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CARBOCYCLIC RING EXPANSION REACTIONS *VIA* FREE RADICAL PATHWAYS - PART III

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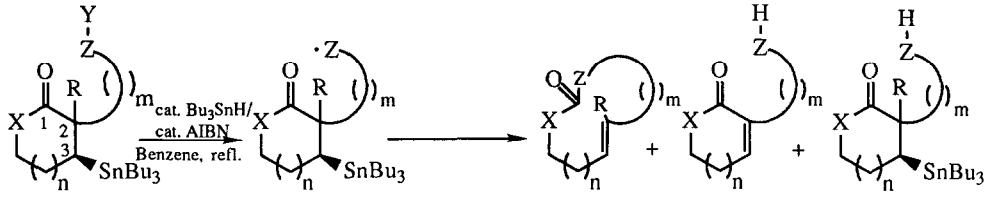
Keywords : Free radical, enolate, ring expansion, alkoxy radical.

Abstract : The free radical ring expansion methodology recently described[1], leading to the formation of medium sized ring ketones from cyclohexanone precursors has been applied to different side chains and ring sizes. In addition precursors based on lactone rings have been prepared and subjected to radical forming reaction conditions.

Introduction

The general methodology[1] for the ring expansion of ketones *via* a radical route, represented in scheme 1, has been extended to the cyclisation of secondary radicals with application to the total synthesis of a naturally occurring insect secretion product. We have also examined the cyclisation of vinyl radicals generated from side-chains possessing an acetylenic linkage or vinylic halide moiety as an alternative method for the preparation of medium ring ketones. The extensions from cyclohexanone precursors to the analogous cyclopentanone and cycloheptanone counterparts, and the viability of applying this methodology for the production of medium ring lactones are also described.



Example: X=CH_2, n=1, m=3 or 4
R=H or alkyl
Y=Br Z· =2° or vinyl radical

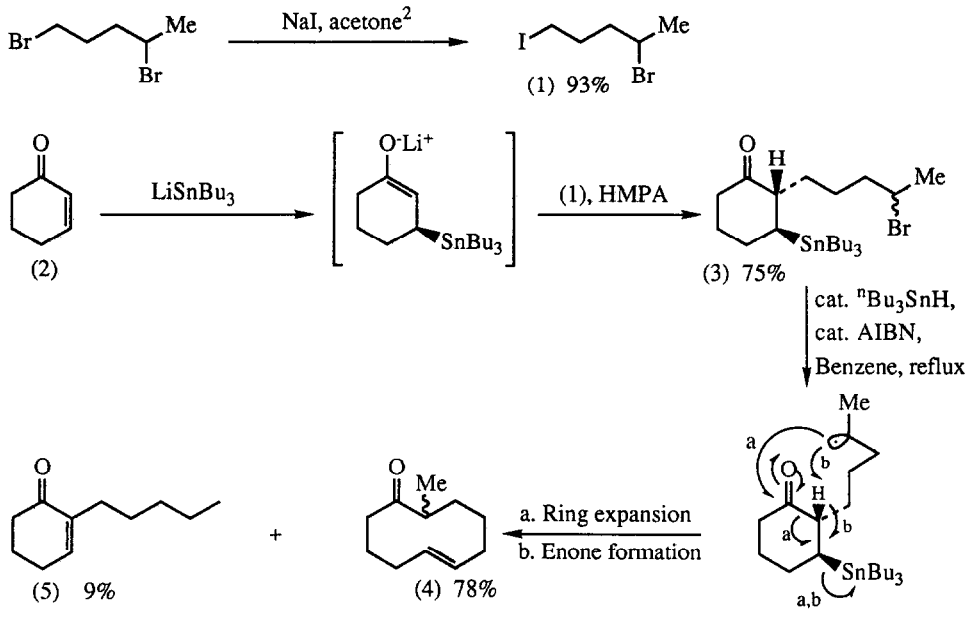
Scheme 1

1. Application to various side-chains situated at the 2-position of the cyclohexanone system

The possible introduction of substituents at the radical forming terminus of the side-chain allows the preparation of medium sized ring compounds selectively mono-substituted α- to the carbonyl functionality, thereby presenting the opportunity of further synthetic manipulation for the preparation of more complex structures. The most logical extension of this methodology, from the cyclisation of simple primary radicals[1], was

to the corresponding secondary counterparts since precursors required for such experiments were readily accessible.

Thus precursor (3), representing a possible four-carbon ring expansion (Scheme 2) with a secondary radical at the termini, was prepared by alkylation of the enolate derived from the reaction of tributyltin lithium and 2-cyclohexen-1-one (2) with 1-iodo-4-bromopentane (1). The sequence required the presence of hexamethylphosphoramide (HMPA) as a co-solvent for the success of the alkylation step. The radical precursor (3) was obtained efficiently by chromatographic separation of the crude material, in 75% yield, free of any tin side-products (namely tetrabutyltin). Subjection of this compound to radical forming conditions (reflux in benzene in the presence of catalytic quantities of AIBN and tributyltin hydride) led to the isolation of 2-methyl-E-cyclodec-6-enone (4)(78%) from desired ring expansion and enone (5)(9%) resulting from direct hydrogen abstraction from the α-position of the cyclohexanone stannane (3) by the secondary radical.

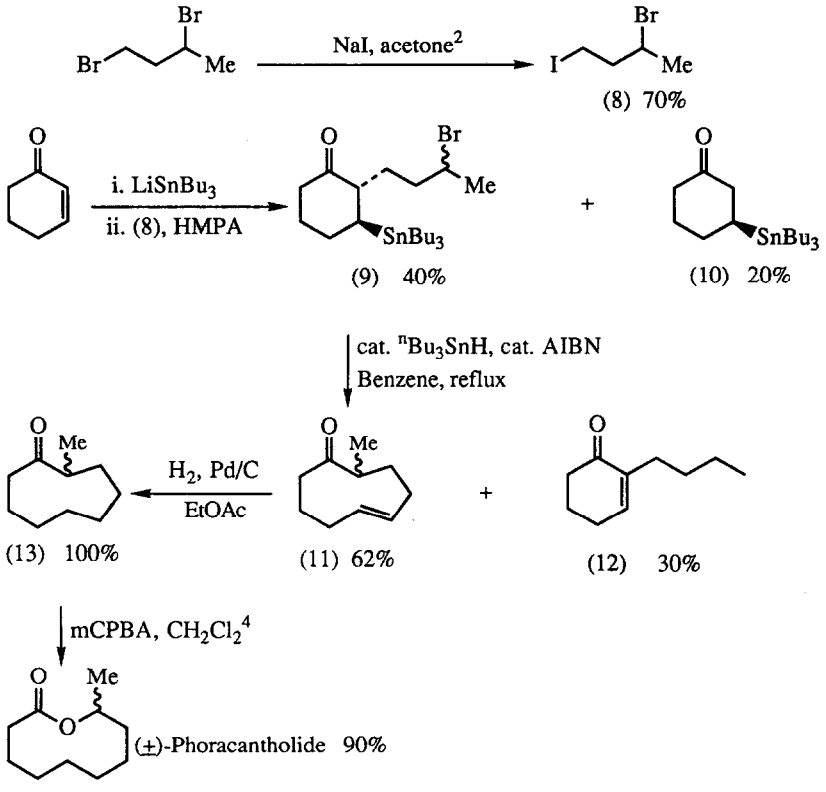


Scheme 2

The formation of the enone system, (pathway b, Scheme 2), was circumvented by the use of 2-methyl-2-cyclohexen-1-one to prepare precursor (6). Treatment of (6) under standard conditions was found to afford cleanly the ring expanded compound (7)(85%). These initial results obtained from the use of secondary radicals are illustrated in table 1 and the above procedure represents a simple method for preparation of such compounds.

The encouraging results obtained with the cyclisation of secondary radicals prompted application to the total synthesis of the naturally occurring 10-membered lactone, (±)-phoracantholide I [(±)-decan-9-olide] (Scheme 3), isolated from the metasternal secretion of the eucalypt longicorn, *Phoracantha Synonyma* [3a]. Previous independent syntheses of racemic phoracantholide I by Ban[3b] and Suginome[3c] utilise ring expansion

procedures whereas the total synthesis by Posner[3d] employed a lead tetraacetate induced fragmentation of a preformed bicyclic hemiketal. The approach that we favoured involved two ring expansion processes. Firstly a three-carbon radical ring expansion reaction which would be followed by a Baeyer-Villiger oxidation[3b], for the introduction of the hetero-atom (Scheme 3).

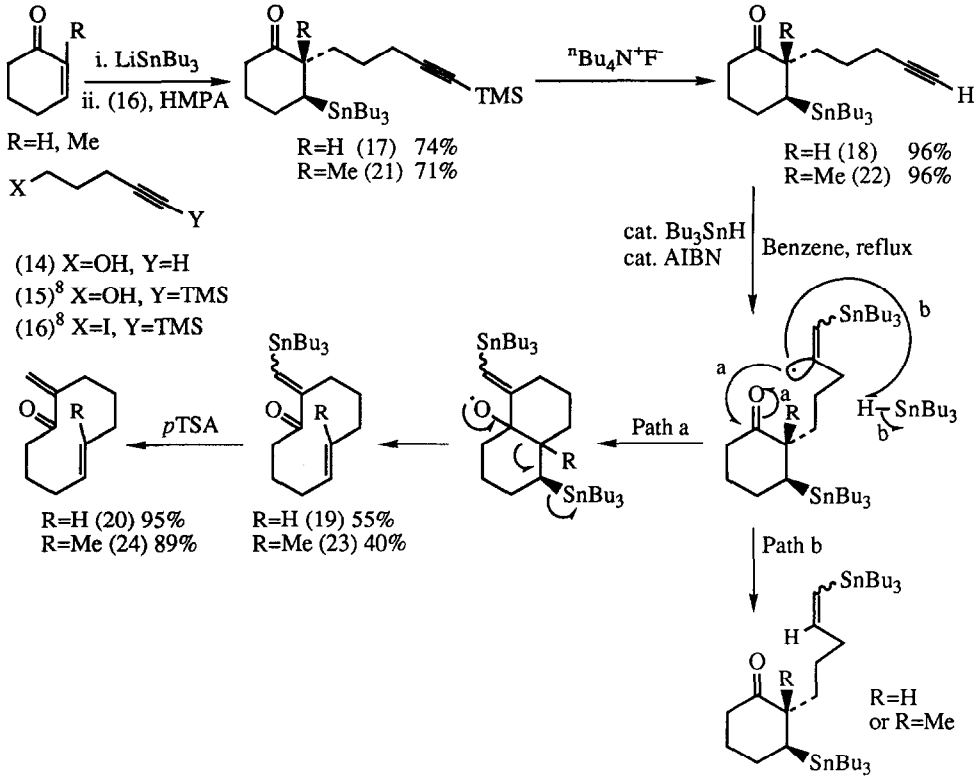


Scheme 3

The radical precursor (9) required for first ring expansion step was prepared by the Michael style addition of LiSnBu3 to 2-cyclohexen-1-one and reaction of the subsequently formed enolate with 1-iodo-3-bromobutane (8), however a substantial amount of the non-alkylated tin containing adduct (10) was also isolated. Fortunately (10) was easily separable from the desired precursor (9) by chromatography. We postulate that the formation of (10) is attributable to β-elimination of (8) by the intermediate enolate. Variation in the delivery system used to introduce the tributylstannyl moiety to the enone from LiSnBu3 to the higher order cuprate [Li2Cu(CN)(Bu)SnBu3][5] gave no improvement in yield of (9) or the ratio of alkylated (9) to non-alkylated (10) adducts. Pleasingly the stannane (9) afforded a chromatographically separable mixture of the ring expanded compound (11)(62%) and enone (12)(30%) after the radical ring expansion reaction sequence. Hydrogenation[6] of olefin (11) at atmospheric pressure with 5% palladium on activated carbon in ethyl acetate gave the cyclo-ketone (13)[3b] in quantative yield without the need for further purification. The Baeyer-Villiger oxidation was

accomplished employing m-CPBA as oxidant in dichloromethane according to the conditions set out by Hesse in his synthesis of A 26771 B[4].

