Heterocyclic Syntheses with Malonyl Chloride. Part 14.[1] A Direct Synthesis of 4,6-Dichloropyrimidines with 5-Benzyl or -Phenyl and 2-Thioalkyl or -Thiophenyl Substituents

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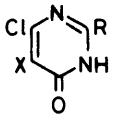
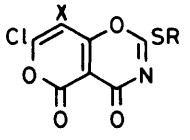
4,6-Dichloropyrimidines are formed direct from benzyl- and phenyl-malonyl chlorides with a variety of organic thiocyanates. Attempted extension to reaction of bromomalonyl chloride with thiocyanates yielded 2-alkylthio-8-bromo-7-chloropyrano[3,4-*e*][1,3]oxazine-4,5-diones.
Possible mechanisms for the two syntheses are discussed.

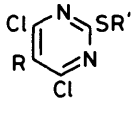
PYRIMIDINES bearing halogens in the active 2-, 4-, or 6-positions were not available by direct ring synthesis [2] until 1968 when we [3] and Bernatek [4] independently found that 2-substituted 4-chloro-6-pyrimidones (1a) were formed from malonyl chloride and certain nitriles. Stensrud and Bernatek extended the synthesis by using mono-substituted malonyl chlorides: these with nitriles at ordinary temperature afforded 2,5-disubstituted 4-chloro-6-pyrimidones (1b),[5] and with organic thiocyanates the 2-thio-substituted analogues (1c).[6] Meanwhile we had shown that at 100 °C thiocyanates behaved differently with malonyl chloride itself, affording the substituted bicyclic pyrano-oxazine products (2a).[7] It thus became pertinent to examine the behaviour of thiocyanates at elevated temperature with substituted malonyl chlorides. With phenyl- and benzyl-malonyl chlorides the reaction provides a new direct synthesis of 4,6-dichloropyrimidines (3).



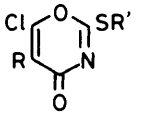
(1) a; X = H
b; X = R'
c; R = SR', X = R''
d; R = SCH_2Ph, X = CH_2Ph



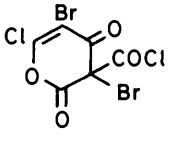
(2) a; X = H
b; X = Br
c; X = Br, R = CH_2Ph
d; X = Br, R = CH_2Cl
e; X = Br, R = Me
f; X = Br, R = Et



(3) a; R = R' = CH_2Ph
b; R = CH_2Ph, R' = Me
c; R = CH_2Ph, R' = CH_2Cl
d; R = H, R' = Me
e; R = Ph, R' = Me
f; R = Ph, R' = CH_2Cl
g; R = Ph, R' = Et
h; R = Ph, R' = CH_2Ph
i; R = R' = Ph



(4)



(5)

Initially it seemed that benzyl- and perhaps phenyl-malonyl chloride might react with thiocyanates under vigorous conditions to give disubstituted 6-chloro-1,3-oxazin-3-ones (4) by analogy with the behaviour of benzylmalonyl chloride with benzonitriles under similar conditions.[8,9] However, interaction of benzylmalonyl chloride with benzyl thiocyanate at 100 °C gave a crystalline compound $C_{18}H_{14}Cl_2N_2S$, the elementary composition of which at once excluded an oxazinone structure. The mass spectrum showed an even molecular ion (P^+) at *m/z* 360, in agreement with an even number of constituent nitrogen atoms, together with $(P + 2)^+$ and $(P + 4)^+$ isotopic ions with intensities relative to P^+ which confirmed the two chlorine atoms in the molecule. This information together with the maximum light absorption at 267 nm,[10] and the strong i.r. absorption at 1 530 cm^{-1},[11] all pointed to the compound being the 5-benzyl-2-benzylthio-4,6-dichloropyrimidine (3a). In similar reactions with benzylmalonyl chloride, methyl and chloromethyl thiocyanates gave products with molecular compositions and physical characteristics in agreement with their being the analogous 4,6-dichloropyrimidines (3b and c). ^{13}C N.m.r. examination confirmed the equivalence of the 4- and 6-carbon atoms of the ring by the line near δ 162 p.p.m. (see Table). For comparison, the ^{13}C n.m.r. spectrum of the known 4,6-dichloro-2-methylthiopyrimidine [12] (3d) was obtained under similar conditions.

