Synthesis of Five-membered Lactams by α-Carbamoyl Radical Cyclisations

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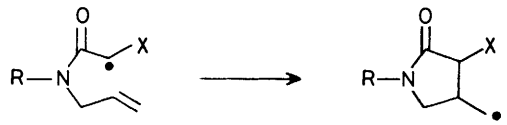
Free-radical cyclisation of *N*-allyl-α-carbamoyl radicals generated by tributyltin radical-mediated cleavage of carbon–chlorine or carbon–sulphur bonds has been studied in some detail. The radicals substituted at the α position by methylthio (phenylthio), chloro, methyl, phenyl, methoxy, or acetoxy groups underwent smooth cyclisation in a 5-*exo*-*trig* manner to give five-membered lactams in which the *trans*-isomer predominated. In contrast, the *N*- or α-unsubstituted, or α-sulphonyl-substituted, radicals gave predominantly or exclusively the reduction products. Cyclisation of the *N*-β-methylallyl system proceeded again regioselectively to give the five-membered lactam.

There have been a great number of studies devoted to the development of useful synthetic methods to the pyrrolidine ring. Perhaps currently the most attractive approaches are based on free-radical cyclisation. So far, α-(*N*-acyl)amino,[1] α-(*N*-sulphonyl)amino,[2] and β-amino radicals[2,3] have been utilised for the construction of pyrrolidine rings. However, the synthesis of five-membered lactams (pyrrolidin-2-ones) using radical cyclisation has received little attention.[4] In the present paper we report a new synthetic method for the five-membered lactams by 5-*exo*-*trig* cyclisation of *N*-allyl-α-carbamoyl radicals. The effect of the substituents on this radical cyclisation is also described.[5]



The reaction of α-methylthio-substituted *N*-allyl-α-chloroacetamides with tributyltin hydride in the presence of azoisobutyronitrile (AIBN) was examined first. The desired α-chloro sulphides (**2a**—**c**) were prepared by *N*-acylation of the corresponding *N*-substituted allylamines with (methylthio)acetyl chloride followed by treatment of the resulting amides (**1a**—**c**) with *N*-chlorosuccinimide (NCS). The *N*-unsubstituted congener (**2d**) was obtained by acylation of allylamine with chloro(methylthio)acetyl chloride.

A mixture of Bu_3SnH (1.1 mol equiv.) and a catalytic amount of AIBN (0.1 mol equiv.) in benzene was added to a 0.06M solution of the chloride (**2a**) in refluxing benzene during 40 min under nitrogen and the resulting mixture was further heated under reflux for 2 h. After removal of solvent, the residue was chromatographed on silica gel to give the lactam (**3a**) and the reduction product (**1a**) in 68 and 16% yield, respectively. The lactam (**3a**) was shown to be a mixture of two diastereoisomers in the ratio 71:29 by g.l.c. analysis. The i.r. spectrum of lactam (**3a**) showed an absorption at 1 690 cm^{-1} typical of a five-membered lactam, and the ^1H n.m.r. spectrum indicated the presence of a *C*-methyl group at δ 1.22 (d, *J* 6.8 Hz for the *trans* isomer) and 1.15 (d, *J* 6.7 Hz for the *cis* isomer). The structure of compound (**3a**) was further confirmed by its transformation to the known unsaturated lactam (**4**) (see Experimental section). The *trans*-stereochemistry for the major isomer was assigned on the basis of thermodynamic considerations and on the fact that treatment of this mixture with sodium ethoxide in refluxing ethanol resulted in an increase in the amount of the major isomer at the expense of the minor one (87:13).

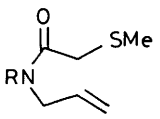
Similarly, the *N*-benzyl (**2b**) and *N*-phenyl derivatives (**2c**) afforded the five-membered lactams (**3b**) and (**3c**) along with the reduction products (**1b**) and (**1c**), respectively (see Table 1). In contrast, the *N*-unsubstituted derivative (**2d**) afforded no cyclised product (**3d**) but only the reduction product (**1d**) in 36% yield. These observations clearly reveal the pronounced influence of the bulkiness of the nitrogen substituent.

The reaction of the *S*-phenyl derivative (**5**) in refluxing benzene was somewhat slower than that of the corresponding *S*-methyl derivative (**2a**), but two isomeric lactams (**7**) and (**8**) were

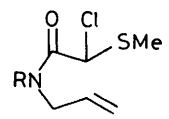
Table 1. Effect of the nitrogen substituents on the α-carbamoyl radical cyclisation[a]

Entry	Chloro sulphide	Product No.	Yield (%)	Ratio of *trans*:*cis*[b]
1	(**2a**)	(**3a**)	68	71:29
		(**1a**)	16	
2	(**2b**)	(**3b**)	80	72:28
		(**1b**)	12	
3	(**2c**)	(**3c**)	90	83:17
		(**1c**)	8	
4	(**2d**)	(**1d**)	36	

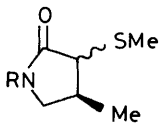
[a] All reactions were carried out using Bu_3SnH (1.1 mol equiv.) in refluxing benzene for 3 h. [b] Determined by g.l.c.



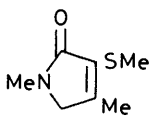
(**1a**–**d**)



(**2a**–**d**)



(**3a**–**d**)



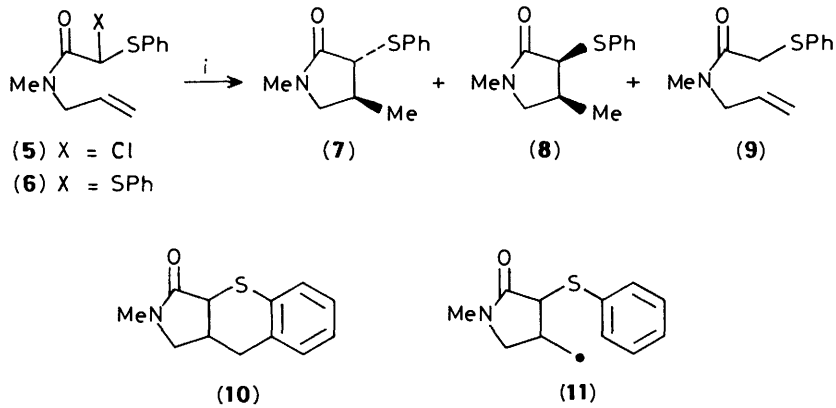
(**4**)

(**1**) – (**3**)
a; R = Me
b; R = CH_2Ph
c; R = Ph
d; R = H

Table 2. Effect of the substituents at the radical centre on the α-carbamoyl radical cyclisation[a]

Entry	Starting material	Reaction temp. (°C)	Reaction time (h)	Product No.	Product Yield (%)	Product Ratio of *trans*:*cis*
1	(**12a**)	80	1	(**13a**)	24	
				(**14a**)	39	
2	(**12b**)	80	6	(**13b**)	12	
				(**14b**)	65	
3	(**12c**)	80	3	(**13c**)	50	73:27[b]
				(**12a**)	29	
4	(**12d**)	80	5	(**13d**)	85	79:21[c]
				(**13b**)	11	
5	(**12e**)	80	3.5	(**13e**)	74	74:26[c]
				(**12e**)	12	
6	(**12f**)	80	2	(**13f**)	94	69:31[d]
7	(**12g**)	110	50	(**13g**)	63	86:14[c]
				(**12g**)	21	
8	(**12h**)	110	10	(**13h**)	67	79:21[c]
				(**18**)	28	74:26[c]
9	(**12i**)	80	8	(**14i**)	34	
				(**12i**)	29	

[a] All reactions were carried out by using Bu_3SnH (1.2—2.0 mol equiv.). [b] Determined by g.l.c. [c] Determined by ^1H n.m.r. spectroscopy. [d] Isolated ratio.



