Synthesis of Thiazolidinones from 1,4-Dithiocyanatobut-2-enes and their Use as Masked 2-Amino-1-Mercaptobut-3-enes

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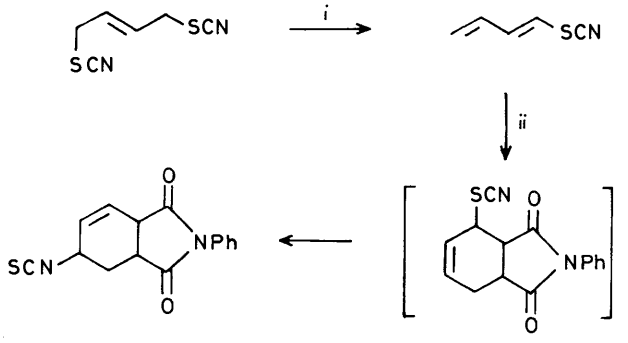
1,4-Dithiocyanatobut-2-enes can be readily prepared from either the appropriate buta-1,3-diene or 1,4-dihalogenobut-2-ene, and give, on heating in methanol, thiazolidinones *via* [3,3]-sigmatropic rearrangement. The initial products of this rearrangement, vicinal isothiocyanatothiocyanates, can be trapped with other nucleophiles: in benzene, amines react to afford dihydrothiazoles. The thiazolidinones are readily transformed to 2-amino-1-mercaptobut-3-enes, the corresponding carbamate esters and to the analogous disulphides. Reaction of these aminothiols with aldehydes and ketones, and with methyl bromoacetate afford respectively thiazolidines and thiomorpholinones.

Allylic thiocyanates undergo [3,3]-sigmatropic rearrangement at 60 °C to give allylic isothiocyanates. Following early studies[1] which indicated the generality of the rearrangement, later mechanistic studies[2] suggested that equilibration of the respective thiocyanate and isothiocyanate occurred *via* a concerted process. Recently the elimination of thiocyanic acid from a 1,4-dithiocyanatobut-2-ene has been described[3] under conditions which do not lead to prior rearrangement of the thiocyanate to an isothiocyanate. Instead the elimination product, a 1-thiocyanatobuta-1,3-diene, can undergo Diels Alder reactions to give adducts which are allylic thiocyanates. These allylic thiocyanates, under the conditions of the Diels Alder addition, then undergo rearrangement to give allylic isothiocyanates as the final products of this reaction sequence (Scheme 1). It



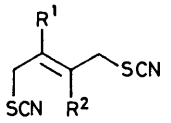
Scheme 1. *Reagents:* i, DBU; ii, *N*-Phenylmaleimide

occurred to us that 1,4-dithiocyanatobut-2-enes might *via* [3,3]-sigmatropic rearrangement by a source of allylic isothiocyanates. Such allylic isothiocyanates (Scheme 2) would be vicinal isothiocyanatothiocyanates, a category of compound known[4] to be useful in the construction of heterocyclic systems. We have previously described[5] our preliminary results, which establish that 1,4-dithiocyanatobut-2-enes undergo the desired [3,3]-sigmatropic rearrangement in preference to elimination and can be used as precursors in the synthesis of thiazolidinones and dihydrothiazoles. In this paper we describe the preparation of a number of 1,4-dithiocyanatobut-2-enes and their use in synthesis based on the trapping of the allylic isothiocyanates produced by thermal rearrangement. A feature of these studies is the synthesis of thiazolidinones, which act as masked 2-amino-1-mercaptobut-3-enes.

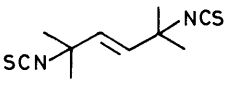
Two routes are available for the synthesis of 1,4-dithiocyanatobut-2-enes, nucleophilic attack of thiocyanate anion on a 1,4-dihalogenobut-2-ene or additon of thiocyanogen to a buta-1,3-diene. 1,4-Dithiocyanatobut-2-ene (**1**) has been prepared by reaction of 1,4-dichlorobut-2-ene with potassium thiocyanate[6] in aqueous ethanol and by reaction of 1,4-dibromobut-2-ene with ammonium thiocyanate[7] in ethanol. This procedure has not been applied generally to the synthesis of other dithiocyanates. The addition of thiocyanogen to alkenes and to dienes has been more studied[8] with reaction to give vicinal dithiocyanates from alkenes possible both by homolytic[9] or heterolytic[10] addition. Addition of thiocyanogen to buta-1,3-diene,[11] isoprene[12] and 2,3-dimethylbuta-1,3-diene[12] is known to give in each case preferentially the 1,4-adducts. A difficulty in such additions is the avoidance of polymerisation of the thiocyanogen, which severely interferes with the isolation of the foul smelling unstable adducts. A number of procedures are described in the older literature to attempt to overcome this problem in which metal thiocyanates are oxidized by a variety of oxidants, and the freshly prepared thiocyanogen is reacted directly with the desired alkene or diene. Such methods have been used extensively by the group of Cambie.[4] An alternative procedure was envisaged of *in situ* electrogeneration of thiocyanogen from thiocyanate ion. Such electrogeneration has been studied[13] and used both in the thiocyanation of alkenes[14,15] and of buta-1,3-diene.[15,16]

We have investigated a number of the above procedures and find (see the Experimental section) that pure 1,4-dithiocyanatobut-2-ene (**1**) is easily prepared, albeit in modest yield by addition of thiocyanogen prepared from sodium thiocyanate and bromine in glacial acetic acid. A solution of 1,4-dithiocyanatobut-2-ene (**1**) in alcoholic solvents is obtained in high yield by reaction of 1,4-dichlorobut-2-ene with potassium thiocyanate.

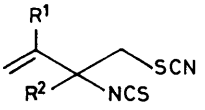
Similarly we find that 2-methyl-1,4-dithiocyanatobut-2-ene (**2**) can be easily isolated in pure conditon by reaction of isoprene with thiocyanogen prepared from sodium thiocyanate and bromine in acetic acid. More conveniently, by prior addition of bromine to isoprene to give a mixture of dibromides and reaction of this mixture with sodium thiocyanate in alcoholic solvents, useful synthetic transformations (*vide infra*) are possible without isolation of the major product 2-methyl-1,4-dithiocyanatobut-2-ene (**2**). From 2,3-dimethylbuta-1,3-diene, either the solid 2,3-dimethyl-1,4-dithiocyanatobut-2-ene (**3**) can be obtained from acetic acid, or alcoholic solutions may be generated by nucleophilic displacement from the mixture of dibromo adducts of 2,3-dimethylbuta-1,3-diene. However, in this case, the direct addition to 2,3-dimethylbutadiene of the thiocyanogen generated *in situ* is the preferable procedure. A further limitation in the efficiency of a general synthesis of 1,4-



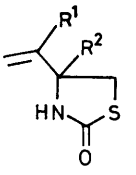
(1) $R^1 = R^2 = H$
(2) R^1 = Me, R^2 = H
(3) $R^1 = R^2$ = Me



(4)



(5) $R^1 = R^2 = H$
(6) R^1 = Me, R^2 = H
(7) R^1 = H, R^2 = Me
(8) $R^1 = R^2$ = Me



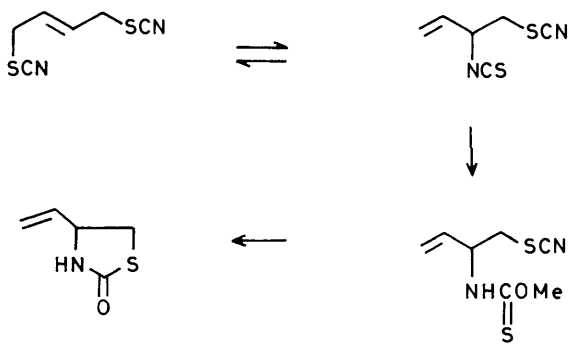
(9) $R^1 = R^2 = H$
(10) R^1 = Me, R^2 = H
(11) R^1 = H, R^2 = Me
(12) $R^1 = R^2$ = Me

dithiocyanatobut-2-enes is exposed by the attempted addition to 2,5-dimethylhexa-2,4-diene. Here equilibration afforded the di-isothiocyanate (**4**) as the only isolated product.