The success of secondary radicals for the generation of medium ring compounds led us to consider the viability of employing vinyl radicals at the terminus of the side-chain. Successful cyclisation of such radicals followed by subsequent fragmentation of the *in situ* alkoxy radical could produce funtionalised 10-membered rings. Reaction of an alkyne carbon-carbon triple bond with trialkylstannane radicals leads to the formation of a vinyl radical; Nishida and co-workers provide recent examples where this has been used in the context of radical ring expansion methodology[7].

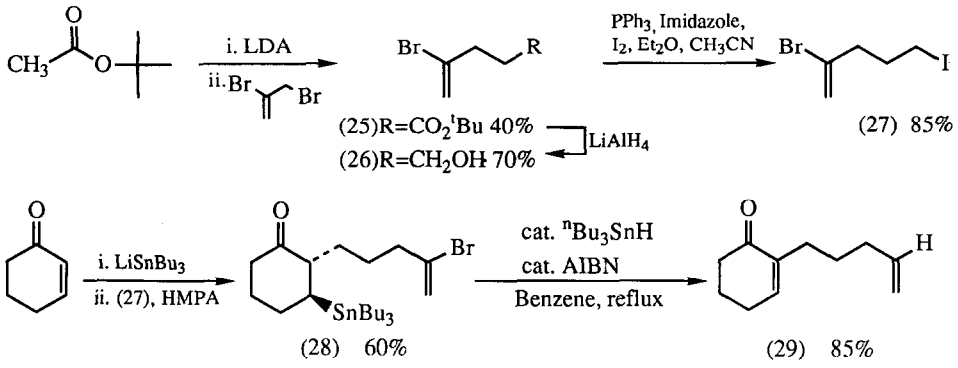


Scheme 4

Derivative (17) was prepared by alkylation of the enolate generated from 2-cyclohexen-1-one with the TMS protected acetylenic iodide (16)(Scheme 4). Deprotection of (17) to (18) was efficiently achieved in near quantative yield by treatment with tetrabutyl ammonium fluoride at room temperature. Stannane (18) was found to undergo radical induced rearrangement leading to the formation of the ring expanded vinyl stannane (19) *via* addition of tributyltin radical to the less sterically hindered terminal end of the acetylenic linkage. Compound (19) was purified by flash chromatography and isolated as a colourless oil in 55% yield along with 30% of the unreacted starting precursor (18). Increase in the reaction time and further additions of AIBN/Bu_3SnH

unfortunately only aided the formation of an alkenylstannane adduct, formed from the direct reduction of the intermediate vinyl radical resulting from the addition of tributyltin radical to the acetylene (path b, Scheme 4). The vinyl stannane (19) was destannylated, to provide the exomethylene product (20) in 95% yield, by simply stirring a solution of (19) at 0°C in THF with slow addition of 1.0 equivalent of *p*TSA (*para*-toluenesulphonic acid). Application of this chemistry to 2-methyl-2-cyclohexen-1-one proved successful albeit in lower yield; a 40% yield in the rearrangement reaction of (22) to (23) was observed. The results obtained from the general cyclisation of vinyl radicals *via* the addition of tributyltin to acetylenic linkage are summarised in table 1.

An alternative approach was sought in order to improve the yields of the ring expanded exomethylene compounds. Another approach for the generation of vinyl radicals equivalent to the cases outlined above was from the corresponding vinyl halides. Stork[9] has used the cyclisation of vinyl radicals for construction of five- and six-membered rings involving vinyl halides as the starting precursors. Thus we decided to demonstrate the feasibility of employing vinyl halides as a source of vinyl radicals for cyclisation, to yield intermediate bicyclo-[4,4,0]-decanyl alkoxy radicals by preparing precursor (28) utilising the standard conjugate addition-alkylation sequence (Scheme 5) with 1-iodo-4-bromo-4-pentene (27). The latter reagent (Scheme 5) was prepared by the initial condensation[10] of the ester enolate derived from *tert*-butyl acetate with 1,2-dibromo-2-propene, followed by reduction[10] of the ester group with lithium aluminium hydride followed by iodination[11] of the derived alcohol using triphenylphosphine/imidazole/iodine.



Scheme 5

Rather surprisingly the vinyl halide precursor (28) when subjected to radical reaction conditions failed to provide any ring expanded product (20), but instead gave the enone (29) as detected by ^{1}H n.m.r. studies. In an attempt to subdue this problem the blocked precursor (30) was prepared from 2-methyl-2-cyclohexen-1-one, however even under reaction conditions whereby tributyltin hydride was added slowly (up to one stoichiometric equivalent) the directly reduced adduct (31) constituted the majority of the isolated material. Results obtained from other vinyl radical precursors are exemplified in table 1.

Table 1

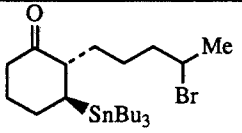
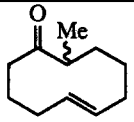
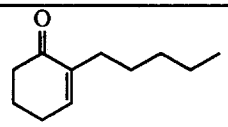
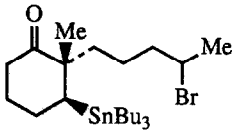
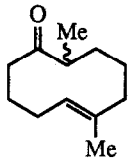
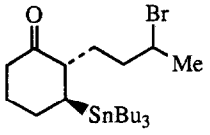
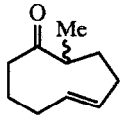
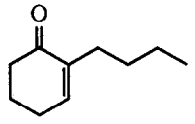
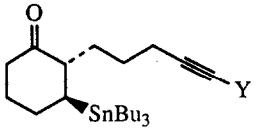
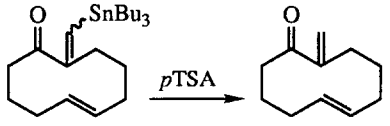
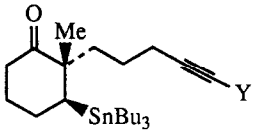
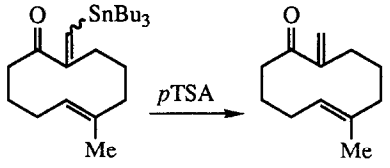
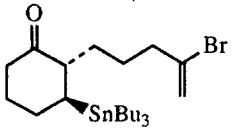
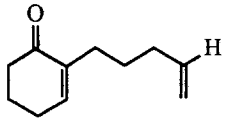
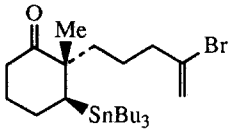
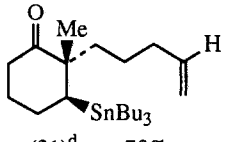
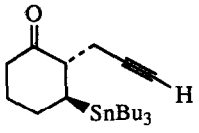
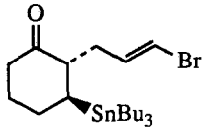
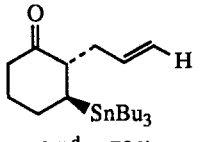
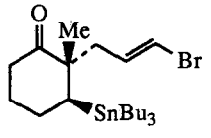
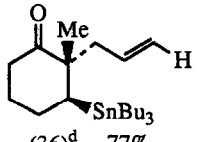
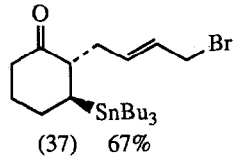
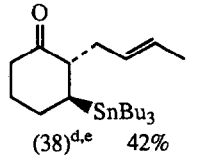
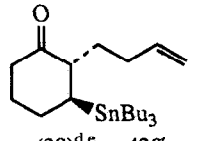
Radical precursor[a]	Radical reaction products[b]
 (3) 75%	 (4) 78%  (5) 9%
 (6) 71%	 (7)[f] 85%
 (9) 40%	 (11)[f] 62%  (12) 30%
 (17) Y=TMS (74%) (18) Y=H (96%)[c]	 (19) 55% (20) 95%
 (21) Y=TMS (71%) (22) Y=H (96%)[c]	 (23)[f] 40% (24)[f] 89%
 (28) 60%	 (29) 85%
 (30) 50%	 (31)[d] 70%

Table 1 continued

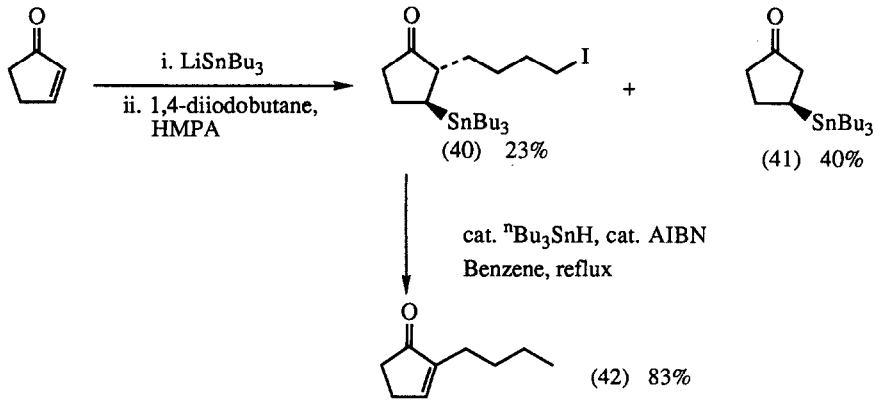
Radical precursor[a]	Radical reaction products[b]
 (32) 82%	COMPLEX MIXTURE OBTAINED
 (33) 53%	 (34)[d] 70%
 (35) 49%	 (36)[d] 77%
 (37) 67%	 (38)[d,e] 42%  (39)[d,e] 42%

Footnotes: a. Yields for reaction of enolate derived from 2-cyclohexen-1-one or 2-methyl-2-cyclohexen-1-one with the relevant alkylating agent; b. Yield from radical ring expansion protocol; c. Yield from desilylation procedure; d. Obtained from the use of 1.0 equiv. of Bu_3SnH; e. Compounds (38) and (39) formed as a mixture in a 1:1 ratio; f. Endo-olefin stereochemistry assigned by analogy to previous work[1].

