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# Iminyl, Amidyl, and Carbamyl Radicals from O-Benzoyl Oximes and O-Benzoyl Hydroxamic Acid Derivatives.

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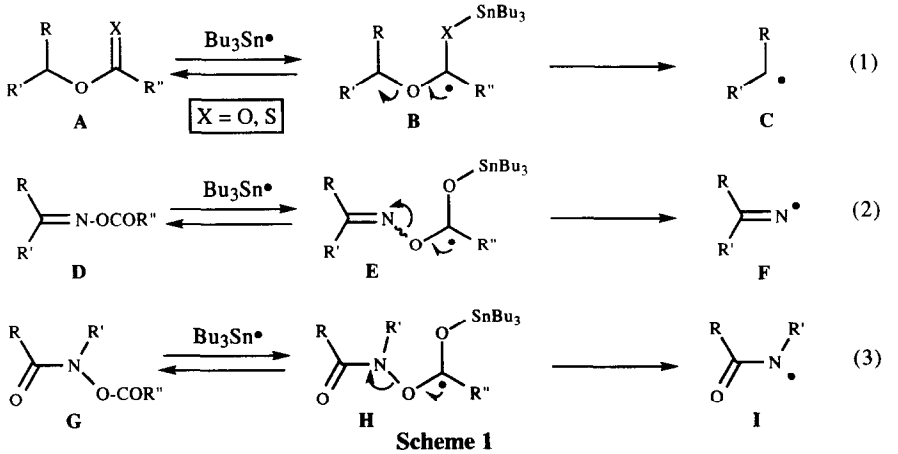
***Abstract***: Oxime benzoates and O-benzoyl hydroxamic acid derivatives react with tributylstannane in the presence of AIBN to give iminyl, amidyl, and carbamyl radicals which can be captured by an internal olefin.

The last decade has witnessed an impressive growth in the development and use of radical processes in organic synthesis.[1] Much of the effort in this area has centered on the creation of C-C bonds using carbon centered radicals. In comparison, nitrogen radicals have not so far attracted the attention they deserve[2], probably because the main precursors, namely N-halo-derivatives, are frequently difficult to prepare and handle, and often display undesirable oxidising properties, especially in the context of complex or fragile molecules. Recently, we[3] and others[2,4] have introduced mild and fairly general methods for the generation of various nitrogen centered radicals. We have in particular shown that iminyls, whose reactivity was the subject of some confusion, undergo in fact clean intramolecular addition reactions to give a variety of pyrrolenine derivatives. Nevertheless, further simple methods to access these species are still needed. As part of a wider study in this area, we found that iminyl, amidyl, and carbamyl radicals can be easily produced by the action of tributylstannane from the corresponding O-acyloximes[3d] and O-acylhydroxamic acids[3f] respectively. In this paper, we wish to give a full account of our work.

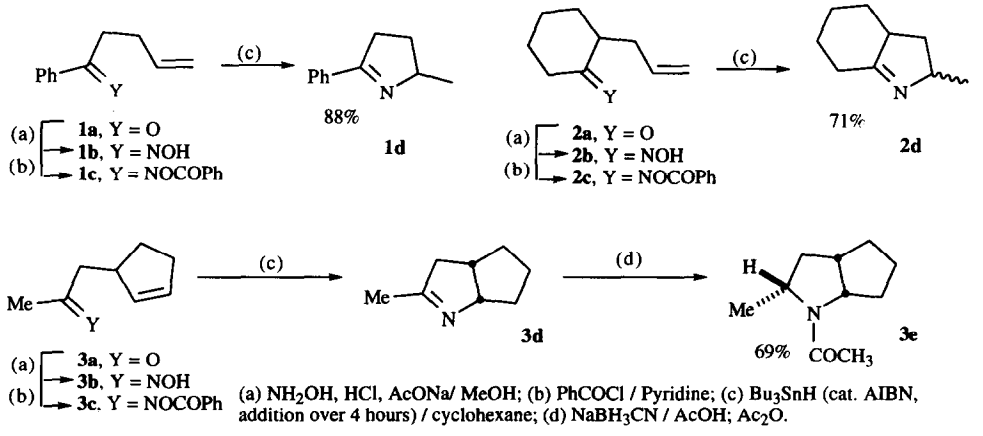



**Scheme 1**

The addition of tributylstannyl radicals to the oxygen of a carbonyl group is well precedented; it has found elegant applications in synthesis, especially when the transient carbon radical thus produced is adjacent to the strained bond of a cyclopropyl or an epoxide ring.[5]

The reaction of ordinary esters with tributylstannane, even though first reported by Koo and Lee more than a quarter of a century ago,[6] has not proved, as a method for deoxygenating alcohols, as powerful as the Barton-McCombie reaction which uses xanthates and other thiocarbonyl derivatives.[7] The reason lies in the much lower reactivity of a carbonyl unit towards tin radicals as compared with a thiocarbonyl group, thus causing the equilibrium in equation 1 (Scheme 1) to shift much more to the left in the former case than in the latter. The consequence of a lower concentration of the intermediate adduct radical **B** is a slower fragmentation rate; hence a shorter chain length. and a rather inefficient overall process. The deoxygenation via carboxylic esters is thus only practical when the final radical produced enjoys special stabilisation (e.g. by resonance), the fragmentation step becoming as a result reasonably rapid. In the case of esters of oximes and hydroxamic acids, it may be argued that the weakness of the N-O bond should also strongly favour the fragmentation step and therefore compensate for a not very effective initial addition of stannyl radicals to the carbonyl group (equations 2 and 3). A recent decarboxylation process using esters of N-hydroxyphthalimide described by Barton and his collaborators[8] presumably hinges on the same effects.

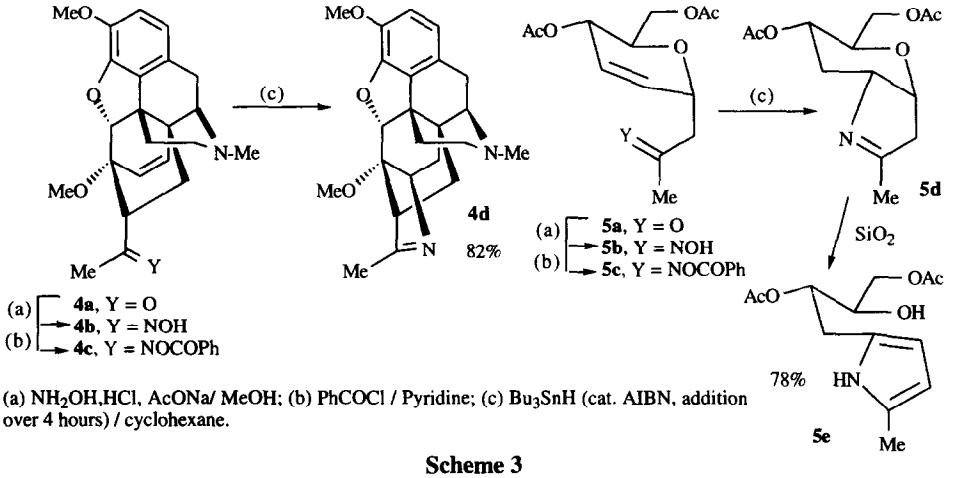
In practice, slow addition of tributylstannane and AIBN to a refluxing solution of oxime benzoate **1c** in deoxygenated cyclohexane produced the expected pyrrolenine **1d** in excellent yield (88%) through capture of the intermediate iminyl radical by the internal olefin. In line with earlier observations[6a], the corresponding acetate was much less reactive towards the stannane so we only used oxime benzoates in our study as shown by the additional examples pictured in schemes 2-5.




