Reactions of Thionyl Chloride with *C*-Methyl Heterocycles. Part 1. The Formation of Dichloro(2-quinolyl)methanesulphenyl Chlorides from 2-Methylquinolines

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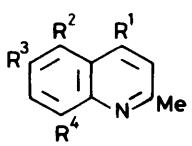
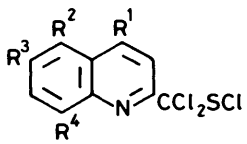
Hot thionyl chloride converts 2-methylquinolines (**1**) into dichloro(2-quinolyl)methanesulphenyl chlorides (**2**) which upon treatment with secondary amines are transformed into thioamides (**7**). Reaction of the novel derivatives (**2**) with amidines gives 5-(2-quinolyl)-1,2,4-thiadiazoles (**8**) and reaction with anionic nucleophiles results in substitution at sulphur.

In this paper we describe the reaction of 2-methylquinolines (**1**) with thionyl chloride to give dichloro(2-quinolyl)-methanesulphenyl chlorides (**2**). These are the first examples of heterocyclic dichloromethanesulphenyl chlorides ($HetCCl_2SCl$) and we have investigated reactions of the parent system (**2a**) with various nucleophiles.

The reactions of some simple methyl heterocycles with thionyl chloride were the subject of an earlier investigation by Davis and Scanlon who reported that complete chlorination of methyl substituents occurred in 2-methylbenzothiazole, 2-methylbenzoxazole, 2-methylbenzimidazole, 4-methylpyridine, 2-methylquinoline, and 2-methylquinoxaline.[1] The products of these reactions were not fully described but it was recognised that loss of the methyl protons in the n.m.r. spectra could be due to formation of several possible chlorine-containing species including trichloromethyl (CCl_3) or dichloromethanesulphenyl chloride (CCl_2SCl) derivatives. In addition to these studies other examples of reactions of methyl heterocycles with thionyl chloride have been described[2] and the reactions of thionyl chloride with active methylene compounds have been reviewed.[3]

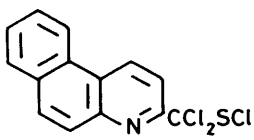


(**1**)



(**2**)

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



(**3**)

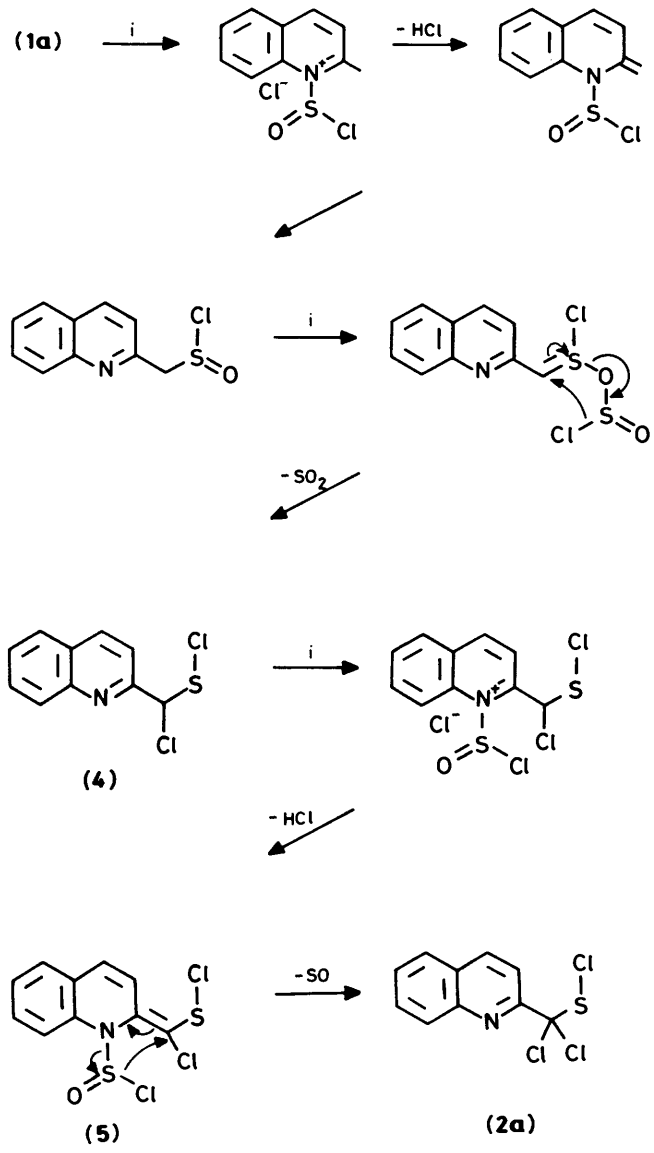
Treatment of 2-methylquinoline (**1a**) with an excess of thionyl chloride (**24h**) gave an ether soluble product in 34% yield which was identified as dichloro(2-quinolyl)methanesulphenyl chloride (**2a**). In a similar manner the derivatives (**2b**), (**2e**), and (**3**) were prepared. When either 6-methoxy or 8-methoxy-2-methylquinoline (**1c**) and (**1d**) were used, the products were the 5-chloro derivatives (**2f**) and (**2g**) which are presumably formed by electrophilic chlorination: the expected 5-unsubstituted products (**2c**) and (**2d**) were not detected.

