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Iminyl Radicals: Part II. Ring Opening of Cyclobutyl- and Cyclopentyliminyl Radicals.

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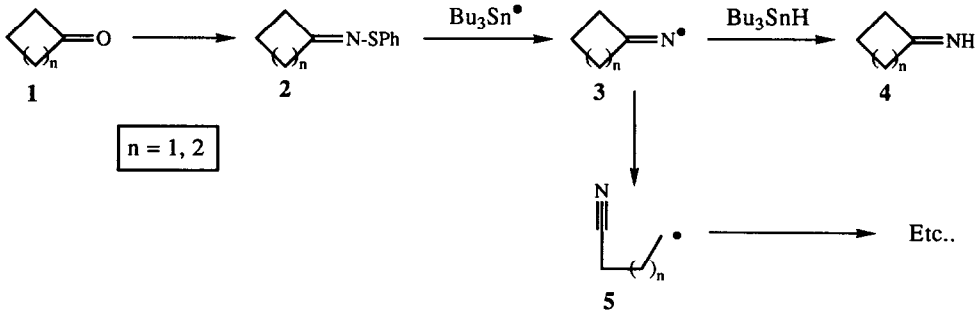
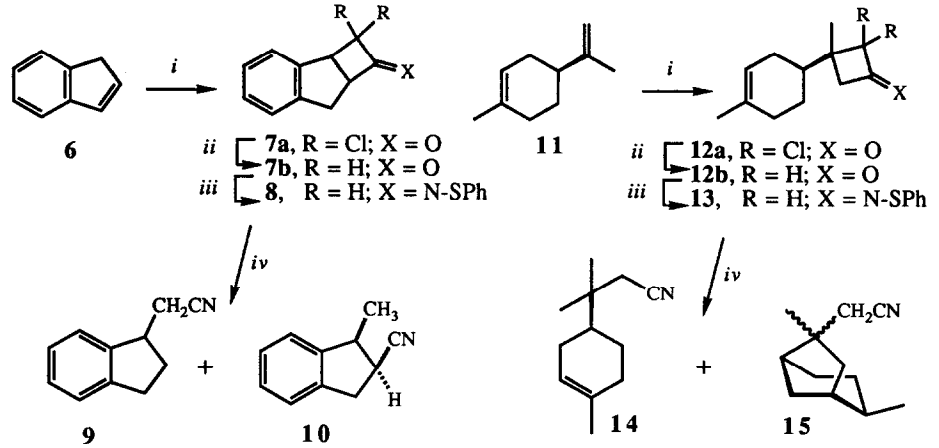
Abstract : Slow addition of tributylstannane to sulphenylimines **2** give the corresponding cycloiminyl radicals **3** which can undergo ring opening, a process that is easily incorporated into complex reaction sequences.

In part one of this series,[1] we described a new and convenient source of iminyl radicals based on sulphenylimines and showed that these species were readily captured by an internal olefin to give Δ^1-pyrrolenines in high yield. Moreover, this process can be easily coupled with an intermolecular addition to an electrophilic olefin allowing the expedient assembly of complex frameworks. We have now addressed another aspect of iminyl radical chemistry, namely the induced opening of small ring systems such as cyclobutanones and some strained cyclopentanones. Part of this work has already appeared in a preliminary communication.[2]



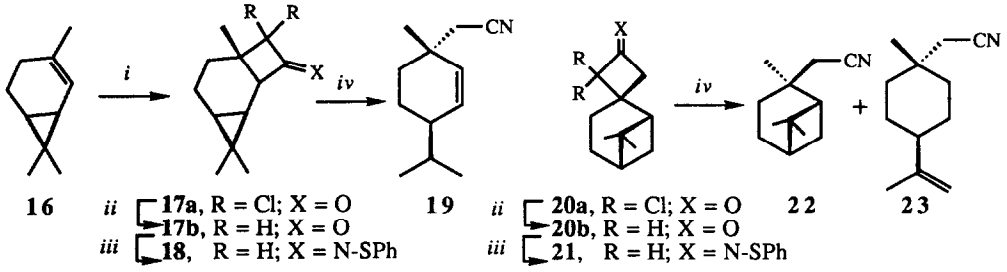
Scheme 1

The ring opening of cycloalkyliminyl radicals has been implicated in a few scattered examples involving mostly radical induced nitrile transfer reactions.[3] Some kinetic studies have also been reported,[4] but the synthetic potential of such processes has hardly been exploited. In the case of cyclobutyliminyl radicals, the rate constant for the ring opening has been estimated by Roberts and Winter[4a] to be greater than $10^3 s^{-1}$ at -73°C. At higher temperatures (such as the boiling point of the common solvents used in radical chemistry), this ring opening should become sufficiently fast to compete with other unwanted side reactions, such as premature hydrogen abstraction from tributylstannane to give the unsubstituted imine **4** (Scheme 1). This latter reaction is, of course, of little synthetic utility as it as imine **4** will simply hydrolyse back to the initial ketone **1** upon work up. However, once the ring opening has occured, the ensuing carbon radical could then be incorporated, as is now common practice in this area, into all kinds of radical sequences thus bringing forward the power of the whole scheme as a synthetic tool.



(*i*) Cl_3CCOCl/ Zn, sonication; (ii) Zn/ NH_4Cl/ MeOH; (iii) PhSN(SiMe3)2/ Bu_4NF Cat.; (iv) Bu_3SnH, AIBN (Cat.), Δ

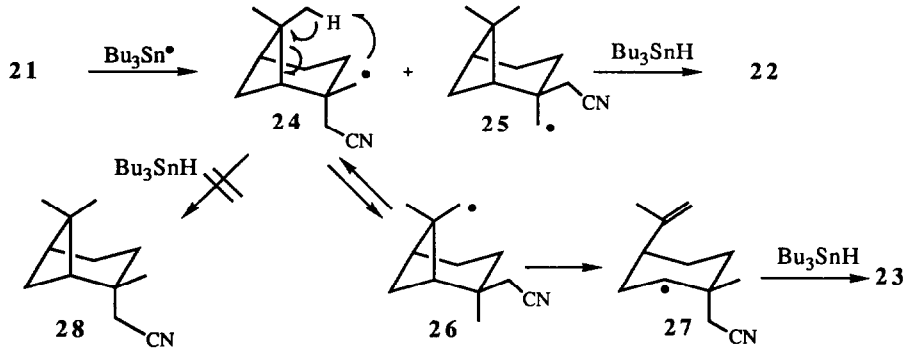
The cyclobutanones in this study have been prepared by cycloaddition of dichloroketene to the appropriate olefin followed by dechlorination with zinc powder. The sulphenylimine precursors were readily obtained by condensing the ketones with $PhSN(SiMe_3)_2$ under fluoride ion catalysis, according to the method of Morimoto and co-workers.[5] The first example we examined is sulphenylimine **8** derived from indene **6** (via **7a** and **7b**). Slow addition (ca. 5 hrs) of n-Bu_3SnH in cyclohexane to a refluxing solution of **8** in the same solvent (in the presence of catalytic amounts of AIBN) resulted in the formation of nitrile **9** in high yield (89%) together with traces of its isomer **10** (3%). The difference in stability between a secondary and a primary radical, reflected in the relative weakness of the bonds being broken, is sufficient to ensure a high regioselectivity in the ring opening step. Under the same conditions, (-)-limonene derivative **13** (from (-)-limonene **11** via **12a** and **12b**) also gave the simple nitrile **14** as the product of ring opening but only in minor amounts (20%). The major product turned out , not unexpectedly, to be the bicyclic compound **15** (73%, diasteriomeric ratio 1.8:1) arising from addition of the intermediate carbon radical onto the endocyclic olefin.



