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Iminyl Radicals: Part I. Generation and Intramolecular Capture by an Olefin.

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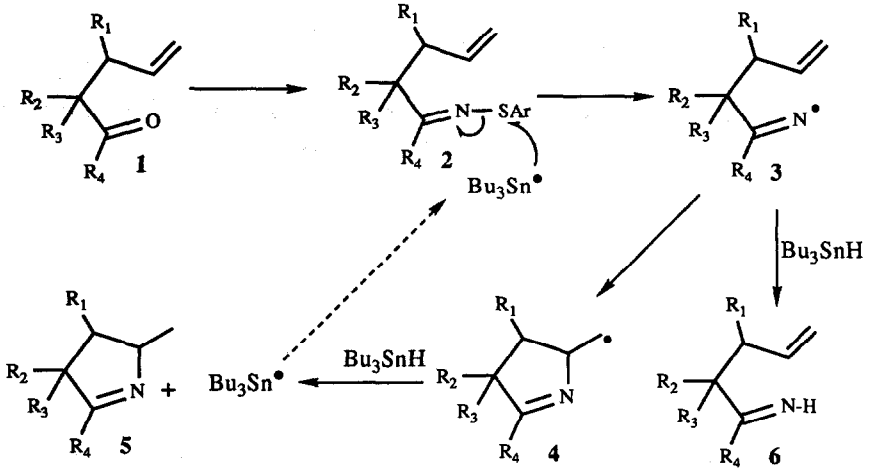
Abstract : Slow addition of tributylstannane to sulphenylimines **2** give the corresponding Δ^1- pyrrolenines **5** by an intramolecular addition of the intermediate iminyl radical, a process which can be easily coupled to an intermolecular addition to an electrophilic olefin.

There has been, over the last decade, an explosive growth in the use of radical reactions in organic synthesis, due in a large measure to their remarkable potential for creating carbon-carbon bonds as well as to the recent availability of a sizeable and rapidly growing body of kinetic data allowing, in many instances, fine control of the regio- and sometimes even the stereochemistry of such reactions.[1,2] Moreover the relative insensitivity of radical processes to solvent effects and steric factors (as far as the radical centre is concerned) provides the chemist with considerable predictive power when applying these kinetic data in the design of synthetic strategies. By far the greater amount of effort has focused on carbon radicals,[2] in contrast to nitrogen and oxygen centered radicals which still have to attract the attention they deserve. Iminyl radicals in particular have been almost completely neglected by synthetic organic chemists. Rare and scattered studies seemed to indicate that these species were rather unreactive[3] and, further compounding these unfavourable reports, was a general lack of convenient methods for generating them. We have, in a series of communications,[4] described our recent contributions to the subject. Contrasting with the earlier impression, we have found that iminyl radicals were indeed exceptionally useful intermediates, capable of mediating a host of synthetically interesting transformations. In this and accompanying papers, we give a full account of our findings.

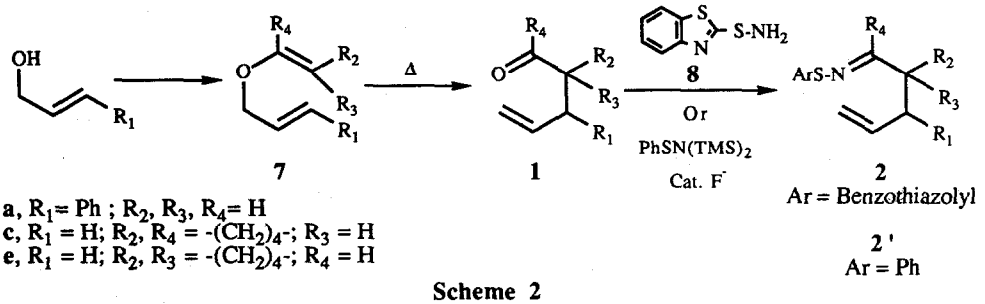
In the first phase of our study, two central problems had to be addressed. The first concerned the development of a mild and generally applicable route to these species. The second was to find out whether they would undergo intramolecular (and later perhaps intermolecular) addition to an olefin with sufficient alacrity to make such cyclisations usefully competitive with other unwanted processes.

Most of the earlier methods for generating iminyl radicals are based on non-chain pyrolytic or photochemical reactions which are ill-suited for preparative work.[5] A notable exception however is the addition of a carbon radical to nitriles which produces iminyls[6a,b] as well as the reduction of N-chloroketimines with tri-n-butylstannane, used by Poutsma and Ibraria[6c] to generate iminyl radicals needed in a mechanistic study. This approach, however, is restricted to the few accessible N-chloroketimines. We therefore considered the possibility of applying stannane chemistry to the more accessible sulphenylimines such as **2** or **2'**. The high thiophilicity of the stannyl radicals as well as the relative weakness of the N-S bond in these systems[7] should constitute a powerful driving force in favour of the formation of the iminyl radical (Scheme 1).



Scheme 1

If the 5-exo cyclisation step is sufficiently rapid, the iminyl radical thus created would proceed to the pyrrolenine **5**; otherwise, premature abstraction of hydrogen from the stannane would simply lead to the unsubstituted imine **6** which would then rapidly hydrolyse back to the starting ketone **1**. The latter process is obviously of little synthetic use. Unlike N-chloroketimines, sulphenylimines are readily available by a number of methods,[7] generally from the corresponding carbonyl derivative or, in some cases, through the oxime.[8] They are easily purified by crystallisation or by chromatography.