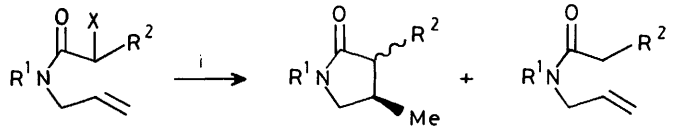
Scheme 1. *Reagents:* i, Bu_3SnH, AIBN

isolated in 47 and 15% yield, respectively, along with the reduction product (**9**) (10%) (Scheme 1). Since the lactam (**8**) was converted completely into the lactam (**7**) when treated with sodium ethoxide in refluxing ethanol, the stereochemistry of the lactams (**7**) and (**8**) was assigned as *trans* and *cis*, respectively. On the other hand, this same chloride (**5**), when heated with Bu_3SnH and AIBN in toluene as solvent in place of benzene, gave a small amount of the tricyclic compound (**10**) in addition to the lactams (**7**) and (**8**). The formation of compound (**10**) is considered to be a result of an intramolecular attack of an aromatic ring on the intermediary radical (**11**).[6]

The phenylthio group has frequently been used as a leaving group in radical reactions. Therefore, the dithioacetal (**6**) was prepared by reaction of the α-chloro sulphide (**5**) with sodium benzenethiolate, and subjected to the cyclisation conditions (Bu_3SnH and AIBN in refluxing benzene). The reaction proceeded in a similar manner to give the *trans*- (**7**) and *cis*-lactam (**8**) in 48 and 14% yield, respectively. Interestingly, the reduction product (**9**) was not detected in the reaction mixture.

Being encouraged by these results, we were then led to examine the behaviour of various α-substituted α-chloro- and α-(phenylthio)-acetamides (**12a—i**) in order to ascertain the effect of the substituents on this radical cyclisation. The desired acetamides were prepared in a straightforward manner; (i) the α-chloroacetamides (**12a—f**) were obtained by direct acylation of *N*-methyl- or *N*-phenyl-allylamine with the corresponding chloroacetyl chlorides, (ii) the α-methoxy sulphide (**12g**) was prepared by nucleophilic substitution of the α-chloro sulphide (**16**) with methoxide ion, (iii) the α-acetoxy sulphide (**12h**) by a Pummerer rearrangement of the sulphoxide (**17**) with acetic anhydride, and (iv) the α-chloro sulphone (**12i**) by oxidation of the α-chloro sulphide (**16**) with *m*-chloroperbenzoic acid (MCPBA).

These radical precursors were then subjected to the cyclisation conditions. The results are summarised in Table 2. In the cases of (**12g**) and (**12h**) whose reactions were slow in refluxing benzene, toluene was used as solvent. The structures of the product were elucidated on the basis of i.r. and ^1H n.m.r. spectroscopic evidence. The dichloroacetamide (**12d**) afforded the expected chloro-substituted lactam (**13d**) and the dechlorinated lactam (**13b**) in 85 and 11% yield, respectively. The latter lactam might be formed by further reduction of the former lactam (**13d**) with Bu_3SnH. In fact, use of 3.3 mol equiv. of Bu_3SnH in this reaction gave only the lactam (**13b**). The *trans*-stereochemistry of the major isomer of (**13e**) from (**12e**) was confirmed in a similar manner to that employed for lactam (**3a**)

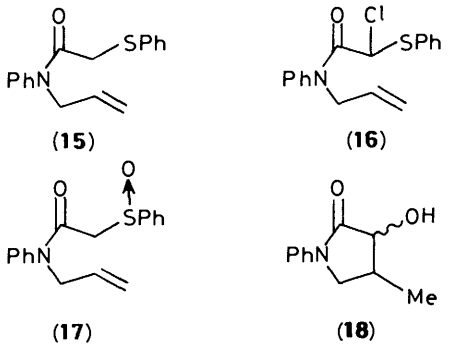


(12a–i) (13a–h) (14a,b,i)

(12)–(14)

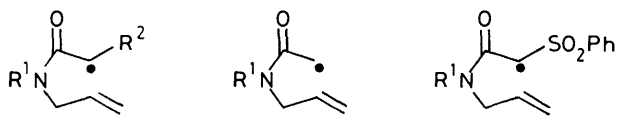
a; R^1 = Me, R^2 = H, X = Cl
b; R^1 = Ph, R^2 = H, X = Cl
c; R^1 = Me, R^2 = Cl, X = Cl
d; R^1 = Ph, R^2 = Cl, X = Cl
e; R^1 = Ph, R^2 = Me, X = Cl
f; R^1 = Ph, R^2 = Ph, X = Cl
g; R^1 = Ph, R^2 = OMe, X = SPh
h; R^1 = Ph, R^2 = OAc, X = SPh
i; R^1 = Ph, R^2 = SO_2Ph, X = Cl

Scheme 2. *Reagents:* i, Bu_3SnH, AIBN



(see Experimental section). The acetoxy lactam (**13h**) formed from the α-acetoxy sulphide (**12h**) appeared to be partially hydrolysed to the hydroxy lactam (**18**) under the reaction conditions (Scheme 2).

The results summarised in the Tables 1 and 2 indicate that (i) the methylthio- (or phenylthio-), chloro-, methyl-, phenyl-, methoxy-, and acetoxy-substituted radicals (**19**) gave preferentially or exclusively the cyclisation products (entries 1—3 in Table 1 and entries 3—8 in Table 2); (ii) when R^2 in (**19**) is hydrogen, *i.e.* radicals (**20**), formation of the reduction product is preferred over the cylisation (entries 1 and 2 in Table 2); and (iii) in the case of the radical substituted by an electron-withdrawing group such as sulphonyl, *e.g.* compound (**21**), the cyclisation was completely suppressed (entry 9 in Table 2). In other words, the radicals (**19**) stabilised either by inductive, mesomeric, or capto-dative effect[7] are more conducive than the less stable primary radical (**20**) for the cyclisation of the α-carbamoyl radicals taking place. These results are somewhat surprising, considering the general observation that so-called 'stabilised' radicals are less reactive than the non-stabilised radicals towards C–C bond-forming reactions with unsaturated bonds.[7,8]

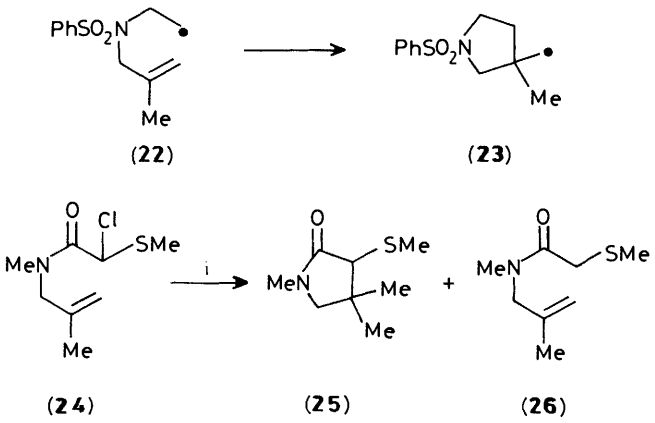


(**19**) R^2 = SMe(SPh), Cl, Me, Ph, OMe, OAc (**20**) (**21**)

A useful guideline for the 5-*exo-trig*-type cyclisation of substituted hex-5-enyl radicals states that 1- or 3-substituted radicals preferentially give *cis*-disubstituted products, while 2- or 4-substituted radicals give mainly *trans* ones.[9] These rules, however, conflict with our data, since all of the α-substituted α-carbamoyl radicals (**19**) gave preferentially *trans*-products (see Tables 1 and 2). It is also known that, if the C-1 substituent is bulky, simple steric factors take precedence, and the *trans*-product predominates.[8,10] However, this argument would not be applicable to our cases, because such a small substituent as methyl also gave the *trans*-rich product (see entry 5 in Table 2).

The preferential formation of *cis*-products from simple 1-substituted hex-5-enyl radicals has been explained in terms of the effects of orbital symmetry or the electrostatic interaction in a dipolar transition state.[11,12] The reason for the preferential formation of *trans*-products from the radicals (**19**) is unclear, but the carbonyl group incorporated into the newly formed ring probably plays an important role in the stereoelectronic preference of the reaction.

