The Preparation of 1-Aryl- and 1-Heteroaryl-alkene-1,2-dithiolates

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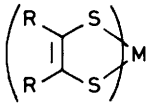
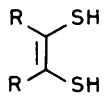
It is shown that alkaline hydrolysis of 2-(*NN*-dialkylamino)-1,3-dithiolium salts produces solutions of ene-1,2-dithiolate salts which are trapped by reaction with iodomethane. The dithiolium salts were prepared by reaction of α-bromoketones with sodium *NN*-dialkyldithiocarbamates, followed by sulphuric acid-catalysed dehydrative ring-closure of the resulting β-oxoalkyl *NN*-dialkyldithiocarbamates.

For some years, transition-metal complexes (**1**) derived formally from the dianions of (*Z*)-alkene-1,2-dithiols (**2**) have attracted attention in view of their interesting structural and electrochemical properties.[1,2]

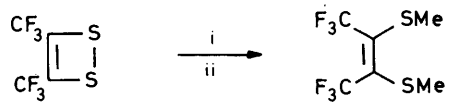


(1)



(2) a; R = H
b; R = CN
c; R = CF_3
d; R = Ph

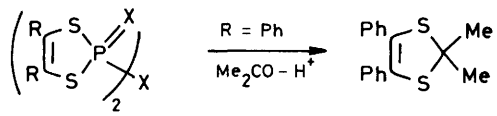
Despite this attention, a general synthetic method for the synthesis of (*Z*)-ene-1,2-dithiols or -1,2-dithiolates has not been reported. This is certainly due, in part, to the instability of ene-1,2-dithiols. The disodium salt of ethylene-1,2-dithiol (**2a**) may be prepared by cleavage of its dibenzyl bis-sulphide using sodium in liquid ammonia;[3] the report[3b] that (**2a**) is stable and may be distilled without decomposition seems likely, in the light of our experience with substituted analogues, to be mistaken. Two of the commonly used ene-1,2-dithiol ligands involve compounds (**2b**) and (**2c**). The disodium salt of the dinitrile (**2b**) is usually synthesised by treating sodium cyanide with carbon disulphide.[4] The dimercury salt of (*Z*)-1,2-bis(trifluoromethyl)-ethylene-1,2-dithiol (**2c**) has been generated by reduction of the dithiete (**3**) with elemental mercury, demonstrated by its subsequent conversion into its bis(methyl sulphide) (**4**) with iodomethane.[5]



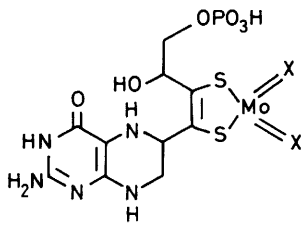
(3) (4)

Reagents: i, Hg; ii, MeI

Cyclic thiophosphate esters (**5**), prepared from benzoins or acyloins and phosphorus pentasulphide, have yielded ene-1,2-dithiolate complexes when treated with transition-metal salts under acidic conditions.[6,7] Hydrolysis, in the absence of transition-metal salts, of the ester (**5**; R = Ph) derived from benzoin has not permitted the free ene-1,2-dithiol (**2d**) to be isolated; however, it can be trapped in low yield as the dithioacetal (**6**).[7]† Furthermore, no synthesis has been reported of an unsymmetrically substituted ene-1,2-dithiol,‡ an especially pertinent structural type relevant to our interest in the molybdenum co-factor (MoCo) of the oxomolybdoenzymes, a



(5) X = O, S (6)



(7) X = O, S

structure (**7**) for which has been suggested by Rajagopalan and co-workers.[8] This structure incorporates a molybdenum complex of an unsymmetrical (*Z*)-ene-1,2-dithiolate, in which the ligand carries a hydroxylated alkyl group at one carbon and a tetrahydrohydropteridin-6-yl unit at the other.