(*i*) Cl_3CCOCl/ Zn, sonication; (ii) Zn/ NH_4Cl/ MeOH; (iii) PhSN(SiMe3)2/ Bu_4NF Cat.; (iv) Bu_3SnH, AIBN (Cat.), Δ

A further illustration of combining two radical processes is the case of derivative **18**, prepared from Δ^2-(+)-carene **16** (via **17a** and **17b**), where rupture of the cyclopropane ring follows the opening of the

cyclobutane-iminyl unit to give finally compound **19** in excellent yield (94%). A much more interesting result was observed when (-)-β-pinene derivative **21** (from (-)-β-pinene via **20a** and **20b**) was subjected to the same treatment. The anticipated nitrile **22** was the minor product (40%) isolated as a *single isomer*, together with a major compound (54%) whose structure **23** was deduced from the ^{1}H and ^{13}C n.m.r. spectra, and from the absence of optical rotation due to the presence of a plane of symmetry. The clean formation of the latter was unexpected at first as it implies a hydrogen atom transfer from a methyl group to a primary radical (to give **26**), followed by a *regiospecific* ring cleavage of the four membered ring (Scheme 2). The presumably reversible abstraction of hydrogen atom *must be fast* compared with quenching of intermediate radical **24** by n-Bu_3SnH under our dilution conditions. None of isomer **28** is formed since the intramolecular hydrogen abstraction step is itself followed by a rapid and essentially irreversible opening of the cyclobutane ring. Isomeric radical **25** cannot undergo a similar 1, 5-hydrogen migration and therefore evolves simply into compound **22**.

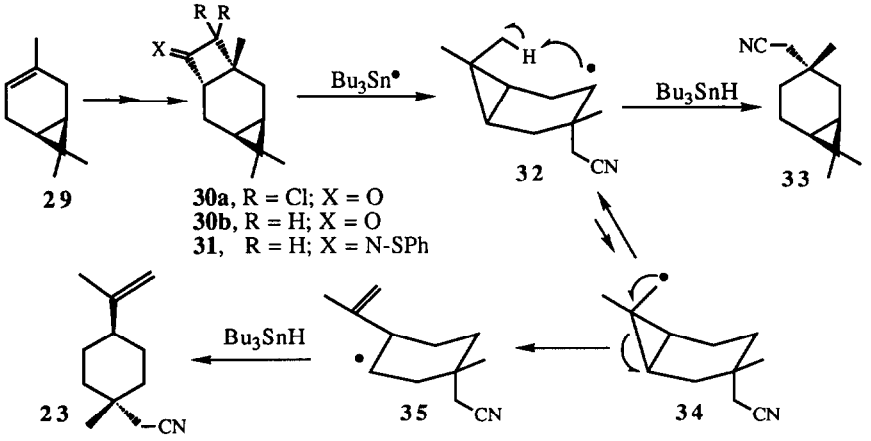


Scheme 2

The high rate of the 1,5 hydrogen migration can be explained by a favourable and rigid conformation[6] placing the migrating hydrogen very close to the radical centre. The striking regiospecificity in the opening of the cyclobutane ring is more difficult to rationalise since both opening modes would produce secondary radicals of very similar stabilities. It could be that steric repulsion causes a slight lengthening (and hence weakening) of the bond closest to the quaternary center thus making it break faster. Small differences in bond lengths are known to have a large effect on the relative rates of bond breaking.[7] It is noteworthy that the remote functionalisation of one of the gem -dimethyl groups in methyl pinanol (via the Barton nitrite photolysis or by the action of lead tetraacetate-iodine and irradiation) has been reported to occur without opening of the cyclobutane ring.[8] Rates for cyclobutyl carbinyl radical opening range from 10^3 to $10^6 s^{-1}$ at 25°C depending on substituents.[9] In our case, the low concentration of the stannane gives the unimolecular process time to occur.

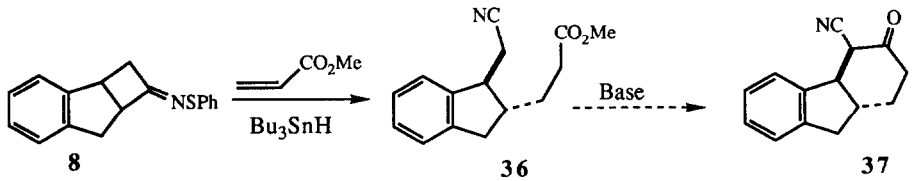
This efficient hydrogen atom transfer prompted us to examine the ring opening of Δ^3 (+)-carene derivative **31** (from Δ^3 (+)-carene **29** via **30a** and **30b**). Indeed, in addition to the "normal" product **33** (70%), a minor compound **23** (19%) was also isolated, identical to the one obtained previously from ß- pinene. The yield of the latter could be easily raised to about 50% by simply adding the stannane even more slowly (over ca. 12 hrs). In this instance, an *a priori* unfavorable equilibrium is established between *secondary* radical **32** and *primary* radical **34**, followed again by a remarkably *regiospecific* cleavage of the cyclopropyl ring to produce radical **35** (Scheme 2).[10] Stabilisation of the primary radical **34** by the cyclopropane ring can hardly be invoked in this case since the geometric disposition, in the transition state, of the atoms involved in the migration of the

hydrogen is not favorable for a stabilising interaction with the cyclopropyl ring which, in any case, is relatively small for radicals (3-4 kcal / mole).[11] Absolute kinetic data on carbon to carbon 1,5-migration of a hydrogen atom are rather scanty[12], and those involving saturated carbons have generally been considered as too sluggish and unselective for synthetic purposes.[12,13] Evidently, such migrations made favourable by proximity in a relatively rigid system, embody a much greater synthetic potential than has been hitherto appreciated, especially when coupled to an irreversible process. Furthermore, the amazingly high selectivity in the opening of the cyclopropane ring has far reaching consequences; its generality and the underlying physical factors need to be examined more thoroughly. It is also interesting to note that compound **23** is arrived at by way of two different (isomeric) radical precursors **27** and **35**, which are both *chiral* . This of course has various synthetic implications which we have not yet exploited.