An internal alkene substitution (*i.e.*, 5-methylhex-5-enyl radical), in general, leads to the enhanced 6-*endo* cyclisation mainly for steric reasons.[11] In this connection, it is interesting to note that Padwa and co-workers[2] observed that cyclisation of the α-(*N*-sulphonyl)amino radical (**22**) gives rise to exclusively the five-membered lactam (**23**). In our system, the *N*-β-methylallyl derivative (**24**) was also found to give regioselec-

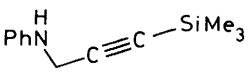


(**22**) (**23**) (**24**) (**25**) (**26**)

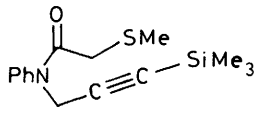
Scheme 3. *Reagents:* i, Bu_3SnH, AIBN

tively the five-membered lactam (**25**) (74%) together with the reduction product (**26**) (14%) (Scheme 3). The structure of compound (**25**) was assigned on the basis of spectroscopic evidence; its i.r. spectrum showed absorption at 1 690 cm^{-1} (typical of a five-membered lactam) and its ^1H n.m.r. spectrum indicated two singlets due to two *C*-methyl protons at δ 1.13 and 1.20. No evidence for the six-membered lactam was detected. No simple explanation for this exclusive formation of the five-membered lactam (**25**) can be offered at the present time.

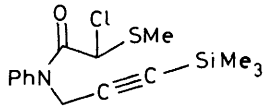
Finally, it was interesting to see whether this radical cyclisation can be applied to alkynyl derivatives. To this end, we prepared the chloride (**29**) in three steps starting from *N*-(prop-2-ynyl)aniline. Treatment of compound (**29**) with Bu_3SnH and AIBN afforded the expected 4-(trimethylsilylmethylene)lactam (**30**) in 40% yield as a single stereoisomer.



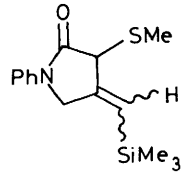
(**27**)



(**28**)



(**29**)



(**30**)

In summary, the present study reveals that the α-carbamoyl radical cyclisation generated by carbon–chlorine or carbon–sulphur bond cleavage provides ready access to five-membered lactams.

Experimental

I.r. spectra were run on a JASCO A-100 spectrophotometer. ^1H N.m.r. spectra were determined with a Varian XL-300 (300 MHz) or JEOL JNM PMX-60 (60 MHz) spectrometer and δ values are quoted relative to tetramethylsilane. Exact mass determinations were obtained on a Hitachi M-80 instrument operating at 20 eV. G.l.c. was carried out on a Shimadzu GC-5APTF gas chromatograph using a SCOT glass capillary column (20 m) coated with Silicone OV-17. Column chromatography was performed on silica gel 60 [Merck PF_{254} for preparative t.l.c. (p.l.c.)] under pressure.

N-*Allyl*-N-*benzyl*-α-(*methylthio*)*acetamide* (**1b**).—According to the reported procedure for the preparation of (**1a**),[13] *N*-allyl-*N*-benzylamine (350 mg, 2.4 mmol) was treated with (methylthio)acetyl chloride[14] (300 mg, 2.4 mmol) to give the *amide* (**1b**) (0.25 g, 44%) as an oil (Found: C, 66.6; H, 7.3; N, 5.85. $C_{13}H_{17}NOS$ requires C, 66.35; H, 7.3; N, 5.95%); $\nu_{max.}(CCl_4)$ 1 640 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.23 (3 H, s), 3.28 (2 H, br s), 3.94 (2 H, m), 4.57 (2 H, s), 4.9—5.4 (2 H, m), 5.45—6.25 (1 H, m), and 7.23 (5 H, br s).

N-*Allyl*-α-(*methylthio*)*acetanilide* (**1c**).—According to the reported procedure for the preparation of (**1a**),[13] *N*-allylaniline (600 mg, 4.5 mmol) was treated with (methylthio)acetyl chloride (560 mg, 4.5 mmol) to give the *amide* (**1c**) (970 mg, 97%) as an oil (Found: C, 64.7; H, 7.0; N, 6.35. $C_{12}H_{15}NOS$ requires C, 65.1; H, 6.8; N, 6.3%); $\nu_{max.}(CCl_4)$ 1 645 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.18 (3 H, s), 3.03 (2 H, s), 4.2—4.4 (2 H, m), 4.85—5.35 (2 H, m), 5.55—6.25 (1 H, m), and 7.0—7.6 (5 H, m).

Preparation and Reaction of N-*Allyl*-α-*chloro*-N-*methyl*-α-(*methylthio*)*acetamide* (**2a**) *with* Bu_3SnH: *General Procedure*.—NCS (310 mg, 2.3 mmol) was added by portions to a solution of the sulphide (**1a**)[13] (360 mg, 2.23 mmol) in CCl_4 (10 ml) at 0 °C and the mixture was stirred at room temperature for 4 h. The precipitated succinimide was filtered off and the filtrate was concentrated under reduced pressure to give, in almost quantitative yield, the chloride (**2a**), which was immediately dissolved in dry benzene (35 ml). To this was added a solution of Bu_3SnH (670 mg, 2.3 mmol) and AIBN (33 mg, 0.2 mmol) in dry benzene (50 ml) *via* a syringe during 40 min under reflux and the mixture was further refluxed for 2 h. After cooling, the solvent was evaporated off and the residue was chromatographed on silica gel (benzene–ethyl acetate, 4:3). The first fraction gave the amide (**1a**)[14] (60 mg, 17%). The second fraction gave 1,4-*dimethyl*-3-*methylthiopyrrolidin*-2-*one* (**3a**) (240 mg, 68%) as an oil (Found: M^+, 159.0719. $C_7H_{13}NOS$ requires *M*, 159.0717); $\nu_{max.}(CCl_4)$ 1 690 cm^{-1}; δ($CDCl_3$; 300 MHz) 1.15 (d, *J* 6.7 Hz, CMe for *cis*), 1.22 (d, *J* 6.8 Hz, CMe for *trans*), 2.15—2.35 (1 H, m, C*H*Me), 2.23 (s, SMe for *trans*), 2.26 (s, SMe for *cis*), 2.87 (3 H, s, NMe), 2.92 (dd, *J* 9.9 and 5.8 Hz, NC*H*H for *trans*), 2.94 (d, *J* 5.8 Hz, SCH for *trans*), 3.07 (dd, *J* 9.9 and 8.4 Hz, NCH*H* for *cis*), 3.33 (dd, *J* 9.9 and 7.8 Hz, NC*H*H for *cis*), 3.34 (d, *J* 8.1 Hz, SCH for *cis*), and 3.51 (dd, *J* 9.9 and 7.9 Hz, NCH*H* for *trans*): the ratio of *trans* and *cis* isomers was shown to be 71:29 by g.l.c., and 69:31 by the integrated intensities of the peak height of the SMe protons in the ^1H n.m.r. spectrum.

Transformation of Compound (**3a**) *to Compound* (**4**).—NCS (65 mg, 0.49 mmol) was added to a solution of compound (**3a**) (60 mg, 0.38 mmol) in CCl_4 at 0 °C and the mixture was stirred at room temperature for 15 h. The precipitated succinimide was filtered off and the solvent was removed by evaporation. The residue was chromatographed on silica gel (ethyl acetate) to give the lactam (**4**)[13] (53 mg, 89%) as an oil.

Treatment of Compound (**3a**) *with Sodium Ethoxide*.—The lactam (**3a**) (20 mg, 0.13 mmol) was added to a solution of sodium ethoxide in ethanol, prepared from sodium (3.1 mg, 0.14 mmol) and ethanol (1 ml), and the mixture was heated under reflux for 10 min. The reaction mixture was poured into water (5 ml) and extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and concentrated, then the residue was chromatographed on silica gel (benzene–ethyl acetate, 4:3) to give the starting lactam (**3a**) (17 mg, 83% recovery), whose ^1H n.m.r. spectrum showed it to be a mixture of two isomers in the ratio 87:13.