In searching for a more generally applicable approach to the synthesis of ene-1,2-dithiolate systems, we have observed that dialkylamino-1,3-dithiolium salts (**9**),[9,10] which can be obtained by dehydration of β-oxoalkyl-*NN*-dialkyldithiocarbamates (**8**), formally incorporate the ene-1,2-dithiol unit. It seemed that not only might it be possible for such salts to be a source of ene-1,2-dithiolates but also that they could be produced with control over the nature of the R^1 and R^2 substituents. Therefore, a rational synthesis of ene-1,2-dithiolates might be developed which had the considerable advantage that unsymmetrically substituted compounds could be generated.

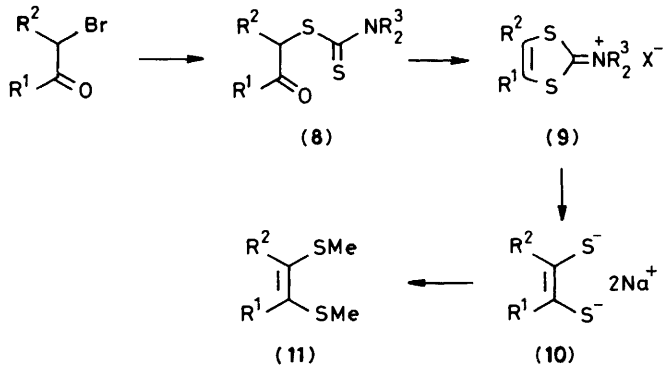
Results and Discussion

Initially, we chose the readily available α-bromoacetophenone as a starting point. Thus, reaction of this compound with

† In view of this and earlier work (S. K. Mitra, *J. Indian Chem. Soc.*, 1938, **15**, 58; R. Mayer and M. Nitzschke, *Chem. Ber.*, 1963, **96**, 2539; G. N. Schrauzer and H. W. Finck, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 133), a claim to have isolated compound (**2d**) following the reduction of 4,5-diphenyl-2H-1-3-dithiole-2-thione [K. M. Pazdro, *Rocz. Chem.*, 1969, **43**, 1089 (*Chem. Abstr.*, 1969, **71**, 91357[6])] seems in error. The saturated compound 1,2-diphenylethane-1,2-dithiol is possibly the correct formulation for the product of this reaction.

‡ Schrauzer *et al.* have mentioned a nickel complex of 1-phenylethylene-1,2-dithiol in their initial communication of the reaction between acyloins and phosphorus pentasulphide,[6a] and later they stated that a thiophosphate ester can be prepared from α-bromoacetophenone or phenylglyoxal,[7] but no details were given in these or subsequent publications.

sodium dimethyl- or diethyl-dithiocarbamate produced the corresponding *NN*-dialkyldithiocarbamates (**8a** and **b**) in good yield.[10a] Dehydrative ring closure, using conc. sulphuric acid,[10b] proceeded smoothly to form the stable, crystalline hydrogen sulphate salts (**9c** and **d**) in excellent yield. This latter step is an improvement over most earlier work,[10a] which involved the use of the more hazardous perchloric acid. Conversion of the precursor salts (**9c** and **d**) into the disodium salt (**10e**) of (*Z*)-1-phenylethylene-1,2-dithiol was achieved with hot methanolic sodium hydroxide; the hydrolysis was confirmed and the salt characterised by trapping with iodomethane, which produced the bis-sulphide (**11f**). This appeared to be the optimum hydrolysis procedure; attempted hydrolyses in aqueous media or using hydrazine hydrate afforded intractable materials. Although the enedithiolate (**10e**) seemed to be relatively stable in basic solution, conversion into the free dithiol by neutralisation of the hydrolysed mixture resulted in the immediate evolution of hydrogen sulphide; extraction of the acidic mixture afforded a multi-component oil which was not investigated further.



Scheme.