**Scheme 2**

Thus, benzoate **2c** derived from 2-allylcyclohexanone gave pyrrolenine **2d** in 71% yield as a 60:40 mixture of diastereomers (Scheme 2). In the same way, compound **3c** afforded derivative **3d** which in this case was reduced *in situ* with sodium cyanoborohydride and acetylated to give finally amide **3e** in 69% yield as one isomer since the reduction takes place from the least hindered exo face. The efficient

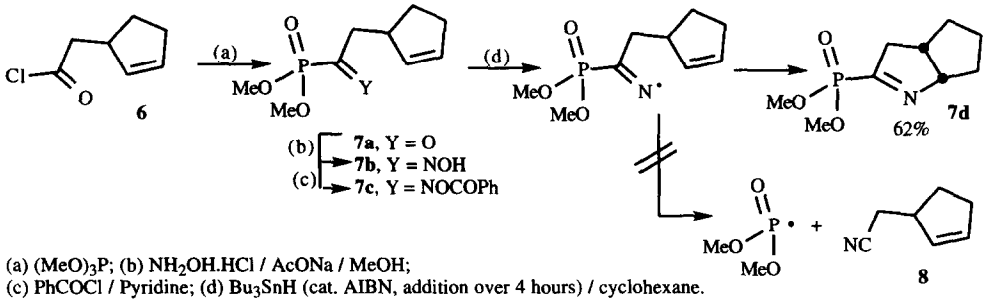
cyclisation of the much more complex derivative of thevinone **4a**, obtained through cycloaddition of methyl vinyl ketone with thebaine[9], could also be accomplished by the same procedure. The polycyclic product **4d**, isolated in 82% yield, was accompanied by a small amount (8%) of starting oxime **4b**. The sugar derivative **5c**, easily accessible from tri-0-acetyl glucal[10] also cyclised smoothly; however, on attempted purification on silica, the primary product **5d** underwent elimination and aromatisation to pyrrole **5e** in 78% overall yield. The reduction of **5c** under these conditions emphasises the fact that only the oxime benzoate is cleaved by the stannyl radicals; the other ester groups are not affected.




(a) $NH_2OH.HCl$, AcONa/ MeOH; (b) PhCOCl / Pyridine; (c) $Bu_3SnH$ (cat. AIBN, addition over 4 hours) / cyclohexane.

**Scheme 3**

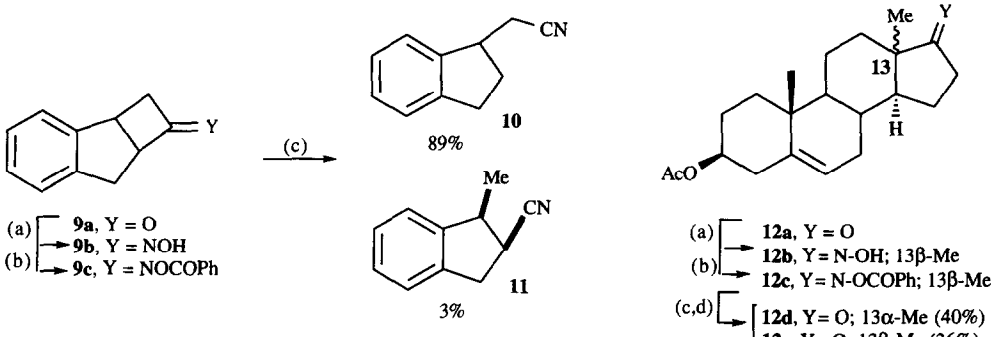
An interesting type of oxime benzoate which also turned out to be a good substrate for the cyclisation is exemplified by compound **7c**, obtained by Arbusov reaction of acid chloride **6** with trimethyl phosphite[11], followed by oximation and benzoylation. We feared in this case that the intermediate iminyl radical would undergo ß-scission to nitrile **8** faster than the desired cyclisation. Fortunately, this did not happen and pyrrolenine **7d** was isolated in 62% yield along with a little (3%) oxime **7b**. It is worthy of note that a compound such as **7d** would be an immediate precursor to the phosphonate analogue of the proline type aminoacid present in Ramipril®[12], a potent inhibitor of Angiotensin Converting Enzyme (ACE).




(a) $(MeO)_3P$; (b) $NH_2OH.HCl$ / AcONa / MeOH;
(c) PhCOCl / Pyridine; (d) $Bu_3SnH$ (cat. AIBN, addition over 4 hours) / cyclohexane.

**Scheme 4**

β-Scission of strained iminyl radicals can be a useful synthetic transformation as we[3b,c, e] and others[13] had shown earlier. For example, under the usual reaction conditions, benzoate **9c** was converted into nitrile **10** in high yield (89%); a small quantity (3%) of isomeric nitrile **11** was also isolated, arising from opening to the less stable intermediate primary carbon radical. The present method however appears to be less effective than our previous processes[3b, e] for accomplishing the epimerisation of the 13-position of steroids through opening and reclosure of the D-ring of iminyls derived from 17-ketosteroids. The reaction of benzoate **12c** with tributylstannane gave 13-episteroid **12d** in only 40% yield. The natural isomer **12e** was the other major product (36%). A small amount (6%) of a mixture of both 3ß-hydroxyketones was also isolated.

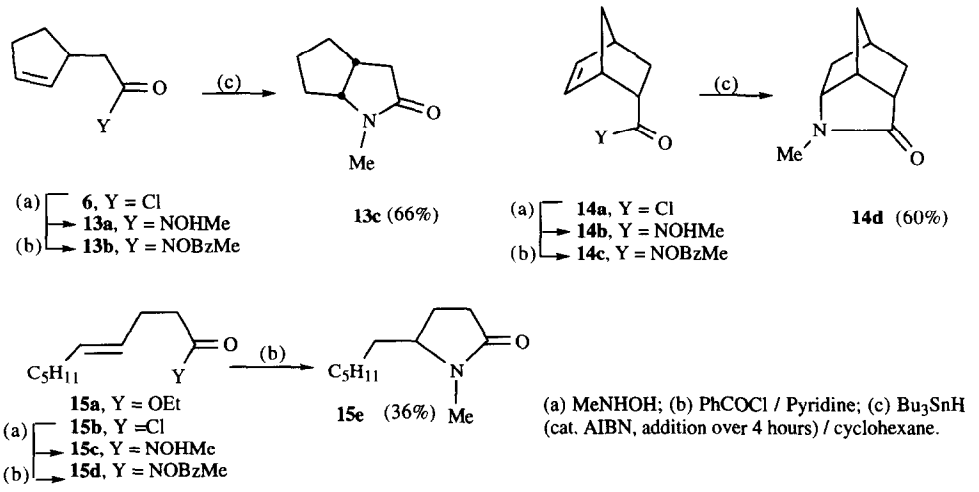



(a) $NH_2OH.HCl$, AcONa/ MeOH; (b) PhCOCl / Pyridine; (c) $Bu_3SnH$ (cat. AIBN, addition over 4 hours) / cyclohexane; (d) AcOH, $H_2O$

**Scheme 5**

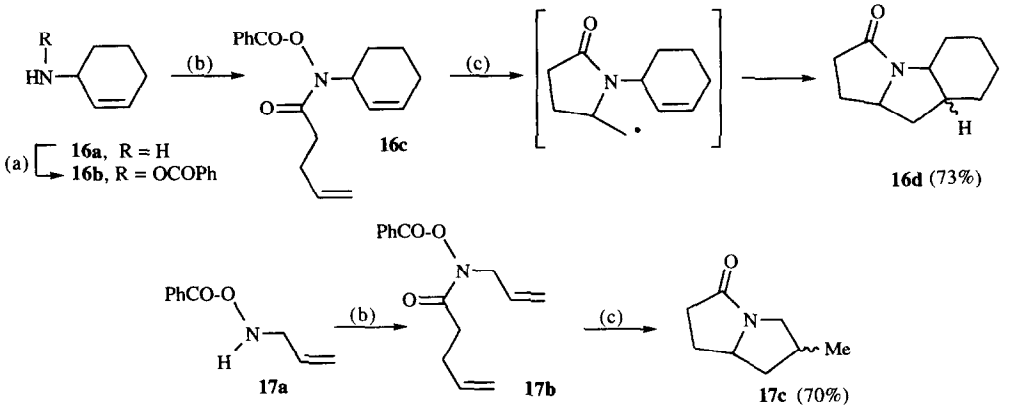
The formation of small amounts of undesired starting oxime in some of these reactions (i.e.**4a** ---> **4b**, **7c** ---> **7b**) is almost certainly due the ability of tin salts to catalyse transesterification (or hydrolysis) processes[14] and to the somewhat activated nature of oxime esters in general. As for the recovery of unwanted natural ketone (**12c** ---> **12e**), it may be ascribed to the increase in the concentration of $Bu_3SnH$ as a result of the relative low reactivity of stannyl radicals towards the carbonyl group of the ester as discussed above. The relatively short chains cause a build up of stannane concentration and allows for premature quenching of the intermediate iminyl radical before opening of ring D has occured.

