Chromatography showed that this product contained two main components. The mixture was purified by m.p.l.c. [chloroform–methanol (9:1) as eluant]. The major product (R_F 0.4) was collected, recrystallised from acetonitrile (200 ml), and identified as *tetrazolo*[1,5-a]-*thiazolo*[5,4-c]*quinolin*-5-(6H)-*one* (**8**) (0.3 g, 25%), buff solid, m.p. 290 °C (decomp.) (Found: C, 49.4; H, 2.25; N, 29.0; S, 13.8. $C_{10}H_5N_5OS$ requires C, 49.4; H, 2.07; N, 28.8; S, 13.2%); $\nu_{max.}$ 760, 860, 1 260, 1 360, 1 420, 1 450, 1 480, 1 500, 1 550, 1 600, and 1 620 cm^{-1}; δ_H([$^2H_6$]DMSO) 2.75—4.25 (v br, exchangeable NH), 7.75—7.95 (m, 2 ArH), 8.5—8.7 (m, ArH), and 8.75—9.0 (m, ArH); *m/z* 243 ($M^{\cdot+}$).

The second component (R_F 0.5) was collected and trituration with acetonitrile (20 ml) afforded 4-*chlorothiazolo*[5,4-c]*quinolin*-2(1H)-*one* (**7**) (0.1 g, 8.5%), yellow solid, m.p. >360 °C (Found: C, 50.9; H, 2.15; N, 11.7; S, 13.1. $C_{10}H_5ClN_2OS$ requires C, 50.75; H, 2.13; N, 11.8; S, 13.55%); $\nu_{max.}$ 770, 850, 880, 970, 1 165, 1 190, 1 250, 1 300, 1 320, 1 480, 1 515, 1 560, and 1 640 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.74—7.98 (m, 2 ArH), 8.08—8.28 (m, ArH), and 8.76—8.94 (m, ArH).

Bis[*dichloro*(4-*quinolyl*)*methyl*]*trisulphanes* (**18**).—2-Chloro-4-methylquinoline (**1c**) (17.8 g, 0.1 mol) was added slowly with stirring to thionyl chloride (119 g, 1 mol) under an argon atmosphere. The yellow solution was then heated under reflux (40 h) and the resulting red solution evaporated. After shaking with ether (150 ml), the solid residue, 2-chloro-4-methylquinoline hydrochloride (8.4 g), was removed. The mother liquor was concentrated to give an oil which was purified by m.p.l.c. (dichloromethane as eluant). The major component (R_F

0.4) was isolated as a pale pink solid (13.6 g, 46%). An analytical sample was prepared by recrystallisation from chloroform–light petroleum (b.p. 60—80 °C) giving *bis*[*dichloro*(2-*chloro*-*quinolin*-4-*yl*)*methyl*]*trisulphane* (**18a**), colourless crystals, m.p. 138—140 °C (Found: C, 41.1; H, 1.60; Cl, 36.2; N, 4.7; S, 16.3. $C_{20}H_{10}Cl_6N_2S_3$ requires C, 40.9; H, 1.72; Cl, 36.2; N, 4.8; S, 16.4%); $\nu_{max.}$ 1 105, 1 155, 1 280, 1 405, 1 500, and 1 570 cm^{-1}; δ_H 7.5—7.9 (m, 4 ArH), 8.0 (s, 2 ArH), 8.05—8.2 (m, 2 ArH), and 8.45—8.6 (m, 2 ArH); *m/z* 587 ($M^{\cdot+}$[^{35}Cl]).

