Synthetic Procedures *via* Rearrangement of 1,4-Dithiocyanatobut-2-enes

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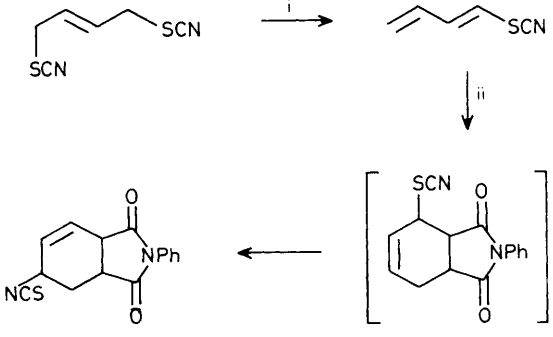
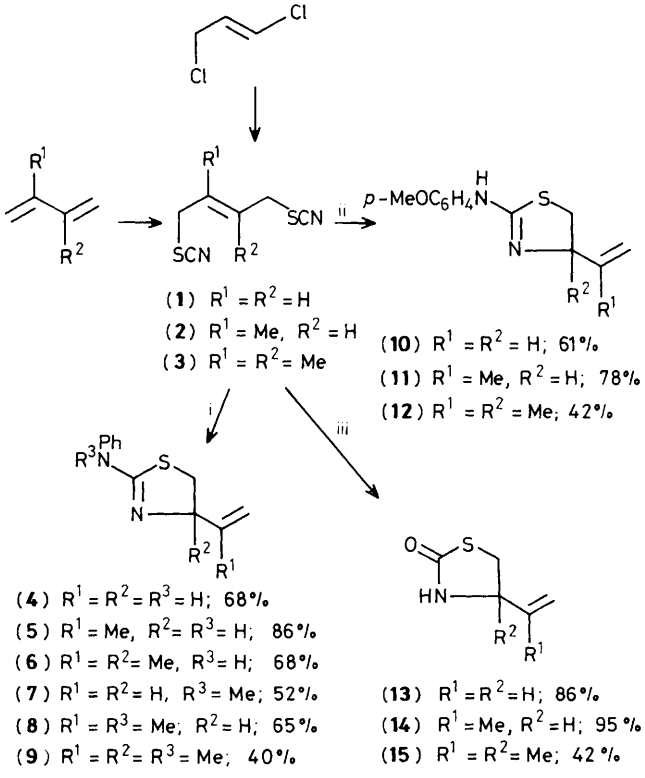
Thermal rearrangement of 1,4-dithiocyanatobut-2-enes, available by either thiocyanogenation of 1,3-dienes or from 1,4-dihalogenobut-2-enes, affords vicinal thiocyanatoisothiocyanates, which are trapped to give thiazolidinones or dihydrothiazoles, or indirectly aminothiols.

A recent paper[1] described the elimination of thiocyanic acid from 1,4-dithiocyanatobut-2-enes with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) to give 1-thiocyanatobuta-1,3-dienes. These dienes in Diels–Alder reactions give initially allylic thiocyanates which rearrange thermally to afford isothiocyanates (Scheme 1). We now find that when the 1,4-dithiocyanatobut-2-enes (**1**)—(**3**) are heated in the presence of weaker bases than DBU reaction by sigmatropic rearrangement to give a vicinal thiocyanatoisothiocyanate takes precedence over a possible elimination reaction. Hence, by using the methods developed by Cambie *et al.*[2] for the trapping of thiocyanatoisothiocyanates the alkenes (**1**)—(**3**), which are readily available, either by an anodic or non-anodic addition[3] of thiocyanogen to buta-1,3-dienes, or by reaction of potassium thiocyanate[4] with *trans*-1,4-dichlorobut-2-ene, are readily transformed to novel heterocyclic systems. Reaction with aromatic amines in hot benzene affords the dihydrothiazoles (**4**)—(**12**)† (Scheme 2). In contrast, because of preferential elimination to give 1-thiocyanato-1,3-dienes aliphatic amines such as dimethylamine and piperidine fail to give good yields of dihydrothiazoles.



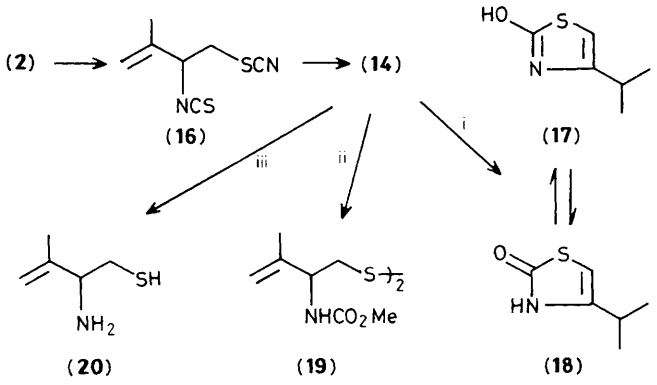
Scheme 1. *Reagents:* i, DBU; ii, *N*-phenylmaleimide.

The dithiocyanates (**1**)—(**3**) are smoothly converted in hot methanol into the thiazolidinones (**13**)—(**15**). By reaction of 1,4-dichlorobut-2-ene with potassium thiocyanate in methanol



Scheme 2. *Reagents:* i, $PhNHR^3$; ii, p-$MeOC_6H_4NH_2$; iii, MeOH.

† All compounds were characterized by i.r. and ^1H and ^{13}C n.m.r. spectroscopy and by high resolution mass spectrometry or microanalysis.



Scheme 3. *Reagents:* i, HCl; ii, KOH, MeOH, air; iii, KOH, aq. dioxane, N_2.

at room temperature for 6 h followed by reaction under reflux for 16 h the thiazolidinone (**13**) is obtained directly in 82% yield. The intermediacy of vicinal thiocyanatoisothiocyanates such as (**16**) is clearly suggested by observation (i.r. and ^{1}H n.m.r.) of those spectral features characteristic of an isothiocyanate when the 1,4-dithiocyanatobut-2-enes (**1**)—(**3**) are heated in benzene in the absence of methanol.

In the case of the dithiocyanate (**2**) two possible sigmatropic rearrangements might occur. Only products from the less hindered isothiocyanate (**16**) are observed. As shown in Scheme 3, this selectivity can be used in regiospecific synthesis of acyclic compounds. Although reaction of (**14**) with acid leads to double bond isomerisation and hence formation of the tautomeric mixture (**17**), (**18**), reaction with potassium hydroxide, under appropriate conditions, affords acyclic compounds such as the disulphide (**19**) and the aminothiol (**20**) in good yields. However, the simple elaboration of dihalides such as 1,4-dichlorobut-2-ene to heterocyclic systems is likely to prove to be more noteworthy in view of the biological activity, and in particular the schistosomicidal activity of such systems.

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