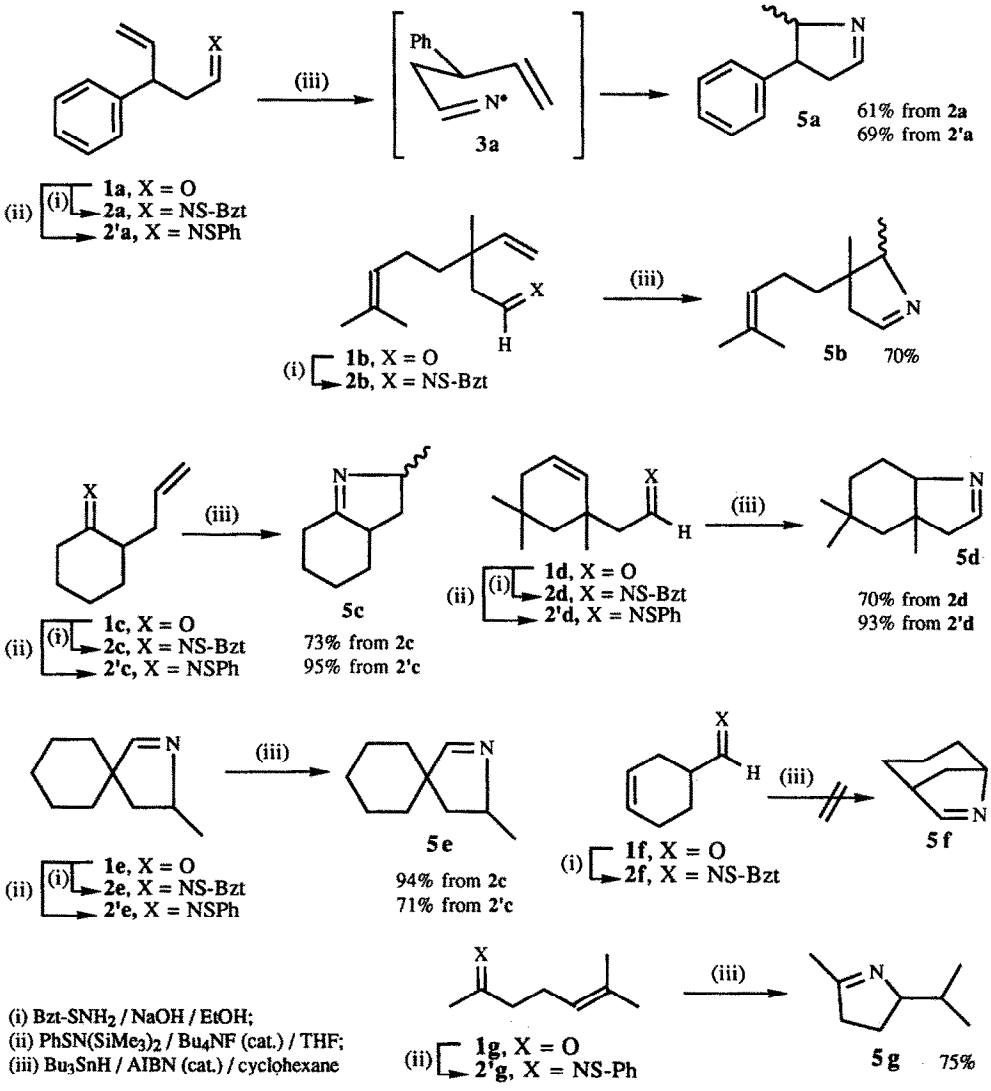


a, R_1 = Ph ; R_2, R_3, R_4 = H
c, R_1 = H; R_2, R_4 = -$(CH_2)_4$-; R_3 = H
e, R_1 = H; R_2, R_3 = -$(CH_2)_4$-; R_4 = H

Scheme 2

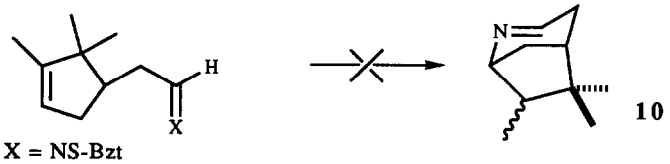
Sulphenylimines **2a-f**, obtained in reasonable yields (43-68%) by direct condensation of the corresponding carbonyl precursor with 2-benzothiazolyl-sulphenamide **8**, were first chosen for this study. Sulphenamide **8** is a stable crystalline solid, easily prepared from 2-mercaptobenzothiazole, ammonia and sodium hypochlorite.[9] The starting γ,δ-unsaturated ketones and aldehydes **1a-f** are themselves readily available, mostly through a Claisen rearrangement as shown in Scheme 2. The preparation of aldehydes **1a**, **1b**, and **1d** required prior isolation of the corresponding intermediate allyl vinyl ether **7**, obtained by the mercuric acetate catalysed reaction of cinnamyl alcohol, geraniol, and isophorol respectively with ethyl vinyl ether.[10] Ketone **1c** and aldehyde **1e** were directly produced from cyclohexanone and cyclohexanecarboxaldehyde respectively by heating with allyl alcohol in the presence of a little acid.[11]

As a precaution against premature reduction of the iminyl radical, the stannane was slowly added to the substrate. Thus, addition over 4-5 hours of tri-n-butylstannane to a refluxing solution of the sulphenylimine **2a** in cyclohexane produced pyrroline **5a** in 61% yield as a 1:9 mixture of cis and trans isomers. The geometry of the two isomers was deduced from the chemical shifts in the NMR spectrum, a phenyl group having a pronounced shielding effect on the vicinal cis-methyl group.[12] The major trans isomer could arise from a chair transition state such as **3a** where the phenyl group occupies an equatorial position. Similarly, **2b** gave **5b** in 70% yield with a similar selectivity (cis:trans ratio 15:85, assuming by analogy with the previous example that the trans isomer dominates in this case also).



Bicyclic and spiro systems are also easily accessible by this approach. Thus, cyclisation of the imine radical from **2c** and **2d** afforded the corresponding bicyclic pyrrolines **5c** and **5d** in 73% and 70% yield respectively, the former consisting of comparable amounts of the two diasterioisomers (40:60). Finally reduction of sulphenylimine **2e** with the stannane gave the spiro pyrroline **5e** in excellent yield (94%). In contrast, no cyclised product was observed from **2f** under the same conditions. Only the initial aldehyde **1f** was isolated indicating that, in this case, cyclisation of the intermediate iminyl radical is too slow to compete effectively with hydrogen abstraction from the stannane.

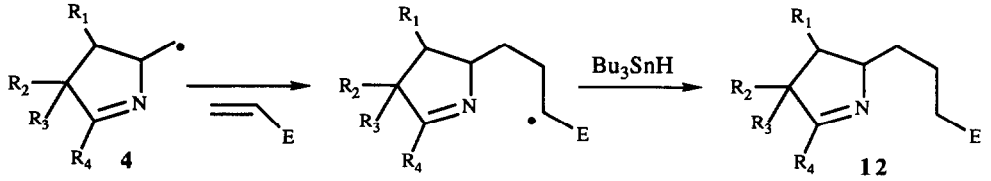
The analoguous S-phenyl sulphenylimines **2'a,c,d,e,g** underwent, in the same way, a clean reductive cyclisation upon treatment with tributylstannane. These substrates are conveniently obtained by a procedure developed by Morimoto and co-workers[13] using a fluoride catalysed condensation of N,N-bis (trimethylsilyl)-phenylsulphenamide with ketones and aldehydes. Through this variant, compounds **5a,c,d,e,g** were produced in comparable yields (69%, 95%, 93%, 71%, and 75% yield respectively).



9, X = NS-Bzt
11, X = O

10

In one attempt to test the possibility of obtaining a six membered ring, we exposed sulphenylimine **9** to the stannane in the usual way but only recovered the starting aldehyde **11**; none of the expected derivative **10** was observed. Although the negative outcome of this experiment does not augur well for the synthesis of six-membered rings by this approach, care must be taken not to generalise from a single, and certainly not the most favourable, example. Further work is planned to examine more thoroughly the scope of the process in this respect. Interestingly, when tributyltin deuteride was used in this experiment, no deuterium was found in the isolated aldehyde **11**, indicating that no intramolecular abstraction of an allylic hydrogen by the intermediate iminyl radical occured. Internal abstraction of the allylic hydrogens is a common problem with 6-exo cyclisations.[1]



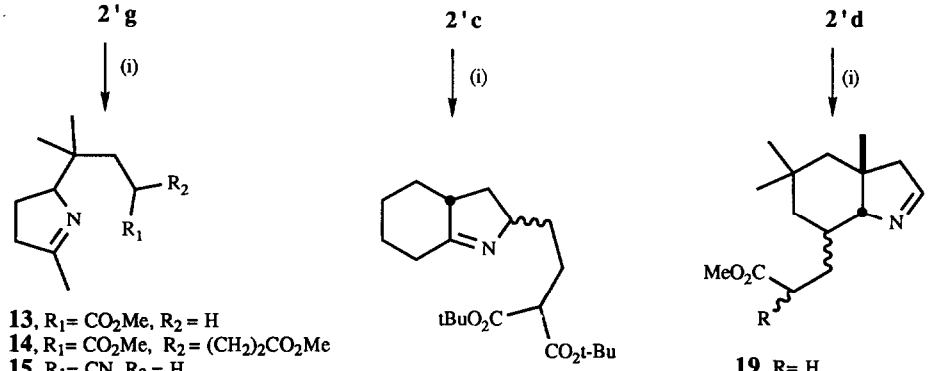
Scheme 3

As demonstrated by the above examples, iminyl radicals turn out to be sufficiently electrophilic to undergo fairly rapid cyclisation, unlike aminyl radicals,[14] which add only sluggishly to unactivated double bonds and usually require protonation or complexation with a transition metal. This drawback has another consequence, uncovered in a recent study by Newcomb and his associates,[15] namely the reduced nucleophilicity of the carbon radical resulting from cyclisation of the protonated aminyl radicals. Thus, further

intermolecular addition of this radical to an electrophilic olefin becomes seriously limited in scope. In the light of these observations, it was important to see whether the imine radical exerted a similar deactivating effect. The possibility of coupling the cyclisation step with an intermolecular radical addition to give derivatives such as **12** (Scheme 3), if successful, would have a considerable synthetic potential for the synthesis of various alkaloid systems.

