Pergamon

Tetrahedron 54 (1998) 13405–13420

TETRAHEDRON

Radical Cyclisation of *N*-(Cyclohexenyl)acrylamides: Synthesis of Bicyclic *N*-Heterocycles

Andrew F. Parsons* and David A.J. Williams

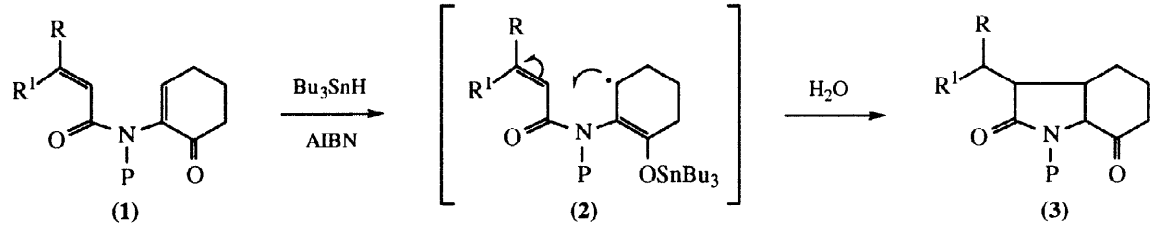
Department of Chemistry, University of York, Heslington, York, YO1 5DD, U.K.

Received 5 June 1998; revised 13 August 1998; accepted 19 August 1998

Abstract: The Bu_3SnH mediated cyclisation of various *N*-acryloxy-2-amino-2-cyclohexenones was explored. This predominantly gave rise to bicyclic lactams but the reaction mechanism was shown to depend upon the substitution of the amide double bond. Preliminary studies targeted towards the preparation of bicyclic lactones are also reported. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Radicals and radical reactions; cyclisation; tin and compounds; enamides.

Cyclisation reactions mediated by Bu_3SnH have been extensively studied over the past twenty years.[1] The reactions generally employ halide, thiophenyl, thiocarbonyl or phenylselenide precursors, but there are limitations with this method. These include the difficulty of removing some tin-containing byproducts (such as tin chlorides/bromides) from products and the reduction and loss of two functional groups (namely R-X and C=C) during the course of the reaction. The need for alternative radical precursors led Enholm and co-workers[2] to investigate the reaction of Bu_3SnH/AIBN with α,β-unsaturated carbonyls to generate allylic *O*-stannyl ketyl radicals. This method is unusual because unsaturated ketones are commonly employed as radical acceptors rather than precursors. The resultant radicals which are stabilised by resonance delocalisation are nucleophilic in character and have been shown to undergo cyclisation reactions using activated alkenes to produce mono- and bicyclic cyclopentanes. We have recently extended this chemistry to pyrrolidine/piperidine synthesis.[3] This method is advantageous as the products retain a versatile ketone functional group; the tin-containing byproducts are easily removed (on column chromatography) and the tin enolate intermediates can undergo subsequent reactions with electrophiles (*e.g.* RX or RCHO).[4]

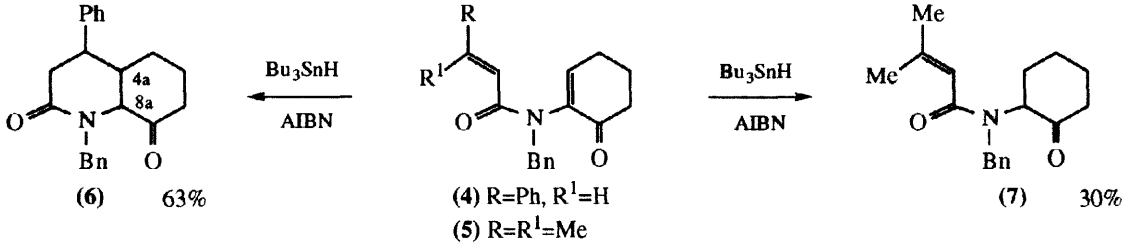


Scheme 1

We became interested in the application of allylic *O*-stannyl ketyl radical reactions to prepare octahydroindolones of type **(3)** (Scheme 1). This ring system is present in a variety of naturally occurring

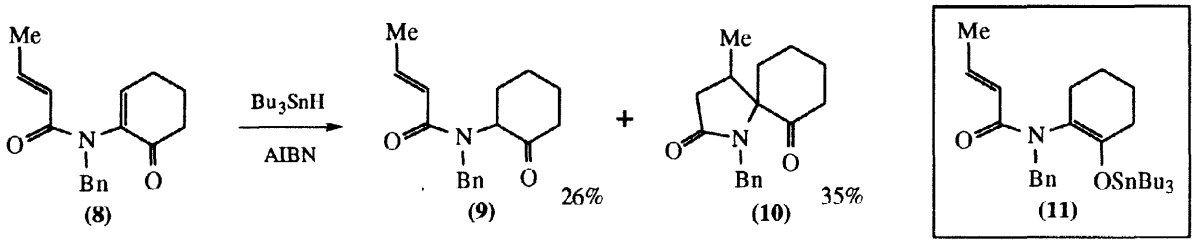
PII: S0040-4020(98)00822-9

alkaloids and the preparation of these types of compounds has attracted considerable synthetic interest. One common approach has employed a Bu_3SnH mediated free-radical cyclisation of haloamide precursors to construct the pyrrolidinone ring present in (**3**).[5] We intended to employ an alternative and novel strategy which centred on the formation of the pyrrolidinone ring by 5-*exo* cyclisation of allylic *O*-stannyl ketyl radical (**2**) prepared from reaction of the cyclohexenone (**1**) with Bu_3SnH.



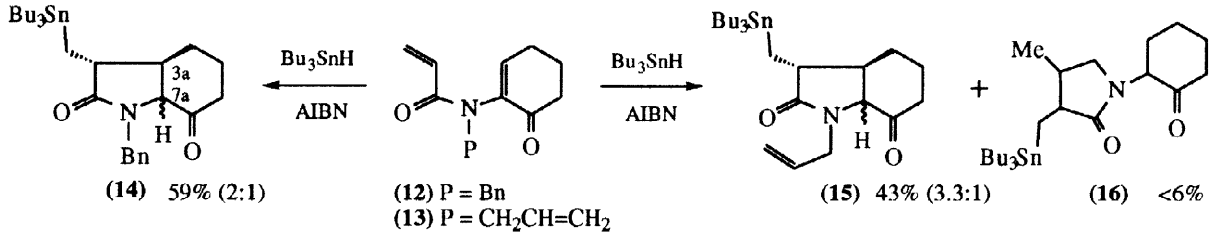
Scheme 2

Initial investigations focused on the reaction of the cinnamamide derivative (**4**) (Scheme 2). This was prepared in 72% yield from treatment of 1,2-cyclohexanedione with benzylamine followed by *trans*-cinnamoyl chloride. Subsequent reaction of (**4**) with Bu_3SnH (1.5 equivalents)/AIBN (0.3 equivalents) in boiling benzene surprisingly resulted in the regioselective formation of the piperidinone (**6**) (as a 1.9:1 mixture of diastereomers) in 63% yield. The spectroscopic data for (**6**) were consistent with a 6- rather than 5-ring lactam, for example, the characteristic amide carbonyl stretch was observed at 1641 cm^{-1} in the IR spectrum. The formation of (**6**), which results from a 6-*endo* cyclisation reaction, can be explained if the cyclisation is reversible and under thermodynamic control as has previously been observed for allylic *O*-stannyl ketyl radical cyclisations leading to substituted cyclopentanes.[2,6] If the reaction is reversible, then slow addition of Bu_3SnH would be expected to improve the stereoselectivity[2] and indeed only one diastereomer [presumably with a *cis*-ring junction ($J_{4a,8a}$ = 5.5 Hz)] was isolated when the Bu_3SnH was added to (**4**) over 5 h. In contrast, reaction of the dimethyl derivative (**5**) (under the same conditions) gave rise to a considerable number of products as shown by the crude ^1H NMR spectrum. Cyclohexanone (**7**) was isolated in 30% yield (after column chromatography), but characterisation of the many other products (formed in small amounts) was not possible. The formation of (**7**) can be explained by reaction of the intermediate *O*-stannyl ketyl radical [of type (**2**)] with Bu_3SnH, rather than the double bond, leading to simple reduction. Simple reduction was also observed on reaction of the *N*-crotonyl derivative (**8**) and the cyclohexane (**9**) was isolated in 26% yield (Scheme 3). In addition, the spiro-pyrrolidinone (**10**) was formed in 35% yield as a separable mixture of two diastereomers (in a ratio of 2.9:1). The mechanism for the unexpected formation of (**10**) is not clear. It could involve the formation of *O*-stannyl ketyl (**11**) which would be required to undergo a disfavoured (5-*endo-trig*) Michael-type addition in order to construct the 5-membered ring.



Scheme 3

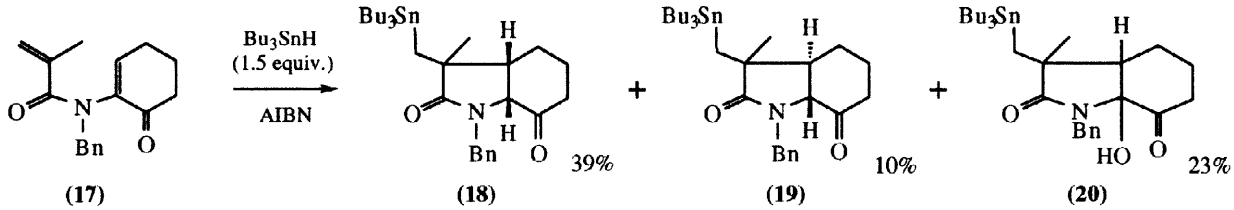
Reaction of the *N*-benzyl acrylamide derivative (**12**) with Bu_3SnH followed an alternative reaction pathway (Scheme 4). In this case regioselective 1,4-addition of the $Bu_3Sn^{\bullet}$ radical to the acrylamide double bond was observed. This was followed by 5-*endo-trig* cyclisation of the intermediate carbamoylmethyl radical[7] to produce the pyrrolidinone (**14**) in 59% yield as a 2:1 mixture of diastereomers. The ^1H NMR spectra indicated that the major diastereomer possessed a *cis*- ring junction ($J_{3a,7a}$ = 8 Hz)[8] while the minor isomer possessed a *trans*- ring junction ($J_{3a,7a}$ = 11.5 Hz). A *trans*- arrangement of the C-3 and C-3a substituents was thought likely on steric grounds and related 5-*exo* carbamoylmethyl radical cyclisations have shown a strong preference for the *trans*- pyrrolidinone diastereomer.[9a,b] Although similar free-radical addition-cyclisation reactions of dienes have been reported[9] this is the first example which makes use of a 5-*endo* (rather than 5-*exo* or 6-*exo*) cyclisation reaction. A similar result was observed when the *N*-allyl derivative (**13**) was reacted with Bu_3SnH and the octahydroindolone (**15**) was isolated as the major product in 43% yield. This is surprising as the intermediate carbamoylmethyl radical could undergo a favoured 5-*exo* cyclisation (rather than 5-*endo* cyclisation) by reaction with the *N*-allyl double bond to form a disubstituted pyrrolidinone. This pathway was thought to be responsible for the formation of minor products (isolated in <6% yield) which included (**16**). Cyclisation of (**13**) could have occurred before or after reduction of the cyclohexenone double bond to form (**16**).



(**14**) 59% (2:1) (**12**) P = Bn (**13**) P = $CH_2CH{=}CH_2$ (**15**) 43% (3.3:1) (**16**) <6%

Scheme 4

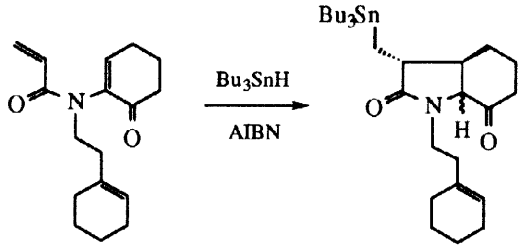
Reaction of the methacrylamide derivative (**17**) also resulted in cyclisation (Scheme 5). The octahydroindolones (**18**) and (**19**), with *cis*- and *trans*- ring junctions respectively, were isolated as diastereomeric mixtures in a combined yield of 49%. In addition, the hydroxy derivative (**20**) was formed in 23% yield as a 2.8:1 mixture of isomers. This may result from reaction of the cyclised radical with molecular oxygen followed by Bu_3SnH reduction of the hydroperoxide intermediate.[10] However, (**20**) was isolated (in similar yield) even after extensive degassing of the solvent although the yield could be reduced when using 3 equivalents of Bu_3SnH. Under these conditions, (**20**) was isolated in 11% yield while (**18**) and (**19**) were formed in 49% and 10% yield respectively. Similar compounds to (**20**) have previously been prepared on hydrolysis of *N*-acyliminium ions[11] but the formation of an intermediate carbocation (under the reducing reaction conditions) is thought to be unlikely in this case.



(**17**) (**18**) (**19**) (**20**)

Scheme 5

The reaction of the *N*-(1-cyclohexenyl)ethyl derivative (**21**) with Bu_3SnH was then investigated (Scheme 6, Table). In this case, the radical resulting from 5-*endo* cyclisation could undergo further 5-*exo* or (more likely) 6-*endo* cyclisation by reaction with the cyclohexenyl double bond. Immediate addition of Bu_3SnH to (**21**) resulted in the formation of octahydroindolone (**22**) in 57% yield while the tetracycle (**23**), derived from 5-*endo*/6-*endo* tandem cyclisation, was formed in only 4% yield. The major isomer of (**22**) possessed a *cis*-ring junction (*cis*-:*trans*- ratio = 3.4:1) while only one isomer of (**23**) was isolated (the stereochemistry of which was not determined). Slow addition of Bu_3SnH (added over 5 or 12 h) improved the yield of (**23**) to 7-9%. The modest yields of (**23**) can be explained by slow cyclisation of the sterically hindered α-amino radical.



