Ring-size and Substituent Effects in Intramolecular Reactions of Alkylidenecarbenes (Carbenoids)

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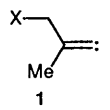
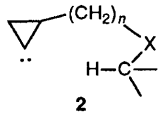
Intramolecular reaction of methylenecarbenes (carbenoids), derived by reaction of 1,1-dibromoalkenes and methyllithium, with 5,6-related C–H bonds leads to cyclopentenes when there is an alkoxy or amino substituent on C-5, but no reaction occurs at a 4,5-related C–H bond when there is a heteroatom on C-4; when there is an alkylthio group either on C-4 or C-5 attack occurs on sulphur and the alkyl group is lost, leading to a 2,3-dihydrothiophene or a 3,4-dihydro-2*H*-thiopyran respectively. If a heteroatom-hydrogen bond is present at the 5,6-position a formal insertion occurs at that bond leading to 2,3-dihydropyrroles, 2,3-dihydrofurans or 2,3-dihydrothiophenes.

The formal insertion of a carbene into a C–H or heteroatom-H bond is well known.[1] The intramolecular version has been applied in, for example, syntheses of modhephene,[2] modified erythromycins,[3] sex attractants,[4] ishwarene[5] and β-lactams.[6] In intermolecular examples, the C–H insertion appears to be favoured by the presence of an adjacent phenyl or alkoxy group.[1,7] This paper examines the effects of distance and the presence of heteroatoms in the intramolecular reactions of alkylidenecarbenes (carbenoids) **1**.

In the case of alkylcarbenes, the normal intramolecular insertion is that into a C(3)–H bond, relative to the carbene centre on C-1, leading to a cyclopropane; this reaction is apparently disfavoured by a range of substituents on C-3 including phenyl and alkoxy.[8] The C(3)–H insertion also occurs for cyclopropylidenes **2**,[9] generated from 1,1-dibromocyclopropanes and methyllithium, particularly when the normal rearrangement to an allene is not favoured; once again, when there is a heteroatom at the 4-position relative to the carbene centre **2** (n = 1), insertion into the C(3)–H bond is normally suppressed, but in this case that into a C(5)–H bond is promoted.[10] When the heteroatom is at the 5- or 6-positions, **2** (n = 2 or 3) no insertion into a C–H bond is seen, although the products of formal insertion into a 5,6-related heteroatom-H bond can be observed.

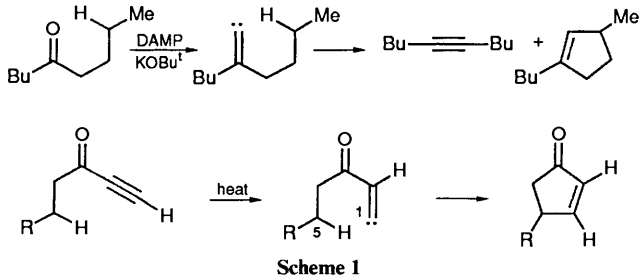


1



2

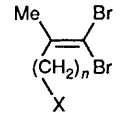
Alkylidenecarbenes **1**[11] have been generated by, for example, base induced elimination of hydrogen halides from 1-halogeno-2,2-disubstituted alkenes,[12] from silylvinyl trifluoromethanesulphonates,[13] *N*-nitrosooxazolidones,[14] base promoted reaction of dimethyl diazomethylphosphonate (DAMP) with carbonyl compounds,[15,16] and thermolysis of alkynes.[2,17] As well as adding to alkenes, they can be trapped by insertion into C(5)–H bonds (Scheme 1).[15,17,3,18]



Scheme 1

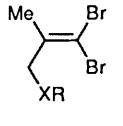
This reaction is observed when there is either a carbon or a heteroatom at the 4-position; no insertion has been reported into other C–H bonds. In this paper we examine the effects of distance and the presence of a heteroatom on the reactions of alkylidenecarbenes **1** or related carbenoids, derived from the reaction of a 1,1-dibromoalkene with methyllithium; the dibromide was chosen in preference to, for example, a monobromoalkene to remove problems of stereoisomerism in the precursor, and to provide a direct parallel with the generation of alkylcarbenes and cyclopropylidenes from the reactions of 1,1-dihalogenoalkanes with an alkyllithium.

The reaction of 1,1-dibromo-2-methylprop-1-ene **3a** with methyllithium in the presence of an alkene is known to give cyclopropanes derived from **1** (X = H).[19,†] The reaction occurs by lithium–bromine exchange which leads to a 1-bromo-1-lithioalkene and this undergoes α-elimination of LiBr; the intermediate can be trapped with CO_2.[20] The corresponding substituted dibromides **4a–i** were prepared by nucleophilic substitution on the tribromide **3b**. Compound **4i** was converted into the alcohol **6a** by hydrolysis, deacylation and reduction, and the alcohol was converted into **6b–f** by standard procedures. The 4-substituted 1,1-dibromobut-1-enes **5** were prepared from the alcohol **5a**. This is readily available from 3-methylbut-3-en-1-ol by bromination and dehydrobromination to an *E*/*Z* mixture of monobromoalkenes,[21] followed by repeating the procedure.



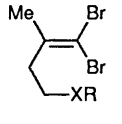
3

a; X = H, n = 1	
b; X = Br, n = 1	
c; X = Br, n = 2	
d; X = Br, n = 3	



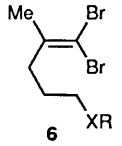
4

	X	R
a;	NPr^i	Pr^i
b;	NMe	Me
c;	O	Me
d;	O	Pr^i
e;	S	Et
f;	S	Allyl
g;	NH	Pr^i
h;	NH	Bu^t
i;	$CHCO_2Et$	Ac



5

	X	R
a;	O	H
b;	NH	H
c;	NPr^i	H
d;	S	H
e;	O	Me
f;	S	Allyl



6

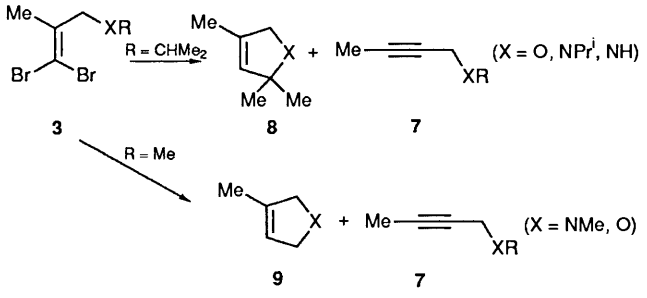
	X	R
a;	O	H
b;	O	Pr^i
c;	NPr^i	Pr^i
d;	S	H
e;	S	Pr^i
f;	NPr^i	H

† Although no methylenecarbene can be trapped in the reaction of 1,1-dibromoprop-1-ene with methyllithium in the presence of an alkene because a very rapid 1,2-hydrogen shift occurs to give propyne, apparently the 1,2-methyl shift in the intermediate carbenes (carbenoids) **1** is slow enough to allow intermolecular trapping to occur.