	R^1	R^2	R^3	X^-
a;	Ph	H	Me	—
b;	Ph	H	Et	—
c;	Ph	H	Me	HSO_4
d;	Ph	H	Et	HSO_4
e;	Ph	H	—	—
f;	Ph	H	—	—
g;	Ph	Me	Me	—
h;	Ph	Me	Me	HSO_4
i;	Ph	Me	—	—
j;	pyridin-2-yl	H	Me	—
k;	pyridin-3-yl	H	Me	—
l;	pyridin-2-yl	H	Me	HSO_4
m;	(1-H-3-pyridinio)$^+$	H	Me	$2HSO_4$
n;	quinoxalin-2-yl	H	Me	—
o;	quinoxalin-2-yl	H	Me	HSO_4
p;	pyridin-2-yl	H	—	—
q;	pyridin-3-yl	H	—	—
r;	quinoxalin-2-yl	H	—	—

In order to assess the generality of the process (Scheme) and to provide ene-1,2-dithiolates and ene-1,2-dithiols which resembled that proposed for the co-factor of the oxomolybdenum enzymes, we have extrapolated the approach discussed above to the synthesis of a (*Z*)-1-aryl-2-alkyl-1,2-enedithiolate and to some (*Z*)-1-heteroarylethylene-1,2-dithiolates.

α-Bromopropiophenone was treated as described above with sodium dimethyldithiocarbamate to give compound (**8g**). Ring closure then afforded the immonium salt (**9h**) and alkaline hydrolysis and trapping proceeded efficiently, as in the simpler case, to give compound (**11i**).

2- and 3-Bromoacetylpyridine hydrobromides[11,12] reacted smoothly with sodium dimethyldithiocarbamate to give (**8j** and **k**). As isolated products from ring closure with sulphuric acid the former carbamate produced a monohydrogen sulphate (**9l**) whilst the latter gave a double salt (**9m**), in which the pyridine nitrogen atom bore a proton.

2-Acetylquinoxaline[13] was similarly brominated in the side chain, after which reaction with sodium dimethyldithiocarbamate and sulphuric acid-catalysed dehydrative ring-closure produced successively the keto ester (**8n**) and the hydrogen sulphate (**9o**).

An anticipated difficulty in the trapping of these iminio-substituted ethylene-1,2-dithiolates (**10**) was competitive reaction of the iodomethane at the ring nitrogen. In practice, this proved not to be a problem and, in each case, hydrolysis and trapping with iodomethane smoothly produced the appropriate bis-sulphides (**11p**), (**11q**), and (**11r**). [The relatively low yield of (**11q**) from (**8m**) (53%) may reflect some competitive *N*-methylation of the dithiolate in this case.]

The 1,3-dithiolium salts described in this paper are readily prepared in high yield from commercially available materials, and are stable. We have shown that simple hydrolysis leads to solutions of the corresponding disodium (*Z*)-ene-1,2-dithiolate salts. The reactions of these salts with metal cations will be reported in subsequent publications. Our approach to the (*Z*)-alkene-1,2-dithiol functionality should enable a large variety of metal complexes containing this grouping to be prepared and studied.

Experimental

M.p.s were determined on a Kofler hot-stage microscope and are uncorrected. U.v. spectra were recorded on a Shimadzu UV-260 instrument with a 1 cm path-length. I.r. spectra were recorded on a Pye-Unicam SP3-200 spectrophotometer. ^1H N.m.r. spectra were recorded at ambient temperature on Perkin-Elmer R34 220 MHz and Varian SC 300 MHz instruments. Mass spectra were measured on a Kratos MS 30 instrument for electron-impact (70 eV source) spectra and a Kratos MS 25 instrument for chemical-ionisation spectra (C.I.M.S.) using ammonia.

2-(NN-*Dimethylamino*)-4-*phenyl*-1,3-*dithiolium Hydrogen Sulphate* (NN-*Dimethyl*-4-*phenyl*-2H-1,3-*dithiol*-2-*iminium Hydrogen Sulphate*) (**9c**).—Conc. sulphuric acid (10 ml) was added dropwise to phenacyl-*NN*-dimethyldithiocarbamate (**8a**) (5.00 g) at room temperature. The mixture was gently warmed for 5 min then poured into diethyl ether (*ca.* 200 ml). The precipitated solid was filtered off and recrystallised from ethanol to give the salt (**9c**) (6.43 g, 96%) as large crystals, m.p. 232—234 °C (lit.,[10b] 232—234 °C); $\lambda_{max.}$ (EtOH) 223, 233sh, 286sh, 300, and 314 nm (log ε 4.13, 4.09, 3.90, 3.95, and 4.00); $\nu_{max.}$ (Nujol) 1 600, 1 240, 1 170, 1 160, 1 050, 840, 760, and 690 cm^{-1}; δ [$(CD_3)_2SO$] 8.02 (1 H, s, 5-H), 7.65 (2 H, m, 2′- and 6′-H) 7.48 (3 H, m, ArH), and 3.46 and 3.51 (6 H, 2 s, $N^+(Me)_2$).