We were delighted to find that slow addition of tributyl stannane (and a catalytic amount of AIBN) to sulphenylimine **2'g** in the presence of 5 equivalents of methyl acrylate produced the expected adduct **13** in 83% yield along with a small amount (12%) of compound **14** arising from double addition to methyl acrylate. Thus, a new carbon-nitrogen bond and carbon-carbon bond, as well as a quaternary centre, are introduced all at once. Clearly, the iminyl moiety does not reduce the nucleophilicity of the intermediate carbon radical **4** to any significant extent. Other electrophilic olefins could also be employed in this modification. For example, acrylonitrile afforded the corresponding adduct **15** in 60% yield again with a small amount (15%) of the double addition product **16**. Di-t-butyl methylenemalonate[16] is much less prone to a radical induced oligomerisation and none of the double addition product was observed in its presence. However, in addition to the expected adduct **17**, obtained in 68% yield, a little (11%) of the simple cyclisation product **5g** was isolated.

This multiple radical addition process was applied to two other sulphenylimines, namely **2'c** and **2'd**. The former furnished **18** in 65% yield (and 30% of **5c**) using di-t-butyl methylenemalonate as the external trap, whereas the latter gave a good yield (81%) of **19** along with a little (10%) of **20** in the presence of methyl acrylate. It is thus possible to capture primary, secondary and tertiary carbon radicals arising from the initial cyclisation of the iminyl.



13, R_1= CO_2Me, R_2 = H
14, R_1= CO_2Me, R_2 = $(CH_2)_2CO_2Me$
15, R_1= CN, R_2 = H
16, R_1= CN, R_2 = $(CH_2)_2CN$
17, R_1= R_2 = CO_2tBu

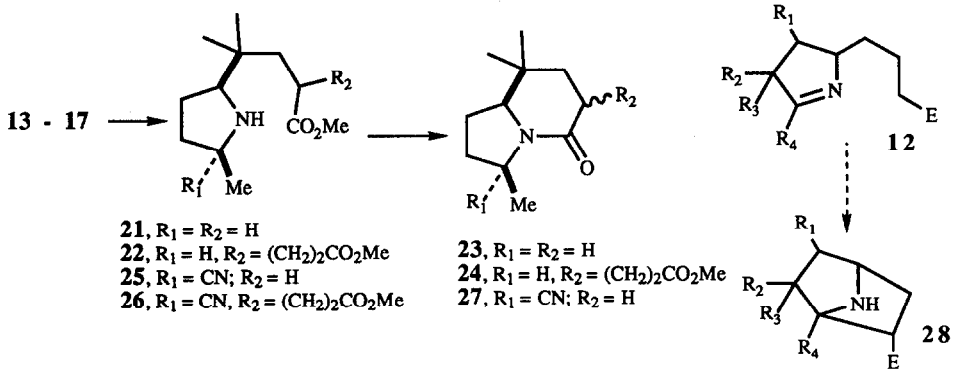
18

19, R= H
20, R= $(CH_2)_2CO_2Me$

(i) Bu_3SnH, AIBN (Cat.), Δ
Electrophilic olefin

The synthetic potential of combining an intra- and an intermolecular radical addition steps is illustrated by the following two experiments. Thus, reduction using sodium cyanoborohydride / acetic acid of the crude mixture of **13** and **14** (85:15) obtained from sulphenylimine **2'g** and methyl acrylate gave lactam **23** (85%), by spontaneous cyclisation of intermediate **21**, and amino ester **22** , very easily separated at this stage. The latter could be cyclised to **24** by heating in toluene for one hour. Lactam **23** is produced as a *single isomer* ;

the attack of the hydride taking place as expected from the less hindered side of the pyrrolenine ring. Alternatively, reaction of the same mixture **13** / **14** with trimethylsilyl cyanide and a catalytic amount of titanium tetrachloride afforded cyanolactam **27** (again as a single isomer) along with cyano amine **26** in a combined yield of 88%. In this case too, lactamisation of intermediate **25** was spontaneous. Both **23** and **27** possess the core skeleton of indolizidine alkaloids and this approach holds much promise for the expedient construction of such systems with efficient control of the relative stereochemistry. Another interesting possibility, which we have not yet explored, is to use the iminyl moiety in the adducts as a partner in an intramolecular mannich reaction to create a tropane type assembly (e.g. **28**).



21, $R_1 = R_2 = H$
22, $R_1 = H$, $R_2 = (CH_2)_2CO_2Me$
25, $R_1 = CN$; $R_2 = H$
26, $R_1 = CN$, $R_2 = (CH_2)_2CO_2Me$

23, $R_1 = R_2 = H$
24, $R_1 = H$, $R_2 = (CH_2)_2CO_2Me$
27, $R_1 = CN$; $R_2 = H$

In summary, we have found that iminyl radicals exhibit sufficient reactivity to allow a number of useful transformations. In addition, the presence of the imine moiety in the cyclised products constitutes a powerful handle for the further, regiospecific, elaboration of the products, especially when the synthetic possibilities of the imine-enamine tautomerism are taken into consideration.

***Acknowledgements**: We wish to express our gratitude to Rhône-Poulenc Agrochimie for very generous financial support.*

Experimental Section

All reactions were performed under inert atmosphere (nitrogen or argon). Melting points were determined with a Köfler or a Reichert hot stage apparatus. ^1H and ^{13}C n.m.r. spectra are for deuteriochloroform solutions with tetramethylsilane as internal standard (δ ppm). The terms primary, secondary, tertiary and quaternary used in conjunction with ^{13}C chemical shifts correspond to the type of carbon in the structure. I.R. spectra are of Nujol mulls unless otherwise stated. Mass spectra (electron impact) were recorded on MS 50 or VG ZAB spectrometers. MATREX 60 (35-70 μm) silica gel was used for column chromatography. Solvents and reagents were purified according to standard laboratory techniques. Compounds **1b**, **1c**, and **1e** were prepared according to references 10b, 11b and 11a respectively.

Typical Procedure for Preparation of Vinyl Ethers 7
Allylic alcohol (80 mmol.) and mercuric acetate (1.27 g, 4 mmol) were added to freshly distilled ethyl vinyl ether (48 ml, 500 mmol.).The reaction mixture was then refluxed (33 °C) for 24 hrs. Dry potassium carbonate (1.11 g, 8 mmol) was added; excess ethyl vinyl ether and ethanol formed in the reaction were distilled off under reduced pressure. The crude residue was purified by distillation and/or by silica gel chromatography and used as such in the next step. The following compounds were prepared by this procedure:

1-Vinyloxy-3-phenyl-2-propene 7a. Purification: the crude residue was dissolved in dichloromethane and washed with a saturated solution of sodium hydrogencarbonate and filtrated over silica gel (eluent petroleum ether / ether: 95/5); yield:77 %; IR (cm^{-1}):1630, 1610, 1180, 960, 810, 730, 680; n.m.r. ^1H: 7.24-7.42 (5H, m), 6.65 (1H, d, J = 16.0 Hz), 6.51 (1H, dd, J = 6.8 Hz, J' = 14.3 Hz), 6.32 (1H, td, J = 5.8 Hz), 4.39 (2H, d), 4.28 (1H, dd, J = J'= 2.1 Hz), 4.07 (1H, dd); n.m.r. ^{13}C:151.5, 136.5, 132.9, 128.6 (2C), 127.9, 126.6 (2C), 124.4, 87.3, 68.8.