The preparation of O-benzoyl derivatives of hydroxamic acids needed to test the second part of our proposal (Scheme 1, equation 3) was readily accomplished either by treatment of the corresponding alkenoyl chloride with N-methylhydroxylamine followed by benzoylation or by oxidation of an allylic amine with dibenzoylperoxide[15] followed by acylation of the resulting N-alkenyl hydroxylamine with a suitable alkenoyl chloride. Slow addition of tributylstannane and AIBN to a refluxing solution of benzoate **13b** in deoxygenated cyclohexane smoothly produced bicyclic lactam **13c** in 66% yield through capture of the intermediate amidyl radical by the internal olefin. The same reaction was readily applied to benzoates **14c**, **15d**, and **16b** which afforded the expected lactams **14d** and **15e** in 60% and 36% yield respectively (Scheme 6).




**Scheme 6**

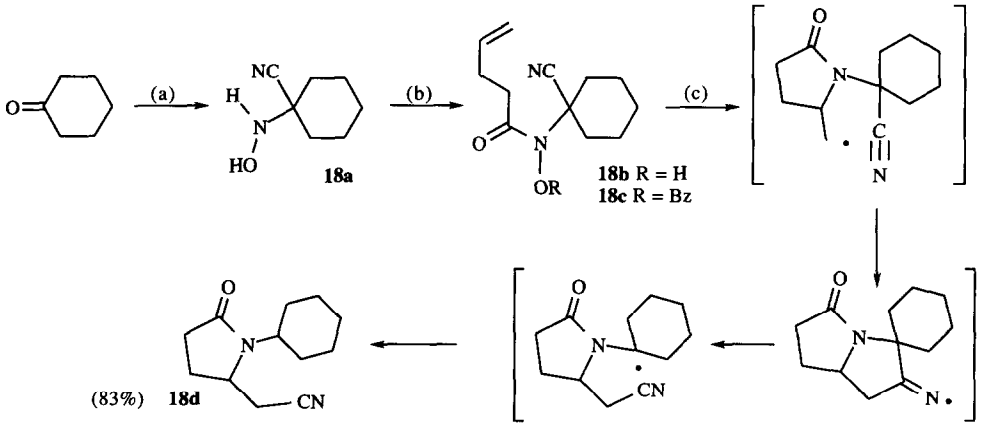
The amidyl radicals were easily incorporated in a number of cascade reactions (Scheme 7). For example, benzoate **16c** gave tricyclic lactam **16d** in 73% yield as an essentially 1:1 mixture of diastereoisomers when it was exposed to tributylstannane under similar conditions. In the same way, compound **17b**, derived from allylamine, afforded lactam **17c** as a 2:1 mixture of epimers in comparable yield (70%). This compound had been prepared by Esker and Newcomb[4a] using an identical sequence but a different amidyl radical precursor (see also ref. 16 for an alternative synthesis).




**Scheme 7**

A more interesting sequence took place with benzoate **18c**. This precursor was easily assembled from cyclohexanone, through reaction with hydroxylamine hydrochloride and sodium cyanide to give hydroxylamine **18a**,[17] followed by acylation with 4-pentenoyl chloride and benzoylation. Slow addition

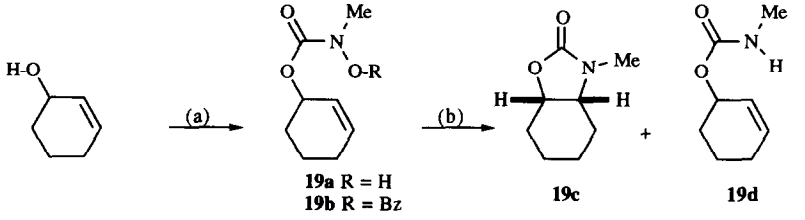
of tributylstannane resulted in the formation of nitrile **18d**, isolated as a crystalline solid in 83% yield. As depicted in Scheme 8, the formation of this compound implies an efficient transfer of the nitrile group,[13] through a transient iminyl radical, after the initial cyclisation of the amidyl radical.




(a) $NH_2OH.HCl$ / NaCN / $H_2O$; (b) 4-pentenoyl chloride / Pyridine; PhCOCl / Pyridine
(c) $Bu_3SnH$ (cat. AIBN, addition over 4 hours) / cyclohexane.

**Scheme 8**

This approach to amidyl radicals could be easily extended to the closely related carbamyl radicals. These species have hardly been studied in the past, and little is known about their reactivity, especially concerning their propensity to undergo 5-exo cyclisations.[18] In fact we are not aware of any example of such a reaction. Starting from 2-cyclohexenol, we therefore prepared the required O-benzoyl-N-hydroxyurethane **19b** by treating the corresponding imidazolide with N-methyl hydroxylamine followed by benzoylation. Slow addition of tributylstannane and a catalytic amount of AIBN to a refluxing solution of **19b** in cyclohexane produced the desired cyclic carbamate **19c**, along with uncyclised material **19d** in a ratio of 40 / 60. The isolated yield of **19c** was however only 20%. The cyclisation step is clearly slower than in the amidyl case but, nevertheless, its success opens the way to the synthesis of cyclic amino alcohols of controlled relative stereochemistry. Important compounds of this type include the aminocyclitols, conduramines, aminocyclopentitols (e.g. the mannostatins) etc.., some of which are potent glycosidase inhibitors.[19]




(a) Carbonyl diimidazole; MeNHOH.HCl / $Et_3N$ / THF; PhCOCl / Pyridine;
(b) $Bu_3SnH$ (cat. AIBN, addition over 4 hours) / cyclohexane.

**Scheme 9**

These new routes to aminyl, amidyl and carbamyl radicals (and other nitrogen centered radicals we have not yet been able study) have the merits of simplicity, mildness, and efficiency. This should allow the conception of novel strategies for the construction of nitrogen containing natural products, especially alkaloids and related substances.

*Acknowledgement* : We wish to thank Rhône-Poulenc Rorer for very generous financial support.

## Experimental Section

All reactions were performed under inert atmosphere (nitrogen or argon)."Usual work-up" involves washing the organic layer successively with water until neutrality, with brine, and drying over sodium sulfate followed by filtration and evaporation of the solvent to dryness under reduced pressure. Melting points were determined with a Köfler or a Reichert hot stage apparatus. $^{1}H$ and $^{13}C$ n.m.r. spectra are for deuteriochloroform solutions with tetramethylsilane as internal standard ($\delta$ ppm). I.R. spectra are for neat films 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. 1-Phenyl-4-penten-1-one **1a**,[20] 2-allylcyclohexanone **2a**,[21] thevinone **4a**,[9] cyclobutanone **9a**,[22] dimethoxy-1-oxo-2-cyclopentene-1-methyl phosphonate **7a**,[11] and ketone **5a** [10] were prepared according to literature procedures.

**2-Cyclopentene-1-acetone 3a.** Methyl lithium (1.6 M solution in ether, 31.1 ml, 3 equivalents) was added dropwise to a cold solution (-78°C) of cyclopenteneacetic acid in ether (8 ml). The reaction mixture was stirred for 30 min. at -78°C, then allowed to warm to -20°C and left under stirring for 30 min. The reaction mixture was diluted with ether (50 ml) and poured into an aqueous saturated solution of ammonium chloride (30 ml). The usual work-up afforded an oily residue which was purified by silica gel chromatography (ether / petroleum ether -1 / 9) to give the title compound **3a** as a colourless oil which was used as such in the next step. Yield: 57 %; IR ($cm^{-1}$):1715; n.m.r.$^{1}H$:5.78-5.50 (m, 2H); 3.11-2.98 (m, 1H); 2.56-2.20 (m, 4H); 2.12 (s, 3H); 1.30-1.50 (m, 2H); n.m.r.$^{13}C$: 208.3; 139.85; 131.12; 49.81; 40.91; 32.02; 30.14; 29.75.