Analogous 4,6-dichloropyrimidines (3e—i) were then prepared from phenylmalonyl chloride and a range of thiocyanates at elevated temperature. The product $C_{11}H_8Cl_2N_2S$ from methyl thiocyanate was shown to be the known 4,6-dichloro-2-methylthio-5-phenylpyrimidine (3e) [13] by comparison with an authentic specimen.

That 4,6-dichloropyrimidines (3) are obtained from benzyl- and phenyl-malonyl chloride with thiocyanates at elevated temperature was thus firmly established. This behaviour was in contrast to the reaction at ordinary temperature, reported [6] to yield 4-chloro-6-pyrimidones. Indeed, we repeated the reaction of benzyl

thiocyanate with benzylmalonyl chloride at 20 °C and confirmed the formation of 5-benzyl-2-benzylthio-4-chloro-6-pyrimidone (1d). Conceivably, then, this last product was an intermediate in our corresponding high temperature reaction. Hence we examined the possible conversion of the chloro-pyrimidone (1d) into the dichloropyrimidine (3a) by reagents present in the reaction mixture. However, the pyrimidone (1d) was recovered in high yield after being refluxed with an excess

TABLE

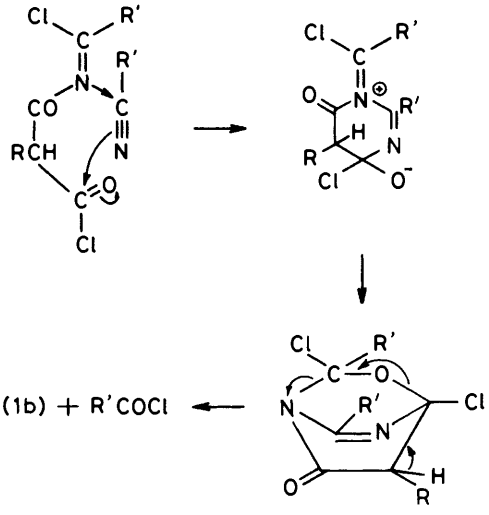
^{13}C N.m.r. shift data (δ) for the 4,6-dichloropyrimidines (3) from ^{1}H coupled and decoupled spectra, omitting benzene resonances

	Carbon				
Compd.	2	4,6	5	2-SMe (or -SCH_2)	5-CH_2
(3d)	174.6	161.4	115.7	14.5	
(3b)	171.0	161.9	136.4	14.1	34.7
(3c)	166.9	162.7	136.2	(44.8)	35.2
(3e)	171.8	160.9	128.2	14.5	
(3f)	167.5	161.3	129.3	(44.6)	
(3g)	171.8	160.9	128.0	(25.8) 14.0 (C-Me)	
(3h)	171.0	160.9	128.5	(35.6)	
(3i)	171.4	161.0	128.5		

of benzylmalonyl chloride in benzene (to give a correct temperature) or with thionyl chloride. Thionyl chloride was just possibly a contaminant of the benzylmalonyl chloride. In a third experiment, the pyrimidone (1d) was heated under reflux with an excess of *S*-ethyl chlorothioformate. This compound was chosen as being an available representative of the by-products known [6] to be formed in the interaction of benzylmalonyl chloride with thiocyanates at ambient temperature (*cf.* also ref. 3) Again, however, the pyrimidone (1d) was unchanged. We therefore conclude that 4-chloro-6-pyrimidones are not intermediates in the high-temperature reaction but that the 4,6-dichloro-pyrimidine products are formed by direct ring synthesis.