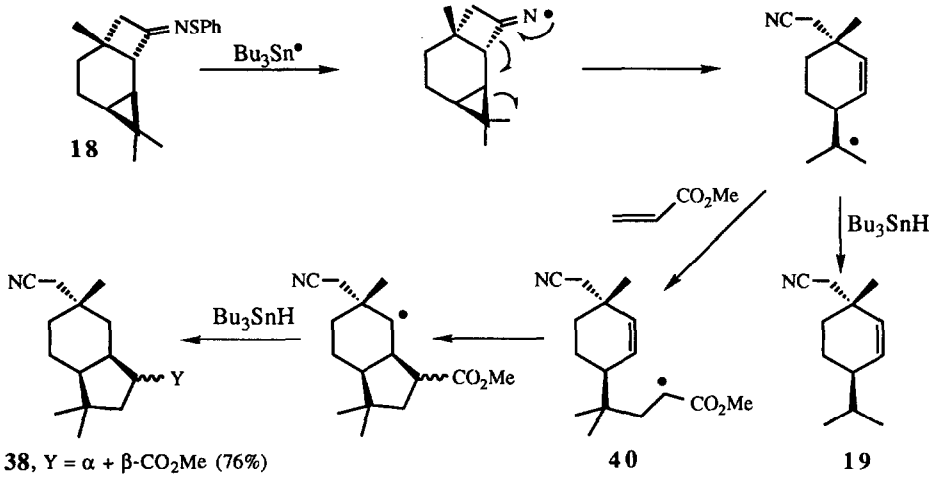
Scheme 3

The intermediate carbon radical may also be captured by an external electrophilic olefin. Thus, in the presence of methyl acrylate, the reaction of sulphenylimine **8** with tributylstannane furnished the trans substituted compound **36** in 65-70% yield. Considering the whole sequence from the starting indene **6**, the overall result is the highly selective creation of two new carbon-carbon bonds accross what originally was an olefin. It is worth noting that a base catalysed Dieckmann type cyclisation between the nitrile and ester containing chains would lead to a *trans- hydrindane* system **37**. Such substructures are of some importance as they constitute the CD ring part of steroids (see below), and work along these lines is currently being pursued.



A more complex radical cascade can be accomplished if the substrate is sulphenylimine **18** derived from Δ^2 (+)-carene. Under the same conditions, bicyclic compound **38** is produced as a mixture of epimers (α/β 3:7) in 76% yield via the sequence displayed in Scheme 4, featuring rupture of the four and three membered rings, and formation of a five membered ring.[14] A small amount of **19** (6%) is also formed but, as mentioned

above, it can be produced in excellent yield in the absence of methyl acrylate. Epimerisation (K_2CO_3/MeOH, 20°C, 48 hrs) and concomitant saponification furnished acid **39** (98%) as a sole isomer. The stereochemistry in the end product is thus completely controlled; it simply follows from the configuration of the starting carene since the cyclisation of radical **40** occurs to give the cis hydrindane system .

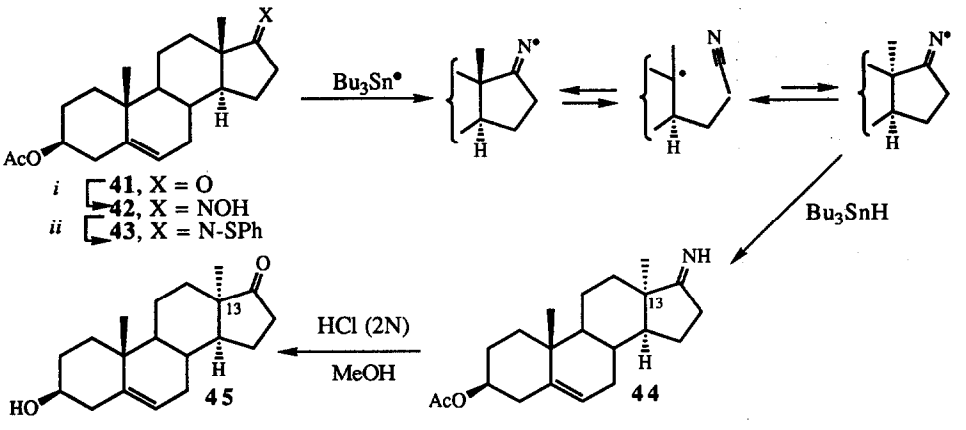


Scheme 4

In contrast to cyclobutyliminyls, the opening of cyclopentyliminyl radicals is a less general process; only those which are somewhat strained and which produce on rupture a relatively stabilised carbon radical undergo the process fast enough to be synthetically useful. One such instance is represented by the iminyl radical derived from a 17-ketosteroid such as **41**. Because of steric hindrance, attempts to prepare the sulphenylimine precursor **43** by the method of Morimoto[5] failed. We therefore applied a procedure we developed some years ago involving treatment of the corresponding oxime with tributyl phosphine and an excess of diphenyl disulphide,[15] and which provided sulphenylmine **43** via oxime **42** in up to 70% yield. This reaction gives sulphenylimines only in the case of hindered ketoximes; ordinary ketoximes are simply reduced to the imine (aldoximes give nitriles). These two methods are thus complementary.

With the required sulphenylimine in hand, we subjected as usual to tributylstannane reduction which resulted in the production of imine **44** with a 13-α-methyl group. In this case, ring opening occurs to give a tertiary radical which then closes back with inversion at the 13-position in order to provide the more thermodynamically stable cis-CD ring junction (Scheme 5). Interestingly, the imine obtained is sufficiently hindered to be resistant to hydrolysis thus allowing its isolation and characterisation.

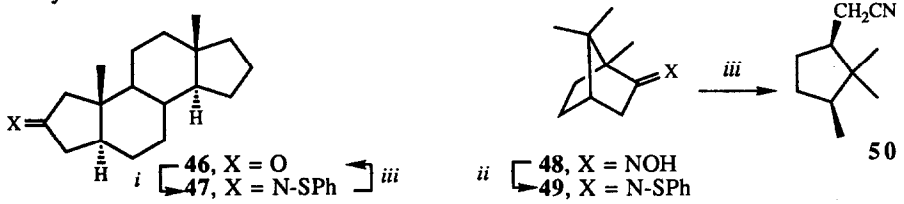
Deliberate hydrolysis with dilute hydrochloric acid finally furnished 13-epi-17-ketosteroid **45** in 88% overall yield. 13-Epi-steroids have previously been prepared by photolysis of 17-ketosteroids[16a-h] or by prolonged heating of 17-acetoximines with acetic anhydride in pyridine.[16i] The former process is based on a reversible Norrish type I fragmentation whereas the latter is not well understood, although iminyl radicals could also be implicated. Subsequently to the present work, we developed a further practical solution to this problem, also proceeding through iminyl radicals generated this time by nickel powder / acetic acid reduction of 17-oxime esters.[17]



(*i*) NH_2OH. HCl/ AcONa/ MeOH; (ii) Bu_3P/ PhSSPh

Scheme 5

A trans hydrindane system is not sufficient to promote fragmentation if the carbon radical produced is only primary. For example, exposure of sulphenylimine **47** to the usual stannane reduction gave back the starting ketone **46** after work up. Five-membered rings locked in [2.2.1] bicyclic systems are also strained, and iminyl radicals of this family can also undergo scission.[3e] This is illustrated by sulphenylimine **49** derived from camphor (again because of steric hindrance, this compound had to be prepared by the Bu_3P / PhSSPh reaction on camphor oxime **48**). In this case, ring opening proceeded smoothly to give the monocyclic derivative **50** in 84% yield as essentially one isomer. Attack of the hydride takes place opposite to the acetonitrile chain thus leading cleanly to the cis isomer.



(*i*) $PhS(N(SiMe_3)_2H$/ Bu_4NF; (*ii*) Bu_3P/ PhSSPh; (*iii*) Bu_3SnH, work-up

In this work we have attempted to survey, albeit briefly, the various synthetic possibilities made accessible by this novel method for generating iminyl radicals. The prospects appear to be particularly bright in the light of the above results and in view of the fact that the starting materials, and especially cyclobutanones, are readily available by a variety of methods,[18] some of which are regio-, stereo-, and even enantioselective.[18e]

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

Experimental Section

General experimental techniques are the same as those in part 1 of this series.