### *General procedure for the preparation of oxime benzoates.*

To a solution of ketone (10 mmol) in methanol (20 ml), sodium acetate (1.1 equiv.) and hydroxylamine hydrochloride (1.1 equiv.) were added successively. The mixture was stirred at 20°C until completion of the reaction, as judged by T.L.C. (20 min. to 4 days). 2-Allylcyclohexanone oxime **2b** and 3β-acetoxyandrostenone oxime **12b** were precipitated from the reaction mixture by slow addition of water. Other oximes were isolated by extraction with dichloromethane followed by the usual work-up. To a solution of the oximes thus obtained (1.14 mmol.) in a mixture of ether (2 ml) and pyridine (1.3 eq.), benzoyl chloride (1.5 eq.) was added dropwise. After completion of the reaction (± 20 min.), water was slowly added. In cases where the product precipitated, it was collected by filtration and dried. Otherwise, a saturated solution of sodium hydrogencarbonate was added and the reaction mixture was stirred for 2 hrs. Extraction with ether, usual work-up, and coevaporation with toluene (30 ml) then afforded the corresponding oxime benzoate. The following compounds were obtained according to this procedure and used without further purification:

**1-Benzoyloximino-1-phenyl-4-pentene 1c.** Obtained as a yellowish syrup after purification by silica gel column chromatography (eluent: ethyl acetate/petroleum ether 30-70); yield: 94%; n.m.r.$^{1}H$: 8.17-8.10 (m, 3H); 7.82-7.77 (m, 2H); 7.66-7.42 (m, 5H); 5.97-5.75 (m,1H); 5.14-5.01 (m, 2H); 3.07 (t, $J_1$ = 7.4 Hz, 2H); 2.42 (td, $J_1$ = 7.4 Hz, $J_2$ = 7,5 Hz, 2H); n.m.r.$^{13}C$: Secondary: 28.18; 30.88; 116.05; Tertiary: 127.45; 128.43; 128.70; 128.92; 129.64; 130.58 (2C); 130.70; 133.39; 134.59; 136.51; Quaternary: 129.1; 133.92; 163.77; 166.78.

**1-Benzoyloximino-2-(2-propenyl)-cyclohexane 2c.** Obtained as a colourless oil following silica gel column chromatography (eluent: ethyl acetate/ petroleum ether 30-70) in 98% yield; IR ($cm^{-1}$):3072; 2935; 2861; 1747; 1630; 1600; 1450; 1260; 1060; 1024; n.m.r.$^{1}H$: 8.08-8.03 (m, 2H); 7.62-7.38 (m, 3H); 5.92-5.72 (m, 1H); 5.12-5.03 (m, 3H); 2.68-2.56 (m, 3H); 2.40-2.25 (m, 1H); 1.85-1.57 (m, 7H); n.m.r.$^{13}C$: Secondary: 22.7; 25.6; 26.3; 31.6; 35.3; 116.6, tertiary: 41.8; 128.4 (2C); 129.5 (2C); 133.02; 136.1, quaternary: 132.5; 164.1; 171.4.

**2-Benzoyloximino-1-(2-cyclopenten-1-yl)-propane 3c.** Obtained as a colourless oil following silica gel column chromatography (eluent: ether/petroleum ether 3-7) in 89% yield; IR ($cm^{-1}$): 3057; 2945; 1745; 1640; 1450; 1243; 1062; n.m.r.$^{1}H$: 8.70 (d, 7.1 Hz, 2H); 7.61-7.41 (m, 3H); 5.80-5.67 (m, $J_1$ = 2 Hz, 2H); 3.1-2.98 (m, $J_1$ = 2 Hz, $J_2$ = 6.0 Hz, 1H); 2.56-2.21 (m, $J_3$ = 6.6 Hz, $J_4$ = 8.3 Hz, $J_5$ = 13.8 Hz, 4H); 2.12 (s, 3H); 2.15-1.98 (m, $J_4$ = 8.3 Hz, 1H); 1.65-1.49 (m, $J_2$ = 6 Hz, 1H); n.m.r.$^{13}C$: Primary: 15.7, secondary: 29.0; 31.7; 41.5, tertiary: 42.4; 128.3 (2C); 129.3 (2C); 131.45; 132.9; 133.2, quaternary: 163.6; 166.5.

**1-Benzoyloximino-1-[(5α)-4,5-epoxy-6-methoxy-17-methyl-6,14-ethenomorphinan-7-yl]-ethane 4c.** Obtained as a yellowish crystalline mixture of two isomers (ratio 7/3) following silica gel column chromatography (eluent: ether/petroleum ether/methanol/triethylamine 35-60-5- 0.5) in 98% yield; m.p. = 79-82°C; ; IR ($cm^{-1}$): 3050; 2950; 1743; 1600; 1450; 1240; 1060. Major isomer: n.m.r.$^1$H: 8.11-8.05 (m, 2H); 7.60-7.26 (m, 3H); 6.59 (AB system, $J_{AB}$ = 11.5 Hz, 2H); 5.69 (AB system, $J_{AB}$ = 8.7 Hz, 2H); 4.74 (s, 1H); 3.83 (s, 3H); 3.59 (s, 3H); 3.30-3.10 (m, 3H); 2.65-3.39 (m, 3H); 2.37 (s, 3H); 1.9-2.1 (m,1H); 1.98 (s, 3H); 1.12-1.33 (m, 1H); 0.82-0.93 ( m, 1H). Minor isomer: n.m.r.$^1$H: 8.11-8.05 (m, 2H); 7.60-7.26 (m, 3H); 6.61 (AB system, $J_{AB}$ = 11.5 Hz, 2H); 5.69 (AB system, $J_{AB}$ = 8.2 Hz, 2H); 4.71 (s, 1H); 3.83 (s, 3H); 3.53 (s, 3H); 3.30-3.10 (m, 3H); 2.65-3.39 (m, 3H); 2.37 (s, 3H); 1.9-2.1 (m,1H); 2.00 (s, 3H); 1.12-1.33 (m, 1H); 0.82-0.93 ( m, 1H). n.m.r.$^{13}$C: secondary and quaternary: 22.5; 30.6; 31.0; 33.5; 34.0; 45.5; 47.7; 79.9; 141.9; 144.3; 163.7; 167.5; 167.8; primary and tertiary: 13.07; 19.93; 36.32; 42.5; 43.4; 51.92; 52.1; 56.6; 59.9; 92.6; 93.4; 113.7; 119.4; 119.5; 128.1; 128.2; 128.5; 128.7; 129.6; 129.8; 133.2; 135.5; 135.7.

**1-[5-(Acetyloxy)-6-[(acetyloxy)-methyl]-5,6-dihydro-2H-pyran-2-yl]-2'-benzoyloximino-propane (2α,5α,6β) 5c.** A 3/2 mixture of two isomers was obtained as an oil following silica gel column chromatography (eluent: ethyl acetate/ ether/petroleum ether 15-15-70) in quantitative yield; IR ($cm^{-1}$): 3070; 2956; 1745 (ester); 1643; 1450; 1371; 1242; 1080; 1061. Major isomer: n.m.r.$^1$H: 8.07-7.97 (m, 2H); 7.57-7.39 (m, 3H); 5.94-5.78 (m, 2H); 5.15-5.09 (m, 1H); 4.65-4.58 (m, 1H); 4.23-3.96 (m, 3H); 3.05-2.56 (m, 2H); 2.18 (s, 3H); 2.05 (s, 3H); 2.01 (s, 3H). Minor isomer: 8.07-7.97 (m, 2H); 7.57-7.39 (m, 3H); 5.94-5.78 (m, 2H); 5.15-5.09 (m, 1H); 4.65-4.58 (m, 1H); 4.23-3.96 (m, 3H); 3.05-2.56 (m, 2H); 2.19 (s, 3H); 2.04 (s, 3H); 2.01 (s, 3H). n.m.r.$^{13}$C: Primary: 15;94; 20.7; 20.9 , secondary: 34.5; 39.1; 62.68; 62.8, tertiary: 64.7; 66.9; 69.7; 124.8; 125; 128.6; 129.5; 131.7; 131.9; 133.2, quaternary: 129.0; 164.3; 164.7; 170.2; 170.6.