By the same procedure phenacyl-*NN*-diethyldithiocarbamate (**8b**) (10.0 g) was cyclised with conc. sulphuric acid (15 ml) and the product was crystallised from ethanol to yield 2-(NN-*diethylamino*)-4-*phenyl*-1,3-*dithiolium hydrogen sulphate* (NN-*diethyl*-4-*phenyl*-2H-1,3-*dithiol*-2-*iminium hydrogen sulphate*) (**9d**) (11.9 g, 92%) as needles, m.p. 200—205 °C; $\lambda_{max.}$ (EtOH) 224sh, 234, 285sh, 300, and 320 nm (log ε 4.32, 4.18, 3.94, 4.00, and 4.08); $\nu_{max.}$ (Nujol) 1 575, 1 540, 1 240, 1 160, 1 050, 850, 830, and 755 cm^{-1}; δ [$(CD_3)_2SO$] 8.32 (1 H, s, 5-H), 7.75 (2 H, m, 2′- and 6′-H), 7.58 (3 H, m, ArH), 3.95 [4 H, m, $N^+(CH_2CH_3)_2$], and 1.39 [6 H, m, $N^+(CH_2CH_3)_2$] (Found: C, 45.1; H, 4.9; N,

4.0; S, 27.45. $C_{13}H_{17}NO_4S_3$ requires C, 44.95; H, 4.95; N, 4.05; S, 27.7%).

1,2-Bis(methylthio)-1-phenylethene (**11f**).—A solution of sodium hydroxide (3.0 g) in methanol (30 ml) was added to a hot solution of salt (**9c**) (1.50 g) in methanol (30 ml) and the resulting mixture was refluxed gently for 90 min. The methanol was then removed under reduced pressure and iodomethane (15 ml) was added. The mixture was shaken periodically at room temperature for 90 min, then the iodomethane was evaporated off. Extraction with diethyl ether (2 × 75 ml) afforded the *bis-sulphide* (**11f**) (0.73 g, 77%) as a pale yellow liquid, b.p. 118—120 °C (0.7 Torr); $\lambda_{max.}$(EtOH) 233, 246sh, and 306 mm; $\nu_{max.}$ (film) 2 940, 1 550, 1 440, 755, and 695 cm^{-1}; δ($CDCl_3$) 7.4 (5 H, m, ArH), 6.43 (1 H, s, 2-H), 3.38 (3 H, s, SCH_3), and 3.04 (3 H, s, SCH_3); *m/z* 196 (M^+, 55%), 181 (7), 166 (8), and 134 (100) (Found: C, 61.0; H, 6.15; S, 32.1%; M^+, 196.0383; $C_{10}H_{12}S_2$ requires C, 61.2; H, 6.15; S, 32.75%; *M*, 196.0385).

By the same procedure the diethyl compound (**9d**) (1.50 g) in methanol (30 ml) was hydrolysed with sodium hydroxide (3.0 g) in methanol (30 ml) and alkylated with iodomethane (15 ml) to give the bis-sulphide (**11f**) (0.804 g, 95%).

1-*Oxo*-1-*phenylpropan*-2-*yl* NN-*Dimethyldithiocarbamate* (**8g**).—A solution of α-bromopropiophenone (10.0 g) in diethyl ether (240 ml) was added dropwise to a refluxing solution of sodium *NN*-dimethyldithiocarbamate dihydrate (10.0 g) in ethanol (20 ml). After the addition was complete the mixture was refluxed for a further 10 min. The solvents were evaporated off and water was added. Extraction with dichloromethane gave an oil which crystallised on being cooled to −40 °C. Recrystallisation from methanol afforded the *dithiocarbamate* (**8g**) (10.5 g, 88%) as large, pale yellow crystals, m.p. 71—73.5 °C; $\nu_{max.}$(Nujol) 1 700, 1 245, 960, 970, and 730 cm^{-1}; δ($CDCl_3$) 7.99 (2 H, m, ArH), 7.40 (3 H, m, ArH), 5.73 (1 H, q, *J* 7 Hz, C*H*Me), 3.40 and 3.20 (6 H, 2 s, NMe_2), and 2.48 (3 H, d, CH_3CH); *m/z* (c.i.m.s.) 254 (MH^+, 36%), 135 (46), 124 (100), 110 (35), and 90 (78) (Found: C, 56.9; H, 6.1; N, 5.5; S, 25.0. $C_{12}H_{15}NOS_2$ requires C, 56.9; H, 5.95; N, 5.55; S, 25.3%).