Cycloadditions of dichloroketene: A solution of trichloroacetyl chloride (3.75 mmol.) in dry ether (20 ml) was added dropwise under sonication over 45 min. to a solution of olefin (2.5 mmol) in dry ether (40 ml) containing zinc powder (490 mg, 7.5 matg), at a rate such that the temperature did not exceed 15-20°C. Sonication was continued for 30 min. after the end of the addition. Ether was then added and the reaction mixture filtered over a pad of Celite. The filtrate was washed successively with water (2 x 25 ml), saturated aqueous sodium carbonate (4 x 25 ml), and brine (2 x 25 ml). The organic layer was dried over sodium sulphate and the solvent removed by evaporation under reduced pressure. The crude residue was purified by silica gel chromatography, when necessary. The following compounds were obtained according to this procedure (derivatives **7a** and **12a** are known compounds: ref. 19):

[1R-(1α,2β,4β,7α]-8,8-Dichloro-3,3,7-trimethyltricyclo[5.2.0.0^{2,4}]nonan-9-one 17a. Used without further purification; yield: 94 %; IR (cm^{-1}): 1795 , 1450, 885, 760 ; n.m.r. ^{1}H: 3.70 (1H, s), 2.02 (1H, m), 1.53 (1H, br. d, J = 13.1 Hz), 1.37 (3H, s), 1.22 (1H, dd, J = 3.5 Hz, J' = 13.1 Hz), 0.80-1.14 (4H, m), 1.04 (3H, s), 0.84 (3H, s); n.m.r. ^{13}C: primary: 15.7, 17.7, 19.7; secondary: 15.7, 31.1; tertiary: 21.3, 27.8, 56.8; quaternary: 17.9, 44.2, 93.2, 196.7.

(1S)-6,6-Dimethylspiro[bicyclo[3.1.1]heptane-2,1'-(2',2'-dichloro)cyclobutan-3'-one 20a. Purified by silica gel chromatography (eluent= petroleum ether / dichloromethane: 85/15) and used as such; yield: 69 %; IR (cm^{-1}): 1805 (cyclobutanone), 1460, 1385, 750 (C-Cl); n.m.r. ^{1}H: two isomers, ratio 58/42: Major product: 3.31 and 3.05 (2H, AB, J = 17.4 Hz), 2.71 (1H, m), 2.16-2.43 (2H, m), 1.91-2.04 (3H, m), 1.49-1.78 (2H, m), 1.28 (3H, s), 0.89 (3H, s); Minor product: 3.23 and 3.11 (2H, AB, J = 17.7 Hz), 2.71 (1H, m), 2.16-2.43 (2H, m), 1.91-2.04 (3H, m), 1.49-1.78 (2H, m), 1.27 (3H, s), 1.06 (3H, s). n.m.r. ^{13}C:

	Major product	Minor product
Primary	: 22.8, 26.9	23.6, 26.9.
Secondary	: 24.3, 24.4, 27.5, 56.1	25.2, 26.2, 28.9, 58.5.
Tertiary	: 38.8, 49.4	39.3, 51.5.
Quaternary	: 39.5, 49.7, 94.6, 194.6	37.7, 51.6, 92.6, 194.9.

[1R-(1α,3β,5β,7α]-9,9-Dichloro-1,4,4,-trimethyltricyclo[5.2.0.0^{3,5}]nonan-8-one 30a. Purification by silica gel chromatography (eluent: petroleum ether / dichloromethane: 90/10) afforded **30a** as white crystals in 86% yield; m.p. = 108-9°C; IR (cm^{-1}): 1790, 1455, 875, 785, 755; n.m.r. ^{1}H: 400 MHz - 3.34 (1H, t, J = 3.5 Hz), 2.36 (1H, dd, J = 15.8 Hz, J' = 8.0 Hz), 2.26 (1H, ddd, J = 3.2 Hz, J' = 8.1 Hz, J" = 15.3 Hz), 1.42 (3H, s), 1.08 (1H, dd, J= J' = 8.5 Hz), 1.01 (3H, s), 0.97 (1H, ddd, J= J' = 4.0 Hz, J" = 8.6Hz), 0.95 (3H, s), 0.76 (1H, q, J = 8.6 Hz), 0.65 (1H, q, J = 8.5 Hz); n.m.r. ^{13}C: primary : 14.7, 18.1, 19.6; secondary: 17.1, 28.0; tertiary: 25.0, 28.1, 60.0; quaternary: 19.2, 44.5, 92.3, 197.8; microanalysis (%): Calc.: C: 58.32, H: 6.53, O: 6.47 for $C_{12}H_{16}OCl_2$.Found: C: 58.48, H: 6.41, O: 6.54.

Dechlorination of α;,α-dichlorocyclobutanones: Ammonium chloride (1.12 g, 21 mmol) and zinc powder (2.6 g, 40 mmol) were successively added to a solution of cyclobutanone (10 mmol) in methanol. The reaction mixture was then heated under reflux for 40 hrs. After cooling, dichloromethane (30 ml) was added and the reaction mixture filtered over Celite to remove zinc chloride and unreacted zinc. The usual work-up afforded a crude residue which was purified by silica gel column chromatography (eluent: petroleum ether / dichloromethane / ether: 50/45/5). The following compounds were obtained according to this procedure (derivative **7b** has already been described[20]):

3-Methyl-3(4-methyl-3-cyclohexenyl)cyclobutanone 12b. Used without further purification; yield: 66 %; IR (cm^{-1}): 1775, 1450, 1440, 1380; n.m.r. ^{1}H: 5.37 (1H, br. s), 2.87 (2H, m), 2.55-2.69 (2H, m), 1.53-2.00 (6H, m), 1.62 (3H, s), 1.34 (1H, m), 1.16 (3H, s); n.m.r. ^{13}C: primary: 21.6, 23.4; secondary: 24.7, 26.8, 31.0, 57.0, 57.5; tertiary: 43.2, 120.3; quaternary: 32.0, 134.0, 208.4.

[1R-(1α,2β,4β,7α]-3,3,7-Trimethyltricyclo[5.2.0.0^{2,4}]non-9-one 17b. Used without further purification; yield: 80 %; IR (cm^{-1}): 1780, 1450, 1375, 1170; n.m.r. ^{1}H: 400 MHz - 2.91 (1H, dd, J = 3.2

Hz, J' = 17.1 Hz), 2.77 (1H, br. s), 2.66 (1H, dd, J = 3.0 Hz, J' = 17.1 Hz), 1.90 (1H, m), 1.59 (1H, dt, J = 12.5 Hz, J' = 3.0 Hz), 1.23 (3H, s), 1.02 (1H, m), 1.01 (3H, s), 0.87 (1H, ddd, J = 2.5 Hz, J' = 5.8 Hz, J'' = 16.5 Hz), 0.81 (3H, s), 0.73-0.83 (2H, m); n.m.r. ^{13}C: primary: 16.0, 18.2, 21.7; secondary: 16.2, 33.2, 59.4; tertiary: 25.7, 27.9, 60.2; quaternary: 17.5, 27.3, 211.3.