Mechanism.—In the original synthesis of 4-chloro-6-pyrimidones (1a) from malonyl chloride and nitriles, we demonstrated [3] that carbon atoms 4—6 were supplied by the malonyl chloride. One molecule of nitrile was obviously incorporated intact into the pyrimidine product, providing N-1, C-2, and the 2-side chain. The second nitrogen, N-3, was necessarily provided by a second nitrile molecule, the remainder of which was concomitantly converted into the corresponding acid chloride, an identified by-product.[3] In our new 4,6-dichloropyrimidine synthesis the ring atoms appear to have the same origins. The remaining problem is to suggest mechanisms whereby the malonyl chloride halogen atoms are not eliminated during the ring building process.

Acid chlorides can be expected to acylate nitriles and thiocyanates on nitrogen. Possible *S*-acylation in the second case does not provide useful subsequent pathways. Normally the *N*-acylation involves transfer of chloride (as a good leaving group), from the carbonyl carbon atom to the cyano-carbon, to give an acylation product RCO·N=C(Cl)R'. When the R group is a malonyl chloride residue, cyclisation to a chloropyridone can be expected, and may in fact occur.[3,14] To explain the formation of 4-chloro-6-pyrimidones (1a) we proposed the cyclisation of an initial diacylation product to an azapyrylium salt,[3] nucleophilic attack by chloride and ring opening, and re-closure then providing the chloropyrimidone (1a) and the acid chloride by-product. Bernatek *et al.*[6] suggested that when the malonyl chloride bore a bulky substituent, a first-formed monoacylation product interacted with a second molecule of nitrile or thiocyanate to yield through a tricyclic transition state, the observed pyrimidone and acid chloride end products. We disagree that the bulk of a malonyl substituent is necessary to direct the reaction to chloropyrimidones because malonyl chloride itself with acetonitrile yields the pyrimidone product and none of the possible chloropyridone.[3,4] Further, we suggest there is an alternative formulation of their pyrimidone synthesis, *via* a bicyclic intermediate, as in Scheme 1. The first intermediate is

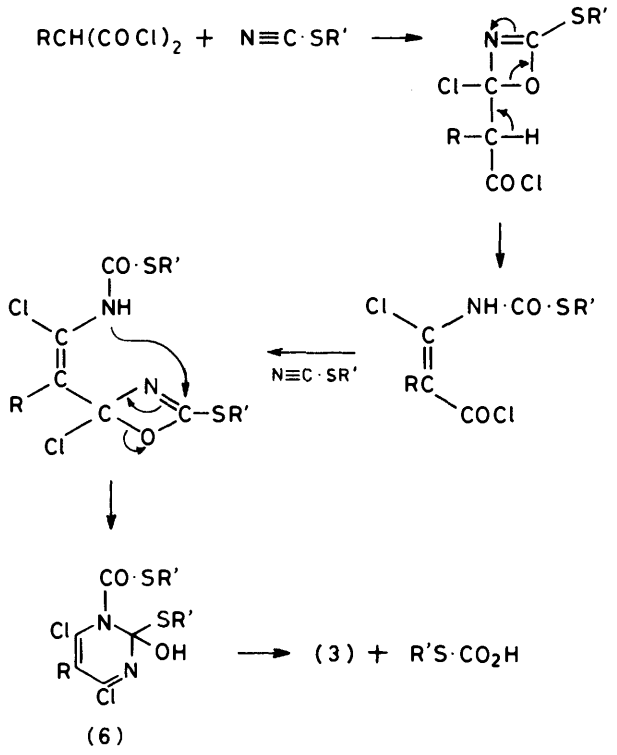


SCHEME 1

dipolar and so might well react further with itself, as indicated, rather than extrude chloride. This removes the requirement for a tricyclic transition state. However, irrespective of whether that is reasonable or not, Scheme 1 does suggest, in principle, how chlorine atoms in a malonyl chloride might be retained (at the bridgehead of a bicyclic system) whilst the oxygen atoms are eliminated.

Given that the vigorous conditions of the thiocyanate reaction could lead initially to a 4-membered ring monoacylation product, as in Scheme 2, then loss of the labile proton would result in ring opening with carbon–oxygen scission: the alternative loss of chloride would not relieve intense angle strain and so would be inhibited. Repetition of the acylation process and internal attack would lead *via* the intermediate (6) to 4,6-

dichloropyrimidine (3) together with a monothiocarbonate mono-ester as immediate by-product. A variety of fates would await the last in the hot reaction mixture.