Preparation and Reaction of N-*Allyl*-N-*benzyl*-α-*chloro*-α-(*methylthio*)*acetamide* (**2b**) *with* Bu_3SnH.—In a manner similar to the preparation of the chloride (**2a**), the sulphide (**1b**) (240 mg, 1.02 mmol) was treated with NCS (160 mg, 1.22 mmol) to give, in almost quantitative yield, the chloride (**2b**), which was then immediately subjected to the cyclisation conditions. After removal of the solvent, the crude material was chromatographed on silica gel (hexane–ethyl acetate, 2:1). The first fraction gave the amide (**1b**) (23 mg, 12%). The second fraction gave a mixture of *trans* and *cis* isomers (72:28 by g.l.c.) of 1-*benzyl*-4-*methyl*-3-*methylthiopyrrolidin*-2-*one* (**3b**) (192 mg, 80%) as an oil (Found: C, 65.9; H, 7.4; N, 6.0. $C_{13}H_{17}NOS$ requires C, 66.35; H, 7.3; N, 5.95%); $\nu_{max.}(CCl_4)$ 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.08 (d, *J* 7 Hz, CMe for *cis*), 1.15 (d, *J* 7 Hz, CMe for *trans*), 1.6—2.5 (1 H, m, C*H*Me), 2.25 (s, SMe for *trans*), 2.28 (s, SMe for *cis*), 2.5—3.4 (m, NCH_2 for *cis*), 2.77 (dd, *J* 10 and 6 Hz, NC*H*H for *trans*),

3.00 (d, *J* 7 Hz, SCH for *trans*), 3.39 (dd, *J* 10 and 8 Hz, NCH*H* for *trans*), 3.39 (d, *J* 7 Hz, SCH for *cis*), 4.44 (2 H, s, NCH_2Ph), and 7.25 (5 H, s, ArH).

Preparation and Reaction of N-*Allyl*-α-*chloro*-α-*methylthio*-N-*phenylacetanilide* (**2c**) *with* Bu_3SnH.—In a manner similar to the preparation of (**2a**), the sulphide (**1c**) (225 mg, 1.01 mmol) was treated with NCS (163 mg, 1.22 mmol) to give quantitatively the chloride (**2c**), which was then immediately subjected to the cyclisation conditions. After removal of the solvent, the crude material was chromatographed on silica gel (hexane–ethyl acetate, 5:1). The first fraction gave a mixture of *trans* and *cis* isomers (83:17 by g.l.c.) of 4-*methyl*-3-*methylthio*-1-*phenylpyrrolidin*-2-*one* (**3c**) (203 mg, 90%) as an oil (Found: C, 65.0; H, 6.7; N, 6.3. $C_{12}H_{15}NOS$ requires C, 65.1; H, 6.8; N, 6.3%); $\nu_{max.}(CCl_4)$ 1 695 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.25 (d, *J* 7 Hz, CMe for *cis*), 1.33 (d, *J* 7 Hz, CMe for *trans*), 1.9—2.85 (1 H, m, C*H*Me), 2.34 (3 H, s, SMe), 3.21 (d, *J* 7 Hz, SCH for *trans*), 3.3—3.9 (m, NCH_2 and SCH for *cis*), 3.48 (dd, *J* 10 and 6 Hz, NC*H*H for *trans*), 4.07 (dd, *J* 10 and 8 Hz, NCH*H* for *trans*), and 7.0—7.95 (5 H, m, ArH). The second fraction gave the amide (**1c**) (17 mg, 8%).

Preparation and Reaction of N-*Allyl*-α-*chloro*-α-(*methylthio*)*acetamide* (**2d**) *with* Bu_3SnH.—To a solution of allylamine (400 mg, 7 mmol) and triethylamine (710 mg, 7 mmol) in diethyl ether (30 ml) was added dropwise a solution of chloro(methylthio)acetyl chloride[15] (1.13 g, 7 mmol) in diethyl ether (5 ml) at 0 °C and the mixture was stirred at room temperature for 30 min. The precipitated triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure to give the chloride (**2d**) (1.06 g, 84%), which was used immediately in the next stage. The chloride (**2d**) (360 mg, 2 mmol) was treated with Bu_3SnH (660 mg, 2.2 mmol) and AIBN (33 mg, 0.2 mmol) in refluxing benzene. After removal of the solvent, the crude material was chromatographed on silica gel (hexane–ethyl acetate, 2:1) to give N-*allyl*-α-(*methylthio*)*acetamide* (**1d**) (100 mg, 36%) as an oil (Found: M^+, 145.0572. $C_6H_{11}NOS$ requires *M*, 145.0560); $\nu_{max.}(CCl_4)$ 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.18 (3 H, s), 3.21 (2 H, s), 3.85—4.1 (2 H, m), 4.9—5.4 (2 H, m), 5.5—6.25 (1 H, m), and 6.5—7.65 (1 H, m).

N-*Allyl*-α-*chloro*-N-*methyl*-α-(*phenylthio*)*acetamide* (**5**).—In a manner similar to the preparation of (**2a**), *N*-allyl-*N*-methyl-α-(phenylthio)acetamide (**9**)[16] (350 mg, 1.58 mmol) was treated with NCS (232 mg, 1.74 mmol) to give, in almost quantitative yield, the chloride (**5**); δ($CDCl_3$; 60 MHz) 2.98 and 3.09 (total 3 H, both s), 3.65—4.5 (2 H, m), 4.95—5.5 (2 H, m), 5.3—6.35 (1 H, m), 5.78 and 5.85 (total 1 H, both s), and 7.1—8.0 (5 H, m). This compound was used immediately in the next stage.

Reaction of Compound (**5**) *with* Bu_3SnH.—(a) *In refluxing benzene.* The chloride (**5**) (384 mg, 1.5 mmol) was treated with Bu_3SnH (570 mg, 1.95 mmol) and AIBN (24 mg, 0.15 mmol) in refluxing benzene (70 ml). After removal of the solvent, the crude material was chromatographed on silica gel (hexane–ethyl acetate, 2:1). The first fraction gave the amide (**9**)[16] (33 mg, 10%). The second fraction gave trans-1,4-*dimethyl*-3-*phenylthiopyrrolidin*-2-*one* (**7**) (156 mg, 47%) as an oil (Found: C, 64.6; H, 6.8; N, 6.5. $C_{12}H_{15}NOS$ requires C, 65.1; H, 6.8; N, 6.3%); $\nu_{max.}(CCl_4)$ 1 700 cm^{-1}; δ($CDCl_3$; 300 MHz) 1.18 (3 H, d, *J* 6.9 Hz), 2.22—2.37 (1 H, m), 2.82 (3 H, s), 2.86 (1 H, dd, *J* 9.6 and 6.2 Hz, NC*H*H), 3.24 (1 H, dd, *J* 9.6 and 7.8 Hz, NCH*H*), 3.30 (1 H, d, *J* 7.3 Hz), 7.25—7.35 (3 H, m), and 7.5—7.6 (2 H, m). The third fraction gave cis-1,4-*dimethyl*-3-*phenylthiopyrrolidin*-2-*one* (**8**) (51 mg, 15%) as an oil (Found: M^+, 221.0845. $C_{12}H_{15}NOS$ requires *M*, 221.0872); $\nu_{max.}(CCl_4)$ 1 700 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.22 (3 H, d, *J* 7 Hz), 2.4—3.9 (3 H, m), 2.81 (3 H, s), 3.87 (1 H, d, *J* 7 Hz), and 6.8—7.7 (5 H, m).

(b) *In refluxing toluene.* The chloride (**5**) (266 mg, 1.04 mmol) was treated with Bu_3SnH (330 mg, 1.14 mmol) and AIBN (17 mg, 0.1 mmol) in refluxing toluene (50 ml). After removal of the solvent, the crude material was chromatographed on silica gel (hexane–ethyl acetate, 1:1). The first fraction gave a trace amount of the reduction product (**9**). The second fraction gave the lactam (**7**) (66 mg, 29%). The third fraction gave a mixture of the lactams (**8**) and (**10**) (total 58 mg), which crystallised after a time. Recrystallisation of this mixture from ethanol gave the pure lactam (**10**) (42 mg, 19%), m.p. 161—162 °C (lit.,[16] 163—164 °C).