(1S)-6,6-Dimethylspiro[bicyclo[3.1.1]heptane-2,1'-cyclobutan-3'-one 20b. Used without further purification; yield: 77 %; IR (cm^{-1}): 1780, 1460, 1380, 1120; n.m.r. ^1H: 2.89 (4H, s), 2.25 (1H, m), 1.84-2.12 (6H, m), 1.23 (3H, s), 1.19 (1H, s), 0.88 (3H, s); n.m.r. ^{13}C: primary: 22.6, 27.0; secondary: 25.0, 27.5, 30.4, 60.3, 62.4; tertiary: 40.1, 52.1; quaternary: 34.0, 39.2, 209.7.

[1S-(1α,3β,5β,7α]-1,4,4,-trimethyltricyclo[5.2.0.0^{3,5}]nonan-8-one 30b. Yield: 88 %; white crystals, m.p.= 41-3°C; IR (cm^{-1}): 1775, 1455, 1390, 1375; n.m.r. ^1H: 2.97 (1H, dd, J = 3.2 Hz, J' = 17.8 Hz), 2.71 (1H, br. s), 2.64 (1H, dd, J = 4.1 Hz, J' = 17.8 Hz) 2.08 (1H, dde, J = 8.1 Hz, J' = 15.1 Hz), 1.93 (1H, dd, J = 7.1 Hz, J' = 14.9 Hz), 1.27 (3H, s) 0.99 (3H, s), 1.02-0.87 (2H, m), 0.57-0.72 (2H, m); n.m.r. ^{13}C: primary: 14.8, 18.5, 18.6; secondary: 18.1, 28.6, 55.8; tertiary: 28.4, 28.5, 62.7; quaternary: 18.0, 27.7, 214.6; microanalysis (%): Calc.: C: 80.85, H: 10.18 for $C_{12}H_{18}O$. Found: C: 80.69, H: 10.06.

Preparation of S-phenyl sulphenylimines: **Method A:** To a solution of phenyl N,N bistrimethylsilylsulphenamide[5] (1.48 g, 5.5 mmol) and carbonyl derivative (5.0 mmol) in anhydrous tetrahydrofurane (15 ml) was added dropwise tetrabutylammonium fluoride (0.1 equivalent, 1.1 M solution in tetrahydrofuran). The reaction mixture was stirred at 20°C during 20-180 min. according to the substrate (T.L.C. monitoring). The solvent was then removed under reduced pressure and the resulting residue was purified by quick filtration through an alumina or silica gel column and the product used as such in most cases. The following compounds were prepared according to this procedure:

N-(2,2a,7,7a-Tetrahydro-1H-cyclobut[α]indene-1-ylidene)-benzenesulfenamide 8. Reaction time: 3 hrs; obtained as a yellow oil after chromatography on neutral alumina (eluent: petroleum ether) and used as such; yield: 77 %, ; IR (cm^{-1}): 1650, 1580, 1475, 1430, 1025, 750, 740, 690; n.m.r. ^1H: 7.47-7.58 (2H, m), 7.17-7.39 (7H, m), 3.98-4.05 (2H, m), 3.12-3.72 (3H, m) 2.82 (1H, dd, J = 17 Hz, J' = 2.5 Hz).

(S)-N-[3-Methyl-3-(4-methyl-3-cyclohexen-1-yl)cyclobutylidene]-benzenesulfenamide 13. Reaction time: 3 hrs; obtained as a yellow oil after chromatography on neutral alumina (eluent: petroleum ether / dichloromethane - 90/10) and used as such; yield: 75 %; IR (cm^{-1}): 1655, 1580, 1480, 1440, 740, 690; n.m.r. ^1H: 7.53 (2H, m), 7.35 (2H, m), 7.22 (1H, m), 5.42 (1H, br. s.), 2.49-2.90 (4H, m), 1.92-2.09 (3H, m), 1.53-1.79 (3H, m), 1.67 (3H, s), 1.28-1.41 (1H, m), 1.17 (3H, s); n.m.r. ^{13}C: mixture of two isomers which could be differentiated only by the chemical shifts of the respective methylene carbons α to the imine function: 169.6, 138.7, 134.0, 129.0 (2C), 126.1, 125.7 (2C), 120.7, 49.5 (49.1), 48.1 (47.6), 42.9 34.9, 31.2, 26.4, 24.3, 23.7, 22.0.

(1S)-N-(6,6-Dimethylspiro[bicyclo[3.1.1]heptane-2,1'-cyclobutan]-3'-ylidene)-benzenesul-fenamide 21. Reaction time: 3 hrs; obtained as a yellow oil after chromatography on neutral alumina (eluent: petroleum ether / dichloromethane - 90/10) and used as such; yield: 79 %; IR (cm^{-1}): 1655, 1585, 1480, 1440, 1025, 745, 690; n.m.r. ^1H: two isomers in equal proportions: Isomer A: 7.49 (2H, m), 7.33 (2H, m), 7.18 (1H, m), 2.73-2.87 (4H, m), 2.13-2.24 (1H, m), 1.80-2.05 (6H, m), 1.22 (3H, s), 1.14-1.19 (1H, m), 0.89 (3H, s); Isomer B: 7.49 (2H, m), 7.33 (2H, m), 7.18 (1H, m), 2.73-2.87 (4H, m), 2.13-2.24 (1H, m), 1.80-2.05 (6H, m), 1.21 (3H, s), 1.14-1.19 (1H, m), 0.86 (3H, s); n.m.r. ^{13}C: mixture of two isomers which could be differentiated only by the chemical shifts of the respective methylene carbons α to the imine function: 170.6, 138.6, 128.9 (2C), 126.1, 125.8 (2C), 54.3 (52.9), 52.8 (51.5), 51.9, 40.3, 39.2, 37.0, 30.8, 27.1 (2C), 25.1, 22.5.

[1R-(1α,2β,4β,7α]-N-(3,3,7-Trimethyltricyclo[5.2.0.0^{2,4}]non-9-yliden)-benzenesulfenamide 18. Reaction time: 3 hrs; obtained as a colourless oil after chromatography on silica gel (eluent: petroleum ether / dichloromethane - 95/15); yield: 94 %; IR (cm^{-1}): 1655, 1580, 1475, 1440, 1025, 740, 690; n.m.r. ^1H: 7.51 (2H, m), 7.34 (2H, m), 7.19 (1H, m), 2.72 (1H, s), 2.62-2.65 (2H, m), 1.81-1.94 (1H, m), 1.42-1.59 (1H, m), 1.14 (3H, s), 1.02-1.11 (2H, m), 1.05 (3H, s), 0.76-0.94 (2H, m), 0.82 (3H, s); n.m.r. ^{13}C: 174.0, 138.8, 128.9 (2C), 126.0, 125.4 (2C), 52.1, 50.1, 33.7, 30.0, 28.1, 25.5, 21.9, 20.2, 17.2,

16.1; microanalysis (%): Calc.: C: 75.54, H: 8.12, N: 4.90 for $C_{18}H_{23}NS$. Found: C: 75.82, H: 8.27, N: 4.80.