1-Vinyloxy-3,5,5-trimethyl-2-cyclohexene 7d. Purification: distillation under reduced pressure (98°C / 20 mm Hg). Filtration over neutral alumina (eluent petroleum ether); yield: 77 %; IR (cm^{-1}): 3115, 1635, 1610, 1195, 815; n.m.r. ^1H: 6.37 (1H, dd, J = 6.7 Hz, J' = 14.2 Hz), 5.48 (1H, s), 4.42 (1H, m), 4.30 (1H, dd, J = 1.4 Hz, J' = 14.2 Hz), 4.01 (1H, dd, J = 1.4 Hz, J' = 14.2 Hz), 1.60-1.92 (3H, m), 1.69 (3H, s), 1.40 (1H, dd, J = 8.7 Hz, J' = 12.7 Hz), 1.00 (3H, s), 0.91 (3H, s); n.m.r. ^{13}C: 150.7, 137.8, 119.9, 88.3, 74.5, 44.3, 41.3, 41.0, 30.9, 26.7, 23.7.

***Claisen Rearrangements*:**

3-Phenyl-4-pentenal 1a. Vinyl ether **7a** (3.50 g, 22 mmol) was heated at 125°C for 22 hrs affording pure **1a** which was used without purification; yield: 100 %; IR (cm^{-1}): 2700, 1715 (aldehyde), 1480, 1450, 915, 755, 700; n.m.r. ^1H: 9.72 (1H, t, J = 2.0 Hz), 7.17-7.36 (5H, m), 5.99 (1H, ddd, J = 6.8 Hz, J = 10.5 Hz, J = 17.2 Hz), 5.11 (1H, d, J = 10.5 Hz), 5.06 (1H, d, J = 17.2 Hz), 3.95 (1H, q, J = 7.2 Hz), 2.83 (2H, m).

(1,5,5-Trimethylcyclohex-2-enyl)ethanal 1d. Vinyl ether **7d** (3.90 g, 20 mmol) was heated in a sealed tube at 215°C for 30 min. The crude product was purified by silica gel chromatography (eluent: petroleum ether / dichloromethane: from 10/0 to 6/4) and used as such in the next step; yield: 75 %; IR (cm^{-1}): 2720, 1725 (aldehyde), 910, 730; n.m.r. ^1H: 9.75 (1H, t, J = 3.1 Hz), 5.68 (1H, td, J = 3.9 Hz, J = 10.1 Hz), 5.52 (1H, d, J = 10.1 Hz), 2.32 (2H, d, J = 3.1 Hz), 1.78 (2H, m), 1.47 (2H, AB, J = 13.9 Hz), 1.17 (3H, s), 0.99 (3H, s), 0.97 (3H, s); n.m.r. ^{13}C: 203.3, 133.2, 125.3, 56.5, 47.9, 38.5, 34.9, 31.2, 29.9, 29.1, 28.7.

Synthesis of Benzothiazolyl Sulphenylimines: General Procedure.

Aqueous sodium hydroxide 2N (0.6 ml) was added to a suspension of benzothiazolyl sulphenamide.[9] (2.00 g, 11.0 mmol.) in ethanol (3.0 ml).The reaction mixture was heated to 65°C, the carbonyl derivative (13.2 mmol.) added, and stirring continued for 20-45 min. until disappearance of the starting material (T.L.C.). After cooling, the reaction mixture was diluted with dichloromethane (40 ml), dried over sodium sulfate, filtered, and evaporated under reduced pressure. The residue was taken-up in dichloromethane (10 ml) et filtered to eliminate some insoluble benzothiazolyl disulphide. Purification was performed either by silica gel chromatography or by crystallisation. The following compounds were prepared according to this procedure:

N-[2-(2-Propenyl)cyclohexylidene]-2-benzothiazolesulfenamide 2c. m.p.= 95-7°C (ethanol,white crystals); yield: 51 %; IR (cm^{-1}): 1625, 1470, 1430, 1030, 1010, 760 (Nujol); n.m.r. ^1H: 7.72-7.98 (2H, m), 7.20-7.51 (2H, m), 5.84-6.06 (1H, m), 5.02-5.18 (2H, m), 2.65-2.90 (2H, m), 1.25-2.48 (9H, m); microanalysis (%): calc.: C: 63.53, H: 6.00, N: 9.26 for $C_{16}H_{18}N_2S_2$; found: C: 62.58, H: 6.38, N: 8.74.

N-[[1-(2-Propenyl)cyclohexyl]methylene]-2-benzothiazolesulfenamide 2e. Silica gel chromatography: eluent dichloro-methane / petroleum ether - 85/15; m.p.= 85-6°C, white crystals; yield: 56 %; IR (cm^{-1}): 1620, 1470, 1430, 1030, 1010, 740 (solution in CH_2Cl_2); n.m.r. ^1H: 7.93 (1H, s), 7.81-7.88 (2H, m), 7.24-7.46 (2H, m), 5.62-5.86 (1H, m), 5.02-5.10 (2H, m), 2.26 (2H, d, J = 7.4 Hz), 1.88-1.94 (2H, m), 1.22-1.66 (8H, m); microanalysis (%): calc.: C: 64.51, H: 6.37, N: 8.85 for $C_{17}H_{20}N_2S_2$; found: C: 64.39, H: 6.52, N: 8.68.

N-(3-Phenyl-4-pentylidene)-2-2-benzothiazolesulfenamide 2a. Silica gel chromatography: eluent dichloromethane / petroleum ether - 70/30; light yellow oil; yield: 56 %; IR (cm^{-1}): 1605, 1450, 1420, 1020, 1000, 740, 690; n.m.r. ^1H: two isomers, ratio 70/30: major product: 7.78-7.90 (3H, m), 7.21-7.45 (7H, m), 5.90-6.11 (1H, m), 5.02-5.21 (2H, m), 3.96 (1H, q, J = 7.0 Hz), 2.90-2.97 (2H, m); minor product: 8.04 (1H, t, J = 4.5 Hz), 7.78-7.90 (2H, m), 7.21-7.45 (7H, m), 5.90-6.11 (1H, m), 5.02-5.21 (2H, m), 3.76 (1H, q, J = 7.0 Hz), 2.74-2.86 (2H, m).

N-(3-Ethenyl-3,7-dimethyl-6-octenylidene)-2-benzothiazolesulfenamide 2b. Silica gel chromatography: eluent dichloromethane / petroleum ether - 90/10; yellow oil; yield: 68 %; IR (cm^{-1}): 1600, 1460, 1420, 1020, 1000, 745, 715; n.m.r. ^1H: two isomers, ratio 70/30: major product: 7.82-7.92 (3H, m), 7.25-7.50 (2H, m), 5.69-5.92 (1H, m), 4.95-5.18 (3H, m), 2.36 (2H, m), 1.82-2.02 (2H, m), 1.68 (3H, s), 1.59 (3H, s), 1.35-1.52 (2H, m), 1.16 (3H, s); minor product: 8.06 (1H, t, J = 5.0 Hz), 7.82-7.92 (2H, m), 7.25-7.50 (2H, m), 5.69-5.92 (1H, m), 4.95-5.18 (3H, m), 2.55 (2H, m), 1.82-2.02 (2H, m), 1.68 (3H, s) 1.59 (3H, s), 1.35-1.52 (2H, m), 1.11 (3H, s); microanalysis (%): calc.: C: 66.24, H: 7.02, N: 8.13 for $C_{19}H_{24}N_2S_2$; found: C: 66.32, H: 7.14, N: 7.85.