The dithiocyanates (**1**)—(**3**) are stable for weeks when stored at 0 °C in the solid state under nitrogen. In solution they are stable at low temperatures but if they are heated in benzene at 60 °C their rearrangement to isothiocyanates is easily monitored by the growth of the absorption peak at 2 060 cm^{-1} associated with the isothiocyanate functionality. Previous studies [2] with allylic monothiocyanates suggests that rearrangement occurs by a [3,3]-sigmatropic process and is not a heterolytic, or even a homolytic cleavage leading to equilibration of thiocyanates with isothiocyanates. These previous studies indicate that such heterolytic cleavages are more favoured with secondary or tertiary thiocyanates. Again on the basis of this earlier work,[2] isomerisation between the dithiocyanates (**1**)—(**3**) and the corresponding products of sigmatropic rearrangement, the vicinal isothiocyanatothiocyanates (**5**)—(**8**), is expected to be an equilibration. Rates of equilibration by sigmatropic rearrangement will not be affected markedly by solvent effects. In agreement with this analysis we find that the dithiocyanate (**1**), when heated in methanol, gives the thiazolidinone (**9**) in 86% yield. Similarly the dithiocyanates (**2**) and (**3**) give the respective thiazolidinones (**10**) and (**12**) in 95% and 42% yield.

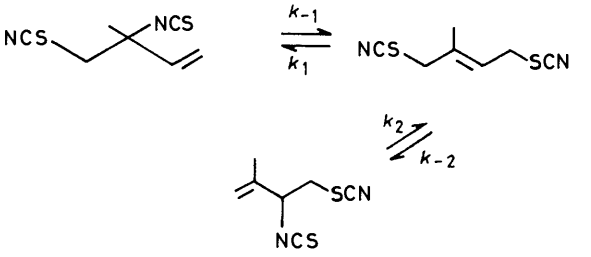
The thiazolidinones (**9**), (**10**), and (**12**) can be prepared most conveniently by reaction of dichloro or dibromo adducts of buta-1,3-diene and isoprene, with potassium thiocyanate in methanol. Initial reaction at room temperature affords the appropriate dithiocyanate which, in subsequent reaction at a higher temperature, affords the thiazolidinone *via* the intermediate isothiocyanatothiocyanate. The likely mechanism of formation of the thiazolidinones based on the recent precedents of Cambie *et al.*[4] is shown in Scheme 2. In the isoprene series two possible thiazolidinones (**10**) and (**11**) can be formed; we have been unable to observe the second thiazolidinone (**11**).

The specificity to give only the thiazolidinone (**10**) might be attributed to either a selectivity in the sigmatropic rearrangement to give preferentially the isothiocyanatothiocyanate (**6**), or an equilibration between the two possible isothiocyanatothiocyanates (**6**) and (**7**) which leads only to the thiazolidinone (**10**) by the preferential trapping of the isothiocyanatothiocyanate (**6**). We prefer the latter explanation of the selectivity for a number of reasons.



Scheme 2.

Although the chemistry of [3,3]-sigmatropic rearrangements has been extensively reviewed [17] there are few precedents upon which the relative rates in Scheme 3 might be predicted. From

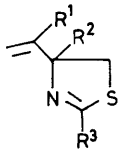


Scheme 3.

the theoretical analysis of Carpenter,[18] whilst the relative rates k_1 and k_2 might be judged to be comparable, it is to be expected that k_{-1} will be substantially greater than k_{-2}. Hence, overall, the isomer (**6**) might be favoured at equilibrium. Recent experimental data [19] concerning the influence of methyl substitution on the rate of [3,3]-sigmatropic processes are consistent with the Carpenter analysis, although other experimental results [20] conflict with the simple Carpenter analysis and suggest limitations to this model. The most pertinent experimental results concern the influence of methyl substituents on the rate of rearrangement of allyl thiocyanates. 2-Methylallyl thiocyanate [21] isomerizes to an isothiocyanate slightly faster than allyl thiocyanate, and it has been shown [2] that 3-methyl substitution in allyl thiocyanate leads to only modest rate enhancement for the [3,3]-sigmatropic rearrangement. Hence, from these results a marked preference for rearrangement of thiocyanate (**2**) to give the isothiocyanate (**6**) would be unexpected.

Two separate observations indicate that the preferential formation of the thiazolidinone is due to the preferential trapping of the less hindered isothiocyanate (**6**). In the buta-1,3-diene series we find that when reaction is conducted in different alcoholic solvents the nature of the solvent markedly determines the yield of the thiazolidinone (**9**). The yield diminishes through the series methanol, ethanol, isopropyl alcohol, and t-butyl alcohol. Our failure to observe reaction intermediates other than isothiocyanates suggests that the slow step in Scheme 3 is the trapping of the isothiocyanates. This view is reinforced by the observation that isolation of the thiazolidinone (**12**) from 2,3-dimethyl-1,4-dithiocyanatobut-2-ene requires substantially longer reaction times than for isolation of the thiazolidinones (**9**) and (**10**). Again, as intermediates other than isothiocyanates are not observed, it is concluded that the rate determining step is the trapping of the isothiocyanate. Hence, in preferential formation of the thiazolidinone (**10**) the selectivity is attributed to the favoured trapping of the less hindered isothiocyanate (**6**).

Cambie *et al.*[4] have shown that vicinal isothiocyanatothiocyanates may be treated with a variety of nucleophiles to give heterocyclic systems. The ability to trap the isothiocyanates (**5**), (**6**), and (**8**) with amines in benzene to give dihydrothiazoles is established by the results in the Table. Two points may be

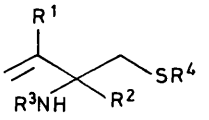


(**13**) $R^1 = R^2 = H$, $R^3 = NHPh$
(**14**) $R^1 = Me$, $R^2 = H$, $R^3 = NHPh$
(**15**) $R^1 = H$, $R^2 = Me$, $R^3 = NHPh$
(**16**) $R^1 = R^2 = Me$, $R^3 = NHPh$
(**17**) $R^1 = R^2 = H$, $R^3 = p\text{-}MeOC_6H_4NH$
(**18**) $R^1 = Me$, $R^2 = H$, $R^3 = p\text{-}MeOC_6H_4NH$
(**19**) $R^1 = R^2 = Me$, $R^3 = p\text{-}MeOC_6H_4NH$
(**20**) $R^1 = R^2 = H$, $R^3 = NMePh$
(**21**) $R^1 = Me$, $R^2 = H$, $R^3 = NMePh$
(**22**) $R^1 = R^2 = Me$, $R^3 = NMePh$
(**23**) $R^1 = Me$, $R^2 = H$, $R^3 = NAcPh$
(**24**) $R^1 = Me$, $R^2 = H$, $R^3 = NBzPh$

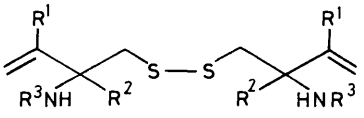
noted which reinforce the above comments. The trapping of the more sterically hindered isothiocyanate (**8**) is markedly less efficient. Secondly, the trapping of the isothiocyanate (**6**) is efficient; no product such as (**15**) is observed from the alternative more hindered isothiocyanate (**7**). It is of interest that, in agreement with the literature, the preferred tautomer is in each case that shown in the Table. In no case were other tautomers observed. The dihydrothiazole (**14**) was further characterized as the acetyl and benzoyl derivatives (**23**) and (**24**).

Thiazolidinones on hydrolysis can afford vicinal aminothiols. Although such aminothiols,[22] formally the adducts of simple alkenes, or their derivatives,[23] can be prepared by a variety of well established methods, in the case of those aminothiols, formally the adducts of conjugated dienes, no preparative procedures have been reported. Hence solvolytic cleavage of the thiazolidinones (**9**) offers a useful regiocontrolled route to 2-amino-1-mercaptobut-3-enes and their derivatives.

Hydrolysis of the thiazolidinones (**9**), (**10**), and (**12**) in aqueous potassium hydroxide under nitrogen affords the aminothiols (**25**)—(**27**). In the presence of air the corresponding disulphides (**34**) and (**35**) are formed as by-products and on standing in air the aminothiols are readily converted to the disulphides. In the case of the disulphides (**34**) and (**35**) mixtures of the (±)- and *meso*-diastereoisomers are obtained; although chromatography gave homogeneous fractions, extra signals were observed in the ^{13}C n.m.r. spectra of the disulphides (**34**) and (**35**), thus indicating formation of a diastereoisomeric mixture. The aminothiol (**25**) was further characterized as the diacetyl derivative (**28**) and the dibenzoyl derivative (**31**), and the aminothiols (**26**) and (**27**) were further characterized as their respective diacetyl derivatives (**29**) and (**30**).