**Dimethyl [1-(Benzoyloxyimino]-2-(2-cyclopenten-1-yl)ethyl]-phosphonate 7c** Obtained as an oil ( 3/5 mixture of two isomers) following .silica gel column chromatography (eluent: ether/petroleum ether 40-60) in 97% yield; IR ($cm^{-1}$): 3050; 2956; 1757; 1600; 1451; 1243; 1038. Major isomer: n.m.r.$^1$H: 8.06-8.02 (m, 2H); 7.68-7.45 (m, 3H); 5.83-5.69 (m, 2H); 3.97 (s, 3H); 3.91 (s, 3H); 3.31-3.22 (m,1H); 2.89-2.65 (m, 2H); 2.44-2.24 (m, 2H); 2.17-2.11 (m, 1H); 1.66-1.55 (m, 1H). Minor isomer: n.m.r.$^1$H: 8.24-8.19 (m, 2H); 7.68-7.45 (m, 3H); 5.83-5.69 (m, 2H); 3.87 (s, 3H); 3.81 (s, 3H); 3.31-3.22 (m,1H); 2.89-2.65 (m, 2H); 2.44-2.24 (m, 2H); 2.17-2.11 (m, 1H); 1.66-1.55 (m, 1H). n.m.r.$^{13}$C:Primary: 53.7 (d, $J_{C\text{-}O\text{-}P}$ = 24 Hz); 52.8 (d, $J_{C\text{-}O\text{-}P}$ = 24 Hz), secondary: 42.5 (d, Jc-p = 22 Hz); 39.1 (d, Jc-p = 60 Hz); 31.4; 31.3; 29.5; 28.8, tertiary: 128.31; 129.2; 129.5; 131.35; 132.72; 132.9; 133.3; 133.32, quaternary: 164.2; 162.4; 162.3; 162; 160.3; 159.04.

**2-Benzoyloximino-1,2a,3,7b-Tetrahydro-2H-cyclobut[α]indene 9c.** Isolated as white crystals (m.p. = 131-4°C, petroleum ether/ethyl acetate/ methanol: 8/1/1) in 93% yield; n.m.r.$^1$H: 7.97 (d, $J_1$ = 7.3 Hz, 2H); 7.60-7.37 (m, $J_1$ = 7.3 Hz, 3H); 7.25 (s, 4H); 4.20-4.10 (td, 1H); 4.08-3.98 (td, $J_3$ = 3 Hz, 1H); 3.61-3.22 ( m, $J_4$ = 17.5 Hz, 3H); 3.03 (dt, $J_4$ = 17.4 Hz; $J_3$ = 3 Hz, $J_4$ = 17.5Hz); n.m.r.$^{13}$C: Secondary:36.96; 40.15, tertiary: 40.5; 47.9; 124.93; 125.34; 127.43; 127.6; 128.45 (2C); 129.6 (2C); 133.2, quaternary: 129.1; 143.2; 144.2; 164; 171.7.

**3β-Acetyloxy-17-Benzoyloximino-androst-5-ene 12c.** Isolated as a colourless syrup following silica gel column chromatography (eluent: ethyl acetate/petroleum ether 4-6) in 95% yield; IR ($cm^{-1}$): 3054; 2985; 1735; 1730; n.m.r.$^1$H: 8.05-8.01(m, 2H); 7.57-7.40 (m, 3H); 5.38 (m, 1H); 4.70-4.50 (m, 1H); 2.78-1.30 (m, 19H); 2.03 (s, 3H); 1.07 (s, 6H); n.m.r.$^{13}$C: 16.83; 19.32; 20.47; 21.35; 23.18; 27.28; 27.71; 31.33; 33.59; 36.7; 36.94; 38.1; 45.13; 50.01; 54.02; 73.72; 121.78; 128.42; 129.48; 132.97; 140.00; 163.93; 170.39; 179.35.

### *General procedure for the generation of iminyls from oxime benzoates.*

The oxime benzoate (1 mmol.) and AIBN (0.1 mmol.) were dissolved in deoxygenated cyclohexane (5 ml) and to the resulting solution, heated under reflux, was slowly added ( 4 hours) tributylstannane (1.2 mmol.) in cyclohexane (5 ml). After cooling to room temperature, the solvent was removed under reduced pressure. The following compounds were obtained according to this procedure:

**3,4-Dihydro-2-methyl-5-phenyl 2-H-pyrrole 1d.** Obtained as a yellowish oil following purification by silica gel column chromatography, (eluent: petroleum ether to petroleum ether / ethyl acetate- 50/50) in 88% yield; IR ($cm^{-1}$): 3051; 2963; 2867; 1614 ( imine ); 1575; 1494; 1447; 1339; 1017; 906; n.m.r.$^1$H: 7.86-7.79 (m, 2H); 7.49-7.26 (m, 3H); 4.38-4.21 (m, J= 6.8 Hz, J' = 6.6 Hz, J''= 7.4 Hz, J'''= 2 Hz, 1H); 3.11 (dddd, J = 17 Hz, J'= 9.8 Hz, J''= 7.7 Hz J'''= 2Hz, 1H); 2.89 (dddd, J = 17 Hz, J' = 9.8 Hz, J'' = 7.7 Hz, J''' = 2 Hz, 1H); 2.25 (dddd, J = 7.4 Hz, J' = 7.7 Hz, 1H); 1.57 (dddd, J = 6.6 Hz, J' = 9.7 Hz, J'' = 9.8 Hz, J''' = 12.7 Hz, 1H); 1.36 (d, J = 6.8 Hz, 3H); n.m.r.$^{13}$C: Primary: 22.17, secondary: 35.26; 30.72, tertiary: 130.32; 128.42 (2C); 127.72 (2C), quaternary: 171.86; 134.74; h.r.m.s.: Calc. for $C_{11}H_{11}N$: 157.08915. Found: 157.08884.

**Cis and trans 3,3a,4,5,6,7-hexahydro-2-methyl-2H-indole 2d.** The inseparable mixture, obtained in 71% yield, was identical to an authentic sample prepared previously[3a]

**5,6,7,8,9a,12,12a,12b-Octahydro-12a-methoxy-7,11-dimethyl-9-H-4,8:8a,12-dimethanobenzofuro[3,2-e]pyrrolo [3,2-g]isoquinoline 4d.** Obtained as a yellowish oil following purification by silica gel column chromatography (eluent: ether /petroleum ether /triethylamine - 30/70/0.5 to methanol / ether / petroleum ether: 10/90) in 82% yield; IR ($cm^{-1}$): 3050; 2933;

1639 (imine); 1502; 1442; 1267; n.m.r.$^1$H: 6.75-6.61 (AB system, $J_{AB}$ = 8 Hz, 2H); 4.90 (s, 1H); 3.8 (s, 3H); 3.42 (s, 3H); 3.17-3.08 (d, 1H); 2.70-1.96 (m, 2H); 2.28 (s, 3H); 2.07 (s, 3H); 1.72-1.62 (m, 3H); 1.30-1.15 (m, 2H); 1.27-0.88 (m, 2H); n.m.r.$^{13}$C: Primary: 19.0; 43.5; 61.3; 62.0, secondary: 21.7; 27.8; 33.2; 45.37, tertiary: 49.7; 53.7; 62.0; 92.3; 114.3; 119.4, quaternary: 38.6; 44.8; 87.5; 128.1; 132.5; 142.6; 147; 181; h.r.m.s.: Calc. for $C_{23}H_{28}N_2O_3$: 380.209444. Found: 380.209887.

**Pyrrole 5e**. Isolated as a colourless, air sensitive, oil following purification by silica gel column chromatography (eluent: ethyl acetate / ether / petroleum ether -5/5/90 to methanol / ether / petroleum ether - 5/80/15) in 78% yield; IR (cm$^{-1}$): 3054; 2986; 1737; 1421; 1039; n.m.r.$^1$H:8.16 (br. s, 1H), 5.85-5.75 (m, 2H); 5.00 (q, J = 5.8 Hz, 1H); 4.23 (dd, $J_2$= 11.8 Hz, $J_3$ = 3 Hz, 1H); 4.09 (dd, J = 11.8 Hz, J' = 6.4 Hz, 1H); 3.92-3.86 (m, J = 3 Hz, J'= 6.4 Hz, 1H); 2.95 (d, J = 5.6 Hz, 2H); 2.76 (br s, 1H); 2.23 (s, 3H); 2.10 (s, 3H); 2.08 (s, 3H); n.m.r. $^{13}$C: Primary: 13.1; 20.8; 21.1; secondary: 29.3; 85.6 , tertiary: 71.0; 74.0; 106.3; 108.0, quaternary: 124.9; 127.4; 170.5; 171.5; m/z: 269 ($M^+$); 209 ($M^+$- AcOH); 149 ($M^+$- 2AcOH).