The structures of the dichloromethanesulphenyl chlorides (**2**) and (**3**) are fully supported by analytical and spectroscopic data. Compound (**2a**) shows i.r. and ^1H n.m.r. spectra which are characteristic of 2-substituted quinolines. In the ^{13}C n.m.r. spectrum of compound (**2a**) the carbon atom of the CCl_2SCl group is observed at 98.4 p.p.m. and two other quaternary carbon atoms are observed at 159.8 and 145.6 p.p.m. The position of the fourth quaternary carbon atom is obscured by signals from the remaining six aromatic carbon atoms. In the mass spectrum the molecular ion of compound (**2a**) [*m/z* 277 (^{35}Cl)] fragments by loss of $Cl^•$ or $SCl^•$ to give fragment ions at *m/z* 242 and *m/z* 210 respectively.

A proposal for the mechanism of formation of compound (**2a**) is shown in Scheme 1. Initial quaternisation of the quinoline followed by deprotonation and a [1,3] shift of the chlorosulphinyl group gives a methanesulphinyl chloride. Subsequent reaction with a second molecule of thionyl chloride followed by a Pummerer-type rearrangement with elimination of SO_2 then leads to the α-chloromethanesulphenyl chloride (**4**). The formation of the proposed intermediate (**4**) has ample precedent in the formation of α-chloromethanesulphenyl chlorides by active α-methylene groups of carboxylic acids and esters, aldehydes, ketones, and nitriles.[2] In contrast, the formation of a dichloromethanesulphenyl chloride from an active methyl group does not have precedent. Pinacolone, for example, gives the α-chlorosulphenyl chloride (Me_3CCOCH-Cl·SCl) (50%) and a trisulphane [$(Me_3CCOCCl_2S)_2S$] (40%).[4] We propose that further reaction of the intermediate (**4**) with thionyl chloride gives, after loss of hydrogen chloride, the *N*-chlorosulphinyl enamine (**5**). Elimination of sulphur monoxide (**5**) ⟶ (**2a**) in a process analogous to the formation of α-monochloro ketones *via* enol-sulphinylation of ketones[3] then gives the observed product (**2a**).

Thermal decomposition of thionyl chloride gives chlorine, sulphur dioxide, and sulphur monochloride (S_2Cl_2).[5] The presence of electrophilic chlorinating agents (*e.g.* Cl_2) in the reaction mixture presumably accounts for the formation of the 5-chloro derivatives (**2f**) and (**2g**) from the methoxyquinolines (**1c**) and (**1d**).

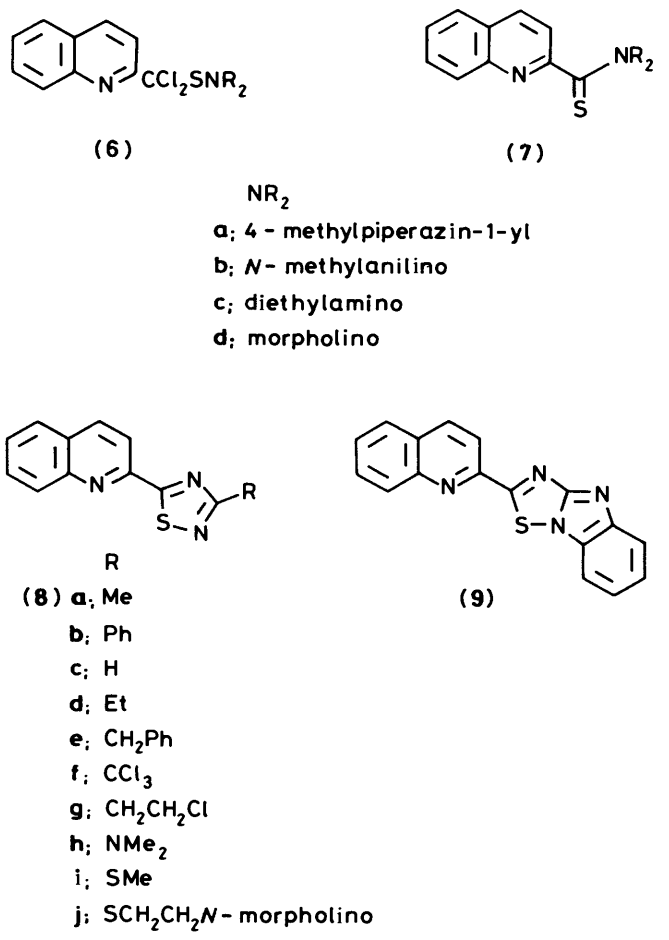
The novel dichloro(2-quinolyl)methanesulphenyl chlorides