Epimerisation of Compounds (**7**) *and* (**8**).—The lactam (**8**) (27 mg, 0.12 mmol) was added to a solution of sodium ethoxide in ethanol, prepared from sodium (4 mg, 0.18 mmol) and ethanol (1 ml), and the mixture was heated under reflux for 15 min. Work-up gave quantitatively the lactam (**7**), which was identical (t.l.c., ^1H n.m.r.) with that obtained by cyclisation of compound (**5**). The lactam (**7**) was recovered unchanged under the same conditions.

Preparation and Reaction of N-*Allyl*-N-*methyl*-α,α-*bis*(*phenylthio*)*acetamide* (**6**) *with* Bu_3SnH.—Benzenethiol (420 mg, 3.77 mmol) was added to a solution of sodium ethoxide in ethanol, prepared from sodium (87 mg, 3.77 mmol) and ethanol (5 ml), and the mixture was stirred at room temperature for 10 min. To the resultant mixture was added a solution of the chloride (**5**) (800 mg, 3.14 mmol) in ethanol (5 ml) and the mixture was stirred at room temperature for 3 h. After removal of the solvent, the residue was dissolved in water (10 ml) and extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and concentrated, then the residue was chromatographed on silica gel (hexane–ethyl acetate, 2:1) to give the *dithioacetal* (**6**) (744 mg, 72%) as an oil (Found: C, 65.3; H, 5.8; N, 4.2. $C_{18}H_{19}NOS_2$ requires C, 65.6; H, 5.8; N, 4.25%); $\nu_{max.}(CCl_4)$ 1 640 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.90 and 2.94 (total 3 H, both s), 3.7—4.05 (2 H, m), 4.8—5.35 (3 H, m), 5.3—6.1 (1 H, m), and 7.05—7.7 (10 H, m). The dithioacetal (**6**) (330 mg, 1.0 mmol) was treated with Bu_3SnH (320 mg, 1.1 mmol) and AIBN (16 mg, 0.1 mmol) in benzene and work-up gave the lactam (**7**) (99 mg, 48%) and the lactam (**8**) (28 mg, 14%).

Preparation and Reaction of N-*allyl*-α-*chloro*-N-*methylacetamide* (**12a**) *with* Bu_3SnH.—Using a standard procedure, *N*-methylallylamine (242 mg, 3.4 mmol) was treated with chloroacetyl chloride (384 mg, 3.4 mmol) to give quantitatively the *amide* (**12a**) as an oil (Found: M^+, 147.0429. $C_6H_{10}ClNO$ requires *M*, 147.0450); $\nu_{max.}(CCl_4)$ 1 660 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.96 and 3.04 (total 3 H, both s), 3.85—4.2 (2 H, m), 4.05 and 4.09 (total 2 H, both s), 4.9—5.45 (2 H, m), and 5.45—6.25 (1 H, m). The chloride (**12a**) (100 mg, 0.67 mmol) was treated with Bu_3SnH (217 mg, 0.75 mmol) and AIBN (11 mg, 0.07 mmol) in benzene. After removal of the solvent, the crude material was chromatographed on silica gel (ethyl acetate). The first fraction gave *N*-allyl-*N*-methylacetamide (**14a**)[17] (30 mg, 39%) as an oil; $\nu_{max.}(CCl_4)$ 1 660 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.06 and 2.09 (total 3 H, both s), 2.91 and 2.94 (total 3 H, both s), 3.75—4.15 (2 H, m), 4.8—5.4 (2 H, m), and 5.4—6.2 (1 H, m). The second fraction gave 1,4-dimethylpyrrolidin-2-one (**13a**)[18] (18 mg, 24%) as an oil; $\nu_{max.}(CCl_4)$ 1 690 cm^{-1}; δ($CDCl_3$; 300 MHz) 1.13 (3 H, d, *J* 6.7 Hz), 2.01 (1 H, dd, *J* 16.0 and 6.4 Hz), 2.35—2.55 (1 H, m), 2.55 (1 H, dd, *J* 16.0 and 8.6 Hz), 2.83 (3 H, s), 2.96 (1 H, dd, *J* 9.6 and 5.9 Hz), and 3.49 (1 H, dd, *J* 9.6 and 7.7 Hz).

Reaction of N-*Allyl*-α-*chloroacetanilide* (**12b**) *with* Bu_3SnH.—The chloride (**12b**)[19] (300 mg, 1.43 mmol) was treated with Bu_3SnH (458 mg, 1.57 mmol) and AIBN (23 mg, 0.14 mmol) in benzene. After removal of the solvent, the crude material was

chromatographed on silica gel (hexane–ethyl acetate, 2:1) to give a mixture of two products (total 193 mg). The ^{1}H n.m.r. spectrum of the mixture showed the major product to be *N*-allylacetanilide (**14b**)[20] [65% based on (**12b**)]; δ($CDCl_3$; 60 MHz) 1.86 (3 H, s), 4.15—4.4 (2 H, m), 4.8—5.25 (2 H, m), 5.5—6.3 (4 H, m), and 6.9—7.7 (5 H, m). The minor product was shown to be 4-*methyl*-1-*phenylpyrrolidin*-2-*one* (**13b**) [12% yield based on (**12b**)], which was identical with an authentic sample prepared by reduction of the lactam (**3c**) with Raney nickel (Found: C, 75.9; H, 7.3; N, 8.5%; M^+, 175.0989. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.5; N, 8.0%; *M*, 175.0996); m.p. 33—33.5 °C (from hexane); $\nu_{max.}$(CCl_4) 1 700 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.18 (3 H, d, *J* 7 Hz), 1.45—3.1 (3 H, m), 3.39 (1 H, dd, *J* 9.5 and 6.5 Hz), 3.90 (1 H, dd, *J* 9.5 and 7.5 Hz), and 7.0—7.7 (5 H, m).

Preparation and Reaction of N-*Allyl*-α,α-*dichloro*-N-*methylacetamide* (**12c**) *with* Bu_3SnH.—By a standard procedure, *N*-methylallylamine (1.5 g, 21 mmol) was treated with dichloroacetyl chloride (3.71 g, 25.2 mmol) to give the *amide* (**12c**) (3.61 g, 95%) as an oil (Found: M^+, 181.0023. $C_6H_9Cl_2NO$ requires *M*, 181.0060); b.p. 95 °C (bath temp.)/1 mmHg; $\nu_{max.}$(CCl_4) 1 670 cm^{-1}; δ($CDCl_3$; 60 MHz) 3.00 and 3.16 (total 3 H, both s), 3.9—4.25 (2 H, m), 4.95—5.45 (2 H, m), 5.5—6.15 (1 H, m), and 6.23 and 6.29 (total 1 H, both s). The chloride (**12c**) (252 mg, 1.5 mmol) was treated with Bu_3SnH (480 mg, 1.65 mmol) and AIBN (82 mg, 0.45 mmol) and the crude material was chromatographed on silica gel (hexane–ethyl acetate, 9:2). The first fraction gave the reduction product (**12a**) (58 mg, 29%). The second fraction gave a mixture of *trans* and *cis* isomers (73:27 by g.l.c.) of 3-*chloro*-1,4-*dimethylpyrrolidin*-2-*one* (**13c**) (100 mg, 50%) as an oil (Found: M^+, 147.0436. $C_6H_{10}ClNO$ requires *M*, 147.0450); $\nu_{max.}$(CCl_4) 1 720 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.20 (d, *J* 7 Hz, CMe for *cis*), 1.24 (d, *J* 7 Hz, CMe for *trans*), 2.1—3.8 (m, NCH_2 for *cis* and C*H*Me), 2.90 (3 H, s, NMe), 3.17 (dd, *J* 9 and 6.5 Hz, NC*H*H for *trans*), 3.56 (dd, *J* 9 and 8 Hz, NCH*H* for *trans*), 3.98 (d, *J* 7 Hz, CHCl for *trans*), and 4.34 (d, *J* 6 Hz, CHCl for *cis*).