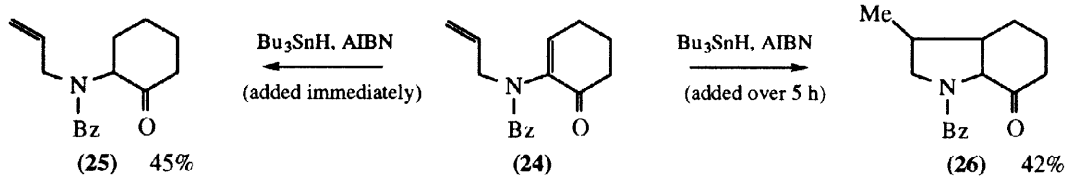
(21) (22) (23)

Scheme 6

Bu_3SnH Addition/h	Yield/% (22)	(23)
Immediate	57	4
5	65	9
12	49	7

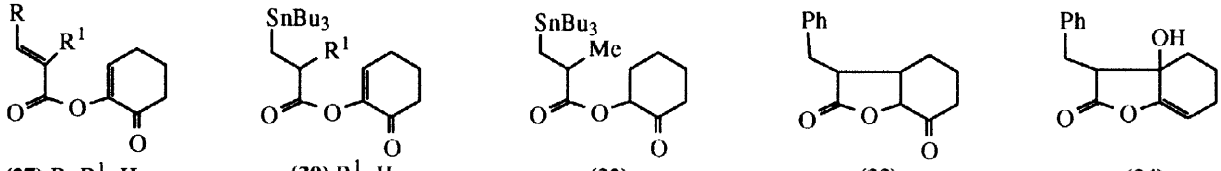
Table

The successful cyclisation of the acrylamides prompted us to explore the reaction of an *N*-allylamine. Hence benzamide (**24**), prepared from 1,2-cyclohexanedione, was reacted with Bu_3SnH using the same conditions as employed earlier. In this case only simple reduction was observed and the cyclohexanone (**25**) was isolated in 45% yield after column chromatography. Clearly the intermolecular reaction of the allylic *O*-stannyl ketyl radical with Bu_3SnH was much quicker than the intramolecular cyclisation. However, reducing the concentration of Bu_3SnH by adding it slowly over 5 h was found to have a pronounced effect and the octahydroindole (**26**) was formed by 5-*exo* cyclisation[12] in 42% yield. No cyclohexanone (**25**) was isolated using these conditions and the ^1H and ^{13}C NMR spectra of (**26**) showed the presence of three diastereomers (in the ratio of 3.4:3:1). Clearly activation of the *N*-allyl double dond is not required for cyclisation of the nucleophilic *O*-stannyl ketyl radical intermediate.



(25) 45% (24) (26) 42%

Scheme 7



(**27**) R=R^1=H
(**28**) R=H, R^1=Me
(**29**) R=Ph, R^1=H
(**30**) R^1=H
(**31**) R^1=Me
(**32**) (**33**) (**34**)

Preliminary studies directed towards the cyclisation of α,β-unsaturated esters have also been carried out. The esters **(27)**-**(29)** were prepared in good yield on acylation of 1,2-cyclohexanedione using acryloyl chloride, methacryloyl chloride or *trans*-cinnamoyl chloride respectively. Reaction of **(27)** with Bu_3SnH (added immediately) in boiling benzene resulted in hydrostannylation of the acryloyl side chain, and the stannane **(30)** was the only product isolated in low yield (typically 24%) after chromatography. Exclusive hydrostannylation could be attributed to the conformational preference of the intermediate ester radical; if the *syn*- conformer is preferred then 5-*endo* cyclisation is less likely. It should be noted however, that related 5-*exo* cyclisation of α-iodo esters can be carried out at 80°C, and at this temperature ester bond rotation is sufficiently rapid to allow cyclisation.[5d] Similar products, namely stannane **(31)** and the saturated ketone **(32)** (derived from hydrolysis of an intermediate *O*-stannyl ketyl) were observed on reaction of **(28)**. In contrast, cinnamate **(29)** underwent cyclisation to form the octa- and hexahydrobenzo[*b*]furans **(33)** and **(34)** in 26% and 10% yield respectively. The IR spectra of **(33)** and **(34)** exhibited C=O stretches at 1784 and 1803 cm^{-1} respectively which are consistent with the formation of butyrolactones. When the Bu_3SnH was added to **(29)** over 5 h, although **(34)** was not isolated, the yield of **(33)** could be improved to 39%. The formation of **(33)** and **(34)** is believed to involve 5-*exo* cyclisation of an intermediate *O*-stannyl ketyl radical. When the ester is in the *anti*-conformation cyclisation gives rise to **(33)** while cyclisation of the *syn*- conformer produces **(34)**. It should be noted that no products resulting from 6-*endo* cyclisation [as observed for **(4)**] were isolated.

This work has demonstrated the novel application of allylic *O*-stannyl ketyl radicals in the formation of *N*-bicycles. The nature of the amide double bond was found to determine the chemoselectivity of the reaction and the formation of an azaspiro[5.4.0]decane is of particular note. Further mechanistic studies are in progress and future work will investigate the application of allylic *O*-stannyl ketyl radical cyclisations in natural product synthesis.

Experimental

^1H NMR (δ^1H) and ^{13}C NMR ($\delta^{13}C$) spectra were recorded on a Jeol EX 270 spectrometer; the carbon spectra were recorded at 67.5 MHz and were assigned using DEPT experiments. Chemical shifts are reported in δ (ppm). Samples were prepared as solutions in $CDCl_3$ containing tetramethylsilane as internal standard or were referenced to an internal chloroform standard. Spectra which were complicated by the presence of conformers at room temperature were recorded in d_8-toluene at 80°C. Coupling constants (*J*) were recorded in Hertz (Hz) to the nearest 0.5 Hz. IR spectra (ν_{max}) were recorded on an ATI Mattison Genesis Series FT IR spectrometer as thin films or solutions in chloroform. Mass spectra (MS) were recorded on a Fisons Instruments VG Analytical Autospec Spectrometer system. Melting points were determined using a Gallenkamp apparatus and are uncorrected. Thin layer chromatography (t.l.c.) was performed on Merck 5554 aluminium-backed silica gel plates. Compounds were visualized under a UV lamp, using alkaline potassium permanganate solution or iodine. Column chromatography was carried out under gravity, using silica gel (Matrex Silica 60, 70-200 micron Fisons, or ICN flash silica 60, 32-63 microns). Commercially available reagents were used as supplied unless otherwise stated. Petroleum ether refers to the fraction of boiling range 40-60°C, which was redistilled before use. Tributyltin hydride was purchased from Lancaster Synthesis Ltd and distilled before use.

General Procedure for the Preparation of Alkenes (4), (5), (8), (12), (13), (17), (21) and (24)

To a stirred solution of 1,2-cyclohexanedione (3.57-8.92 mmol) in benzene or toluene (50-70 cm^3) at room temperature was added the amine (3.93-9.81 mmol). The solution was heated at reflux in a Dean-Stark water separator until t.l.c. indicated that no starting material remained (approx. 3 h). After cooling to 0 °C, the acid chloride (3.93-9.81 mmol) was added dropwise. Triethylamine (3.93-9.81 mmol) was then added and the

solution allowed to warm to room temperature. After stirring overnight (15 h) no starting material remained by t.l.c.. The solution was washed with water, brine, dried (magnesium sulfate) and the solvent evaporated under reduced pressure to afford the crude alkene which was purified by column chromatography (silica) (47-72%).

(E)-N-*Benzyl*-N-*(6-oxo-cyclohex-1-enyl)cinnamamide* (4)

Benzylamine (0.47 cm^3, 4.28 mmol), *trans*-cinnamoyl chloride (0.65 g, 3.93 mmol) and triethylamine (0.55 cm^3, 3.93 mmol) were reacted with 1,2-cyclohexanedione (0.40 g, 3.57 mmol) in benzene (50 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 1:1) afforded alkene (**4**) (0.84 g, 72%) as an off-white crystalline solid (m.p. 101-105 °C); R_f 0.14 (diethyl ether-petroleum ether, 1:1); ν_{max} (thin film) 3059 (w), 3029 (w), 2929 (w), 1685 (s), 1655 (s), 1614 (s), 1495 (m), 1451 (m), 1392 (s), 1361 (m), 1343 (m), 1224 (m), 977 (w), 764 (m), 727 (m), 702 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.73 (1H, d, *J*=15.5, CH=C<u>H</u>Ph), 7.42-7.22 (10H, m, aromatics), 6.55 (1H, t, *J*=4, C<u>H</u>=C), 6.42 (1H, d, *J*=15.5, C<u>H</u>=CHPh), 5.49 (1H, d, *J*=15, NC<u>H</u>Ph), 4.08 (1H, d, *J*=15, NC<u>H</u>Ph), 2.58-2.33 (4H, m, $C\underline{H}_2CO$ and $C\underline{H}_2CH$), 2.06-1.96 (2H, m, $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 194.6 ($CH_2\underline{C}O$), 165.8 (N<u>C</u>O), 149.8 (<u>C</u>H=C), 142.1 (CH=<u>C</u>HPh), 138.0 (<u>C</u>=CH), 137.1, 134.8 (<u>C</u>=CH aromatics), 129.3, 128.7, 128.4, 128.1, 127.5, 127.1 (<u>C</u>H=C aromatics), 117.9 (<u>C</u>H=CHPh), 50.4 ($N\underline{C}H_2Ph$), 38.1 ($\underline{C}H_2CO$), 25.7 ($\underline{C}H_2CH$), 22.2 ($CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 332 ($M+H^+$, 100%), 200 (M-COCH=CHPh, 15); Found: $M+H^+$, 332.1649. $C_{22}H_{21}NO_2$ requires for $M+H^+$, 332.1651.

N-*Benzyl*-N-*(6-oxo-cyclohex-1-enyl)-3,3-dimethylacrylamide* (5)

To a solution of 1,2-cyclohexanedione (0.60 g, 5.35 mmol) in benzene (70 cm^3) was added benzylamine (0.64 cm^3, 5.89 mmol), 3,3-dimethylacryloyl chloride (0.66 cm^3, 5.89 mmol) and triethylamine (0.82 cm^3, 5.89 mmol) according to the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 3:2) afforded alkene (**5**) (0.82 g, 54%) as an oil; R_f 0.16 (diethyl ether-petroleum ether, 3:2); ν_{max} (thin film) 2932 (m), 1687 (s), 1652 (s), 1627 (s), 1449 (m), 1395 (w), 1370 (w), 1270 (m), 1178 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.31-7.20 (5H, m, aromatics), 6.46 (1H, t, *J*=4, C<u>H</u>=C), 5.55 (1H, s, $C\underline{H}=C(CH_3)_2$), 5.40 (1H, br d, *J*=13.5, NC<u>H</u>Ph), 3.95 (1H, br d, *J*=13.5, NC<u>H</u>Ph), 2.51-2.41 and 2.41-2.26 (2 x 2H, br m, $C\underline{H}_2CO$ and $C\underline{H}_2CH$), 2.07 (3H, s, $CC\underline{H}_3$), 2.02-1.90 (2H, br m, $CH_2C\underline{H}_2CH_2$), 1.77 (3H, s, $CC\underline{H}_3$); δ_C (67.5 MHz, $CDCl_3$) 194.1 ($CH_2\underline{C}O$), 166.5 (N<u>C</u>O), 148.8 ($\underline{C}(CH_3)_2$), 148.3 (<u>C</u>H=C), 138.0, 136.8 (N<u>C</u>=CH and <u>C</u>=CH aromatic), 127.9, 127.5, 126.2 (<u>C</u>H=C aromatics), 116.6 ($\underline{C}H=C(CH_3)_2$), 49.2 ($N\underline{C}H_2Ph$), 37.7 ($\underline{C}H_2CO$), 26.1 ($C\underline{C}H_3$), 25.0 ($\underline{C}H_2CH$), 21.6 ($CH_2\underline{C}H_2CH_2$), 19.3 ($C\underline{C}H_3$); *m/z* (CI, NH_3) 284 ($M+H^+$, 100%), 200 (M-COCH=C$(CH_3)_2$, 15), 83 (10); Found: $M+H^+$, 284.1652. $C_{18}H_{21}NO_2$ requires for $M+H^+$, 284.1651.