2-(NN-*Dimethylamino*)-4-*methyl*-5-*phenyl*-1,3-*dithiolium Hydrogen Sulphate* (4,NN-*Trimethyl*-5-*phenyl*-2H-1,3-*dithiol*-2-*iminium Hydrogen Sulphate*) (**9h**).—The dithiocarbamate (**8g**) was treated with conc. sulphuric acid (7 ml) and the reaction mixture was worked up as described for the phenyl analogue (**9c**) above to give the *salt* (**9h**) (5.65 g, 86%) as fine needles (from ethanol), m.p. 204—205.5 °C; $\lambda_{max.}$(EtOH) 259 and 312 nm (log ε 3.85 and 4.01); $\nu_{max.}$(Nujol) 1 620, 1 250, 1 160, 1 060, 850, 765, and 700 cm^{-1}; δ [$(CD_3)_2SO$] 7.50 (5 H, s, Ph), 3.46 (6 H, s, N^+Me_2), and 2.32 (3 H, s, 4-CH_3) (Found: C, 43.3; H, 4.5; N, 4.2; S, 28.9. $C_{12}H_{15}NO_4S_3$ requires C, 43.2; H, 4.55; N, 4.2; S, 28.85%).

Z-1,2-*Bis(methylthio)*-1-*phenylprop*-1-*ene* (**11i**).—A hot solution of the salt (**9h**) (0.327 g) in methanol (10 ml) was hydrolysed with sodium hydroxide (1.0 g) in methanol (10 ml) as described above (reflux period 1 h) and the product was methylated with iodomethane (5 ml) at room temperature (1 h) to give the *bis-sulphide* (**11i**) (0.133 g, 64%) as a pale yellow liquid, $\lambda_{max.}$(EtOH) 218, 246sh, and 286 nm; $\nu_{max.}$(film) 2 940, 1 440, 1 130, 740, and 700 cm^{-1}; δ($CDCl_3$) 7.2—7.4 (5 H, m, Ph), 2.34 (3 H, s, SCH_3), 1.90 (3 H, s, 3-Me or SCH_3), and 1.82 (3 H, s, SCH_3 or 3-Me); *m/z* 210 (M^+, 82%), 195 (6), 180 (8), 164 (16), 148 (100), 147 (58), and 115 (62) (Found: M^+ 210.0538. $C_{11}H_{14}S_2$ requires *M*, 210.0537).

2-*Oxo*-2-(*pyridin*-2-*yl*)*ethyl* NN-*Dimethyldithiocarbamate* (**8j**).—A solution of 2-(bromoacetyl)pyridinium hydrobromide (30.0 g) in water (100 ml) was added to a refluxing solution of sodium *NN*-dimethyldithiocarbamate dihydrate (45.0 g) in ethanol. After the addition was complete the mixture was refluxed for a further 15 min, then diluted with water (*ca.* 200 ml). After the mixture had cooled, the crystalline product was filtered off and recrystallised from ethanol to yield the *dithiocarbamate* (**8j**) (22.7 g, 89%) as large, pale pink crystals, m.p. 126—130 °C; $\nu_{max.}$(Nujol) 1 695, 1 510, 1 250, 990, 775, and 665 cm^{-1}; δ($CDCl_3$) 8.70 (1 H, dq, *J* 5 and 2 Hz, py 6-H), 8.04 (1 H, dt, *J* 7.5 and 1.5 Hz, py 3-H), 7.84 (1 H, m, py 4-H), 7.49 (1 H, m, py 5-H), 5.08 (2 H, s, CH_2S), and 3.44 and 3.49 (6 H, 2s, NMe_2); *m/z* 240 (M^+, 1%), 152 (13), 88 (100), and 78 (11) (Found: C, 49.7; H, 5.0; N, 11.6; S, 26.2. $C_{10}H_{12}N_2OS_2$ requires C, 50.0: H, 5.05; N, 11.65; S, 26.7%).