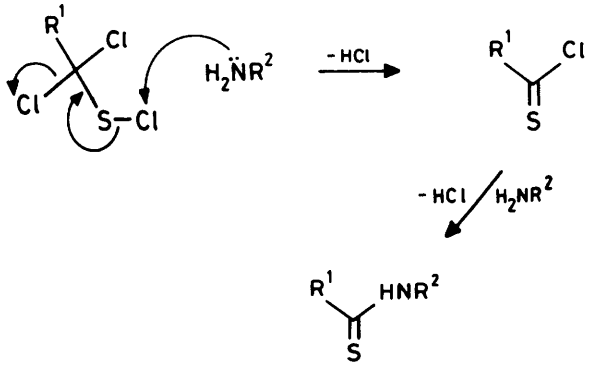
Scheme 1. *Reagents:* i, $SOCl_2$

(**2**) are stable, crystalline compounds with sharp melting points. The mode of reaction of the parent compound (**2a**) with secondary amines differs from those reported for alkyl- and carbamoyl-dichloromethanesulphenyl chlorides which give dichloromethanesulphenamides ($RCCl_2SNR_2$).[6,7] When compound (**2a**) was treated with *N*-methylpiperazine in CH_2Cl_2 the product was not the expected sulphenamide (**6a**) but was identified as the thioamide (**7a**). In a similar manner the thioamides (**7b**)—(**7d**) were obtained using *N*-methylaniline, diethylamine and morpholine. In these reactions the dichloromethanesulphenyl chloride (**2a**) is behaving as a 'masked' thioacyl chloride (RCS·Cl) rather than as a conventional sulphenylchloride (RSCl), but the structural features which determine this change in behaviour are not clear.

It is tempting to speculate on the mechanism of formation of the thioamides (**7**). Phillips and Ratts[7] found that treatment of *N*,*N*-dimethylcarbamoyl-α,α-dichloromethanesulphenyl chloride ($Me_2NCO{\cdot}CCl_2SCl$) with liquid ammonia gave 1-cyano-*N*,*N*-dimethylformamide ($Me_2NCO{\cdot}CN$), which is probably formed *via* the thioamide ($Me_2NCO{\cdot}CSNH_2$). They



proposed a mechanism in which formation of the thioacyl chloride is promoted by nucleophilic attack of ammonia on the sulphenyl chlorine atom (Scheme 2; $R^1 = Me_2NCO$; $R^2 = H$). A similar mechanism may account for the formation of the

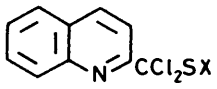


Scheme 2.

thioamides (**7**) but alternative mechanisms involving initial ionisation cannot be excluded.

In contrast to the results obtained using secondary amines, treatment of compound (**2a**) with amidines gave products analogous to those reported using carbamoyldichloromethanesulphenyl chlorides ($R_2NCO{\cdot}CCl_2SCl$)[7] and trichloromethanesulphenyl chloride (CCl_3SCl).[8] Typically, compound (**2a**) and acetamidine gave the 5-(2-quinolyl)-1,2,4-thiadiazole (**8a**) (yield 37%) and further derivatives (**8b**)—(**8g**) were obtained in moderate yield. Use of guanidines or *S*-alkyl-

isothioureas gave analogous products (**8h**)—(**8j**) and reaction with 2-aminobenzimidazole gave the 1,2,4-thiadiazolo[2,3-*a*]benzimidazole (**9**).



X

(**10**) **a**; SCN
b; *p*-$MeC_6H_4SO_2$
c; OPh
d; CN
e; phthalimido
f; $PO(OMe)_2$

The reaction of compound (**2a**) with several anionic nucleophiles led, in all cases, to substitution at sulphur. Potassium thiocyanate gave the sulphenyl thiocyanate (**10a**) (16%), sodium *p*-tolysulphinate gave the aryl thiosulphonate (**10b**) (27%), potassium phenoxide gave the phenyl sulphenate (**10c**) (8%), potassium cyanide gave the thiocyanate (**10d**) (6%), and potassium phthalimide gave the sulphenamide (**10e**) (20%). These results are in agreement with the observed reactions of other dichloromethanesulphenyl chlorides with C, N, O, and S nucleophiles.[8] Similarly, when trimethylphosphite was used as nucleophile, initial attack at sulphur occurred and a subsequent Arbuzov reaction[9] gave a high yield (94%) of the *O*,*O*-dimethyl thiophosphate (**10f**).

Experimental

^{1}H N.m.r. spectra were recorded on Varian CFT-20 (80 MHz) and XL-200 (200 MHz) spectrometers; i.r. spectra on a Pye-Unicam SP3-200 spectrometer, m.s. on a V.G. Micromass 6F or V. G. 7070E spectrometer, and analyses on a Carlo-Erba 1106. Unless otherwise stated, i.r. spectra were measured using KBr discs and 80 and 200 MHz n.m.r. spectra in deuteriochloroform (tetramethylsilane as internal reference). Only significant bands from i.r. spectra are quoted.