(E)-N-*Benzyl*-N-*(6-oxo-cyclohex-1-enyl)-3-methylacrylamide* (8)

Following the general procedure 1,2-cyclohexanedione (0.50 g, 4.46 mmol) in benzene (60 cm^3) was reacted with benzylamine (0.49 cm^3, 4.46 mmol), crotonyl chloride (90% pure, 0.52 g, 4.46 mmol) and triethylamine (0.69 cm^3, 4.91 mmol). Column chromatography (silica; ethyl acetate-petroleum ether, 2:3) afforded alkene (**8**) (0.62 g, 52%) as an oil; R_f 0.18 (ethyl acetate-petroleum ether, 2:3); ν_{max} (thin film) 2933 (m), 1665 (s), 1623 (s), 1445 (m), 1393 (m), 1360 (m), 1343 (m), 1290 (m), 1256 (w), 1226 (m), 1190 (w), 1079 (w), 967 (m), 724 (m), 703 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.32-7.14 (5H, m, aromatics), 6.95 (1H, dq, *J*=15 and 7, C<u>H</u>CH_3), 6.50 (1H, br t, *J*=4, C<u>H</u>=C), 5.84 (1H, br d, *J*=15, C<u>H</u>=$CHCH_3$), 5.40 (1H, d, *J*=15, NC<u>H</u>Ph), 3.99 (1H, d, *J*=15, NC<u>H</u>Ph), 2.53-2.25 (4H, m, $C\underline{H}_2CO$ and $C\underline{H}_2CH$), 2.02-1.91 (2H, m, $CH_2C\underline{H}_2CH_2$), 1.81 (3H, dd, *J*=7 and 1.5, $CHC\underline{H}_3$); δ_C (67.5 MHz, $CDCl_3$) 195.0 ($CH_2\underline{C}O$), 166.1 (N<u>C</u>O), 149.8 (<u>C</u>H=C), 142.0 (CH=<u>C</u>HCH_3), 138.4, 137.5 (N<u>C</u>=CH and <u>C</u>=CH aromatic), 128.9, 128.3, 127.3 (<u>C</u>H=C aromatics), 122.1 (<u>C</u>H=$CHCH_3$), 50.5 ($N\underline{C}H_2Ph$), 38.4 ($\underline{C}H_2CO$), 25.9 ($\underline{C}H_2CH$), 22.4 ($CH_2\underline{C}H_2CH_2$), 18.1 ($CH\underline{C}H_3$); *m/z* (CI, NH_3) 270 ($M+H^+$, 100%), 200 (M-COCH=$CHCH_3$, 15), 176 (20); Found: $M+H^+$, 270.1491. $C_{17}H_{19}NO_2$ requires for $M+H^+$, 270.1494.

N-*Benzyl*-N-*(6-oxo-cyclohex-1-enyl)acrylamide* (12)

Benzylamine (0.58 cm^3, 5.35 mmol), acryloyl chloride (0.45 cm^3, 5.35 mmol) and triethylamine (0.82 cm^3, 5.89 mmol) were reacted with 1,2-cyclohexanedione (0.60 g, 5.35 mmol) in benzene (70 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 4:1) afforded alkene (**12**) (0.68 g, 50%) as an oil; R_f 0.17 (diethyl ether-petroleum ether, 4:1); ν_{max} (thin film) 3061 (w), 3030 (w), 2945 (m), 2871 (w), 1687 (s), 1657 (s), 1617 (m), 1413 (m), 1263 (m), 1080 (m), 702 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.31-7.20 (5H, m, aromatics), 6.51 (1H, t, *J*=4, C<u>H</u>=C), 6.39 (1H, dd, *J*=16.5 and 2, CH=C<u>H</u>$_A$H$_B$), 6.16 (1H, dd, *J*=16.5 and 10, C<u>H</u>=CH$_2$), 5.60 (1H, dd, *J*=10 and 2, CH=CH$_A$<u>H</u>$_B$), 5.39 (1H, d, *J*=14.5, NC<u>H</u>Ph), 4.05 (1H, d, *J*=14.5, NC<u>H</u>Ph), 2.52-2.32 (4H, m, C<u>H</u>$_2$CO and C<u>H</u>$_2$CH), 2.04-1.92 (2H, m, CH$_2$C<u>H</u>$_2$CH$_2$); δ_C (67.5 MHz, $CDCl_3$) 194.6 (CH$_2$<u>C</u>O), 165.5 (N<u>C</u>O), 149.7 (<u>C</u>H=C), 137.9, 137.0 (N<u>C</u>=CH and <u>C</u>=CH aromatic), 128.7, 128.1, 127.9, 127.2 (<u>C</u>H=C aromatic and <u>C</u>H=CH$_2$), 127.7 (CH=<u>C</u>H$_2$), 50.3 (N<u>C</u>H$_2$Ph), 38.1 (<u>C</u>H$_2$CO), 25.6 (<u>C</u>H$_2$CH), 22.1 (CH$_2$<u>C</u>H$_2$CH$_2$); *m/z* (CI, NH_3) 273 (M+NH_4^+, 10%), 256 (M+H^+, 100), 200 (M-COCH=CH_2, 10); Found: M+H^+, 256.1337. $C_{16}H_{17}NO_2$ requires for M+H^+, 256.1338.

N-*Allyl*-N-*(6-oxo-cyclohex-1-enyl)acrylamide* (13)

Following the general procedure 1,2-cyclohexanedione (0.50 g, 4.46 mmol) in benzene (60 cm_3) was reacted with allylamine (0.37 cm^3, 4.91 mmol), acryloyl chloride (0.40 cm^3, 4.91 mmol) and triethylamine (0.69 cm^3, 4.91 mmol). Column chromatography (silica; diethyl ether-petroleum ether, 4:1) afforded alkene (**13**) (0.43 g, 47%) as an oil; R_f 0.15 (diethyl ether-petroleum ether, 4:1); ν_{max} ($CHCl_3$) 3007 (m), 2956 (w), 2934 (w), 1690 (s), 1657 (s), 1619 (m), 1413 (m), 1347 (w), 1261 (m), 1237 (m), 1119 (w), 977 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.92 (1H, t, *J*=4, C<u>H</u>=C), 6.32 (1H, dd, *J*=16.5 and 2, NCOCH=C<u>H</u>$_A$H$_B$), 6.14 (1H, dd, *J*=16.5 and 10, NCOC<u>H</u>), 5.84-5.69 (1H, m, NCH$_2$C<u>H</u>), 5.58 (1H, dd, *J*=10 and 1.5, NCOCH=CH$_A$<u>H</u>$_B$), 5.11 (1H, d, *J*=10.5, NCH$_2$CH=C<u>H</u>$_A$H$_B$), 5.10 (1H, d, *J*=16.5, NCH$_2$CH=CH$_A$<u>H</u>$_B$), 4.48 (1H, dd, *J*=14 and 4, NC<u>H</u>), 3.76 (1H, dd, *J*=14 and 7, NC<u>H</u>), 2.61-2.53 (4H, m, C<u>H</u>$_2$CO and CH$_2$C<u>H</u>$_2$CH), 2.09 (2H, appt. quint, *J*=6.5, CH$_2$C<u>H</u>$_2$CH$_2$); δ_C (67.5 MHz, $CDCl_3$) 194.5 (CH$_2$<u>C</u>O), 165.0 (N<u>C</u>O), 149.1 (<u>C</u>H=C), 138.1 (<u>C</u>=CH), 132.8 (NCH$_2$<u>C</u>H), 127.8 (NCO<u>C</u>H), 127.2 (NCOCH=<u>C</u>H$_2$) 117.6 (NCH$_2$CH=<u>C</u>H$_2$), 49.9 (N<u>C</u>H$_2$), 37.6 (<u>C</u>H$_2$CO), 25.5 (CH$_2$<u>C</u>H$_2$CH), 21.7 (CH$_2$<u>C</u>H$_2$CH$_2$); *m/z* (CI, NH_3) 206 (M+H^+, 100%), 150 (M-COCH=CH_2, 20); Found: M+H^+, 206.1179. $C_{12}H_{15}NO_2$ requires for M+H^+, 206.1181.

N-*Benzyl*-N-*(6-oxo-cyclohex-1-enyl)methacrylamide* (17)

To a solution of 1,2-cyclohexanedione (0.60 g, 5.35 mmol) in benzene (70 cm^3) was added benzylamine (0.64 cm^3, 5.89 mmol), 2-methylacryloyl chloride (0.85 cm^3, 5.89 mmol) and triethylamine (0.82 cm^3, 5.89 mmol) according to the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 1:1) afforded alkene (**17**) (0.76 g, 53%) as an off-white crystalline solid (m.p. 71-74 °C); R_f 0.35 (diethyl ether); ν_{max} ($CHCl_3$) 3032 (w), 3008 (m), 2956 (w), 2936 (w), 1690 (s), 1655 (m), 1620 (s), 1452 (m), 1414 (w), 1397 (w), 1366 (w), 1345 (w), 1238 (w), 1190 (w), 1153 (w), 1122 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.32-7.20 (5H, m, aromatics), 6.47 (1H, t, *J*=4.5, C<u>H</u>=C), 5.20 (1H, br s, NC<u>H</u>Ph), 5.11-5.08 (1H, br m, C=C<u>H</u>$_A$H$_B$), 5.04 (1H, br s, C=CH$_A$<u>H</u>$_B$), 4.25 (1H, br s, NC<u>H</u>Ph), 2.43-2.30 (4H, m, C<u>H</u>$_2$CO and C<u>H</u>$_2$CH), 1.92-1.86 (5H, m, CH$_2$C<u>H</u>$_2$CH$_2$ and CC<u>H</u>$_3$); δ_C (67.5 MHz, $CDCl_3$) 194.7 (CH$_2$<u>C</u>O), 171.9 (N<u>C</u>O), 145.4 (<u>C</u>H=C), 141.3, 139.8, 137.3 (<u>C</u>=CH, <u>C</u>=CH aromatic and <u>C</u>=CH$_2$), 128.4, 128.2, 127.2 (<u>C</u>H=C aromatics), 116.9 (C=<u>C</u>H$_2$), 50.9 (N<u>C</u>H$_2$Ph), 38.3 (<u>C</u>H$_2$CO), 25.6 (<u>C</u>H$_2$CH), 22.0 (CH$_2$<u>C</u>H$_2$CH$_2$), 19.8 (C<u>C</u>H$_3$); *m/z* (CI, NH_3) 287 (M+NH_4^+, 10%), 270 (M+H^+, 100), 200 (M-COC(CH$_3$)=CH_2, 15); Found: M+H^+, 270.1490. $C_{17}H_{19}NO_2$ requires for M+H^+, 270.1494.

N-*2-(Cyclohex-1-enyl)ethyl*-N-*(6-oxo-cyclohex-1-enyl)acrylamide* (21)

2-(Cyclohex-1-enyl)ethylamine (1.25 cm^3, 8.92 mmol), acryloyl chloride (0.76 cm^3, 8.92 mmol) and triethylamine (1.37 cm^3, 9.81 mmol) were reacted with 1,2-cyclohexanedione (1.00 g, 8.92 mmol) in benzene (70 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 4:1) afforded alkene (**21**) (1.41 g, 58%) as an oil; R_f 0.29 (diethyl ether); ν_{max} ($CHCl_3$) 3007 (m), 2932 (m), 2837 (w), 1691 (s), 1656 (s), 1615 (m), 1417 (m), 1266 (m), 1236 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.93 (1H, t, *J*=4, COC=C<u>H</u>), 6.28 (1H, dd, *J*=17 and 2, CH=C<u>H</u>$_A$H$_B$), 6.13 (1H, dd, *J*=17 and 10, C<u>H</u>=CH$_2$), 5.53 (1H, dd, *J*=10

and 2, $CH=CH_A\underline{H}_B$), 5.39 (1H, br s, $CH_2C=C\underline{H}CH_2$), 3.89 (1H, m, NC$\underline{H}$), 3.22 (1H, m, NC$\underline{H}$), 2.62-2.53 (4H, m, $C\underline{H}_2CO$ and $COCH=CHC\underline{H}_2$), 2.16-2.06 and 1.98-1.88 (2 x 4H, m, $NCH_2C\underline{H}_2$, $CC\underline{H}_2$, $CH_2C=CHC\underline{H}_2$ and $COC=CHCH_2C\underline{H}_2$), 1.59-1.52 (4H, m, $CCH_2C\underline{H}_2$ and $CH_2C=CHCH_2C\underline{H}_2$); δ_C (67.5 MHz, $CDCl_3$) 194.3 ($CH_2\underline{C}O$), 164.8 (N$\underline{C}$O), 148.6 (COC=$\underline{C}$H), 138.5 (CO$\underline{C}$=CH), 134.2 ($NCH_2CH_2\underline{C}$), 127.8 ($\underline{C}H=CH_2$), 126.4 ($CH=\underline{C}H_2$), 122.0 ($CH_2C=\underline{C}H$) 45.5 ($N\underline{C}H_2$), 37.8, 35.4 ($\underline{C}H_2CO$ and $NCH_2\underline{C}H_2$), 27.6, 25.4, 24.6 ($\underline{C}H_2C=CH$, $\underline{C}H_2CH=CCO$ and $\underline{C}H_2CH=CCH_2$), 22.2, 21.9, 21.7 ($COCH_2\underline{C}H_2$, $CCH_2\underline{C}H_2$ and $C=CHCH_2\underline{C}H_2$); *m/z* (CI, NH_3) 274 ($M+H^+$, 100%); Found: $M+H^+$, 274.1807. $C_{17}H_{23}NO_2$ requires for $M+H^+$, 274.1807.

N-*Allyl*-N-*(6-oxo-cyclohex-1-enyl)benzamide* (24)

Following the general procedure 1,2-cyclohexanedione (0.50 g, 4.46 mmol) in benzene (60 cm^3) was reacted with allylamine (0.37 cm^3, 4.91 mmol), benzoyl chloride (0.57 cm^3, 4.91 mmol) and triethylamine (0.69 cm^3, 4.91 mmol). Column chromatography (silica; diethyl ether-petroleum ether, 3:2) afforded alkene (**24**)[13,14] (0.60 g, 53%) as an oil; R_f 0.15 (diethyl ether-petroleum ether, 3:2); ν_{max} (thin film) 2929 (w), 1688 (s), 1652 (s), 1429 (m), 1388 (m), 1296 (m), 700 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.40-7.23 (5H, m, aromatics), 6.68 (1H, br s, C$\underline{H}$=C), 5.93-5.79 (1H, m, C$\underline{H}$=CH_2), 5.19-5.11 (2H, m, CH=C$\underline{H}_2$), 4.54 (1H, br s, NC$\underline{H}$), 3.90 (1H, br s, NC$\underline{H}$), 2.40-2.15 (4H, br s, $C\underline{H}_2CO$ and $CH_2C\underline{H}_2CH$), 1.90-1.72 (2H, br s, $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 194.4 ($CH_2\underline{C}O$), 170.5 (N$\underline{C}$O), 148.2 ($\underline{C}H$=C), 139.4, 135.9 (N$\underline{C}$=CH and $\underline{C}$=CH aromatic), 132.8 ($\underline{C}H=CH_2$), 129.2, 127.3, 127.0, ($\underline{C}H$=C aromatic), 117.6 ($CH=\underline{C}H_2$), 50.0 ($N\underline{C}H_2CH$), 37.7 ($\underline{C}H_2CO$), 25.3 ($CH_2\underline{C}H_2CH$), 21.7 ($CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 256 ($M+H^+$, 100%), 150 (M-COPh, 15); Found: $M+H^+$, 256.1338. $C_{16}H_{17}NO_2$ requires for $M+H^+$, 256.1338.