Preparation and Reaction of N-*Allyl*-α,α-*dichloroacetanilide* (**12d**) *with* Bu_3SnH.—By a standard procedure, *N*-allylaniline (1.07 g, 8 mmol) was treated with dichloroacetyl chloride (1.42 g, 9.6 mmol) to give the *anilide* (**12d**) (1.69 g, 86%) as an oil (Found: C, 53.85; H, 4.6; N, 5.7. $C_{11}H_{11}Cl_2NO$ requires C, 54.1; H, 4.5; N, 5.7%); $\nu_{max.}$(CCl_4) 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 4.26 and 4.36 (total 2 H, both br s), 4.85—5.4 (2 H, m), 5.5—6.3 (1 H, m), 5.82 (1 H, s), and 7.05—7.6 (5 H, m). The chloride (**12d**) (376 mg, 1.54 mmol) was treated with Bu_3SnH (490 mg, 1.69 mmol) and AIBN (25 mg, 0.15 mmol) and the crude material was chromatographed on silica gel (hexane–ethyl acetate, 9:2). The first fraction gave a mixture of *trans* and *cis* isomers (79:21 by n.m.r.) of 3-*chloro*-4-*methyl*-1-*phenylpyrrolidin*-2-*one* (**13d**) (274 mg, 85%) (Found: C, 62.9; H, 5.8; N, 6.6. $C_{11}H_{12}ClNO$ requires C, 63.0; H, 5.8; N, 6.7%); m.p. 139—140 °C (from hexane–ethanol); $\nu_{max.}$(CCl_4) 1 710 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.26 (d, *J* 7 Hz, CMe for *cis*), 1.31 (d, *J* 7 Hz, CMe for *trans*), 2.2—3.0 (1 H, m, C*H*Me), 3.48 (dd, *J* 10 and 7.5 Hz, NC*H*H for *trans*), 3.55—4.0 (m, NCH_2 for *cis*), 3.96 (dd, *J* 10 and 8 Hz, NCH*H* for *trans*), 4.14 (d, *J* 8 Hz, CHCl for *trans*), 4.47 (d, *J* 6 Hz, CHCl for *cis*), and 7.0—7.8 (5 H, m). The second fraction gave the lactam (**13b**) (30 mg, 11%) which was identical with that obtained by reaction of the chloride (**12b**) with Bu_3SnH.

A similar reaction of (**12d**) (350 mg, 1.43 mmol) in the presence of Bu_3SnH (3.3 mol equiv.) (1.38 g, 4.72 mmol) and AIBN (46 mg, 0.28 mmol) afforded a mixture of the lactam (**13b**) and the amide (**14b**) (total 231 mg) in the ratio 81:19 (g.l.c.).

Preparation and Reaction of N-*Allyl*-α-*chloropropionanilide* (**12e**) *with* Bu_3SnH.—By a standard procedure, *N*-allylaniline (800 mg, 6.0 mmol) was treated with 2-chloropropionyl chloride (840 mg, 6.61 mmol) to give the *anilide* (**12e**) quantitatively (1.35 g) as an oil (Found: C, 64.2; H, 6.35; N, 6.5. $C_{12}H_{14}ClNO$ requires C, 64.4; H, 6.3; N, 6.3%); $\nu_{max.}$(CCl_4) 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.57 (3 H, d, *J* 7 Hz), 4.0—4.5 (3 H, m), 4.8—5.3 (2 H, m), 5.55—6.25 (1 H, m), and 7.05—7.6 (5 H, m). The chloride (**12e**) (400 mg, 1.78 mmol) was treated with Bu_3SnH (570 mg, 1.97 mmol) and AIBN (29 mg, 0.17 mmol) and the crude material was chromatographed on silica gel (hexane–ethyl acetate, 7:1). The first fraction gave the starting material (**12e**) (41 mg, 12%). The second fraction gave a mixture of *trans* and *cis* isomers (74:26 by n.m.r.) of 3,4-dimethyl-1-phenylpyrrolidin-2-one (**13e**) (267 mg, 74%); $\nu_{max.}$(CCl_4) 1 710 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.07 (d, *J* 7 Hz, Me for *cis*), 1.18 (d, *J* 7 Hz, Me for *cis*), 1.19 (d, *J* 6 Hz, Me for *trans*), 1.25 (d, *J* 6 Hz, Me for *trans*), 1.75—3.1 (2 H, m, 2 × C*H*Me), 3.33 (t, *J* 10 Hz, NC*H*H for *trans*), 3.45 (dd, *J* 10 and 4 Hz, NC*H*H for *cis*), 3.78 (dd, *J* 10 and 8 Hz, NCH*H* for *trans*), 3.86 (dd, *J* 10 and 7 Hz, NCH*H* for *cis*), and 6.85—7.8 (5 H, m, ArH). This material crystallised after a time. Recrystallisation of this mixture from hexane gave the pure trans-*isomer* of (**13e**) (Found: C, 76.2; H, 8.15; N, 7.4. $C_{12}H_{15}NO$ requires C, 76.2; H, 8.0; N, 7.4%); m.p. 94—96 °C. This compound (7 mg) was recovered quantitatively when treated with sodium ethoxide (2.5 mg) in refluxing ethanol (3 ml) for 30 min.

Preparation and Reaction of N-*Allyl*-α-*chloro*-α-*phenylacetanilide* (**12f**) *with* Bu_3SnH.—By a standard procedure, *N*-allylaniline (1.0 g, 7.5 mmol) was treated with α-chlorophenylacetyl chloride (1.42 g, 7.5 mmol) to give the *anilide* (**12f**) quantitatively (2.14 g) as an oil (Found: C, 71.4; H, 5.55; N, 4.9. $C_{17}H_{16}ClNO$ requires C, 71.45; H, 5.6; N, 4.9%); $\nu_{max.}$(CCl_4) 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 4.2—4.45 (2 H, m), 4.8—5.45 (2 H, m), 5.29 (1 H, s), 5.5—6.25 (1 H, m), and 6.9—7.6 (10 H, m). The chloride (**12f**) (400 mg, 1.39 mmol) was treated with Bu_3SnH (530 mg, 1.82 mmol) and AIBN (23 mg, 0.14 mmol) and the crude material was chromatographed on silica gel (hexane–ethyl acetate, 9:2). The first fraction gave trans-4-*methyl*-1,3-*diphenylpyrrolidin*-2-*one* (**13f**) (227 mg, 65%) (Found: C, 81.2; H, 6.9; N, 5.5. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); m.p. 94.5—95 °C (from hexane); $\nu_{max.}$(CCl_4) 1 715 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.20 (3 H, d, *J* 6 Hz, Me), 2.05—2.95 (1 H, m, C*H*Me), 3.36 (1 H, d, *J* 12 Hz, C*H*Ph), 3.46 (1 H, dd, *J* 12 and 9 Hz, NC*H*H), 3.90 (1 H, dd, *J* 9 and 8 Hz, NCH*H*), and 6.85—7.85 (10 H, m, ArH). The second fraction gave the cis-*isomer* of the *lactam* (**13f**) (101 mg, 29%) (Found: C, 81.25; H, 6.8; N, 5.6. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); m.p. 139—139.5 °C (from hexane–ethyl acetate); $\nu_{max.}$(CCl_4) 1 710 cm^{-1}; δ($CDCl_3$; 60 MHz) 0.78 (3 H, d, *J* 7 Hz, Me), 2.45—3.25 (1 H, m, C*H*Me), 3.55 (1 H, dd, *J* 10 and 6 Hz, NC*H*H), 3.83 (1 H, dd, *J* 17 and 10 Hz, NCH*H*), 3.94 (1 H, d, *J* 9 Hz, C*H*Ph), and 6.9—7.9 (10 H, m, ArH).