**Dimethyl (3,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrol-2-yl phosphonate 7d**. Obtained as a yellowish oil following purification by silica gel column chromatography (eluent: ether / petroleum ether - 1/4 to ether / petroleum ether / methanol - 60 / 35 / 5) in 62% yield; IR (cm$^{-1}$): 3054; 2055; 2865; 2241; 1688; 1608; 1450; 1260; 1033; n.m.r.$^1$H: 4.81 (m e, 1H); 3.87 (s, 3H); 3.06 (ddd, J = 18.1 Hz, J' = 8.6 Hz; J" = 1.8 Hz ); 2.80-2.66 (m, 1H); 2.58 (dd, J = 18.1 Hz, J' = 6.2 Hz, 1H); 1.95-1.25 (m, 6H); n.m.r.$^{13}$C: Primary: 53.5; 53.4, secondary: 47.4 (d, $J_{C-P}$ = 122 Hz); 34.7; 32.6 (d, $J_{C-P}$= 12 Hz); 24 .0; tertiary: 82.8 (d, $J_{C-P}$ = 134 Hz); 38.4 (d, $J_{C-P}$ = 24 Hz); quaternary: 171.2 (d, $J_{C-P}$ = 206Hz); h.r.m.s.: Calc. for $C_9H_{16}NO_3P$ ( M+1) Calc.: 218.094598. Found: 218.094058.

**2,3-Dihydro-1H-indene-1-acetonitrile 10**.[3b, 23]. Obtained after silica gel column chromatography (eluent: petroleum ether/dichloromethane- 1/0 to 4/1) in 89% yield; IR (cm$^{-1}$): 2230; 1475; 1455; 750; n.m.r.$^1$H: 7.22 (m, 4H); 3;47 (m, 1H); 2.94 (m, 2H); 2.71 (1H, dd, J = 16.7 Hz); 2.54 (dd, j= 7.6 Hz, 1H); 2.45 (m, J = 5.6 Hz, J' = 7.7 Hz , J"= 7.8 Hz, J'" = 13.1 Hz, 1H); 1.88 (m, J = 6.9 Hz, J' = 7.0 Hz, J" = 8.4 Hz, J'" = 13.1 Hz, 1H); 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 (3%) of **cis-2,3-dihydro-1-methyl-1H-indene-2-carbonitrile 11** [3b] was also isolated

**1-Acetyl-octahydro-2-methyl-(2α,3aβ,6aβ)-cyclopentan[b]pyrrole 3e**. Sodium cyanoborohydride (3 eq.) was added to a solution in tetrahydrofurane (1 ml) of the crude residue obtained from reduction of **3c** by tributylstannane The reaction mixture was stirred for a few minutes at 20°C and acetic acid (1 ml) was then added. After completion of the reduction, as judged by T.L.C., acetic anhydride (3 ml) was added, and the reaction mixture was heated at 40°C for 18 hrs. After cooling and addition of ether (20 ml), the crude reaction mixture was poured into saturated aqueous sodium hydrogen carbonate (50 ml). Extraction with ether and usual work-up afforded the title compound.as a light yellow oil. Purification by silica gel column chromatography (eluent: ether /petroleum ether -4/1 to methanol / ether - 1/9), yield: 62 %, mixture of two rotamers, ratio 4:1, IR (cm$^{-1}$): 2956; 1618; 1420; major rotamer: n.m.r.$^1$H: 4.2-4.05 (m, 2H); 2.52-2.70 (m, 1H); 2.3-1.30 (m, 8H); 2.04 (s, 3H); 1.28 (d, J = 6 Hz, 3H), minor rotamer: 4.35-4.45 (m, 2H); 2.82-2.95 (m, 1H); 2.3-1.30 (m, 8H); 2.03 (s, 3H); 1.30 (d, J = 6 Hz, 3H). n.m.r. $^{13}$C::20.35; 21.75; 22.29; 22.86; 23.38; 23.53; 23.80; 23.99; 24.14; 25.00; 29.99; 0.57; 31.99; 32.43; 32.50; 33.44; 33.96; 34.49; 35.08; 36.05; 36.84; 38.24; 38.39; 39.08; 40.03; 41.36; 42.15; 42.88; 48.30; 54.97; 55.60; 62.28; 63.53; 64.29; 65.20; 70.56; 80.93; 116.59; 166.70; 168.67; h.r.m.s.: Calc.:for $C_{10}H_{17}NO$ 167.131013. Found: 167.1310137.

**(13α-Methyl) 3β-acetoxy-androst-5-en-17-one 12d** and **3β-acetoxy-androst-5-en-17-one 12e**. These two compounds were isolated in 40% and 36% yield respectively and were identical to authentic samples. [3b, 24]

### *General Procedure for the Preparation of N-Benzoyloxyamides*

Oxalyl chloride (2 mmol.) was added to an ice-cooled solution of the alkenoic acid (1 mmol.) in dichloromethane 2.5 ml) containing one drop of N,N-dimethylformamide. The reaction mixture was stirred for 10 min. at 0°C and for one hour at room temperature. The solvent and excess reagent were removed by evaporation under reduced pressure, and the crude acid chloride thus obtained was added to an ice cooled suspension of N-methylhydroxylamine hydrochloride ( 2 mmol.), anhydrous sodium carbonate (4 mmol.) in dry ether (14 ml), containing 3 drops of pyridine. The reaction mixture was left overnight at room temperature. Water was then added and the organic layer was separated and washed with an aqueous solution (1 M) of citric acid . Work-up afforded a crude residue which was dissolved in dry ether (2 ml) containing triethylamine (1.3 mmol) and the resulting soloution cooled to 0°C. Benzoyl chloride (1.5 mmol.) was added dropwise and the temperature allowed to rise to 20°C. The mixture was stirred for 30 min. then poured into saturated aqueous hydrogen carbonate. After stirring overnight., the organic layer was separated and washed with an aqueous solution (1 M) of citric acid. The usual work-up procedure and silica gel column chromatography afforded the following N-benzoyloxyamides which were used directly in the next step:

**N-benzoyloxy-N-methyl-2-(cyclopent-2-enyl)-acetamide 13b**. Obtained as a light yellow oil (eluent: dichloromethane/ pentane/ ether- 50/ 48/2) from 2-cyclopentenylacetic acid in 64% overall yield; IR (cm$^{-1}$): 2937; 1762; 1687; 1243; 1012; n.m.r. $^1$H ($CDCl_3$; 300 MHz): 1.37-1.5 (m, 1H); 2.1-2.46(m, 5H); 3.16(m, 1H); 3.4(s, 3H); 5.7(m, 2H); 7.5(m, 2H); 7.67(m, 1H); 8.07(m, 2H); n.m.r. $^{13}$C ($CDCl_3$): 30.46; 32.41; 38.88; 42.07; 127.49; 129.5; 130.6; 131.9; 134.67; 135.04; 169.91.

**N-benzoyloxy-N-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxamide 14c**. Obtained as a colourless oil (eluent: heptane/ ether-4/1) from endo-norbornenecarboxylic acid in 70% overall yield; IR ($cm^{-1}$): 2968; 1762; 1668; 1243; 1031; 1012; n.m.r. $^1H$ ($CDCl_3$; 300 MHz): 1.3-1.58 (m, 2H); 1.6-1.7 (m, 1H); 1.93-2.04 (m, 1H); 3.01 (br. s, 1H); 3.16-3.23 (m, 1H); 3.3 (br. s, 1H); 3.54 (s, 3H); 6.20-6.24 (m, 1H); 6.3-6.37 (m, 1H); 7.66-7.71 (m, 2H); 7.8-7.86 (m, 1H); 8.26-8.3 (m, 2H); n.m.r. $^{13}C$ ($CDCl_3$): 30.07; 41.91; 42.46; 45.49; 49.51; 127.04 ; 128.94; 29.94;132.68; 134.40; 136.95; 164.29; 174.88.