General Procedure for the Preparation of Alkenes (27)-(29)

To a stirred solution of 1,2-cyclohexanedione (5.35 mmol) in dichloromethane (40 cm^3) at room temperature was added the acid chloride (5.89 mmol) and triethylamine (5.89 mmol). The solution was stirred at room temperature until t.l.c. indicated that no starting material remained (approx. 2 h). The solution was washed with water, brine, dried (magnesium sulfate) and the solvent evaporated under reduced pressure to afford the crude alkene which was purified by column chromatography (silica) (67-83%).

***(6-Oxocyclohex-1-enyl) acrylate* (27)**

To a solution of 1,2-cyclohexanedione (0.60 g, 5.35 mmol) in dichloromethane (40 cm^3) was added acryloyl chloride (0.48 cm^3, 5.89 mmol) and triethylamine (0.82 cm^3, 5.89 mmol) according to the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 1:1) afforded alkene (**27**) (0.67 g, 75%) as an oil; R_f 0.27 (diethyl ether-petroleum ether, 1:1); ν_{max} ($CHCl_3$) 3032 (w), 2955 (w), 2933 (w), 1743 (s), 1692 (s), 1406 (w), 1255 (w), 1217 (w), 1175 (m), 1156 (s), 1106 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.64 (1H, t, *J*=4.5, C$\underline{H}$=C), 6.51 (1H, dd, *J*=17 and 1.5, $CH=C\underline{H}_A\underline{H}_B$), 6.23 (1H, dd, *J*=17 and 10.5, C$\underline{H}$=CH_2), 5.98 (1H, dd, *J*=10 and 1.5, $CH=CH_A\underline{H}_B$), 2.56-2.49 (4H, m, $C\underline{H}_2CO$ and $C\underline{H}_2CH$), 2.06 (2H, appt. quint., *J*=6.5, $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 191.0 ($CH_2\underline{C}O$), 163.1 (O$\underline{C}$O), 144.5 ($\underline{C}$=CH), 136.0 ($\underline{C}H$=C), 132.2 ($CH=\underline{C}H_2$), 126.6 ($\underline{C}H=CH_2$), 37.3 ($\underline{C}H_2CO$), 24.1 ($\underline{C}H_2CH$), 21.8 ($CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 184 ($M+NH_4^+$, 100%), 167 ($M+H^+$, 55), 55 (15); Found: $M+NH_4^+$, 184.0965. $C_9H_{10}O_3$ requires for $M+NH_4^+$, 184.0974.

***(6-Oxo-cyclohex-1-enyl) methacrylate* (28)**

Following the general procedure 1,2-cyclohexanedione (0.60 g, 5.35 mmol) in dichloromethane (40 cm^3) was reacted with methacryloyl chloride (0.57 cm^3, 5.89 mmol) and triethylamine (0.82 cm^3, 5.89 mmol). Column chromatography (silica; diethyl ether-petroleum ether, 1:1) afforded alkene (**28**) (0.80 g, 83%) as an oil; R_f 0.36 (diethyl ether-petroleum ether, 1:1); ν_{max} ($CHCl_3$) 3033 (w), 3010 (w), 2956 (w), 2936 (w), 1734 (s), 1692 (s), 1456 (w), 1357 (w), 1320 (m), 1296 (m), 1239 (m), 1209 (m), 1176 (s), 1143 (s) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.63 (1H, t, *J*=4.5, C$\underline{H}$=C), 6.25 (1H, br s, $C=C\underline{H}_A\underline{H}_B$), 5.73-5.70 (1H, br m, $C=CH_A\underline{H}_B$), 2.58-2.50 (4H, m, $C\underline{H}_2CO$ and $C\underline{H}_2CH$), 2.08 (2H, appt. quint., *J*=6.5, $CH_2C\underline{H}_2CH_2$), 1.99 (3H, br s, $CC\underline{H}_3$); δ_C (67.5

MHz, $CDCl_3$) 191.3 ($CH_2\underline{C}O$), 164.7 ($O\underline{C}O$), 145.0 ($\underline{C}$=CH), 135.8 ($\underline{C}H$=C), 134.7 ($\underline{C}$=CH_2), 127.0 (C=$\underline{C}H_2$), 37.5 ($\underline{C}H_2CO$), 24.4 ($\underline{C}H_2CH$), 22.1 ($CH_2\underline{C}H_2CH_2$), 17.8 ($C\underline{C}H_3$); *m/z* (CI, NH_3) 198 ($M+NH_4^+$, 85%), 181 ($M+H^+$, 100), 152 (10), 86 (10), 69 (85); Found: $M+NH_4^+$, 198.1129. $C_{10}H_{12}O_3$ requires for $M+NH_4^+$, 198.1130.

(E)-*(6-Oxo-cyclohex-1-enyl) cinnamate* (29)

Trans-cinnamoyl chloride (0.98 g, 5.89 mmol) and triethylamine (0.82 cm^3, 5.89 mmol) were reacted with 1,2-cyclohexanedione (0.60 g, 5.35 mmol) in dichloromethane (40 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 1:1) afforded alkene (**29**) (0.86 g, 67%) as a white solid (m.p. 114-116 °C); R_f 0.25 (diethyl ether-petroleum ether, 1:1); ν_{max} ($CHCl_3$) 3034 (w), 3010 (w), 2953 (w), 2937 (w), 1727 (s), 1692 (s), 1635 (m), 1451 (w), 1356 (w), 1309 (m), 1238 (m), 1202 (w), 1175 (m), 1145 (s), 1106 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.77 (1H, d, *J*=16, CH=C$\underline{H}$Ph), 7.53-7.48 (2H, m, aromatics), 7.39-7.35 (3H, m, aromatics), 6.64 (1H, t, *J*=4, C$\underline{H}$=C), 6.54 (1H, d, *J*=16, C$\underline{H}$=CHPh), 2.57-2.45 (4H, m, $C\underline{H}_2CO$ and $C\underline{H}_2CH$), 2.04 (2H, appt. quint., *J*=6.5, $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 191.6 ($CH_2\underline{C}O$), 164.3 ($O\underline{C}O$), 146.4 (CH=$\underline{C}$HPh), 144.9 ($\underline{C}$=CH), 136.1 (C=$\underline{C}$H), 133.7 ($\underline{C}$=CH aromatic), 130.3, 128.4, 127.7 ($\underline{C}$H=C aromatics), 116.2 ($\underline{C}$H=CHPh), 37.7 ($\underline{C}H_2CO$), 24.5 ($\underline{C}H_2CH$), 22.2 ($CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 260 ($M+NH_4^+$, 80%), 243 ($M+H^+$, 35), 166 (20), 148 (25), 131 (100); Found: $M+NH_4^+$, 260.1286. $C_{15}H_{14}O_3$ requires for $M+NH_4^+$, 260.1287.

General Procedure for Treatment of Precursors with Bu_3SnH

To a 0.1 mol dm^{-3} solution of the alkene (**4**), (**5**), (**8**), (**12**), (**13**), (**17**), (**21**), (**24**) and (**27**)-(**29**) (1eq., 0.56-0.89 mmol) in boiling degassed benzene (6-9 cm^3) was added tributyltin hydride (1.5 eq., 0.85-1.33 mmol) and azobisisobutyronitrile (0.3 eq., 0.17-0.27 mmol). The solution was heated at reflux under nitrogen and monitored by t.l.c.. After 18 h, if starting material remained a further 0.3 eq. of azobisisobutyronitrile were added. When no starting material remained by t.l.c. the solvent was evaporated under reduced pressure to afford crude product which was purified by flash column chromatography (silica).

Treatment of* (E)-N-*benzyl*-N-*(6-oxo-cyclohex-1-enyl)cinnamamide* (4) *with tributyltin hydride

Following the general procedure, alkene (**4**) (0.20 g, 0.61 mmol) in degassed benzene (6 cm^3) was treated with tributyltin hydride (0.27 g, 0.91 mmol) and azobisisobutyronitrile (30 mg). Column chromatography (silica; ethyl acetate-petroleum ether, 1:3) afforded *1-benzyl-4-phenyldecahydroquinoline-2,8-dione* (**6**) (128 mg, 63%) as a separable 1.9:1 mixture of diastereomers.

1-Benzyl-4-phenyldecahydroquinoline-2,8-dione (Major diastereomer): R_f 0.14 (ethyl acetate-petroleum ether, 1:3); ν_{max} ($CHCl_3$) 3007 (m), 2949 (m), 1724 (s), 1641 (s), 1495 (w), 1452 (m), 1248 (w), 788 (w), 704 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37-7.04 (10H, m, aromatics), 5.74 (1H, d, *J*=15, NC$\underline{H}$Ph), 4.11 (1H, d, *J*=5.5, COC$\underline{H}$N), 3.60 (1H, d, *J*=15, NC$\underline{H}$Ph), 2.86-2.66 (3H, m, NCHC$\underline{H}$ and $C\underline{H}_2CON$), 2.61-2.49 (2H, m, C$\underline{H}$Ph and $CH_2C\underline{H}COC$), 2.40-2.28 (1H, m, $CH_2C\underline{H}COC$), 1.78-1.61 (4H, m, $CH_2C\underline{H}_2CH$ and $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 207.2 ($CH_2\underline{C}OCH$), 169.1 ($N\underline{C}O$), 140.7, 136.7 ($\underline{C}$=CH aromatic), 128.9, 128.1, 127.5, 127.3, 127.2, 126.9 ($\underline{C}$H=C aromatic), 66.6 (CO$\underline{C}$HN), 49.0 ($N\underline{C}H_2Ph$), 43.5 ($\underline{C}$HPh), 40.9, 40.1 ($\underline{C}H_2COCH$ and $NCO\underline{C}H_2$), 38.9 (NCH$\underline{C}$H) 25.9 ($CH_2\underline{C}H_2CH$), 22.2 ($CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 334 ($M+H^+$, 100%), 268 (65), 204 (20); Found: $M+H^+$, 334.1799. $C_{22}H_{23}NO_2$ requires for $M+H^+$, 334.1807. *(Minor diastereomer)*: R_f 0.17 (ethyl acetate-petroleum ether, 1:3); ν_{max} ($CHCl_3$) 3031 (w), 3007 (w), 2951 (w), 1718 (m), 1641 (s), 1449 (w), 1412 (w), 1247 (w), 704 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.39-7.03 (10H, m, aromatics), 5.06 (1H, d, *J*=15, NC$\underline{H}$Ph), 4.11-4.04 (2H, m, NC$\underline{H}$Ph and COC$\underline{H}$N), 3.31-2.15 (6H, m, $C\underline{H}_2COC$, $NCOC\underline{H}_2$, NCHC$\underline{H}$ and C$\underline{H}$Ph), 2.04-1.20 (4H, m, $CH_2C\underline{H}_2CH_2$ and $CH_2C\underline{H}_2CH$); δ_C (67.5 MHz, $CDCl_3$) 209.4 ($CH_2\underline{C}OCH$), 170.1 ($N\underline{C}O$), 140.0, 136.5 ($\underline{C}$=CH aromatic), 129.5, 129.0, 128.5, 128.0, 127.6, 127.2 ($\underline{C}$H=C aromatic), 68.9 (CO$\underline{C}$HN), 48.2 ($N\underline{C}H_2Ph$), 43.9, 41.1 ($\underline{C}$HPh and $CH_2CH_2\underline{C}H$), 38.6, 32.9 ($\underline{C}H_2COCH$ and $NCO\underline{C}H_2$), 25.6 ($CH_2\underline{C}H_2CH$), 19.7 ($CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 334 ($M+H^+$, 100%), 272 (10), 204 (10); Found: $M+H^+$, 334.1803. $C_{22}H_{23}NO_2$ requires for $M+H^+$, 334.1807.

Treatment of* N-*benzyl*-N-*(6-oxo-cyclohex-1-enyl)-3,3-dimethylacrylamide* (5) *with tributyltin hydride
Following the general procedure, alkene (**5**) (0.18 g, 0.63 mmol) in degassed benzene (6 cm^3) was treated with tributyltin hydride (0.27 g, 0.94 mmol) and azobisisobutyronitrile (31 mg). Column chromatography (silica; ethyl acetate-petroleum ether, 4:1) afforded *N-benzyl-N-(2-oxo-cyclohexyl)-3,3-dimethylacrylamide* (**7**) (54 mg, 30%). R_f 0.28 (diethyl ether-petroleum ether, 4:1); ν_{max} ($CHCl_3$) 3038 (w), 3005 (m), 2944 (m), 2871 (w), 1706 (s), 1649 (m), 1618 (s), 1451 (m), 1415 (w), 1352 (w), 1234 (w), 1179 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37-7.20 (5H, m, aromatics), 5.79-5.77 (1H, br m, NCOCH), 4.99 (1H, dd, *J*=12 and 5.5, COCHN), 4.84 (1H, d, *J*=18, NCHPh), 4.31 (1H, d, *J*=18, NCHPh), 2.57-2.32 (4H, m, CH_2CO and CH_2CH), 2.03-1.50 (10H, m, CH_2CH_2CO, CH_2CH_2CH and 2 x CCH_3); δ_C (67.5 MHz, $CDCl_3$) 206.7 (CH_2CO), 169.6 (NCO), 149.7 ($C(CH_3)_2$), 138.5 (C=CH aromatic), 128.5, 127.0, 126.0 (C=CH aromatics), 117.4 ($CH=C(CH_3)_2$), 62.8 (COCHN), 50.4 (NCH_2Ph), 41.3 (CH_2CO), 31.5 (CH_2CH), 26.6 (CCH_3), 26.1, 24.6 (CH_2CH_2CO and CH_2CH_2CH), 20.4 (CCH_3); *m/z* (CI, NH_3) 286 ($M+H^+$, 100%); Found: $M+H^+$, 286.1810. $C_{18}H_{23}NO_2$ requires for $M+H^+$, 286.1807.