The following compounds were similarly prepared from 2-chloro-4,7-dimethylquinoline (**1d**) and 4-methyl-8-nitroquinoline (**1e**) respectively: *bis*[*dichloro*(2-*chloro*-7-*methylquinolin*-4-*yl*)*methyl*]*trisulphane* (**18b**) (9.3 g, 30%), colourless crystals, m.p. 179—181 °C (Found: C, 42.7; H, 2.22; Cl, 34.3; N, 4.6; S, 15.5. $C_{22}H_{14}Cl_6N_2S_3$ requires C, 43.0; N, 2.29; Cl, 34.6; N, 4.6; S, 15.6%); $\nu_{max.}$ 1 110, 1 170, 1 270, 1 410, 1 500, and 1 575 cm^{-1}; δ_H 2.6 (s, 2 Me), 7.4 (dd, *J* 1 and 8 Hz, 2 ArH), 7.85 (d, *J* 1 Hz, 2 ArH), 7.95 (s, 2 ArH), and 8.4 (d, *J* 8 Hz, 2 ArH); *bis*[*dichloro*(2-*chloro*-8-*nitro*-*quinolin*-4-*yl*)*methyl*]*trisulphane* (**18c**) (0.65 g, 3%), buff solid, m.p. 147—149 °C (Found: C, 39.8; H, 1.61; Cl, 23.3; N, 9.2; S, 15.2. $C_{20}H_{10}Cl_4N_4S_3O_4$ requires C, 39.5; H, 1.66; Cl, 23.3; N, 9.2; S, 15.8%); $\nu_{max.}$ 715, 810, 860, 875, 925, 1 035, 1 065, 1 425, 1 555, and 1 600 cm^{-1}; δ_H 7.65 (dt, *J* 1 and 8 Hz, 2 ArH), 8.00 (dd, *J* 1 and 8 Hz, 2 ArH), 8.10 (d, *J* 5 Hz, 2 ArH), 8.75 (dd, *J* 1 and 8 Hz, 2 ArH), and 9.10 (d, *J* 5 Hz, 2 ArH).

Reactions of Bis[*dichloro*(4-*quinolyl*)*methyl*]*trisulphanes* (**18**).—(a) *With amines.* Compound (**18a**) (5.87 g, 0.01 mol) in dichloromethane (50 ml) was added slowly to a stirred solution of diethylamine (7.3 g, 0.1 mol) in dichloromethane (50 ml) at −9 °C. The orange solution was stirred at room temperature (1 h) and then evaporated. The residue was extracted with dichloromethane (3 × 20 ml) and the extract was purified by m.p.l.c. (dichloromethane as eluant). The major component (R_F 0.25) was collected and crystallisation from dichloromethane gave 2-*chloro*-4-(N,N-*diethylthiocarbamoyl*)*quinoline* (**21**; R^1 = H, R^2 = R^3 = Et) (2.9 g, 52%), colourless crystals, m.p. 132—134 °C (Found: C, 60.3; H, 5.33; Cl, 12.7; N, 9.9; S, 11.8. $C_{14}H_{15}ClN_2S$ requires C, 60.3; H, 5.42; Cl, 12.7; N, 10.0; S, 11.5%); $\nu_{max.}$ 1 150, 1 270, 1 320, 1 435, 1 465, 1 500, 1 580, 2 940, and 2 980 cm^{-1}; δ_H 1.12 (t, *J* 8 Hz, CH_2*Me*), 1.52 (t, *J* 8 Hz, CH_2*Me*), 3.34 (m, *J* 8 Hz, 2 H), 4.0 (m, *J* 8 Hz, 1 H), 4.46 (m, *J* 8 Hz, 1 H), 7.24 (s, ArH), 7.54—7.62 (m, ArH), 7.7—7.8 (m, 2 ArH), and 8.0—8.06 (m, ArH); *m/z* 278 (M + H^+ [^{35}Cl]).