N-[2-(1,5,5-Trimethyl-2-cyclohexen-1-yl)ethylidene]-2-benzothiazolesulfenamide 2d. Silica gel chromatography: eluent dichloromethane / petroleum ether - 60/40; Yellow syrup; Yield: 48 %; IR (cm^{-1}): 635, 1455, 1195, 1045, 820; n.m.r. ^1H: mixture of two isomers, ratio 70/30: Major product: 7.80-7.93 (3H, m), 7.24-7.45 (2H, m), 5.62-5.78 (1H, m), 5.45 (1H, d, J = 10.0 Hz), 2.31 (2H, m), 1.74-1.83 (2H, m), 1.47 (2H, m), 1.19 (3H, s), 0.98 (6H, s); Minor product: 8.08 (1H, t, J = 5.7 Hz), 7.80-7.93 (2H, m), 7.24-7.45 (2H, m), 5.62-5.78 (1H, m), 5.51 (1H, d, J = 8.0 Hz), 2.45 (2H, d, J = 6.0 Hz), 1.74-1.83 (2H, m), 1.38-1.56 (2H, m), 1.15 (3H, s), 0.98 (6H, s).

N-[(3-cyclohexen-1yl)methylidene]-2-benzothiazolesulfenamide 2f. The crude reaction mixture was taken up in dichloromethane and washed with a 35% aqueous solution of sodium bisulfite. Usual work-up afforded the title compound in 68 % yield; ^1H: 8.08 (1H, d, J = 4.0 Hz), 7.72-7.79 (2H, m), 7.22-7.43 (2H, m), 5.71 (2H, s), 2.70 (1H, m), 1.55-2.35 (6H, m). This compound was used without further purification.

N-[2-(2,2,3-Trimethyl-3-cyclopenten-1-yl)ethylidene]-2-benzothiazolesulfenamide 9. Silica gel chromatography: eluent dichloromethane; m.p.: 55-7°C, yellow crystals; yield: 61%; IR (cm^{-1}): 1620, 1470, 1430, 1025, 1005, 755, 735 (film); n.m.r. ^1H: mixture of two isomers, ratio 60/40: major product: 7.61-7.70 (3H, m), 7.22-7.47 (2H, m), 5.25 (1H, s), 1.90-2.70 (5H, m), 1.63 (3H, s), 1.02 (3H, s), 0.85 (3H, s); minor product: 8.14 (1H, t, J = 5.0 Hz), 7.61-7.70 (2H, m), 7.22-7.47 (2H, m), 5.25 (1H, s) 1.90-2.70 (5H, m), 1.62 (3H, s), 1.05 (3H, s), 0.85 (3H, s); microanalysis (%): Calc.: C: 64.51, H: 6.37, N: 8.85 for $C_{17}H_{20}N_2S_2$; found: C: 64.50, H: 6.33, N: 8.80.

Preparation of S-Phenyl Sulphenylimines: General Procedure.

Tetrabutylammonium fluoride (0.1 equivalent, 1.1 M solution in tetrahydrofurane) was added dropwise to a solution of phenyl N,N bistrimethylsilylsulphenamide (1.48 g, 5.5 mmol, prepared according to reference 13), and carbonyl derivative (5.0 mmol) in anhydrous tetrahydrofurane (15 ml). The reaction mixture was stirred at 20°C during 20-180 min. depending on the substrate (T.L.C. monitoring). The solvent was then removed under reduced pressure and the resulting residue was purified by quick filtration through alumina or silica gel. The product was used as such in the next step. The following compounds were prepared according to this procedure:

N-[(6-Methyl)-5-hepten-2-ylidene]benzenesulfenamide 2g. Chromatography on neutral alumina, eluent: petroleum ether; yield: 94 % (colourless oil); IR (cm^{-1}): 1610, 1580, 1475, 1440, 1020, 735, 685. ; ^1H: mixture of two isomers, ratio 75/25: major product: 7.53 (2H, m), 7.33 (2H, m), 7.15 (1H, m), 5.15 (1H, t, J = 6.9 Hz), 2.26-2.48 (4H, m), 2.05 (3H, s), 1.70 (3H, s), 1.62 (3H, s); minor product: 7.53 (2H, m), 7.33 (2H, m), 7.15 (1H, m), 5.15 (1H, t, J = 6.9 Hz), 2.26-2.48 (4H, m), 2.10 (3H, s), 1.70 (3H, s), 1.66 (3H, s); n.m.r. ^{13}C: major product: 168.2, 139.4, 132.3, 128.8 (2C), 125.6, 124.0 (2C), 123.5, 42.5, 25.8, 25.0 22.5, 17.8; minor product: 169.4, 139.2, 133.2, 128.8 (2C), 125.8, 125.3 (2C), 122.7, 37.6, 27.3, 25.0 23.7, 17.8.

N-[2-(2-Propenyl)cyclohexylidene]-2-benzenesulfenamide 2'c. Chromatography on neutral alumina, eluent: petroleum ether / dichloromethane - 80/20; yield: 68 % (light yellow oil); IR (cm^{-1}): 1615, 1480, 1440, 1025, 740, 690. ; n.m.r. ^1H: 7.53 (2H, m), 7.32 (2H, m), 7.13 (1H, m), 5.77-5.89 (1H, m), 4.98-5.09 (2H, m), 2.70-2.80 (2H, m), 2.10-2.38 (3H, m), 1.26-2.02 (6H, m); n.m.r. ^{13}C: 172.4, 139.7, 137.5, 128.8 (2C), 125.4, 124.5 (2C), 116.0, 47.8, 35.6, 34.4, 33.1, 26.6 24.6; microanalysis (%): calc.: C: 73.42, H: 7.80, N: 5.70 for $C_{15}H_{19}NS$; found: C: 73.21, H: 7.69, N: 5.47.

N-[[1-(2-Propenyl)cyclohexyl]methylene]-2-benzenesulfenamide 2'e. Silica gel chromatography, eluent: petroleum ether / dichloromethane - 80/20; yield: 58 % (yellow oil); IR (cm^{-1}): 1625, 1470, 1430, 1010, 730, 680. ; n.m.r. ^1H: 7.76 (1H, s), 7.48 (2H, m), 7.34 (2H, m), 7.20 (1H, m), 5.65-5.80 (1H, m), 4.95-5.05 (2H, m), 2.17 (2H, d, J = 7.4 Hz), 1.26-1.85 (10H, m); n.m.r. ^{13}C: 168.9, 138.2, 134.0, 129.0 (2C), 126.0 (2C), 126.3, 117.7, 45.3, 44.0, 33.6 (2C), 26.1, 22.4 (2C).

N-(3-Phenyl-4-pentylidene)-2-benzenesulfenamide 2'a. Silica gel chromatography, eluent: petroleum ether / dichloro-methane - 70/30; yield: 60 % (yellow oil); ; IR (cm^{-1}): 1615, 1460, 1430, 1010, 740, 690; n.m.r. ^1H: mixture of two isomers, ratio 55/45: major product: 7.80 (1H, t, J = 6.2 Hz), 7.18-7.51 (10H, m), 5.90-6.06 (1H, m), 5.01-5.16 (2H, m), 3.69 (1H, sext, J = 7.2 Hz), 2.71-2.83 (2H, m); minor product: 7.63 (1H, t, J = 4.5 Hz), 7.18-7.51 (10H, m), 5.90-6.06 (1H, m), 5.01-5.16 (2H, m), 3.69 (1H, sext, J = 7.2 Hz), 2.71-2.83 (2H, m).