2. Application to ring sizes other than 6-membered precursors

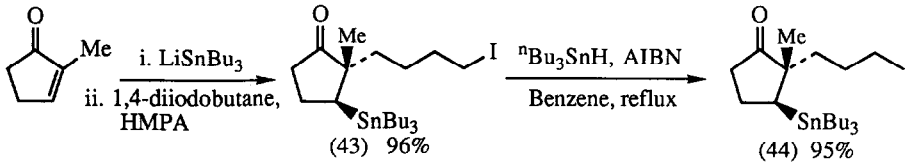
In view of the general success of various cyclohexanone precursors presented in table 1 and in previous publications originating from our laboratories[1] the extension of this methodology to other ring sizes was seen as a means of investigating steric factors that may effect the radical ring expansion process.

A potential four-carbon ring expansion precursor was prepared (Scheme 6) from 2-cyclopenten-1-one by conjugate addition of $LiSnBu_3$ and alkylation with 1,4-diiodobutane.



Scheme 6

Problems were encountered in the preparation of (40) in that the major product was non-alkylated stannane (41) but fortunately the required product (40) was separable from (41) by flash chromatography. After subjection of alkylated stannane (40) to standard ring expansion conditions the only product (42)(83%) isolated corresponded to that resulting from direct hydrogen abstraction from the α-position (Scheme 6).



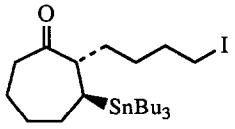
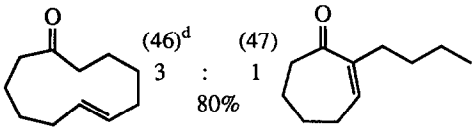
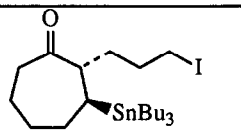
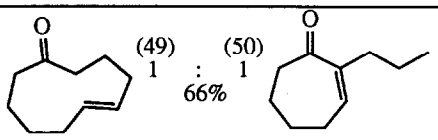
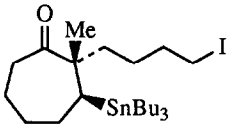
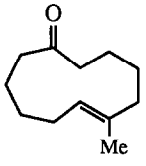
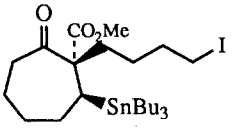
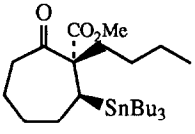
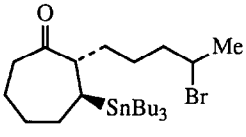
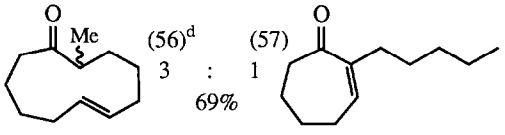
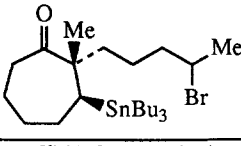
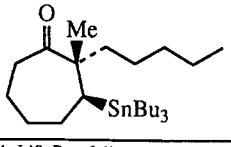
Scheme 7

Interestingly the precursor (43) (Scheme 7) from 2-methyl-2-cyclopenten-1-one was prepared in high yield, free from any non-alkylated compound (unlike the preparation of (40))[12]. The radical expansion reaction of (43) under normal conditions (cat. $^{n}Bu_3SnH$) however gave low yields of the directly reduced adduct (44), the yield was then optimised by adding a stoichiometric equivalent of tributyltin hydride. The results from 5-membered ring systems may be accounted for by the lower reactivity towards nucleophilic radical attack for cyclopentanone as compared to cyclohexanone.This is due to the increased hinderance and the eclipsing interactions about the carbonyl group which occur on addition[13].

The chemistry developed for the cyclohexenone system proved to be practical for the preparation of precursors involving α,β-unsaturated cycloheptenone derivatives. Table 2, exemplifies the the results obtained from various *trans* -cycloheptanone substrates; in general it was observed that both, in terms of preparation of radical precursors and their subsequent radical reactions, the results were less satisfactory when compared to analogous cyclohexanone counterparts. Recently Pattenden *et al* have observed inefficient free radical ring expansion of a cycloheptanone to a cyclooctanone structure in a related system[14]. Additionally for the 7-membered rings the success of the alkylation step was limited to the preparation of structures possessing side-

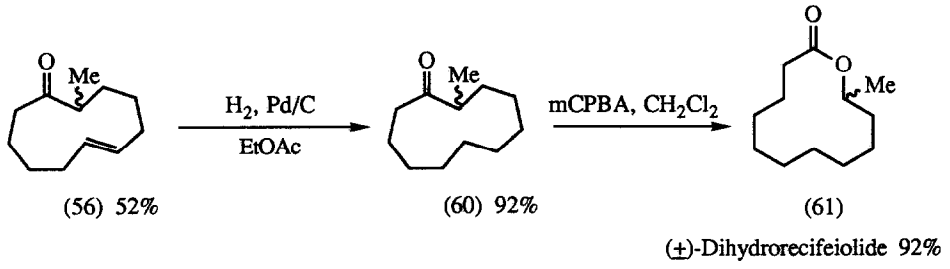
chains with three- and four-carbon atoms; phenylselenomethylene bromide could not be used as an enolate alkylation agent[1].

Table 2

Radical precursor[a]	Radical reaction product[b]
 (45) 66%	 (46)[d] : (47) = 3 : 1, 80%
 (48) 55%	 (49) : (50) = 1 : 1, 66%
 (51) 60%	 (52)[d] 72%
 (53) 58%	 (54)[c] 80%
 (55) 63%	 (56)[d] : (57) = 3 : 1, 69%
 (58) 59%	 (59)[c] 75%

Footnotes: a. Yields from combination of the relevant enone with $LiSnBu_3$ followed by enolate quench with standard alkylating agents; b. Yields from radical reaction protocol; c. Obtained from the use of 1.0 equiv. Bu_3SnH; d. Olefin stereochemistry assigned by analogy to previous work[1].

The ring expanded compound (56)(Table 2) was converted to naturally occurring 12-membered ring lactone (±)-dihydrorecifeiolide[3e] (61)(Scheme 8) using the methodology described earlier for the synthesis of (±)-phoracantolide I (Scheme 3)



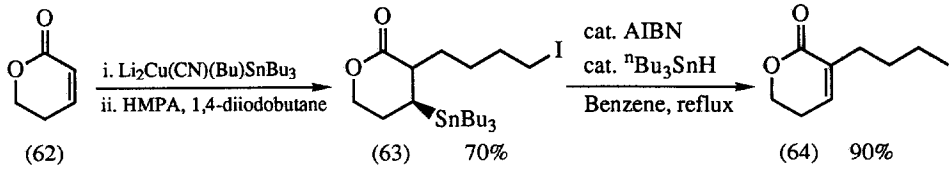
(56) 52% (60) 92% (61)

(±)-Dihydrorecifeiolide 92%

Scheme 8

3. Application to ring systems possessing a hetero-atom

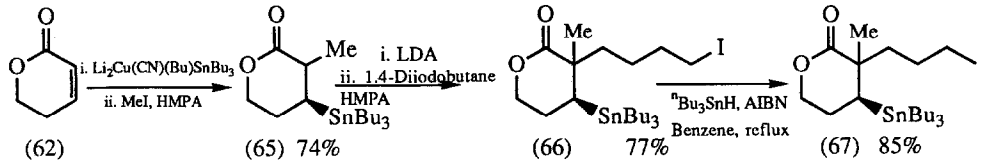
The use of α,β-unsaturated lactones as starting materials provided another potential application of the general ring expansion methodology for generating medium ring structures. It was postulated however that preparation of medium ring lactones would indeed be difficult due to the inherently reduced reactivity of then lactone carbonyl functionality towards radicalophilic attack compared to ketones. A simple lactone precursor (63) was prepared by the conjugate addition of a higher order cuprate to the α,β–unsaturated lactone (62) followed by alkylation with 1,4-diiodobutane (Scheme 9). Subjection of compound (63) to radical expansion conditions only led to product (64) from preferential direct hydrogen abstraction.



(62) (63) 70% (64) 90%

Scheme 9

In an attempt to circumvent this problem the α–position was blocked by the introduction of a methyl group. Thus derivative (65)(Scheme 10) was alkylated[15] to (66); in this case however subjection of precursor (66) to radical expansion conditions (catalytic to one equivalent Bu_3SnH) led solely to the directly reduced adduct (67).



(62) (65) 74% (66) 77% (67) 85%

Scheme 10

Summary

In this report we have shown that the radical ring expansion methodology represented in scheme 1 has general application to various side chains situated at the α-position with respect to the carbonyl group as well as application to different ring size of the initial enone. We have also demonstrated that this methodology can be used to generate substrates for the synthesis of naturally occurring molecules as shown by the synthesis of (±)-phoracantholide I (Scheme 3) and (±)-dihydrorecifeiolide (Scheme 8).

EXPERIMENTAL

Infrared (IR) spectra were obtained using a Perkin-Elmer 681 spectrometer. ^{1}H and ^{13}C nuclear magnetic resonance were obtained using a Varian Gemini 200MHz machine at 200 and 50.3MHz respectively in chloroform-d_1, unless otherwise stated. Chemical shifts are quoted in parts per million (δ p.p.m.) using chloroform as an internal reference and the coupling constants (*J*) are given to the nearest 0.5Hz. Mass spectra were recorded on a GCMS/TRIO-1 a V.G. Micromass 16F (ACE-alternative E.I./C.I.), a V.G. Micromass 30F (E.I./C.I.) or a V.G. Micromass ZAB IF (E.I./D.C.I./F.I./F.D.) and in general only the major observed isotope is quoted. Microanalyses were performed in the Dyson Perrins Laboratory.

All reactions were performed under an atmosphere of argon unless otherwise indicated. The molarity of n-Butyl lithium was checked by titration employing 1,3-diphenylacetone *p*-tosylhydrazone as indicator. All solvents were distilled prior to use: tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl, hexamethylphosphoramide (HMPA) from calcium hydride, dichloromethane from calcium hydride, light petroleum ether (boiling range 30 - 40°C) was distilled to remove any high boiling impurities and will be referred to as 'petrol'. Copper (I) cyanide used to prepare compounds (63) and (65) was dried over phosphorous pentoxide for a period of 24hours prior to use. The drying agent used after workup procedure refers to magnesium sulphate. Flash chromatography was performed on silica gel (Merck Kieselgel 60GF_{254} 230-400 mesh). Preparative layer chromatography (p.l.c.) was performed on silica gel (HF-Blend 41/KG) coated to 1mm on 200x200mm glass plates; these were pre-eluted with dichloromethane before use.