Separations by column chromatography were carried out using Merck Kieselgel 60 (230—400 mesh). Evaporation refers to the removal of volatile materials under reduced pressure. Substances stated to be identical were so with respect to m.p.s, mixed m.p.s, and i.r. spectra. M.p.s are uncorrected. For all preparations May & Baker colourless laboratory chemical grade (>99% $SOCl_2$) thionyl chloride was used without further purification.

WARNING. Reaction of thionyl chloride with certain *C*-methyl heterocycles can be vigorous. We recommend preliminary experiments on a small scale and addition of substrate to thionyl chloride (NOT *vice versa*).

Dichloro(2-quinolyl)methanesulphenyl Chlorides (**2**).—2-Methylquinoline (**1a**) (71.5 g, 0.5 mol) was slowly added to thionyl chloride (595 g, 5 mol), stirred under an argon atmosphere at room temperature and the solution was carefully heated under reflux. A green colouration was observed. After maintaining reflux (24 h), the solution was evaporated to give a green solid which was extracted with ether (4 × 200 ml). Concentration of the ethereal extracts gave *dichloro(2-quinolyl)-methanesulphenyl chloride* (**2a**) (47.4 g, 34%), buff solid, m.p. 104—106 °C (Found: C, 43.1; H, 2.3; Cl, 38.3; N, 4.9; S, 11.2. $C_{10}H_6Cl_3NS$ requires C, 43.1; H, 2.2; Cl, 38.2; N, 5.0; S, 11.5%); $\nu_{max.}$ 730, 770, 790, 810, 830, 925, 975, 1 120, 1 310, 1 380, 1 430, 1 510, and 1 595 cm^{-1}; δ_H 7.66 (dt, *J* 1 and 8 Hz, 6- or 7-ArH), 7.8 (dt, *J* 1 and 8 Hz, 6- or 7-ArH), 7.89 (dd, *J* 1 and 8 Hz, 5-ArH), 8.02 (d, *J* 8 Hz, 3-ArH), 8.05 (dd, *J* 1/2 and 8 Hz, 8-ArH), and 8.38 (dd, *J* 1/2 and 8 Hz, 4-ArH); δ_C 98.36 (CCl_2SCl), 119.51 (ArCH), 129.62 (ArCH), 130.11 (ArCH), 130.35 (ArCH), 132.84 (ArCH), 140.90 (ArCH), 145.57 (ArC), and 159.77 (ArC); *m/z* 277 [$M^{\cdot+}$ (^{35}Cl)], 242 (*M* − Cl), 210 (*M* − SCl), 207, 172, 149, 145, 128, 101, and 86.

The following compounds were similarly prepared from 4-chloro-2-methylquinoline (**1b**), 6-methoxy-2-methylquinoline (**1c**), 8-methoxy-2-methylquinoline (**1d**), 2,6-dimethylquinoline (**1e**), and 3-methylbenzo[*f*]quinoline respectively: *dichloro(4-chloroquinolin-2-yl)methanesulphenyl chloride* (**2b**) (9.3 g, 21%), colourless solid, m.p. 103—105 °C (Found: C, 38.0; H, 1.5; Cl, 45.3; N, 4.3; S, 10.2. $C_{10}H_5Cl_4NS$ requires C, 38.4; H, 1.6; Cl, 45.3; N, 4.5; S, 10.2%); δ_H 7.6—8.35 (m, 5 ArH); *dichloro(5-chloro-6-methoxyquinolin-2-yl)methanesulphenyl chloride* (**2f**) (6.4 g, 16%), colourless solid, m.p. 155—157 °C (Found: C, 38.8; H, 2.0; N, 4.1; S, 8.9. $C_{11}H_7Cl_4NOS$ requires C, 38.5; H, 2.1; N, 4.1; S, 9.35%); δ_H 4.1 (s, OMe), 7.6 (d, *J* 9 Hz, ArH), 8.02 (d, *J* 9 Hz, ArH), 8.1 (d, *J* 9 Hz, ArH), and 8.75 (d, *J* 9 Hz, ArH); dichloro-(5-chloro-8-methoxyquinolin-2-yl)methanesulphenyl chloride (**2g**) (1.2 g, 7%), yellow solid, m.p. 170—172 °C; δ_H 4.04 (s, OMe), 6.95 (d, *J* 8 Hz, ArH), 7.56 (d, *J* 8 Hz, ArH), 8.06 (d, *J* 8 Hz, ArH), and 8.66 (d, *J* 8 Hz, ArH), used without further characterisation; dichloro(6-methylquinolin-2-yl) methanesulphenyl chloride (**2e**) (27% crude yield) obtained as a dark oil and used without further purification; *(benzo[f]quinolin-2-yl)-dichloromethanesulphenyl chloride* (**3**) (4.2 g, 16%), off-white solid, m.p. 143—145 °C (Found: C, 51.5; H, 2.3; Cl, 32.4; N, 4.2. $C_{14}H_8Cl_3NS$ requires C, 51.2; H, 2.5; Cl, 32.4; N, 4.3%); δ_H 7.74 (m, 2 ArH), 7.86 (d, *J* 9 Hz, ArH), 7.94 (m, ArH), 8.03 (d, *J* 9 Hz, ArH), 8.18 (d, *J* 9 Hz, ArH), 8.59 (d, *J* 9 Hz, ArH), and 9.10 (d, *J* 9 Hz, ArH).