(**25**) $R^1 = R^2 = R^3 = R^4 = H$
(**26**) $R^1 = Me$, $R^2 = R^3 = R^4 = H$
(**27**) $R^1 = R^2 = Me$, $R^3 = R^4 = H$
(**28**) $R^1 = R^2 = H$, $R^3 = R^4 = Ac$
(**29**) $R^1 = Me$, $R^2 = H$, $R^3 = R^4 = Ac$
(**30**) $R^1 = R^2 = Me$, $R^3 = R^4 = Ac$
(**31**) $R^1 = R^2 = H$, $R^3 = R^4 = PhCO$
(**32**) $R^1 = R^2 = R^4 = H$, $R^3 = CO_2Me$
(**33**) $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = CO_2Me$



(**34**) $R^1 = R^2 = R^3 = H$
(**35**) $R^1 = Me$, $R^2 = R^3 = H$
(**36**) $R^1 = R^2 = H$, $R^3 = CO_2Me$
(**37**) $R^1 = Me$, $R^2 = H$, $R^3 = CO_2Me$

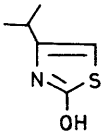
Cleavage of the thiazolidinones (**9**) and (**10**) in basic methanol afforded carbamate esters. The initially formed thiols (**32**) and (**33**) could be isolated directly or further oxidation afforded the disulphides (**36**) and (**37**), which again were recognized by ^{13}C n.m.r. to be mixtures of diastereoisomers. Although there is literature precedent[24] for the acid catalysed hydrolysis of thiazolidinones, such a method using hydrochloric acid in dioxane fails in the case of thiazolidinones (**9**) and (**10**). After attempted reaction, the thiazolidinone (**9**) is recovered un-

Table. Preparation of 4,5-dihydrothiazoles in benzene

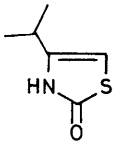
	Reactants	Product	Reflux time (h)	Yield (%)
(1)	Aniline	(**13**)	18	68
(2)	Aniline	(**14**)	24	86
(3)	Aniline	(**16**)	144	68
(1)	$p\text{-}MeOC_6H_4NH_2$	(**17**)	20	61
(2)	$p\text{-}MeOC_6H_4NH_2$	(**18**)	24	77
(3)	$p\text{-}MeOC_6H_4NH_2$	(**19**)	72	42
(1)	PhNHMe	(**20**)	24	52
(2)	PhNHMe	(**21**)	72	65
(3)	PhNHMe	(**22**)	144	40

changed, but under the same conditions the thiazolidinone (**10**) is converted by isomerization of the double bond to the thiazole (**38**). Although such thiazoles in the solid state can exist as the amide tautomer, in common with the normal behaviour,[25] in solution the product is considered to exist as the thiazole tautomer (**38a**) rather than the alternative form (**38b**).

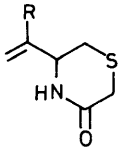
An important feature of the chemistry of vicinal aminothiols is their use in the synthesis of a variety of heterocyclic systems by reaction with biselectrophiles. The aminothiols (**25**) and (**26**) behave in the expected manner. Reaction with methyl bromoacetate affords the respective thiomorpholinones (**39**) and (**40**).



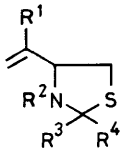
(**38a**)



(**38b**)



(**39**) R = H
(**40**) R = Me



(**41**) $R^1 = R^2 = H$, $R^3 = R^4 = Me$
(**42**) $R^1 = R^3 = R^4 = Me$, $R^2 = H$
(**43**) $R^1 = R^2 = H$, R^3R^4 = Ph, and H or H and Ph
(**44**) R^1 = Me, $R^2 = H$, R^3R^4 = Ph and H or H and Ph
(**45**) $R^1 = R^3 = R^4 = H$, $R^2 = Me$
(**46**) $R^1 = R^2 = Me$, $R^3 = R^4 = H$

Reaction with acetone affords the respective thiazolidines (**41**) and (**42**). Benzaldehyde with the aminothiol (**25**) gives an inseparable mixture of stereoisomeric thiazolidines (**43**) and similarly the aminothiol (**26**) gives the inseparable mixture (**44**). Formaldehyde reacts according to the recently described method[26] to give the *N*-methylthiazolidine (**45**) from the aminothiol (**25**) and the *N*-methylthiazolidine (**46**) from the aminothiol (**26**). Thus, this method offers a route to the unreported secondary amines 1-mercapto-2-*N*-methylaminobut-3-enes.

A number of valuable processes stem from the above [3,3]-sigmatropic rearrangement of the 1,4-dithiocyanatobut-2-enes. Their efficient trapping leads to thiazolidinones and dihydrothiazoles. The intermediate thiazolidinones may be used in a regiocontrolled synthesis of unsaturated aminothiols, and the latter may in turn be used as intermediates in the synthesis of a variety of heterocyclic systems.

Experimental

M.p.s. were determined in a capillary tube and are uncorrected. I.r. spectra were obtained using a Perkin-Elmer 157G grating spectrometer. ^1H and ^{13}C n.m.r. spectra were obtained using a Bruker 360 MHz spectrometer. Tetramethylsilane was used as internal standard and deuteriochloroform was used as the solvent unless otherwise stated. Mass spectra were obtained at 70 eV unless otherwise stated, using a Kratos MS-30 spectrometer equipped with a DS 505 Data System. Flash chromatography was carried out on Macherey Nagel silica gel 60. Organic solutions were dried over anhydrous magnesium sulphate and solvent evaporation was carried out at reduced pressure using a rotatory evaporator. Elemental analyses were performed at University College, London.

Synthesis of 1,4-*Dithiocyanatobut-2-enes.*—1,4-*Dithiocyanatobut-2-ene* (**1**). To a cold (0 °C) solution of potassium thiocyanate (11.64 g) in chloroform (300 ml) iodine (19.24 g) was added, and the solution was stirred at 0 °C for 2 h. A solution of buta-1,3-diene (3.24 g) in chloroform (100 ml) was then added and the solution was stirred at room temperature for 24 h. The solution was washed with sodium sulphite solution (10%) and then water, and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded a yellow crystalline residue. Recrystallization [ethyl acetate–light petroleum (b.p. 40—60 °C)] gave the title compound (**1**) as white crystals (2.55 g, 25%), m.p. 82—84 °C (lit.,[6,7] 82—84 °C); $\nu_{max.}$(Nujol) 2 160 cm^{-1}; δ_H (360 MHz) 3.61—3.65 (4 H, d *J* 6 Hz, $2CH_2$) and 5.95 (2 H, m, CH); δ_C (p.p.m.) 35.2 (CH_2), 111.5 (SCN), and 129.5 (CH); *m/z* 170 (M^+, 2%), 112 (72%), and 78 (100%).

Addition to buta-1,3-diene was achieved in glacial acetic acid using the following procedure. To a solution of sodium thiocyanate (36 g) in glacial acetic acid (335 ml) buta-1,3-diene (7 g) in glacial acetic acid (35 ml) was added. To the resulting vigorously stirred solution at 5 °C a solution of bromine (11 ml) in glacial acetic acid (65 ml) was slowly added dropwise over 15 min. The solution was set aside in a refrigerator at 0 °C for 18 h after which the resulting yellow precipitate was removed by filtration and washed with glacial acetic acid (50 ml). The washings and filtrate were combined and water (800 ml) added and the solution was basified by careful addition of solid sodium carbonate. The resulting yellow waxy precipitate was skimmed off, washed with cold water and dissolved in cold benzene (50 ml). The benzene solution was first filtered and the filtrate was slowly added with stirring to light petroleum (b.p. 40—60 °C) (100 ml). The yellow needle like crystals were obtained by filtration, and recrystallisation [ethyl acetate—light petroleum (b.p. 40—60 °C)] afforded 1,4-dithiocyanatobut-2-ene (**1**) (7.7 g 35% yield), m.p. 82—84 °C.

2-*Methyl*-1,4-*dithiocyanatobut*-2-*ene* (**2**). Iodine (12.9 g) was added to a cold (0 °C) solution of potassium thiocyanate (9.7 g) in chloroform (300 ml), and the solution was stirred at 0 °C for 2 h. Isoprene (3.4 g) was added and the solution stirred at room temperature for 20 h. The solution was washed successively with water, and sodium sulphite solution (10%) and water, and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded a brown oil. Flash chromatography [eluant ethyl acetate–light petroleum (1:3)] gave the title compound (**2**) as white crystals (1.28 g, 16%), m.p. 75—76 °C; $\nu_{max.}$(Nujol) 2 160 cm^{-1}; δ_H 1.90 (3 H, s, Me), 3.60 (2 H, s, CH_2), 3.70 (2 H, d, CH_2), and 5.75 (1 H, t, CH); δ_C 15.02 (Me), 31.36 (CH_2), 42.53 (CH_2), 111.14 (SCN), 114.41 (SCN), 124.13 (CH), and 136.78 (*C*Me); *m/z* 184 (M^+, 1%), 126 (40%), and 67 (100%).