Treatment of* (E)-N-*benzyl*-N-*(6-oxo-cyclohex-1-enyl)-3-methylacrylamide* (8) *with tributyltin hydride
Following the general procedure, alkene (**8**) (0.15 g, 0.56 mmol) in degassed benzene (6 cm^3) was treated with tributyltin hydride (0.25 g, 0.85 mmol) and azobisisobutyronitrile (28 mg). Column chromatography (silica; ethyl acetate-petroleum ether, 3:2) afforded N-*benzyl*-N-*(2-oxo-cyclohexyl) methylacrylamide* (**9**) (42 mg, 26%), and *1-benzyl-1-azaspiro[5.4.0]decane-2,6-dione* (**10**) (54 mg, 35%) as a separable 2.9:1 mixture of diastereomers.
(E)-N-*Benzyl*-N-*(2-oxo-cyclohexyl) methylacrylamide* (**9**): R_f 0.35 (ethyl acetate-petroleum ether, 3:2); ν_{max} (thin film) 3007 (m), 2946 (m), 1718 (m), 1660 (s), 1611 (s), 1449 (m), 1420 (m), 1349 (w), 1234 (w), 964 (m), 754 (w), 727 (w), 701 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.38-7.21 (5H, m, aromatics), 6.98 (1H, dq, *J*=15 and 7, $CHCH_3$), 6.11 (1H, dq, *J*=15 and 1.5, $CH=CHCH_3$), 5.10-5.04 (1H, br m, COCHN), 4.88 (1H, d, *J*=18.5, NCHPh), 4.34 (1H, d, *J*=18.5, NCHPh), 2.57-2.33 (2H, m, CH_2CO), 2.10-1.94 (2H, m, CH_2CH), 1.87-1.50 (7H, m, CH_2CH_2CO, CH_2CH_2CH and $CHCH_3$); δ_C (67.5 MHz, $CDCl_3$) 206.6 (CH_2CO), 167.9 (NCO), 143.3 ($CHCH_3$), 138.4 (C=CH aromatic), 128.6, 127.1, 125.9 (CH=C aromatics), 121.8 ($CH=CHCH_3$), 63.3 (COCHN), 49.7 (NCH_2Ph), 41.3 (CH_2CO), 31.5 (CH_2CH), 26.2, 24.6 (CH_2CH_2CO and CH_2CH_2CH), 18.1 ($CHCH_3$); *m/z* (CI, NH_3) 272 ($M+H^+$, 85%), 193 (10), 176 (100); Found: $M+H^+$, 272.1648. $C_{17}H_{21}NO_2$ requires for $M+H^+$, 272.1651.
(4R*S*,5R*S*)-*1-Benzyl-1-azaspiro[5.4.0]decane-2,6-dione* (**10**). *(Major diastereomer)*: R_f 0.20 (ethyl acetate-petroleum ether, 3:2); ν_{max} (thin film) 3006 (m), 2946 (m), 2871 (w), 1707 (s), 1690 (s), 1451 (m), 1405 (s), 1355 (w), 707 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.28-7.20 (5H, m, aromatics), 4.94 (1H, d, *J*=16, NCHPh), 4.03 (1H, d, *J*=16, NCHPh), 2.74 (1H, dd, *J*=8 and 16.5, CHCON), 2.59-2.44 (2H, m, CH_2COC or $NCCH_2$), 2.29 (1H, ddd, *J*=15, 13 and 6.5, CHCOC or NCCH), 2.08 (1H, dd, *J*=16.5 and 5, CHCON), 2.05-1.94 (1H, m, CHCOC or NCCH), 1.82-1.46 (5H, m, $CHCH_3$, CH_2CH_2C and CH_2CH_2CO), 1.05 (3H, d, *J*=7, $CHCH_3$); δ_C (67.5 MHz, $CDCl_3$) 208.2 (CH_2COC), 175.2 (NCO), 138.9 (C=CH aromatic), 128.7, 128.0, 127.3 (CH=C aromatics), 76.5 (COCN), 45.7 (NCH_2Ph), 42.4, 38.4 (CH_2COC and CH_2CON), 37.5 (CH_2CN), 36.4 ($CHCH_3$), 25.7, 22.8 (CH_2CH_2CO and CH_2CH_2C), 18.1 ($CHCH_3$); *m/z* (CI, NH_3) 272 ($M+H^+$, 100%); Found: $M+H^+$, 272.1646. $C_{17}H_{21}NO_2$ requires for $M+H^+$, 272.1651. *(Minor diastereomer)*: R_f 0.16 (ethyl acetate-petroleum ether, 3:2); ν_{max} (thin film) 3006 (m), 2946 (m), 2871 (w), 1707 (s), 1690 (s), 1451 (m), 1405 (s), 1356 (w), 707 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.30-7.18 (5H, m, aromatics), 5.16 (1H, d, *J*=16.5, NCHPh), 3.58 (1H, d, *J*=16.5, NCHPh), 2.61-1.96 (4H, m, CH_2CON and CH_2COC), 2.11-1.96 (2H, m, $NCCH_2$), 1.88-1.51 (5H, m, $CHCH_3$, CH_2CH_2C and CH_2CH_2CO) 1.12 (3H, d, *J*=7, $CHCH_3$); δ_C (67.5 MHz, $CDCl_3$) 209.3 (CH_2COC), 176.2 (NCO), 139.4 (C=CH aromatic), 128.8, 128.0, 127.3 (CH=C aromatics), 76.6 (COCN), 45.2 (NCH_2Ph), 39.4 (CH_2COC), 37.8 (CH_2CON), 33.0 ($CHCH_3$), 32.5 (CH_2C) 26.3, 21.9 (CH_2CH_2CO and CH_2CH_2C), 16.3 ($CHCH_3$); *m/z* (CI, NH_3) 272 ($M+H^+$, 100%); Found: $M+H^+$, 272.1646. $C_{17}H_{21}NO_2$ requires for $M+H^+$, 272.1651.

Treatment of* N-*benzyl*-N-*(6-oxo-cyclohex-1-enyl)acrylamide* (12) *with tributyltin hydride
Following the general procedure, alkene (**12**) (0.23 g, 0.89 mmol) in degassed benzene (9 cm^3) was treated with tributyltin hydride (0.39 g, 1.33 mmol) and azobisisobutyronitrile (44 mg). Column chromatography

(silica; ethyl acetate-petroleum ether, 3:7) afforded *1-benzyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**14**) (283 mg, 59%) as a separable 2:1 mixture of diastereomers.

(3R*,3aR*,7aS*)-*1-Benzyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**14**) *(Major diastereomer)*: R_f 0.31 (ethyl acetate-petroleum ether, 3:7); ν_{max} (thin film) 2957 (m), 2927 (m), 2872 (w), 2855 (w), 1727 (m), 1695 (s), 1453 (m), 1418 (m), 1207 (w), 1076 (w), 702 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.33-7.16 (5H, m, aromatics), 5.25 (1H, d, *J*=15, NCHPh), 4.17 (1H, d, *J*=15, NCHPh), 3.69 (1H, d, *J*=8, COCHN), 2.38-2.19 (4H, m, CH_2CO, CHCON and $CHCHCH_2$), 2.01-1.60 (4H, m, CH_2CH_2CH and $CH_2CH_2CH_2$), 1.49 (6H, appt quin, *J*=8, 3 x $SnCH_2CH_2$), 1.31 (6H, appt sext, *J*=7, 3 x CH_2CH_3), 1.02 (1H, dd, *J*=5 and 13, CHCHSn), 0.89 (15H, appt t, *J*=7.5, 3 x CH_2CH_3 and $SnCH_2CH_2$), 0.72 (1H, dd, *J*=13 and 9.5, CHCHSn); δ_C (67.5 MHz, $CDCl_3$) 209.8 (CH_2CO), 176.2 (NCO), 136.5 (C=CH aromatic), 128.6, 128.3, 127.4 (CH=C aromatics), 62.7 (COCHN), 48.1 (NCOCH or CH_2CH_2CH), 46.2 (NCH_2Ph), 42.3 (NCOCH or CH_2CH_2CH), 40.2 (CH_2CO), 29.1, 27.3 (CH_2CH_3 and $SnCH_2CH_2$), 25.0, 22.5 (CH_2CH_2CH and $CH_2CH_2CH_2$), 13.6 (CH_2CH_3), 10.2 ($SnCH_2CH_2$), 8.1 ($SnCH_2CH$); *m/z* (CI, NH_3) 548 (M^{120}+H^+, 2%), 546 (M^{118}+H^+, 2), 544 (M^{116}+H^+, 1), 490 (100), 256 (25); Found: M^{116}+H^+, 544.2545. $C_{28}H_{45}NO_2Sn$ requires for M^{116}+H^+, 544.2546.

(3R*,3aR*,7aR*)-*1-Benzyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**14**) *(Minor diastereomer)*: R_f 0.37 (ethyl acetate-petroleum ether, 3:7); ν_{max} (thin film) 2950 (s), 2923 (s), 2868 (s), 1688 (s), 1452 (m), 1392 (m), 1355 (w), 701 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.31-7.13 (5H, m, aromatics), 5.20 (1H, d, *J*=14, NCHPh), 4.44 (1H, d, *J*=14, NCHPh), 3.47 (1H, d, *J*=11.5, COCHN), 2.32-1.99 (4H, m, CH_2CO, CHCON and $CHCHCH_2$), 1.79-1.60 (2H, m, CH_2CH_2CH or $CH_2CH_2CH_2$), 1.57-1.40 (8H, m, 3 x $SnCH_2CH_2$ and CH_2CH_2CH or CH_2CH_2CO) 1.32 (6H, appt sext, *J*=7, 3 x CH_2CH_3), 1.09-0.75 (17H, m, 3 x CH_2CH_3 and $SnCH_2CH_2$, $SnCH_2CH$); δ_C (67.5 MHz, $CDCl_3$) 205.7 (CH_2CO), 177.5 (NCO), 136.5 (C=CH aromatic), 128.6, 128.5, 127.5 (CH=C aromatics), 65.9 (COCHN), 53.8 (NCOCH), 46.9 (CH_2CH_2CH), 45.0 (NCH_2Ph), 39.9 (CH_2CO), 29.1 ($SnCH_2CH_2$ or CH_2CH_3), 27.6, (CH_2CH_2CH or $CH_2CH_2CH_2$), 27.4 ($SnCH_2CH_2$ or CH_2CH_3), 27.0 (CH_2CH_2CH or $CH_2CH_2CH_2$), 13.7 (CH_2CH_3), 10.2 ($SnCH_2CH_2$), 8.1 ($SnCH_2CH$); *m/z* (CI, NH_3) 546 (M^{118}+H^+, 1%), 544 (M^{116}+H^+, 1), 490 (100), 256 (25); Found: M^{116}+H^+, 544.2544. $C_{28}H_{45}NO_2Sn$ requires for M^{116}+H^+, 544.2546.

Treatment of* N-*allyl*-N-*(6-oxo-cyclohex-1-enyl)acrylamide* (13) *with tributyltin hydride

To a solution of alkene (**13**) (0.19 g, 0.92 mmol) in degassed benzene (10 cm^3) was added tributyltin hydride (0.40 g, 1.38 mmol) and azobisisobutyronitrile (45 mg) according to the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 3:7) afforded *1-allyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**15**) (196 mg, 43%) as a separable 3.3:1 mixture of diastereomers.

(3R*,3aR*,7aS*)-*1-Allyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**15**) *(Major diastereomer)*: R_f 0.23 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 3006 (m), 2956 (s), 2926 (s), 2872 (m), 1718 (s), 1690 (s), 1454 (m), 1416 (m), 1267 (w), 1238 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.70 (1H, m, $CH=CH_2$), 5.17-5.09 (2H, m, $CH=CH_2$), 4.56 (1H, appt. ddt, *J*=15.5, 4.5 and 1.5, NCH), 3.96 (1H, d, *J*=8.5, COCHN), 3.67 (1H, dd, *J*=15.5 and 8, NCH), 2.41-2.37 (3H, m, CH_2CO and CHCON), 2.26-2.16 (1H, m, CH_2CH_2CH), 2.06-1.94 and 1.85-1.74 (2 x 2H, m, $CH_2CH_2CH_2$ and CH_2CH_2CH), 1.55-1.41 (6H, m, 3 x $SnCH_2CH_2$), 1.29 (6H, appt sext, *J*=7, 3 x CH_2CH_3), 1.01 (1H, dd, *J*=13 and 5, CHCHSn), 0.91-0.83 (15H, m, 3 x CH_2CH_3 and $SnCH_2CH_2$), 0.70 (1H, dd, *J*=13 and 9.5, CHCHSn); δ_C (67.5 MHz, $CDCl_3$) 209.5 (CH_2CO), 176.0 (NCO), 132.6 ($CH=CH_2$), 118.0 ($CH=CH_2$), 63.1 (COCHN), 48.1 (NCOCH or CH_2CH_2CH), 45.0 (NCH_2 or CH_2CO), 42.4 (NCOCH or CH_2CH_2CH), 40.2 (NCH_2 or CH_2CO), 29.2, 27.3 ($SnCH_2CH_2$ and CH_2CH_3), 25.1, 22.6 (CH_2CH_2CH and $CH_2CH_2CH_2$), 13.7 (CH_2CH_3), 10.1 ($SnCH_2CH_2$), 8.6 ($SnCH_2CH$); *m/z* (CI, NH_3) 500 (M^{122}+H^+, 2%), 498 (M^{120}+H^+, 2), 496 (M^{118}+H^+, 1), 494 (M^{116}+H^+, 1), 440 (100), 308 (5), 208 (10); Found: M^{116}+H^+, 494.2389. $C_{24}H_{43}NO_2Sn$ requires for M^{116}+H^+, 494.2389.