[1R-(1α,2β,4β,7α]-N-(1,4,4-Trimethyltricyclo[5.2.0.0^{3,5}]nonan-8-ylidene-benzenesulfen-amide 31. Reaction time: 3 hrs; obtained as white crystals after chromatography on silica gel (eluent: petroleum ether / dichloromethane - 95/15); yield: 90 %; m.p.= 67-73°C; IR (cm^{-1}; solution in CCl_4): 1650, 1580, 1475, 1450, 1440, 1025, 740, 690; n.m.r. ^{1}H: two isomers, ratio 60/40: Major product: 7.50 (2H, m), 7.33 (2H, m), 7.17 (1H, m), 2.88 (1H, dd, J = 3.6 Hz, J' = 15.1 Hz), 2.74 (1H, m), 2.55 (1H, dd, J = 1.8 Hz, J' = 13.6 Hz), 2.16 (1H, m) 1.78 (1H, d, J = 6.9 Hz), 1.20 (3H, s), 1.03 (3H, s), 0.97 (3H, s), 0.82-0.94 (2H, m) 0.63-0.75 (2H, m); Minor product: 7.50 (2H, m), 7.33 (2H, m), 7.17 (1H, m), 2.96 (1H, dd, J = 3.6 Hz, J' = 15.1 Hz), 2.74 (1H, m), 2.46 (1H, dd, J = 1.8 Hz, J' = 13.9 Hz), 2.23 (1H, m) 1.85 (1H, d, J = 6.6 Hz), 1.18 (3H, s), 1.03 (3H, s), 1.02 (3H, s), 0.82-0.94 (2H, m) 0.63-0.75 (2H, m); n.m.r. ^{13}C: Major product: 174.9, 138.9, 128.9 (2C), 125.9, 125.5 (2C), 54.6, 45.7, 30.3, 28.8, 28.6, 28.4, 20.1, 18.7, 18.3, 17.8, 15.1; Minor product: 173.5, 139.1, 128.9 (2C), 125.9, 125.4 (2C), 54.1, 46.9, 29.4, 28.9, 28.6, 28.1, 19.0, 18.5, 17.7, 17.3, 15.1; microanalysis (%): Calc.: C: 75.54, H: 8.12, N: 4.90 for $C_{18}H_{23}NS$. Found: C: 76.01, H: 8.30, N: 4.90.

Method B[14]**:** Diphenyldisulphide (1.44 g, 6.6 mmol) and tributylphosphine (700 µl, 2.8 mmol) were added successively, at 20°C, to a solution of oxime (2.0 mmol) in dry pyridine (8.0 ml). The reaction mixture was stirred for 5 min., then poured into 5% aqueous potassium carbonate (100 ml). Extraction with a 4/1 pentane / dichloromethane mixture (2 x 50 ml), drying over sodium sulphate and evaporation of the solvant under reduced pressure afforded the corresponding S-phenyl sulphenylimine. The following compounds were prepared according to this procedure:

N-(1,7,7-Trimethyl-bicyclo[2.2.1]heptan-2-ylidene) benzenesulfenamide 49. Obtained as a colourless oil following silica gel chromatography (eluent: petroleum ether / benzene - 80/20) and used as such; yield: 75 %; IR (cm^{-1}): 1630, 1475, 1440, 1385, 1030, 690 (solution in CCl4); n.m.r. ^{1}H: 7.53 (2H, m), 7.35 (2H, m), 7.19 (1H, m), 2.50 (1H, m), 2.04 (1H, t, J = 4.2 Hz), 1.83-2.00 (2H, m), 1.73 (1H, td, J = 12.1 Hz, J' = 3.6 Hz), 1.47 (1H, td, J = 8.8 Hz, J' = 3.6 Hz), 1.28 (1H, m), 1.10 (3H, s), 0.96 (3H, s), 0.79 (3H, s); n.m.r. ^{13}C: primary: 11.1, 19.1, 19.7; secondary: 27.5, 32.2, 39.5; tertiary: 44.7, 124.5 (2C), 125.4, 128.8 (2C); quaternary: 48.6, 56.5, 139.8, 181.2.

N-(3β-Acetoxy-androst-5-en-17-ylidene) benzenesulfenamide 43. Obtained as white crystals following chromatography over neutral alumina (eluent: petroleum ether / dichloromethane / ether - 70/20/10); yield: 68 %; m.p.= 165-7°C (lit[14].m.p. 163-5°C); IR (cm^{-1}; solution in CCl_4): 1730, 1630, 1480, 1440, 1370, 1365, 1240, 1030; n.m.r. ^{1}H: 7.49 (2H, m), 7.32 (2H, m), 7.13 (1H, m), 5.39 (1H, d, J = 4.6 Hz), 4.61 (1H, m), 2.29-2.45 (4H, m), 1.85-2.16 (4H, m), 2.02 (3H, s), 1.40-1.71 (7H, m), 1.02-1.38 (3H, m), 1.05 (3H, s), 0.91 (3H, s); n.m.r. ^{13}C: primary: 16.3, 19.4, 21.4; secondary: 20.6, 23.9, 27.8, 31.3, 32.0, 33.7, 37.0, 38.2; tertiary: 31.6, 50.3, 53.9, 73.8, 122.1, 124.6 (2C), 125.5, 128.7 (2C); quaternary: 36.8, 47.7, 139.7, 140.0, 170.5, 182.1; microanalysis (%): Calc.: C: 74.10, H: 8.06, N: 3.20 for $C_{27}H_{35}NO_2S$. Found: C: 74.04, H: 8.22, N: 3.11.

Ring opening of aryl-sulphenylimines derived from cyclobutanones: 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 (2.4 mmol.) in deoxygenated cyclohexane (6 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:

2,3-Dihydro-1H-indene-1-acetonitrile 9.[21] Purified by silica gel chromatography (eluent: petroleum ether / dichloromethane - 100/0 to 80/20); yield: 89 %; IR (cm^{-1}): 2230, 1475, 1455, 750; n.m.r. ^{1}H: 7.22 (4H, m), 3.47 (1H, m), 2.94 (2H, m), 2.71 (1H, dd, J = 6.1 Hz, J' = 16.7 Hz), 2.54 (1H, dd, J = 7.6 Hz, J' = 16.7 Hz), 2.45 (1H, m, J = 5.6 Hz, J' = 7.7 Hz, J" = 7.8 Hz, J"' = 13.1 Hz), 1.88 (1H, m, J = 6.9 Hz, J' = 7.0 Hz, J" = 8.4 Hz, J"' = 13.1 Hz).; n.m.r. ^{13}C: 143.8, 143.4, 127.8, 126.8, 124.9, 123.5, 118.8, 41.5, 31.9, 31.0, 23.0. A small amount (4%) of cis-2,3-Dihydro-1-methyl-1H-indene-2-carbonitrile **10** could also be isolated ; IR (cm^{-1}): 2230, 1475, 1455, 750; n.m.r. ^{1}H: 7.22 (4H, m), 3.42 (1H, m), 3.27 (2H, m), 2.50 (1H, m), 1.43 (3H, d, J = 7.0 Hz); n.m.r. ^{13}C: 145.1, 143.8, 127.6, 127.5, 124.6, 123.8, 118.8, 53.4, 41.3, 35.9, 17.3.