In an alternative method isoprene (3.5 g) in glacial acetic acid (17.5 ml) was added to a solution of sodium thiocyanate (18 g) in glacial acetic acid (168 ml). To the resulting vigorously stirred solution at 5 °C a solution of bromine (5.5 ml) in glacial acetic acid (35 ml) was slowly added dropwise over 10 min. The solution was left in a refrigerator for 12 h after which the resulting yellow precipitate was removed by filtration and washed with glacial acetic acid (25 ml). The washings and filtrate were combined, water (300 ml) was added, and the solution basified by careful addition of solid sodium carbonate. The resulting yellow waxy precipitate was skimmed off, washed with cold water and dissolved in cold benzene (50 ml). The benzene solution was first filtered and the filtrate was slowly added, with stirring, to light petroleum (b.p. 40—60 °C) (100 ml). The pale yellow plate-like crystals which separated were isolated by filtration. Recrystallisation [benzene–light petrol-

eum (b.p. 40—60 °C)] afforded the title compound (**2**) (2 g, 21%) m.p. 75—76 °C.

2,3-*Dimethyl*-1,4-*dithiocyanatobut*-2-*ene* (**3**). 2,3-Dimethylbuta-1,3-diene (3 g) in glacial acetic acid (15 ml) was added to a cold (0 °C) solution of potassium thiocyanate (14.4 g) in glacial acetic acid (100 ml). To the resulting vigorously stirred solution at 5 °C, a solution of bromine (3.7 ml) in glacial acetic acid (22 ml) was added dropwise over 15 min. The solution was left in a refrigerator at 0 °C for 12 h after which the resulting precipitate was filtered off and washed successively with water, ethyl alcohol and then ether, and dissolved in hot benzene. This solution was filtered hot and, on cooling, afforded yellow needles. After filtration these needles were recrystallised (ethyl acetate) to afford the title compound (**3**) (1.6 g, 22%), m.p. 130—131 °C (lit.[12] m.p. 130—131 °C); $\nu_{max.}$(Nujol) 2 160 cm^{-1}; δ 1.95 (6 H, s, Me) and 3.70 (4 H, s, CH_2); *m/z* 198 (M^+, 0.3%), 140 (52%), and 126 (100%).

2,5-*Di-isothiocyanato*-2,5-*dimethylhex*-3-*ene* (**4**). 2,5-Dimethylhexa-2,4-diene (3.3 g) was added to a cold solution (0 °C) of potassium thiocyanate (5.8 g) and iodine (7.8 g) in chloroform (330 ml) which had been stirred for 2 h, and the solution was stirred in the dark for 24 h. After work up as described above and flash chromatography [eluant ethyl acetate–light petroleum (1:3)], a colourless oil (1.09 g) was isolated. Further chromatographic purification of this fraction afforded the *title compound* (**4**) as an unstable oil (700 mg, 10% yield); $\nu_{max.}$(neat) 2 980, 2 925, and 2 060 cm^{-1}; δ_H 1.35 (3 H, s, Me), 1.55 (3 H, s, Me), 1.7 (3 H, s, Me), 1.8 (3 H, s, Me), 4.46 (1 H, d, *CH*SCN), and 5.15 (1 H, d, *J* 7 Hz C=C*H*); δ_C 18.24 (Me), 22.27 (Me), 25.84 (Me), 26.00 (Me), 63.23 (CH), 90.90 (NCS), 118.22 (CH), and 140.92 (quaternary C); *m/z* 181 (100%), 127 (16%), and 69 (13%).

Synthesis of Thiazolidinones.—4-*Vinylthiazolidin*-2-*one* (**9**). 1,4-Dithiocyanatobut-2-ene (**1**) (0.2 g) was heated under reflux in ethanol (5 ml) for 18 h. The solvent was evaporated under reduced pressure and the yellow oily residue was chromatographed over silica gel. Elution with ethyl acetate–light petroleum (1:1) gave the *title compound* (**9**) as a colourless oil (114 mg, 76%). A sample was further purified by distillation (110 °C/0.1 mmHg) to give pure *title compound* (**9**) (Found: C, 46.1; H, 5.3; N, 10.7. C_5H_7NOS requires C, 46.5; H, 5.4; N, 10.85%); *m/z* 129 (3%) and 86 (100%); $\nu_{max.}$(neat) 3 240 and 1 680 cm^{-1}; δ_H 3.15 (1 H, q, *J* 11 and 7 Hz), 3.52 (1 H, q, *J* 11 and 7 Hz), 4.39 (1 H, q, *J* 7, 7 and 7 Hz), 5.17 (1 H, d, *J* 11 Hz), 5.35 (1 H, d, *J* 17 Hz), 5.58 (1 H, m, CH), and 7.00 (1 H, br, NH); δ_C 35.18 (CH_2), 57.67 (CH), 117.68 (CH_2), 135.96 (CH), and 175.59 (CO). The reaction was repeated in different solvents with the following results. At reflux in methanol 4-vinylthiazolidin-2-one (**9**) was obtained in 86% yield. At reflux in isopropyl alcohol a yield of 61% was obtained. At reflux in t-butyl alcohol a yield of 20% was obtained.

4-*Vinylthiazolidin*-2-*one* (**9**) *from* 1,4-*dichlorobut*-2-*ene*. 1,4-Dichlorobut-2-ene (6.25 g) was added to a solution of potassium thiocyanate (9.7 g) in aqueous methanol (90%, 100 ml) and the resulting solution was stirred at room temperature for 6 h. Potassium chloride was removed by filtration and the filtrate was heated under reflux for 26 h. Removal of methanol under reduced pressure gave a yellow oily residue. Flash chromatography [eluant ethyl acetate–light petroleum (1:1)] afforded compound (**9**).

4-*Isopropenylthiazolidin*-2-*one* (**10**). 2-Methyl-1,4-dithiocyanatobut-2-ene (**2**) (0.5 g) was heated under reflux in methanol (50 ml) for 20 h. Work up as described above and flash chromatography [eluant ethyl acetate–light petroleum (1:1)] gave a crystalline residue. Recrystallization (ethyl acetate–pentane) afforded the *title compound* (**10**) (370 mg, 95% yield), m.p. 91—92 °C (Found: C, 50.4; H, 6.4; N, 9.8; C_6H_9NOS requires C, 50.3; H, 6.3; N, 9.8%); *m/z* 102 (9%) and 100 (100%); $\nu_{max.}$($CHCl_3$), 3 300—3 200 and 1 680 cm^{-1}; δ_H 1.70 (3 H, s, Me), 3.18 (1 H, q, *J* 11 and 8 Hz), 3.48 (1 H, q, *J* 11 and 8 Hz), 4.38 (1 H, t, *J* 8 Hz, CHN), 4.95 (1 H, s, vinylic CH_2), 5.08 (1 H, s, vinylic CH_2), and 7.15 (1 H, br, NH); δ_C 17.91 (Me), 33.91 (CH_2), 60.22 (CH), 113.01 (CH_2), 142.54 (*C*Me), and 175.71 (CO).

4-*Isopropenylthiazolidin*-2-*one* (**10**) *from* 1,4-*dibromo*-2-*methylbut*-2-*ene*. Bromine (16 g) was added slowly to a solution of isoprene (6.8 g) in chloroform (100 ml) with stirring. After the brown colour had faded the solvent was evaporated off under reduced pressure and was replaced by a solution of potassium thiocyanate (17 g) in methanol (100 ml). The solution was stirred at room temperature for 6 h and then filtered to remove the precipitated salts. The filtrate was heated under reflux for 20 h, and subsequent evaporation of the solvent under reduced pressure and flash chromatography afforded compound (**10**) (8.65 g, 61% w.r.t. isoprene).

