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Generation of Aminyl Radicals using Sulfenamides as Synthetic Precursors

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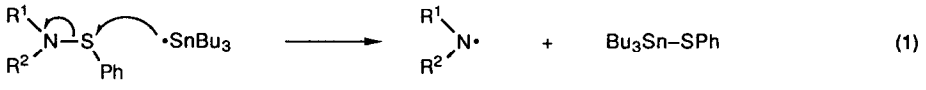
Key Words: sulfenamides; aminyl radicals; tributyltin hydride; radical-cyclisation; *N*-(benzenesulfenyl)phthalimide

Abstract: Sulfenamides are synthesised from reaction between amines and *N*-(benzenesulfenyl)-phthalimide or benzenesulfenyl chloride. The sulfenamides undergo reaction with tributyltin hydride to yield aminyl radicals which can be cyclised onto suitable alkenes.

We have reported[1,2] our initial results on the use of sulfenamides as precursors of aminyl radicals, which are generated using tributyltin hydride (Bu_3SnH) for S_H2 abstraction of the benzenesulfenyl group (equation 1). Since our initial report Beckwith and Tsanakatsidis[3] have also reported the use of sulfenamides to generate aminyl radicals. In this report we discuss the full details and further progress on our studies of the generation of aminyl radicals using sulfenamides. Application to the synthesis of nitrogen heterocycles using radical cyclisation is also discussed.



(1)

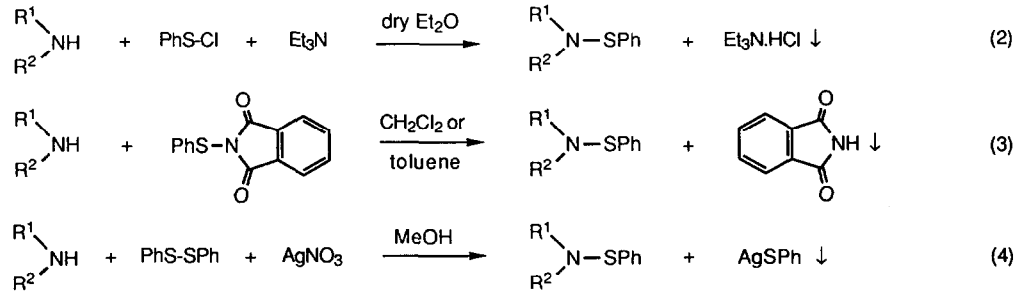
The use of radicals in synthesis, especially cyclisation reactions, has developed into a major branch of modern organic chemistry in recent years,[4] and many new methodologies have been developed for producing carbon-centred radicals in synthetic reactions. Nitrogen heterocycles are important because of their occurrence in a large number of natural products and pharmaceutical drugs. However, the application of aminyl radical cyclisation to their synthesis has been surprisingly limited. There are numerous examples of the use of carbon-centred radical cyclisation to synthesise pyrrolidine derivatives; *e.g.* cyclisation of α-aminoalkyl[5] and β-aminoalkyl[6] radicals onto alkenes and the cyclisation of carbinyl-radicals onto enamines.[7] Although several methods for generating aminyl radicals have been developed[8,9] there is no general facile methodology.

Two methods of generating aminyl radicals have shown practical application to the synthesis of nitrogen heterocycles. The older and most widely used method which uses photolysis or metal induced one-electron reduction of *N*-chloramines has been reviewed[9] and applications are still reported.[10] The recent development of the use of *N*-hydroxypyridine-2-thione carbamates (PTOC = 2-thioxopyridinyloxycarbonyl) by Newcomb and co-workers[11,12] has provided a major new method with wide synthetic possibilities. PTOC carbamates have also been used to generate aminium,[11c-f] amidyl,[13] and iminyl radicals.[14] Other methods for generating aminyl radicals have obvious drawbacks, *e.g.* photolysis of nitrosamines,[15] decomposition of tetrazines,[16] and anodic oxidation of lithium amides.[17] The aim of our studies was to develop a new and widely applicable methodology for generating synthetically useful aminyl radicals.

N-Chloramines provide good precursors for generating aminyl radicals whereas chloroalkanes are poor radical precursors because the N-Cl bond is weaker than the C-Cl bond. Alkylsulfides are poor precursors due to a relatively strong C-S bond and alkylselenides with the weaker C-Se bond are often used in radical generation.[4,18] However, their nitrogen counterparts, sulfenamides and selenamides, have much weaker N-S or N-Se bonds. We therefore considered that sulfenamides and selenamides would make excellent precursors of aminyl radicals. Sulfenamides are well characterised compounds[19] and have been prepared by various methods. Although selenamides[20] and sulfenamides of amides[21] are known compounds we found their preparation troublesome and did not investigate them further. In our investigations benzenesulfenamides (PhS–NR^1R^2) were used because they are stable and easily synthesised.[19] S_H2 abstraction of benzenesulfenyl groups by tributyltin radicals has proved useful for generating alkyl radicals,[4,18] alkoxyl radicals,[22] and iminyl radicals.[23] We have found that this method is also very effective for generating aminyl radicals from sulfenamides.

Synthesis of Benzenesulfenamide Precursors

Two methods for the synthesis of sulfenamides were developed and used for all the precursors. Reaction between amines and benzenesulfenyl chloride[24] was rapid and gave quantitative yields of sulfenamides (equation 2).[23] However, diphenyl disulfide impurities formed in some of these reactions were problematic to remove. Sulfenamides were also synthesised in high yield by reaction between amines[25] and *N*-(benzenesulfenyl)phthalimide (equation 3).[26] The reactions were slow at room temperature but faster in refluxing solvent, and gave cleaner products. Phthalimide was removed by filtration and unreacted *N*-(benzenesulfenyl)phthalimide separated by chromatography. With more hindered amines no reaction took place and benzenesulfenyl chloride had to be used. A third method, the reaction between amines and diphenyl disulfide in the presence of silver nitrate (equation 4), was also investigated.[27] The method requires a large excess of amine, which made it unsuitable for our purposes. Synthesis of sulfenamides using the reaction between thiolates and *N*-chloramines has been recently reported and could prove useful.[28]



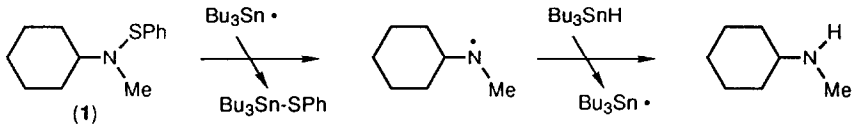
The benzenesulfenamides were found to be stable to light, refluxing toluene, and anhydrous acids. The sulfenamides were however hydrolysed rapidly by aqueous acid and on silica gel chromatography. Purification was therefore carried out using flash-sinter or column chromatography on neutral alumina.

Generation of Aminyl Radicals

Reactions were carried out under nitrogen and a syringe pump was normally used for adding a solution of Bu_3SnH and AIBN to the sulfenamide over a period of 2-10 h. AIBN needs to be continuously added because of its short half-life at elavated temperatures.[4b] The reactions were followed by TLC and terminated when the sulfenamide was used up. The problems of separating tributyltin derivatives from products were circumvented by extraction of amine product mixtures into dilute hydrochloric acid, basification and extraction. Tributylstannyl phenyl sulfide (Bu_3Sn-SPh) was separated and identified as evidence for the abstraction reaction (equation 1). This by-product has the advantage of being stable under the reaction and work-up conditions and can be separated from products by chromatography. A range of solvents were found to be satisfactory for

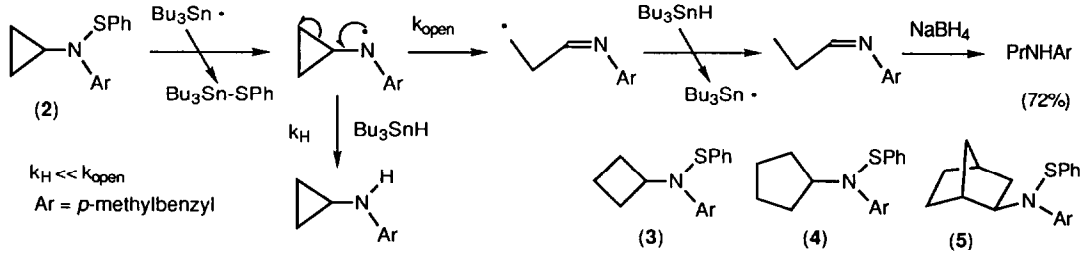
carrying out the reaction; acetonitrile, cyclohexane, THF, toluene, and benzene (now a listed carcinogen and not further used). The use of cyclohexane in reactions using a syringe pump was precluded because of the limited solubility of AIBN although could still be used by adding portions of AIBN. Initial attempts at homolytic cleavage of several sulfenamides using photolysis[21] failed and the sulfenamides were recovered unaltered.

N-(Benzenesulfenyl)-*N*-methylcyclohexylamine (**1**) was chosen for initial studies to determine whether aminyl radicals were in fact formed from the reaction between sulfenamides and Bu_3SnH. Reaction under normal radical conditions (Bu_3SnH, AIBN, 15 min in refluxing cyclohexane) gave *N*-methylcyclohexylamine in 93% yield (GLC) and 53% isolated yield in a separate experiment. The sulfenamide was stable in refluxing toluene or cyclohexane (2 h, 100% recovery). When the reaction was repeated under an atmosphere of oxygen in place of nitrogen, no AIBN, and in the dark, the formation of product was completely inhibited and the starting sulfenamide was recovered unreacted (15 min, 100% by GLC), clearly indicating a radical reaction (equation 5).



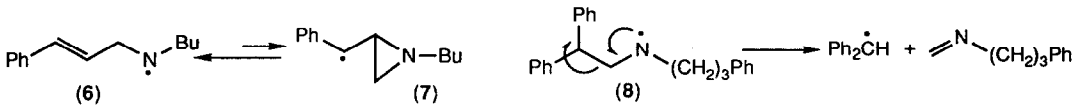
(5)

We chose a series of 3-, 4-, 5-, and 6-membered ring cycloalkyl sulfenamides (**1**)-(**5**) to further prove the intermediacy of aminyl radicals. The rate of ring-opening of *N*-propylcyclobutylaminyl and *N*-butylcyclopropylaminyl radicals is fast (2.5×10^7 s^{-1} and 5×10^5 s^{-1} at 50°C respectively)[11a] and therefore the aminyls resulting from sulfenamides (**2**) and (**3**) should readily give ring-opened products. On the other hand, the 5- and 6-membered ring cyclopentylaminyl and cyclohexylaminyl radicals would not be predicted to undergo ring-opening. The imines resulting from the rearrangement of the cyclopropyl- (**2**) and cyclobutyl-aminyl (**3**) radicals were reduced prior to work-up to avoid problems with hydrolysis. As predicted, the cyclobutyl- and cyclopropyl-sulfenamides (**2**) and (**3**) gave only ring-opened products under radical conditions to yield *N*-butyl- and *N*-propyl-*p*-methylbenzylamines in 73% and 42% isolated yields respectively, thereby providing clear evidence for the formation of aminyl radicals. No traces of non ring-opened cyclobutyl- or cyclopropyl-amine were detected. A solution of the cyclopropyl sulfenamide (**2**) was also refluxed with Bu_3SnH under non-radical conditions for the same time (oxygen atmosphere, absence of light, and no AIBN) and 100% recovery of starting material was obtained. $LiAlH_4$ can reductively ring-open cyclopropylamines by a non-radical mechanism but this obviously does not take place with Bu_3SnH. As expected, reaction under radical conditions between Bu_3SnH and the cyclohexyl (**1**), cyclopentyl (**4**), and strained bicycloheptyl (**5**) sulfenamides gave only the non ring-opened amines in 53%, 54%, in 69% isolated yields respectively.



The aminyl radical (**6**) was generated from the corresponding sulfenamide by reaction with Bu_3SnH to examine the possibility that benzylic stabilisation of the cyclised radical (**7**) would be sufficient to overcome the ring strain. We obtained only non-cyclised amine (53%), even when a syringe pump was used for slow addition of Bu_3SnH. The benzylic stabilisation of the radical is not sufficient to overcome the ring strain.

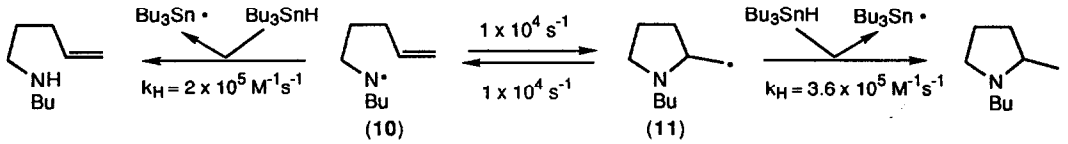
Aminyl radical (**8**) was generated in the expectation that β-fission would take place to give a stabilised radical. Our experiment showed that indeed diphenylmethane (67%) was formed, via the stable diphenylmethyl radical.



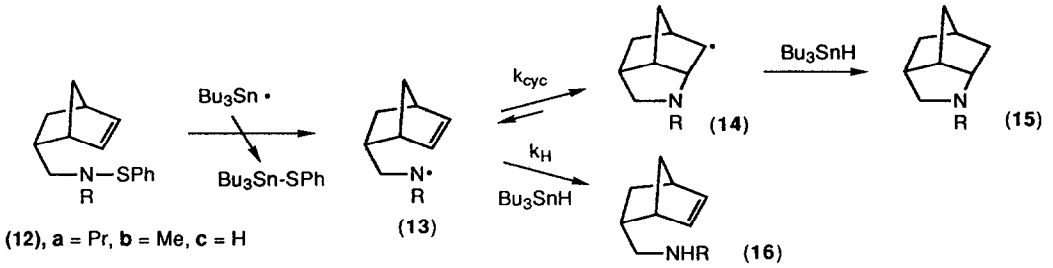
The initial assumption that the S_H2 abstraction by $Bu_3Sn^{\bullet}$ radicals of PhS from sulfenamides (N-SPh bond-fission) would be much faster than the abstraction from sulfides (C-SPh bond-fission) was tested. Comparison reactions were carried out under the same conditions using Bu_3SnH/AIBN and cyclohexane as solvent. 1-Cyclohexyl-3-phenyl-1-propyl phenyl sulfide (**9**) gave the alkane, 1-cyclohexyl-3-phenylpropane, (32%) and unreacted sulfide (30%) after 7 h refluxing. In contrast, the sulfenamide (**1**) gave N-methyl-cyclohexylamine (75%) and unreacted sulfenamide (23%) after only 15 min. When a mixture of the sulfide (**9**) and sulfenamide (**1**) and were treated with Bu_3SnH/AIBN under the same reaction conditions for 15 min only abstraction of PhS from the sulfenamide was observed. This clearly indicating the difference between N-S and C-S bonds in S_H2 abstraction reactions, *i.e.* the sulfenamides are the nitrogen counterparts of selenides (C-SePh) in radical reactions.