Table 1 Reactions of the dibromides **4** with methyllithium

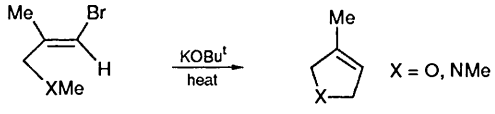
Starting dibromide	Products	Ratio
4c	**7** (X = O, R = Me), **8** (X = O)	1.8:1
4d	**7** (X = O, R = Pr^i), **9** (X = O)	1:3
4i	**7** (X = NH, R = Pr^i), **8** (X = NH)	1:1
4b	**7** (X = NMe, R = Me), **9** (X = NMe)	1:2
4a	**7** (X = NPr^i, R = Pr^i), **8** (X = NPr^i)	1.1:1
4h	**7** (X = NH, R = Bu^t)	—

Reaction of **4a–d** with methyllithium led to a mixture of the corresponding alkyne **7**, derived by a 1,2-alkyl shift in the corresponding carbene **1**, and either **8** or **9**, the product of insertion of the carbene (carbenoid) into a 5,6-related C–H bond (see Table 1). The ratio of insertion product to alkyne was



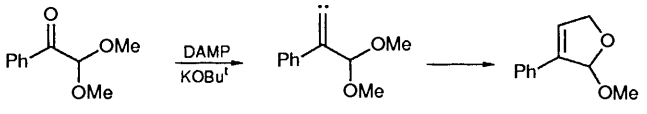
3 **8** **7** **9** **7**

greater for **4d** than **4c**, possibly because in the latter case the C–H bond was tertiary; however, this did not hold for **4a**, **4b** or, indeed **4g**. It is interesting to note that in the case of **4g**, insertion occurred into the 5,6-related CH bond, rather than the 4,5-related NH bond; in the same way **4h** gave only the alkyne **7** (X = NH, R = Bu^t). The cyclisation to **8** or **9** is as expected from the reaction of **10** (X = O, NMe) with base; in that case, however, no alkyne was observed, perhaps reflecting the different reaction conditions used.[22,23]

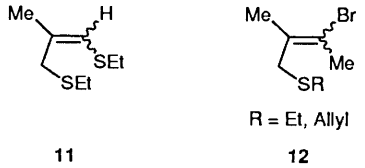


10 **9**

A similar insertion into the C–H bonds of acetals has been reported.[18]

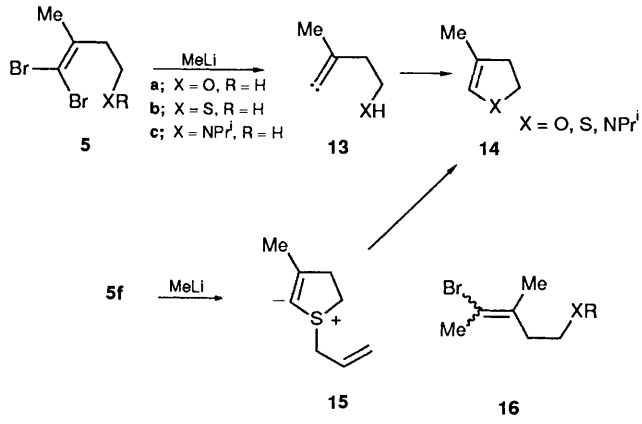


Reaction of the sulphides **4e** and **4f** with methyllithium did not lead to dihydrothiophenes, and instead **4e** led to **11** and **12** (R = Et), of undefined stereochemistry, while **4f** led to **12** (R = allyl). The disulphide **11** may possibly arise by trapping of the carbene by starting material to form an *S*-ylide, followed by protonation and dealkylation by reaction with MeLi.[24]



11 **12**

Treatment of the alcohol **5a** with methyllithium at 20 °C gave the dihydrofuran **14** (X = O) in 58% yield; the most general route to substituted 2,3-dihydrofurans is from derivatives of 4-hydroxybutyraldehyde.[25] Reaction of **5b** with methyllithium gave the 2,3-dihydropyrrole **14** (X = NPr^i) in 49% yield. A small amount of residue was obtained which gave an extremely complicated NMR spectrum and was not investigated further; 2,3-dihydropyrroles have been prepared by several methods, including condensation of γ-amino ketones,[26] and the acid catalysed thermal rearrangement of cyclopropyl imines.[27] Treatment of the thiol **5d** or sulphide **5f** with methyllithium also gave the corresponding dihydrothiophene **14** (X = S) in 71 and 57% yield respectively.

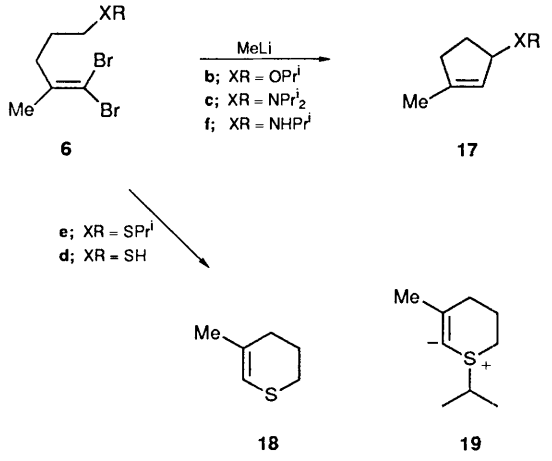


5 **13** **14** **15** **16**

In the latter case, the residue gave a complicated NMR spectrum and GLC showed it to contain several components. The production of **14** (X = S) in this reaction may involve the generation of the ylide **15** by interaction of the sulphur lone pair with the carbene **1** (X = $CH_2SAllyl$); this can then undergo protonation and dealkylation.[24] By analogy with other sulphur ylides **15** might have been expected to undergo a 2,3-sigmatropic shift; this was not observed. The synthesis of substituted 2,3-dihydrothiophenes is not well documented, although treatment of 4,5-dihydrothiophen-3(2*H*)-one with a Grignard reagent followed by dehydration formally leads to 3-substituted derivatives.[28] The cyclisations of **5a**, **c**, **d** apparently involve formal insertion of the carbene **13** into the 5,6-related HX-bond; however, the mechanisms of such insertions are often more complex,[29] and, in reactions involving MeLi, removal of the acidic hydrogen may compete with lithium–halogen exchange. It should be noted that 2 mol equiv. of MeLi were required in the case of **5a**. Reaction the methyl ether **5e** with methyllithium gave a volatile component which was assigned as **7** (XR = CH_2OMe) on the basis of its ^1H NMR spectrum, which included a methyl signal at δ 1.79 showing a coupling of 1 Hz to the protons of C-2 typical of such systems. The residue was tentatively assigned as a *ca.* 1:1 mixture of *E*- and *Z*-**16** (XR = OMe); GCMS showed two components with identical fragmentation patterns, and an accurate mass measurement was in agreement with the formula $C_7H_{13}O$, consistent with loss of a bromine atom from the ethers. The carbene derived from **5e** may have been expected to insert into the 4,5- or 6,7-related C–H bond. Clearly this mode of reaction is disfavoured.