(1R-trans)-1-Methyl-4-(1-methylethyl)-2-cyclohexene-1-acetonitrile 19. Purified by silica gel chromatography, (eluent: petroleum ether / dichloromethane - 90/10); yield: 94 %.; IR (cm^{-1}): 2240, 1460, 1360, 805, 740.; n.m.r. ^1H: 5.64 (1H, br. d, J = 10.2 Hz), 5.47 (1H, br. d, J = 10.2 Hz), 2.27 (2H, s), 1.92 (1H, m), 1.37-1.70 (5H, m), 1.13 (3H, s), 0.90 (3H, d, J = 6.8 Hz), 0.87 (3H, d, J = 6.8 Hz); n.m.r. ^{13}C: 132.8, 132.1, 118.3, 41.6, 34.6, 34.5, 31.9, 31.7, 26.5, 21.8, 19.7, 19.3; primary: 19.3, 19.7, 26.5; secondary: 21.8, 31.7, 34.6; tertiary: 31.9, 41.6, 132.1, 132.8; quaternary: 34.5, 118.3; HRMS: Calc.: 177.1517 for $C_{12}H_{19}N$. Found: 177.1510.

[1R-(2endo,6exo)]-2,6-Dimethyl-bicyclo[3.2.1]octane-6-acetonitrile 15. Purified by silica gel chromatography, (eluent: petroleum ether / dichloromethane - 80/20); yield: 73 %; IR (cm^{-1}): 2230, 1465, 1450; n.m.r. ^1H: Mixture of two diastereoisomers, ratio 1.8/1: Major product: 2.47 (2H, s), 1.90-2.10 (2H, m), 1.25-1.76 (8H, m), 1.23 (3H, s), 0.84-1.12 (1H, m), 0.75 (3H, d, J = 6.4 Hz); Minor product: 2.31 (2H, s), 1.90-2.10 (2H, m), 1.25-1.76 (8H, m), 1.27 (3H, s), 0.84-1.12 (1H, m), 0.75 (3H, d, J = 6.4 Hz).

n.m.r. ^{13}C:	Major product	Minor product
Primary:	20.2, 30.0	20.8, 30.0
Secondary:	25.3, 27.7, 28.3, 37.2, 39.2	25.3, 27.7, 28.0, 37.2, 39.3
Tertiary:	36.2, 41.6, 43.3	36.3, 41.8, 42.8
Quaternary:	32.6, 119.6	32.6, 119.3

Microanalysis (%): Calc.: C: 81.29, H: 10.80 for $C_{12}H_{19}N$. Found: C: 81.60, H: 10.76.

(S)-β,β,4-Trimethyl-3-cyclohexene-1-propanenitrile 14. Purified by silica gel chromatography (eluent: petroleum ether / dichloromethane - 80/20; Yield: 20 %); IR (cm^{-1}): 2240, 1470, 1370.; n.m.r. ^1H: 5.36 (1H, br. s), 2.28 (2H s), 1.90-2.09 (3H, m), 1.65-1.87 (2H, m), 1.64 (3H, s), 1.15-1.58 (2H, m), 1.05 (3H, s), 1.02 (3H, s); n.m.r. ^{13}C: primary: 23.3, 24.2, 24.5; secondary: 24.1, 26.5, 29.2, 31.2; tertiary: 42.0, 120.3; quaternary: 35.3, 118.8, 134.2; microanalysis (%): Calc.:C: 81.29, H: 10.80 for $C_{12}H_{19}N$. Found: C: 81.41, H: 10.80.

[1S-(1α,2β,5α)]-2,6,6-Trimethyl-bicyclo[3.1.1]heptane-2-acetonitrile 22. Purified by silica gel chromatography, (eluent: petroleum ether / dichloromethane - 100/0 to 80/20); yield: 40 %.; IR (cm^{-1}): 2230, 1460, 1380.; n.m.r. ^1H: 2.52-2.40 (2H, AB, J = 16.7 Hz), 2.26 (1H, m), 1.80-1.94 (4H, m), 1.64 (2H, m), 1.25 (3H, s), 1.21 (1H, s), 1.18 (3H, s), 1.04 (3H, s); n.m.r. ^{13}C: 119.0, 51.5, 40.7, 39.4, 37.4, 31.0, 29.7, 28.7, 28.1 (2C), 25.5, 23.9; primary: 23.9, 28.1, 29.7, secondary: 25.5, 28.1, 28.7, 31.0; tertiary: 40.7, 51.5; quaternary: 37.4, 39.4, 119.0; microanalysis (%): Calc.: C: 81.29, H: 10.80 for $C_{12}H_{19}N$. Found:C: 81.07, H: 10.58.

trans-1-Methyl-4-(1-methylethenyl)-cyclohexaneacetonitrile 23. Purified by silica gel chromatography (eluent: petroleum ether / dichloromethane - 100/0 to 80/20); yield: 54 % from **13**; 19 % from **31** (tin hydride addition over 5 hrs); 50 % from **31** (tin hydride addition over 12 hrs); IR (cm^{-1}): 2230, 1640, 1460, 1440, 1380, 885; n.m.r. ^1H: 4.71 (2H, s), 2.22 (2H, s), 1.83 (1H, tt, J = 3.2 Hz, J = 11.4 Hz), 1.73 (3H, s), 1.57-1.71 (4H, m), 1.34-1.46 (4H, m), 1.08 (3H, s); n.m.r. ^{13}C: 149.9, 118.2, 108.6, 44.9, 37.0 (2C), 33.5, 32.9, 27.1 (2C), 22.1, 21.0; primary: 21.0, 22.1; secondary: 27.1 (2C), 33.5, 37.0, 108.6; tertiary: 44.9; quaternary: 32.9, 118.2, 149.9; microanalysis (%): Calc.: C: 81.29, H: 10.80 for $C_{12}H_{19}N$. Found: C: 81.30, H: 10.76.

[1R-(1α,3α,6α)]-3,7,7-Trimethyl-bicyclo[4.1.0]heptane-3-acetonitrile 28. Silica gel chromatography (eluent: petroleum ether/dichloromethane - 100/0 to 80/20); yield: 70 % from **31** (tin hydride addition over 5 hrs); 42 % from **31** (tin hydride addition over 12 hrs); IR (cm^{-1}): 2240, 1450, 1425, 1375; n.m.r. ^1H: 2.31-2.39 (2H, AB system, J = 16.9 Hz), 1.72-1.83 (2H, m), 1.65 (1H, dd, J = 7.6 Hz, J' = 15.3 Hz), 1.38 (1H, dddd, J = 1.5 Hz, J' = 2.5 Hz, J'' = 8.0 Hz, J''' = 14.2 Hz), 1.01 (3H, s), 0.98 (3H, s), 0.87-0.89 (2H, m), 0.91 (3H, s), 0.62 (1H, ddd, J = 4.9 Hz, J' = 9.4 Hz, J'' = 14.2 Hz), 0.50 (1H, t, J = 8.7 Hz); n.m.r. ^{13}C: 118.9, 32.5, 31.1, 30.8, 29.0, 28.2, 25.8, 17.7, 17.5, 17.0, 15.7, 15.0; primary: 15.0, 17.0, 17.7; secondary: 15.7, 25.8, 30.8, 32.5; tertiary: 28.2, 29.0; quaternary: 17.5, 31.1, 118.9; H.R.M.S.: Calc.: 177.1517 for $C_{12}H_{19}N$. Found: 177.1511.