4-*Isopropenyl*-4-*methylthiazolidin*-2-*one* (**12**). 2,3-Dimethyl-1,4-dithiocyanatobut-2-ene (**3**) (800 mg) was heated under reflux in methanol (100 ml) for 72 h. Work up as described above and flash chromatography [eluant ethyl acetate–light petroleum (1:1)] afforded two fractions. Following the less polar mixture of isothiocyanates and unrearranged thiocyanates, there was obtained a more polar fraction, the title compound (**12**) as a colourless oil (270 mg, 42% yield); *m/z* (e.i.), 157.0561. $C_7H_{11}NOS$ requires 157.0558; $\nu_{max.}$(neat), 3 200 and 1 685 cm^{-1}; δ_H 1.55 (3 H, s, Me), 1.85 (3 H, s, Me), 3.18 (1 H, d *J* 11 Hz), 3.38 (1 H, d, *J* 11 Hz), 4.92 (1 H, s, vinylic CH_2), 5.05 (1 H, s, vinylic CH_2) and 7.25 (1 H, br, NH); δ_C 18.81 (Me), 25.56 (Me), 39.82 (CH_2), 63.60 (*C*Me), 111.59 (CH_2), 146.14 (CMe), and 174.60 (CO); *m/z* 157 (M^+, 10%), 114 (55%), and 82 (100%).

2-*Anilino*-4-*vinyl*-4,5-*dihydrothiazole* (**13**).—A solution of aniline (186 mg) and 1,4-dithiocyanatobut-2-ene (**1**) (170 mg) in benzene (10 ml) were heated under reflux for 18 h. Evaporation of the solvent under reduced pressure afforded an oily residue. Flash chromatography [eluant ethyl acetate–light petroleum (1:3)] and purification by recrystallization (ethyl acetate–pentane) afforded the *title compound* (**13**) (139 mg, 68%), m.p. 80—82 °C (Found: C, 64.8; H, 5.9; N, 13.7. $C_{11}H_{12}N_2S$ requires C, 64.7; H, 5.9; N, 13.7%); *m/z* 204 (M^+, 99%); $\nu_{max.}$ ($CHCl_3$), 3 405, 1 595, and 695 cm^{-1}; δ_H 2.98 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.30 (1 H, q, *J* 11 and 7 Hz, CH_2S), 4.40 (1 H, m, CHN), 5.10 (1 H, d, *J* 10 Hz), 5.25 (1 H, d, *J* 17 Hz), 5.9 (1 H, m, CH), and 7.0—7.3 (6 H, complex); δ_C 36.46 (CH_2), 63.65 (CH), 118.56 (CH_2), and 148.27 (C=N).

Preparation of other 4,5-*Dihydrothiazoles.*—The above procedure, modified as indicated in the Table, was used to prepare the following 4,5-dihydrothiazoles. 2-*Anilino*-4-*isopropenyl*-4,5-*dihydrothiazole* (**14**), m.p. 105—107 °C (Found: C, 66.2; H, 6.2; N, 12.7. $C_{12}H_{14}N_2S$ requires C, 66.05; H, 6.4; N, 12.8%); δ_H 1.79 (3 H, s, Me), 3.07 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.34 (1 H, q, *J* 11 and 7 Hz, CH_2S), 4.42 (1 H, t, *J* 7 Hz, CHN), 4.87 (1 H, s, vinylic CH_2), 5.06 (1 H, s, vinylic CH_2), and 6.95—7.35 (6 H, complex); δ_C 18.53 (Me), 35.59 (CH_2), 67.07 (CH), 112.61 (CH_2) and other resonances.

2-*Anilino*-4-*isopropenyl*-4-*methyl*-4,5-*dihydrothiazole* (**16**). M.p. 105—106 °C (Found: C, 67.1; H, 6.9; N, 11.8. $C_{13}H_{16}N_2S$ requires C, 67.2; H, 6.9; N, 12.1%); δ_H 1.45 (3 H, s, Me), 1.85 (3 H, s, Me), 3.09 (1 H, d, *J* 11 Hz, CH_2S), 3.25 (1 H, d, *J* 11 Hz, CH_2S), 4.90 (1 H, s, vinylic CH_2), 5.15 (1 H, s, vinylic CH_2), 7.00—7.30 (5 H, ArH), and 7.55 (1 H, br, NH); δ_C 19.42 (Me), 25.48 (Me), 40.86 (CH_2), 68.86 (quaternary C), 111.38 (CH_2) and other resonances.

2-p-*Anisidino*-4-*vinyl*-4,5-*dihydrothiazole* (**17**). M.p. 96—98 °C (Found: C, 61.4; H, 6.0; N, 11.8. $C_{12}H_{14}N_2OS$ requires C, 61.5; H, 6.0; N, 12.0%); δ_H 3.02 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.34 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.76 (3 H, s, OMe), 4.44 (1 H,

m, CHN), 5.12 (1 H, d, *J* 10 Hz, vinylic CH_2), 5.29 (1 H, d, *J* 17 Hz, vinylic CH_2), 5.85 (1 H, m, vinylic CH), 6.25 (1 H, br, NH), and 6.80 and 7.00 (4 H, ArH); δ_C 36.68 (CH_2), 55.54 (OMe), 64.25 (CH), 114.33 (CH), 116.80 (CH_2) and other resonances.

2-p-*Anisidino*-4-*isopropenyl*-4,5-*dihydrothiazole* (**18**). M.p. 98—100 °C (Found: C, 63.0; H, 6.5; N, 10.9. $C_{13}H_{16}N_2OS$ requires C, 62.9; H, 6.45; N, 11.3%); δ_H 1.75 (3 H, s, Me), 3.00 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.27 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.75 (3 H, s, OMe), 4.41 (1 H, t, *J* 7 Hz, CHN), 4.83 (1 H, s, vinylic CH_2), 5.05 (1 H, s, vinylic CH_2), 6.75 and 6.95 (4 H, ArH), and 7.3 (1 H, br, NH); δ_C 18.34 (Me), 35.24 (CH_2), 55.28 (OMe), 66.43 (CH), 112.45 and other resonances.

2-p-*Anisidino*-4-*isopropenyl*-4-*methyl*-4,5-*dihydrothiazole* (**19**). M.p. 144—145 °C (Found: C, 63.7; H, 6.8; N, 10.4. $C_{14}H_{18}N_2OS$ requires C, 64.1; H, 6.9; N, 10.7%); δ_H 1.40 (3 H, s, Me), 1.78 (3 H, s, Me), 3.00 (1 H, d, *J* 11 Hz, CH_2S), 3.20 (1 H, d, *J* 11 Hz, CH_2S), 3.78 (3 H, s, OMe), 4.88 (1 H, s, vinylic CH_2), 5.12 (1 H, s, vinylic CH_2), 6.75 and 6.95 (4 H, ArH), and 7.25 (1 H, br, NH); δ_C 19.38 (Me), 25.49 (Me), 40.88 (CH_2), 55.44 (OMe), 63.57 (quaternary carbon), 111.23 (CH_2) and other resonances.

2-(N-*Methylanilino*)-4-*vinyl*-4,5-*dihydrothiazole* (**20**). As an oil, *m/z* 218.0858. $C_{12}H_{14}N_2S$ requires 218.0878; δ_H 3.05 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.40 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.42 (3 H, s, NMe), 4.6 (1 H, m, CHN), 5.15 (1 H, d, *J* 10 Hz, vinylic CH_2), 5.35 (1 H, d, *J* 17 Hz, vinylic CH_2), 6.00 (1 H, m, vinylic CH), and 7.15—7.45 (5 H, complex, ArH); δ_C 40.47 (CH_2), 40.83 (NMe), 77.15 (CH), 115.11 (CH_2) and other resonances.

2-(N-*Methylanilino*)-4-*isopropenyl*-4,5-*dihydrothiazole* (**21**). As an oil, *m/z* 232.0982. $C_{13}H_{16}N_2S$ requires 232.1034; δ_H 1.81 (3 H, s, Me), 3.05 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.37 (1 H, q, *J* 11 and 7 Hz, CH_2S), 3.42 (3 H, s, NMe), 4.82 (1 H, t, *J* 7 Hz), 4.85 (1 H, s, vinylic, CH_2), 5.07 (1 H, s, vinylic CH_2), and 7.25 (5 H, complex, ArH); δ_C 18.94 (Me), 39.69 (CH_2), 40.61 (NMe), 77.51 (CH), 110.89 (CH_2) and other resonances.