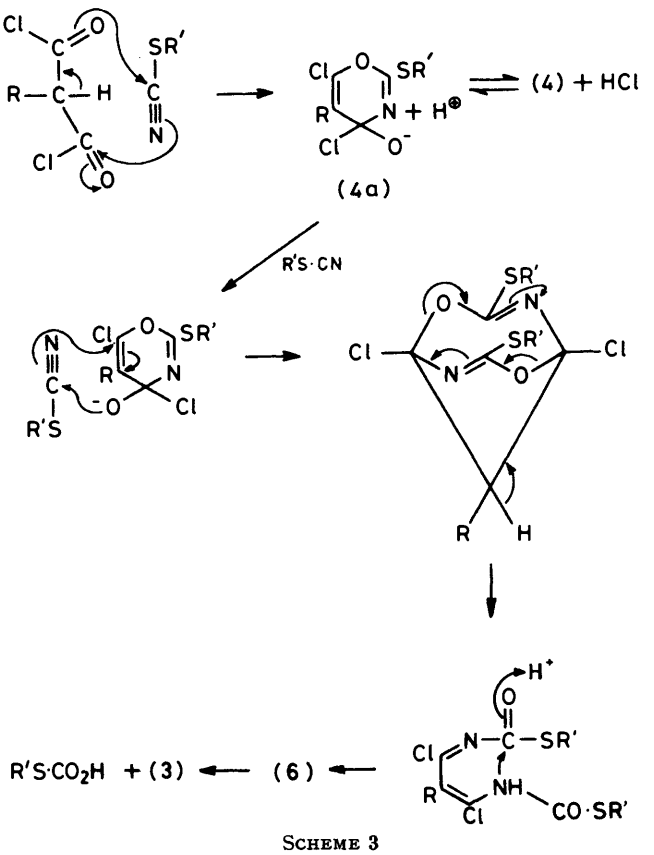


Scheme 2

An alternative possibility, shown in Scheme 3, is to assume that the reaction begins as for formation of an oxazinone (4), but that under the vigorous conditions an equilibrium is achieved between the oxazinone (4), chloride, and the first intermediate (4a). The resultant effective persistence of the last would then allow further reaction with thiocyanate, to provide dichloropyrimidine (3) plus the same by-product $R'S{\cdot}CO_2H$ as before. Whilst 1 : 2-proportions of a malonyl chloride and a thiocyanate would appear optimum for the formation of the dichloropyrimidine products, we found 1 : 1 proportions gave the best yields. This observation discourages us from here elaborating a further possible mechanism involving dimerisation of the nitrile function whilst the latter is acylated initially: the necessary two such steps would consume 4 proportions of thiocyanate.

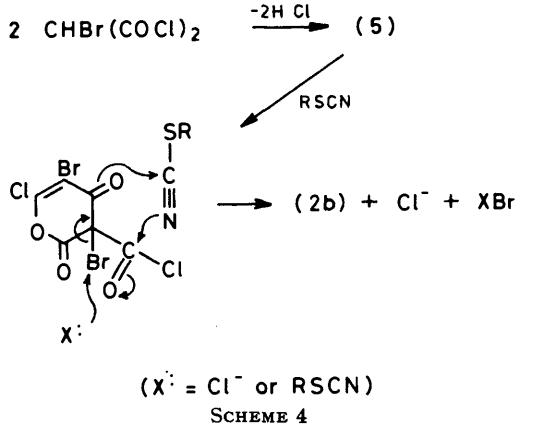
Reaction with Bromomalonyl Chloride.—In attempting to extend the new pyrimidine synthesis to the interaction of bromomalonyl chloride with thiocyanates, only bicyclic 2-alkylthio-8-bromo-7-chloropyrano[3,4-*e*][1,3]oxazine-4,5-diones (2b) were isolated. The u.v. spectra were similar, though bathochromically shifted, to those of the previously prepared 8-unsubstituted analogues (2a), whilst in the i.r. region, the new compounds showed the expected two high-frequency carbonyl bands.[7]