Cyclisation of Aminyl Radicals

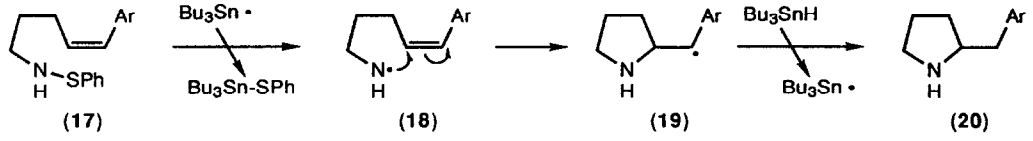
Our attempts to cyclise *N*-butylpent-4-en-1-aminyl radicals (**10**) generated from *N*-butyl-*N*-(benzenesulfenyl)pent-4-en-1-amine and Bu_3SnH gave poor yields of the cyclised pyrrolidine. Reports in the literature[3,11] at this time suggested that the cyclisation was unfavourable and therefore the reaction was not further investigated. The rate of cyclisation of (**10**) is within experimental error the same as the rate of ring-opening of the cyclised radical (**11**)[11d,29] and the rate of hydrogen abstraction from Bu_3SnH by the aminyl radical (**10**)[11b,29] is similar to that of the primary carbinyl radical (**11**).[30] These rates indicate the reason for the poor yields of cyclised products from aminyl radicals (**10**).



We therefore sought procedures in which cyclisation would be more favourable. The use of t-BuSH as a hydrogen source[11b,29] has been shown to be even less helpful than Bu_3SnH; the thiol is an electrophilic source of hydrogen and reacts faster with the nucleophilic aminyl ($2\text{-}3 \times 10^6\ M^{-1}s^{-1}$). The problem of the nucleophilicity of aminyl radicals has been overcome in the use of *N*-hydroxypyridine-2-thione carbamates (PTOC) by carrying out the reaction in the presence of acid to generate electrophilic aminium radicals and using t-BuSH as an electrophilic hydrogen source.[11,12] The electrophilic aminium radical cyclises rapidly and irreversibly and reacts very slowly with the electrophilic t-BuSH but the nucleophilic cyclised carbinyl radical readily abstracts hydrogen from t-BuSH. Unfortunately thiols do not act as radical chain carriers with sulfenamides and react with the alkenes. The use of malonic acid or magnesium dibromide in sulfenamide reactions presumably gave aminium radicals but these reacted rapidly with Bu_3SnH to yield uncyclised amines. Amidyl radicals[13] are also electrophilic and exhibit the same problems with Bu_3SnH, so that t-BuSH also needs to be used with the PTOC amidyl radical precursors. To overcome these disadvantages we chose three methods to force cyclisation: the use of aminyl radicals which cyclise rapidly, aminyls which cyclise to yield stable benzylic radicals, and trapping the cyclised radicals in tandem reactions. The latter methodology is reported in the following paper.

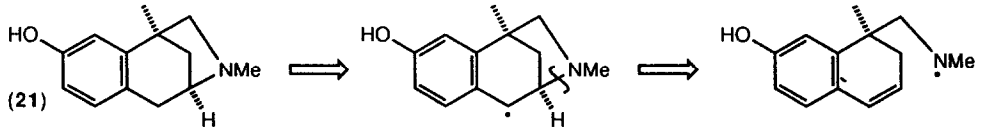


The first method required an intermediate aminyl radical which would be predicted to have a faster rate of cyclisation than the rate of the reverse ring-opening reaction. *endo*-(Bicyclo[2.2.1]hept-5-en-2-yl)methylaminyl radicals (**13**) were considered because the butressed aminyl radicals are correctly orientated to react rapidly with the strained alkene. Carbinyl radical equivalents have been shown to have fast rates of cyclisation,[31] *e.g.* the rate of *exo*-cyclisation of *endo*-2-(bicyclo[2.2.1]hept-5-en-2-yl)ethyl radicals[31a] is 1×10^7 s^{-1}. The sulfenamides (**12a-c**) were prepared from 2-cyano-bicyclo[2.2.1]hept-5-ene or bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde. The *exo* and *endo* isomers were not separated except after the radical reactions; the yields were calculated from the *endo* isomer only. Moderate yields of cyclisation were obtained, (**12a**) gave an isolated yield (29%) of cyclised material (**15a**). ^{1}H NMR analysis of the reaction mixture showed a 4:1 ratio of cyclised (**15a**):uncyclised (**16a**). The improvement in yield of cyclised material was as predicted, *i.e.* the rate of cyclisation > rate of ring-opening.

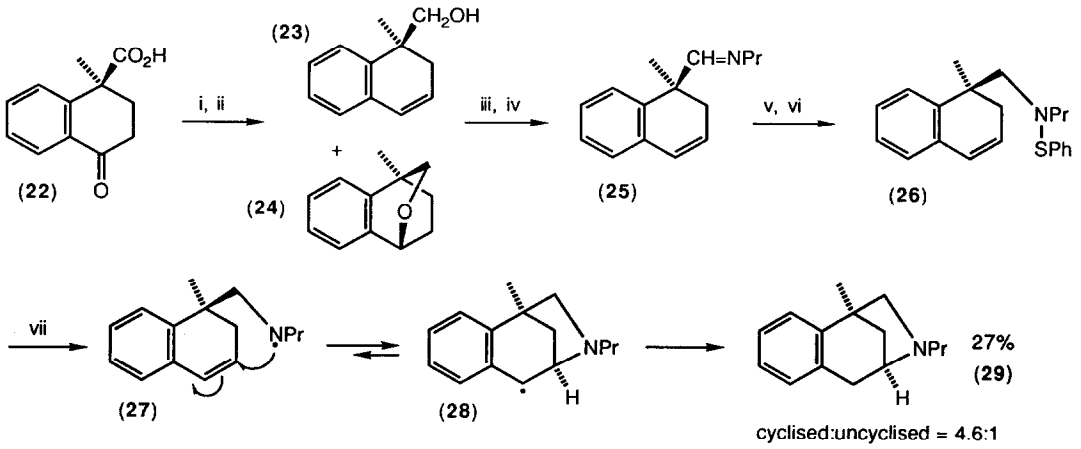


The second methodology for improving aminyl radical cyclisation, use of a stabilised cyclised radical, proved more successful. An initial test reaction using a simple precursor (**17**, Ar = 4-isopropylphenyl), carried out by syringe pump addition of Bu3SnH and AIBN to a refluxing solution of (**17**) in THF over 5 h, gave the pure cyclised product (**20**) (65%). The primary sulfenamide was stable and readily reacted to yield the primary aminyl radical (**18**) which cyclised exclusively to the stabilised radical (**19**). No uncyclised amine was detected.

The requirement for a stabilising group on the alkene is obviously a limitation; however, many retro-syntheses can be envisaged which have an intermediate stabilised radical. This methodology was tested on the aphanorphine skeleton[10a] as an example of the potential for application of sulfenamides to natural product synthesis. The retrosynthesis of aphanorphine (**21**) illustrates the cyclisation to an intermediate benzylic radical.



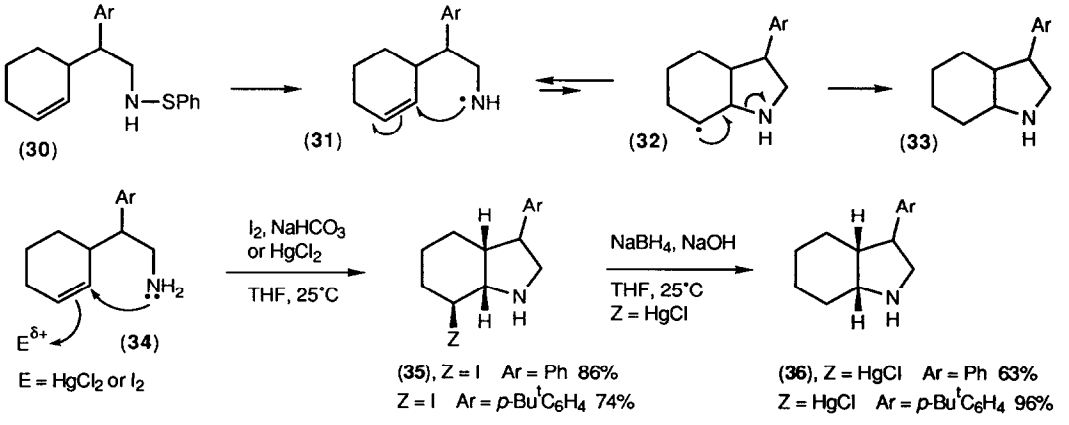
A sulfenamide precursor (**26**) with the aphanorphine skeleton was synthesised as shown below using standard procedures and the steps were not optimised. The acid (**22**) was prepared using a literature procedure.[32] The acid (**22**) was initially converted to the propylamide, the ketone reduced, and the resulting



i. $LiAlH_4$/THF, ii. refluxing toluene/*p*TSA, iii. Swern oxidation, iv. $PrNH_2$/$-H_2O$, v. $LiAlH_4/Et_2O$, vi. $PhSCl/Et_3N/Et_2O$, vii. Bu_3SnH/AIBN, refluxing toluene, 5 h

alcohol dehydrated to yield an alkene. However, the amide could not be successfully reduced with $LiAlH_4$ even after prolonged heating. The successful route involved reduction of (**22**) to a diol, followed by acid catalysed dehydration to yield the hydroxyalkene (**23**). The unwanted cyclic ether (**24**) which was also formed in the acid catalysed dehydration step was removed by chromatography. A route via reduction of the methyl ester of (**22**) also led to unwanted by-products. The imine (**25**) was readily reduced to the required amine which was converted to the sulfenamide precursor (**26**). Reaction between (**26**) and Bu_3SnH gave the predicted cyclised amine (**29**) and a small amount of uncyclised amine indicating that the cyclisation of the intermediate aminyl radical (**27**) to the stabilised radical (**28**) was not exclusive. The benzylic stabilisation was not sufficient to exclude direct reduction of (**27**) to yield uncyclised amine. The conversion of uncylised amine via sulfenamide (**23**) to the aphanorphine analogue (**29**) was achieved in 27% isolated yield.

The sulfenamide methodology appeared to provide a route to our synthetic targets, arylhexahydroindolines (**33**), by *exo* cyclisation of aminyl radicals (*e.g.* **31**) onto a cyclohexene moiety. The sulfenamide precursors (**30**) were readily prepared from the corresponding amines using benzenesulfenyl chloride but attempts to prepare the sulfenamides using *N*-(benzenesulfenyl)phthalimide failed completely, probably due to steric hindrance.



E = $HgCl_2$ or I_2

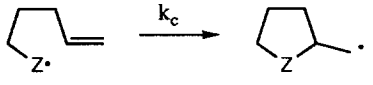
(**35**), Z = I Ar = Ph 86%
Z = I Ar = *p*-Bu^{t}C$_6$H$_4$ 74%

(**36**), Z = HgCl Ar = Ph 63%
Z = HgCl Ar = *p*-Bu^{t}C$_6$H$_4$ 96%

Attempts at radical cyclisation by reaction between (**30**, Ar = *p*-Bu^t-C_6H_4) and Bu_3SnH (added at low concentration using a syringe pump) gave only uncyclised amine (quantitative recovery) and no cyclised material (**33**) could be detected. Attempts using tristrimethylsilylsilane,[4,33] $(Me_3Si)_3SiH$, which reacts more slowly than Bu_3SnH with intermediate radicals and is therefore more favourable for cyclisation, also yielded only uncyclised amine (71%). Cyclisation of the aminyl radical (**31**) is sterically favourable but the hexahydroindoline radical (**32**) is not stabilised and cyclisation is not favoured.

However, the use of electrophiles, mercury (II) chloride and iodine, to activate the alkene to nucleophilic attack by the amine,[34] proved successful. In this case the alternative non-radical cyclisation proved more useful. High yields of the iodides (**35**, Ar = Ph and *p*-Bu^t-C_6H_4) were obtained from the corresponding amines (**34**). Similarly, high yields were obtained using $HgCl_2$; the intermediate mercury adducts were not purified and directly reduced to the hexahydroindoline (**36**) in overall high yield.