Reaction of **6b** or **6c** with methyllithium led to the corresponding cyclopentenes **17** by apparent insertion of the derived carbene into a 5,6-related C–H bond inside the heteroatom at the 6-position; no alkyne was obtained in these cases. Compound **6f** also led to a cyclopentane, although the yield was very low; no reaction at nitrogen was observed in this case. It appears that in these carbenes, a heteroatom at the 6-position does favour insertion into the C(5)–H bond more than a heteroatom at the 4-position does, in contrast with the selectivity seen for cyclopropylidenes. Treatment of either **6e** or **6d** with methyllithium led to the dihydrothiopyran **18**. In the case of the thiol

6e, the product may be formed by insertion of the derived carbene into the 6,7-related S–H bond or by intramolecular reaction of the thiolate with the carbene centre followed by protonation. The formation of **18** from the sulphide **6d** is less clear, and may again involve formation of the ylide **19** which then undergoes protonation and dealkylation, the exact order of which has not been established. Such dealkylations are known to occur with alkyllithiums and sulphonium salts.[24]



Experimental

Organic solutions were dried over anhydrous sodium or magnesium sulphate. TLC was performed on Schleicher and Schull F15054 silica gel plates. Column chromatography was performed using Merck 7736 silica gel under low pressure eluting with (a) light petroleum b.p. 40–60 °C, (b) light petroleum–diethyl ether (4:1) or (c) light petroleum–diethyl ether (9:1). GLC was conducted using a Packard 427 gas chromatograph with a quartz SE30 capillary column or, for preparative work, a Varian Aerograph 2700 gas chromatograph with a 2 M 10% SE30 on Celite 60–85 column. Unless otherwise stated, all new compounds were pure by TLC or GLC. Melting points were determined on a Kofler hot-stage apparatus. Elemental analyses were performed with a Carlo-Erba Instrumentazione model 1106 CHN analyser. IR spectra were recorded on a Nicolet 20 SX B F.T. spectrometer. NMR spectra were recorded for deuteriochloroform solutions with tetramethylsilane as the internal standard unless otherwise stated. ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R24B at 60 MHz, a Bruker WP 200 at 200 MHz or a Bruker WM 300-WB at 300 MHz, and ^{13}C NMR spectra on the WP200 at 50 MHz or WM300-WB at 75 MHz. *J* Values are recorded in Hz. EI mass spectra were recorded on an AEI MS 9 or Kratos MS80RF; Br and Cl refer to the isotopes ^{79}Br and ^{35}Cl.

3,3-*Dibromo-2-methylprop-2-enyl Ethers.* Reaction of 1,1,3-tribromo-2-methylprop-1-ene **3b**[30] with sodium methoxide in methanol or sodium isopropoxide in isopropyl alcohol (reflux 2 h) gave **4c** (65%), b.p. 26–28 °C at 0.5 mmHg [δ_H 1.86 (3 H, s), 3.23 (3 H, s), 3.99 (2 H, s)] and **4d** (80%), b.p. 40–42 °C at 0.07 mmHg [δ_H 3.95 (2 H, s), 3.44 (1 H, septet, *J* 6), 1.81 (3 H, s), 1.07 (6 H, d, *J* 7].

3,3-*Dibromo-2-methylprop-2-enylamines.*—The tribromide **3b** was refluxed for 18 h with the corresponding amine or, for volatile amines, a solution of this in ethanol. Work-up gave the amines **4a** (79%) (Found: M$^+$, 310.9860. $C_{10}H_{19}Br_2N$ requires *M*, 310.9884), δ_H 0.95 (12 H, d, *J* 6.5), 1.86 (3 H, s), 2.93 (2 H, septet, *J* 6.5) and 3.2 (2 H, s); **4b** (77%) (Found: M$^+$, 254.9253. $C_6H_{11}Br_2N$ requires *M*, 254.9258), δ_H 1.93 (3 H, s), 2.66 (6 H, s) and 2.99 (2 H, s); **4g** (71%) (Found: M$^+$, 268.9429. $C_7H_{13}Br_2N$ requires *M*, 268.9415), δ_H 0.8 (1 H, br s, NH), 1.05 (6 H, d, *J* 6.5), 1.91 (3 H, s), 2.75 (1 H, sep, *J* 6.5) and 3.34 (2 H, s); and **4h** (69%) (Found: M$^+$, 282.9559. $C_8H_{13}Br_2N$ requires *M*, 282.9571), δ_H 0.71 (1 H, br s, NH), 1.03 (9 H, s), 1.96 (3 H, s) and 3.27 (2 H, s).

3,3-*Dibromo-2-methylprop-2-enyl Sulphides.*—Prop-2-enethiol (1.1 g, 14.8 mmol) was stirred for 30 min with sodium methoxide (800 mg, 14.8 mmol) in methanol (10 ml). The tribromide **3b** (3.5 g, 12 mmol) in methanol (5 ml) was added and the mixture was refluxed for 18 h. It was then cooled, poured into water (50 ml), and extracted with ether (50 ml). The organic layer was dried and evaporated at 14 mmHg to give an oil; column chromatography[a] gave 1-allylthio-3,3-dibromo-2-methylprop-1-ene **4f** (2.3 g, 67%) (Found: M$^+$, 283.8891. $C_7H_{10}Br_2S$ requires: *M*, 283.8870); δ_H 6.16–4.97 (3 H, m), 3.34 (2 H, s), 3.10 (2 H, d, *J* 6) and 2.0 (3 H, s); ν_{max}/cm^{-1} 1425m, 1375s and 1230s. Reaction as above using ethanethiol (820 mg, 13.3 mmol) in place of prop-2-enethiol gave 1,1-dibromo-3-ethylthio-2-methylprop-1-ene **4e** (2.3 g, 70%); δ_H 3.33 (2 H, s), 2.50 (2 H, q, *J* 7), 2.0 (3 H, s) and 1.27 (3 H, t, *J* 7); ν_{max}/cm^{-1} 1375, 1435, 1590 and 2960.

Reaction of 3,3-*Dibromo-2-methylprop-2-enes with Methyllithium.*—(a) Methyllithium (1 mol dm^{-3}; 4 ml) was added over 1 min to a stirred solution of the ether **4c** (0.5 g) in ether (5 ml). After 3 min, the mixture was quenched with water (5 ml) and worked up as above. The organic extract contained two components in the ratio 1.8:1 (GLC); the bulk of the ether was removed by careful distillation at 760 mmHg until the volume of the residue was *ca.* 0.5 ml and this was then flash distilled at 14 mmHg. Preparative GLC gave but-2-ynyl methyl ether,[31] and 3-methyl-2,5-dihydrofuran[23] (70% combined based on NMR spectroscopy).