Reactions of Dichloro(quinolin-2-yl)methanesulphenyl Chloride (**2a**) *with Secondary Amines.*—A solution of compound (**2a**) (5.58 g, 0.02 mol) in dichloromethane (100 ml) was slowly added with stirring to a cold (0 °C) solution of *N*-methylpiperazine (10.02 g, 0.1 mol) in dichloromethane (50 ml). During addition the temperature was maintained below 5 °C. After being stirred at room temperature (1 h) the solution was evaporated and the residue was extracted with ethyl acetate (3 × 50 ml). Evaporation of the extracts gave an oil which was purified by m.p.l.c. (chloroform as eluant). The major component was recrystallised from ether–light petroleum (b.p. 40—60 °C) to give 2-[(4-*methylpiperazin*-1-*yl*)*thiocarbonyl*]*quinoline* (**7a**) (0.4 g, 7%), fine yellow needles, m.p. 95—97 °C (Found: C, 66.5; H, 6.5; N, 15.6; S, 11.7. $C_{15}H_{17}N_3S$ requires C, 66.4; H, 6.3; N, 15.5; S, 11.8%); $\nu_{max.}$ 1 495, 2 795, and 2 940 cm^{-1}; δ_H 2.36 (s, NMe), 2.45 (t, *J* 5 Hz, NCH_2), 2.68 (t, *J* 5 Hz, NCH_2), 3.66 (t, *J* 5 Hz, NCH_2), 4.50 (t, *J* 5 Hz, NCH_2), 7.43—7.90 (m, 4 ArH), and 8.01—8.26 (m, 2 ArH).

The following compounds were similarly prepared from *N*-methylaniline, diethylamine, and morpholine respectively: 2-(N-*methylanilino*)*thiocarbonylquinoline* (**7b**) (0.9 g, 16%), yellow solid, m.p. 146—148 °C (Found: C, 73.1; H, 4.9; N, 10.1; S, 11.6. $C_{17}H_{14}N_2S$ requires C, 73.35; H, 5.1; N, 10.1; S, 11.5%); $\nu_{max.}$ 1 385 and 1 495 cm^{-1}; δ_H 4.0 (s, NMe), 7.10 (m, Ph), 7.35—8.05 (m, 6 ArH); 2-[(*diethylamino*)*thiocarbonyl*]*quinoline* (**7c**) (1.15 g, 24%), colourless solid, m.p. 123—125 °C (Found: C, 68.8; H, 6.6; N, 11.3; S, 13.3. $C_{14}H_{16}N_2S$ requires C, 68.8; H, 6.6; N, 11.5; S, 13.1%); $\nu_{max.}$ 1 430, 1 500, 1 510, and 2 985 cm^{-1}; δ_H 1.24 (t, *J* 7 Hz, CH_2*Me*), 1.45 (t, *J* 7 Hz, CH_2*Me*), 3.50 (q, *J* 7 Hz, CH_2Me), 4.16 (q, *J* 7 Hz, CH_2Me), 7.40—7.90 (m, 4 ArH), and 8.00—8.24 (m, 2 ArH); 2-[(*morpholino*)*thiocarbonyl*]*quinoline* (**7d**) (0.5 g, 24%), yellow solid, m.p. 172—174 °C (Found: C, 65.4; H, 5.61; N, 10.8; S, 12.3. $C_{14}H_{14}N_2OS$ requires C, 65.1; H, 5.46; N, 10.8; S, 12.4%); $\nu_{max.}$ 1 420, 1 490, 2 860, and 2 980 cm^{-1}; δ_H 3.7 (s, br, 4 H), 3.8—4.0 (m, 2 H), 4.4—4.6 (m, 2 H), 7.5—7.9 (m, 4 ArH), and 7.9—8.3 (m, 2 ArH).

Reaction of Dichloro(2-quinolyl)methanesulphenyl Chloride (**2a**) *with Amidines and Related Species.*—Sodium hydroxide (5M, 10 ml) was slowly added to a stirred solution of acetamidine hydrochloride (0.95 g, 0.01 mol) and compound (**2a**) (2.8 g, 0.01 mol) in dichloromethane (20 ml) at 0 °C and the temperature was maintained below 5 °C. The solution was stirred at room temperature (1 h), the organic layer was collected, washed with water (2 × 20 ml), and dried ($MgSO_4$). Evaporation gave a dark oil which was purified by m.p.l.c. (chloroform as eluant). Collection and concentration of the major component followed by trituration with ether gave 2-(3-*methyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8a**) (0.85 g, 37%), colourless solid, m.p. 130—131 °C (Found: C, 63.0; H, 3.71; N, 18.3; S, 14.1. $C_{12}H_9N_3S$ requires C, 63.4; H, 3.99; N, 18.5; S, 14.1%); $\nu_{max.}$ 1 290, 1 315, 1 420, 1 500, and 1 590 cm^{-1}; δ_H 2.78 (s, Me), 7.45—7.95 (m, 3 ArH), and 8.05—8.33 (m, 3 ArH); *m/z* 227 ($M^{\cdot+}$).