The apparent nucleophilicity of aminyl radicals is notable, particularly in contrast to the electrophilicity of alkoxyl radicals. Several rate studies provide evidence for the nucleophilic behaviour of aminyl radicals. The rate of cyclisation onto weakly nucleophilic alkenes at 50°C is in the order: alkoxyl >> carbinyl > aminyl. Similarly, the nucleophilicity of aminyl radicals is further supported by the bimolecular rate of hydrogen abstraction at 50°C from Bu_3SnH, a nucleophilic source of hydrogen, which is in the same order as cyclisation: aminyl[29] ($R_2N^\bullet$ at 50°C) = 2 x 10^5 $M^{-1}s^{-1}$ < carbinyl[35] ($RCH_2^\bullet$ at 50°C) = 3.9 x 10^6 $M^{-1}s^{-1}$ < alkoxyl (t-BuO•) = *ca.* 10^8 $M^{-1}s^{-1}$ (30°C[36]), 6.6 x 10^8 $M^{-1}s^{-1}$ (80°C[22]). The rate of reaction between dialkylaminyl radicals and Bu_3SnH is 8 x 10^4 $M^{-1}s^{-1}$ at 50°C whereas the rate with t-BuSH, an electrophilic source of hydrogen, is 2-3 x 10^6 $M^{-1}s^{-1}$ at 50°C.[11c] The rate of addition of $Me_2N^\bullet$ to substituted styrenes is enhanced by electron withdrawing substituents on the phenyl ring of the styrene.[37] The role of the lone pair of electrons is crucial to the reactivity of aminyl radicals. When the lone pair is delocalised (aminium and amidyl radicals or complexed with Lewis acids) aminyl radicals become electrophilic in nature and react more rapidly in cyclisation reactions and in abstraction from Bu_3SnH.



Z = O, $k_c = 5.2 \times 10^8\ s^{-1}$ (ref. 22)
Z = CH_2, $k_c = 3.6 \times 10^5\ s^{-1}$ (ref. 30)
Z = NBu, $k_c = 1 \times 10^4\ s^{-1}$ (ref. 29)

In conclusion, we believe that our initial results show that amines are easily converted into sulfenamides which in turn are good substrates for the facile generation of aminyl radicals. This route provides a simple new method for generating aminyl radicals for use in synthesis and is an important addition to the methodology using *N*-hydroxypyridine-2-thione carbamates (PTOC carbamates) developed by Newcomb and co-workers.[11]

Acknowledgements

We gratefully thank Rhone-Poulenc Agriculture for a Post-graduate Research Studentship (DNC), the S.E.R.C. for a Post-doctoral Fellowship (RJM), Professor Martin Newcomb for advice on the nucleophilicity of aminyl radicals and for sending pre-publication results, the SERC High Field NMR Service at the University of Warwick, and the SERC MS Service at University College, Swansea.

EXPERIMENTAL

General Procedures

IR spectra were obtained using a Pye Unicam PU9516 spectrometer and a Nicolet 205 FT-IR. Elemental analyses were carried out at Brunel University. Mass spectra were run on a Kratos MS80 spectrometer and also carried out by the SERC Mass Spectrometry Service at University College, Swansea. All mass spectra are electron impact (E.I.) spectra. ^1H NMR spectra were run at 250 MHz using a Bruker AC 250 spectrometer unless otherwise stated. 300 MHz NMR spectra were provided by Rhone-Poulenc Agriculture (Ongar) and 400

MHz and nOe difference spectra were provided by the SERC High Field NMR Service at the University of Warwick. $CDCl_3$ was used as the NMR solvent with TMS as internal standard. Temperatures quoted for Kugelrohr distillations are those of the heating bath. Solvents were purified by standard procedures. Light petroleum refers to the b.p. 40-60°C fraction. TLC was performed on aluminium plates coated with Merck silica gel 60F254 or neutral alumina, and compounds were visualised by UV light, iodine vapour, or Dragendorff's reagent. Flash chromatography was carried with TLC alumina as absorbent.

Benzenesulfenyl chloride

Chlorine gas was bubbled through carbon tetrachloride (200 ml) with stirring until the solution turned yellow (usually about 15 min). Benzenethiol (10.0 g, 91 mmol) in carbon tetrachloride (100 ml) was added over a period of 20 min, and the chlorine gas bubbled through the mixture for a further 2 h. The orange solution was neutralised with anhydrous sodium carbonate (30 g) and distilled to yield benzenesulfenyl chloride (b.p. 94-96°C at 1 mm Hg) (6.2 g, 47%); υ_{max} (neat)/cm^{-1} 3060, 1578, 1474, and 748; δ_H 7.15.

Synthesis of sulfenamides using benzenesulfenyl chloride

(a) N-*(Benzenesulfenyl)phthalimide. General procedure for the synthesis of sulfenamides using benzenesulfenyl chloride.* Benzenesulfenyl chloride (34.6 g, 0.31 mol) was added dropwise over a period of 20 min to a solution of phthalimide (45.6 g, 0.31 mol) and triethylamine (37.6 g, 0.37 mol) in dry diethyl ether (100 ml). The precipitate of triethylamine hydrochloride was filtered and the filtrate evaporated to dryness to yield the sulfenamide as colourless crystals. Recrystallisation (ethanol) gave pure *N*-(benzenesulfenyl)phthalimide (41.9 g, 53%); m.p. 158-160°C (lit.[26] 160-161°C); υ_{max} (Nujol)/cm^{-1} 1605, 1465, 715, and 685; δ_H 7.02 (4 H, s, Ph-H) and 7.81 (4 H, d, phthalimide-H). TLC [light petroleum/alumina] showed the sulfenamide as the only product.

(b) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclobutylamine* (3). N-(p-*Methylbenzyl)cyclobutylamine. General procedure for the synthesis of amines via imines.* A solution of tolualdehyde (4.7 g, 39 mmol) and a crystal of p-toluenesulfonic acid as catalyst in toluene (50 ml) was added dropwise to cyclobutylamine (2.8 g, 39 mmol) in toluene (50 ml). The mixture was refluxed for 2 h using a Dean-Stark water separator. Removal of the solvent yielded *N-(p*-methylbenzylidene)cyclobutylamine as a brown oil; υ_{max} (neat)/cm^{-1} 3020, 1636, 1610, 1510, and 814; δ_H 2.03 (6 H, m, cyclobutyl CH_2), 2.21 (3 H, s, Me), 4.15 (1 H, q, cyclobutyl CH), 7.34 (4 H, ABq, Ar-H), and 8.07 (1 H, s, N=CH). The imine was reduced (2 h) using sodium borohydride (4.5 g, 0.117 mol, 3 equiv.) in refluxing dry methanol (100 ml). The mixture was diluted with water and the amine extracted into dichloromethane. The solution was evaporated to dryness to yield a brown oil which was not further purified (5.9 g, 86%); υ_{max} (neat)/cm^{-1} 3292, 3044, 1614, 1512, and 806; δ_H 1.65 (6 H, m, cyclobutyl-CH_2), 2.24 (3 H, s, Me), 3.28 (1 H, m, CHN), 3.65 (2 H, s, NHCH_2), and 7.02 (4 H, s, Ar-H); δ_C 13.54, 29.24, 31.26, 53.58, 59.22, 59.54, and 125.09-140.14 (Ar-C); m/z 175.1361 (M^+, $C_{12}H_{17}N$ requires 175.1361), 147 (50%), 105 (100), 77 (10), 51 (4), 39 (5), and 27 (6). TLC (ethyl acetate/alumina) showed one spot.

N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclobutylamine* (3). The general procedure for sulfenamide formation was used with N-(p-methylbenzyl)cyclobutylamine (1.0 g, 57 mmol) to yield a red oil. Column chromatography with alumina as absorbent and light petroleum as eluent yielded *N*-(benzenesulfenyl)-*N*-(*p*-methylbenzyl)cyclobutylamine (3) as a clear oil (1.2 g, 73%); υ_{max} (neat)/ cm^{-1} 3052, 1580, 1474, and 808; δ_H 1.54 (2 H, m, cyclobutyl CH_2), 1.93 (4 H, m, cyclobutyl CH_2), 2.18 (3 H, s, Me), 3.54 (1 H, m, C*H*NSPh), 3.92 (2 H, s, CH_2N), and 7.10 (9 H, m, Ph-H); δ_C 13.49, 21.16, 29.24, 59.14, and 59.46. *m/z* 284.1473 [$(M+H)^+$, $C_{18}H_{21}NS$+H requires 284.1473], 218 (7%), 176 (15), 147 (38), 105 (100), 77 (9), 65 (11), and 39 (10). TLC showed one spot.

(c) N-*(Benzenesulfenyl)*-N-*(2,2-diphenylethyl)-3-phenylprop-1-ylamine* (8). N-*(2,2-Diphenylethyl)-3-phenyl-prop-1-ylamine.* A mixture of 2,2-diphenylethylamine (4.0 g, 20 mmol) and 3-phenylpropionyl chloride (3.4 g, 20 mmol) in dry diethyl ether (50 ml) and triethylamine (50 ml) were stirred for 1 h. The precipitate of triethylamine hydrochloride was filtered off and the filtrate washed with aq. hydrochloric acid and

aq. sodium carbonate solution. The solution was evaporated to dryness to yield *N*-(2,2-diphenylethyl)-3-phenylpropionamide as orange crystals (m.p. 89.5-91°C); υ_{max} (Nujol)/cm^{-1} 3436, 3320, 3060, 3024, 1656, 1600, 1510, and 784; δ_H 1.05 (1 H, m, NH), 2.23 (2 H, m, C*H*$_2$CH$_2$Ph), 2.86 (2 H, t, CH$_2$NH), 3.92 (2 H, t, C*H*$_2$Ph), 5.85 (1 H, m, Ph$_2$C*H*), and 7.13 (15 H, s, Ph-H). Reduction of the amide using $LiAlH_4$ in dry THF yielded *N*-(2,2-diphenylethyl)-3-phenylprop-1-ylamine as a yellow oil (2.9 g, 78% overall); υ_{max} (neat)/cm^{-1} 3324, 3056, 3024, 1600, 1492, and 744; δ_H 1.11 (1 H, m, NH), 1.74 (2 H, m, CH$_2$C*H*$_2$CH$_2$), 2.63 (4 H, tt, NC*H*$_2$CH$_2$C*H*$_2$Ph), 3.15 (2 H, d, Ph$_2$CHC*H*$_2$N), 4.12 (1 H, t, Ph$_2$C*H*), and 7.12 (15 H, s, Ph-H). TLC showed one spot and the amine was not further purified.

N-*(Benzenesulfenyl)*-N-*(2,2-diphenylethyl)-3-phenylprop-1-ylamine* (**8**). *N*-(2,2-Diphenylethyl)-3-phenylprop-1-ylamine (1.0 g) was reacted using the general procedure for preparing sulfenamides with benzenesulfenyl chloride to yield an oil which was purified by chromatography on alumina to yield *N*-(benzenesulfenyl)-*N*-(2,2-diphenylethyl)-3-phenylprop-1-ylamine (**8**) as a clear oil (670 mg, 50%); υ_{max} (neat)/cm^{-1} 3060, 3024, 1600, 1492, and 740; δ_H 1.84 (2 H, m, NCH$_2$C*H*$_2$), 2.41 (2 H, t, C*H*$_2$Ph), 2.87 (2 H, t, NC*H*$_2$), 3.54 (2 H, d, CHC*H*$_2$N), 4.43 (1 H, t, Ph$_2$C*H*), and 7.24 (20 H, m, Ph-H); δ_C 31.45 (*C*H$_2$Ph), 33.49 (*C*H$_2$CH$_2$Ph), 49.18 (N*C*H$_2$), 51.16 (Ph$_2$*C*H), 54.49 (CH*C*H$_2$N), and 128.26-129.32 (Ar-C). TLC showed one spot.

(d) N-*(Benzenesulfenyl)*-N-*butyl-3-phenylprop-2-en-1-ylamine* (**6**). N-*Butyl-3-phenylprop-2-en-1-ylamine.* Butylamine (20 ml, large excess) was added to a stirred solution of cinnamyl bromide (5.0 g, 25 mmol) in dry diethyl ether (50 ml). The resulting suspension was stirred at room temperature for 90 min when TLC indicated absence of cinnamyl bromide. The precipitate of butylamine hydrobromide was filtered off and washed with diethyl ether. The ether fractions were combined and evaporated to dryness to yield the *N*-butyl-3-phenylprop-2-en-1-ylamine as a clear oil, (3.3 g, 69%); υ_{max} (neat)/cm^{-1} 3309, 3026, 1496, and 692; δ_H 0.94 (3 H, t, Me), 1.33 (2 H, m), 1.49 (2 H, tt), 2.64 (2 H, t, CH$_2$N), 3.41 (2 H, d, 1-H$_2$), 6.29 (1 H, dt, 2-H), 6.41 (1 H, d, 3-H), and 7.25 (5 H, m, Ph-H); δ_C 14.04 (Me), 20.50 (CH$_2$), 32.25 (CH$_2$), 49.19 (CH$_2$N), 51.96 (1-C), 128.19-137.14 (Ar and alkene-C); m/z 190.1596 [(M+H)$^+$ (49%). $C_{13}H_{19}N$ requires 190.1596], and 74 (100).

N-*(Benzenesulfenyl)*-N-*butyl-3-phenylprop-2-en-1-ylamine* (**6**). *N*-Butyl-3-phenylprop-2-en-1-ylamine was reacted using the general procedure (room temperature, 2.5 h) to yield *N*-(benzenesulfenyl)-*N*-butyl-3-phenylprop-2-en-1-ylamine (**6**) as a clear oil (83%); υ_{max} (neat)/cm^{-1} 3026, 1582, 1476, and 691; δ_H 0.89 (3 H, t, Me), 1.17 (2 H, m), 1.33 (2 H, tt), 2.94 (2 H, t, CH$_2$N), 3.76 (2 H, d, 1-H), 6.29 (1 H, dt, 2-H), 6.46 (1 H, d, 3-H), and 7.30 (10 H, m, Ph-H); δ_C 13.99 (Me), 20.14 (CH$_2$), 30.53 (CH$_2$), 56.33 (CH$_2$N), 61.42 (1-C), and 125.27-136.96 (Ph-C and 2,3-C); m/z 298.1629 [MH$^+$ (100%). $C_{19}H_{23}NS$+H requires 298.1629], 190 (98), 117 (42), and 109 (6).

Synthesis of sulfenamides using *N*-(benzenesulfenyl)phthalimide.