(b) Methyllithium (1 mol dm^{-3}; 4 ml) was added over 1 min to the ether **4d** (0.5 g) in ether (5 ml). After work-up as above, GLC of the ether layer showed two products in the ratio *ca.* 3:1. The ether was carefully removed at 14 mmHg until the volume of the residue was *ca.* 0.5 ml; this was flash distilled at 14 mmHg and the two components were separated by preparative GLC. The first was 2,2,4-trimethyl-2,5-dihydrofuran.[23] The second was but-2-ynyl isopropyl ether;[32] δ_H 3.93 (2 H, q, *J* 2.5), 3.71 (1 H, septet, *J* 6), 1.80 (3 H, t, *J* 2.5) and 1.12 (6 H, d, *J* 6) (70% combined by NMR spectroscopy).

(c) Methyllithium (1 mol dm^{-3}; 4 ml) was added as above to the amine **4g** (0.5 g) in ether (5 ml). After work-up as above, GLC showed the presence of two products in the ratio *ca.* 1:1. The solvent was removed carefully at 760 mmHg until the volume was *ca.* 0.5 ml. Flash distillation at 14 mmHg and 40 °C gave a residue (35 mg) and a distillate (170 mg) which was separated by GLC to give 2,2,4-trimethyl-2,5-dihydropyrrole,[23] and *N*-isopropylbut-2-ynylamine (Found: M$^+$, 111.1041. $C_7H_{13}N$ requires *M*, 111. 1048); δ_H 3.25 (2 H, q, *J* 2.5), 2.97 (1 H, septet, *J* 6), 1.77 (3 H, t, *J* 2.5), 1.63 (1 H, br s, NH) and 1.01 (6 H, d, *J* 6).

(d) Methyllithium (1 mol dm^{-3}; 4 ml) was added as above to the amine **4b** (0.5 g) in ether (5 ml). After work-up as above the solvent was carefully removed at 760 mmHg to leave a *ca.* 2:1 mixture (130 mg) of the pyrroline **9** (X = NMe)[23] and the alkyne **7** (XR = NMe_2) which showed only one peak on GLC (Found: M$^+$, 97.0877. Calc. for $C_6H_{11}N$: *M*, 97.0891); δ_H (for the pyrroline)[33] 5.23 (1 H, br s), 3.27 (4 H, br s), 2.12 or 2.32 (3 H, s), and 1.68 (3 H, s), and (for the alkyne) 3.08 (2 H, q, *J* 2.5), 2.12 or 2.32 (6 H, s) and 1.80 (3 H, t, *J* 2.5).

(e) Methyllithium (1 mol dm^{-3}; 8 ml) was added to the amine **4a** (1.0 g) in ether (10 ml). Work-up as above and GLC showed the presence of two components in the ratio 1.1:1. The solvent

was removed carefully at 14 mmHg and 20 °C and the residue (480 mg) was separated into the two components by preparative GLC. The first was *N*-isopropyl-2,2,4-trimethyl-2,5-dihydropyrrole (Found: M^+, 153.1512. $C_{10}H_{19}N$ requires *M*, 153.1517); δ_H 5.08 (1 H, m), 3.44 (2 H, br s), 3.04 (1 H, septet, *J* 6), 1.69 (3 H, br s) and 0.98–1.16 (12 H, m); ν_{max}/cm^{-1} 2950, 1680, 1460, 1390 and 830. The second was *N*,*N*-diisopropylbut-2-ynylamine (Found: M^+, 153.1510); δ_H 3.26 (2 H, q, *J* 2.3), 3.13 (2 H, septet, *J* 6), 1.75 (3 H, t, *J* 2.3) and 1.04 (12 H, d, *J* 6); ν_{max}/cm^{-1} 2940, 2320, 1480, 1390 and 1190.

(f) Methyllithium (1 mol dm^{-3}; 8 ml) was added over 1 min to the amine **4h** (1.0 g) in ether (10 ml). After work-up as above, careful removal of the solvent gave an oil which was characterised as N-*tert*-butylbut-2-ynylamine, b.p. 60–62 °C at 14 mmHg (0.31 g, 70%) (Found: M^+, 125.1202. $C_8H_{15}N$ requires *M*, 125.1204); δ_H 3.19 (2 H, q, *J* 2.75), 2.25 (1 H, br s), 1.76 (3 H, t, *J* 2.75) and 1.03 (9 H, s); ν_{max}/cm^{-1} 3280, 2920, 2300, 1480, 1370 and 1230.

(g) Methyllithium (0.74 mol dm^{-3}; 6 ml) was added as above to the sulphide **4e** (1.0 g) in ether (10 ml). After work-up as above, TLC showed the presence of two products which were separated by column chromatography.[a] The first was characterised as 3-bromo-2-methylbut-2-enyl ethyl sulphide **12** (R = Et) (160 mg) (Found: M^+, 207.9933. $C_7H_{13}BrS$ requires *M*, 207.9921); δ_H 3.21 (2 H, s), 2.67–2.22 (5 H, m), 1.83 (3 H, s) and 1.17 (3 H, t, *J* 7); ν_{max}/cm^{-1} 1215, 1460 and 2980. The second was 1,3-bis(ethylthio)-2-methylprop-1-ene **11** (70 mg); δ_H 5.64 (1 H, s), 3.1 (2 H, s), 2.83–2.16 (4 H, m), 1.83 (3 H, s) and 1.47–1.02 (6 H, m); ν_{max}/cm^{-1} 1230, 1375, 1445 and 2935.

The above reaction was repeated using dibromide (1.2 g) and methyllithium (6 ml) at −50 °C. Work-up gave **12** (R = Et) (230 mg).

(h) Methyllithium (0.74 mol dm^{-3}; 3 ml) was added to the sulphide **4f** (0.5 g) in ether (10 ml) at 20 °C. After work-up as before, chromatography[a] afforded two fractions. The first fraction was 1-allylthio-3-bromo-2-methylbut-2-ene **12** (R = allyl) (90 mg) (Found: M^+, 219.9925. $C_8H_{13}BrS$ requires *M*, 219.9921); δ_H 6.0–4.87 (3 H, m), 3.33 (2 H, s), 3.12 (2 H, d, *J* 7), 2.36 (3 H, s) and 1.90 (3 H, s); ν_{max}/cm^{-1} 1225, 1420, 1630 and 2980. The second fraction (45 mg) was not characterised.