4-*Isopropenyl*-2-(N-*methylanilino*)-4-*methyl*-4,5-*dihydrothiazole* (**22**). An an oil, *m/z* 246.1168. $C_{14}H_{18}N_2S$ requires 246.1190; δ_H 1.48 (3 H, s, Me), 1.85 (3 H, s, Me), 3.05 (1 H, d, *J* 11 Hz, CH_2S), 3.28 (1 H, d, *J* 11 Hz, CH_2S), 3.42 (3 H, s, NMe), 4.85 (1 H, s, vinylic, CH_2), 5.08 (1 H, s, vinylic CH_2), and 7.2—7.4 (5 H, complex, ArH); δ_C 19.55 (Me), 26.18 (Me), 40.68 (NMe), 43.88 (CH_2), 77.49 (quaternary C), 111.38 (CH_2) and other resonances.

Reaction of 2-anilino-4-isopropenyl-4,5-dihydrothiazole (**13**) with acetic anhydride and subsequent purification by flash chromatography afforded as an oil 2-(N-*acetylanilino*)-4-*isopropenyl*-4,5-*dihydrothiazole* (**23**); *m/z* 260.0982. $C_{14}H_{16}N_2OS$ requires M^+ 260.0983; δ_H 1.84 (3 H, s, Me), 2.67 (3 H, s, COMe), 2.94 (1 H, d, *J* 11 Hz, CH_2S), 3.38 (1 H, q, *J* 11 and 8 Hz, CH_2S), 4.98 (2 H, s, vinylic, CH_2), 5.32 (1 H, d, *J* 8 Hz, CHN), 6.95 (2 H, ArH), 7.12 (1 H, ArH), and 7.32 (2 H, ArH); δ_C 19.77 (Me), 25.67 (COMe), 30.66 (CH_2), 62.19 (CH), 111.69 (CH_2) and other resonances.

Reaction of 2-anilino-4-isopropenyl-4,5-dihydrothiazole (**13**) with benzoyl chloride and subsequent purification by flash chromatography afforded as an oil 2-(N-*benzoylanilino*)-4-*isopropenyl*-4,5-*dihydrothiazole* (**24**); *m/z* 322.1139. $C_{19}H_{18}N_2OS$ requires M^+, 322.1140; $\nu_{max.}$(neat) 3 000, 1 680, 1 670, and 1 600 cm^{-1}; δ_H 1.68 (3 H, s, Me), 3.10 (1 H, t, *J* 11 Hz, CH_2S), 3.45 (1 H, q, *J* 11 and 9 Hz, CH_2S), 4.67 (1 H, m, CHN), 4.78 (1 H, s, vinylic CH_2), 4.84 (1 H, s, vinylic CH_2), and 7.2—7.5 (10 H, ArH); δ_C 19.37 (Me), 38.70 (CH_2), 76.08 (CH), 111.64 (CH_2) and other resonances.

Preparation of Aminothiols from Thiazolidinones.—The thiazolidinone (0.01 mol) in water (100 ml) containing added potassium hydroxide (0.2 mol) was heated under reflux under nitrogen for 48 h. The cold solution was neutralized (to pH8) with dilute hydrochloric acid and extracted with ether (3 × 50 ml). The combined extracts were washed with water (1 × 50 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure to afford the appropriate crude aminothiols as unstable yellow oils. The aminothiols were characterized by reaction overnight with acetic anhydride to afford as stable solids the diacetylated amide esters.

4-Vinylthiazolidin-2-one (**9**) (1.29 g) afforded 2-*amino*-1-*mercaptobut*-3-*ene* (**25**) (0.70 g, 68%), $\nu_{max.}$($CHCl_3$), 3 380, 2 550, and 1 640 cm^{-1}; δ_H 1.65 (3 H, s, NH_2 and SH), 2.68 (2 H, m, CH_2S), 3.48 (1 H, m, CHN), 5.15 (2 H, m, C=CH_2), and 5.80 (1 H, m, C=CH). The aminothiol (**25**) gave, as white crystals, the diacetylated product (**28**), m.p. 52—54 °C (Found: C, 51.4; H, 7.1; N, 7.5. $C_8H_{13}NO_2S$ requires C, 51.3; H, 6.95; N, 7.5%); $\nu_{max.}$($CHCl_3$), 3 420, 1 695, and 1 660 cm^{-1}; δ_H 1.98 (3 H, s, NCOMe), 2.38 (3 H, s, SCOMe), 3.12 (2 H, m, CH_2S), 4.64 (1 H, m, CHN), 5.20 (2 H, m, C=CH_2), 5.78 (1 H, m, C=CH), and 6.26 (1 H, br, NH); δ_C 23.19 (Me), 30.52 (Me), 33.12 (CH_2), 51.51 (CH), 116.32 (C=CH_2), 136.32 (C=CH), 169.72 (NH*CO*Me), and 193.98 (S*CO*Me). The aminothiol (**25**) gave, as white crystals, the dibenzoyl derivative (**31**) m.p. 118—119 °C (Found: C, 69.0; H, 5.5; N, 4.4. $C_{18}H_{17}NO_2S$ requires C, 69.4; H, 5.5; N, 4.6%); $\nu_{max.}$($CHCl_3$) 3 440, 3 015, 1 680, 1 600, and 1 585 cm^{-1}; δ_H 3.37 (1 H, dd, *J* 14, 5 Hz) and 3.49 (1 H, dd, *J* 14, 9 Hz) (CH_2S), 4.92 (1 H, m, CHN), 5.28 (2 H, m, CH_2), 5.94 (1 H, m, C=CH), 6.90 (1 H, d, *J* 8 Hz NH), and 7.35—8.0 (10 H, m, ArH); δ_C 32.97 (CH_2), 52.65 (CH), 166.99 (CO), 192.93 (CO) and other resonances.

4-Isopropenylthiazolidin-2-one (**10**) (1.43 g) afforded 2-*amino*-1-*mercapto*-3-*methylbut*-3-*ene* (**26**) (0.90 g, 77% yield), $\nu_{max.}$($CHCl_3$) 3 095, 2 550, and 1 650 cm^{-1}; δ_H 1.65 (3 H, s, NH_2 and SH), 1.75 (3 H, s, Me), 2.45—3.25 (2 H, m, CH_2S), 3.65 (1 H, m, CHN), and 4.78 (2 H, m, C=CH_2). The aminothiol (**26**) gave, as white crystals, the diacetylated product (**29**), m.p. 48—50 °C (Found: M^+ 158.0653. $C_9H_{15}NO_2S$ requires 158.0640); *m/z* 158 (3%) 122 (25%) and 70 (100%); $\nu_{max.}$($CHCl_3$) 3 420 and 1 680 cm^{-1}; δ_H 1.78 (3 H, s, Me), 1.98 (3 H, s, NCOMe), 2.37 (3 H, s, SCOMe), 3.11 (2 H, m, CH_2S), 4.52 (1 H, m, CH), 4.94 (2 H, *m*, C=CH_2), and 5.98 (1 H, br, NH).

4-Isopropenyl-4-methylthiazolidin-2-one (**12**) (1.57 g) afforded 2-*amino*-1-*mercapto*-2,3-*dimethylbut*-3-*ene* (**27**) (0.60 g, 46%), $\nu_{max.}$($CHCl_3$) 3 160, 2 550, and 1 650 cm^{-1}; δ_H 1.49 (3 H, s, Me), 1.65 (3 H, s, NH_2 and SH), 1.75 (3 H, s, Me), 2.45—3.25 (2 H, m, CH_2S), and 4.95 (2 H, s, C=CH_2). The aminothiol (**27**) gave as white crystals, the diacetylated product (**30**) m.p. 89—90 °C (Found: M^+ 172.0807. $C_{10}H_{17}NO_2S$ requires 172.0796); *m/z* 172 (31%) 128 (24%), and 84 (100%); $\nu_{max.}$($CHCl_3$) 3 350 and 1 680 cm^{-1}; δ_H 1.49 (3 H, s, Me), 1.78 (3 H, s, Me), 1.96 (3 H, s, NCOMe), 2.36 (3 H, s, SCOMe), 3.22 (1 H, d) and 3.55 (1 H, d) (CH_2S), 4.95 (2 H, s, C=CH_2), and 6.12 (1 H, br, NH); δ_C 19.38 (Me), 23.72 (Me), 23.87 (Me), 30.42 (Me), 38.27 (CH_2), 59.47 (CN), 111.68 (C=CH_2), 146.93 (*C*=CH_2), 169.33 (N*CO*Me), and 196.63 (S*CO*Me).