(a) N-*(Benzenesulfenyl)*-N-*methylcyclohexylamine* (**1**). *General procedure for the synthesis of sulfenamides using* N-*(benzenesulfenyl)phthalimide.* A solution of *N*-methylcyclohexylamine (2.0 g, 18 mmol) and *N*-(benzenesulfenyl)phthalimide (4.5 g, 18 mmol) in CH_2Cl_2 (50 ml) was stirred for 30 min under an atmosphere of nitrogen. The precipitate of phthalimide was filtered off and the solution evaporated to dryness to yield an oil which was purified by column chromatography (alumina/light petroleum) to yield pure *N*-(benzenesulfenyl)-*N*-methylcyclohexylamine (**1**) as a yellow oil (3.7 g, 93%); (Found: C, 70.62; H, 8.61; N, 6.03: $C_{13}H_{19}NS$ requires: C, 70.54; H, 8.65; N, 6.33%); υ_{max} (neat)/cm^{-1} 3060, 1582, 1474, 728, and 692; δ_H 1.26-1.60 (8 H, m), 1.92 (2 H, m), 2.74 (1 H, m, CHN), 2.87 (3 H, s, Me), and 7.01-7.25 (5 H, m, Ph-H); δ_C 143.2 (C), 128.5, 124.7, and 122.9 (CH), 66.0 (Me), 43.8 (*C*HN), 30.6, 30.5, 25.9, 25.8, and 25.7 (CH$_2$); m/z 221 (100%), 178, 139, 109, 83, 70, and 55. TLC showed one spot. A repeat reaction (15 h) gave a yield of 76%.

(b) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclopropylamine* (**2**). Tolualdehyde (4.2 g, 35 mmol) and cyclopropylamine (2.0 g, 35 mmol) were reacted using the general procedure to yield *N*-(*p*-methylbenzylidene)-cyclopropylamine as a brown oil; υ_{max} (neat)/cm^{-1} 3088 and 3008; δ_H 0.92 (4 H, d, cyclopropyl CH$_2$), 2.25 (3

H, s, Me), 2.93 (1 H, m, cyclopropyl CH), 7.00-7.57 (4 H, ABq Ph-H), and 8.23 (1 H, s, N=CH). The imine was reduced with sodium borohydride using the general procedure to yield a brown oil which was not further purified (4.8 g, 85%); υ_{max} (neat)/cm^{-1} 3312, 3084, 1612, 1512, and 804; δ_H 0.46 (4 H, d, cyclopropyl CH_2), 1.95 (1 H, s, cyclopropyl CH), 2.23 (3 H, s, Me), 3.68 (2 H, s, NHC*H*$_2$), and 6.90 (4 H, s, Ar-H). TLC (ethyl acetate/alumina) showed one spot.

N-(*p*-Methylbenzyl)cyclopropylamine (1.0 g, 6.2 mmol) was reacted using the general procedure (CH_2Cl_2, r.t. 2 days) to yield pure *N*-(benzenesulfenyl)-*N*-(*p*-methylbenzyl)cyclopropylamine (**2**) as a brown oil (1.2 g, 72%); υ_{max} (neat)/cm^{-1} 3052, 3004, 1612, 1512, 730, 692, and 808; δ_H 0.61 (4 H, d, cyclopropyl-CH_2), 2.31 (3 H, s, Me), 2.43 (1 H, m, C*H*N), 4.08 (2 H, s, NCH_2), and 7.19 (9 H, m, Ar-H); δ_C 9.81 (cyclopropyl-CH_2), 21.15 (Me), 39.33 (*C*HN), 61.75 (NCH_2), and 123.93-129.13 (Ar-C); m/z 270.1316 [$(MH)^+$ (2%). $C_{17}H_{20}NS$ requires 270.1316], 160 (31), 105 (100), 77 (14), 65 (9), 51 (6), and 39 (12). TLC showed one spot.. A repeat reaction (toluene, reflux, 1 h) gave a yield of 30%.

(c) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclobutylamine* (**3**). (44%, toluene, 1 h reflux).

(d) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclopentylamine* (**4**). Cyclopentylamine and *p*-tolualdehyde were reacted together using the general procedure to yield the imine; υ_{max} (neat)/cm^{-1} 3020, 1638, 1610, 1510, and 814; δ_H 1.84 (8 H, m, CH_2), 2.23 (3 H, s, Me), 3.85 (1 H, m, C*H*N), 7.32 (4 H, ABq, Ar-H), and 8.25 (1 H, s, C*H*=N). Reduction of the imine yielded the amine as an oil (98% overall); υ_{max} (neat)/cm^{-1} 3044, 1512, and 806; δ_H 1.73 (8 H, m, CH_2), 2.26 (3 H, s, Me), 2.70 (1 H, m, CHN), 3.14 (1 H, m, NH), 3.72 (2 H, s, NHC*H*$_2$), 7.10 (4 H, s, Ar-H); m/z 189.1517 (M^+. $C_{13}H_{19}N$ requires 189.1517) 160 (40%), 105 (100), 84 (11), 41 (6).

N-(*p*-Methylbenzyl)cyclopentylamine (1.0 g, 53 mmol) was reacted using the general procedure (15 h reflux) to yield *N*-(benzenesulfenyl)-*N*-(*p*-methylbenzyl)cyclopentylamine (**4**) as a pale yellow oil (300 mg, 20%); υ_{max} (neat)/cm^{-1} 3050, 3000, 1612, 1580, 1512, 1472, 808, and 738; δ_H 1.44 (8 H, m, CH_2), 2.17 (3 H, s, Me), 3.49 (1 H, q, CHN), 4.18 (2 H, s, NCH_2), and 7.32 (9 H, m, Ar-H); δ_C 21.16, 24.07, 30.71, 62.44, 65.67 and 123.45-135.27 (Ar-C); m/z 297.1551 (M^+. $C_{19}H_{23}NS$ requires 297.1551), 218 (13%), 192 (23), 105 (100), 77 (11), 41 (11).

(e) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)bicyclo[2.2.1]hept-exo-2-ylamine* (**5**). *exo*-2-Aminobicyclo-[2,2,1]heptane was prepared using the general procedure via the imine; υ_{max} (neat)/cm^{-1} 3024, 1638, 1606, 1508, and 812; δ_H 1.13 (4 H, m, 5-H 6-H), 1.50 (4 H, m, 7-H, 3-H), 2.23 (3 H, s, Me), 2.90 (2 H, s, 1-H, 4-H), 3.21 (1 H, m, 2-H), 7.43 (4 H, ABq, Ar-H), and 8.14 (1 H, s, N=CH); to yield N-(p-*methylbenzyl)bicyclo[2.2.1]hept-exo-2-ylamine* as a yellow oil (95% overall); υ_{max} (neat)/cm^{-1} 3532, 3044, 1512, and 806; δ_H 1.07 (4 H, m, 5-H, 6-H), 1.50 (4 H, m, 3-H, 7-H), 2.06 (2 H, s, 1-H, 4-H), 2.31 (3 H, s, Me), 2.60 (1 H, m, 2-H), 3.68 (2 H, ABq, NHC*H*$_2$), and 7.22 (4 H, ABq, Ar-H); δ_C 21.08 (Me), 26.91 (6-C), 28.62 (5-C), 34.94 (7-C), 35.67 (4-C), 40.19 (3-C), 40.68 (1-C), 51.61 (NHCH_2), 61.11 (2-C), and 128.13-137.80 (Ar-C); m/z 215.1674 (M^+. $C_{15}H_{21}N$ requires 215.1674], 105 (100%), 77 (12), and 41 (10). TLC showed one spot.

N-(p-*methylbenzyl)bicyclo[2,2,1]hept-exo-2-ylamine* (1.2 g, 56 mmol) was reacted using the general procedure (toluene 2 days reflux) to yield *N*-(benzenesulfenyl)-*N*-(*p*-methylbenzyl)bicyclo[2.2.1]hept-*exo*-2-ylamine as an orange oil (767 mg, 43%); (Found C, 77.84; H, 7.84; N, 4.56. $C_{21}H_{25}NS$ requires: C, 77.97; H, 7.79; N, 4.33%); υ_{max} (neat)/cm^{-1} 3056, 3016, 1604, 1578, 1510, 1474, 808, and 740; δ_H 1.05 (4 H, m, 5-H and 6-H), 1.48 (3 H, m, 7-H and 3-H), 2.24 (2 H, s, 1-H, 4-H), 2.35 (3 H, s, Me), 2.58 (1 H, s, 3-H), 2.95 (1 H, m, 2-H), 4.08 (2 H, ABq, NCH_2), 7.23 (5 H, d, Ph-H, and 7.30 (4 H, ABq Ar-H); δ_C 21.16 (Me), 27.33 (6-C), 28.44 (5-C), 35.48 (7-C), 35.74 (4-C), 39.61 (3-C), 40.77 (1-C), 59.61 (NCH_2), 67.71 (2-C), and 125.48-129.12 (Ar-C); m/z 323.1708 (M^+. $C_{21}H_{25}NS$ requires 323.1708), 216 (21%), 105 (100), 95 (15), 77 (20), 67 (22), and 39 (18). TLC showed one spot.

(f) N-*(Benzenesulfenyl)*-N-*(2,2-diphenylethyl)-3-phenylprop-1-ylamine* (**8**). (34%, benzene, 1 h reflux).

Synthesis of sulfenamides using diphenyl disulfide.

N-*(Benzenesulfenyl)*-N-*methylcyclohexylamine* (**1**). Silver nitrate (85 mg, 0.5 mmol) was dissolved in methanol (4.4 ml) and diphenyl disulfide (109 mg, 0.5 mmol) added giving a pale yellow suspension which was cooled to 0°C. *N*-methylcyclohexylamine (0.33 ml, 2.5 mmol) was added dropwise to the suspension. The suspension was warmed to room temperature and stirred for 48 h. The mixture was filtered and the filtrate evaporated. The residue was dissolved in diethyl ether which was washed with water, dried, and evaporated to dryness to yield a yellow oil (139 mg). Chromatography on basic alumina with diethyl ether/light petroleum gave a clear oil of pure (**1**) (96 mg, 86%) identical to authentic material.

Reactions between sulfenamides and Bu_3SnH

(a) N-*(benzenesulfenyl)*-N-(p-*methylbenzyl)bicyclo[2,2,1]hept-2-exo-ylamine* (**5**). *General procedure for reactions between sulfenamides and Bu_3SnH.* Nitrogen gas was passed through a solution of sulfenamide (**5**) (350 mg, 1.1 mmol) in dry cyclohexane (30 ml) for 30 min. A solution of Bu_3SnH (400 mg, 1.8 mmol, 1.7 equiv.) and AIBN (30 mg) in dry cyclohexane (20 ml) was purged with nitrogen for 30 min and the solution was added in one portion to the reaction solution (or transferred to a syringe pump and added over 6 h to the refluxing solution of the sulfenamide). The reaction was followed by TLC until complete consumption of the sulfenamide was observed (1 h). The reaction was allowed to cool to room temperature and the solvent evaporated to dryness to yield an oily residue. The amine products were extracted with 1M hydrochloric acid, the acid solution neutralised with sodium carbonate solution followed by aq. sodium hydroxide solution until pH 14. The aqueous layer was extracted with diethyl ether, the ether extracts combined, washed with water, dried, evaporated to dryness, and the residue purified by flash-sinter chromatography using TLC alumina and light petroleum as eluent to yield *N-(p*-methylbenzyl)bicyclo[2,2,1]hept-2-exo-ylamine (**5**) as a pale yellow oil (162 mg, 69%). The TLC and IR and ^1H NMR spectra of the amine were identical to those of authentic material. The use of the syringe pump gave a similar yield. No ring opened products were detected in either reaction.

(b) N-*(Benzenesulfenyl)*-N-*methylcyclohexylamine* (**1**). A solution of sulfenamide (**1**) (117 mg, 0.53 mmol), Bu_3SnH (262 mg, 0.9 mmol), and AIBN (30 mg, 0.18 mmol) in cyclohexane (5 ml) was refluxed for 15 min. The reaction mixture was analysed by GLC (capillary BP1, 12 m) using cyclohexylamine as an internal standard and found to contain only *N*-methycyclohexylamine (93%). A repeat reaction under the same conditions in which light was excluded and oxygen was bubbled through the solution gave a quantitative recovery of unaltered sulfenamide (**1**) with no traces of *N*-methycyclohexylamine (analysis by ^1H NMR spectroscopy using *p*-dimethoxybenzene as an internal standard). Further purification by chromatogaphy using neutral alumina as absorbent and light petroleum as eluent gave pure (**1**) (86 mg, 74%).

Preparation of tri-n-butyltinphenylsulphide. In a reaction between *N*-(benzenesulfenyl)-*N*-methylcyclohexylamine (**1**) (222 mg, 1 mmol) and Bu_3SnH (437 mg, 1.5 mmol) in acetonitrile, the diethyl ether extracts were dried and evaporated to dryness after extraction of basic material with dil. hydrochloric acid to yield an oil (599 mg). Chromatography on basic alumina with light petroleum followed by further chromatography on silica with light petroleum gave *tri-n-butyltinphenylsulphide* as a clear oil (205 mg, 51%). (Found: C; 54.41, H; 7.99, S; 8.08. $C_{18}H_{32}SSn$ requires: C; 54.16, H; 8.08, S; 8.02); υ_{max} (neat)/cm^{-1} 2952, 1578, 1474, 1460, 1084, 1024, 742, and 694; δ_H 7.40 (2 H, m, Ph-H), 7.13 (3 H, m, Ph-H), 1.53 (2 H, m), 1.32 (2 H, sextuplet, J = 7.0 Hz), 1.09 (2 H, t, J = 7.0 Hz), 0.87 (3 H, t, J = 7.0 Hz); δ_C 134.7, 128.5, 125.6, 28.5, 27.0, 14.3, and 13.6; m/z 400 (presence of 404, 400, 398, and 396 confirmed), 229, 177, 153, 110, 77, 51, and 29; .