4,4-*Dibromo*-2-*methylbut*-3-*en*-1-*ol* **5a**.—Bromine (10.1 ml, 0.18 mol) in dichloromethane (200 ml) was added to a solution of (*E*)- and (*Z*)-4-bromo-3-methylbut-3-en-1-ol[21] (29.3 g, 0.17 mol) in dichloromethane (500 ml) at −78 °C. After 24 h at 20 °C the solution was concentrated at 14 mmHg to give 3,4,4-tribromo-3-methylbutan-1-ol (53.5 g, 93%); ν_{max}(film)/cm^{-1} 3290br s, 1379m, 1049s and 669m cm^{-1}; δ_H 1.98 (1 H, s), 2.01 (3 H, s), 2.26–2.54 (2 H, m), 3.89–4.10 (2 H, complex multiplet) and 6.03 (1 H, s); δ_C 28.8 (q), 43.7 (t), 55.0 (d), 60.6 (t) and 69.6 (s); *m*/*z* 322/324/326 (0.2:0.4:0.2% of base peak). A solution of potassium hydroxide in methanol (5 mol dm^{-3}; 40 ml) was added to the tribromide (52 g, 0.16 mol) with cooling and stirring. After 5 h at 20 °C, the mixture was poured into water (500 ml) and extracted with dichloromethane (5 × 150 ml). The organic extracts were washed with hydrochloric acid (1 mol dm^{-3}; 200 ml) and saturated aq. sodium hydrogen carbonate (200 ml), dried and concentrated at 14 mmHg. Chromatography[b] gave the title compound **5a** (22.2 g, 56%) as an oil, b.p. 85–87 °C, 0.1 mmHg, which solidified with time and was crystallised from light petroleum, m.p. 39–40 °C (Found: C, 24.7; H, 3.3%; M^+, 241.8952. $C_5H_8Br_2O$ requires C, 24.6; H, 3.3%; M, 241.8942); ν_{max}/cm^{-1} 3343 br s, 1046s and 820s; δ_H 1.8 (1 H, br s, OH), 1.95 (3 H, s), 2.6 (2 H, t, *J* 6) and 3.8 (2 H, t, *J* 6); δ_C 23.7 (q), 41.1 (t), 59.9 (t), 86.8 (s) and 139.1 (s).

1,1-*Dibromo*-4-*methoxy*-2-*methylbut*-1-*ene* **5e**.—Dibromide **5a** (3 g, 0.012 mol) and tetrabutylammonium iodide (0.04 g, 1 mol %) in dichloromethane (10 ml) were stirred vigorously with 50% aq. sodium hydroxide (1.25 ml, 0.031 mol). Dimethyl sulphate (1.7 ml, 0.018 mol) was added dropwise with cooling. After 18 h at 20 °C, conc. aq. ammonia (3 ml) was added and the mixture was stirred for 30 min. It was then poured into water (100 ml) and extracted with dichloromethane (3 × 50 ml); the organic layer was washed with water (50 ml), dried and concentrated at 14 mmHg. Chromatography[a] of the residue gave the title compound **5e** (2.21 g, 71%) (Found: M^+, 255.9092. $C_6H_{10}Br_2O$ requires *M*, 255.9099) as a colourless oil; ν_{max}/cm^{-1} 2826m, 1116s and 822s; δ_H 1.93 (3 H, s), 2.56 (2 H, t, *J* 7), 3.33 (3 H, s) and 3.49 (2 H, t, *J* 7); δ_C 23.3 (q), 38.1 (t), 58.6 (q), 69.6 (t), 86.4 (s) and 139.4 (s).

1,1,4-*Tribromo*-2-*methylbut*-1-*ene* **3c**.—Phosphorus tribromide (0.82 ml, 4.2 mmol) was added to the alcohol **5a** (3 g, 0.012 mol) in ether (30 ml) at 0 °C. The solution was stirred at 20 °C for 24 h, washed with hydrochloric acid (1 mol dm^{-3}) saturated aq. sodium hydrogen carbonate and water, dried and concentrated at 14 mmHg. Chromatography[a] of the residue gave the title compound **3c** (1.7 g, 45%) (Found: M^+, 303.8135. $C_5H_7Br_3$ requires *M*, 303.8118); ν_{max}/cm^{-1} 1600w, 1270m, 1217m and 819s; δ_H 1.95 (3 H, s), 2.85 (2 H, t, *J* 7) and 3.45 (2 H, t, *J* 7 Hz); δ_C 22.9 (q), 27.9 (t), 40.9 (t), 88.5 (s) and 138.9 (s).

4,4-*Dibromo*-3-*methylbut*-3-*enylamine* **5b***.—Methanesulphonyl chloride (5.6 g, 0.05 mol) was added to the alcohol **5a** (11.0 g, 0.045 mol) in dry pyridine (20 ml) at 0 °C. The mixture was stirred at 20 °C for 2 h, poured into ether (200 ml) and washed with hydrochloric acid (1 mol dm^{-3}; 2 × 30 ml) and saturated aq. sodium hydrogen carbonate (30 ml), dried and concentrated at 14 mmHg. Chromatography[c] of the residue gave the mesylate (14.3 g, 98%) (Found: M^+, 319.8689. $C_6H_{10}Br_2SO_3$ requires *M*, 319.8717); ν_{max}/cm^{-1} 2939w, 1355s, 1174s, 955s and 822s; δ_H 1.9 (3 H, s), 2.7 (2 H, t, *J* 6), 3.0 (3 H, s) and 4.25 (2 H, t, *J* 6). The mesylate (5 g, 0.016 mol) and sodium azide (1.1 g, 0.017 mol) were stirred at reflux in dimethylformamide (25 ml) for 3 h. The mixture was allowed to cool, ether (150 ml) was added and the organic layer was washed with hydrochloric acid (1 mol dm^{-3}; 3 × 30 ml), brine (30 ml) and water (30 ml), dried and concentrated at 14 mmHg to give 1-azido-4,4-dibromo-3-methylbut-3-ene (3.5 g, 84%) (Found: $M^+ + 1$, 267.9125. $C_5H_7Br_2N_3$ requires $M + 1$, 267.9095); ν_{max}/cm^{-1} 2931m, 2099s, 1266m, 1135m and 821s; δ_H 1.9 (3 H, s), 2.55 (2 H, m) and 3.4 (2 H, m). Lithium aluminium hydride (0.19 g, 0.005 mol) was added to the azide (2.6 g, 0.01 mol) in ether (20 ml) in small portions. The reaction was followed by TLC until the azide had been consumed (*ca.* 10 min). The reaction mixture was quenched with ethyl acetate, diluted with water, filtered, and the organic layer separated and concentrated at 14 mmHg. The residue was taken up in hydrochloric acid (1 mol dm^{-3}; 50 ml) and extracted with ether (25 ml). The aqueous layer was made basic with aq. sodium hydroxide (1 mol dm^{-3}) and then extracted with ether (3 × 30 ml). The organic layer was dried and concentrated at 14 mmHg to give the title compound **5b** (1.45 g, 60%) (Found: $M^+ + 1$, 241.9136. $C_5H_9Br_2N$ requires $M + 1$, 241.9180); ν_{max}/cm^{-1} 3360m, 3240m, 2927m, 1600m, 1134m and 817s; δ_H 1.74 (2 H, br s, NH), 1.91 (3 H, s), 2.46 (2 H, t, *J* 7) and 2.86 (2 H, t, *J* 7). Prolonged reaction times in the reduction led to a product which showed a ^1H NMR spectrum consistent with reduction of the vinylic bromides.