This formation of the compounds (2b) was unexpected for two reasons. Firstly the related chloromalonyl



Scheme 3

chloride had given the best yields of 4-chloro-6-pyrimidones in reaction with thiocyanates and with nitriles.[5,6] Secondly, the formation of an annelated pyrone was not expected from a *substituted* malonyl chloride. The induced self-condensation of bromomalonyl chloride



Scheme 4

would be expected to yield the bromo(chloro)chlorocarbonylpyrone (5). Evidently this latter undergoes 3-debromination either before the cyclisation with thiocyanate or concomitantly with that process. Chloride or thiocyanate could be responsible for abstraction of the (positive) bromine in question, and so the overall mechanism is presumably as shown in Scheme 4.

EXPERIMENTAL

U.v. ($CHCl_3$) and i.r. (Nujol) spectra were obtained with Pye Unicam SP 1800 and SP 200 spectrophotometers, respectively. ^1H and ^{13}C N.m.r. spectra were obtained using a Bruker WH 90 DS Fourier-transform instrument operating at 90 and 22.63 MHz respectively: solutions at 25 °C contained $SiMe_4$. Mass spectra were recorded with an AEI MS 12 instrument.

Reactions of Benzylmalonyl Chloride with Thiocyanates.—(i) Benzylmalonyl chloride [5] (4.62 g, 0.02 mol) was heated with benzyl thiocyanate [15] (2.98 g, 0.02 mol) at 100 °C until the evolution of gases ceased: atmospheric moisture was rigorously excluded. The solid was washed with a little cold dry ether and recrystallised several times from light petroleum (b.p. 40—60 °C) (charcoal) to give *5-benzyl-2-benzylthio-4,6-dichloropyrimidine* (3a) (1 g, 28%), m.p. 111—113 °C (Found: C, 60.0; H, 3.9; Cl, 19.5; N, 7.7; S, 8.8. $C_{18}H_{14}Cl_2N_2S$ requires C, 59.8; H, 3.9; Cl, 19.6; N, 7.75; S, 8.9%), *m/z* 364 [$(P + 4)^+$, 18%], 362 [$(P + 2)^+$, 64%], 360 (M^+); $\lambda_{max.}$ 267 nm (ε 25 000); $\nu_{max.}$ 1 730, 1 580w, 1 550w, and 1 530s cm^{-1}; δ[$(CD_3)_2CO$] 4.2 (s, CH_2). 4.4 (s, SCH_2), and 7.2—7.55 (m, 2 × Ph). (ii) Similarly from methylthiocyanate (1.46 g, 0.02 mol), *5-benzyl-4,6-dichloro-2-methylthiopyrimidine* (3b) (0.7 g, 24%) was obtained, m.p. 72 °C (Found: C, 50.5; H, 3.6; Cl, 24.85; N, 9.7; S, 11.1. $C_{12}H_{10}Cl_2N_2S$ requires C, 50.5; H, 3.5; Cl, 24.9; N, 9.8; S, 11.2%), $\lambda_{max.}$ 266 nm (ε 25 500); $\nu_{max.}$ 1 740, 1 592w, and 1 540s cm^{-1}. (iii) Chloromethyl thiocyanate (2.15 g, 0.02 mol) at 140 °C similarly gave *5-benzyl-4,6-dichloro-2-chloromethylthiopyrimidine* (3c) (0.7 g, 21%), m.p. 107—108 °C (Found: C, 45.9; H, 2.8; Cl, 32.7; N, 8.55; S, 9.9. $C_{12}H_9Cl_3N_2S$ requires C, 45.1; H, 2.8; Cl, 33.3; N, 8.8; S, 10.0%), *m/z* 324 $(P + 6)^+$, 322 $(P + 4)^+$, 320 $(P + 2)^+$, 318 (M^+); $\lambda_{max.}$ 259 nm (ε 22 800); $\nu_{max.}$ 1 740, 1 590w, 1 560w, and 1 540s cm^{-1}; δ($CDCl_3$) 4.22 (s, CH_2), 5.2 (s, SCH_2Cl), and 7.26 (Ph).