N-*(Benzenesulfenyl)*-N-*methylcyclohexylamine* (**1**) *(Ph_3SnH).* A solution of the sulfenamide (**1**) (0.3 g, 1.36 mmol), triphenyltin hydride (0.8 g, 2.31 mmol, 1.7 equiv.), and AIBN (0.07 g, 4 mmol) in cyclohexane (30 ml) was purged with nitrogen for 30 min. The flask was then placed in a pre-heated oil bath and the solution refluxed for 30 min after which time TLC showed that no sulfenamide was present. The amine products were extracted with 1M hydrochloric acid, neutralised with sodium carbonate solution followed by aq. sodium hydroxide solution until pH 14, and re-extracted into CH_2Cl_2. The solution was evaporated to dryness to yield *N*-methylcyclohexylamine (81 mg, 53%). The product was identified by IR and ^1H NMR spectroscopy.

(c) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclopropylamine* (**2**). Sulfenamide (**2**) (0.2 g, 0.74 mmol) was reacted using the general procedure (cyclohexane, 2.5 h reflux). At the end of the reaction, $NaBH_4$ (0.3 g, 7.43 mmol) in dimethylformamide (20 ml) was added and the mixture stirred at room temperature for 60 min. Standard work-up produced pure *N*-(*p*-methylbenzyl)propylamine as a yellow liquid (88 mg, 73%). The TLC and IR and ^1H NMR spectra of the amine were identical to those of authentic material prepared by the reaction between propylamine and *p*-methylbenzyl bromide. The m.p. of the hydrochloride salt, m.p. 177-179°C, was the same as that of authentic material.

(d) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclobutylamine* (**3**). Sulfenamide (**3**) (400 mg, 1.4 mmol) was reacted using the general procedure (cyclohexane, 2 h, reflux) and the product mixture reduced with $NaBH_4$ to yield pure *N*-(*p*-methylbenzyl)cyclobutylamine as a clear oil (106 mg, 42%); The TLC and IR and ^1H NMR spectra of the amine were identical to those of authentic material prepared by the reaction between butylamine and *p*-methylbenzylbromide.

(e) N-*(Benzenesulfenyl)*-N-(p-*methylbenzyl)cyclopentylamine* (**4**). Sulfenamide (**4**) (288 mg, 0.9 mmol) (cyclohexane, 30 min, reflux) gave *N*-(*p*-methylbenzyl)cyclopentylamine as a colourless oil (99 mg, 54%). The TLC and IR and ^1H NMR spectra of the amine were identical to those of authentic material. No ring opened product derived from *N*-(*p*-methylbenzyl)cyclopentylamine, was detected.

(f) N-*(Benzenesulfenyl)*-N-*butyl-3-phenylprop-2-enylamine* (**6**). Sulfenamide (**6**) (benzene, 6 h, reflux) yielded pure *N*-butyl-3-phenylprop-2-enylamine (53%) as a clear oil and no cyclised material was observed. The TLC and IR and ^1H NMR spectra of the amine were identical to those of authentic material.

(g) N-*(Benzenesulfenyl)*-N-*(2,2-diphenylethyl)-3-phenylprop-1-ylamine* (**8**). Sulfenamide (**8**) (233 mg, 0.6 mmol) (cyclohexane, 2 h, reflux) gave two products which were reduced using $NaBH_4$ in DMF. The amine products were extracted into dil. hydrochloric acid and the neutral diphenylmethane into CH_2Cl_2. The amine fraction was unfortunately lost in the extraction stage. ^1H NMR using an internal standard (*p*-dimethoxybenzene) was used to determine the yield of diphenylmethane (67%). The TLC and IR and ^1H NMR spectra of the product were identical to those of authentic diphenylmethane. No *N*-(2,2-diphenylethyl)-3-phenylprop-1-ylamine was detected in the crude product mixture.

1-Cyclohexyl-3-phenyl-1-propyl phenyl sulfide (9)

1-Cyclohexyl-3-phenylpropanol. The Grignard reagent from cyclohexylbromide, and 4-phenylpropionaldehyde, were reacted in diethyl ether to give a white solid of 1-cyclohexyl-3-phenylpropanol; m.p. 59-60°C; υ_{max} (Nujol)/cm^{-1} 3296, 3024, 1602, 1494, 1032, 960, 920, 904, 846, 746, and 696; δ_H 1.10 (6 H, m), 1.70 (8 H, m), 2.65 (1 H, m), 2.80 (1 H, m), 3.37 (1 H, m), and 7.24 (5 H, m, Ar-H); δ_C 142.4, 128.4, 125.7, 75.6, 43.8, 35.9, 32.4, 29.2, 27.8, 28.5, 28.3, and 28.2; m/z 218, 200, 133, 117, 104, 91, and 83.

1-Cyclohexyl-1-mesyl-3-phenylpropane. The 1-cyclohexyl-3-phenylpropanol was reacted with methanesulfonyl chloride in dry pyridine to yield 1-cyclohexyl-1-mesyl-3-phenylpropane (70%); υ_{max} (Nujol)/cm^{-1} 3024, 2932, 1602, 1494, 1450, 1346, 1174, 970, 906, 734, and 700; δ_H 1.18 (5 H, m), 1.75 (6 H, m), 2.00 (2 H, m), 2.70 (2 H, m), 2.99 (3 H, s, Me), 4.65 (1 H, q, J = 6.4 Hz, C*H*OMs), and 7.25 (5 H, m, Ph-H); δ_C 25.95, 26.0, 26.2, 28.3, 31.4, 33.1 (CH_2), 38.7 (CH), 41.3 (Me), 87.5 (*C*HOMs), 128.1, 128.3, 128.5 (Ph-CH), and 141.1 (Ar-C); m/z 296 (M^+), 200, 117, 104 (100%), 91, 67,and 55.

1-Cyclohexyl-3-phenyl-1-propyl phenyl sulfide (**9**). Benzenethiol (463 mg, 4.2 mmol) in diethyl ether was added to a suspension of NaH (50% dispersion in oil, 192 mg, 4 mmol) in dry diethyl ether (8 ml) and the solution stirred for 10 min. A solution of 1-cyclohexyl-1-mesyl-3-phenylpropane (470 mg, 1.6 mmol) in diethyl ether was added dropwise and the mixture stirred at r.t. overnight and at reflux for 2 h and cooled to r.t. The ether solution was washed with sat. ammonium chloride solution, water, and brine, dried, and evaporated to dryness to yield an oil. The oil was purified by flash chromatography using silica gel as absorbent and CH_2Cl_2/light petroleum as eluent to yield a colourless oil of *1-cyclohexyl-3-phenyl-1-propyl phenyl sulfide* (**9**); (Found C, 81.33; H, 8.53. $C_{21}H_{26}S$ requires C, 81.23; H, 8.44%); υ_{max} (neat)/cm^{-1} 3024, 2924, 1602, 1582, 1478, 1448, 1026, 746, and 700; δ_H 1.05-1.33 (5 H, m), 1.45-2.05 (8 H, m), 2.70 (1 H, m, C*H*SPh), 2.92 (2

H, m, CH_2Ph), and 7.06-7.37 (10 H, m Ph-H); δ_C 26.28, 29.86, 33.62, 33.91 (CH_2), 42.05 (CH), 55.24 (CH), 125.78, 126.06, 128.30, 128.46, 128.77, 130.91 (Ar-CH), 137.2, and 142.0 (Ar-C); m/z 310 (M^+), 219, 201, 104, 97, 91 (100%), 83, 77, 67, and 55.

Reaction between Bu_3SnH and 1-cyclohexyl-3-phenyl-1-propyl phenyl sulfide (**9**). *1-Cyclohexyl-3-phenyl-1-propyl phenyl sulfide* (**9**) (155 mg, 0.5 mmol), Bu_3SnH (247 mg, 0.85 mmol), and AIBN (28 mg, 0.17 mmol) were reacted in refluxing cyclohexane for 7 h using the general procedure to yield a crude oil (317 mg). Flash chromatography using silica gel as absorbent and diethyl ether/petroleum ether as eluent gave tributylstannyl phenyl sulfide (46 mg, 30%) and pure *3-cyclohexyl-1-phenylpropane* (32 mg, 32%); (Found C, 88.56; H, 11.63. $C_{15}H_{22}$ requires C, 89.04; H, 10.96); υ_{max} (neat)/cm^{-1} 3024, 2920, 1602, 1494, 1448, 1030, 890, 746, and 698; δ_H 0.87 (2 H, m), 1.20 (6 H, m), 1.70 (7 H, m), 2.57 (2 H, t, CH_2Ph), and 7.20 (5 H, m, Ph-H); δ_C 26.4, 26.7, 28.8, 33.4, 36.3, and 37.2 (CH_2), 37.6 (CH), 125.5, 128.2, and 128.4 (Ph-C), and 143.0 (Ph-C); m/z 202.1722 (M^+. $C_{15}H_{22}$ requires 202.1722) 117, 106, 92 (100%), 83, 79, 65, and 55.

In a repeat reaction the sulfide (**9**) (77.5 mg, 0.25 mmol) and the sulfenamide (**1**) (55.3 mg, 0.25 mmol) were reacted under the same conditions for 15 min. ^1H NMR spectroscopic analysis using *p*-dimethoxybenzene as an internal standard indicated (**1**) (31%) and (**9**) (98%). GLC analysis showed *N*-methylcyclohexylamine (56%) and HPLC analysis (reverse-phase, 8% water in MeOH) showed that no 3-cyclohexyl-1-phenylpropane was present. A repeat reaction under identical conditions with sulfenamide (**1**) and without sulfide (**9**) indicated *N*-methylcyclohexane (76% by GLC) and sulfenamide (**1**) (23% by ^1H NMR spectroscopy).

N-(Benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamines (12).

N-Propyl(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**16a**). A solution of bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (2.00 g, 16.4 mmol) in diethyl ether (2.5 ml) was added to a mixture of 4Å molecular sieves (2 g) and diethyl ether (10 ml) and cooled to 0°C. A solution of propylamine (1.94 g, 32.8 mmol) in diethyl ether (2.5 ml) was added and stirred for 20 min. The mixture was filtered and evaporated to dryness to an orange oil (2.64 g) of the imine; υ_{max} (neat)/cm^{-1} 2960, 1662, 1454, 1378, 1336, and 720. A solution of the crude imine (2.64 g, 16.2 mmol) in diethyl ether was added to a suspension of $LiAlH_4$ (923 mg, 24.3 mmol) in diethyl ether (40 ml) and stirred for 30 min. Aq. sodium hydroxide solution (1 M) was added dropwise until a grey granular precipitate had formed. The solution was filtered, and the filtrate evaporated to dryness to yield an orange oil. Chromatography using basic alumina as absorbent and 1% MeOH in chloroform as eluent gave a pale yellow oil of *exo-* and *endo-N*-propyl(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**16a**) (2.29 g, 85%); υ_{max} (neat)/cm^{-1} 3384, 2956, 2188, 1636, 1568, 1456, 1338, 1126, 906, and 720; δ_H 0.48 (1 H, ddd, J = 11.44, 4.20, 2.59 Hz, *endo*-3-H), 0.86 (3 H, t, Me), 1.22 (1 H, m, 7-H), 1.37 (1 H, m, 7-H), 1.44 (2 H, t, CH_2Me), 1.81 (1 H, ddd, J = 11.50, 8.69, 3.86 Hz, *exo*-3-H), 2.18 (1 H, m, 2-H), 2.50 (2 H, t, J = 7.45 Hz, CH_2CH_2N), 2.70 (2 H, m, $CHCH_2N$), 2.79 (1 H, brs, 4-H), 2.84 (1 H, brs, 1-H), 5.87 (1 H, dd, J = 5.70, 2.87 Hz, 6-H), and 6.07 (1 H, dd, J = 5.71, 2.68 Hz, 5-H); δ_C 11.8 (Me), 23.2 (CH_2), 30.7 (CH_2), 39.3, 43.3, 44.4 (CH), 49.6, 52.2, 54.4 (CH_2), 132.1 and 137.3 (5, 6-C), and for the minor isomer, 23.3, 31.5 (CH_2), 41.7, 44.6 (CH), 45.2, 55.9 (CH_2), 136.5 and 137.3 (5, 6-C), and 3 carbons could not be observed; m/z 166 (MH^+), 136, 123, 98, 91,79, 72, 66, 56, and 41.

N-Methyl(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**16b**). Methylamine (50 mmol, 33% solution in ethanol) was reacted using the procedure as for (**16a**) to yield the corresponding methylimine (747 mg); δ_H 0.90-2.30 (5 H, m), 2.75 (2 H, m), 3.00 (3 H, s, Me), 5.85 (2 H, m), and 7.35 (1 H, m, CH=N). The crude imine was reduced using the procedure as for (**16a**) to yield *N*-methyl(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**16b**) as a pale yellow oil (295 mg, 43%); υ_{max} (neat)/cm^{-1} 3296, 2900, 1633, 1468, 1342, 1150, 836, 754, and 720; δ_H 1.37 (1 H, m, 7-H), 1.82 (1 H, ddd, J = 13.35, 8.82, 3.85 Hz, *exo*-3-H), 2.21 (1 H, m, 2-H), 2.28 (2 H, brs, CH_2N), 2.39 (3 H, s, Me), 2.74 (1 H, brs, 4-H), 2.82 (1 H, brs, 1-H), 5.89 (1 H, dd, J = 5.71, 2.87 Hz, 6-H), and 6.09 (1 H, dd, J = 5.73, 3.02 Hz, 5-H); δ_C 30.4 (3-C), 36.3 (2-C), 38.5 (4-C), 42.1 (1-C), 44.1 (Me), 49.4 (7-C), 56.2 (CH_2N), 131.8 (6-C), and 137.2 (5-C); m/z 137.1204 (M^+. $C_9H_{15}N$ requires 137.1204), 122, 108, 96, 91, 77, 70, and 44 (100%).