N-*Isopropyl*-4,4-*dibromo*-3-*methylbut*-3-*enylamine* **5c**.—Bromocresol Green (1 drop) was added to the amine **5b** (1.4 g,

* The direct conversion of **10a** into **10b** using hydrazoic acid and diethyl azodicarboxylate gave only a 21% yield.[34]

5.8 mmol) in methanol (15 ml). A solution of hydrochloric acid in methanol (2 mol dm^{-3}) was added dropwise to give a yellow colour. Acetone (0.36 g, 6.4 mmol) was added, followed by sodium cyanoborohydride (0.18 g, 2.6 mmol) and a few 4 Å sieves. The mixture was stirred at 20 °C for 24 h and then brought to pH 2 by dropwise addition of concentrated hydrochloric acid; the mixture was then concentrated at 14 mmHg. The residue was taken up in water (10 ml) and extracted with ether (3 × 20 ml). The aqueous solution was brought to pH 10 with solid potassium hydroxide, saturated with sodium chloride and extracted with ether (5 × 20 ml). The organic extracts were dried and concentrated at 14 mmHg to give the title compound **5c** (1.2 g, 73%) (Found: $M^+ + 1$, 283.9635. $C_8H_{15}Br_2N$ requires $M + 1$, 283.9660); ν_{max}/cm^{-1} 3350br m, 2964s, 1471m, 1442m, 1132m and 817s; δ_H 1.07 (6 H, d, J 6.2), 1.41 (1 H, br s, NH), 1.92 (3 H, s), 2.45 (2 H, m) and 2.65–2.95 (3 H, complex multiplet).

4,4-*Dibromo*-3-*methylbut*-3-*enethiol* **5d**.—A mixture of the above mesylate (0.8 g, 2.5 mmol) and thiourea (0.21 g, 2.75 mmol) in ethanol (10 ml) was stirred under reflux for 6 h. Potassium carbonate (0.7 g), sodium metabisulphite (2.3 g), and water (5 ml) were added and the mixture was stirred for 18 h, concentrated at 14 mmHg and partitioned between dichloromethane (25 ml) and hydrochloric acid (1 mol dm^{-3}; 20 ml). The organic layer was washed with water (20 ml), dried and concentrated at 14 mmHg. Chromatography,[a] gave 4,4-dibromo-3-methylbut-3-enethiol **5d** (0.47 g, 72%) (Found: $M^+ - 1$, 256.8620. $C_5H_8Br_2S$ requires $M - 1$, 256.8636); ν_{max}/cm^{-1} 2934m, 2564w, 1445m, 1153m and 813s; δ_H 1.45 (1 H, t, J 7.7, SH), 1.91 (3 H, s) and 2.53–2.70 (4 H, m); δ_C 21.7 (t), 22.9 (q), 42.2 (t), 87.4 (s) and 139.8 (s).

1,1-*Dibromo*-4-*chloro*-2-*methylbut*-1-*ene*.—The above mesylate (13.8 g, 0.043 mol) and lithium chloride (9 g, 0.22 mol) in acetone (100 ml) were refluxed for 60 h, concentrated at 14 mmHg and partitioned between dichloromethane (150 ml) and water (100 ml); the aqueous layer was extracted with dichloromethane (2 × 150 ml) and the combined organic extracts were washed with water (100 ml), dried and concentrated at 14 mmHg. Chromatography[a] gave 1,1-dibromo-4-chloro-2-methylbut-1-ene (Found: M^+, 259.8633. $C_5H_7Br_2Cl$ requires M, 259.8604) as a colourless oil (8.53 g, 76%); ν_{max}/cm^{-1} 2961w, 1600w, 1147m and 820s; δ_H 1.95 (3 H, s), 2.7 (2 H, m) and 3.55 (2 H, m); δ_C 23.1 (q), 40.7 (t), 40.8 (t), 88.4 (s) and 138.2 (s).

Allyl 4,4-*Dibromo*-3-*methylbut*-3-*enyl Sulphide* **5f**.—A solution of sodium prop-2-enyl sulphide in dimethylformamide (2.8 mol dm^{-3}), prepared from sodium methoxide and prop-2-enethiol, was added dropwise to 1,1-dibromo-4-chloro-2-methylbut-1-ene (1.5 g, 5.7 mmol) in dimethylformamide (5 ml) at 20 °C until no starting material remained (TLC). Brine was added and the mixture was extracted with ether (2 × 50 ml). The combined organic extracts were washed with hydrochloric acid (1 mol dm^{-3}; 30 ml) and water (30 ml), dried and concentrated at 14 mmHg. Chromatography[a] gave the title compound (0.45 g, 26%) (Found: $M^+ - Br$, 220.9846. $C_8H_{12}Br_2S$ requires M, 220.9823); ν_{max}/cm^{-1} 2915m, 1625w, 989s, 917s and 815s; δ_H 1.91 (3 H, s), 2.54 (4 H, br s), 3.17 (2 H, d, J 7), 5.12 (1 H, d, J 10), 5.14 (1 H, d, J 16) and 5.80 (1 H, ddt, J 16, 10, 7); δ_C 23.0 (q), 27.5 (t), 34.9 (t), 38.3 (t), 86.8 (s), 117.3 (t), 134.4 (d) and 140.3 (s).

Reaction of 4,4-*Dibromo*-3-*methylbut*-3-*enes with Methyllithium*.—(a) Methyllithium (1.5 mol dm^{-3}; 4.4 ml, 6.5 mmol) was added as above to the alcohol **5a** (0.75 g, 3.1 mmol) in ether (5 ml) at 20 °C. After work-up as above, the solvent was removed at −40 °C and 1 mmHg; flash distillation at 20 °C and 1 mmHg gave 4-methyl-2,3-dihydrofuran **14**. (X = O) (0.15 g, 58%) as a colourless liquid (Found: $M^+ + 1$, 85.0653. C_5H_8O requires $M^+ + 1$, 85.0653); $\nu_{max}(CCl_4)/cm^{-1}$ 3116w, 1673s, 1300m, 1089m and 925m; δ_H 1.67 (3 H, s, shows fine coupling, $W_{\frac{1}{2}}$ 5), 2.52 (2 H, t, J 9.5 shows fine coupling) and 4.30 (2 H, t, J 9.5).