2-*Oxo*-2-(*pyridin*-3-*yl*)*ethyl* NN-*Dimethyldithiocarbamate* (**8k**).—In a similar procedure to that described above for (**8j**) a refluxing solution of sodium dimethyldithiocarbamate dihydrate (25.0 g) in ethanol (50 ml) was treated with a solution of crude 3-(bromoacetyl)pyridinium hydrobromide (21.1 g) in hot water (100 ml) and the product was recrystallised from ethanol to give the *dithiocarbamate* (**8k**) (11.0 g, 62%) as off-white feathery needles, m.p. 116—117 °C; $\nu_{max.}$(Nujol) 1 685, 1 580, 1 510, 1 275, and 710 cm^{-1}; δ($CDCl_3$) 9.35 (1 H, d, *J* 2 Hz, py 2-H), 8.85 (1 H, dd, *J* 2 and 5 Hz, py 6-H), 8.39 (1 H, m, py 4-H), 7.48 (1 H, m, py 5-H), 4.83 (2 H, s, CH_2S), and 3.45 and 3.52 (6 H, 2 s, NMe_2); *m/z* 240 (M^+, 1%), 207 (5), 206 (3), 121 (13), 107 (17), 106 (31), 88 (98), 78 (31), and 72 (100) (Found: C, 49.7; H, 5.0; N, 11.45; S, 26.4%).

The dithiocarbamates (**8j** and **k**) were cyclised as described for the phenyl compound (**8a**) above to give respectively 2-(NN-*dimethylamino*)-4-(*pyridin*-2-*yl*)-1,3-*dithiolium hydrogen sulphate* [NN-*dimethyl*-4-(*pyridin*-2-*yl*)-2H-1,3-*dithiol*-2-*iminium hydrogen sulphate*] (**8l**) (11.1 g, 82%) from (**8j**) (10.2 g) and 35 ml conc. sulphuric acid (35 ml), buff plates, m.p. 276 °C (from ethanol); $\lambda_{max.}$(MeOH) 228 and 312 nm (log ε 4.20 and 4.26); $\nu_{max.}$(Nujol) 1 600, 1 170, 1 150, 1 000, and 790 cm^{-1}; δ [$(CD_3)_2SO$] 8.64 (1 H, d, *J* 4.5 Hz, py 6-H), 8.47 (1 H, s, 5-H), 8.19 (1 H, d, *J* 8 Hz, py 3-H), 8.05 (1 H, t, *J* 8 Hz, py 4-H), 7.54 (1 H, m, py 5-H), and 3.53 and 3.58 (6 H, 2 s, N^+Me_2) (Found: C, 37.3; H, 3.75; N, 8.7; S, 29.5. $C_{10}H_{12}N_2O_4S_3$ requires C, 37.5; H, 3.8; N, 8.75; S, 30.0%), and 2-(NN-*dimethylamino*)-4-(*pyridinium*-3-*yl*)-1,3-*dithiolium bis(hydrogen sulphate)* [NN-*dimethyl*-4-(1H-3-*pyridinio*)-2H-1,3-*dithiol*-2-*iminium bis(hydrogen sulphate)*] (**9m**) (2.37 g, 68%) from (**9k**) (2.00 g) and acid (5 ml), very deliquescent off-white crystals, m.p. 147—148 °C (from methanol); $\lambda_{max.}$(MeOH) 225 and 307 nm (log ε 4.19 and 4.11); $\nu_{max.}$(Nujol) *ca.* 2 900v br, 1 580, 1 230, and 1 150 cm^{-1}; δ(D_2O) 9.16 (1 H, d, *J* 0.5 Hz, py 2-H), 8.91 (1 H, d, *J* 5.5 Hz, py 6-H), 8.85 (1 H, m, py 4-H), 8.23 (1 H, m, py 5-H), 8.06 (1 H, s, 5-H), and 3.60 and 3.56 (6 H, 2 s, N^+Me_2) (Found: C, 28.2; H, 3.4; N, 6.7; S, 30.1. $C_{10}H_{14}N_2O_8S_4$ requires C, 28.7; H, 3.4; N, 6.7; S, 30.65%).