Using compound (**18b**) (6.15 g, 0.01 mol) and butylamine (7.3 g, 0.1 mol), the following product was obtained in a similar manner; 4-(N-*butylthiocarbamoyl*)-2-*chloro*-7-*methylquinoline* (**21**; R^1 = Me, R^2 = Bu, R^3 = H) (3.46 g, 59%), colourless crystals, m.p. 156—157 °C (Found: C, 61.5; H, 5.9; Cl, 12.3; N, 9.5; S, 10.8. $C_{15}H_{17}ClN_2S$ requires C, 61.5; H, 5.85; Cl, 12.1; N, 9.6; S, 11.0%); $\nu_{max.}$ 1 300, 1 360, 1 400, 1 500, 1 550, 1 620, 2 930, 2 960, 3 050, and 3 220 cm^{-1}; δ_H 1.1 (t, *J* 6 Hz, CH_2*Me*), 1.4—2.1 (m, CH_2CH_2Me), 2.5 (s, Me), 4.0 (q, *J* 7 Hz, CH_2), 7.1 (s, ArH), 7.3 (dd, *J* 1 and 8 Hz, ArH), 7.45 (d, *J* 1 Hz, ArH), 7.8 (d, *J* 8 Hz, ArH), and 8.5 (br s, exchangeable NH); *m/z* 292 (M + H^+ [^{35}Cl]).

(b) *With amidines.* Compound (**18a**) (11.74 g, 0.02 mol) was stirred in dichloromethane (100 ml) with acetamidine hydrochloride (3.78 g, 0.04 mol) at 0 °C. Sodium hydroxide (50% w/v; 25 ml) was added at a rate which maintained the temperature below 5 °C and the solution was then stirred at room temperature (0.5 h). The organic layer was collected, washed (2 × 50 ml), and dried (Na_2SO_4). Evaporation gave a dark brown oil which was purified by m.p.l.c. (dichloromethane as eluant). Collection of the major component (R_F 0.2) gave 2-*chloro*-4-(3-*methyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**22**; R = Me) (3.7 g, 36%), colourless solid, m.p. 111—112 °C (Found: C, 55.0; H, 3.0; Cl, 13.7; N, 15.9; S, 12.1. $C_{12}H_8ClN_3S$ requires C, 55.1; H, 3.08; Cl, 13.5; N, 16.1; S, 12.3%); $\nu_{max.}$ 1 270, 1 285, 1 420, 1 440, 1 485, 1 550, and 1 575 cm^{-1}; δ_H 2.85 (s, Me), 7.55—7.95 (m, 2 ArH), 7.80 (s, ArH), 8.05—8.20 (m, ArH), and 9.0—9.25 (m, ArH); *m/z* 261 (M + H^+ [^{35}Cl]).

In a similar manner, the following derivatives were prepared from compound (**18a**) using *S*-methylisothiourea hydrogen sulphate and benzamidine hydrochloride respectively: 2-*chloro*-4-(3-*methylthio*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**22**; R = SMe) (0.55 g, 9%), tiny pale yellow crystals, m.p. 122—124 °C (Found: C, 49.2; H, 2.74; N, 14.2; S, 22.0. $C_{12}H_8ClN_3S_2$ requires C, 49.1; H, 2.74; N, 14.3; S, 21.8%); $\nu_{max.}$ 1 100, 1 150, 1 215, 1 415, 1 460, 1 475, 1 550, and 1 580 cm^{-1}; δ_H 2.8 (s, SMe), 7.55—7.95 (m, 3 ArH), 8.05—8.25 (m, ArH), and 8.5—8.7 (m, ArH); *m/z* 293 ($M^{\cdot+}$); 2-*chloro*-4-(3-*phenyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**22**; R = Ph) (3.2 g; 39%), buff solid, m.p. 147—149 °C (Found: C, 63.3; H, 3.07; Cl, 10.8; N, 12.9; S, 9.7. $C_{17}H_{10}ClN_3S$ requires C, 63.1; H, 3.11; Cl, 10.95; N, 13.0; S, 9.9%); $\nu_{max.}$ 710, 750, 780, 855, 885, 1 100, 1 230, 1 280, 1 340, 1 420, 1 510, and 1 570 cm^{-1}; δ_H 7.48—7.58 (m, 3 ArH), 7.72 (dt, *J* 1 and 8 Hz, ArH), 7.84 (s, ArH), 7.85 (dt, *J* 1 and 8 Hz, ArH), 8.12 (dd, *J* 1 and 8 Hz, ArH), 8.36—8.44 (m, 2 ArH), and 8.72 (dd, *J* 1 and 8 Hz, ArH); *m/z* 323 (M + H^+ [^{35}Cl]).

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