(b) Methyllithium (1.3 mol dm^{-3}; 3.3 ml, 4.3 mmol) was added as above to **5e** (1.0 g, 3.9 mmol) in ether (5 ml) at 20 °C. After work-up as above, the solvent was removed at −40 °C and 1 mmHg; flash distillation at 20 °C and 1 mmHg gave a colourless oil characterised as 1-methoxypent-3-yne (0.14 g, 36%) (Found: $M^+ - 1$, 97.0661. C_6H_9O requires $M - 1$, 97.0654); ν_{max}(film)/cm^{-1} 2827m, 1453m, 1380m, 1191m and 1117s; δ_H 1.79 (3 H, t, J 1), 2.3–2.4 (2 H, m), 3.37 (3 H, s) and 3.47 (2 H, t, J 7); m/z 97 (64%), 83 (80) and 45 (100). The residue was purified by Kugelrohr distillation (b.p. 50 °C and 1 mmHg) to give a mixture of (*E*)- and (*Z*)-2-bromo-5-methoxy-3-methylpent-2-enes (0.35 g, 47%) (Found: $M^+ + Br$, 113.0972. $C_7H_{13}O$ requires $M - Br$, 113.0966); ν_{max}(film)/cm^{-1} 2826m, 1648w, 1449m, 1382m, 1115s and 1067m; δ_H 1.78 (3 H, q, J 1), 1.88 (3 H, q, J 1.5), 2.28 (3 H, shows fine coupling), 2.31 (3 H, shows fine coupling), 2.41 (2 H, t, J 7), 2.53 (2 H, t, J 7), 3.33 (3 H, s), 3.35 (3 H, s), 3.40 (2 H, t, J 7) and 3.45 (2 H, t, J 7); m/z 113, 69 and 45.

(c) Methyllithium (1.5 mol dm^{-3}; 2.8 ml, 4.2 mmol) was added as above to the amine **5c** (1.07 g, 3.8 mmol) in ether (5 ml). Work-up as above, removal of the solvent at −40 °C and 1 mmHg, and flash distillation at 20 °C and 1 mmHg gave *N*-isopropyl-4-methyl-2,3-dihydropyrrole **14** (X = NPr^i) (Found: M^+, 125.1200. $C_8H_{15}N$ requires M, 125.1204) as a colourless oil (0.23 g, 49%); $\nu_{max}(CCl_4)/cm^{-1}$ 2969s, 2872m, 1718m, 1381m and 908m; δ_H 1.08 (6 H, d, J 6), 1.67 (3 H, m), 2.32 (2 H, t, J 8.5, further broadened), 2.75 (1 H, septet, J 6), 3.0 (2 H, t, J 8.5) and 5.72 (1 H, q, J 1.6).

(d) Methyllithium (1.4 mol dm^{-3}; 5.2 ml, 7 mmol) was added as above to the thiol **5d** (0.9 g, 3.5 mmol) in ether (5 ml) at 20 °C. After work-up as above, the solvent was removed at −40 °C and 1 mmHg; flash distillation at 20 °C and 1 mmHg gave a colourless oil, 4-methyl-2,3-dihydrothiophene **14** (X = S) (0.25 g, 71%) (Found: M^+, 100.0370. C_5H_8S requires M, 100.0347); ν_{max}/cm^{-1} 3059w, 2926s, 1626w, 1442s, 1232m and 799s; δ_H 1.77 (3 H, s, fine coupling), 2.64 (2 H, t, J 8, further broadened), 3.24 (2 H, t, J 8) and 5.67 (1 H, q, J 1.8); δ_C 16.8 (q), 32.3 (t), 39.7 (t), 117.8 (d) and 132.6 (s).

(e) Methyllithium (1.4 mol dm^{-3}; 1 ml, 1.4 mmol) was added as above to the sulphide **5f** (0.4 g, 1.3 mmol) in ether (5 ml) at 20 °C. Work-up and flash distillation at 20 °C and 1 mmHg gave 4-methyl-2,3-dihydrothiophene **14** (X = S) (0.076 g, 57%), identical (NMR, IR and MS) with that above. The residue gave a complex NMR spectrum and contained several components by GLC.

5,5-*Dibromo*-4-*methylpent*-4-*enoic Acid*.—The tribromide **3b** (8.7 g) was refluxed for 18 h with a solution prepared from ethyl acetoacetate (4.7 g) and sodium methoxide [from sodium (830 mg) in methanol (60 ml)]. Work-up as before gave ethyl 2-acetyl-5,5-dibromo-4-methylpent-4-enoate **4i** (7.2 g, 70%) (Found: M^+, 339.9337. $C_{10}H_{14}Br_2O_3$ requires M, 339.9310); δ_H 4.2 (2 H, q, J 7), 3.60 (1 H, t, J 7), 2.75 (2 H, d, J 7), 2.22 (3 H, s), 1.90 (3 H, s) and 1.32 (3 H, t, J 7); ν_{max}/cm^{-1} 1740, 1725 and 820. The above keto ester (2.2 g) was refluxed for 3 h with sodium methoxide (1.2 g) in water (1.2 g) and ethanol (10 ml). The solvent was removed at 14 mmHg and the residue was extracted with ether (50 ml). The extract was washed with water (25 ml), dried and evaporated at 14 mmHg to give 5,5-dibromo-4-methylpent-4-enoic acid (1.7 g) (Found: M^+, 269.8891. $C_6H_8Br_2O$ requires M, 269.8912); δ_H 10.33 (1 H, br s), 2.5 (4 H, br s) and 1.9 (3 H, s); ν_{max}/cm^{-1} 3600, 2400, 1705 and 823. The above acid (5.2 g) was refluxed for 2 h with methyl iodide (1.2 ml) and potassium carbonate (1.5 g) in

butan-2-one (40 ml). After work-up, chromatography gave methyl 5,5-dibromo-4-methylpent-4-enoate (4.5 g, 82%); δ_H 3.67 (3 H, s), 2.4–2.6 (4 H, m) and 1.93 (3 H, s); ν_{max}/cm^{-1} 1730 and 823.

5,5-Dibromo-4-methylpent-4-en-1-ol **6a**.—Lithium aluminium hydride (375 mg) was added to methyl 5,5-dibromo-4-methylpent-4-enoate (5.5 g) in tetrahydrofuran (10 ml). After 10 min, the mixture was quenched by careful addition of water and worked up as above to give 5,5-dibromo-4-methylpent-4-en-1-ol **6a** (4.4 g) (Found: M^+, 255.9099. $C_6H_{10}Br_2O$ requires *M*, 255.9112); δ_H 3.8 (1 H, br s), 3.52 (2 H, t, *J* 6), 2.3 (2 H, m), 1.9 (3 H, s) and 1.7 (2 H, m); ν_{max}/cm^{-1} 3370, 1635 and 815.

5-Bromo-4-methylpent-4-en-1-ol.—Methyllithium (1.2 ml) was added to the alcohol **6a** (250 mg) in ether (10 ml). Work-up as before gave a single major product which was purified by column chromatography[b] and characterised as 5-bromo-4-methylpent-4-en-1-ol (70 mg) (Found: M^+, 177.9956. $C_6H_{11}BrO$ requires *M*, 177.9943); δ_H 5.8 (1 H, br s), 3.5 (2 H, t, *J* 7), 2.8 (1 H, br s, OH), 2–2.3 (2 H, br m), 1.8 (3 H, s) and 1.5–1.8 (2 H, br m).