PREPARATION OF ALKYLATING AGENTS

Preparation of 1-Iodo-4-bromopentane (1)

To a solution of 1,4-dibromopentane (5.00g, 21.7mmol) in acetone (50ml) was added sodium iodide (3.0 equiv., 9.80g, 65mmol) and the resultant mixture was stirred overnight at room temperature. After *in vacuo* removal of the acetone, the remaining solid mass was extracted with ether and the solvent removed *in vacuo* to afford a pale yellow oil. The crude product was subjected to flash column chromatography (petrol) to yield (1) as a colourless oil (5.60g, 93%). $\nu_{max.}$ (thin film) 2985 (m), 2960 (s), 2920 (s), 2860 (m), 2940 (m), 1445 (s), 1380 (m); δ_H 1.75 (3H, d, *J* 8Hz), 1.8 - 2.15 (4H, m), 3.22 (2H, t, *J* 8Hz), 4.15 (1H, q, *J* 8Hz); m/z (E.I.) 197 (M^+ - Br, 12%), 149 (27), 127 (15), 69 (100), 53 (12).

Preparation of 1-Iodo-3-bromobutane (8)

Use of the procedure for the preparation of (1) on 1,3-dibromobutane (5.00g, 23.4mmol) afforded 1-iodo-3-bromobutane (8)(4.29g, 70%) as a colourless oil. $\nu_{max.}$ (thin film) 2980 (s), 2960 (s), 2880 (s), 1450 - 1420 (s), 1375 (s), 975 (w); δ_H 1.75 (3H, d, *J* 6.5Hz), 2.23 (2H, q, *J* 6Hz), 3.25 - 3.38 (2H, m), 4.04 - 4.24 (1H, m);

m/z (GCMS, C.I., NH_3) 262 (M^+, 20%), 152 (22), 135 (30), 120 (12), 108 (13), 94 (12), 84 (17), 72 (65), 58 (100).

Preparation of 1-Trimethylsilyl-2-pentyn-5-ol (15)

To a solution of 4-pentyn-1-ol (14)(5.00g, 59.4mmol) in anhydrous THF (200ml) at -78°C was added n-butyl lithium (1.6M, 2.0 equiv., 119mmol, 74.3ml) over a 20min period, then the white suspension was stirred for a further 45minutes at -78°C. The resultant dianion was then quenched by the addition of chlorotrimethylsilane (2.1 equiv., 15.8ml, 125mmol) and the resultant mixture allowed to warm up to room temperature slowly. This led to the clean formation of 1-(trimethylsilyl)-2-pentyn-5-trimethylsilyl ether as indicated by ^1H NMR. After the solution had reached room temperature it was poured into a mixture of 10% hydrochloric acid/ether (1:1 200ml) and the resultant mixture was stirred vigorously overnight. The organic phase was separated, the aqueous phase was extracted with ether and the combined organic layers were washed with brine (2 x 30ml), dried, filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography using dichloromethane as the solvent to elute (15) as a colourless oil (8.53g, 92%). $\nu_{max.}$ (thin film) 3340 (s, broad), 2960 (s), 2900 (s), 2880 (m), 2180 (s), 1445 - 1410 (m), 1250 (s), 1070 (s), 1050 (s); δ_H 0.16 (9H, s), 1.64 (1H, s, broad), 1.79 (2H, quintet, *J* 8Hz), 2.37 (2H, t, *J* 8Hz), 3.78 (2H, t , *J* 8Hz); δ_C (50.3 MHz) 0.00, 16.02, 31.02, 60.75, 84.62, 106.74; *m/z* (GCMS, C.I., NH_3) 174 (MNH_4^+, 10%), 157 (MH^+, 100), 141 (31), 90 (47), 85 (30), 74 (15), 60 (3).

Preparation of 1-Trimethylsilyl-2-pentyn-5-iodide (16)

To a solution of (15) (5.00g, 32.1mmol) in ether : acetonitrile (3:1, 200ml) was added triphenylphosphine (1.1 equiv., 9.24g, 35.3mmol) and imidazole (1.1 equiv., 2.26g, 35.3mmol). The resultant clear solution was cooled in a ice bath, iodine (1.1 equiv., 8.96g, 35.3mmol) was added portion wise, then the mixture was stirred at room temperature for one hour, filtered under reduced pressure, the solid being thoroughly washed with cold ether then the solvent was removed *in vacuo* . This led to the preciptation of more triphenylphosphine oxide, the product was carefully extracted with ether and washed successively with 10% sodium thiosulphate and brine. Drying, filtration and removal of the solvent *in vacuo* led to the isolation of syrupy oil contaminated with triphenylphosphine oxide. Subjection of this material to flash column chromatography (neat petrol) afforded completely pure (16) (7.68g, 90%). $\nu_{max.}$ (thin film) 2960 (s), 2900 (m), 2180 (s), 1430 (m), 1250 (s), 1220 (s), 1170 (m), 1020 (m); δ_H 0.16 (9H, s), 2.00 (2H, ca.quintet, *J* 8Hz), 2.35 (2H, t, *J* 8Hz), 3.30 (2H, t, *J* 8Hz); δ_C (50.3 MHz) 0.00, 4.92, 20.79, 31.97, 85.80, 104.89; *m/z* (GCMS, C.I., NH_3) 268 (100%), 266 (M^+, 30), 140 (18), 139 (10), 90 (60), 74 (38), 73 (8).

Preparation of *tert*-butyl 4-bromo-4-pentenonate (25)

A solution of LDA in anhydrous THF (75ml) prepared at 0°C from diisopropylamine (1.3 equiv., 7.84ml) and n-butyl lithium (1.5M, 1.0 equiv., 28.7ml) was cooled to -78°C. To this was added *tert*-butyl acetate (5.00g, 43mmol) as a solution in THF (10ml) dropwise, the resultant mixture stirred for 30min., followed by the addition of 2,3-dibromopropene (1.1 equiv., 4.89ml). After stirring the mixture at room temperature overnight a saturated solution of ammonium chloride was added, the aqueous layer separated, extracted with ether, the combined organic extracts washed with brine, dried and the solvent removed *in vacuo* to afford crude product (25). Purification by flash chromatography (gradient elution 20:1 petrol : ether to 3:1 petrol : ether) afforded

(25)(4.00g, 40%) as a colourless oil. $\nu_{max.}$ (thin film) 3010 (w), 2980 (s), 2930 (m), 1730 (s), 1630 (m), 1470 - 1420 (m), 1390 (m), 1365 (m), 1250 (m), 1150 (s), 890 (m), 845 (m); δ_H 1.55 (9H, s), 2.48 (2H, t, *J* 7Hz), 2.70 (2H, t, *J* 7Hz), 5.40 (1H, s), 5.63 (1H, s); δ_C (50.3 MHz, DEPT) CH_3: 27.82, CH_2: 33.87, 36.81, 117.30, C: 80.30, 132.63, 171.29; *m/z* (ZAB1F, C.I., NH_3) 252 (MNH_4^+, 100%), 236 (25), 220 (18), 192 (70), 175 (27), 136 (27), 116 (15), 74 (38), 58 (14).

Preparation of 4-bromo-4-pentenol (26)

To a slurry of lithium aluminium hydride (2.1 equiv., 1.00g, 27mmol) in anhydrous THF (50ml) cooled to 0°C was added ester (25)(3.00g, 12.8mmol) dropwise as a solution in THF (20ml) with constant stirring maintaining the temperature in the reaction vessel below 5°C. The reaction mixture was allowed to warm to room temperature, stirred for 3hours, cooled to 0°C and quenched by the dropwise addition of a 10% solution of sodium sulphate. The product was extracted with ether from the aqueous phase, washed with brine, dried and concentrated *in vacuo* . Purification by flash chromatography (5:1 petrol : ether) yielded (26)(1.33g, 70%) as a colourless oil. $\nu_{max.}$ (thin film) 3500 - 3200 (br), 2940 (s), 2880 (s), 1630 (s), 1470 - 1410 (m), 1050 (s), 885 (m); δ_H 1.76 (2H, quintet, *J* 7Hz), 2.48 (2H, t, *J* 7Hz), 3.12 (1H, broad s), 3.59 (2H, t, *J* 7Hz), 5.37 (1H, s), 5.57 (1H, s); δ_C (50.3 MHz) 30.58, 37.61, 60.93, 117.02, 134.05; *m/z* (ZAB1F, C.I., NH_3) 182 (MNH_4^+, 20%), 164 (M^+, 7), 125 (5), 85 (100), 67 (8), 58 (20), 53 (7).

Preparation of 2-bromo-5-iodo-1-pentene (27)

The protocol for the preparation of (16) was used to convert (26) (2.00g, 12.1mmol) to the corresponding iodo-compound (27)(2.84g, 85%). $\nu_{max.}$ (thin film) 2960 (s), 2940 (s), 2840 (m), 1630 (s), 1450 - 1410 (m), 1220 (s), 1170 (m), 890 (m); δ_H 2.05 (2H, quintet, *J* 7Hz), 2.65 (2H, t, *J* 7Hz), 3.20 (2H, t, *J* 7Hz), 5.50 (1H, s), 5.70 (1H, s); *m/z* (E.I.) 276/274 (M^+, ^{81}Br, ^{79}Br, 37%), 235 (14), 208 (7), 147 (55), 127 (17), 119 (18), 107 (14), 91 (10), 79 (18), 67 (100), 53 (12).

GENERAL PROCEDURE FOR THE PREPARATION OF *TRANS*-CYCLOHEXANONE AND CYCLOPENTANONE RING EXPANSION PRECURSORS

To a rapidly stirred solution of bis(tributyltin) (1.05 equiv.) in anhydrous THF (2ml/mmol of enone) at 0°C was added n-butyllithium (1.0 equiv.) dropwise, and the resultant yellow coloured solution stirred for 15 min at 0°C. After this period the solution was cooled to -78°C, the desired enone (1.0 equiv.) added dropwise as a solution in THF (0.5ml/mmol) and the mixture stirred at -78°C for 30min. The reaction flask was then warmed to -23°C whereupon HMPA (12 equiv.) was added, the resultant suspension stirred for 10min and then the relevant alkylating agent added slowly. The reaction mixture was then allowed to warm to room temperature slowly and stirred overnight. The mixture was then quenched with saturated ammonium chloride solution (5ml), ether (20ml) added, the organic layer separated and the aqueous phase thoroughly extracted with ether (4x30ml). The combined organic extracts were washed with brine then dried, filtered and solvent removed *in vacuo* . The residue was purified by flash column chromatography employing petrol/ether (as indicated) as solvent system.