The following compounds were similarly prepared from benzamidine hydrochloride, formamidine acetate, propionamidine hydrochloride, phenylacetamidine hydrochloride, trichloroacetamidine hydrochloride, 3-chloropropionamidine hydrochloride, *N,N*-dimethylguanidine hydrochloride, *S*-methylisothiourea sulphate, *S*-(2-morpholinoethyl)isothiourea dihydrochloride, and 2-aminobenzimidazole respectively; 2-(3-*phenyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8b**) (2.4 g, 42%), colourless solid, m.p. 184—185 °C (Found: C, 70.7; H, 3.78; N, 14.6; S, 11.2. $C_{17}H_{11}N_3S$ requires C, 70.6; H, 3.83; N, 14.5; S, 11.1%); $\nu_{max.}$ 1 320, 1 415, 1 430, 1 500, and 1 590 cm^{-1}; δ_H 7.40—8.50 (m, 11 ArH); 2-(1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8c**) (0.7 g, 16%), buff solid, m.p. 131—132 °C (Found: C, 61.9; H, 3.25; N, 19.4; S, 14.5. $C_{11}H_7N_3S$ requires C, 61.95; H, 3.3; N, 19.7; S, 15.0%); $\nu_{max.}$ 1 500 and 1 590 cm^{-1}; δ_H 7.50—7.94 (m, 3 ArH), 8.10—8.35 (m, 3 ArH), and 8.82 (s, ArH); 2-(3-*ethyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8d**) (2.0 g, 41%), off-white solid, m.p. 100—102 °C (Found: C, 64.5; H, 4.50; N, 17.4; S, 13.0. $C_{13}H_{11}N_3S$ requires C, 64.7; H, 4.60; N, 17.4; S, 13.3%); $\nu_{max.}$ 1 420, 1 500, and 1 590 cm^{-1}; δ_H 1.45 (t, *J* 8 Hz, CH_2Me), 3.10 (q, *J* 8 Hz, CH_2Me), 7.50—7.94 (m, 4 ArH), and 8.05—8.29 (m, 2 ArH); 2-(3-*benzyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8e**) (2.85 g, 47%), off-white solid, m.p. 148—150 °C (Found: C, 71.3; H, 4.3; N, 13.7; S, 10.3. $C_{18}H_{13}N_3S$ requires C, 71.3; H, 4.3; N, 13.85; S, 10.6%); $\nu_{max.}$ 1 310, 1 450, 1 495, and 1 590 cm^{-1}; δ_H 4.36 (s, CH_2), 7.16—7.53 (m, 5 ArH), and 7.57—8.26 (m, 6 ArH); 2-(3-*trichloromethyl*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8f**) (3.7 g, 56%), off-white solid, m.p. 119—120 °C (Found: C, 43.8; H, 1.7; Cl, 32.5; N, 12.9; S, 9.9. $C_{12}H_6Cl_3N_3S$ requires C, 43.6; H, 1.8; Cl, 32.2; N, 12.7; S, 9.7%); $\nu_{max.}$ 1 500 and 1 590 cm^{-1}; δ_H 7.60—7.70 (m, ArH), 7.75—7.91 (m, 2 ArH), 8.10—8.17 (m, ArH), and 8.27—8.37 (m, 2 ArH); 2-[3-(2-*chloroethyl*)-1,2,4-*thiadiazol*-5-*yl*]*quinoline* (**8g**) (1.4 g, 34%), buff solid, m.p. 137—139 °C (Found: C, 56.7; H, 3.49; Cl, 12.7; N, 15.2; S, 11.8. $C_{13}H_{10}ClN_3S$ requires C, 56.6; H, 3.66; Cl, 12.9; N, 15.2; S, 11.6%); $\nu_{max.}$ 1 365, 1 420, 1 500, and 1 590 cm^{-1}; δ_H 3.55 (t, *J* 8 Hz, CH_2CH_2), 4.10 (t, *J* 8 Hz, CH_2CH_2), 7.45—7.93 (m, 3 ArH), and 8.05—8.30 (m, 3 ArH); 2-(3-*dimethylamino*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8h**) (1.3 g, 22%), yellow solid, m.p. 148—151 °C (Found: C, 61.0; H, 4.7; N, 22.0; S, 11.9. $C_{13}H_{12}N_4S$ requires C, 60.9; H, 4.7; N, 21.9; S, 12.5%); $\nu_{max.}$ 1 410, 1 500, and 1 550 cm^{-1}; δ_H 3.15 (s, NMe_2), 7.45—7.90 (m, 3 ArH), and 7.98—8.22 (m, 3 ArH); 2-(3-*methylthio*-1,2,4-*thiadiazol*-5-*yl*)*quinoline* (**8i**) (0.6 g, 12%), pale pink plates, m.p. 181—183 °C (Found: C, 55.6; H, 3.34; N, 16.2; S, 24.7. $C_{12}H_9N_3S_2$ requires C, 55.6; H, 3.5; N, 16.2; S, 24.7%); $\nu_{max.}$ 1 315, 1 380, 1 445, 1 490, and 1 585 cm^{-1}; δ_H 2.78 (s, SMe), 7.50—7.95 (m, 3 ArH), and 8.07—8.35 (m, 3 ArH); 2-[3-(2-*morpholinoethylthio*)-1,2,4-*thiadiazol*-5-*yl*]*quinoline* (**8j**) (0.15 g, 6%), off white solid, m.p. 114—115 °C (Found: C, 56.6; H, 5.0; N, 15.4; S, 17.8. $C_{17}H_{18}N_4OS_2$ requires C, 57.0; H, 5.1; N, 15.6; S, 17.9%); $\nu_{max.}$ 1 445, 1 495, 1 590, 2 820, 2 860, 2 935, and 2 965 cm^{-1}; δ_H 2.45—2.63 (m, 4 H), 2.80 (dt, *J* 7 and 1 Hz, 2 H), 3.48 (dt, *J* 7 and 1 Hz, 2 H), 3.65—3.80 (m, 4 H), 7.45—7.95 (m, 3 ArH), and 8.05—8.40 (m, 3 ArH); 2-(2-*quinolyl*)-[1,2,4]*thiadiazolo*[2,3-a]*benzimidazole* (**9**) (0.52 g, 12%), yellow solid, m.p. 270—272 °C (Found: C, 67.8; H, 3.3; N, 18.5; S, 10.9. $C_{17}H_{10}N_4S$ requires C, 67.5; H, 3.3; N, 18.5; S, 10.6%); $\nu_{max.}$ 1 505, 1 590, and 1 615 cm^{-1}; δ_H 7.34—7.42 (m, 2 ArH), 7.74—7.99 (m, 4 ArH), 8.10—8.19 (m, 2 ArH), 8.38 (d, *J* 8 Hz, ArH), and 8.73 (d, *J* 8 Hz, ArH); *m/z* 302 ($M^{\cdot+}$).