1,1,5-Tribromo-2-methylpent-1-ene **3d**.—Dibromide **6a** (1.25 g) and pyridine (0.5 g) were added to phosphorus tribromide (0.5 g) in light petroleum (b.p. 40–60 °C; 15 ml). The mixture was stirred for 1.5 h at 20 °C after which it was washed with ice-water (25 ml), saturated aq. sodium hydrogen carbonate (25 ml) and water (25 ml) and evaporated at 14 mmHg to give an oil (1.1 g). This was purified by chromatography[a] and characterised as 1,1,5-tribromo-2-methylpent-1-ene **3d** (0.7 g) (Found: M^+, 317.8289. $C_6H_9Br_3$ requires *M*, 317.8255); δ_H 3.38 (2 H, t, *J* 6), 1.70–2.63 (6 H, m) and 1.90 (3 H, s); ν_{max}/cm^{-1} 825 and 813.

5,5-Dibromo-N-isopropyl-4-methylpent-4-enylamine **6f**.—The tribromide **3d** (500 mg) was refluxed for 18 h with isopropylamine (5 ml). Excess of amine was removed at 14 mmHg and the residue was dissolved in ether (50 ml) and extracted with hydrochloric acid (4 mol dm^{-3}). The aqueous layer was brought to pH 10 by addition of sodium hydroxide (4 mol dm^{-3}) and extracted with ether (2 × 50 ml). The combined extracts were dried and evaporated at 14 mmHg to give an oil which was purified by chromatography and characterised as the title compound **6f** (250 mg); δ_H 2.0–2.9 (6 H, m), 1.9 (3 H, s), 1.5–1.9 (2 H, m) and 1.00 (6 H, d, *J* 6).

5,5-Dibromo-4-methylpent-4-enyl Isopropyl Sulphide **6e**.—The tribromide **3d** (500 mg) was refluxed for 18 h with propane-2-thiol (150 mg) and sodium methoxide (25% in methanol; 450 mg) in methanol (10 ml). Work-up as before and chromatography gave the title compound **6e** (400 mg); δ_H 2.80 (1 H, septet, *J* 7), 2.1–2.6 (4 H, m), 1.85 (3 H, s), 1.5–2.0 (2 H, m) and 1.22 (6 H, d, *J* 6); ν_{max}/cm^{-1} 1695.

5,5-Dibromo-4-methylpent-4-enethiol **6d**.—The tribromide **3d** (510 mg), thiourea (150 mg), sodium metabisulphite (75 mg) and potassium carbonate (75 mg) were refluxed in methanol (18 ml) and water (6 ml) for 2 h. Work-up as before and chromatography gave the title compound **6d** (90 mg); δ_H 2.1–2.8 (4 H, m), 1.90 (3 H, s), 1.6–1.9 (2 H, m) and 1.25 (1 H, t, *J* 7) and bis(5,5-dibromo-4-methylpent-4-enyl) disulphide; δ_H 2.3–2.9 (8 H, m), 1.9 (6 H, s) and 1.7–2.0 (4 H, m).

5,5-Dibromo-N,N-diisopropyl-4-methylpent-4-enylamine **6c**.—The tribromide **3d** (1.1 g) was refluxed for 18 h with diisopropylamine (0.5 g) in ethanol (10 ml). Work-up as before and chromatography gave the title compound (270 mg) (Found: M^+, 339.0197. $C_{12}H_{23}Br_2N$ requires *M*, 339.0188); δ_H 2.95 (2 H, septet, *J* 7), 1.3–2.5 (6 H, m), 1.85 (3 H, s) and 1.00 (12 H, d, *J* 6).

5,5-Dibromo-4-methylpent-4-enyl Isopropyl Ether **6b**.—The tribromide **3d** (500 mg) was refluxed for 2 h with sodium isopropoxide [from Na (200 mg) in isopropyl alcohol (10 ml)]. Work-up as before and chromatography gave the title compound **6b** (266 mg, 82%) (Found M^+, 297.9570. $C_9H_{16}Br_2O$ requires *M*, 297.9568); δ_H 3.10–3.67 (3 H, m), 2.0–2.4 (2 H, m), 1.82 (3 H, s), 1.3–1.8 (2 H, m) and 1.06 (6 H, d, *J* 6); ν_{max}/cm^{-1} 2980 and 830.

Reaction of 5,5-Dibromo-4-methylpent-4-enes with Methyllithium.—(a) Methyllithium (1 mol dm^{-3}; 2 ml) was added over 2 min to the sulphide **6e** (300 mg) in ether (10 ml). Addition of water and work-up as above gave an oil which was a single major spot on TLC; flash distillation at 14 mmHg gave 5-methyl-3,4-dihydro-2*H*-thiopyran (85 mg, 68%) (Found: M^+, 114.0507. $C_6H_{10}S$ requires *M*, 114.0503); δ_H 5.67 (1 H, s), 2.75 (2 H, m), 2.04 (4 H, m) and 1.7 (3 H, s).

(b) Methyllithium (1 mol dm^{-3}; 0.5 ml) was added as above to thiol **6d** (80 mg) in ether (10 ml). Work-up as above gave a single product identical with that obtained above (30 mg, 90%).

(c) Methyllithium (1 mol dm^{-3}; 2 ml) was added as above to the ether **6b** (260 mg) in ether (10 ml) at 20 °C. Work-up as above gave a single product which was purified by chromatography and characterised as isopropyl 3-methylcyclopent-2-enyl ether (95 mg, 89%) (Found: M^+, 140.1205. $C_9H_{16}O$ requires *M*, 140.1201); δ_H 5.4 (1 H, br s), 4.4 (1 H, vbr s), 3.5 (1 H, septet, *J* 7), 1.6–2.4 (4 H, m), 1.7 (3 H, br s) and 1.1 (6 H, d, *J* 7).

(d) Methyllithium (1 mol dm^{-3}; 1.2 ml) was added as above to the amine **6c** (310 mg) in ether (10 ml). Work-up as before gave a single compound which was purified by chromatography and characterised as *N,N*-diisopropyl-3-methylcyclopent-2-enylamine (145 mg, 87%) (Found: M^+, 181.1819. $C_{12}H_{23}N$ requires *M*, 181.1830); δ_H 5.22 (1 H, br s), 4.06 (1 H, br m), 3.08 (2 H, septet, *J* 6.5), 2.3–1.9 (4 H, m), 1.73 (3 H, s), 1.01 (6 H, d, *J* 6.5) and 0.99 (6 H, d, *J* 6.5); ν_{max}/cm^{-1} 3000, 2960 and 2880.

(e) Methyllithium (1 mol dm^{-3}; 1 ml) was added as above to the amine **6f** in ether (10 ml). Work-up and chromatography as before gave *N*-isopropyl-3-methylcyclopent-2-enylamine (15%) (Found: M^+, 139.1366. $C_9H_{17}N$ requires *M*, 139.1361); δ_H 5.1 (1 H, br s), 4.1 (1 H, vbr s), 3.1 (1 H, septet, *J* 7), 2.0–2.4 (4 H, m), 1.65 (3 H, br s) and 1.0 (6 H, d, *J* 7). A number of unidentified components were also obtained.

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