N-[2-(1,5,5-Trimethyl-2-cyclohexen-1-yl)ethylidene]-2-benzenesulfenamide 2'd. Chromatography on neutral alumina, eluent: petroleum ether / dichloromethane - 50/50); yield: 89 % (colourless oil); IR (cm^{-1}): 1605, 1580, 1480, 1020, 740, 690. ; n.m.r. ^1H: mixture of two isomers, ratio 60/40: Major product: 7.93 (1H, t, J = 5.8 Hz), 7.54 (2H, m), 7.36 (2H, m), 7.22 (1H, m), 5.61-5.78 (1H, m), 5.58 (1H, t, J = 10 Hz), 2.38 (2H, m), 1.75-1.84 (2H, m), 1.30-1.50 (2H, m), 1.20 (3H, s), 1.01 (3H, s), 0.98 (3H, s); Minor product: 7.74 (1H, t, J = 4.8 Hz), 7.54 (2H, m), 7.36 (2H, m), 7.22 (1H, m), 5.61-5.78 (1H, m), 5.58 (1H, t, J = 10 Hz), 2.21 (2H, m), 1.75-1.84 (2H, m), 1.30-1.50 (2H, m), 1.12 (3H, s), 1.03 (3H, s), 0.98 (3H, s); microanalysis (%): calc.: C: 74.67, H: 8.48, N: 5.12 for $C_{17}H_{23}NS$; found: C: 74.45, H: 8.35, N: 4.89.

Cyclisation Reactions: General Procedure:.

Aryl-sulphenylimine (2.0 mmol) and AIBN (0.1 mmol) were dissolved in deoxygenated cyclohexane (10 ml). The reaction mixture was heated to reflux and a solution of freshly prepared tributylstannane (2.2 mmol.) in cyclohexane (10 ml) was added dropwise over 4 hrs. After cooling, the solvent was evaporated under reduced pressure and the crude residue purified by silica gel chromatography. The following compounds were obtained according to this procedure:

3,3a,4,5,6,7-Hexahydro-2-methyl-2H-indole-cis and trans 5c. Silica gel chromatography, eluent: dichloromethane / ether - 100/0 to 0/100; yellow liquid; yield: 73 % from benzothiazolyl sulphenylimine **2c**; 95 % from S-phenyl sulphenylimine **2'c**. IR (cm^{-1}): 1645, 1450, 930, 910; n.m.r. ^1H: mixture of two isomers, ratio 60/40: major product: 3.90 (1H, m), 2.67 (1H, br. s.), 2.35 (1H, dd, J = 6.7 Hz, J' = 12.5 Hz), 0.89-2.28 (9H, m), 1.27 (3H, d, J = 6.9 Hz); minor product: 4.15 (1H, m), 2.73 (1H, br. s.), 2.31 (1H, dd, J = 7.5 Hz, J' = 12.5 Hz), 0.89-2.28 (9H, m), 1.07 (3H, d, J = 6.9 Hz); ^{13}C: major product: 178.5, 65.9, 49.0, 38.7, 35.0, 31.7, 26.6, 25.3, 22.9; minor product: 178.5, 65.9, 47.5, 36.9, 34.8, 32.0: 26.9, 25.5, 22.2; M.S : 137, 122, 109, 95.

3-Methyl-2-azaspiro[4.5]dec-1-ene 5e. Silica gel chromatography, eluent: dichloromethane / ether - 100/0 to 0/100, yellow liquid; yield: 94 % from benzothiazolyl sulphenylimine **2e**; 71 % from S-phenyl sulphenylimine **2'e**; IR (cm^{-1}): 1630, 1450; n.m.r. ^1H: 7.26 (1H, d, J = 2.4 Hz), 4.09 (1H, sex.d, J = 2.4 Hz, J' = 6.8 Hz, J'' = 7.6 Hz, J''' = 7.1 Hz) 2.01 (1H, dd, J = 7.6 Hz, J' = 12.8 Hz), 1.24-1.72 (10H, m), 1.29 (3H, d, J = 6.8 Hz), 1.16 (1H, dd, J = 7.1 Hz, J'= 12.8 Hz); n.m.r. ^{13}C: 173.1, 67.3, 55.1, 41.9, 35.8, 33.2, 25.7, 23.2, 23.1, 23.0; H.R.M.S.: calc.: 151.1361 for $C_{10}H_{17}N$; found: 151.1362.

3,4-Dihydro-2-methyl-3-phenyl-2H-pyrrole-cis and trans 5a. Silica gel chromatography, eluent: dichloromethane / ether- 100/0 to 40/60, yellow liquid; yield: 61 % from benzothiazolyl sulphenylimine **2a**; 69 % from S-phenyl sulphenylimine **2'a**; IR (cm^{-1}): 1610, 1595, 1480, 1440, 740, 690; n.m.r. ^1H: mixture of two isomers, ratio: 9/1: major product: 7.61 (1H, br. s.), 7.16-7.35 (5H, m), 4.06 (1H, m, J= 2.3 Hz, J' = 6.8 Hz, J'' = 7.1 Hz,), 3.12 (1H, dddd, J = 2.3 Hz, J' = 1.3 Hz, J'' = 7.3 Hz, J''' = 17.3 Hz), 2.88 (1H, ddd, J = 7.1 Hz, J' = 7.3 Hz, J'' = 8.7 Hz), 2.69 (1H, dddd, J = 2.3 Hz, J' = 17.3 Hz, J'' = 8.7 Hz, J''' = 0.9 Hz,), 1.35 (3H, d, J = 6.8 Hz); minor product: 7.72 (1H, br. s.) ;7.16-7.35 (5H, m), 4.36 (1H, m), 3.51 (1H, q, J = 7.9 Hz), 2.90 (2H, m), 0.84 (3H, d, J = 7.0 Hz); ^{13}C: 164.4, 128.8, 128.5, 128.1, 127.1, 127.2, 126.6, 76.5, 50.2, 46.5, 21.2; H.R.M.S.:calc: 159.1048 for $C_{11}H_{13}N$; found: 159.1047.

3,4-Dihydro-2,3-dimethyl-3-(4-methyl-3-pentenyl)-2H-pyrrole-cis and trans 5b. Silica gel chromatography, eluent: dichloromethane / ether- 100/0 to 0/100, yellow liquid; yield: 70 % ; IR (cm^{-1}): 1610, 1450, 1370; n.m.r. ^1H: mixture of two isomers, ratio 85/15: 7.52 (1H, s), 5.09 (1H, t, J = 7.0 Hz), 3.64 (1H, m), 2.26-2.48 (2H, m), 1.83-2.08 (2H, m), 1.68 (3H, s), 1.60 (3H, s), 1.26-1.46 (2H, m), 1.19 (3H, d, J = 7.2 Hz), 0.87 (3H, s); n.m.r. ^{13}C: 165.4, 131.5, 124.5, 74.8, 50.5, 43.0, 41.1, 25.7, 24.2, 20.4, 17.6, 15.5; H.R.M.S.: calc.: 179.1674 for $C_{12}H_{21}N$; found: 179.1677.

3a,4,5,6,7,7a-Hexahydro-3a,5,5-trimethyl-3H-indole 5d. Silica gel chromatography, eluent: dichloromethane / ether- 100/0 to 0/100, yellow liquid; yield: 70 % from benzothiazolyl sulphenylimine **2d**; 93 % from S-phenyl sulphenylimine **2'd**; IR (cm^{-1}): 1620, 1460; n.m.r. ^1H: 7.59 (1H, s), 3.46 (1H, m), 2.46 (1H, d, J = 17.1 Hz), 2.23 (1H, dd, J = 17.1 Hz, J' = 2.2 Hz), 1.80-1.94 (2H, m), 1.16-1.26 (4H, m), 1.18 (3H, s), 0.95 (3H, s), 0.86 (3H, s); n.m.r. ^{13}C: 166.8, 75.6, 54.2, 47.0, 39.8, 34.0, 32.4, 29.8, 28.5, 27.7, 24.4; H.R.M.S.: calc.: 165.1517 for $C_{11}H_{19}N$; found: 165.1516.