2-(*Bromoacetyl*)*quinoxalinium Bromide*.—A solution of bromine (1.86 g) in acetic acid (3 ml) was added to a solution of 2-acetylquinoxaline (2.00 g) in acetic acid. The mixture was heated on a steam-bath for 10 min, then cooled to 0 °C. Filtration afforded the *title bromide* (3.30 g, 85%) as greenish needles, m.p. 141—146 °C (decomp.) which was used in the next stage without further purification.

Recrystallisation from ethanol (charcoal) afforded 2-*bromoacetylquinoxaline* as off-white plates, m.p. 113—117 °C; $\nu_{max.}$(Nujol) 1 700, 990, 950, 760, and 670 cm^{-1}; δ($CDCl_3$) 9.34 (1 H, s, 3-H), 8.05 (2 H, m, ArH), 7.87 (2 H, m, ArH), and 4.78 (2 H, s, CH_2); *m/z* (c.i.m.s.) 253 and 251 (MH^+, 8.8%), and 173 (100) (Found: C, 48.0; H, 2.7; N, 11.2; Br, 31.6. $C_{10}H_7BrN_2O$ requires C, 47.85; H, 2.8; N, 11.15; Br, 31.8%).

2-*Oxo*-2-(*quinoxalin*-2-*yl*)*ethyl* NN-*Dimethyldithiocarbamate* (**8n**).—Treatment of a solution of sodium dimethyldithiocarbamate dihydrate (4.6 g) in hot ethanol (15 ml) with 2-(bromoacetyl)quinoxaline hydrobromide (2.70 g) as described above for the pyridine analogue (**8j**) gave a dark brown product which was purified by passage through a short silica column [eluant dichloromethane–ethyl acetate (10:1)] and recrystallised from ethanol to give the *dithiocarbamate* (**8n**) (1.58 g, 67%) as orange crystals, m.p. 157—159 °C; $\nu_{max.}$(Nujol) 1 710, 955, and 770 cm^{-1}; δ($CDCl_3$) 9.47 (1 H, s, quin 3-H), 8.20 (2 H, m, ArH), 7.87 (2 H, m, ArH), 5.09 (2 H, s, CH_2), and 3.41 and 3.45 (6 H, 2 s, NMe_2); *m/z* (c.i.m.s.) 292 (MH^+, 7%), 258 (28) 228 (11), 173 (99), 155 (58), and 90 (100) (Found: C, 53.3; H, 4.5; N, 14.3; S, 22.3. $C_{13}H_{13}N_3OS_2$ requires C, 53.6; H, 4.5; N, 14.4; S, 22.0%).

Cyclisation of the dithiocarbamate (**8n**) (1.00 g) with conc. sulphuric acid (3 ml) as described above gave 2-NN-*dimethylamino*)-4-(*quinoxalin*-2-*yl*)-1,3-*dithiolium hydrogen sulphate* [NN-*dimethyl*-4-(*quinoxalin*-2-*yl*)-2H-1,3-*dithiol*-2-*iminium hydrogen sulphate*] (**9o**) (1.03 g, 81%) as buff needles, m.p. 302—303 °C (from methanol) $\lambda_{max.}$(MeOH) 249, 300, 346, and 362 nm (log ε 4.42, 4.21, 4.32, and 4.28); $\nu_{max.}$(Nujol) 1 590, 1 360, 1 330, 1 040, 835, and 780 cm^{-1}; δ[$(CD_3)_2SO$] 9.69 (1 H, s, quin 3-H), 8.87 (1 H, s, 5-H), 8.19 (1 H, m, ArH), 8.10 (1 H, m, ArH), 7.95 (2 H, m, ArH), and 3.56 and 3.62 (6 H, 2 s, N^+Me_2) (Found: C, 41.7; H, 3.5; N, 11.25; S, 25.6. $C_{13}H_{13}N_3O_4S_3$ requires C, 42.0; H, 3.55; N, 11.3; S, 25.9%).