2-(Aminomethyl)bicyclo[2.2.1]hept-5-ene (**16c**). 2-Cyanobicyclo[2.2.1]hept-5-ene (3.0 g, 25 mmol) in dry diethyl ether (10 ml) was added slowly to a cooled suspension of $LiAlH_4$ (1.0 g, 27 mmol) in dry diethyl ether (10 ml). After stirring for 30 min, water was added, the lithium salts removed by filtration, and the solution evaporated to dryness to yield a mixture of *exo*- and *endo*-2-(aminomethyl)bicyclo[2.2.1]hept-5-ene (**16c**) as a yellow oil (3.1 g, 99%); υ_{max} (neat)/cm^{-1} 3368, 3056, and 1660; δ_H 0.53 (1 H, ddd, 3-*endo*-H, *endo*), 1.12-1.45 (3 H, m, 7-H and 3-*endo*-H, *exo*), 1.52 (2 H, s, NH_2), 1.84 (1 H, ddd, 2-H, *endo*), 2.08 (1 H, ddd, 2-H, *exo*), 2.36-2.42 (2 H, m, CH_2N), 2.64-2.87 (3 H, m, 1-H, 1-H, and 3-*exo*-H *exo* and *endo*), 5.92 (1 H, dd, 5-H), 6.11 (1 H, dd, 6-H); δ_C 30.21 (6-C), 41.86 (2-C), 42.75 (4-C), 45.61 (1-C), 46.73 (7-C), 49.52 (CH_2NH_2). TLC showed one spot but the ^1H NMR spectrum showed a mixture of *endo*- and *exo*-isomers (50:50). The isomers were not separated.

N-*(Benzenesulfenyl)*-N-*propyl(bicyclo[2.2.1]hept-5-en-2-yl)methylamine* (**12a**). *exo*- and *endo*-*N*-propyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**16a**) was reacted with *N*-(benzenesulfenyl)phthalimide using the general procedure (5 h, toluene, reflux) to yield *exo*- and *endo*-*N*-(benzenesulfenyl)-*N*-propyl(bicyclo[2.2.1]-hept-5-en-2-yl)methylamine (**12a**) as a colourless oil (79%); υ_{max} (neat)/cm^{-1} 2960, 1582, 1474, 1342, 1082, 908, and 692; δ_H 0.53 (1 H, ddd, J = 11.53, 4.34, 2.60 Hz, *endo*-3-H), 0.88 (3 H, t, Me), 1.27 (1 H, m, 7-H), 1.40 (1 H, ddd, J = 8.06, 4.22, 1.95 Hz, 7-H), 1.65 (2 H, sestet, CH_2Me), 1.81 (1 H, ddd, J = 12.81, 8.96, 3.86 Hz, *exo*-3-H), 2.48 (1 H, m, 2-H), 2.67 (2 H, dd, J = 7.63, 2.21 Hz, $CHCH_2N$), 2.75 (1 H, brs, 4-H), 2.92 (3 H, m, 1-H, NCH_2CH_2), 5.93 (1 H, dd, J = 5.69, 2.81 Hz, 5-H), 6.10 (1 H, dd, 5.68, 3.02 Hz), 7.12-7.48 (5 H, m, Ph-H); δ_C 11.5 (Me), 21.6 (CH_2), 30.6 (CH_2), 38.1, 43.3, 42.0, 44.6 (CH), 49.5, 60.8, 62.3 (CH_2), 125.0, 125.3, 128.5, (Ph-CH), 132.7 and 137.1 (5, 6-C), and 141.2 (Ph-C), for the minor isomer, 21.8, 31.3 (CH_2), 38.2, 42.4 (CH), 45.3, 64.2 (CH_2), 136.5 and 136.6 (5, 6-C); m/z 273.1560 [MH^+ (20%), $C_{17}H_{23}NS$ requires 273.1551], 244 (97), 180 (100), 164 (30), 150 (29), 134 (15), 122 (15), 109 (65), 91 (22), 79 (30), and 66 (38).

N-*(Benzenesulfenyl)*-N-*methylbicyclo[2.2.1]hept-5-en-2-yl)methylamine* (**12b**). *exo*- and *endo*-*N*-Methyl-bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**16b**) (247 mg, 1.8 mmol) was reacted with *N*-(benzenesulfenyl)-phthalimide (400 mg, 1.6 mmol) using the general procedure (toluene, reflux, overnight) to yield *exo*- and *endo*-*N*-(benzenesulfenyl)-*N*-methylbicyclo[2.2.1]hept-5-en-2-yl)methylamine (**12b**) as a pale yellow oil (237 mg, 54%); υ_{max} (neat)/cm^{-1} 3056, 2960, 1580, 1474, 1438, 752, 722, and 692; δ_H 0.52 (1 H, ddd, J = 11.56, 4.22, 2.62 Hz, *exo*-3-H), 1.25 (1 H, 7-H), 1.41 (1 H, m, 7-H), 1.81 (1 H, ddd, J = 11.67, 8.81, 3.84 Hz, 5-H), 2.46 (1 H, m, 2-H), 2.57 (2 H, m, CH_2N), 2.76 (1 H, brs, 4-H), 2.79 (3 H, s, Me), 2.86 (1 H, brs, 1-H), 5.93 (1 H, dd, J = 5.68, 2.88 Hz, 6-H), and 6.10 (1 H, dd, J = 5.73, 3.02 Hz, 5-H); δ_C 30.4 (3-C), 37.8 (2-C), 42.3 (4-C), 44.5 (1-C), 47.0 (Me), 49.4 (7-C), 63.8 (CH_2N), 126.2, 127.1, 128.5, 132.6 (Ph-CH), 132.6 and 137.0 (5, 6-C), and 138.3 (Ph-C); m/z 245.1238 [M^+ (100%). $C_{15}H_{19}NS$ requires 245.1238], 212, 152, 136, 122, 109, 94, and 82.

N-*(Benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine* (**12c**). *exo*- and *endo*-2-(Aminomethyl)-bicyclo[2.2.1]hept-5-ene (**16c**) were reacted using the general procedure (diethyl ether, 2 h) to yield *exo*- and *endo*-*N*-(benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**12c**) as a clear oil (41%); υ_{max} (neat)/cm^{-1} 3328, 3056, 1580, 1476, 738, and 692; δ_H 0.52 (1 H, ddd, 3-*endo*-H, *endo*), 1.28 (3 H, m, 7-H and 3-*endo*-H, *exo*), 1.83 (1 H, ddd, 2-H, *endo*), 2.76 (2 H, m, 1-H, 1-H, *exo* and *endo*), 3.19 (2 H, m, CH_2N), 5.91 (1 H, dd, 5-H), 6.11 (1 H, dd, 6-H), and 7.35 (5 H, m, Ph-H), other signals could not be assigned; δ_C 30.18 and 31.00 (3-C), 39.59 and 39.62 (4-C), 41.58 and 42.29 (1-C), 44.09 and 44.21 (2-C), 47.16 (*exo*-7-C), 49.28 (*endo*-7-C), 56.35 and 57.85 (CH_2N), 132.05, 132.43, 136.59 and 137.33 (5, 6-C), and 126.0-137.0 (Ar-C); m/z 232.1160 $[MH]^+$ (100%). ($C_{14}H_{17}NS$+H) requires 232.1160], 218 (80), 189 (49), 93 (15), and 65 (27).

Reaction between Bu_3SnH and N-*(benzenesulfenyl)*-N-*propyl(bicyclo[2.2.1]hept-5-en-2-yl)methylamine* (**12a**). The sulfenamide (**12a**) (273 mg, 1 mmol) was reacted with Bu_3SnH (495 mg, 1.7 mmol) using the general procedure (syringe pump, THF, 12 h). The ^1H NMR spectrum of the crude product showed a ratio of

(**15a**):uncyclised amine of 4:1. The crude product was treated with acetic anhydride (24 h at room temperature) to remove the *exo*-isomer as the corresponding acetate. The crude mixture was subjected to chromatography using neutral alumina as absorbent with MeOH/$CHCl_3$ as eluent to yield the cyclic amine (**15a**) as an oil (31 mg, 29% allowing for the *exo*-isomer); υ_{max} (neat)/cm^{-1} 3397, 2958, 2872, 2514, 1645, 1455, 1069, and 753; δ_H 1.35 (4 H, m, 5, 7-H), 1.48 (2 H, sestet, J = 7.47, CH_2Me), 1.89 (1 H, m, *exo*-3-H), 2.11 (1 H, brs, 4-H), 2.26 (1 H, m, 2-H), 2.44 (1 H, d, J = 10.03 Hz, CHCH_2N), 2.51 (2 H, t, J = 6.72 Hz, CH_2CH_2N), 2.59 (1 H, m, 1-H), 3.17 (1 H, dd, J = 6.26, 10.00 Hz, CHCH_2N), 3.33 (1 H, m, 6-H); δ_C 11.9 (Me), 22.2 (CH_2Me), 32.0 (CH_2), 34.5 (CH), 37.5 (CH_2), 40.9 (CH_2), 46.0 (CH), 56.6 (CH_2N), 60.8 (CH_2N), and 63.6 (6-CH); m/z 165.1517 [M^+ (14%). $C_{11}H_{19}N$ requires 165.1517], 150 (15), 136 (100), 129 (19), 122 (33), 110 (12), 94 (10), 80 (20), 68 (12), and 55 (10).

Reaction between Bu_3SnH and N-*(benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamines*, (**12b**) and (**12c**). Both sulfenamides was reacted using the standard procedure and the products were analysed as mixtures and not separated. The sulfenamide (**12b**) (237 mg, 0.97 mmol) gave the cyclised amine (**15b**) (75 mg, 57%) and uncyclised amine (**16b**). The sulfenamide (**12c**) (cyclohexane, reflux, syringe pump, 6 h) gave a mixture of the cyclised amine (**15c**) and uncyclised amine (**16c**) (38%); δ_H 1.28 (2 H, m, 5-H), 1.61 (2 H, m, 7-H), 1.85 (2 H, m, 3-H), 2.17 (1 H, m, 4-H), 2.57 (1 H, m, 1-H), 2.80 (1 H, s, 2-H), 3.06 (2 H, m, CHCH_2N), and 3.43 (1 H, m, 6-H); δ_C 26.04 (3-C), 26.17 (5-C), 29.72 (2-C), 31.08 (7-C), 41.69 (4-C), 53.81 (1-C), 65.86 (CH_2N), and 69.37 (6-C).

cis-N-(Benzenesulfenyl)-5-(4-isopropylphenyl)pent-4-enylamine

cis-*5-(4-Isopropylphenyl)pent-4-enylamine*. 3-Cyanopropyl triphenyl phosphonium bromide was prepared as colourless crystals from reaction between 4-bromobutyronitrile and triphenylphosphine (toluene, 72 h, reflux) (79%); m.p. 215-217°C; δ_H 1.96 (2 H, dt, $CH_2CH_2CH_2$), 3.11 (2 H, t, CH_2CN), 4.14 (2 H, m, CH_2P), and 7.85 (15 H, m, Ph-H). The anion of the phosphonium bromide was formed by reaction with NaH in dry THF. A solution of 4-isopropylbenzaldehyde in dry THF was added dropwise and the mixture stirred for 17 h under an atmosphere of nitrogen. Work-up of the reaction mixture and purification on a dry silica column using diethyl ether/light petroleum as eluent yielded *cis*-4-cyano-1-(4-isopropylphenyl)but-1-ene as a clear oil, (80%); υ_{max} (neat)/cm^{-1} 3017, 2246, 1512, 1461, and 847; δ_H 1.25 (6 H, d, Me_2), 2.41 (2 H, t, CH_2CN), 2.65 (2 H, dt, 3-CH_2), 2.90 (1 H, q, C*H*Me_2), 5.59 (1 H, dt, 2-H), 6.56 (1 H, d, 3-H), and 7.16 (4 H, ABq, Ar-H); δ_C 17.58 (4-C), 23.93 (Me), 24.51 (3-C), 33.84 (2-C), 124.93 (CN), 128.39-148.00 (Ar-C and 1-C); m/z 199.1361 (M^+, $C_{14}H_{17}N$ requires 199.1361), 199 (87%), 159 (32), 117 (100), and 91 (12). The *cis*-4-cyano-1-(4-isopropylphenyl)but-1-ene was reduced with $LiAlH_4$ in dry diethyl ether at room temperature (2 h) to yield *cis*-5-(4-isopropylphenyl)pent-4-enylamine as a clear oil (95%); υ_{max} (neat)/cm^{-1} 3367, 3297, 3008, 1511, 1460, and 845; δ_H 1.24 (6 H, d, Me_2), 1.60 (2 H, q, 2-H), 2.36 (2 H, t, 3-H), 2.73 (2 H, t, 1-H), 2.87 (1 H, m, C*H*Me_2), 5.59 (1 H, dt, 4-H), 6.41 (1 H, d, 5-H), and 7.23 (4 H, s, Ph-H); δ_C 23.97 (Me), 25.99 (2-C), 33.81 (C*H*Me_2), 34.04 (3-C), 41.84 (1-C), and 128.67-141.34 (Ar-H and 4,5-C); m/z 204.1752 [$(M+H)^+$. $C_{14}H_{21}N$+H requires 204.1752], 204 (37%), 186 (34), 143 (100), 128 (26), and 56 (37).

cis-N-*(Benzenesulfenyl)-5-(4-isopropylphenyl)pent-4-enylamine* (**17**). *cis*-5-(4-Isopropylphenyl)pent-4-enylethylamine was reacted using the general procedure for synthesising sulfenamides using *N*-(benzenesulfenyl)phthalimide (CH_2Cl_2, 3 h, reflux) to yield *cis-N*-(benzenesulfenyl)-5-(4-isopropylphenyl)pent-4-enylamine (**17**) as a clear oil, (2.2 g, 72%); υ_{max} (neat)/cm^{-1} 3344, 3007, 1583, 1477, 1460, 845, and 692; δ_H 1.26 (6 H, d, Me_2), 1.72 (2 H, q, 2-H), 2.37 (2 H, dt, 1-H), 2.83 (1 H, m, C*H*Me_2), 2.95 (2 H, m, 3-H), 5.58 (1 H, dt, 4-H), 6.41 (1 H, d, 5-H), and 7.15 (9 H, m, Ph-H); δ_C 23.86 (Me_2), 25.88 (2-C), 30.38 (1-C), 33.71 (CH), 51.51 (3-C), and 124.86-130.34 (Ph-C and 4, 5-C); m/z 312.1790 (MH^+, $C_{20}H_{25}NS$+H requires 312.1790), 202 (100), 109 (25), and 70 (94).