(3R*,3aR*,7aR*)-*1-Allyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**15**) *(Minor diastereomer)*: R_f 0.27 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 3003 (w), 2958 (m), 2928 (m), 2871 (m), 1691 (s), 1636 (m), 1457 (w), 1396 (m), 1341 (w), 1288 (w), 1244 (w), 1185 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.75-5.60 (1H, m, $CH=CH_2$), 5.11 (1H, br d, *J*=17.5, $CH=CH_AH_B$), 5.09 (1H, br d, *J*=9.5, $CH=CH_AH_B$), 4.44 (1H, br dd, *J*=15 and 4.5, NCH), 3.96 (1H, dd, *J*=15 and 8.5, NCH), 3.81 (1H, d, *J*=11, COCHN), 2.49-2.09 (4H, m, CH_2CO, CHCON and $CHCHCH_2$), 1.82-1.55 (4H, m, $CH_2CH_2CH_2$ and CH_2CH_2CH), 1.54-1.41 (6H, m, 3 x

$SnCH_2\underline{C}H_2$), 1.30 (6H, appt sext, *J*=7, 3 x $C\underline{H}_2CH_3$), 1.03 (1H, dd, *J*=13 and 5.5, CHC<u>H</u>Sn), 0.91-0.83 (15H, m, 3 x $CH_2C\underline{H}_3$ and $SnC\underline{H}_2CH_2$), 0.77 (1H, dd, *J*=13 and 9.5, CHC<u>H</u>Sn); δ_C (67.5 MHz, $CDCl_3$) 205.5 ($CH_2\underline{C}O$), 177.3 (N<u>C</u>O), 132.2 ($\underline{C}H{=}CH_2$), 118.4 (CH=$\underline{C}H_2$), 66.6 (CO<u>C</u>HN), 54.1, 46.5 (NCO<u>C</u>H and $CH_2CH_2\underline{C}H$), 44.1, 40.0 (N<u>C</u>H_2 and $\underline{C}H_2CO$), 29.0 ($SnCH_2\underline{C}H_2$ or $\underline{C}H_2CH_3$), 27.8 ($CH_2\underline{C}H_2CH$ or $CH_2\underline{C}H_2CH_2$), 27.4 ($SnCH_2\underline{C}H_2$ or $\underline{C}H_2CH_3$), 27.2 ($CH_2\underline{C}H_2CH$ or $CH_2\underline{C}H_2CH_2$), 13.7 ($CH_2\underline{C}H_3$), 10.1 ($Sn\underline{C}H_2CH_2$), 8.2 ($Sn\underline{C}H_2CH$); *m/z* (CI, NH_3) 500 (M^{122}+H^+, 2%), 440 (100), 206 (5); Found: M^{116}+H^+, 494.2392. $C_{24}H_{43}NO_2Sn$ requires for M^{116}+H^+, 494.2389.

Treatment of N-benzyl-N-(6-oxo-cyclohex-1-enyl)methacrylamide* (17) *with tributyltin hydride

Following the general procedure, alkene (**17**) (0.20 g, 0.74 mmol) in degassed benzene (7 cm^3) was treated with tributyltin hydride (0.32 g, 1.12 mmol) and azobisisobutyronitrile (37 mg). Column chromatography (silica; diethyl ether-petroleum ether, 1:4) afforded *1-benzyl-3-methyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**18**) (162 mg, 39%), *1-benzyl-3-methyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**19**) (41 mg, 10%) and *1-benzyl-3-methyl-3-tributylstannanylmethyl-7a-hydroxyoctahydroindole-2,7-dione* (**20**) (98 mg, 23%) as an inseparable mixture except for the major isomer of (**18**).

(3R*S*,3aR*,7aS*)-*1-Benzyl-3-methyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**18**) *(Major diastereomer)*: R_f 0.30 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 2956 (s), 2925 (s), 2872 (m), 2246 (w), 1720 (s), 1684 (s), 1458 (m), 1422 (m), 1265 (w), 1077 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.34-7.17 (5H, m, aromatics), 5.04 (1H, d, *J*=14.5, NC<u>H</u>Ph), 4.20 (1H, d, *J*=14.5, NC<u>H</u>Ph), 3.75 (1H, d, *J*=9, COC<u>H</u>N), 2.49-2.12 (3H, m, $C\underline{H}_2CO$ and NCHC<u>H</u>), 1.91-1.80 (3H, m, $CH_2C\underline{H}_2CH_2$ and $CH_2C\underline{H}CHN$ or $CH_2C\underline{H}_2CH$ and $CH_2C\underline{H}CH_2$), 1.63-1.41 (7H, m, $CH_2C\underline{H}CHN$ or $CH_2C\underline{H}CH_2$ and 3 x $SnCH_2C\underline{H}_2$), 1.37-1.21 (6H, m, 3 x $C\underline{H}_2CH_3$), 1.03-0.96 (5H, m, $SnC\underline{H}_2C$ and $CC\underline{H}_3$), 0.92-0.75 (15H, m, 3 x $CH_2C\underline{H}_3$ and $SnC\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 210.3 ($CH_2\underline{C}O$), 179.9 (N<u>C</u>O), 136.4 (<u>C</u>=CH aromatic), 128.5, 127.5 (<u>C</u>H=C aromatics), 62.2 (CO<u>C</u>HN), 48.8 (NCH<u>C</u>H), 46.8 ($\underline{C}CH_3$), 46.0 (N<u>C</u>H_2Ph), 39.1 ($\underline{C}H_2CO$), 29.1, 27.4 ($\underline{C}H_2CH_3$ and $SnCH_2\underline{C}H_2$), 23.4, 22.8 ($CH_2\underline{C}H_2CH$ and $CH_2\underline{C}H_2CH_2$), 22.3 ($C\underline{C}H_3$), 21.1 ($Sn\underline{C}H_2C$), 13.7 ($CH_2\underline{C}H_3$), 10.6 ($Sn\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 562 (M^{120}+H^+, 1%), 504 (100), 272 (35), 230 (10), 193 (5), 176 (30), 114 (10). *(Minor diastereomer)*: The presence of this was indicated by δ_H (270 MHz, $CDCl_3$) 5.03 (1H, d, *J*=15, NC<u>H</u>Ph), 4.18 (1H, d, *J*=15, NC<u>H</u>Ph), 3.74 (1H, d, *J*=8.5, COC<u>H</u>N); δ_C (67.5 MHz, $CDCl_3$) 210.4 ($CH_2\underline{C}O$), 180.0 (N<u>C</u>O), 62.2 (CO<u>C</u>HN); *m/z* (CI, NH_3) 562 (M^{120}+H^+, 1%).

(3R*S*,3aR*,7aR*)-*1-Benzyl-3-methyl-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**19**) *(Major diastereomer)*: The presence of this was indicated by δ_H (270 MHz, $CDCl_3$) 5.18 (1H, d, *J*=14, NC<u>H</u>Ph), 4.39 (1H, d, *J*=14, NC<u>H</u>Ph), 3.44 (1H, d, *J*=12, COC<u>H</u>N); δ_C (67.5 MHz, $CDCl_3$) 206.4 ($CH_2\underline{C}O$), 180.2 (N<u>C</u>O), 64.3 (CO<u>C</u>HN); *m/z* (CI, NH_3) 562 (M^{120}+H^+, 1%). *(Minor diastereomer)*: The presence of this was indicated by δ_H (270 MHz, $CDCl_3$) 5.11 (1H, d, *J*=14.5, NC<u>H</u>Ph), 4.44 (1H, d, *J*=14.5, NC<u>H</u>Ph), 3.55 (1H, d, *J*=12, COC<u>H</u>N); δ_C (67.5 MHz, $CDCl_3$) 64.5 (CO<u>C</u>HN); *m/z* (CI, NH_3) 562 (M^{120}+H^+, 1%).

(3R*S*,3aR*S*,7aR*S*)-*1-Benzyl-3-methyl-3-tributylstannanylmethyl-7a-hydroxyoctahydroindole-2,7-dione* (**20**) *(Major diastereomer)*: The presence of this was indicated by ν_{max} ($CHCl_3$) 3468 (br w, OH) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.06 (1H, s, CO<u>H</u>), 4.74 (1H, d, *J*=15, NC<u>H</u>Ph), 3.76 (1H, d, *J*=15, NC<u>H</u>Ph); δ_C (67.5 MHz, $CDCl_3$) 209.3 ($CH_2\underline{C}O$), 182.2 (N<u>C</u>O), 88.4 (<u>C</u>OH); *m/z* (CI, NH_3) 578 (M^{120}+H^+, 5%). *(Minor diastereomer)*: The presence of this was indicated by ν_{max} ($CHCl_3$) 3468 (br w, OH) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.10 (1H, s, CO<u>H</u>), 4.74 (1H, d, *J*=15, NC<u>H</u>Ph), 3.76 (1H, d, *J*=15, NC<u>H</u>Ph); δ_C (67.5 MHz, $CDCl_3$) 88.2 (<u>C</u>OH); *m/z* (CI, NH_3) 578 (M^{120}+H^+, 5%).

Treatment of* N-*2-(cyclohex-1-enyl)ethyl*-N-*(6-oxo-cyclohex-1-enyl)acrylamide* (21) *with tributyltin hydride

Tributyltin hydride (0.41 g, 1.42 mmol) and azobisisobutyronitrile (46 mg) were reacted with alkene (**21**) (0.26 g, 0.94 mmol) dissolved in degassed benzene (10 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 1:4) afforded *1-(2-(cyclohex-1-enyl)ethyl)-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**22**) (301 mg, 57%) as a separable 3.4:1 mixture of diastereomers and *7-tributylstannanylmethyl-perhydroerythrinan-4,8-dione* (**23**) (21 mg, 4%).

(3R*,3aR*,7aS*)-*1-(2-(Cyclohex-1-enyl)ethyl)-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**22**) *(Major diastereomer)*: R_f 0.13 (diethyl ether-petroleum ether, 1:4); ν_{max} ($CHCl_3$) 3023 (m), 2999 (w), 2953

(s), 2927 (s), 2872 (m), 1716 (m), 1687 (s), 1457 (m), 1425 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.39 (1H, br s, C=CH), 4.00 (1H, dt, *J*=14 and 7.5, NCHCH$_2$), 3.96 (1H, d, *J*=8.5, COCHN), 3.10 (1H, dt, J=14 and 6.5, NCHCH$_2$), 2.42-2.30 (3H, m, CH$_2$CO and CHCON), 2.18-1.74 (11H, m, NCHCH, NCH$_2$CH$_2$, CH$_2$C=CH, CH$_2$CH=C, CH$_2$CH$_2$CO and NCHCHCH$_2$), 1.62-1.41 (10H, m, C=CHCH$_2$CH$_2$, CH=CCH$_2$CH$_2$ and 3 x SnCH$_2$CH$_2$), 1.29 (6H, appt sext, *J*=7, 3 x CH$_2$CH$_3$), 0.99-0.73 (16H, m, CHCHSn, 3 x CH$_2$CH$_3$ and SnCH$_2$CH$_2$), 0.64 (1H, dd, *J*=13 and 9.5, CHCHSn); δ_C (67.5 MHz, $CDCl_3$) 209.7 (CH$_2$CO), 176.3 (NCO), 135.0 (C=CH), 122.9 (CH=C), 63.8 (COCHN), 48.1, 42.7 (NCOCH and NCHCH), 40.4, 40.1 (NCH$_2$ and CH$_2$CO), 35.5 (CCH$_2$CH$_2$), 29.2 (CH$_2$CH$_3$ or SnCH$_2$CH$_2$), 27.8 (CH$_2$C=C) 27.4 (SnCH$_2$CH$_2$ or CH$_2$CH$_3$), 25.3, 25.2, 22.8, 22.7, 22.3 (CH$_2$C=C and 4 x CH$_2$CH$_2$), 13.7 (CH$_2$CH$_3$), 10.2 (SnCH$_2$CH$_2$), 9.1 (SnCH$_2$CH); *m/z* (CI, NH_3) 566 (M^{120}+H$^+$, 1%), 564 (M^{118}+H$^+$, 1), 524 (2), 508 (100), 276 (40).