3,4-Dihydro-2-(1-methylethyl)-5-methyl-2H-pyrrole 5g. Silica gel chromatography, eluent: dichloromethane / ether - 100/0 to 20/80), orange liquid; yield: 75 %; IR (cm^{-1}): 1640, 1460, 1430, 1370, 730; n.m.r. ^1H: 3.71 (1H, m), 2.44 (2H, m), 2.02 (3H, d, J = 1.7 Hz), 1.71-1.98 (2H, m), 1.50 (1H, m), 1.01 (3H, d, J = 6.7 Hz), 0.86 (3H, d, J = 6.7 Hz); n.m.r. ^{13}C: 173.3, 78.5, 38.7, 32.9, 25.4, 19.5, 19.3, 18.1.

Cyclisation-Addition Reactions: General Procedure.

Phenylsulphenylimine (2.0 mmol), olefin (2-5 equivalents), and AIBN (0.1 mmol) were dissolved in deoxygenated cyclohexane (10 ml). The reaction mixture was heated to reflux and a solution of freshly prepared tributylstannane (2.4 mmol.) in cyclohexane (6 ml) was added dropwise over 5 hrs. After cooling, the solvent was evaporated under reduced pressure and the crude residue purified by silica gel chromatography, eluent: dichloromethane / ether - 80/20 to 0/100 then ether / methanol - 95/5. The following compounds were obtained according to this procedure:

3,4-Dihydro-γ,γ,5-trimethyl-2H-pyrrole-2-butanenitrile 15. Olefin: Acrylonitrile (5 equivalents); yield: 60 %; IR (cm^{-1}): 2220 , 1640 ; n.m.r. ^1H: 3.71 (1H, m), 2.36-2.51 (4H, m), 2.03 (3H, br. s), 1.68-1.93 (3H, m), 1.55 (1H, m), 0.92 (3H, s), 0.86 (3H, s); n.m.r. ^{13}C: primary: 19.8, 22.5, 23.7; secondary: 12.6, 24.0, 35.5, 39.3; tertiary: 80.8; quaternary: 36.9, 120.8, 174.9; H.R.M.S.: calc.: 178.1470 for $C_{11}H_{18}N_2$; found: 178.1425.

Methyl 3,4-dihydro-γ,γ,5-trimethyl-2H-pyrrole-2-butanoate 13. Olefin: Methyl acrylate (5 equivalents); yield: 83 %; IR (cm^{-1}): 1735, 1165 , 1645 ; n.m.r. ^1H: 3.74 (1H, m), 3.66 (3H, s), 2.31-2.49 (4H, m), 2.03 (3H, d, J = 1.1 Hz), 1.84 (1H, m), 1.61-1.71 (3H, m), 0.90 (3H, s), 0.84 (3H, s); n.m.r. ^{13}C: primary: 19.9, 23.1, 23.5, 51.6; secondary: 24.0, 29.5, 34.5, 39.4; tertiary: 81.4; quaternary: 36.4, 174.5, 175.0; H.R.M.S.: calc.: 211.1572 for $C_{12}H_{21}NO_2$; found: 211.1567.

t-Butyl-α-(t-butyloxycarbonyl)-γ,γ,5-trimethyl-3,4-dihydro-2H-pyrrole-2-butanoate 17. Olefin: Di-t-butylmethylenemalonate[16] (2 equivalents); yield: 68 %; IR (cm^{-1}): 1720, 1130 , 1640 ; n.m.r. ^1H: 3.74 (1H, m), 3.29 (1H, t, J = 6.2 Hz), 2.45 (2H, m), 2.04 (3H, s), 1.88 (2H, d, J = 6.2 Hz), 1.55-1.84 (2H, m), 1.46 (18H, s), 0.95 (3H, s), 0.83 (3H, s); n.m.r. ^{13}C: primary: 19.6, 22.7, 24.2, 27.9 ; secondary: 24.0, 37.1, 39.3; tertiary: 50.2, 81.5; quaternary: 36.6, 81.3 , 175.1, 169.8 ; H.R.M.S.: calc.: 353.2566 for $C_{20}H_{35}NO_4$; found: 353.2569.

t-Butyl-α-(t-butyloxycarbonyl)-3,3a,4,5,6,7-hexahydro-2H-indole-2-butanoate 18. Olefin: Di-t-butylmethylene-malonate (2 equivalents); yield: 65 %; IR (cm^{-1}): 1725, 1140, 1650; n.m.r. ^1H: mixture of two isomers, ratio 65/35: major product: 3.75 (1H, m), 3.17 (1H, t, J = 7.1 Hz), 2.47-2.67 (2H, m), 0.88-2.36 (13H, m), 1.48 (18H, s); minor product: 4.02 (1H, m), 3.13 (1H, t, J = 7.5 Hz), 2.47-2.67 (2H, m), 0.88-2.36 (13H, m), 1.48 (18H, s).

^{13}C:	Major product	Minor product
Primary:	27.89 .	27.89 .
Secondary:	36.5, 34.8, 31.7, 26.8 ;26.0, 25.2.	34.9, 34.6, 34.0, 31.9 ;27.1, 25.6, 25.4.

Tertiary:	70.5, 54.0, 48.3.	70.5, 54.0, 47.6.
Quaternary:	178.6, 168.8, 81.2.	178.9, 168.8, 81.2.

H.R.M.S.: calc.:365.2566 for $C_{21}H_{35}NO_4$; found: 365.2565.

Methyl 3a,4,5,6,7,7a-hexahydro-3a,5,5-trimethyl-3H-indole-7-propanoate, (3aα,7α,7aα) and (3aα,7β,7aα) 19. Olefin: methyl acrylate (5 equivalents); yield: 81 %; IR (cm^{-1}): 1735, 1165, 1630; n.m.r. ^1H: mixture of two isomers, ratio 65/35: major product: 7.53 (1H, s), 3.65 (3H, s), 3.23 (1H, d, J = 9.6 Hz), 2.59 (1H, d, J = 17.8 Hz) 2.19 (1H, d, J = 17.8 Hz), 1.72-2.45 (3H, m), 1.62 (1H, m), 1.53 (1H, d, J = 14.4 Hz) 1.35 (1H, d, J = 11.5 Hz), 0.85-1.21 (3H, m), 1.01 (3H, s), 0.96 (3H, s), 0.92 (3H, s); minor product: 7.64 (1H, d, J = 2.4 Hz), 3.67 (3H, s), 3.32 (1H, m), 1.72-2.48 (7H, m), 1.35 (1H, d, J = 11.5 Hz), 0.85-1.21 (3H, m), 1.25 (3H, s), 0.95 (3H, s), 0.83 (3H, s).

^{13}C:	Major product	Minor product
Primary:	28.4, 31.8, 33.6, 51.4.	25.5, 27.0, 31.9, 51.4.
Secondary:	30.3, 32.2, 41.7, 46.7, 51.5.	29.5, 32.1, 39.9, 46.7, 55.5.
Tertiary:	38.5, 82.8, 165.9.	34.5, 77.9, 168.2.
Quaternary:	39.5, 174.4.	41.4, 174.4.

H.R.M.S.: calc.: 251.1885 for $C_{15}H_{25}NO_2$; found: 251.1886.