***trans*-2-(4'-Bromopentyl)-3-tributylstannylcyclohexanone (3)**

Using the described general procedure compound (3)(1.26g, 75%) was obtained as a colourless oil after purification by flash chromatography (petrol:ether 20:1) from 2-cyclohexen-1-one (0.30g, 3.12mmol) and 1-

iodo-4-bromopentane (3.0 equiv., 2.59g, 9.38mmol). (Found: C, 51.40; H, 8.72. $C_{23}H_{45}BrOSn$ requires C, 51.52; H, 8.46%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 1710 (s), 1465 - 1420 (m), 1380 (w), 1075 (w); δ_H 0.75 - 1.05 (15H, m), 1.20 - 2.25 (26H, m), 2.27 - 2.50 (3H, m), 4.15 (1H, quintet, *J* 8Hz); *m/z* (D.C.I., NH_3) 554 (MNH_4^+, ^{120}Sn, ^{79}Br, 20%), 537 (MH^+, ^{120}Sn, ^{79}Br, 2), 378 (19), 330 (21), 308 (77), 184 (65), 167 (100), 149 (80).

***trans*-2-Methyl-2-(4'-bromopentyl)-3-tributylstannylcyclohexanone (6)**

Use of the general protocol afforded (6)(1.07g, 71%) as a colourless oil after purification by flash chromatography (petrol:ether 20:1) starting from 2-methyl-2-cyclohexen-1-one[16] (0.30g, 2.73mmol) and 1-iodo-4-bromopentane (3.0 equiv., 2.26g, 8.18mmol). (Found: C, 52.32; H, 8.78. $C_{24}H_{47}BrOSn$ requires C, 52.39; H, 8.61%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 1710 (s), 1460 - 1415 (m), 1380 (m), 1075 (w), 870 (w); δ_H 0.8 - 1.05 (15H, m), 1.1 (3H, s), 1.18 - 2.05 (26H, m), 2.2 - 2.52 (2H, m), 4.15 (1H, quintet, J 8Hz); m/z (D.C.I., NH_3) 493 (M^+ - ^nBu, ^{120}Sn, ^{79}Br, 10%), 471 (28), 413 (7), 388 (49), 291 (23), 181 (29), 163 (100).

***trans*-2-(3'-Bromobutyl)-3-tributylstannylcyclohexanone (9)**

The general procedure was applied to 2-cyclohexen-1-one (0.50g, 5.2mmol) and 1-iodo-3-bromobutane (8)(5.0 equiv., 6.80g, 26mmol) to yield stannane (9)(1.09g, 40%) as a colourless oil and 3-tributylstannylcyclohexanone (0.40g, 20%) after purification by flash chromatography (petrol:ether 20:1). For (9); (Found: C, 50.44; H, 8.52. $C_{22}H_{43}BrOSn$ requires C, 50.60; H, 8.30%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2870 (s), 2860 (s), 1710 (s), 1465 - 1440 (m), 1380 (m), 1340 (w), 1225 (m), 1070 (m), 960 (w), 875 (w); δ_H 0.88 - 0.95 (15H, m), 1.28 - 1.95 (21H, m), 1.70 (3H, d, J 6.5Hz), 2.15 - 2.50 (3H, m), 4.06 - 4.22 (1H, m); *m/z* (C.I., Direct) 523 (MH^+, ^{120}Sn, ^{79}Br, 2%), 513 (5), 465 (10), 443 (45), 385 (30), 361 (15), 308 (12), 291 (12), 153 (100), 135 (47), 55 (2).

***trans*-2-(5'-Trimethylsilyl-4'-pentyn)-3-tributylstannylcyclohexanone (17)**

Application of the general procedure yielded (17)(1.21g, 74%) as a colourless oil after purification by flash chromatography (petrol:ether 20:1) from the reaction between 2-cyclohexen-1-one (0.30g, 3.12mmol) and alkylating agent (16) (3.0 equiv., 2.49g, 9.38mmol). (Found: C, 59.03; H, 9.69. $C_{26}H_{50}SiOSn$ requires C, 59.43; H, 9.59%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 2180 (m), 1710 (s), 1460 (m), 1420 (m), 1250 (m), 1070 (m), 840 (m), 760 (m); δ_H 0.15 (9H, s), 0.8 - 1.05 (15H, m), 1.1 - 2.0 (21H, m), 2.1 - 2.22 (1H, m), 2.3 - 2.5 (4H, m); δ_C (50.3 MHz, DEPT) C: 85.15, 105.44, 217.75, CH: 34.14, 54.33, CH_2: 9.02, 20.05, 26.86, 27.41, 28.94, 29.34, 30.82, 32.59, 42.79, CH_3: 0.00, 13.53; *m/z* (D.C.I., NH_3) 527 (MH^+, ^{120}Sn, 5%), 469 (5), 308 (30), 265 (100), 235 (13), 212 (50), 109 (37), 90 (22).

***trans*-2-Methyl-2-(5'-trimethylsilyl-4'-pentyn)-3-tributylstannylcyclohexanone (21)**

The stannane (21)(1.04g, 71%) was afforded as a colourless oil after purification by flash chromatography (petrol:ether 20:1) using the general protocol from 2-methyl cyclohexen-1-one (0.30g, 2.73mmol) and alkylating agent (16)(3.0 equiv., 2.18g, 8.18mmol). (Found: C, 59.95; H, 9.68. $C_{27}H_{52}SiOSn$ requires C, 60.11; H, 9.72%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2870 (m), 2190 (m), 1710 (s), 1465 (s), 1455 (m), 1375 (w), 1250 (m), 840 (m), 760 (m); δ_H 0.15 (9H, s), 0.80 - 1.00 (15H, m), 1.05 (3H, s), 1.20 - 1.70 (19H, m), 1.80 - 1.95 (2H, m), 2.05 - 2.25 (2H, m), 2.30 - 2.45 (2H, m); δ_C (50.3 MHz, DEPT) C: 51.66, 84.89, 104.67, 216.09, CH: 38.06, CH_2: 10.09, 20.22, 23.44, 25.40, 27.38, 28.90, 29.09, 29.87, 38.69, CH_3: 0.00, 13.48, 24.11; *m/z* (D.C.I., NH_3) 558 (MNH_4^+, ^{120}Sn, 2%), 541 (MH^+, ^{120}Sn, 15), 483 (34), 308 (100), 291 (48), 250 (19), 233 (18), 90 (23), 73 (25).

***trans*-2-(4'-bromo-4'-pentenyl)-3-tributylstannylcyclohexanone (28)**

Application of the general protocol to 2-cyclohexen-1-one (0.20g, 2.08mmol) and (27)(3.0 equiv., 1.71g, 6.24mmol) afforded the stannane (28)(667mg, 60%) as a colourless oil after chromatographic purification (petrol:ether 20:1). (Found: C, 51.60; H, 8.40. $C_{23}H_{43}BrOSn$ requires C, 51.71; H, 8.11%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2870 (s), 2860 (s), 1710 (s), 1630 (m), 1460 - 1420 (m), 1375 (w), 1170 (w), 885 (m); δ_H 0.79 - 0.95 (15H, m), 1.18 - 2.15 (21H, m), 2.31 - 2.39 (5H, m), 5.33 (1H, s), 5.53 (1H, m); δ_C (50.3MHz, DEPT) CH_3: 13.48, CH_2: 8.96, 25.96, 27.37, 28.88, 29.07, 30.10, 32.68, 41.51, 42.84, 116.65, CH: 34.33, 54.42, C: 134.53, 214.03; *m/z* (D.C.I., NH_3) 552 (MNH_4^+, ^{120}Sn, ^{79}Br, 35%), 535 (MH^+, ^{120}Sn, ^{79}Br, 32), 477 (40), 308 (100), 165 (28).

***trans*-2-Methyl-2-(4'-bromo-4'-pentenyl)-3-tributylstannylcyclohexanone (30)**

The stannane (30)(498mg, 50%) was obtained as a colourless oil after chromatography (petrol:ether 15:1) from the reaction between 2-methylcyclohexen-1-one(0.20g, 1.81mmol) and (27)(3.0 equiv., 1.49g). (Found: C, 52.74; H, 8.39. $C_{24}H_{45}BrOSn$ requires C, 52.58; H, 8.27%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2870 (s), 2860 (s), 1705 (s), 1630 (m), 1460 - 1410 (m), 1375 (m), 885 (m); δ_H 0.82 - 0.94 (15H, m), 1.11 (3H, s), 1.22 - 1.55 (16H, m), 1.82 - 1.98 (5H, m), 2.32 - 2.42 (4H, m), 5.41 (1H, s), 5.59 (1H, s); *m/z* (ZAB1F, D.C.I., NH_3) 566 (MNH_4^+, ^{120}Sn, ^{79}Br, 8%), 549 (MH^+, ^{120}Sn, ^{79}Br, 17), 308 (100), 179 (15), 58 (2).

***trans*-2-(2'-Propyn)-3-tributylstannylcyclohexanone (32)**

The general procedure given for the preparation of *trans*-substrates afforded the stannane (32)(0.73g, 82%) as a colourless oil after purification by chromatography (petrol:ether 20:1), starting from 2-cyclohexen-1-one (0.20g, 2.08mmol) and propargyl bromide (5.0 equiv., 80% solution in toluene) as the alkylating agent. (Found: C, 59.41; H, 9.13. $C_{21}H_{38}OSn$ requires C, 59.32; H, 9.01%); $\nu_{max.}$ (thin film) 3320 (m), 2960 (s), 2920 (s), 2880 (s), 2860 (s), 1710 (s), 1465 - 1455 (m), 1220 (w), 1165 (w), 1080 (w), 860 (w); δ_H 0.85 - 1.05 (15H, m), 1.21 - 1.60 (17H, m), 1.70 - 1.90 (2H, m), 2.00 (1H, t, 2.0Hz), 2.21 - 2.65 (3H, m); δ_C (50.3 MHz, DEPT) C: 82.41, 211.30, CH: 31.62, 31.74, 69.47, CH_2: 8.85, 19.84, 27.34, 29.05, 30.21, 31.62, 42.23, CH_3: 13.44; *m/z* (D.C.I., NH_3) 444 (MNH_4^+, ^{120}Sn, 2%), 427 (MH^+, ^{120}Sn, 16), 369 (68), 308 (100), 291 (57), 135 (40), 119 (15), 97 (25), 91 (26), 79 (12), 68 (11), 58 (12).