**N-Benzoyloxy-N-methyl-4-decenamide 15d.** Oct-1-en-3-ol (3.61 ml, 23.4 mmol.) and propionic acid (0.1 ml, 1.4 mmol.) were dissolved in triethylorthoacetate (30ml, 0.16 mol.). The resulting solution was heated at 120°C and the ethanol formed during the reaction was continuously removed by distillation. When all the starting material was consumed, as judged by T.L.C., the temperature of the oil bath was raised to 160°C and reflux was maintained for 2 hrs. Bulb to bulb distillation gave ester **15a** as a colourless oil (4.54g; 98 %). This compound was saponified with 2N sodium hydroxide in methanol to give the corresponding crude acid which was converted into the title compound **15d** according to the general procedure described above. Compound **15d** was obtained as a colourless oil following purification by silica gel column chromatography (eluent: dichloromethane) in 86% yield; IR ($cm^{-1}$): 2930; 1762; 1682; 1250; 1011; n.m.r. $^1H$ ($CDCl_3$; 300 MHz): 0.85 (t, J=7 Hz, 3H); 1.21-1.33 (m, 6H); 1.93 (m, 2H); 2.32-2.37 (m, 4H); 3.41 (s, 3H); 5.39-5.42 (m, 2H); 7.49-7.54 (m, 2H); 7.65-7.69 (m, 1H); 8.08-8.11 (m, 2H); n.m.r. $^{13}C$ ($CDCl_3$): 14.04; 22.51; 27.4; 29.01; 31.36; 32.4; 35.79 ; 126.8; 128.15; 128.9; 131.8; 130.0; 134.43; 164.31.

**N-Benzoyloxy-N-(2-propenyl)-4-pentenamide 17b**. Allylamine (1.5 ml, 20 mmol.) was added dropwise to a cold (+ 5°C) solution of benzoyl peroxide (4.84 g, 20 mmol.) in chloroform. Potassium carbonate (4.8 g) was added (in order to liberate the amine which had partly precipitated as its benzoate salt) at such a rate that the temperature did not exceed +6°C. The reaction mixture was then allowed to warm to 20°C, and after stirring for 12 hrs, it was then cooled to +5°C . Triethylamine (2.79 ml, 20 mmol.) and a solution of 4-pentenoyl chloride (20 mmol.) in chloroform (10 ml) were successively added. After 12 hrs at room temperature the reaction mixture was poured into saturated sodium bicarbonate and stirring was continued overnight. The organic layer was washed with an aqueous solution of citric acid (0.1 M), dried over sodium sulfate and concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography (eluent: ether/ pentane-4/1 to ether) to give benzoate 17b in 34% yield as an oil; IR ($cm^{-1}$): 3075; 2987; 2931; 1768; 1681; 1237; 1037; 1012 $cm^{-1}$; n.m.r. $^1H$ ($CDCl_3$; 250 MHz): 2.4 (s, 4H); 4.43 (d, J= 7Hz, 2H); 5.02 (d, J=7 Hz, 1H); 5.03 (d, J=17.5 Hz, 1H); 5.2 (d, J=12.5 Hz, 1H); 5.26 (d, J=17.5 Hz, 1H); 5.7-6 (m, 2H); 7.4-7.7 (m, 3H); 8.08 (d, J=7.3 Hz, 2H); n.m.r. $^{13}C$ ($CDCl_3$): 28.73; 32.14; 51.52; 115.9; 119.17; 129.35; 130.43; 131.87; 134.91; 137.42; 164.94.

**Pent-4-enoic acid benzoyloxy-cyclohex-2-enyl-amide 16c**. 3-Aminocyclohexene (1.69 g, 7 mmol.) was converted into **17c** by the same procedure as for **17b**. Purification by silica gel column chromatography (eluent: ether/ pentane-4/1 to ether) gave **16c** as a colourless oil in 37% overall yield; IR ($cm^{-1}$): 2943;1768; 1675; 1237; 1018; n.m.r. $^1H$ ($CDCl_3$; 200 MHz): 1.56-2.07 (m, 6H); 2.51 (m, 4H); 4.97 (d, J=7 Hz, 1H); 5.05 (d, J=17.5 Hz, 1H); 5.27 (m, 1H 5.58-5.91 (m, 3H); 7.46-7.53 (m, 2H); 7.61-7.67 (m, 1H); 8.06(d, J=7.3 Hz, 2H); n.m.r. $^{13}C$ ($CDCl_3$): 20.01; 23.63; 25.85; 31.31; 53.59; 114.57; 129.13; 129.25; 133.6; 138.4; 164.45.

**1-Hydroxyamino-cyclohexanecarbonitrile 18a** A solution of hydroxylamine hydrochloride (11.5g , 0.16mol.) in water (50 ml) was added to cyclohexanone (15.54 ml, 0.15 mol.). The reaction mixture was stirred for 15 min. at room temperature. A solution of sodium cyanide (7.6g , 0.155mol) in water (25 ml) was then added dropwise over 30 min. The reaction mixture was stirred for 6 days. The white precipitate was collected by filtration, dried, and used directly in the next step (14.92g; 70 %)

**N-(1-Cyanocyclohexyl)-N-hydroxy-4-pentenamide 18b**. 4-Pentenoyl chloride (20 mmol.) was added dropwise, with stirring, to an ice-cooled suspension of **18a**.(3.36g, 24 mmol.) and anhydrous sodium carbonate (2.54 g; 24 mmol.) in dry ether (50 ml). After 5 minutes, the reaction mixture was allowed to warm to 20°C and kept stirring for 18 hrs. Water was then added and the organic layer was washed with 1M aqueous citric acid, dried over sodium sulfate and concentrated under reduced pressure to give a residue which was used directly in the next step.

**Pent-4-enoic acid benzoyloxy-(1-cyano-cyclohexyl)-amide 18c**. Benzoylation of **18b** as above gave the title compound **18c** as a colourless oil in 42% overall yield following purification by silica gel column chromatography (eluent: dichloromethane/ pentane/ ether- 48/ 50/ 2 ); IR ($cm^{-1}$): 2943; 2862; 2256; 1768; 1700; 1450; 1237; 1037; 1012; n.m.r. $^1H$ ($CDCl_3$; 200 MHz): 1.1-2.64 (m, 14H); 4.94 (d, J= 8.5 Hz, 1H); 5.01 (d, J= 16Hz, 1H); 5.76 (m, 1H); 7.53-7.62 (m, 2H); 7.7-7.8 (m, 1H); 8.14 (d, J= 7.3 Hz, 2H); n.m.r. $^{13}C$ ($CDCl_3$): 23.33; 25.22; 28.60; 33.65; 62.24; 116.44; 118.56; 126.34; 130.12; 130.94; 135.94; 137.41; 165.75; 174.72.

**O-(2-cyclohexenyl)-N-hydroxy-N-methyl carbamate 19a**. To a solution of 2-cyclohexen-1-ol (2 ml, 20.4 mmol.) in tetrahydrofurane (40 ml) was added 1,1' carbonyldiimidazole (4.13 g, 25.5 mmol.). The reaction mixture was stirred at 20°C until the starting alcohol had disappeared (± 7 hrs) as judged by T.L.C. (eluent ether/ pentane -1/1). Triethylamine (3.34 ml, 24 mmol.) and N-methylhydroxylamine hydrochloride (2 g, 24 mmol.) were then added. The reaction mixture was stirred for 48 hrs, then concentrated under reduced pressure. After addition of water, the product was extracted with ether. The organic layer was washed with aqueous citric acid (1 M) and worked-up in the usual way. The crude product thus obtained was used in the next step without further purification.

**O-(2-Cyclohexenyl)-N-benzoyloxy-N-methyl carbamate 19b.** This compound was obtained from **19a** according to the general procedure described above for the preparation of N-benzoyloxyamides. Purification by silica gel column chromatography (eluent: ether/ pentane-3/7) gave 19b as a yellowish oil in 60% overall yield; IR ($cm^{-1}$): 2950; 1743; 1725; 1243; 1156; 1018; n.m.r. $^1H$ ($CDCl_3$; 250MHz): 1.52-2.12 (m, 6H); 3.38 (s, 3H); 5.2-5.3 (m, 1H); 5.68-5.78 (m, 1H); 5.86-5.97 (m, 1H); 7.4-7.5 (m, 2H); 7.54-7.64 (m, 1H); 8.05 (d, J=7.3 Hz, 2H); n.m.r. $^{13}C$ ($CDCl_3$): 24.28; 27.86; 37.50; 70.13; 124.92; 126.96; 128.11-129.38; 132.39; 133.4; 155.58; 164.06.