Reactions of Phenylmalonyl Chloride with Thiocyanates.—(a) A mixture of phenylmalonyl chloride [5] (4.34 g, 0.02 mol) and methyl thiocyanate (1.46 g, 0.02 mol), protected from moisture, was slowly heated to 150 °C and kept at that temperature until gas evolution ceased. Trituration of the cold product with heptane and recrystallisation (heptane–charcoal) gave yellow 4,6-dichloro-2-methylthio-5-phenylpyrimidine (3e) (0.6 g, 22%), m.p. 107—109 °C (Found: C, 48.7; H, 3.0; Cl, 26.1; N, 10.2. Calc. for $C_{11}H_8Cl_2N_2S$: C, 48.7; H, 3.0; Cl, 26.15; N, 10.3%), $\lambda_{max.}$ 268 nm (ε 25 300); $\nu_{max.}$ 1 600w, 1 560s, and 1 540sh cm^{-1}; δ [$(CD_3)_2CO$] 2.62 (s, SMe) and 7.33—7.66 (m, Ph), identical with an authentic sample (Aldrich Co.).

(b) From the appropriate thiocyanates, the following *4,6-dichloro-5-phenylpyrimidines* were similarly obtained: (i) at 160 °C, *2-chloromethylthio-* (3f) (0.4 g, 13%), m.p. 104—106 °C (Found: C, 43.2; H, 2.3; Cl, 34.7; N, 9.2; S, 10.3. $C_{11}H_7Cl_3N_2S$ requires C, 43.2; H, 2.3; Cl, 34.8; N, 9.2; S, 10.5%), $\lambda_{max.}$ 262 nm (ε 20 600); $\nu_{max.}$ 1 600w and 1 550s cm^{-1}; (ii) at 170 °C, *2-ethylthio-* (3g) (0.4 g, 14%), m.p. 99—101 °C (Found: C, 50.45; H, 3.5; Cl, 24.8; N, 9.9. $C_{12}H_{10}Cl_2N_2S$ requires C, 50.5; H, 3.5; Cl, 24.9; N, 9.8%), $\lambda_{max.}$ 270 nm (ε 26 900); $\nu_{max.}$ 1 600 and 1 560s cm^{-1}; (iii) at 150 °C, 2-benzylthio- (3h) (0.45 g, 13%), m.p. 127—129 °C (Found: C, 58.9; H, 3.6; N, 8.1. $C_{17}H_{12}Cl_2N_2S$ requires C, 58.8; H, 3.5; N, 8.1%), $\lambda_{max.}$ 270 nm (ε 24 300); $\nu_{max.}$ 1 600w, 1 550s, 1 540sh, and 1 500sh cm^{-1}; (iv) at 130 °C, *2-phenylthio-*(3i) (1 g, 30%), m.p. 108—110 °C [by extraction into heptane, evaporation, and crystallisation from light petroleum (b.p. 40—60 °C)–charcoal] (Found: C, 58.05; H, 3.2; N, 8.4; S, 9.3. $C_{16}H_{10}Cl_2N_2S$ requires C, 57.7; H, 3.0; N, 8.4; S, 9.6%), $\lambda_{max.}$ 270 nm (ε 20 300), $\nu_{max.}$ 1 600w, 1 550s, and 1 540sh cm^{-1}.

5-Benzyl-2-benzylthio-4-chloro-6-pyrimidone [6] (1d).—(a) *Preparation.* During 6 days a mixture of benzylmalonyl chloride (1 mol equiv.) and benzyl thiocyanate (2 mol equiv.), protected from atmospheric moisture, gave a crude solid. This was washed with and recrystallised from acetic acid to give the product, m.p. 205—206 °C, $\nu_{max.}$ 1 650s, 1 600w, 1 580w, and 1 550s cm^{-1}.

(b) *Attempted conversion into the 4,6-dichloro-pyrimidine.* The pyrimidone (1d) (0.5 g, portions) was recovered, m.p. and mixed m.p. 205—206 °C, $\nu_{max.}$ unchanged, by evaporation, washing of the residue with dry ether, and recrystallisation (acetic acid), after being refluxed (i) for 4 h with an excess of benzylmalonyl chloride in benzene, (ii) for 3 h with an excess of thionyl chloride, and (iii) for 4 h with an excess of *S*-ethyl chlorothioformate (Fluka).