***trans*-2-(3'-Bromo-2'-propenyl)-3-tributylstannylcyclohexanone (33)**

Use of the general protocol yielded (33)(0.84g, 53%) as a colourless oil after purification by chromatography (petrol:ether 15:1) from 2-cyclohexen-1-one (0.30g, 3.12mmol) and 1,3-dibromo-1-propene (3.0 equiv., 1.85g, 9.36mmol). (Found: C, 49.59; H, 8.04. $C_{21}H_{39}BrOSn$ requires C, 49.83; H, 7.77%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2890 (s), 2860 (s), 1710 (s), 1620 (w), 1460 - 1420 (m), 1225 (w), 1160 (w), 1080 (w), 960 (w), 660 (m); δ_H 0.79 - 1.00 (15H, m), 1.20 - 1.51 (17H, m), 1.70 - 1.90 (2H, m), 2.10 - 2.50 (2H, m), 2.55 - 2.70 (1H, m), 6.10 - 6.26 (2H, m); δ_C (50.3 MHz, DEPT) C: 215.45, CH: 33.88, 53.66, 108.07, 133.61, CH_2: 9.07, 27.38, 29.10, 30.32, 31.71, 32.64, 42.71, CH_3: 13.50; *m/z* (D.C.I., NH_3) 524 (MNH_4^+, ^{120}Sn, ^{79}Br, 42%), 507 (MH^+, ^{120}Sn, ^{79}Br, 20), 449 (45), 447 (18), 308 (100), 137 (12).

***trans*-2-Methyl-2-(3'-bromo-2'-propenyl)-3-tributylstannylcyclohexanone (35)**

From 2-methyl-2-cyclohexen-1-one (0.30g, 2.73mmol) and 1,3-dibromo-1-propene (3.0 equiv., 1.62g, 8.18mmol) following the general procedure the stannane (35) was isolated as a colourless oil (0.69g, 49%) after purification by flash chromatography (petrol:ether 20:1). (Found: C, 50.66; H, 8.03. $C_{22}H_{41}BrOSn$ requires C, 50.80; H, 7.94%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 1710 (s), 1620 (w), 1460 - 1420 (m), 1380 (m), 1140 (w), 1080 (w), 950 (w), 650 (m); δ_H 0.79 - 1.00 (15H, m), 1.13 (3H, s), 1.20 - 1.50 (17H, m),

1.70 - 2.15 (2H, m), 2.30 - 2.60 (2H, m), 6.10 - 6.26 (2H, m); *m/z* (D.C.I., NH_3) 538 (MNH_4^+, ^{120}Sn, ^{79}Br, 32%), 521 (MH^+, ^{120}Sn, ^{79}Br, 25), 463 (50), 308 (100), 252 (5), 151 (12), 111 (10).

***trans*-2-(4'-Bromo-2'-butenyl)-3-tributylstannylcyclohexanone (37)**

The general procedure gave (37) (1.09g, 67%) as a colourless oil after flash chromatography (petrol:ether 20:1) from 2-cyclohexen-1-one (0.30g, 3.12mmol) and 1,4-dibromo-2-butene (3.0 equiv., 1.98g, 9.36mmol). (Found: C, 50.76; H, 8.25. $C_{22}H_{41}BrOSn$ requires C, 50.80; H, 7.94%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 1710 (s), 1650 (w), 1465 - 1410 (m), 1380 (m), 1170 (m), 970 (w); δ_H 0.79 - 1.00 (15H, m), 1.20 - 1.85 (17H, m), 1.86 - 2.20 (2H, m), 2.25 - 2.50 (3H, m), 3.92 (2H, d, *J* 7Hz), 5.60 - 5.89 (2H, m); δ_C (50.3 MHz, DEPT) C: 215.78, CH: 33.53, 54.42, 127.65, 134.59, CH_2: 13.47, 27.34, 29.05, 30.21, 32.25, 32.73, 32.86, 42.66, CH_3: 13.47; *m/z* (D.C.I., NH_3) 538 (MNH_4^+, ^{120}Sn, ^{79}Br, 5%), 441 (22), 308 (15), 291 (12), 151 (100), 133 (57).

***trans*-2-(4'-Iodobutyl)-3-tributylstannylcyclopentanone (40)**

Application of the general procedure to 2-cyclopenten-1-one (100mg, 1.22mmol) and 1,4-diiodobutane (0.64ml, 4.85mmol) afforded 3-tributylstannylcyclopentanone (41)(180mg, 40%) as a colourless oil after flash chromatography (petrol:ether 20:1).$\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 1730 (s), 1470 - 1400 (m), 1375 (m), 1235 (m), 1185 (m), 1070 (m), 1000 (w), 960 (w), 870 (m); δ_H 0.72 - 1.05 (15H, m), 1.16 - 2.36 (19H, m); *m/z* (E.I.) 375 (31%), 374 (M^+,^{120}Sn, 100), 373 (31), 372 (73), 371 (32), 370 (31) and the required alkylated material *trans*-2-(4'-Iodobutyl)-3-tributylstannylcyclopentanone (40)(157mg, 23%). (Found: C, 45.76; H, 7.70. $C_{21}H_{41}OISn$ requires C, 45.43; H, 7.44%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 1735 (s), 1460 (m), 1375 (m), 1155 (m), 1075 (m), 960 (m), 870 (m); δ_H 0.82 - 0.97 (15H, m), 1.20 - 1.67 (18H, m), 1.72 - 1.93 (2H, m), 1.96 - 2.41 (4H, m), 3.19 (2H, t, *J* 7Hz); *m/z* (F.I.) 429 (M^+-I,100%), 427 (45), 426 (81), 425 (34), 424 (51).

***trans*-2-Methyl-2-(4'-iodobutyl)-3-tributylstannylcyclopentanone (43)**

The general procedure described for the preparation of *trans*-cyclohexanone precursors was employed to prepare the 5-membered precursor (43) as a colourless oil (2.85g, 96%) after purification by flash chromatography (petrol:ether 20:1) from 2-methyl-cyclohexen-1-one (0.50g, 5.21mmol) and 1,4-diiodobutane (3.0 equiv., 4.84g, 15.6mmol). (Found: C, 46.57; H, 7.80. $C_{22}H_{43}IOSn$ requires C, 46.43; H, 7.61%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1730 (s), 1465 - 1410 (m), 1380 (m), 1185 (w), 1075 (w); δ_H 0.81 - 1.00 (18H, m), 1.20 - 1.92 (21H, m), 2.00 - 2.49 (2H, m), 3.18 (2H, *J* 6.5Hz); δ_C (50.3 MHz, DEPT) C: 52.34, 216.03, CH: 32.10, CH_2: 6.34, 9.03, 23.52, 25.65, 27.34, 29.09, 33.70, 35.56, 39.14, CH_3: 13.49, 24.19; *m/z* (D.C.I., NH_3) 588 (MNH_4^+, ^{120}Sn, 23%), 513 (M^+ - ^nBu, ^{120}Sn, 8), 387 (17), 308 (27), 135 (100), 109 (5).

GENERAL PROCEDURE FOR THE DESILYLATION OF SUBSTRATES (17) AND (21)

To a stirred solution of the relevant substrate in anhydrous THF (3ml/mmol of substrate) at 0°C was added tetrabutylammonium fluoride (TBAF)(1.05 equiv., 1M solution in THF), the resultant solution stirred for 30 min and the progress of the reaction monitored by t.l.c analysis. The reaction usually reached completion within 35 min whereupon saturated solution of ammonium chloride (1ml), distilled water (2ml) and ether (15ml) were added. The aqueous layer was separated, extracted with ether, the combined organic layers washed with brine, dried and concentrated *in vacuo* . The crude desilylated acetylenic compounds were purified by flash column chromatography (petrol:ether 20:1).

***trans*-2-(4'-Pentyn)-3-tributylstannylcyclohexanone (18)**

Deprotection of (17)(0.50g, 0.95mmol) employing TBAF (1ml) according to the general procedure yielded compound (18) as a colourless oil (0.41g, 96%). (Found: C, 60.93; H, 9.63. $C_{23}H_{42}OSn$ requires C, 60.95; H, 9.34%); $\nu_{max.}$ (thin film) 3320 (m), 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1710 (s), 1465 (m), 1455 (m), 1380 (w), 1070 (w), 875 (w); δ_H 0.80 - 1.00 (15H, m), 1.2 - 1.82 (21H, m), 1.95 (1H, t, *J* 2Hz), 2.10 - 2.25 (2H, m), 2.30 - 2.45 (3H, m); δ_C (50.3 MHz, DEPT) C: 103.39, 214.24, CH: 28.90, 34.32, 54.27, CH_2: 9.01, 18.50, 26.72, 27.37, 29.09, 30.40, 30.59, 32.61, 42.82, CH_3: 13.48; *m/z* (D.C.I., NH_3) 472 (MNH_4^+, ^{120}Sn, 3%), 455 (MH^+, ^{120}Sn, 15), 397 (24), 308 (100), 231 (60), 189 (14), 163 (15), 107 (13), 58 (7).

***trans*-2-Methyl-2-(4'-pentyn)-3-tributylstannylcyclohexanone (22)**

Following the general protocol detailed above deprotection of (21)(0.50g, 0.93mmol) was achieved using TBAF (0.97ml) to afford (22)(0.42g, 96%) as a colourless oil. (Found: C, 61.72; H, 9.73. $C_{24}H_{44}OSn$ requires C, 61.69; H, 9.49%); $\nu_{max.}$ (thin film) 3320 (m), 2960 (s), 2920 (s), 2880 (s), 1710 (s), 1465 (m), 1455 (m), 1070 (w), 870 (w); δ_H 0.80 - 1.00 (15H, m), 1.10 (3H, s), 1.21 - 1.70 (21H,m), 1.80 - 2.00 (3H, m, *J* 2Hz), 2.05 - 2.20 (1H, m), 2.31 - 2.49 (1H, m); δ_C (50.3 MHz, DEPT) C: 52.05, 104.57, 216.75, CH: 38.21, CH_2: 10.06, 13.47, 18.82, 23.29, 24.24, 27.40, 29.09, 30.29, 38.77, CH_3: 13.47, 24.24; *m/z* (D.C.I., NH_3) 486 (MNH_4^+, ^{120}Sn, 1%), 469 (MH^+, ^{120}Sn, 10), 308 (100), 291 (33), 250 (11), 235 (10), 196 (8), 179 (8), 161 (9), 138 (14), 121 (10), 93 (10), 81 (7), 55 (6).

GENERAL PROCEDURE FOR THE PREPARATION OF *TRANS*-CYCLOHEPTANONE DERIVATIVES

To a stirred solution of bis(tributyltin) (1.05 equiv.) in anhydrous THF (2ml/mmol of enone) at 0°C was added n-butyl lithium (1.0 equiv.), the resultant yellow solution stirred for 15min and then cooled to -78°C. The relevant enone[17,18] was added dropwise as a solution in THF (0.5ml/mmol) and the mixture allowed to stir for 60min at -78°C. After this period had elapsed the reaction mixture was warmed to -23°C, HMPA (12 equiv.) was added and the resultant suspension was stirred for 15min. The enolate was then quenched by the addition of the desired alkylating agent (4.0 equiv.) as a solution in THF (1ml/mmol of enone) and after being allowed to warm up to room temperature over ca.5hr the reaction mixture was stirred at room temperature for 24hrs. The mixture was quenched with saturated ammonium chloride solution (5ml), the aqueous layer extracted with ether (4x30ml), the combined organic extracts washed with brine, dried, filtered and concentrated *in vacuo* . Purification of the crude oils was achieved by flash column chromatography (petrol:ether as indicated). Compounds in this series were isolated isomerically pure with assumed *trans*-2-alkyl-3-stannyl-stereochemistry on the basis of mechanistic and thermodynamic considerations, and by analogy to the related *trans*-2-alkyl-3-tributylstannyl-cyclohexanone series.