### *General Procedure for the Radical Cyclisations of N-Benzoyloxyamides.*

A solution of tributylstannane (1.2 mmol.) and AIBN (0.1 mmol.) in a deoxygenated mixture of cyclohexane (2.5 ml) and toluene (2.5 ml) was added dropwise over 6 hrs. to a refluxing solution of N-benzoyloxyamide (1 mmol.) in deoxygenated cyclohexane ( 5 ml). The reaction was monitored by T.L.C. and, after an additional period of 12 hrs under reflux, a further amount of tributylstannane (0.6 mmol.) was added in the same way if necessary. The solvents were then evaporated under reduced pressure and the residue purified by silica gel column chromatography.

**1-Methyl-hexahydro-cyclopenta-[b]-pyrrol-2-one 13c.** Obtained as a light yellow oil (eluent: ether:methanol- 9/1) in 66% yield; IR ($cm^{-1}$): 2950; 1687; 1406; n.m.r. $^1H$ ($CDCl_3$; 300 MHz): 1.41-1.9 (m, 6H); 2.1 (q, J= 9 Hz, J= 21 Hz, 1H); 2.67 (q, J= 9 Hz, J= 21 Hz, 1H); 2.7(m, 1H); 2.8 (s, 3H); 3.93 (m, 1H); n.m.r. $^{13}C$ ($CDCl_3$): 23.67; 28.04 ; 30.95; 34.16; 39.29; 34.17; 65.65; 182.7; h.r.m.s.: Calc.:for $C_8H_{13}NO$ 139.0997. Found: 139.1005.

**4-Aza-4-methyl-tricyclo[4.2.1.0 $^{3,7}$]nonan-5-one 14d.** Obtained as a colourless oil (eluent: pentane/ ether 1/1 to methanol/ ethyl acetate 1/5) in 60% yield; IR ($cm^{-1}$): 2956; 1687; 1681; 1437; 1400; 1087; n.m.r. $^1H$ ($CDCl_3$; 300 MHz): 1.28 (m, 1H); 1.47 (m, 1H); 1.53 (m, 2H); 1.56 (m, 1H); 1.82 (m, 1H); 2.36 (m, 1H); 2.43 (m, 1H); 2.78 (s, 3H); 2.98 (m, 1H); 3.51 (m, 1H,); n.m.r. $^{13}C$ ($CDCl_3$): 29.29; 34.91; 35.71; 37.97; 38.01; 42.92; 45.45; 61.63; 180.45; h.r.m.s.: Calc.:for $C_9H_{13}NO$: 151. 0997. Found: 151.1004.

**5-Hexyl-1-methyl-pyrrolidin-2-one 15e.** Obtained as a yellowish oil (eluent: ether/methanol -95/ 5 to ethyl acetate/methanol -4/1) in 36% yield; IR ($cm^{-1}$): 2931; 2856; 1700; 1462; 1425; 1400; n.m.r. $^1H$ ($CDCl_3$; 250 MHz): 0.9 (t, J=7 Hz, 3H); 1.18-1.43 (m, 17H); 1.6-1.79 (m, 2H); 2.07-2.20 (m, 1H); 2.24-2.46 (m, 2H); 2.79 (s, 3H); 3.42-3.52 (m, 1H); n.m.r. $^{13}C$ ($CDCl_3$): 14.25; 22.78; 24.15; 24.38; 24.62; 29.55; 30.41; 31.61; 32.45; 27.87; 60.22; 175.32; h.r.m.s.: Calc. for $C_{11}H_{21}NO$: 183.1623. Found: 183.1635.

**Decahydro-3H pyrrolo [1.2-a] indol-3-one 16d.** Isolated in 73% yield (eluent: ether, ether/ methanol- 9/1) as a 1:1 mixture of cis and trans isomers (by CG-MS). [16]

Isomer A : IR ($cm^{-1}$): 1683; 1450; 1398; 1275 ; n.m.r. $^1H$ ($CDCl_3$; 300Mhz): δ 1.14-1.21 (m, 2H); 1.31-1.34 (m, 1H); 1.45-1.52 (m, 2H); 1.54-1.59 (m, 1H); 1.61-1.74 (m, 3H 1.78 (ddd, J=J'=4Hz, J"=12Hz, 1H); 1.94 (dt, J=8Hz, J'=12Hz, 1H); 2.24-2.36(m, 3H); 2.6(ddd, J=16Hz, J'=13Hz, J"=8Hz, 1H); 3.85-3.94 (m, 1H); 4.11(tt, J=5Hz, J'=10Hz, 1H); n.m.r. $^{13}C$ ($CDCL_3$; 300Mhz): δ 21.33; 22.61; 26.70; 27.02; 30.10; 35.10; 38.54; 54.28; 59.47; 176.46.

Isomer B : IR ($cm^{-1}$):1687;.1456; 1406; 1300; 1175; n.m.r $^1H$ ($CDCl_3$; 400Mhz): δ 1.14-1.21 (m, 2H); 1.31-1.34 (m, 1H); 1.45-1.52 (m, 2H); 1.54-1.59 (m, 1H); 1.61-1.74 (m, 3H 1.78 (ddd, J=J'=4Hz, J"=12Hz, 1H); 2.22 (ddd, J=5.5Hz, J'=7.5Hz, J"=12Hz, 1H); 2.42 (dd, J=8Hz, J'=16Hz, 1H); 2.48-2.56 (m, 1H); 2.57-2.62 (m, 1H); 2.67 (ddd, J=16Hz, J'=13Hz, J"=7.5Hz, 1H); 3.56-3.61 (m, 1H); 3.95 (tt, J=5Hz, J'=10Hz, 1H); n.m.r.$^{13}C$ ($CDCL_3$; 250Mhz): δ 21.40; 23.06; 26.67; 27.92; 35.0; 41.03; 53.09; 63.12; 173.39; h.r.m.s.: Calc. for $C_{11}H_{17}NO$: 179.13101. Found: 179.1316

**Hexahydro-6-methyl-pyrrolizin-3-one 17c.** Isolated in 70% yield (eluent: ether/ pentane-1/1, ether, ether/ methanol- 95/5) as a 2:1 mixture of isomers; lit. ref.4a,16.

**(1-Cyclohexyl-2-oxo-5-pyrrolidinacetonitrile 18d** Isolated in 83% yield as white crystals (eluent: ether/methanol -95/ 5 to ethyl acetate/methanol -4/1); m.p. 82°C (from ether); IR ($cm^{-1}$, Nujol): 2243; 1662; 1462; 1418; 1281; n.m.r. $^1H$ ($CDCl_3$; 300 MHz): 1.06-2.04 (m, 12H); 2.24-2.42 (m, 2H); 2.55-2.72 (m, 2H); 3.7-3.81 (m, 1H); 3.92-4.0 (m, 1H); n.m.r. $^{13}C$ ($CDCl_3$): 25.45; 26.18; 26.49; 26.64; 26.72; 30.58; 30.91; 32.60; 53.72; 54.23; 117.77; 175.29; microanalysis (%): Calc. for $C_{12}H_{17}NO_2$: C: 69.87; H: 8.80; N: 13.58. Found: C: 69.98; H: 8.71; N: 13.47.

**Hexahydro-benzoxazol-2-one 19c.** Isolated in 20% yield as a colourless oil (eluent: ether/methanol -4/ 1 to ethyl acetate/methanol -4/1) (some mechanical loss occured on purification since the nmr spectrum of the crude indicated the presence of 40% **19c** and 60% of reduced product **19d**); IR ($cm^{-1}$): 2944; 2864; 1749 (C=0); 1431; 1392; 1114; 1019; n.m.r. $^1H$ ($CDCl_3$; 250 MHz): 1.3-1.92 (m, 8H); 2.8 (s, 3H); 3.61 (dt, J=6 Hz, J= 6Hz); 4.49 (dt, J=6 Hz, J=6 Hz); n.m.r. $^{13}C$ ($CDCl_3$): 19.86; 20.04; 25.64; 27.38; 29.11; 56.72; 73.59; 159.65; h.r.m.s.: Calc.:for $C_8H_{11}NO_2$: 155.0946. Found: 155. 0956.

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