Other Reactions of Dichloro(2-quinolyl)methanesulphenyl Chloride (**2a**).—(a) *With potassium thiocyanate.* A solution of potassium thiocyanate (0.97 g, 0.01 mol) in water (30 ml) was added to a stirred solution of compound (**2a**) (2.79 g, 0.01 mol) in dichloromethane (100 ml) at room temperature. The solution was stirred (1 h), the organic layer was collected, washed with water (30 ml), dried (Na_2SO_4) and evaporated to give a dark oil which was extracted with light petroleum (b.p. 60—80 °C) (4 × 50 ml). Cooling of the petroleum extracts to 0 °C gave *dichloro*(2-*quinolyl*)*methanesulphenyl thiocyanate* (**10a**) (0.48 g, 16%), buff solid, m.p. 93—95 °C (Found: C, 44.1; H, 2.0; Cl, 23.7; N, 9.2; S, 20.8. $C_{11}H_6Cl_2N_2S_2$ requires C, 43.9; H, 2.0; Cl, 23.5; H, 9.3; S, 21.3%); $\nu_{max.}$ 1 505, 1 590, and 2 160 cm^{-1}; δ_H 7.58—7.67 (m, ArH), 7.72—7.88 (m, 2 ArH), 7.98 (d, *J* 8 Hz, ArH), 8.06 (m, ArH), and 8.32 (d, *J* 8 Hz, ArH).

(b) *With sodium toluene*-p-*sulphinate.* Compound (**2a**) (2.78 g, 0.01 mol) was slowly added to a stirred solution of sodium *p*-tolylsulphinate (1.78 g, 0.01 mol) and triethylamine (1.11 g, 0.01 mol) in acetonitrile (20 ml) at 0 °C. Stirring was continued at room temperature (0.25 h), the solution was evaporated, and the resulting brown oil was subjected to m.p.l.c. (dichloromethane as eluant). Collection of the major component, evaporation, and recrystallisation from ether–light petroleum gave S-[*dichloro*-(2-*quinolyl*)*methyl*]*toluene*-p-*thiosulphonate* (**10b**) (0.8 g, 27%), colourless plates, m.p. 99—101 °C (Found: C, 51.1; H, 3.2; Cl, 17.7; N, 3.4; S, 15.9. $C_{17}H_{13}Cl_2NO_2S_2$ requires C, 51.3; H, 3.3; Cl, 17.8; N, 3.5; S, 16.1%); $\nu_{max.}$ 1 340 and 1 590 cm^{-1}; δ_H 2.33 (s, Me), 7.13 (d, *J* 8 Hz, 2 ArH), 7.56—7.84 (m, 5 ArH), 7.94 (d, *J* 8 Hz, ArH), 8.01 (d, *J* 8 Hz, ArH), and 8.21 (d, *J* 8 Hz, ArH).