4-*Isopropylthiazole*-2(3H)-*one* (**38b**).—4-Isopropenylthiazolidin-2-one (**10**) (500 mg) was heated under reflux in dioxane (10 ml) and water (30 ml), to which hydrochloric acid (2M) (10 ml) had been added, for 24 h under nitrogen. The cold solution was extracted with ether (3 × 30 ml) and the ether extract dried ($MgSO_4$). After filtration and evaporation of the solvent under reduced pressure, chromatography [eluant ethyl acetate–light petroleum (1:1)] afforded the *title compound* (**38b**) as a yellow oil (350 mg, 70%) (Found: M^+ 143.0402. C_6H_9NOS requires 143.0405); $\nu_{max.}$(neat) 3 160, 2 995, 1 660, and 1 470 cm^{-1}; δ_H 1.25 (6 H, d, *J* 7 Hz, Me), 2.78 (1 H, m, CH), 5.66 (1 H, s, vinylic CH), and 10.98 (1 H, br, NH); δ_C 20.55 (Me), 28.65 (CH), 94.97 (vinylic CH), 141.65 (CNH), and 176.80 (CO).

Preparation of Disulphides from Thiazolidinones.—4-Vinylthiazolidin-2-one (**9**) (0.52 g) was heated under reflux in water (50 ml) containing added potassium hydroxide (4.5 g) in the presence of air for 48 h. Dilute hydrochloric acid (25 ml) was added to adjust the solution to pH 8. The solution was extracted with dichloromethane (4 × 20 ml) and the organic phases back extracted with further dilute hydrochloric acid (2 × 20 ml). The combined acid fractions were neutralized with 10% sodium hydroxide solution and extracted with ether (3 × 20 ml). The ether extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give, as a colourless oil, a mixture of meso- and (±)-*bis*(2-*aminobut*-3-*enyl*) *disulphide* (**34**) (0.35 g, 43%), $\nu_{max.}$($CHCl_3$) 3 380, 3 095, and 1 640 cm^{-1}; δ_H 1.65 (4 H, s, NH_2), 2.55—2.95 (4 H, m, CH_2S), 3.68 (2 H, m, CHN), 5.14 (2 H, d, *J* 10 Hz) and 5.24 (2 H, d, *J* 17 Hz) (C=CH_2), and 5.85 (2 H, m, C=CH); δ_C 47.05 and 47.32 (CH_2), 52.95 and 53.10 (CH), 114.95 (C=CH_2), and 140.78 (C=CH); *m*/*z* 102 (67%) and 56 (100%).

Similarly 4-isopropenylthiazolidin-2-one (**10**) (0.57 g) afforded, as a colourless oil, a mixture of meso- and (±)-*bis*(2-*amino*-3-*methylbut*-3-*enyl*) *disulphide* (**35**) (0.42 g, 45%), $\nu_{max.}$ ($CHCl_3$), 3 380, 3 095, and 1 650 cm^{-1}; δ_H 1.70 (4 H, s, NH_2), 1.75 (6 H, s, Me), 2.62 and 2.94 (4 H, CH_2), 3.59 (2 H, m, CHN), 4.85 (2 H, s, C=CH_2), and 4.98 (2 H, s, C=CH_2); δ_C 18.42 (Me), 45.51 and 45.81 (CH_2), 55.65 and 55.79 (CH), 111.12 (C=CH_2), and 146.71 (C=CH_2); *m*/*z* 116 (4%) and 70 (100%).

4-Vinylthiazolidin-2-one (**9**) (2.58 g) was heated under reflux in methanol (100 ml) containing added potassium hydroxide (1.12 g) in the presence of air for 20 h. The cold solution was extracted with dichloromethane (4 × 20 ml) after dilution with water. The aqueous phase after neutralization with dilute hydrochloric acid and subsequent work-up afforded 1-*mercapto*-2-*methoxycarbonylaminobut*-3-*ene* (**32**) as a yellow oil (2.18 g, 68%) (Found: M^+, 161.0518. $C_6H_{11}NO_2S$ requires 161.0510); *m*/*z* 161 (2%), 115 (34%), 85 (100%), and 83 (98%); $\nu_{max.}$ 3 440, 1 720, and 1 640 cm^{-1}; δ_H 1.39 (1 H, q, *J* 9, 7 Hz, SH), 2.75 (2 H, m, CH_2), 3.68 (3 H, s, OMe), 4.45 (1 H, m, CHN), 5.2—5.3 (2 H, m, vinylic CH_2), 5.3—5.4 (1 H, br, NH), and 5.78 (1 H, m, vinylic CH); δ_C 29.43 (CH_2), 51.73 (Me), 54.15 (CH), 116.05 (C=CH_2), 136.23 (C=CH), and 156.43 (CO). From the combined dichloromethane extracts work-up afforded, as a yellow oil, the disulphide (**36**) (1.09 g, 17%); *m*/*z* 160 (2%) and 114 (100%); $\nu_{max.}$($CHCl_3$) 3 445, 1 730, and 1 650 cm^{-1}; δ_H 2.84 (4 H, m, CH_2S), 3.65 (6 H, s, OMe), 4.34 (2 H, m, CHN), 4.9—5.25 (6 H, C=CH_2 and NH), and 5.4—6.0 (2 H, m, C=CH).

4-Isopropenylthiazolidin-2-one (**10**) (3 g) was similarly heated in methanol containing added potassium hydroxide (1.2 g) in the presence of air for 20 h. From the alkaline phase work-up afforded as a yellow oil 1-*mercapto*-2-*methoxycarbonylamino*-3-*methylbut*-3-*ene* (**33**) (2.8 g, 76%) (Found: M^+, 175.0649. $C_7H_{13}NO_2S$ requires 175.0667); *m*/*z* 175 (28%), 128 (55%), and 100 (100%); $\nu_{max.}$($CHCl_3$), 3 440, 3 340, 1 730, and 1 655 cm^{-1}; δ_H 1.30 (1 H, dd, *J* 9, 7 Hz, SH), 1.68 (3 H, s, Me), 2.55—2.8 (2 H, m, CH_2S), 3.62 (3 H, s, OMe), 4.21 (1 H, m, CHN), 4.88 (2 H, C=CH_2), and 5.42 (1 H, br, NH); δ_C 19.65 (Me), 27.67 (CH_2), 52.08 (OMe), 57.04 (CH), 112.71 (C=CH_2), 142.51 (C=CH_2), and 156.36 (CO). From the dichloromethane extract work-up afforded, as a yellow oil, the disulphide (**37**) (1.2 g, 16%); *m*/*z* 174 (7%), 143 (5%), 142 (42%), and 128 (100%); $\nu_{max.}$(neat) 3 440, 3 330, and 1 740 cm^{-1}; δ_H 1.72 (6 H, s, Me), 2.8—3.05 (4 H, m, CH_2), 3.68 (6 H, s, OMe), 4.35 (2 H, m, CHN), 4.95 (4 H, C=CH_2), and 5.38 (2 H, br, NH); δ_C 19.43 (Me), 19.56 (Me), 43.24 (CH_2), 43.42 (CH_2), 52.21 (OMe), 55.47 (CH), 55.96 (CH), 112.60 (C=CH_2), 143.42 (C=CH_2), 143.59 (C=CH_2), and 156.61 (CO).

5-*Vinylthiomorpholin*-3-*one* (**39**).—2-Amino-1-mercaptobut-3-ene (**25**) (309 mg) and methyl bromoacetate (459 mg) were heated under reflux for 24 h under nitrogen in absolute ethanol containing sodium ethoxide (138 mg). Acetic acid was added to the cold solution to neutralize any excess of alkali, the solvent was evaporated under reduced pressure, and the crystalline residue was recrystallized from ethyl acetate–pentane to afford the *title compound* (**39**) as white crystals (300 mg, 70%), m.p. 108—109 °C (Found: C, 50.5; H, 6.4; N, 9.6. C_6H_9NOS requires C, 50.3; H, 6.3; N, 9.8%); $\nu_{max.}$($CHCl_3$) 3 400 and 1 660 cm^{-1}; δ_H 2.64 (1 H, dd, *J* 12, 8 Hz) and 2.86 (1 H, dd, *J* 12, 4 Hz) (CH_2S), 3.30 (2 H, m, $COCH_2S$), 4.24 (1 H, m, CHN), 5.28 (1 H, d, *J* 12 Hz, C=CH_2), 5.34 (1 H, d, *J* 17 Hz, C=CH_2), 5.87 (1 H, m, C=CH), and 7.01 (1 H, s, NH).