Reaction of Bromomalonyl Chloride with Thiocyanates.—(a) Benzyl thiocyanate (2.98 g, 0.02 mol) was heated with bromomalonyl chloride [16] (4.38 g, 0.02 mol) at 120—130 °C with rigid exclusion of moisture until gas evolution ceased. Next day, the dark product was repeatedly crystallised (CCl_4–charcoal) to give yellow *2-benzylthio-8-bromo-7-chloropyrano*[3,4-e][1,3]*oxazine-4,5-dione* (2c) (0.3 g), m.p. 190 °C (Found: C, 41.9; H, 1.7; Br, 19.8; Cl, 8.95; N, 3.4; S, 7.9. $C_{14}H_7BrClNO_4S$ requires C, 42.0; H, 1.8; Br, 19.9; Cl, 8.85; N, 3.5; S, 8.0%), $\lambda_{max.}$ 270, 294, 304, 355, and 364 nm (ε × 10^{-3} 8.6, 10, 9.4, 20 and 20.2 respectively), $\nu_{max.}$ 1 775, 1 720s, 1 570s, 1 530, and 1 500s cm^{-1}; δ($CDCl_3$) 4.4 (s, CH_2) and 7.35 (Ph).

(b) Chloromethyl thiocyanate (3.21 g) with bromomalonyl chloride (6.57 g) similarly afforded yellow needles, m.p. 159—161 °C, of the *2-chloromethylthio-analogue* (2d) (0.7 g, 13%) (Found: C, 26.8; H, 0.5; Br, 22.45; Cl, 19.55; N, 4.0; S, 8.8. $C_8H_2BrCl_2NO_4S$ requires C, 26.8; H, 0.6; Br, 22.3; Cl, 19.75; N, 3.9; S, 8.9%), $\lambda_{max.}$ 268, 291, 301, 351, and 360 nm (ε × 10^{-3} 10, 9.9, 8.49, 16.17, and 15.29 respectively); δ[$(CD_3)_2CO$] 5.46 (s, CH_2).

(c) Methyl thiocyanate (1.74 g, 0.02 mol) was similarly treated at 100 °C. The crude product was washed with a little cold dry ether. Repeated crystallisation [light petroleum (b.p. 80—100 °C)–charcoal] gave pale yellow leaflets, m.p. 178—180 °C, of the *2-methylthio-analogue* (2e) (0.46 g, 14.1%) (Found: C, 29.7; H, 0.85; Br, 24.5; Cl, 11.0; N, 4.4; S, 10.0. $C_8H_3BrClNO_4S$ requires C, 29.6; H, 0.9; Br, 24.6; Cl, 10.9; N, 4.3; S, 9.9%), $\lambda_{max.}$ 270, 294, 304, 355, and 364 nm (ε × 10^{-3} 8.4, 9.24, 9.03, 18, and 18 respectively); δ($CDCl_3$) 2.64 (s, Me).

(d) At 120 °C, but otherwise as in (c), ethyl thiocyanate gave the *2-ethylthio-analogue* (2f) (0.35 g, 10.3%) as fine yellow needles (from CCl_4–charcoal), m.p. 140 °C (Found: C, 31.8; H, 1.35; Br, 23.7; Cl, 10.5; N, 4.1; S, 9.6. $C_9H_5BrClNO_4S$ requires C, 31.9; H, 1.5; Br, 23.6; Cl, 10.5; N, 4.1; S, 9.5%), $\lambda_{max.}$ 271, 295, 304, 355, and 364 nm (ε × 10^{-3} 9.5, 10.3, 10.2, 20.4, and 20.7 respectively); $\nu_{max.}$ 1 780sh, 1 740s, 1 570, and 1 520sh cm^{-1}; δ($CDCl_3$) 1.46 (t, Me, *J* 6 Hz) and 2.24 (q, CH_2).

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