(3R*,3aR*,7aR*)-*1-(2-(Cyclohex-1-enyl)ethyl)-3-tributylstannanylmethyloctahydroindole-2,7-dione* (**22**) *(Minor diastereomer)*: R_f 0.23 (diethyl ether-petroleum ether, 1:4); ν_{max} ($CHCl_3$) 3023 (m), 2954 (s), 2927 (s), 2870 (m), 1721 (m), 1691 (s), 1455 (w) 1400 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.38 (1H, br s, C=CH), 3.91-3.78 (2H, m, COCHN and NCHCH$_2$), 3.52 (1H, dt, J=13.5 and 6.5, NCHCH$_2$), 2.48-1.70 (14H, m, CH$_2$CO, CHCON, NCHCH, NCH$_2$CH$_2$, CH$_2$C=CH, CH$_2$CH=C, CH$_2$CH$_2$CO and NCHCHCH$_2$), 1.61-1.41 (10H, m, C=CHCH$_2$CH$_2$, CH=CCH$_2$CH$_2$ and 3 x SnCH$_2$CH$_2$), 1.28 (6H, appt sext, *J*=7, 3 x CH$_2$CH$_3$), 1.00 (1H, dd, *J*=13 and 5, CHCHSn), 0.91-0.80 (15H, m, 3 x CH$_2$CH$_3$ and SnCH$_2$CH$_2$), 0.73 (1H, dd, *J*=13 and 10, CHCHSn); δ_C (67.5 MHz, $CDCl_3$) 205.8 (CH$_2$CO), 177.1 (NCO), 135.4 (C=CH), 123.1 (CH=C), 67.3 (COCHN), 54.5, 46.5 (NCOCH and NCHCH), 40.1, 39.5 (NCH$_2$ and CH$_2$CO), 35.7 (CCH$_2$CH$_2$), 29.2 (CH$_2$CH$_3$ or SnCH$_2$CH$_2$), 27.9, 27.8 (2 x CH$_2$=C), 27.4 (CH$_2$CH$_3$ or SnCH$_2$CH$_2$), 27.3, 25.3, 22.8, 22.4 (4 x CH$_2$CH$_2$) 13.7 (CH$_2$CH$_3$), 10.2 (SnCH$_2$CH$_2$), 9.8 (SnCH$_2$CH); *m/z* (CI, NH_3) 566 (M^{120}+H$^+$, 2%), 564 (M^{118}+H$^+$, 2), 525 (2), 508 (100), 274 (20).

7-tributylstannanylmethyl-perhydroerythrinan-4,8-dione (**23**): R_f 0.15 (diethyl ether-petroleum ether, 1:4); ν_{max} ($CHCl_3$) 3021 (m), 2928 (s), 2856 (m), 1700 (m), 1674 (s), 1456 (w), 1425 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 4.10 (1H, ddd, *J*=13, 5.5 and 1.5, NCH), 3.49 (1H, ddt, J=3.5, 1.5 and 13, NCH), 2.54-2.25 (3H, m, CH$_2$CO, CHCON), 2.07-1.03 (29H, m, NCHCH, NCH$_2$CH$_2$CH, NCH$_2$CH$_2$CHCH, 3 x CH$_2$CH$_2$CH$_2$, 4 x CH$_2$CH$_2$CH, 3 x SnCH$_2$CH$_2$ and 3 x CH$_2$CH$_3$), 0.98-0.80 (16H, m, CHCHSn, 3 x CH$_2$CH$_3$ and SnCH$_2$CH$_2$), 0.72 (1H, dd, *J*=13 and 9.5, CHCHSn); δ_C (67.5 MHz, $CDCl_3$) 212.6 (CH$_2$CO), 174.3 (NCO), 69.2 (COCN), 54.3, 53.8 (NCOCH and NCOCHCH), 43.0 (NCH$_2$ or CH$_2$CO), 41.9 (NCH$_2$CH$_2$CH or NCH$_2$CH$_2$CHCH), 38.8 (NCH$_2$ or CH$_2$CO), 34.9 (NCH$_2$CH$_2$CH or NCH$_2$CH$_2$CHCH), 34.2, 32.2, 30.0 (3 x CH$_2$CH$_2$), 29.3 (CH$_2$CH$_3$ or SnCH$_2$CH$_2$), 27.8 (CCH$_2$CH$_2$), 27.4 (SnCH$_2$CH$_2$ or CH$_2$CH$_3$), 26.9, 25.5, 19.8 (3 x CH$_2$CH$_2$), 13.8 (CH$_2$CH$_3$), 10.2 (SnCH$_2$CH$_2$), 10.1 (SnCH$_2$CH); *m/z* (CI, NH_3) 566 (M^{120}+H$^+$, 1%), 564 (M^{118}+H$^+$, 1), 508 (100), 274 (5).

Treatment of* N-*allyl*-N-*(6-oxo-cyclohex-1-enyl)benzamide* (24) *with tributyltin hydride

Tributyltin hydride (0.23 g, 0.81 mmol) and azobisisobutyronitrile (26 mg) were reacted with alkene (**24**) (0.14 g, 0.54 mmol) dissolved in degassed benzene (6 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 7:3) afforded N-*allyl*-N-*(2-oxo-cyclohexyl)benzamide* (**25**) (62 mg, 45%). R_f 0.24 (diethyl ether-petroleum ether, 7:3); ν_{max} ($CHCl_3$) 3007 (m), 2947 (m), 2871 (w), 1721 (s), 1630 (s), 1449 (m), 1414 (m), 1316 (w), 1255 (w), 1125 (w) cm^{-1}; δ_H (270 MHz, toluene-d_8, 80 °C) 7.41-7.37 (2H, m, aromatics), 7.15-7.00 (3H, m, aromatics), 5.76-5.65 (1H, m, CH=CH$_2$), 4.98 (1H, d, *J*=16.5, CH=CH$_A$H$_B$), 4.93 (1H, d, *J*=10, CH=CH$_A$H$_B$), 4.33 (1H, t, *J*=9.5, COCHN), 4.02 (1H, br d, *J*=14, NCH), 3.62 (1H, dd, *J*=16.5 and 5, NCH), 2.32 (1H, br d, *J*=15.5, CHCO), 1.92-1.79 (3H, m, CHCO and CH$_2$CH), 1.59-1.15 (4H, m, CH$_2$CH$_2$CO and CH$_2$CH$_2$CH); δ_C (67.5 MHz, $CDCl_3$) 205.3 (CH$_2$CO), 172.3 (NCO), 136.2 (C=CH aromatic), 134.9 (CH=CH$_2$), 129.4, 128.1, 126.5 (CH=C aromatic), 116.9 (CH=CH$_2$), 63.3 (COCHN), 51.3 (NCH$_2$), 41.1 (CH$_2$CO), 30.6 (CH$_2$CH), 25.5, 24.5 (CH$_2$CH$_2$CO and CH$_2$CH$_2$CH); *m/z* (CI, NH_3) 258 (M+H$^+$, 100%), 105 (15); Found: M+H$^+$, 258.1495. $C_{16}H_{19}NO_2$ requires for M+H$^+$, 258.1494.

Reaction of* N-*allyl*-N-*(6-oxo-cyclohex-1-enyl)benzamide* (24) *with tributyltin hydride added over 5 h

A 0.014 mol dm^{-3} solution of tributyltin hydride (1.5 eq., 0.33 g, 1.15 mmol) and azobisisobutyronitrile (0.3 eq., 38 mg) in degassed benzene (82 cm^3) was added dropwise over 5 h *via* a syringe pump to a 0.024 mol dm^{-3} solution of alkene (**24**) (0.20 g, 0.76 mmol) in boiling degassed benzene (25 cm^3) whilst the latter was stirred

under nitrogen. The solution was then heated overnight at reflux after which t.l.c. indicated that no starting material remained and the solvent was removed under reduced pressure to afford crude product. Column chromatography (silica; diethyl ether) afforded *1-benzoyl-3-methyloctahydroindole-7-one* (**26**) (83 mg, 42%) as a mixture of 3 inseparable diastereomers in the ratio 3.4:3:1.

1-Benzoyl-3-methyloctahydroindole-7-one (Diastereomer 1): R_f 0.20 (diethyl ether); ν_{max} ($CHCl_3$) 3006 (m), 2963 (m), 2940 (m), 2879 (w), 1727 (s), 1670 (m), 1627 (s), 1446 (m), 1424 (m), 1309 (m), 1259 (w), 1232 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.57-7.30 (5H, m, aromatics), 4.31 (1H, d, *J*=7.5, COC<u>H</u>N), 3.86 (1H, dd, *J*=12 and 9, NC<u>H</u>), 3.27 (1H, dd, *J*=12 and 9.5, NC<u>H</u>), 2.71-2.27 (3H, m, NCHC<u>H</u> and C<u>H</u>$_2$CO), 2.23-1.64 (5H, m, C<u>H</u>CH_3, $CH_2C\underline{H}_2CH$, $CH_2C\underline{H}_2CH_2$), 1.06 (3H, d, *J*=6.5, CHC<u>H</u>$_3$); δ_C (67.5 MHz, $CDCl_3$) 206.8 ($CH_2\underline{C}O$), 170.6 (N<u>C</u>O), 136.9 (<u>C</u>=CH aromatic), 128.0, 126.7, 126.5 (C=<u>C</u>H aromatic), 69.5 (CO<u>C</u>HN), 51.8 (N<u>C</u>H_2), 48.1 (CH<u>C</u>HCH_2 or <u>C</u>HCH_3), 40.2 (<u>C</u>H_2CO), 34.0 (CH<u>C</u>HCH_2 or <u>C</u>HCH_3), 23.4, 23.1 ($CH_2\underline{C}H_2CH_2$ and $CH_2\underline{C}H_2CH$); *m/z* (CI, NH_3) 258 ($M+H^+$, 100%); Found: $M+H^+$, 258.1491. $C_{16}H_{19}NO_2$ requires for $M+H^+$, 258.1494. *(Diastereomer 2)*: The presence of this was indicated by: δ_H (270 MHz, $CDCl_3$) 5.02 (1H, d, *J*=7, COC<u>H</u>N), 3.65 (1H, dd, *J*=10 and 8.5, NC<u>H</u>), 2.90 (1H, appt. t, *J*=10, NC<u>H</u>), 0.94 (3H, d, *J*=6.5, CHC<u>H</u>$_3$); δ_C (67.5 MHz, $CDCl_3$) 205.7 ($CH_2\underline{C}O$), 169.9 (N<u>C</u>O), 136.6 (<u>C</u>=CH aromatic), 66.6 (CO<u>C</u>HN), 54.9 (N<u>C</u>H_2), 50.0 (CH<u>C</u>HCH_2 or <u>C</u>HCH_3), 40.3 (<u>C</u>H_2CO), 31.6 (CH<u>C</u>HCH_2 or <u>C</u>HCH_3), 23.4, 23.0 ($CH_2\underline{C}H_2CH$ and CH<u>C</u>HCH). *(Diastereomer 3)*: The presence of this was indicated by: δ_H (270 MHz, $CDCl_3$) 4.45 (1H, d, *J*=6.5, COC<u>H</u>N), 3.54 (1H, appt. t, *J*=9, NC<u>H</u>), 3.34 (1H, appt. t, *J*=9, NC<u>H</u>), 0.98 (3H, d, *J*=7, CHC<u>H</u>$_3$); δ_C (67.5 MHz, $CDCl_3$) 208.3 ($CH_2\underline{C}O$), 170.4 (N<u>C</u>O), 135.9 (<u>C</u>=CH aromatic), 67.8 (CO<u>C</u>HN), 54.7 (N<u>C</u>H_2), 45.5 (CH<u>C</u>HCH_2 or <u>C</u>HCH), 37.6 (<u>C</u>H_2CO), 36.6 (CH<u>C</u>HCH_2 or <u>C</u>HCH_3), 25.4, 21.8 ($CH_2\underline{C}H_2CH_2$ and $CH_2\underline{C}H_2CH$).

Treatment of 6-Oxocyclohex-1-enyl acrylate* (27) *with tributyltin hydride

Following the general procedure, alkene (**27**) (0.18 g, 1.05 mmol) in degassed benzene (11 cm^3) was treated with tributyltin hydride (0.46 g, 1.58 mmol) and azobisisobutyronitrile (52 mg). Column chromatography (silica; diethyl ether-petroleum ether, 1:4) afforded *6-oxocyclohex-1-enyl 3-tributylstannanylpropanoate* (**30**) (126 mg, 26%).

6-Oxocyclohex-1-enyl 3-tributylstannanylpropanoate (**30**): R_f 0.33 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 3006 (w), 2957 (s), 2926 (s), 2872 (m), 2853 (m), 1754 (s), 1692 (s), 1461 (w), 1174 (m), 1143 (s), 1112 (s) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.57 (1H, t, *J*=4.5, C<u>H</u>=C), 2.77-2.63 (2H, m, OCOC<u>H</u>$_2$), 2.58-2.48 (4H, m, C<u>H</u>$_2$COC and C<u>H</u>$_2$CH), 2.07 (2H, appt. quint., *J*=6.5, $CH_2C\underline{H}_2CH_2$), 1.60-1.42 (6H, m, 3 x $SnCH_2C\underline{H}_2$), 1.30 (6H, appt. sext., *J*=7, 3 x C<u>H</u>$_2CH_3$), 1.18-1.02 (2H, m, $OCOCH_2\underline{C}H_2$), 0.98-0.73 (15H, m, 3 x $CH_2C\underline{H}_3$ and $SnC\underline{H}_2CH_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 191.8 ($CH_2\underline{C}OC$), 173.4 (O<u>C</u>O), 144.4 (<u>C</u>=CH), 135.8 (<u>C</u>H=C), 38.0 (<u>C</u>H_2COC), 30.9 (<u>C</u>H_2COO), 29.1, 27.3 ($SnCH_2\underline{C}H_2$ and $\underline{C}H_2CH_3$), 24.7, 22.5 (<u>C</u>H_2CH and $CH_2\underline{C}H_2CH_2$), 13.6 ($CH_2\underline{C}H_3$), 8.8 ($Sn\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 476 ($M^{120}+NH_4^+$, 20%), 459 ($M^{120}+H^+$, 2), 440 (10), 401 (100), 308 (25), 291 (5), 186 (5), 130 (5); Found: $M^{116}+NH_4^+$, 472.2188. $C_{21}H_{38}O_3Sn$ requires for $M^{116}+NH_4^+$, 472.2182.