Reaction between Bu_3SnH and cis-N-*(benzenesulfenyl)-5-(4-isopropylphenyl)pent-4-enylamine* (**17**). The sulfenamide (**17**) (695 mg, 2.24 mmol) was reacted using the general procedure for Bu_3SnH reactions (benzene, 5 h, reflux, Bu_3SnH added by syringe pump) to yield pure 2-(4-isopropylbenzyl)pyrrolidine as a clear oil, (295 mg, 65%); υ_{max} (neat)/cm^{-1} 3308, 1514, and 1463; δ_H 1.27 (6 H, d, Me_2), 1.76 (5 H, m, 3-H,

4-H and NH), 2.70 (2 H, d, ArCH_2), 2.82 (2 H, m, 5-H), 3.01 (1 H, m, CHMe$_2$), 3.20 (1 H, dt, 2-H), 7.17 (4 H, s, Ph-H); δ_C 24.06 (Me), 24.86 (3-C), 31.29 (2-C), 33.69 (*C*HMe$_2$), 41.99 (Ar*C*H$_2$), 46.20 (5-C), 60.56 (2-C), 126.14 and 128.89 (Ar-*C*H), and 137.53 and 146.52 (Ar-C); m/z 204.2110 [MH$^+$ (100%). $C_{14}H_{21}N$+H requires 204.2110] and 70 (32). No uncyclised amine or other products were detected.

Synthesis of the aphanorphine analogue (29)

4-Hydroxy-1-hydroxymethyl-1-methyl-1,2,3,4-tetrahydronaphthalene. $LiAlH_4$ (2.33 g, 61.3 mmol) was added in portions to a solution of 1-carboxy-1-methyl-4-oxo-1,2,3,4-tetrahydronaphthalene (**22**) (5.0 g, 24.5 mmol) in THF (120 ml) and diethyl ether (30 ml). After 30 min the suspension was diluted with diethyl ether and 1 M aq. NaOH solution added. The mixture was filtered and the filtrate evaporated to dryness. The residue was purified by flash-chromatograpy using silica gel with EtOAc/light petroleum as eluent to yield a colourless solid of 4-hydroxy-1-hydroxymethyl-1-methyl-1,2,3,4-tetrahydronaphthalene as a mixture of diastereoisomers (4.56 g, 97%); υ_{max} (neat)/cm^{-1} 3350; δ_H 1.20 (3 H, s, Me), 1.25 (3 H, s, Me), 1.35 (1 H, m), 1.60-2.10 (6 H, m), 2.16 (1 H, m), 3.39 (2 H, m), 3.50 (1 H, d, J = 11 Hz), 3.73 (1 H, d, J = 11 Hz), 4.60 (2 H, m), 7.20 (8 H, m); δ_C 26.25 and 26.38 (Me), 28.03, 28.19, 28.63, and 28.79 (CH_2), 39.05, 39.26 (C), 68.14, 68.46 (CH), 70.84, 71.01 (CH_2), 126.19, 126.29, 126.50, 126.54, 127.61, 127.84, 128.33, 129.31 (Ar-CH), 139.58, 140.18, 141.47, and 141.49 (Ar-C); m/z 192 , 175, 157, 144, 128, and 115.

1,2-Dihydro-1-hydroxymethyl-1-methylnaphthalene (**23**). 4-Hydroxy-1-hydroxymethyl-1-methyl-1,2,3,4-tetrahydronaphthalene (3.12 g, 16 mmol) and *p*-toluenesulfonic acid (1.52 g, 8 mmol) were refluxed in toluene with a Dean-Stark water-separator for 15 min. The cooled solution was washed with aq. sodium carbonate solution, dried, and evaporated to dryness. Flash chromatography of the resulting residue using silica gel with EtOAc/light petroleum as eluent gave two products: 1,2-dihydro-1-hydroxymethyl-1-methylnaphthalene (**23**) as a colourless solid; m.p. 88-89°C; υ_{max} (neat)/cm^{-1} 3315, 1106, and 1026; δ_H 1.28 (3 H, s, Me), 1.75 (1 H, s), 2.19 (1 H, d, J = 17.5 Hz), 2.41 (1 H, d, J = 17.5 Hz), 3.50 (2 H, q, J = 10 Hz), 5.89 (1 H, m), 6.41 (1 H, d, J = 10 Hz), and 7.18 (4 H, m, Ar-H); δ_C 23.1 (Me), 33.3 (2-C), 38.7 (1-C), 68.5 (*C*H$_2$OH), 125.1, 126.8, 126.9, and 127.4 (Ar-CH), 133.7, and 139.3 (Ar-C); m/z (E.I. and C.I.) 192.1388 [(M + NH$_4$)$^+$. ($C_{12}H_{14}O$ + NH$_4$) requires 192.1388], 174, 156, 143, 128, 115, 102, and 91; and the cyclic ether (**24**) (18%) as a clear oil; υ_{max} (neat)/cm^{-1} 3020, 2956, 1486, 1461, 1380, 1044, 1020, 929, 873, and 753; δ_H 1.33 (1 H, m), 1.34 (3 H, s, 1-Me), 1.55 (1 H, t), 1.73 (1 H, t), 2.32 (1 H, m), 3.13 (1 H, d, J = 11.8 Hz, OC*H*), 3.77 (1 H, d, J = 11.9 Hz, OC*H*), 4.83 (1 H, 4-H), and 7.27 (4 H, m, Ar-H); δ_C 18.30 (Me), 27.55 and 30.00 (2-C, 3-C), 34.82 (1-C), 69.84 (4-CH), 72.87 (*C*H$_2$O), 120.71, 122.35, 126.10, and 127.66 (Ar-CH), 140.22, and 143.13 (Ar-C); m/z 175.1123 [(MH)$^+$ (3%). ($C_{12}H_{14}O$ + H) requires 175.1123], 157 (21), 144 (100), 115 (25), 103 (10), 91 (12), 77 (15), and 61 (10).

1,2-Dihydro-1-methylnaphthalene-1-carboxaldehyde. A solution of oxalyl chloride (3.24 g, 25.5 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a solution of DMSO (4,3 g, 55.7 mmol) in CH_2Cl_2 (5 ml) at -78°C and stirred for 15 min. A solution of 1,2-dihydro-1-hydroxymethyl-1-methylnaphthalene (**23**) (2.01 g, 11.6 mmol) CH_2Cl_2 (15 ml) was added dropwise to the solution. After 40 min, a solution of Et_3N (16.1 ml) in CH_2Cl_2 (15 ml) was added slowly and the solution allowed to warm up to room temperature, water added, and the mixture extracted with CH_2Cl_2. The combined extracts were washed with 2 M hydrochloric acid, saturated sodium carbonate solution, and brine, dried, and evaporated to dryness to yield an oil. The oil was purified by flash chromatography using silica gel as absorbent and light petroleum/diethyl ether as eluent to give a colourless oil of 1,2-dihydro-1-methylnaphthalene-1-carboxaldehyde (1.809 g, 90%); b.p. 195-200°C at 0.05 mm Hg; υ_{max} (neat)/cm^{-1} 1726, 1486, 1450, 786, and 755; δ_H 2.27 (1 H, ddd, J = 17.4, 3.76, 2.21 Hz, 2-H), 2.74 (1 H, ddd, J = 17.5, 4.85, 1.55 Hz, 2-H), 5.97 (1 H, dt, J = 9.8, 4.0 Hz, 3-H), 6.43 (1 H, dt, J = 9.8, 1.55 Hz, 4-H), 7.12 (2 H, m, Ar-H), 7.24 (2 H, m, Ar-H), and 9.49 (1 H, s, CHO); δ_C 20.1 (Me), 31.1 (3-C), 49.6 (1-C), 125.9, 127.0, 127.5, 127.9 (Ar and alkene-CH), 133.8 and 134.2 (Ar-C), and 201.5 (CHO); m/z 172.0888 (M$^+$. $C_{12}H_{12}O$ requires 172.0888), 157, 143, 128, and 115.

N-*[(1,2-Dihydro-1-methylnaphth-1-yl)methyl]*-N-*propylamine*. Propylamine (3.84 g, 65 mmol) and 1,2-dihydro-1-methylnaphthalene-1-carboxaldehyde (1.809 g, 6.5 mmol) were reacted using the procedure as for (**16a**) to yield the imine (**25**) (1.22 g); υ_{max} (neat)/cm^{-1} 1666; δ_H 0.8 (3 H, t, Me), 1.3 (3 H, s, Me), 1.5 (2 H, m), 2.1 (1 H, d, J = 18 Hz), 2.6 (1 H, J = 18 Hz), 3.3 (1 H, t), 5.9 (1 H, m), 6.4 (1 H, d, J = 10.5 Hz), 7.1 (4 H, m), and 7.6 (1 H, s, CH=N). The imine (**25**) (1.22 g) was reduced with $LiAlH_4$ using the procedure as for (**16a**) to yield an oil which was distilled to give *N*-[(2,3-dihydro-1-methylnaphth-1-yl)methyl]-*N*-propylamine (1.00 g, 74%) as a clear oil; b.p. 218°C at 0.05 mm Hg; υ_{max} (neat)/cm^{-1} 3343, 3033, 2930, 1485, 1458, 1123, 786, and 755; δ_H 0.78 (1 H, brs), 0.84 (3 H, t, CH_2CH_3), 1.27 (3 H, s, 1-Me), 1.42 (1 H, sestet, CH_2Me), 2.16 (1 H, ddd, 2-H), 2.54 (4 H, CH_2N), 2.76 (1 H, d, 2-H), 5.92 (1 H, dt, 3-H), 6.38 (1 H, dt, 4-H), and 7.02-7.20 (4 H, m, Ar-H); δ_C 11.68 (CH_2CH_3), 23.03 (CH_2Me), 25.34 (1-Me), 34.73 (2-C), 37.62 (1-C), 52.60 and 57.43 (CH_2N), 124.63, 126.39, 126.70, 127.21, and 127.32 (Ar-CH, alkene-C), 133.65 and 141.18 (Ar-C); m/z 216.1752 [MH$^+$. $C_{15}H_{21}N$+H requires 216.1752], 216 (2%), 142 (29), 128 (28), 115 (15), 102 (3), 89(3), and 72 (100).

N-*(Benzenesulfenyl)*-N-*[(2,3-dihydro-1-methylnaphth-1-yl)methyl]*-N-*propylamine* (**26**). *N*-[(2,3-dihydro-1-methylnaphth-1-yl)methyl]-*N*-propylamine (235 mg, 1.1 mmol) was reacted using the general procedure for benzenesulfenyl chloride (diethyl ether, reflux 30 min) to yield the sulfenamide (**26**) (355 mg, with traces of PhSSPh); δ_H 0.80 (3 H, t, CH_2CH_3), 1.43 (3 H, s, 1-Me), 1.50 (2 H, sestet, CH_2Me), 2.16-2.86 (4 H, m), 3.13 (2 H, CH_2N), 5.90 (1 H, dt, 3-H), 6.40 (1 H, dd, 4-H), and 7.0.16 (9 H, m, Ar-H). (**26**) was used without complete purification.

Reaction between sulfenamide (**26**) *and* Bu_3SnH. The sulfenamide (**26**) (355 mg, 1.1 mmol) was reacted using the general procedure (toluene, 5 h, reflux, syringe pump) to yield a crude oil. ^{1}H NMR spectroscopy was used to determine the ratio of cyclised amine (**29**) to uncyclised amine, *N*-(2,3-dihydro-1-methylnaphth-1-yl)-*N*-propylmethylamine (4.6:1). The oil was mixed with acetic anhydride (2 ml), Et_3N (5 ml), and CH_2Cl_2 (5 ml) and stirred for 4 h. The solution was poured into aq. sodium carbonate solution and extracted with CH_2Cl_2. The organic extracts were evaporated to dryness to yield a residue which was purified by flash chromatography using alumina as absorbent to yield (**29**) as a clear oil 65 mg, 27%); υ_{max} (neat)/cm^{-1} 2967, 1665, 1456, 1166, 1042, 795, and 734; δ_H 0.87 (3 H, t, CH_2CH_3), 1.46 and 1.49 (3 H, 2 x s, 1-Me), 1.84 (1 H, d, J = 10.8 Hz, 2-H), 2.00 (1 H, ddd, J = 10.9, 5.7, 1.4 Hz, 2-H), 2.53 (2 H, m, $MeCH_2$), 2.79 (2 H, 2 x s, C-CH_2N), 2.90 (1 H, dd, J = 17.0, 3.3 Hz, 4-H), 3.04 (1 H, d, J = 16.9 Hz, 4-H), 3.49 (1 H, m, CHN, 4-H), 7.14 (3 H, m), and 7.21 (1 H, m); δ_C 11.83 (CH_2CH_3), 21.51 (1-Me), 22.67 (CH_2Me), 36.74 (4-C), 41.51 (2-C, CH_2), 42.07 (1-C), 57.02 (CH_2CH_2N), 59.01 (3-C, CHN), 69.67 (C-CH_2N), 122.76, 126.39, 125.55, 126.03, and 129.30 (Ar-CH), 134.42 and 146.88 (Ar-C); m/z 216.1752 [MH$^+$ (3%). $C_{15}H_{21}N$+H requires 216.1752], 200 (14), 186 (35), 172 (5), 158 (8), 142 (45), 129 (100), 115 (28), 84 (12), and 49 (25).