N-*Allyl*-α-(*phenylthio*)*acetanilide* (**15**).—Using a procedure similar to that for the preparation of compound (**6**), the chloride (**12b**) (4.22 g, 20 mmol) was treated with sodium benzenethiolate (22 mmol) to give the *anilide* (**15**) (5.5 g, 97%) as an oil (Found: C, 71.9; H, 5.9; N, 5.15. $C_{17}H_{17}NOS$ requires C, 72.05; H, 6.05; N, 4.9%); $\nu_{max.}$(CCl_4) 1 665 cm^{-1}; δ($CDCl_3$; 60 MHz) 3.51 (2 H, s), 4.15—4.45 (2 H, m), 4.8—5.3 (2 H, m), 5.5—6.25 (1 H, m), and 7.0—7.7 (10 H, m).

N-*Allyl*-α-*chloro*-α-(*phenylthio*)*acetanilide* (**16**).—In a manner similar to the preparation of compound (**2a**), the anilide (**15**) (560 mg, 1.97 mmol) was treated with NCS (290 mg, 2.17 mmol) to give quantitatively the chloride (**16**); δ($CDCl_3$; 60 MHz) 4.2—4.45 (2 H, m), 4.9—5.35 (2 H, m), 5.42 (1 H, s), 5.55—6.35 (1 H, m), and 7.1—7.9 (10 H, m). This compound was used without purification in the next stage.

Preparation and Reaction of N-*Allyl-α-methoxy-α-(phenylthio)acetanilide* (**12g**) *with* Bu_3SnH.—The chloride (**16**) (626 mg, 1.97 mmol) was added to a solution of sodium methoxide in methanol, prepared from sodium (50 mg, 2.17 mmol) and methanol (5 ml), at room temperature and the mixture was stirred at the same temperature for 15 h, then heated under reflux for 2 h. The solvent was evaporated off, the residue was diluted with CH_2Cl_2 (10 ml), and the whole was washed with water, then dried (Na_2SO_4). The solvent was evaporated off and the residue was chromatographed on silica gel (hexane–ethyl acetate, 9:2) to give the *monothioacetal* (**12g**) (402 mg, 65%) (Found: C, 68.8; H, 6.4; N, 4.6. $C_{18}H_{19}NO_2S$ requires C, 69.0; H, 6.1; N, 4.5%); $\nu_{max.}(CCl_4)$ 1 670 cm^{-1}; δ($CDCl_3$; 60 MHz) 3.39 (3 H, s), 4.15—4.45 (2 H, m), 4.85—5.3 (2 H, m), 5.5—6.3 (1 H, m), and 7.0—7.5 (10 H, m).

A solution of Bu_3SnH (347 mg, 1.19 mmol) and AIBN (18 mg, 0.1 mmol) in dry toluene (40 ml) was added to a refluxing solution of compound (**12g**) (340 mg, 1.08 mmol) in dry toluene (20 ml) *via* a syringe during 1 h, and the mixture was further refluxed for 38 h. An additional solution of Bu_3SnH (157 mg, 0.5 mmol) and AIBN (9 mg, 0.05 mmol) in dry toluene (10 ml) was added and the mixture was again heated under reflux for a further 12 h. After cooling, the solvent was evaporated off and the residue was chromatographed on silica gel (hexane–ethyl acetate, 7:1). The first fraction gave the amide (**12g**) (70 mg, 21%). The second fraction gave a mixture of *trans* and *cis* isomers (86:14 by n.m.r.) of 3-methoxy-4-methyl-1-phenylpyrrolidin-2-one (**13g**); $\nu_{max.}(CCl_4)$ 1 715 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.11 (d, *J* 7 Hz, CMe for *cis*), 1.26 (d, *J* 7 Hz, CMe for *trans*), 1.95—2.8 (1 H, m, C*H*Me), 3.30 (dd, *J* 10 and 8 Hz, NC*H*H for *trans*), 3.54 (higher-field peak of doublet, CH–O for *trans*), 3.67 (3 H, s, OMe), 3.80 (dd, *J* 10 and 8 Hz, NCH*H* for *trans*), 3.90 (d, *J* 7 Hz, CH–O for *cis*), and 6.9—7.7 (5 H, m, ArH). This material crystallised after a time. Recrystallisation from hexane gave the pure trans-*isomer* of (**13g**) (Found: C, 70.6; H, 7.6; N, 7.00. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.4; N, 6.8%); m.p. 83—84 °C.

*Preparation and Reaction of α-Acetoxy-*N-*allyl-α-(phenylthio)acetanilide** (**12h**) *with* Bu_3SnH.—A solution of sodium metaperiodate (415 mg, 1.94 mmol) in water (5 ml) was added by portions to a stirred solution of the sulphide (**15**) (500 mg, 1.76 mmol) in acetone (10 ml) at 0 °C and the mixture was stirred at room temperature for 15 h. The precipitated salts were removed by filtration and the acetone was evaporated off. The residual aqueous solution was extracted with $CHCl_3$, the extract was dried (Na_2SO_4), and the solvent was evaporated off. The residue was chromatographed on silica gel (hexane–ethyl acetate, 1:1) to give *N*-allyl-α-phenylsulphinylacetanilide (**17**) (380 mg, 72%) as an oil; δ($CDCl_3$; 60 MHz) 3.48 and 3.84 (total 2 H, AB q, *J* 13.8 Hz), 4.2—4.4 (2 H, m), 4.8—5.3 (2 H, m), 5.4—6.2 (1 H, m), and 6.6—7.85 (10 H, m). This sulphoxide (475 mg, 1.58 mmol) was dissolved in acetic anhydride (3 ml) containing sodium acetate (330 mg, 3.97 mmol) and the mixture was heated under reflux for 5 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (20 ml) and the whole was washed thoroughly with saturated aq. $NaHCO_3$, then dried (Na_2SO_4). The solvent was evaporated off and the residue was chromatographed on silica gel (hexane–ethyl acetate, 2:1) to give the *anilide* (**12h**) (464 mg, 86%) as an oil (Found: C, 66.8; H, 5.9; N, 4.2. $C_{19}H_{19}NO_3S$ requires C, 66.8; H, 5.6; N, 4.1%); $\nu_{max.}(CCl_4)$ 1 750 and 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 2.08 (3 H, s), 4.15—4.45 (2 H, m), 4.9—5.35 (1 H, m), 5.5—6.25 (1 H, m), 5.93 (1 H, s), 7.18 (5 H, s), and 7.37 (5 H, s). The anilide (**12h**) (500 mg, 1.46 mmol) was treated with Bu_3SnH (935 mg, 3.2 mmol) and AIBN (48 mg, 0.29 mmol) in toluene. After removal of the solvent, the crude material was chromatographed on silica gel (hexane–ethyl acetate, 5:1). The first fraction gave a mixture of *trans* and *cis* isomers (79:21 by n.m.r.) of 3-acetoxy-4-methyl-1-phenylpyrrolidin-2-one† (**13h**); $\nu_{max.}(CCl_4)$ 1 750 and 1 725 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.07 (d, *J* 7 Hz, CMe for *cis*), 1.24 (d, *J* 7 Hz, CMe for *trans*), 1.8—2.9 (1 H, m, C*H*Me), 2.15 (3 H, s, COMe), 3.33 (t, *J* 9.5 Hz, NC*H*H for *trans*), 3.48 (dd, *J* 10 and 3 Hz, NC*H*H for *cis*), 3.83 (t, *J* 9 Hz, NCH*H* for *trans*), 3.92 (dd, *J* 10 and 6 Hz, NCH*H* for *cis*), 5.21 (d, *J* 9.5 Hz, CH–O for *trans*), 5.48 (d, *J* 8 Hz, CH–O for *cis*), and 6.9—7.75 (5 H, m, ArH). This material crystallised after a time. Recrystallisation from hexane gave the pure trans-*isomer* of (**13h**) (Found: C, 66.8; H, 6.4; N, 6.3. $C_{13}H_{15}NO_3$ requires C, 67.0; H, 6.5; N, 6.0%); m.p. 85—86 °C. The second fraction gave a mixture of *trans* and *cis* isomers (74:26 by n.m.r.) of 3-*hydroxy*-4-*methyl*-1-*phenylpyrrolidin*-2-*one* (**18**) (78 mg, 28%) (Found: C, 69.1; H, 7.0, N, 7.3. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.85; N, 7.3%); m.p. 131—132 °C (from hexane–ethanol); $\nu_{max.}(CCl_4)$ 1 715 cm^{-1}; δ ($CDCl_3$; 60 MHz) 1.12 (d, *J* 7 Hz, CMe for *cis*), 1.29 (d, *J* 7 Hz, CMe for *trans*), 1.9—2.95 (1 H, m, C*H*Me), 3.29 (t, *J* 10 Hz, NC*H*H for *trans*), 3.3—4.3 (m, NCH_2 and CH–O for *cis*), 3.78 (t, *J* 9 Hz, NCH*H* for *trans*), 4.02 (br d, *J* 10 Hz, CH–O for *trans*), 4.25—4.65 (1 H, br, OH), and 6.85—7.75 (5 H, m, ArH).