Treatment of 6-Oxo-cyclohex-1-enyl methacrylate* (28) *with tributyltin hydride

Tributyltin hydride (0.48 g, 1.66 mmol) and azobisisobutyronitrile (54 mg) were reacted with alkene (**28**) (0.20 g, 1.10 mmol) dissolved in degassed benzene (11 cm^3) following the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 3:7) afforded *6-oxocyclohex-1-enyl 2-methyl-3-tributylstannanylpropanoate* (**31**) (51 mg, 10%) and *2-oxocyclohexyl 2-methyl-3-tributylstannanylpropanoate* (**32**) (102 mg, 20%) as a mixture of isomers.

6-Oxocyclohex-1-enyl 2-methyl-3-tributylstannanylpropanoate (**31**): R_f 0.33 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 3080 (m), 3053 (m), 2957 (s), 2926 (s), 2872 (w), 2854 (w), 1749 (s), 1692 (s), 1460 (w), 1237 (w), 1175 (m), 1142 (s), 1110 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.55 (1H, t, *J*=4.5, C<u>H</u>=C), 2.88-2.75 (1H, m, OCOC<u>H</u>), 2.57-2.46 (4H, m, C<u>H</u>$_2$COC and C<u>H</u>$_2$CH=C), 2.07 (2H, appt. quint., *J*=6.5, $CH_2C\underline{H}_2CH_2$), 1.59-1.42 (6H, m, 3 x $SnCH_2C\underline{H}_2$), 1.37-1.20 (10H, m, SnC<u>H</u>CH, CHC<u>H</u>$_3$ and 3 x C<u>H</u>$_2CH_3$), 1.03 (1H, dd, *J*=13 and 9.5, SnC<u>H</u>CH), 0.98-0.73 (15H, m, 3 x $CH_2C\underline{H}_3$ and $SnC\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 191.8 ($CH_2\underline{C}O$), 176.0 (O<u>C</u>O), 145.4 (<u>C</u>=CH), 135.7 (<u>C</u>H=C), 38.1 (<u>C</u>H_2CO), 37.2 (<u>C</u>HCH_3), 29.1, 27.4 ($SnCH_2\underline{C}H_2$ and $\underline{C}H_2CH_3$), 24.9, 22.6 ($CH_2\underline{C}H_2CH$ and $CH_2\underline{C}H_2CH_2$), 20.7 (CH<u>C</u>H$_3$), 14.2 ($Sn\underline{C}H_2CH$),

13.7 ($CH_2\underline{C}H_3$), 9.4 ($Sn\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 490 ($M^{120}+NH_4^+$, 10%), 473 ($M^{120}+H^+$, 5), 415 (100), 345 (15), 321 (10), 308 (30), 183 (5), 130 (5); Found: $M+NH_4^+$, 486.2330. $C_{22}H_{40}O_3Sn$ requires for $M+NH_4^+$, 486.2339.

2-Oxocyclohexyl 2-methyl-3-tributylstannanylpropanoate (**32**): R_f 0.39 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 2956 (s), 2927 (s), 2871 (m), 1724 (s), 1460 (w), 1377 (w), 1240 (w), 1176 (w), 1110 (w), 1070 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.18-5.10 (1H, br m, $COC\underline{H}O$), 2.81-2.68 (1H, br m, $OCOC\underline{H}$), 2.53-2.23 (2H, m, $C\underline{H}_2CO$), 2.13-1.93 (2H, br m, $OCHC\underline{H}_2$), 1.86-1.41 (10H, m, $C\underline{H}_2CH_2CO$, $C\underline{H}_2CH_2CH$ and 3 x $C\underline{H}_2CH_3$), 1.36-1.11 (10H, m, $SnC\underline{H}CH$, $CHC\underline{H}_3$ and 3 x $C\underline{H}_2CH_3$), 1.06-0.75 (16H, m, $SnC\underline{H}CH$ and 3 x $CH_2C\underline{H}_3$ and $SnC\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 204.6 and 204.5 ($CH_2\underline{C}O$), 177.2 and 177.1 ($O\underline{C}O$), 76.1 ($CO\underline{C}HO$), 40.7 ($\underline{C}H_2CO$), 37.3 and 37.2 ($\underline{C}HCH_3$), 33.0 ($CH_2\underline{C}H_2CH$), 29.1, 27.4 ($SnCH_2\underline{C}H_2$ and $\underline{C}H_2CH_3$), 27.1, 23.7 ($\underline{C}H_2CH_2CO$ and $\underline{C}H_2CH_2CH$), 21.0 and 20.6 ($CH\underline{C}H_3$), 14.3 and 14.2 ($Sn\underline{C}H_2CH$), 13.6 ($CH_2\underline{C}H_3$) 9.3 ($Sn\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 492 ($M^{120}+NH_4^+$, 3%), 475 ($M^{120}+H^+$, 10), 417 (100), 321 (25), 308 (45), 291 (5), 202 (5), 185 (15), 132 (5); Found: $M+H^+$, 471.2227. $C_{22}H_{42}O_3Sn$ requires for $M+H^+$, 471.2230.

Treatment of (6-oxo-cyclohex-1-enyl) 2-phenylacrylate* (29) *with tributyltin hydride

To a solution of alkene (**29**) (0.18 g, 0.72 mmol) in degassed benzene (8 cm^3) was added tributyltin hydride (0.32 g, 1.08 mmol) and azobisisobutyronitrile (35 mg) according to the general procedure. Column chromatography (silica; diethyl ether-petroleum ether, 3:7 then diethyl ether) afforded *3-benzyloctahydrobenzofuran-2,7-dione* (**33**) (46 mg, 26%) and *3-benzyl-3a-hydroxy-2,3,3a,4,5,6-hexahydrobenzofuran-2-one* (**34**) (17 mg, 10%) as single diastereomers.

3-Benzyloctahydrobenzofuran-2,7-dione (**33**): R_f 0.26 (diethyl ether); ν_{max} ($CHCl_3$) 3033 (w), 2935 (m), 2872 (w), 1784 (s), 1730 (s), 1496 (w), 1453(w), 1158 (w), 1129 (w), 1067 (w), 1044 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.33-7.17 (5H, m, aromatics), 4.76 (1H, d, *J*=8.5, $COC\underline{H}O$), 3.16 (1H, dd, *J*=14 and 5, $CHC\underline{H}Ph$), 2.94-2.83 (1H, m, $CHC\underline{H}CH_2$), 2.88 (1H, dd, *J*=14 and 7, $CHC\underline{H}Ph$), 2.51 (1H, ddd, *J*=12, 7 and 5, $C\underline{H}COO$), 2.45-2.37 (2H, m, $C\underline{H}_2CO$), 1.97-1.60 (4H, m, $CH_2C\underline{H}_2CH$ and $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 205.8 ($CH_2\underline{C}O$), 176.4 ($O\underline{C}O$), 137.2 ($\underline{C}$=CH aromatic), 129.0, 128.7, 126.9 (C=$\underline{C}$H aromatics), 80.2 ($CO\underline{C}HO$), 44.2, 42.2 ($CH\underline{C}HCH_2$ and $\underline{C}HCH_2Ph$), 39.5, 34.2 ($\underline{C}H_2CO$ and $CH\underline{C}H_2Ph$), 24.7, 22.1 ($CH_2\underline{C}H_2CH$ and $CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 262 ($M+NH_4^+$, 100%), 218 (30), 201 (5), 114 (10); Found: $M+NH_4^+$, 262.1437. $C_{15}H_{16}O_3$ requires for $M+NH_4^+$, 262.1443.

3-Benzyl-3a-hydroxy-2,3,3a,4,5,6-hexahydrobenzofuran-2-one (**34**): R_f 0.18 (diethyl ether-petroleum ether, 3:7); ν_{max} ($CHCl_3$) 3602 (m), 3033 (w), 2930 (m), 2869 (w), 2848 (w), 1803 (s), 1703 (s), 1497 (w), 1453 (w), 1258 (w), 1208 (w), 1171 (w), 1136 (w), 1112 (w), 1066 (s) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.31-7.21 (5H, m, aromatics), 5.38 (1H, dd, *J*=4.5 and 3, C=C$\underline{H}$), 3.28 (1H, dd, *J*=14.5 and 4.5, $CHC\underline{H}Ph$), 3.07 (1H, dd, J=14.5 and 10.5, $CHC\underline{H}Ph$), 2.75 (1H, dd, *J*=10.5 and 4.5, $OCOC\underline{H}$), 2.28-1.98 (2H, m, $C=CHC\underline{H}_2$), 1.69-1.57 (2H, m, $C\underline{H}_2COH$), 1.46-1.15 (2H, m, $CH_2C\underline{H}_2CH_2$); δ_C (67.5 MHz, $CDCl_3$) 174.7 ($O\underline{C}O$), 151.0 ($\underline{C}$=CH), 138.8 ($\underline{C}$=CH aromatic), 129.1, 128.6, 126.6 (C=$\underline{C}$H aromatics), 104.3 (C=$\underline{C}$H), 72.6 ($\underline{C}OH$), 53.1 ($\underline{C}HCH_2Ph$), 33.6, 29.6 ($CH\underline{C}H_2Ph$ and $\underline{C}H_2CH$), 22.7, 17.4 ($\underline{C}H_2COH$ and $CH_2\underline{C}H_2CH_2$); *m/z* (CI, NH_3) 262 ($M+NH_4^+$, 100%), 244 (15), 227 (25); Found: $M+NH_4^+$, 262.1446. $C_{15}H_{16}O_3$ requires for $M+NH_4^+$, 262.1443.

Acknowledgements

We thank the EPSRC for a research studentship and Pfizer for financial contributions.

References

1. (a) Giese, B.; Kopping, B.; Göbel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K.J.; Trach, F. *Organic Reactions*, **1996**, *48*, 301.
   (b) Aldabbagh, F.; Bowman, W.R. *Contemp. Org. Synth.*, **1997**, 261.
2. (a) Enholm, E.J.; Kinter, K.S. *J. Am. Chem. Soc.*, **1991**, *113*, 7784.
   (b) Enholm, E.J.; Kinter, K.S. *J. Org. Chem.*, **1995**, *60*, 4850.

3. (a) Parsons, A.F.; Pettifer, R.M. *Tetrahedron Lett.*, **1997**, *38*, 5907.
(b) Parsons, A.F.; Pettifer, R.M. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 651.
4. (a) Enholm, E.J.; Whitley, P.E. *Tetrahedron Lett.*, **1995**, *36*, 9157.
(b) Enholm, E.J.; Whitley, P.E. *Tetrahedron Lett.*, **1996**, *37*, 559.
(c) Enholm, E.J.; Whitley, P.E.; Xie, Y. *J. Org. Chem.*, **1996**, *61*, 5384.
5. (a) Ishibashi, H.; So, T.S.; Okochi, K.; Sato, T.; Nakamura, N.; Nakatani, H.; Ikeda, M. *J. Org. Chem.*, **1991**, *56*, 95.
(b) Stork, G.; Mah, R. *Heterocycles*, **1989**, *28*, 723.
(c) Ishibashi, H.; Fuke, Y.; Yamashita, T.; Ikeda, M. *Tetrahedron: Asymmetry*, **1996**, *7*, 2531.
(d) Curran, D.P.; Tamine, J. *J. Org. Chem.*, **1991**, *56*, 2746.
(e) Jolly, R.S.; Livinghouse, T. *J. Am. Chem. Soc.*, **1988**, *110*, 7536.
6. For thermodynamically controlled radical reactions leading to 6-*endo-trig* cyclisations see:
(a) Julia, M. *Acc. Chem. Res.*, **1971**, *4*, 386.
(b) Julia, M. *Pure Appl. Chem.*, **1974**, *40*, 553.
7. (a) Goodall, K.; Parsons, A.F. *Tetrahedron*, **1996**, *52*, 6739.
(b) Sato, T.; Nakamura, N.; Ikeda, K.; Okada, M.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 2399.
8. Knapp, S.; Levorse, A.T. *J. Org. Chem.*, **1988**, *53*, 4006.
9. (a) De Riggi, I.; Gastaldi, S.; Surzur, J.-M.; Bertrand, M.P. *J. Org. Chem.*, **1992**, *57*, 6118.
(b) Hanessian, S.; Reinhold, U.; Ninkovic, S. *Tetrahedron Lett.*, **1996**, *37*, 8967 and 8971.
(c) Naito, T.; Honda, Y.; Miyata, O.; Ninomiya, I. *J. Chem. Soc., Perkin Trans. 1*, 1995, 19.
10. (a) Nakamura, E.; Inubushi, T.; Aoki, S.; Machii, D. *J. Am. Chem. Soc.*, **1991**, *113*, 8980.
(b) Mayer, S.; Prandi, J. *Tetrahedron Lett.*, **1996**, *37*, 3117.
11. Morzycki, J.W.; Wilczewska, A.Z. *Tetrahedron*, **1996**, *52*, 14057.
12. For a related cyclisation see Clive, D.L.J.; Mohammed, A.Y. *Heterocycles*, **1989**, *28*, 1157.
13. Toda, F.; Miyamoto, H.; Takeda, K.; Matsugawa, R.; Maruyama, N. *J. Org, Chem.*, **1993**, *58*, 6208.
14. Ikeda, M.; Uchino, T.; Takahashi, M.; Ishibashi, H.; Tamura, Y.; Kido, M. *Chem. Pharm. Bull.*, **1985**, *33*, 3279.