***trans*-2-(4'-Iodobutyl)-3-tributylstannylcycloheptanone (45)**

Following the general protocol the stannane (45)(0.70g, 66%) was isolated as a colourless oil after chromatography (petrol:ether 20:1) from 2-cyclohepten-1-one[17] (0.20g, 1.82mmol) and 1,4-diiodobutane (2.25g, 7.27mmol). (Found: C, 47.67; H, 8.05. $C_{23}H_{45}IOSn$ requires C, 47.37; H, 7.78%); $\nu_{max.}$ (thin film) 3000 (m), 2960 (s), 2930 (s), 2900 (s), 2870 (m), 2840 (m), 1700 (s), 1440 (s), 1430 (s), 1360 (m), 1160 (s), 950 (m); δ_H 0.80 - 1.00 (15H, m), 1.21 - 1.60 (25H, m), 2.30 - 2.60 (3H, m), 3.15 (2H, t, *J* 7.5Hz); δ_C (50.3 MHz, DEPT) C: 215.16, CH: 29.08, 56.80, CH_2: 6.01, 9.25, 24.94, 27.38, 28.44, 28.89, 31.91, 32.91,

33.34, 40.30, 54.07, CH_3: 13.51; *m/z* (E.I.) 527 (M^+ - ^nBu, ^{120}Sn, 59%), 401 (27), 361 (53), 291 (60), 247 (30), 235 (25), 177 (50), 167 (32), 149 (25), 121 (34), 95 (52), 81 (47), 67 (95), 55 (100).

***trans*-2-(3'-Iodopropyl)-3-tributylstannylcycloheptanone (48)**

Use of the standard procedure afforded compound (48)(0.57g, 55%) as a colourless oil after purification by flash chromatography (petrol:ether 20:1) from 2-cyclohepten-1-one (0.20g, 1.82mmol) and 1,3-diiodopropane (2.15g, 7.27mmol). (Found: C, 46.11; H, 7.85. $C_{22}H_{43}IOSn$ requires C, 46.43; H, 7.61%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2880 (s), 1705 (s), 1470 - 1410 (m), 1370 (m), 1170 (m), 1070 (m); δ_H 0.80 - 1.00 (15H, m), 1.19 - 1.70 (23H, m), 1.79 - 2.70 (3H, m), 3.15 (2H, t, *J* 7.5Hz); *m/z* (E.I.) 513 (M^+ - ^nBu, ^{120}Sn, 14%), 361 (122), 345 (100), 289 (26), 231 (28), 177 (54), 149 (52), 121 (32), 67 (31), 55 (71).

***trans*-2-Methyl-2-(4'-iodobutyl)-3-tributylstannylcycloheptanone (51)**

The stannane (51) was obtained as a colourless oil (0.87g, 60%) after chromatographic purification (petrol:ether 15:1) starting from 2-methyl-2-cyclohepten-1-one[18] (0.30g, 2.41mmol) and 1,4-diiodobutane (5.0 equiv., 3.75g, 12.1mmol) using the general procedure. (Found: C, 48.01; H, 7.91. $C_{24}H_{47}IOSn$ requires C, 48.27; H, 7.93%); $\nu_{max.}$ (thin film) 2960 (s), 2929 (s), 2870 (s), 2850 (s), 1705 (s), 1465 - 1440 (m), 1380 (m), 1140 (w), 1070 w); δ_H 0.84 - 0.95 (15H, m), 1.03 (3H, s), 1.21 - 1.96 (25H, m), 2.15 - 2.24 (1H, m), 2.85 - 2.97 (1H, m), 3.14 (2H, t, *J* 7Hz); δ_C (50.3 MHz) 10.31, 13.51, 21.62, 25.24, 26.71, 27.41, 28.99, 29.19, 29.38, 32.56, 33.74, 37.85, 38.05, 39.86, 54.24, 217.58; *m/z* (D.C.I., NH_3) 616 (MNH_4^+, ^{120}Sn, 42%), 599 (MH^+, ^{120}Sn, 52), 541 (13), 415 (8), 378 (15), 308 (95), 291 (25), 198 (15), 181 (70), 163 (100), 58 (8).

***cis*-2-Carbomethoxy-2-(4'-iodobutyl)-3-tributylstannylcycloheptanone (53)**

Application of the general protocol to 2-carbomethoxy-cyclohepten-1-one[19] (0.30g, 1.79mmol) and 1,4-diiodobutane (5.0 equiv., 2.77g, 8.93mmol) afforded (53) as a colourless oil (0.67g, 58%) after purification (flash column petrol:ether 5:1) of the crude residue. (Found: C, 47.01; H, 7.63. $C_{25}H_{47}IO_3Sn$ requires C, 46.83; H, 7.39%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1735 (s), 1705 (s), 1465 - 1420 (m), 1380 (m), 1160 (m), 1075 (m), 875 (w); δ_H 0.79 - 1.00 (15H, m), 1.15 - 2.02 (25H, m), 2.40 - 2.70 (2H, m), 3.15 (2H, t, *J* 7.5Hz), 3.73 (3H, s); δ_C (50.3 MHz, DEPT) C: 52.78, 175.89, 216.05, CH: 34.43, CH_2: 10.12, 24.84, 27.38, 28.86, 29.05, 30.40, 32.27, 33.87, 34.43, 37.10, 41.02, CH_3: 13.49, 51.86; m/z (D.C.I., NH_3) 643 (MH^+, ^{120}Sn, 8%), 585 (14), 459 (10), 401 (8), 378 (9), 308 (30), 291 (14), 225 (100), 210 (15), 193 (25), 169 (12), 58 (4).

***trans*-2-(4'-Bromopentyl)-3-tributylstannylcycloheptanone (55)**

Following the general procedure (55) was produced as a colourless oil (0.95g, 63%) after purification by flash chromatography (petrol:ether 20:1) from 2-cyclohepten-1-one (0.3g, 2.73mmol) and 1-iodo-4-bromopentane (4.0 equiv., 3.01g, 10.9mmol). (Found: C, 52.45; H, 8.63. $C_{24}H_{47}BrOSn$ requires C, 52.39; H, 8.61%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2870 (s), 2860 (s), 1700 (s), 1465 - 1430 (m), 1380 (m), 1250 (m), 1075 (w); δ_H 0.76 – 1.09 (15H, m), 1.14 - 2.03 (28H, m), 2.27 - 2.32 (1H, m), 2.49 - 2.69 (2H, m), 4.12 (1H, sextet, *J* 6Hz); *m/z* (D.C.I., NH_3) 541 (3%), 413 (10), 345 (15), 308 (23), 291 (7), 198 (12), 181 (78), 163 (100), 151 (3), 138 (7), 121 (8), 95 (10), 81 (12), 58 (4).

***trans*-2-Methyl-2-(4'-bromopentyl)-3-tributylstannylcycloheptanone (58)**

The use of the general procedure to 2-methyl-2-cyclohepten-1-one (0.30g, 2.42mmol) and 1-iodo-4-bromopentane (4.0 equiv., 2.67g, 9.67mmol) afforded the stannane (58) as a colourless oil (0.80g, 59%) after purification by flash chromatography (petrol:ether 20:1). (Found: C, 53.04; H, 8.89. $C_{25}H_{49}BrOSn$ requires C, 53.22; H, 8.75%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2870 (s), 2850 (s), 1700 (s), 1465 - 1440 (m), 1375

(m), 1260 (w), 1150 (m), 1075 (m); δ_H 0.81 - 0.95 (15H, m), 1.00 (3H, s), 1.19 - 1.56 (21H, m), 1.64 (3H, d, *J* 6.5Hz), 1.71 - 1.88 (4H, m), 2.13 - 2.20 (1H, m), 2.83 - 2.94 (1H, m), 4.06 (1H, sextet, *J* 6.5Hz); *m/z* (D.C.I., NH_3) 565 (MH^+, ^{120}Sn, ^{79}Br, 2%), 507 (5), 427 (5), 359 (4), 308 (11), 291 (5), 195 (45), 177 (100), 109 (8), 95 (10), 55 (2).

PREPARATION OF LACTONE PRECURSORS

3-(4'-Iodobutyl)-4-tributylstannyl-5,6-dihydro-2H-pyran-2-one (63)

To dry copper (I) cyanide (1.1 equiv., 92mg, 1.1mmol) under a stream of argon was added anhydrous THF (4ml) to form a slurry, which was cooled to -78°C and n-butyllithium (2.0 equiv., 1.5M, 1.36ml) added dropwise. The reaction flask was removed from the cooling bath for a few seconds and then cooled to -78°C again.To the resultant suspension was added n-tributyltin hydride (2.0 equiv., 70%, 0.72ml) (a rapid a colour change with evolution of gas was observed at this stage) and stirring continued for a further 10min. After this period 5,6-dihydro-2H-pyran-2-one (62)(0.10g, 1.0mmol) was added dropwise as a solution in THF (0.4ml), the newly formed brown solution stirred at -78°C for 60min, then warmed to -23°C, followed by the successive addition of HMPA (24 equiv., 4.2ml, 24mmol) and 1,4-diiodobutane (5.0 equiv., 1.55g, 5mmol). The reaction mixture was allowed to warm to room temperature slowly and subsequently stirred overnight. The mixture was quenched 10% NH_4OH/ 90% saturated ammonium chloride (3ml), the organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were washed with brine, dried, filtered and concentrated *in vacuo* . The crude product was purified by flash chromatography (gradient elution, petrol : ether 20:1 to petrol : ether 5:1), to afford the stannane lactone (63) as a colourless oil (0.41g, 70%). (Found: C, 44.30; H, 7.24. $C_{21}H_{41}IO_2Sn$ requires C, 44.16; H, 7.24%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2860 (s), 2840 (s), 1760 (s), 1460 - 1410 (m), 1380 (w), 1265 (m), 1170 (m), 1075 (m), 870 (w); δ_H 0.88 - 0.95 (15H, m), 1.25 - 2.15 (21H, m), 2.59 -2.69 (1H, m), 3.2 (2H, t, *J* 7.0Hz), 4.34 (2H, m); δ_C (50.3 MHz, DEPT) C: 174.56, CH: 21.45, 43.86, CH_2: 6.28, 8.64, 26.79, 27.35, 27.80, 29.04, 31.50, 33.52, 70.02, CH_3: 13.50; *m/z* (D.C.I., NH_3) 590 (MNH_4^+, ^{120}Sn, 6%), 573 (MH^+, ^{120}Sn, 11), 515 (93), 445 (9), 389 (7), 378 (6), 361 (6), 308 (8), 291 (8), 172 (55), 155 (100), 81 (7), 58 (7).