Preparation and Reaction of N-*Allyl-α-chloro-α-phenylsulphonylacetanilide* (**12i**) *with* Bu_3SnH.—MCPBA (80%) (1.75 g, 8.1 mmol) was added by portions to a solution of the chloride (**16**) (1.12 g, 3.52 mmol) in CH_2Cl_2 at 0 °C and the mixture was stirred at room temperature for 20 h. The precipitate was removed by filtration, the solvent was evaporated off, and the residue was chromatographed on silica gel (hexane–ethyl acetate, 3:1) to give quantitatively the *sulphone* (**12i**) (Found: C, 58.3; H, 4.6; N, 4.1. $C_{17}H_{16}ClNO_3S$ requires C, 58.4; H, 4.6; N, 4.0%); m.p. 79.5—80.0 °C (from hexane–ethyl acetate); $\nu_{max.}(CCl_4)$ 1 680 cm^{-1}; δ($CDCl_3$; 60 MHz) 4.15—4.45 (2 H, m), 4.9—5.35 (2 H, m), 5.16 (1 H, s), 5.5—6.3 (1 H, m), and 7.1—8.1 (10 H, m).

The sulphone (**12i**) (350 mg, 1 mmol) was treated with Bu_3SnH (466 mg, 1.6 mmol) and AIBN (24 mg, 0.15 mmol) and the crude material was chromatographed on silica gel (hexane–ethyl acetate, 3:1). The first fraction gave the unchanged sulphone (**12i**) (100 mg, 29%). The second fraction gave N-*allyl-α-phenylsulphonylacetanilide* (**14i**) (108 mg, 34%) (Found: C, 64.7; H, 5.45; N, 4.40. $C_{17}H_{17}NO_3S$ requires C, 64.7; H, 5.4; N, 4.4%); m.p. 82.5—83.0 °C (from hexane–ethyl acetate); $\nu_{max.}(CCl_4)$ 1 665 cm^{-1}; δ($CDCl_3$; 60 MHz) 3.94 (2 H, s), 4.1—4.45 (2 H, m), 4.8—5.3 (2 H, m), 5.4—6.15 (1 H, m), and 6.9—8.1 (10 H, m).

*Preparation and Reaction of α-Chloro-*N-*methyl-*N-*(2-methylprop-2-enyl)-α-(methylthio)acetamide* (**24**) *with* Bu_3SnH.—The amide (**26**)[11] (200 mg, 1.15 mmol) was treated with NCS (185 mg, 1.38 mmol) to give quantitatively the chloride (**24**). This compound, without purification, was dissolved in dry toluene (20 ml) and treated with Bu_3SnH (370 mg, 1.27 mmol) and AIBN (20 mg, 0.1 mmol). The crude material was chromatographed on silica gel (benzene–ethyl acetate, 4:3). The first fraction gave the starting amide (**26**) (29 mg, 14% recovery). The second fraction gave 1,4,4-*trimethyl*-3-*methylthiopyrrolidin*-2-*one* (**25**) (147 mg, 74%) as an oil (Found: M^+, 173.0851. $C_8H_{15}NOS$ requires *M*, 173.0873); $\nu_{max.}(CCl_4)$ 1 690 cm^{-1}; δ($CDCl_3$; 60 MHz) 1.13 (3 H, s, CMe), 1.20 (3 H, s, CMe), 2.27 (3 H, s, SMe), 2.87 (3 H, s, NMe), 2.96 (1 H, d, *J* 9 Hz, NC*H*H), 2.98 (1 H, s), and 3.19 (1 H, d, *J* 9 Hz, NCH*H*).

N-(3-*Trimethylsilylprop*-2-*ynyl*)*aniline* (**27**).—Butyl-lithium (15% hexane solution) (5.9 ml, 9.53 mmol) and chlorotrimethyl-

* *N*-Allyl-*N*-phenylcarbamoyl(phenylthio)methyl acetate.

† 4-Methyl-2-oxo-1-phenylpyrrolidin-3-yl acetate.

silane (830 mg, 7.6 mmol) were successively added to a solution of *N*-(prop-2-ynyl)aniline[21] (500 mg, 3.8 mmol) in dry tetrahydrofuran (20 ml) at −78 °C and the mixture was stirred at the same temperature for 1 h, then at room temperature for 30 min. After removal of the solvent, the residue was dissolved in diethyl ether (20 ml) and washed with water, then dried (Na_2SO_4). The solvent was evaporated off and the residue was chromatographed on silica gel (hexane–ethyl acetate, 7:1) to give the *silane* (**27**) (700 mg, 91%) as an oil (Found: C, 70.5; H, 8.6; N, 6.75. $C_{12}H_{17}NSi$ requires C, 70.9; H, 8.4; N, 6.9%); δ($CDCl_3$; 60 MHz) 0.14 (9 H, s), 3.90 (3 H, br s), and 6.5—7.4 (5 H, m).

α-*Methylthio*-N-(3-*trimethylsilylprop*-2-*ynyl*)*acetanilide* (**28**).—According to the reported procedure for the preparation of compound (**1a**),[13] compound (**27**) (430 mg, 2.1 mmol) was treated with (methylthio)acetyl chloride (260 mg, 2.1 mmol) to give the *anilide* (**28**) (417 mg, 68%) as an oil (Found: C, 61.9; H, 7.3; N, 5.05. $C_{15}H_{21}NOSSi$ requires C, 61.8; H, 7.3; N, 4.8%); $\nu_{max.}$(CCl_4) 2 180 and 1 655 cm^{-1}; δ($CDCl_3$; 60 MHz) 0.11 (9 H, s), 2.18 (3 H, s), 3.03 (2 H, br s), 4.51 (2 H, s), and 7.35 (5 H, s).

Preparation and Reaction of α-*Chloro*-α-*methylthio*-N-(3-*trimethylsilylprop*-2-*ynyl*)*acetanilide* (**29**) *with* Bu_3SnH.—The sulphide (**28**) (200 mg, 0.68 mmol) was treated with NCS (110 mg, 0.82 mmol) to give quantitatively the chloride (**29**). This compound, without purification, was dissolved in benzene (15 ml) and the mixture was treated with Bu_3SnH (220 mg, 0.75 mmol) and AIBN (11 mg, 0.07 mmol). The crude material was chromatographed on silica gel (hexane–ethyl acetate, 7:1) to give 3-*methylthio*-1-*phenyl*-4-*trimethylsilylmethylenepyrrolidin*-2-*one* (**30**) (81 mg, 40%) (Found: M^+, 291.1085. $C_{15}H_{21}NOSSi$ requires *M*, 291.1111); m.p. 101.5—102 °C (from hexane); $\nu_{max.}$(CCl_4) 1 700 and 1 380 cm^{-1}; δ($CDCl_3$; 60 MHz) 0.23 (9 H, s, $SiMe_3$), 2.31 (3 H, s, SMe), 4.00 (1 H, br s, SCH), 4.29 and 4.56 (1 H each, br AB q, *J* 13.2 Hz, NCH_2), 5.65—5.85 (1 H, m, C=CH), and 7.0—7.8 (5 H, m, ArH).

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