5-*Isopropenylthiomorpholin*-3-*one* (**40**).—Following the above procedure 2-amino-1-mercapto-3-methylbut-3-ene (**26**) (351 mg) and ethyl bromoacetate (459 mg) afforded a crude product which was purified by chromatography (eluant ethyl acetate) to give a white residue, which was recrystallised from ethyl acetate–pentane to give the *title compound* (**40**) (350 mg, 74%), m.p. 101—103 °C (Found: M^+, 157.0565. $C_7H_{11}NOS$ requires 157.0561); *m*/*z* 157 (82%), 111 (83%), and 68 (100%); $\nu_{max.}$($CHCl_3$) 3 400, 3 200, and 1 660 cm^{-1}; δ_H 1.78 (3 H, s, Me), 2.68 (1 H, dd, *J* 14 and 10 Hz), and 2.84 (1 H, dd, *J* 14 and 4 Hz) (CH_2S), 3.25 (1 H, d, *J* 17 Hz) and 3.40 (1 H, d, *J* 17 Hz) (CH_2CO), 4.20 (1 H, dd, *J* 10, 4 Hz, CHN), 5.02 (1 H, s, vinylic H), 5.07 (1 H, s, vinylic H), and 619 (1 H, br, NH).

2,2-*Dimethyl*-4-*vinylthiazolidine* (**41**).—A solution of 2-amino-1-mercaptobut-3-ene (**25**) (0.24 g) in acetone (10 ml) was kept at room temperature for 24 h, and the solvent was then evaporated under reduced pressure. Chromatography of the residue [eluant ethyl acetate—light petroleum (2:3)] afforded the *title compound* (**41**) as a pale yellow oil (0.24 g, 72%) (Found: M^+, 143.0770. $C_7H_{13}NS$ requires 143.0769); *m*/*z* 143 (7%), 128 (30%), and 56 (100%); $\nu_{max.}$($CHCl_3$) 3 420 and 1 650 cm^{-1}; δ_H 1.58 (3 H, s, Me), 1.70 (3 H, s, Me), 2.20 (1 H, br, NH), 2.55—3.0 (2 H, m, CH_2S), 3.96 (1 H, m, CHN), 5.0—5.4 (2 H, m, C=CH_2), and 5.9 (1 H, m, CH=C).

4-*Isopropenyl*-2,2-*dimethylthiazolidine* (**42**).—Following the above procedure 2-amino-1-mercapto-3-methylbut-3-ene (**26**) (0.34 g) in acetone (10 ml) was kept at room temperature for 24 h. Work-up and chromotography [eluant ethyl acetate–light petroleum (2:3)] afforded the *title compound* (**42**) as a yellow oil (0.32 g; 70% yield) (Found: M^+, 157.0904. $C_8H_{15}NS$ requires 157.0925); *m*/*z* 157 (5%), 142 (22%), and 70 (100%); $\nu_{max.}$(neat) 3 290 and 1 650 cm^{-1}; δ_H 1.58 (3 H, s, Me), 1.70 (3 H, s, Me), 1.85 (3 H, s, Me), 1.92 (1 H, br, NH), 2.79 (1 H, t, *J* 10 Hz, CH_2S), 3.27 (1 H, dd, *J* 10, 6 Hz, CH_2S), 3.92 (1 H, m, CHN), 4.92 (1 H, s, vinylic), and 4.97 (1 H, s, vinylic).

cis- *and* trans-2-*Phenyl*-4-*vinylthiazolidine* (**43**).—2-Amino-1-mercaptobut-3-ene (**25**) (0.31 g) was dissolved in benzaldehyde (0.64 g) and left at room temperature for 18 h. Chromatography [eluant ethyl acetate–light petroleum (1:4)] afforded, as a colourless oil which crystallized below 0 °C, a mixture of the *title compounds* (**43**) (0.29 g, 50%) (Found: M^+, 191.0758. $C_{11}H_{13}NS$ requires 191.0769); *m*/*z* 191 (30), 144 (35%), and 106 (100%); $\nu_{max.}$($CHCl_3$) 3 395 and 1 640 cm^{-1}; δ_H 2.09 (NH), 2.83 and 3.22 (CH_2), 3.81 and 4.08 (CHN), 5.15—5.4 (vinylic H), 5.65 (benzylic H), 5.85—6.05 (vinylic CH), and 7.2—7.55 (ArH); δ_C 40.46 and 40.86 (CH_2), 65.17 and 67.51 (CH), 70.88 and 72.38 (CH), 116.15 and 116.68 (C=CH_2) and other resonances.

cis- *and* trans-4-*Isopropenyl*-2-*phenylthiazolidine* (**44**).—Following the above procedure 2-amino-1-mercapto-3-methylbut-3-ene (**26**) (0.29 g) and benzaldehyde (0.53 g) afforded as a colourless oil which crystallized below 0 °C, a mixture of the *title compounds* (**44**) (0.26 g, 51%) (Found: M^+, 205.0925.

$C_{12}H_{15}NS$ requires 205.0925); *m/z* 205 (1%), 158 (13%), and 106 (100%); $\nu_{max.}$($CHCl_3$) 3 300 and 1 650 cm^{-1}; δ_H 1.88 (Me), 2.07 (NH), 2.85—3.0 and 3.2—3.35 (CH_2), 3.76—3.82 (CH), 4.94 and 5.05 (vinylic H), 5.68 (benzylic H), and 7.2—7.55 (ArH); δ_C 19.13 and 20.38 (Me), 40.17 and 44.14 (CH_2), 70.22, 70.90, 72.27, and 75.08 (CH), 111.29 and 111.48 (C=CH_2) and other resonances.

3-*Methyl*-4-*vinylthiazolidine* (**45**).—A solution of formic acid [2.3 ml, (90% solution)], formaldehyde [1.5 g (35% solution)], and 2-amino-1-mercaptobut-3-ene (**25**) (0.60 g) were heated at 110 °C for 90 min, and the excess of formic acid was removed under reduced pressure. The residue was basified with aqueous sodium hydrogen carbonate and extracted with ether (3 × 15 ml). The combined ether extracts were dried ($MgSO_4$) and after evaporation of the solvent under reduced pressure the residue was chromatographed. Elution with ethyl acetate–light petroleum (1:4) afforded, as a yellow oil, the *title compound* (**45**) (0.54 g, 72% yield) (Found: M^+, 129.0685. $C_6H_{11}NS$ requires 129.0612); *m/z* 129 (14%), 114 (16%), and 85 (100%); $\nu_{max.}$($CHCl_3$) 3 095 and 1 645 cm^{-1}; δ_H 2.35 (3 H, s, Me), 2.84 (1 H, dd, *J* 10, 7 Hz) and 3.04 (1 H, dd, *J* 10, 6 Hz) (CH_2N), 3.45 (1 H, m, CHN), 3.88 (1 H, d, *J* 8 Hz, CH_2N) and 4.10 (1 H, d, *J* 8 Hz, CH_2N), 5.25 (2 H, m, CH_2=C), and 5.79 (1 H, m, C=CH); δ_C 33.40 (CH_2S), 39.26 (Me), 60.02 (CH_2N), 71.21 (CHN), 116.98 (CH_2=C), and 136.74 (CH=C).

4-*Isopropenyl*-3-*methylthiazolidine* (**46**).—Following the above procedure 2-amino-1-mercapto-3-methylbut-3-ene (**26**) (0.80 g) on treatment with formic acid (2.7 ml) and formaldehyde (1.78 g), work-up and purification by chromatography [eluant ethyl acetate–light petroleum (1:4)] afforded, as a pale yellow oil, the *title compound* (**46**) (0.84 g, 86%) (Found: M^+, 143.0757. $C_7H_{13}NS$ requires 143.0769); $\nu_{max.}$ 3 095 and 1 660 cm^{-1}; δ_H 1.78 (3 H, s, Me), 2.24 (3 H, s, NMe), 2.92 (1 H, dd, *J* 11, 7 Hz) and 2.95 (1 H, dd, *J* 11, 7 Hz) (CH_2S), 3.24 (1 H, t, *J* 7 Hz, CHN), 3.79 (1 H, d, *J* 8 Hz, CH_2N) and 4.04 (1 H, d, *J* 8 Hz, CH_2N), 4.92 (1 H, s, vinyl), and 4.97 (1 H, s, vinyl); δ_C 19.42 (Me), 32.39 (CH_2), 39.04 (NMe), 60.16 (CH_2N), 74.41 (CHN), 113.10 (CH_2=C), and 143.11 (MeC=C).

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