(c) *With potassium phthalimide.* Compound (**2a**) (4.2 g, 0.015 mol) was added to a stirred solution of potassium phthalimide (2.8 g, 0.015 mol) and triethylamine (1.68 g, 0.017 mol) in dimethylformamide (20 ml) at 0 °C. After the slightly exothermic reaction was complete, the brown solution was stirred for a short period (0.25 h). After evaporation, the residue was extracted with dichloromethane (3 × 100 ml), the extract was subjected to m.p.l.c. (dichloromethane as eluant), and the major component was collected and isolated as a colourless solid (3.1 g) which was recrystallised from dichloromethane giving N-[*dichloro*(2-*quinolyl*)*methanesulphenyl*]*phthalimide* (**10e**) (1.2 g, 20%), colourless prisms, m.p. 193—197 °C (Found: C, 55.8; H, 2.5; Cl, 18.1; N, 7.2; S, 8.2. $C_{18}H_{10}Cl_2N_2O_2S$ requires C, 55.5; H, 2.6; Cl, 18.2; N, 7.2; S, 8.2%); $\nu_{max.}$ 1 335, 1 710, and 1 740 cm^{-1}; δ_H 7.58—7.80 (m, 2 ArH), 7.81—7.89 (m, 3 ArH), 7.94—8.06 (m, 4 ArH), and 8.33 (d, *J* 8 Hz, ArH).

(d) *With potassium cyanide.* A solution of potassium cyanide (0.65 g, 0.01 mol) in water (30 ml) was added to a stirred solution of compound (**2a**) (2.79 g, 0.01 mol) in dichloromethane (100 ml) at room temperature. The solution was stirred (1 h), and the organic layer was collected, washed with water (30 ml), and dried (Na_2SO_4). Evaporation gave a dark oil which was subjected to m.p.l.c. (dichloromethane as eluant). Collection of the major component, evaporation, and recrystallisation from light petroleum (b.p. 40—60 °C) gave *dichloro*(2-*quinolyl*)-*methyl thiocyanate* (**10d**) (0.16 g, 6%), colourless needles, m.p. 101—103 °C (Found: C, 48.7; H, 2.1; Cl, 26.1; N, 10.1; S, 12.0. $C_{11}H_6Cl_2N_2S$ requires C, 49.1; H, 2.25; Cl, 26.3; N, 10.4; S, 11.9%); $\nu_{max.}$ 1 430, 1 510, 1 590, and 2 160 cm^{-1}; δ_H 7.47—

7.56 (m, ArH), 7.6—7.76 (m, 2 ArH), 7.85 (d, *J* 8 Hz, 3-H), 7.92 (m, ArH), and 8.23 (d, *J* 8 Hz, 4-H).

(e) *With trimethyl phosphite.* Trimethyl phosphite (1.36 g, 0.011 mol) was added with stirring to a cold (0 °C) solution of compound (**2a**) (2.79 g, 0.010 mol) in dichloromethane (100 ml). During addition the temperature was maintained below 5 °C. After being stirred at room temperature (1 h) the solution was evaporated and the residue triturated with light petroleum (b.p. 40—60 °C) (30 ml). Cooling (0 °C) gave S-*dichloro*(2-*quinolyl*)-*methyl* O,O-*dimethyl thiophosphate* (**10f**) (3.3 g, 94%), buff solid, m.p. 75—76 °C (Found: C, 40.5; H, 3.3; Cl, 19.8; N, 3.8; S, 9.5. $C_{12}H_{12}Cl_2NO_3PS$ requires C, 40.9; H, 3.4; Cl, 20.1; N, 4.0; S, 9.1%); $\nu_{max.}$ 2 960, 2 860, 1 600, and 1 505 cm^{-1}; δ_H 3.75 (s, Me), 3.95 (s, Me), 7.6—7.95 (m, 6 ArH); *m/z* 352 ($M^{\bullet+}$).

(f) *With potassium phenoxide.* Potassium phenoxide (1.32 g, 0.01 mol) was added with stirring to a cold (0 °C) solution of compound (**2a**) (2.79 g, 0.01 mol) in dichloromethane (100 ml). During addition the temperature was maintained below 5 °C. The solution was stirred at room temperature (1 h), water (2 × 50 ml) was added, and the organic layer was collected and dried (Na_2SO_4). Evaporation gave a dark oil which was extracted with light petroleum (b.p. 60—80 °C) (2 × 50 ml). Cooling of the petroleum extracts to 0 °C gave *phenyl dichloro*-(2-*quinolyl*)*methanesulphenate* (**10c**) (0.26 g, 8%), buff solid, m.p. 76—78 °C (Found: C, 57.1; H, 3.2; Cl, 21.5; N, 4.1; S, 9.8. $C_{16}H_{11}Cl_2NOS$ requires C, 57.15; H, 3.3; Cl, 21.1; N, 4.2; S, 9.5%); $\nu_{max.}$ 1 590, 1 490, and 1 480 cm^{-1}; δ_H 6.85—7.5 (m, OPh), 7.6—8.15 (m, 5 ArH), and 8.35 (d, *J* 8 Hz, 4-H).

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