Formation of Lactam 23 . Sodium cyanoborohydride (3 equivalents) was added to a solution of imine **13** (100 mg, 0.47 mmol) in acetic acid (5.0 ml). After 15 min. at 20°C, ether was added, and the reaction mixture was poured slowly into a saturated solution of aqueous sodium hydrogencarbonate (50 ml). Extraction with ether (3 x 25 ml), followed by the usual work-up afforded a crude residue which was purified by silica gel chromatography, eluent: petroleum ether/ether: 20/80; yield: 85 %; IR (cm^{-1}): 1640 ; n.m.r. ^1H: 400 MHz - 4.21 (1H, m), 3.27 (H_4, dd, J= 11.6 & 5.4 Hz), 2.35 (2H, m), 1.89 (1H, m), 1.79 (1H, m), 1.66 (1H, m), 1.53-1.60 (3H , m), 1.19 (3H, d, J = 6.4 Hz), 0.99 (3H, s), 0.88 (3H, s); n.m.r. ^{13}C: primary: 17.8, 19.2, 27.4; secondary: 25.1, 29.8, 30.3, 36.9; tertiary: 52.8, 68.5; quaternary: 31.9, 168.8; H.R.M.S.: calc.: 181.1467 for $C_{11}H_{19}NO$; found: 181.1468.

Formation of α-cyanolactam 27. Cyanotrimethylsilane (3 equivalents) and titanium tetrachloride (0.1 equivalent) were added successively to a solution of imine **13** (80 mg, 0.38 mmol) in dichloromethane (4.0 ml). After 48 hrs at 20°C, sodium hydrogencarbonate was added and the reaction mixture was extracted with dichloromethane (3 x 20 ml). Usual work-up and column chromatography of the residue over silica gel (eluent: petroleum ether / ether: 50/50) afforded the title compound **27**; yield: 88 %; IR (cm^{-1}): 2230 , 1650 ; n.m.r. ^1H: 400 MHz - 3.47 (1H, dd, J= 11.8 & 5.0 Hz), 2.33-2.44 (3H, m), 2.14 (1H, dd, J= 12.8 & 6.5 Hz), 1.93 (1H, m), 1.60-1.70 (3H, m), 1.69 (3H, s), 1.02 (3H, s), 0.88 (3H, s); n.m.r. ^{13}C: primary: 17.7, 23.8, 27.3; secondary: 25.0, 29.8, 36.3, 37.7; tertiary: 68.9; quaternary: 32.1, 55.1, 121.1, 168.7; H.R.M.S.: calc.: 206.1419 for $C_{12}H_{18}N_2O$; found: 206.1415.

References and notes:

1. Giese, B., *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Curran, D. P. *Synthesis* **1988**, 417, 489. (c) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (d) Hart, D. J. *Science* **1984**, *223*, 883. (e) Curran, D. P. in *Comprehensive Organic Synthesis* Trost, B. M.; Fleming, I. Eds.; Pergamon Press: Oxford, 1991, Vol 4, pp 715-831.

2. Two volumes in the Houben-Weyl series are solely dedicated to carbon radicals: *Houben-Weyl Methoden der Organischen Chemie* ; Regitz, M.; Giese, B., Eds; Georg. Thieme Verlag: Stuttgart, 1989 (Band E19a)

3. See for example: (a) Symons, M. C. R. *Tetrahedron* **1973**, *29*, 615. (b) Roberts, B. P.; Winter, J. *J. Chem. Soc. Perkin Trans. 2* **1979**, 1353. (c) Griller, D.; Mendenhall, G. D.; Van Hoof, W.; Ingold, K. U. *J. Amer. Chem. Soc.* **1974**, *96*, 6068.

4. Boivin, J.; Fouquet, E.; Zard, S..Z. *Tetrahedron Lett.* **1990**, *31*, 85; 3545. (b) idem. *J. Am. Chem. Soc.* **1991**, *113*, 1054. (c) idem. *Tetrahedron Lett.* **1991**,*32*, 4299. (d) Boivin, J.; Schiano, A.-M..; Zard, S. Z. *Tetrahedron Lett.*. **1992**, *33*, 7849.

5. Forrester, A. R., 'International Review of Science, Organic Chemistry Series Two: Free Radical Reactions', Vol. 10, Chap. 5, Butterworths & Co., London, 1975 ; McNab *J. Chem. Soc., Chem. Commun.* **1980**, 422; idem. *J. Chem. Soc. Perkin Trans. 1* **1982**, 1941 ; Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Chem. Commun.* **1976**, 539; Hasebe, M.; Kogawa, K.; Tsuchiya, *Tetrahedron Lett.* **1984**, *25*, 3887. Forrester, A. R., Gill, M.; Meyer, C. J.; Sadd, J. S.; Thomson, R. H. *J. Chem. Soc. Perkin Trans. 1* **1979**, 606.

6. (a) Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc. Chem. Commun.* **1987**, 666. (b) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565. (c) Poutsma, M. L.; Ibraria, P. A. *J. Org. Chem.* **1969**, *34*, 2848.

7. For an excellent recent review on sulphenamides and sulphenylimines, see Craine, L.; Raban, M. *Chem. Rev.* **1989**, *89*, 689.

8. Barton, D. H. R.; Motherwell, W. B.; Simon, E. S.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1984**, 337; idem. *J. Chem. Soc. Perkin Trans. 1* **1986**, 2243.

9. (a) Barltrop, J. A.; Morgan, K. J. *J. Chem. Soc.* **1957**, 3072. (b) D'Amico, J. J. *J. Org. Chem.* **1961**, *26*, 3436.

10. (a) Burgstahler, A.W.; Nordin, I. C. *J. Amer. Chem. Soc.* **1961**, *83*, 198. (b) Julia, S.; Julia, M.; Linares, H.; Blondel, J-C. *Bull. Soc. Chim. Fr.* **1962**, 1947.

11. (a) Lorette, N. B.; Howard, W. L. *J. Org. Chem.*, **1961**, *26*, 3112. (b) Brannock, K. C. *J. Amer. Chem . Soc.* **1959**, *81*, 3379.

12. (a) Molander, G.A.; Hoberg, J.O. *J. Amer. Chem . Soc.*, **1992**, *114*, 3123. (b) Scribe, P. *Compt. Rend.*, **1965**, *261*, 160.

13. Morimoto, T.; Nezu, T.; Achiwa, K.; Sekia, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1584.

14. (a) Russell Bowman, W.; Clark, D. N.; Marmon, R. J. *Tetrahedron Lett.* **1992**, *33*, 4993; **1991**, *32*, 6441. (b) Beckwith, A. L. J.; Maxwell, B. J.; Tsanakatidis, J. *Aust. J. Chem.* **1991**, *44*, 1809. (c) Tokuda, M.; Yamada, Y.; Takagi, T., Suginome, H.; Furusaki, A. *Tetrahedron* **1987**, *43*, 281; ibid. *Tetrahedron Lett.* **1985**, *26*, 6085. (d) Newcomb, M.; Deeb, T. M. *J. Amer. Chem. Soc.*, **1987**, *109*, 3163. (e) Gasc, M-B.; Lattes, A.; Perie, J-J. *Tetrahedron* **1983**, *39*, 703. (f) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337; (g) Beckwith, A. L. J.; Ingold K. U., in *Rearrangements in Ground and Excited States*; de Mayo, P. Ed., Academic Press: New York, 1980, Vol 1.

15. Newcomb, M.; Deeb, T. M.; Marquardt, D. J. *Tetrahedron* **1990**, *46*, 2317; 2329. (b) Newcomb, M.; Marquardt, D. J.; Udaya kumar, M. *Tetrahedron* **1990**, *46*, 2352.

16. Ballesteros, P.; Roberts, B.W.; Wong, J. *J. Org. Chem.* **1983**, *48*, 3603.

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