Generation and Alkylation of Sodium Ene-1,2-*dithiolates* (**10**).—The hydrolyses of the dithiolium salts were carried out as described above for the phenyl analogue. In each case a solution of sodium hydroxide (1.0 g) in methanol (10 ml) was added to a refluxing solution of the appropriate dithiolium salt in methanol, and alkylation was carried out with iodomethane (5 ml) at room temperature. The weight of salt, volume of methanol, reflux period, methylation period, and yield of bissulphide are given; (Z)-1,2-*bis*(*methylthio*)-1-(*pyridin*-2-*yl*)*ethylene* (**11p**) (0.389 g; 10 ml; 2 h; 1 h; 84%), yellow liquid, $\lambda_{max.}$(EtOH) 215, 236, 278, and 326 nm; $\nu_{max.}$(film) 2 930, 1 580, 1 530, 1 450, 1 420, 840, 770, and 665 cm^{-1}; δ($CDCl_3$) 8.56 (1 H, d, *J* 4 Hz, py 6-H), 7.72 (2 H, m, py 3- and 4-H), 7.67 (1 H, s, 2-H), 7.13 (1 H, t, *J* 4 Hz, py 5-H), 2.45 (3 H, s, SCH_3), and 2.16 (3 H, s, SCH_3); *m/z* 197 (M^+, 44%), 182 (100), 167 (23), 150 (81), 135 (42), 104 (43), and 78 (21) (Found: C, 54.85; H, 5.7; N, 7.1; S, 32.8%; M^+, 197.0335. $C_9H_{11}NS_2$ requires C, 54.8; H, 5.6; N, 7.1; S, 32.5%; *M*, 197.0333).

(Z)-1,2-*Bis*(*methylthio*)-1-(*pyridin*-3-*yl*)*ethylene* (**11q**) (0.374 g; 10 ml; 2 h; 30 min; 53%), pale yellow oil, $\lambda_{max.}$(EtOH) 226sh, 245sh, and 345 nm; $\nu_{max.}$(film) 2 920, 1 670, 1 575, 1 550, 1 415, 800, and 715 cm^{-1}; δ($CDCl_3$) 8.74 (1 H, d, *J* 0.5 Hz, py 2-H), 8.55 (1 H, m, py 6-H), 7.83 (1 H, d, *J* 8 Hz, py 4-H), 7.32 (1 H, m, py 5-H), 6.61 (1 H, s, 2-H), 2.44 (3 H, s, SCH_3), and 2.08 (3 H, s, SCH_3); *m/z* 197 (M^+, 100%), 182 (15), 167 (31), and 135 (39) (Found: M^+, 197.0329).

(Z)-1,2-*Bis*(*methylthio*)-1-(*quinoxalin*-2-*yl*)*ethylene* (**11r**) (0.173 g; 25 ml; 2 h; 1 h; 77%), orange oil, which slowly crystallised from hexane as orange–yellow crystals, m.p. 58—62 °C; $\lambda_{max.}$(EtOH) 216, 242, 293, and 388 nm; $\nu_{max.}$(film) 2 910, 1 510, 1 330, 1 015, 795, and 760 cm^{-1}; δ($CDCl_3$) 9.18 (1 H, s, quin 3-H), 8.10 (2 H, m, ArH), 7.94 (1 H, s, 2-H), 7.77 (2 H, m, ArH), 2.57 (3 H, s, SCH_3), and 2.28 (3 H, s, SCH_3); *m/z* 248 (M^+, 27%), 233 (100), 218 (10), 186 (27), 168 (13), 155 (41), and 129 (16) (Found: C, 58.1; H, 4.8; N, 11.4; S, 25.4%; M^+, 248.0446. $C_{12}H_{12}N_2S_2$ requires C, 58.0; H, 4.85; N, 11.3; S, 25.8%; *M*, 248.0442).

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