Ring opening of S-phenyl-sulphenylimines 8 and 18 in the presence of methyl acrylate. General procedure: The sulphenylimine (2.0 mmol), AIBN (0.2 mmol), and methyl acrylate (5 equivalents) were dissolved in deoxygenated cyclohexane (16 ml). The reaction mixture was heated to reflux and freshly prepared tributylstannane (650 µl, 2.4 mmol.) was added dropwise over 4 hrs.with the aid of a syringe pump. 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:

Methyl trans-1-cyanomethyl-2,3-dihydro-1H-indene-2-propanoate 36. Purified by silica gel chromatography (eluent: petroleum ether / dichloromethane / ether - 50/50/0 then 50/45/5; Yield: 70 %; IR (cm^{-1}): 2240, 1730, 1435, 1200, 750.; n.m.r. ^1H: 7.23 (4H, m), 3.70 (3H, s), 3.09-3.25 (2H, m), 2.65-2.75 (2H, ABX system, J = 5.9, 6.5, and 16.0 Hz), 2.60 (1H, m), 2.45 (2H, m), 2.23 (1H, m), 2.06 (1H, m), 1.77 (1H, m); n.m.r. ^{13}C: primary: 51.7; secondary: 21.8, 29.4, 32.3, 37.1; tertiary: 45.0, 46.7, 123.5, 124.9, 126.9, 127.8; quaternary: 118.5, 142.1, 142.5, 173.5.

Methyl [1R-(1a,3aα,6a,7aα)] and [1S-(1a,3aα,6β,7aβ)]-6-(cyanomethyl)octahydro-3,3,6-trimethyl-1H-indene-1-carboxylate 38 . Purified by silica gel chromatography (eluent: petroleum ether/dichloromethane/ether - 50/50/0 to 0/50/50); yield: 76 %; IR (cm^{-1}): 2240, 1725, 1460, 1435, 1170, 730; n.m.r. ^1H: two isomers, ratio 70/30: Major product: 3.68 (3H, s), 2.66 (1H, q, J = 8.1 Hz), 2.45 (1H, m), 2.22-2.28 (2H, AB, J = 15.6 Hz), 1.82 (1H, dd, J = 8.2 Hz, J' = 13.0 Hz), 1.15-1.72 (8H, m), 1.14 (3H, s), 1.03 (3H, s), 0.92 (3H, s); Minor product: 3.68 (3H, s), 2.98 (1H, t, d, J = 7.3 Hz, J = 12.0 Hz), 2.38 (1H, m), 2.29-2.35 (2H, AB, J = 17.0 Hz), 1.98 (1H, t, J = 12.5 Hz), 1.75 (1H, m), 1.21-1.68 (7H, m), 1.09 (3H, s), 1.08 (3H, s), 0.99 (3H, s); n.m.r. ^{13}C: Major product: 176.9 (15), 118.4 (11), 51.9 (16), 48.3 (9), 47.9 (6), 44.1 (8), 41.9 (7), 39.7 (2), 39.5 (1), 35.1 (4), 32.6 (3), 30.6 (10), 29.6 (14), 27.5 (12), 24.5 (13), 19.6 (5); Minor product: 174.2 (15), 118.3 (11), 51.6 (16), 46.4 (6), 45.8 (9), 41.4 (8), 39.8 (1), 39.4 (7), 34.0 (4), 33.3 (2), 33.0 (12), 32.4 (3), 30.0 (13), 28.2 (14), 26.3 (10), 20.3 (5); M.S.: 263 ($M^{+\bullet}$), 248 (M - CH_3), 232 (M - CH_3O), 223 (M - CH_2CN or M - 2 x CH_3), 204 (M - $COOCH_3$), 188 and 128.

[1R-(1a,3aα,6a,7aα)]-6-(cyanomethyl) octahydro-3,3,6-trimethyl-1H-indene-1-carboxylic acid 39: A solution of ester **38** (110 mg, 0.42 mmol) in anhydrous methanol (6 ml) containing potassium carbonate (174 mg, 1.26 mmol) and methyl formate (50 mg, 0.84 mmol) was refluxed for 48 hrs. The solvent was evaporated and the residue taken-up in dichloromethane (20 ml). The organic layer was extracted with water (2 x 30 ml). The aqueous layer acidified with dilute (1N) hydrochloric acid. and extracted with dichloromethane (3 x 20 ml). The organic layer was dried over sodium sulfate and evaporated to dryness; yield: 100 %; IR (cm^{-1}): 3060, 2260, 1720, 1475, 1435, 1300, 1225; n.m.r. ^1H: 2.70 (1H, m), 2.49 (1H, m), 2.22-2.28 (2H), 1.83 (1H, dd, J=12.9 & 8.7Hz), 1.72 (1H, dd, J=12.9 & 9.3Hz), 1.68 (1H, dd, J=14.1 & 5.9Hz), 1.64 (1H, m), 1.50-1.57 (2H, m), 1.44 (1H, dd, J=14.1 & 9.1Hz), 1.23-1.36 (2H, m), 1.14 (3H, s), 1.04 (3H, s), 0.93 (3H, s); n.m.r. ^{13}C: 182.7 , 118.4 , 48.2 , 48.0 , 43.8 , 42.0, 39.7, 39.5, 35.0, 32.6, 30.8, 29.6, 27.4, 24.5, 19.6; HRMS: Calc: 249.1728 for $C_{15}H_{23}NO_2$. Found: 249.1729.

Ring opening of aryl-sulphenylimines derived from cyclopentanones: Aryl-sulphenylimine (2.0 mmol) and AIBN (0.1 mmol) were dissolved in deaerated cyclohexane (10 ml). The reaction mixture was heated to reflux and a solution of freshly prepared tributylstannane (2.4 mmol.) in deaerated cyclohexane (6 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. Compound **50** has already been described.[22]

(13α-Methyl) 3β-acetoxy-17-imino-androst-5-ene 44 and (13α-methyl) 3β-hydroxy-androst-5-en-17-one 45. Compound 44 was obtained after purification by silica gel chromatography (eluent: dichloromethane / ether - 100/0 to 0/100); yield: 86 %; IR (cm^{-1}): 1730, 1650, 1470, 1460, 1230, 1030, 905.; n.m.r. ^1H: 7.20 (1H, br. s), 5.39 (1H, br. s), 4.60 (1H, m), 0.91-2.60 (19H,m), 2.00 (3H, s), 0.98 (3H, s), 0.85 (3H, s); n.m.r. ^{13}C: primary and tertiary: 121.9, 73.6, 52.6, 48.3, 33.4, 27.8, 21.3, 18.9; secondary: 37.7, 36.5, 32.8, 32.4, 32.3, 27.4,23.0,21.9; quaternary: 193.8, 170.3, 138.9, 47.5,36.6; M.S. 330, 329, 286, 270; Compound **45** was obtained by acidic hydrolysis of **44**: a solution of **44** (70 mg) in a mixture of methanol (10 ml) and 2N hydrochloric acid (3 ml) was heated under reflux for 2 hrs. Usual work-up gave the corresponding ketone **45** which was crystallised from pentane; yield: 82 %; m.p. 179-182°C, $[\alpha]_D$ -161° ($CHCL_3$); (lit.[16] 180-4°C, $[\alpha]_D$ -162°).

References and notes:

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