N-(Benzenesulfenyl)-2-(4-t-butylphenyl)-2-(cyclohex-2-enyl)ethylamine

2-(4-t-Butylphenyl)-2-(cyclohex-2-enyl)ethylamine (**34**, Ar = 4-t-butylphenyl). 4-t-Butylbenzyl cyanide was prepared from reaction between sodium cyanide and 4-t-butylbenzyl chloride in ethanol and water (reflux, 4.5 h). Purification on a dry silica column using hexane and diethyl ether as eluent yielded 4-t-butylbenzyl cyanide (70%) as a clear liquid; δ_H 1.33 (9 H, s, t-Bu), 3.71 (2 H, s, CH_2CN), and 7.32 (4 H, ABq, Ar-H); δ_C 23.12 (CH_2CN), 31.32 (t-Bu), 34.59 (Me_3C), 118.16-127.71 (Ar-C), and 151.16 (CN). 4-t-Butylbenzyl cyanide was reacted using the above procedure to yield: *2-(4-t-butylphenyl)-2-(cyclohex-2-enyl)acetonitrile* (98%); (Found C: 85.07, H: 8.95, N: 5.58. $C_{18}H_{23}N$ requires C: 85.32, H: 9.15, N: 5.53); δ_H 1.35 (9 H, s, t-Bu), 1.52 (2 H, m, 5'-H), 1.73 (2 H, m, 6'-H), 2.01 (2 H, m, 4'-H), 2.59 (1 H, m, 1'-H), 3.71 (1 H, dd, 2-H), 5.48 (1 H, d, 3'-H), 5.76 (1 H, d, 2'-H), and 7.32 (4 H, ABq, Ar-H); δ_C 18.72 (5'-C), 20.66 (6'-C), 27.40 (4'-C), 31.23 (t-Bu), 34.49 (CMe_3), 40.45 (1'-C), 42.92 (2-C), 124.90-133.38 (Ar-C and olefin-C), and 151.00 (CN); m/z 253, 173 (70), 158 (100), 130 (26); *2-(4-t-butylphenyl)-2-(cyclohex-2-enyl)ethylamine* (**34**) as a clear oil (79%). (Found C: 83.62, H: 10.52, N: 5.55; $C_{18}H_{27}N$ requires, C: 83.98, H: 10.57, N: 5.44); δ_H 1.32 (9 H, s, t-Bu), 1.50-1.71 (6 H, m, 4', 5', 6'-H), 1.96 (2 H, s, NH_2), 2.51 (2 H, m, 1', 2-H),

2.93 (1 H, t, 1-H), 3.13 (1 H, dt, 1-H), 5.37 (0.5 H, d, 3'-H), 5.62 (0.5 H, d, 3'-H), 5.84 (1 H, dd, 2'-H), and 7.24 (4 H, ABq, Ar-H); δ_C 21.97 (5'-C), 25.23 (6'-C), 27.25 (4'-C), 31.41 (*CMe*$_3$), 34.37 (*C*Me$_3$), 39.08 (1'-C), 44.52 (2-C), 54.45 (1-C), 124.95-130.35 (Ar-CH and 2', 3'-C), 139.26 and 149.09 (Ar-C); m/z 257 (17%), 240 (38), 183 (66), 176 (100), 147 (96), 133 (90), and 105 (61).

N-*(Benzenesulfenyl)-2-(4-t-butylphenyl)-2-(cyclohex-2-enyl)ethylamine* (**30**, Ar = 4-t-butylphenyl). The amine (**34**) was reacted with benzenesulfenyl chloride (2 h) using the general procedure to yield the sulfenamide (**30**, R = 4-t-butylphenyl) as a light yellow oil, (90%); δ_H 1.31 (2 H, m, 5'-H), 1.35 (9 H, s, t-Bu), 1.42 (2 H, m, 6'-H), 1.64 (2 H, m, 4'-H), 1.89 (1 H, s, NH), 3.11 (1 H, m, 1'-H), 3.62 (2 H, m, 1, 2-H), 3.95 (1 H, m, 1-H), 5.42 (1 H, d, 3'-H), 5.63 (1 H, d, 2'-H), 7.25 (9 H, m, Ar-H); δ_C 22.09 (5'-C), 25.32 (6'-C), 27.00 (4'-C), 31.51 (*CMe*$_3$), 34.60 (*C*Me$_3$), 38.71 (1'-C), 49.46 (2-C), 67.52 (1-C), 124.95-129.79 (Ar-C and 2,3-C), 139.13 and 149.01 (Ar-C); m/z 366 (5%), 351 (52), 271 (56), 258 (90), 126 (100). Attempts to prepare the sulfenamides (**30**, Ar = Ph and 4-t-butylphenyl) using the general procedure for *N*-(benzenesulfenyl)phthalimide (CH_2Cl_2, 3 days, reflux) gave only unaltered starting amine.

Reaction between N-*(benzenesulfenyl)-2-(4-t-butylphenyl)-2-(cyclohex-2-enyl)]ethylamine and Bu$_3$SnH, and tris(trimethylsilyl)silane*. The sulfenamide (100 mg, 0.27 mmol) was reduced with Bu$_3$SnH using the general procedure (THF, 6 h, reflux, addition of Bu$_3$SnH by syringe pump) to give pure 2-(4-t-butylphenyl)-2-(cyclohex-2-enyl)ethylamine (**34**) (100%) and no expected cyclised product (**33**) was observed. The sulfenamide (200 mg, 0.55 mmol) was also reduced with tris(trimethylsilyl)silane (THF, 3 h, reflux, addition of (Me$_3$Si)$_3$SiH by syringe pump) to yield the amine (**34**) (100 mg, 71%). No other products and no evidence for cyclised amine was observed.

Cyclisations using electrophiles (I_2 and $HgCl_2$)

2-(Cyclohex-2-enyl)-2-phenylethylamine (**34**, Ar = Ph). Phenylacetonitrile (12.0 g, 0.102 mol) and benzyltriethylammonium chloride (1.1 g, 4.65 mmol) were both added to a stirred solution of sodium hydroxide (100 ml, 50% w/v). The resulting two phase system was cooled to 25°C and 1 equiv. of 3-bromocyclohexene was added dropwise. The suspension was stirred at 40°C for 6 h, and overnight at room temperature. The reaction was diluted with water and acidified to pH 2 using conc. hydrochloric acid and extracted with diethyl ether. The ether extracts were combined and washed with water, dried, and evaporated to dryness to yield a brown oil. Purification on a silica column using diethyl ether and hexane as eluent yielded 2-(cyclohex-2-enyl)-2-phenylacetonitrile as a light yellow oil (16.8 g, 92%); υ_{max} (neat)/cm^{-1} 3029, 2240, 1496, and 676; δ_H (300 MHz) 1.35 (2 H, m, 5'-H), 1.67 (2 H, m, 6'-H), 1.88 (2 H, d, 4'-H), 2.55 (1 H, m, 1'-H), 3.68 (1 H, dd, 2-H), 5.32 (0.5 H, d, 2'-H), 5.69 (0.5 H, d, 2'-H), 5.76 (1 H, m, 3-H), and 7.23 (5 H, m, Ph-H); δ_C 21.01 (5'-C), 25.01 (6'-C), 26.28 (4'-C), 40.45 (1'-C), 43.38 (2-C), 124.38-129.05 (Ar-C and alkene-C), and 134.51 (CN); m/z 197(15%), 117 (100), and 105 (26). The 2-(cyclohex-2-enyl)-2-phenylacetonitrile (700 mg, 3.55 mmol) was reduced with $LiAlH_4$ in dry diethyl ether to yield pure 2-(cyclohex-2-enyl)-2-phenylethylamine (**34**) as a clear oil, (690 mg, 97%); υ_{max} (neat)/cm^{-1} 3372, 3060, 1648, 1583, 1494, and 680; δ_H 1.24 (2 H, m, 5'-H), 1.48 (2 H, m, 6'-H), 1.75 (2 H, m, 4'-H), 1.97 (2 H, s, NH_2), 2.49 (2 H, m, 1', 2-H), 2.91 (1 H, t, 1-H), 3:15 (1 H, dt, 1-H), 5.32 (0.5 H, d, 3'-H), 5.64 (0.5 H, d, 3'-H), 5.82 (1 H, dd, 2'-H), and 7.09-7.25 (5 H, m, Ph-H); δ_C 21.90 (5'-C), 25.39 (6'-C), 27.35 (4'-C), 38.46 and 39.03 (1', 2-C), 44.86 (1-C), 125.09-131.81 (Ph-CH and alkene-C), and 142.54 (Ph-C); m/z 201 (19%), 184 (100), 120 (66), and 103 (42).

3-Phenyl-8-iodohexahydroindoline (**35**, Z = I, Ar = Ph). A solution of iodine (5.1 g, 19 mmol) in THF (15 ml) was added to a stirred solution of 2-(cyclohex-2-enyl)-2-phenylethylamine (**34**, Ar = Ph) (2.0 g, 9.95 mmol) in tetrahydrofuran (10 ml) and saturated sodium bicarbonate solution (15 ml) and stirred for 24 h. After this time, a saturated solution of sodium thiosulfate (50 ml) was added and the product was extracted with ethyl acetate. The ethyl acetate extracts were dried and evaporated to dryness to yield the 3-phenyl-8-iodoperhydroindole (**35**, Z = I, Ar = Ph) as a brown oil (2.0 g, 61%) after purification on a alumina column using hexane and diethyl ether as eluent; δ_H (300 MHz) 1.87 (6 H, m, 4, 5, 6-H), 2.41 (1 H, m, NH), 3.08 (1 H, t, 3a-H), 3.62 (1 H, t, 3-H), 3.85 (1 H, m, 7a-H), 4.18 (2 H, m, 2-H), 4.85 (1 H, m, 7-H), and 7.29 (5 H, s,

Ph-H); δ_C 14.11 (5-C), 16.53 (6-C), 26.05 (7-C), 41.83 (4-C), 47.77 (2-C), 50.35 (3-C), 62.26 (9-C), 72.80 (8-C), and 127.03-128.79 (Ph-C); m/z 329, 261 (97%), and 244 (100).

3-(4-t-Butylphenyl)-8-iodohexahydroindoline (**35**, Z = I, Ar = 4-t-butylphenyl). 2-(4-t-Butylphenyl)-2-(cyclohex-2-enyl)ethylamine (**34**, Ar = 4-t-butylphenyl) (100 mg, 0.38 mmol) was reacted with iodine under the same conditions as the previous experiment to yield 3-(4-t-butylphenyl)-8-iodohexahydroindoline as an oil, (110 mg, 74%); δ_H (300 MHz)1.21 (9 H, s, t-Bu), 1.48 (6 H, m, 5, 6, 7-H), 2.40 (1 H, m, NH), 2.73 (1 H, ddd, 4-H), 3.60 (1 H, dt, 3-H), 3.82 (1 H, m, 9-H), 4.15 (2 H, m, 2-H), 4.87 (1 H, m, 7-H), and 7.19 (4 H, dd, Ar-H); δ_C 14.14 (5-C), 17.18 (6-C), 25.06 (7-C), 31.33 (t-Bu), 34.45 (*C*Me$_3$), 41.87 (4-C), 50.13 (2-C), 49.78 (3-C), 59.92 (9-C), 72.86 (8-C), and 125.38-127.83 (Ar-C); m/z 383 (10%), 299 (100), 231 (85), and 145 (81).

3-Phenylhexahydroindoline (**36**, Ar = Ph). A solution of 2-(cyclohex-2-enyl)-2-phenylethylamine (**34**, Ar = Ph) (100 mg, 0.49 mmol) in dry THF (10 ml) was added to a stirred solution of mercuric (II) chloride (203 mg, 0.75 mmol) in dry THF (15 ml). The reaction was then stirred at room temperature under an atmosphere of nitrogen for 2 h. A white precipitate of the mercury adduct (**35**, Z = HgCl), m.p. 224-227°C (dec.) was filtered off and suspended in tetrahydrofuran (4 ml). A solution of $NaBH_4$ (19 mg, 0.5 M solution) in 3 M sodium hydroxide (1 ml) was added to the suspension and the resulting suspension stirred for 2 h. After this time, a drop of mercury could be observed in the bottom of the reaction flask. The organic solution was decanted off, dried, and evaporated to dryness to yield pure 3-phenylhexahydroindoline (**36**, Ar = Ph) as a clear oil, (30 mg, 50%); δ_H 1.35 (9 H, m, 4, 5, 6, 7-H and NH), 3.17 (1 H, ddd, 3a-H), 3.34 (1 H, m, 3-H), 3.71 (2 H, m, 2-H), 4.13 (1 H, m, 7a-H), and 7.01-7.28 (5 H, m, Ph-H).

3-(4-t-Butylphenyl)hexahydroindoline (**36**, Ar = 4-t-butylphenyl). 2-(4-t-Butylphenyl)-2-(cyclohex-2-enyl)-ethylamine (**34**, Ar = 4-t-butylphenyl) (200 mg, 0.78 mmol) was reacted with mercury (II) chloride under the same conditions as the previous experiment to yield the corresponding mercury adduct (**35**, Z = HgCl), m.p. 243-250°C (dec.), which was reduced to yield 3-(4-t-butylphenyl)hexahydroindoline (**36**, Ar = 4-t-butylphenyl) as an oil (120 mg, 96%); δ_H 1.25 (9 H, s, t-Bu), 1.38 (9 H, m, 4, 5, 6, 7-H and NH), 3.08 (2 H, m, 3, 3a-H), 3.42 (2 H, dd, 2-H), 3.71 (1 H, m, 7a-H), and 7.34 (4 H, dd, Ar-H); δ_C 20.88 (5-C), 23.19 (6-C), 25.12 (4-C), 27.03 (7-C), 31.32 (*C*Me$_3$), 34.36 (*C*Me$_3$), 46.46 (3a-C), 60.06 (3-C), 65.35 (7a-C), 66.81 (2-C), and 125.29-130.29 (Ar-C).

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