3-Methyl-4-tributylstannyl-5,6-dihydro-2H-pyran-2-one (65)

The protocol to prepare (63) was employed to prepare (65) as a colourless oil (0.61g, 74%) from 5,6-dihydro-2H-pyran-2-one (62)(0.20g, 2mmol) and methyliodide (6.0 equiv., 1.7g, 12mmol). (Found: C, 53.55; H, 8.83. $C_{18}H_{36}O_2Sn$ requires C, 53.62; H, 9.00%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1740 (s), 1460 - 1410 (m), 1380 (w), 1265 (m), 1185 (m), 1160 (m), 1100 (m), 1070 (m), 1050 (m), 1040 (m), 865 (w); δ_H 0.89 – 0.96 (15H, m), 1.22 – 1.62 (16H, m), 1.89 - 2.20 (2H, m), 2.65 (1H, sextet, *J* 7Hz), 4.35 (2H, m); δ_C (50.3 MHz, DEPT) C: 175.51, CH: 23.90, 38.76, CH_2: 8.59, 14.78, 27.32, 29.01, 69.85, CH_3: 13.44, 17.91; *m/z* (C.I., NH_3) 422 (MNH_4^+, ^{120}Sn, 3%), 405 (MH^+, ^{120}Sn, 11), 283 (100), 133 (63), 105 (10), 91 (32), 74 (17), 58 (3).

3-Methyl-3-(4'-iodobutyl)-4-tributylstannyl-5,6-dihydro-2H-pyran-2-one (66)

To a stirred solution of di-isopropylamine (1.5 equiv., 0.1ml, 0.71mmol) in anhydrous THF (2ml) at 0°C was added n-butyl lithium (1.05 equiv., 1.5M, 0.33ml, 0.49mmol), which was stirred for 20min at 0°C and then cooled to -78°C. The stannane (65)(0.19g, 0.47mmol) was added dropwise as a solution in THF (0.3ml), the resultant mixture allowed to stir for a further 20min, followed by the slow dropwise addition of a mixture of HMPA (5.0 equiv., 0.43ml), 1,4-diodobutane (5.0 equiv., 0.72ml) and THF (0.5ml). Stirring was continued at -

78°C for another 10min after which the reaction mixture was warmed to -23°C and allowed to warm to room temperature overnight. The mixture was quenched with saturated ammonium chloride solution and the aqueous layer thoroughly extracted with ether. The organic layers were combined, washed with brine, dried, filtered and solvent removed *in vacuo* . Purification of the crude residue was achieved by flash column chromatography, initially using petrol : ether 20:1 to elute excess diiodide followed by petrol : ether 5:1 to afford pure stannane (66) as a colourless oil (0.224g, 77%). (Found: C, 45.12; H, 7.56. $C_{22}H_{43}IO_2Sn$ requires C, 45.16; H, 7.41%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2880 (m), 2860 (m), 1740 (s), 1465 - 1420 (m), 1380 (m), 1270 (w), 1140 (m), 1080 (w), 1045 (w); δ_H 0.88 - 0.96 (15H, m), 1.20 - 2.25 (24H, m), 3.08 - 3.25 (2H, m), 4.20 - 4.50 (2H, m); δ_C (50.3 MHz, DEPT) C: 46.84, 176.45, CH: 28.86, CH_2: 6.50, 9.81, 25.05, 25.89, 27.36, 27.96, 29.05, 33.46, 72.50, CH_3: 13.48, 28.56; *m/z* (D.C.I., NH_3) 604 (MNH_4^+, ^{120}Sn, 2%), 587 (MH^+, ^{120}Sn, 19), 529 (3), 499 (20), 403 (10), 308 (14), 291 (20), 186 (20), 169 (100), 151 (21), 113 (13), 58 (12).

GENERAL PROCEDURE FOR RADICAL REACTIONS

A solution of the relevant precursor in benzene (5mM) was degased with argon for 1hour, after which AIBN (0.1equiv) and tributyltin hydride (0.1equiv) were added. The resultant solution was degassed for a further 20 minutes after which the reaction mixture was heated to reflux and monitored by ^1H nmr at regular periods. The solvent was removed *in vacuo* and the crude material purified by flash column chromatography (as indicated), followed by preparative thin layer chromatography where necessary. In some reactions a full stoichiometic equivalent of $^nBu_3SnH$ and further AIBN were added as indicated.

Radical reaction of precursor (3)

The stannane (3) (0.20g, 0.37mmol) was subjected to the general procedure and was found to be consumed after 12hours of reflux. The benzene was removed *in vacuo* and the remaining residue purified by flash column chromatography using petrol : ether (20:1). The compounds E-2-methylcyclodec-6-enone (4)(48.5mg, 78%) and 2-pentyl-2-cyclohexen-1-one (5)(5.4mg, 9%) proved to be separable by chromatography and were isolated in a 9:1 ratio respectively with total yield of 87%. Data for (4); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2930 (s), 2860 (m), 1710 (s), 1460 - 1410 (m), 1370 - 1340 (m), 1160 (m), 1060 (m), 1050 (m), 980 (m), 900 (w), 860 (w); δ_H 0.97 (3H, d, *J* 7.5Hz), 1.55 - 2.40 (12H, m), 2.45 - 2.59 (1H, sextet, *J* 7Hz), 5.04 - 5.28 (1H, ABX_2, J_{AB} 16Hz, J_{AX} 4Hz), 5.30 - 5.38 (1H, ABX_2, J_{AB} 16Hz, J_{BX} 4Hz); δ_C (50.3 MHz, DEPT) C: 216.00, CH: 50.37, 131.31, 134.67, CH_2: 27.59, 28.07, 31.52, 32.41, 33.86, 52.67, CH_3: 20.86; *m/z* (GCMS, C.I., NH_3) 184 (MNH_4^+, 11%), 167 (MH^+, 31), 166 (M^+,5), 149 (100), 133 (4), 105 (3), 95 (4), 91 (5), 81 (3), 58 (2). Data for (5); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2930 (s), 2870 (s), 1675 (s), 1635 (w), 1460 (m), 1435 (m), 1380 (m), 1175 (m), 1120 (m), 1095 (m), 900 (m), 730 (w); δ 0.87 (3H, t, *J* 6.5Hz), 1.29 - 1.42 (6H, m), 1.89 - 1.99 (2H, m), 2.17 (2H, t, *J* 7Hz), 2.31 - 2.46 (4H, m), 6.71 (1H, t, *J* 4Hz); δ_C (125 MHz, DEPT) CH: 144.75, CH_2: 22.51, 23.18, 26.07, 28.28, 29.48, 31.63, 38.63, CH_3: 14.03; *m/z* (GCMS, C.I., NH_3) 184 (MNH_4^+, 15%), 167 (MH^+, 100), 151 (5), 137 (3), 123 (2), 95 (1), 81 (1).

Radical reaction of precursor (6)

Application of the general procedure for radical reactions to (6)(0.15g, 0.27mmol) produced (2-methyl)-E-6-methylcyclodec-6-enone (7) as a fragrant oil (41.7mg, 85%) after purification by flash chromatography (petrol:ether 20:1); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2920 (s), 2870 (s), 2860 (s), 1705 (s), 1625 (m), 1460

- 1410 (m), 1370 (w), 1170 (w), 1150 (w), 1075 (m), 970 (w), 840 (w); δ_H 0.98 (3H, d, *J* 7.0Hz), 1.70 (3H, s), 1.80 - 2.40 (11H, m), 2.45 - 2.73 (2H, m), 4.95 (1H, m); δ_C (50.3 MHz, DEPT) C: 48.16, 215.95, CH: 48.15, 129.15, CH_2: 24.65, 28.02, 31.98, 39.45, 40.52, 51.89, CH_3: 14.53, 28.72; *m/z* (E.I.) 180 (M^+, 29%), 162 (72), 147 (32), 137 (67), 133 (30), 124 (66), 119 (20), 111 (37), 109 (92), 105 (25), 95 (81), 81 (92), 67 (94), 55 (100).

Radical reaction of precursor (9)

The stannane (9)(0.30g, 0.57mmol) was subjected to general radical reaction conditions after which purification by flash column chromatography (20:1 petrol : ether) led to the racemic ring expanded compound E-2-methyl-cyclonon-5-enone (11)(54.2mg, 62%) which eluted firstly (R_f = 0.6, petrol : ether 5:1) followed by 2-butyl-2-cyclohexen-1-one[20] (12)(26.2mg, 30%)(R_f = 0.4, petrol : ether 5:1). Data for (11); $\nu_{max.}$ (thin film) 3030 (w), 2960 (s), 2930 (s), 2860 (s), 1700 (s), 1460 - 1440 (m), 1370 (w), 1350 (w), 1135 (m), 985 (m); δ_H 0.95 (3H, d, *J* 7Hz), 1.60 - 2.68 (11H, m), 5.00 - 5.23 (1H, m), 5.40 - 5.70 (1H, m); *m/z* (GCMS, E.I.) 152 (M^+, 27%), 134 (100), 119 (57), 105 (27), 91 (57), 82 (40), 67 (98), 54 (88). Data for (12); $\nu_{max.}$ (thin film) 3030 (w), 2960 (s), 2930 (s), 2860 (s), ; δ_H 0.92 (3H, t, *J* 7.5Hz), 1.26 - 1.39 (4H, m), 1.97 (2H, sextet, *J* 7.5Hz), 2.19 (2H, td, *J* 8.5, 1.5Hz), 2.32 - 2.36 (2H, m), 2.41 - 2.45 (2H, m), 6.71 (1H, td, *J* 5, 1.5Hz); *m/z* (GCMS, E.I.) 152 (M^+, 56%), 133 (2), 123 (100), 109 (10), 95 (63), 91 (15), 84 (34), 81 (49), 79 (50), 67 (65), 55 (35), 54 (52).

Radical reaction of precursor (18)

The precursor (18)(0.20g, 0.44mmol) was refluxed in benzene for 72h with addition of tributyltin hydride/AIBN(0.1 equiv.) every 24h. Removal of benzene *in vacuo* and flash chromatography of crude material (petrol : ether 20: 1) produced 2-exomethylene-(E(?)-1'-tributylstannyl)-E-cyclodec-6-enone (19)(0.11g, 55%) as colourless oil. [In addition to which some starting material was recovered (20%)]. For (19); (Found: C, 61.01; H, 9.51. $C_{23}H_{42}OSn$ requires C, 60.95; H, 9.34%); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2900 (s), 1675 (s), 1575 (m), 1470 - 1440 (m), 1420 (m), 1380 (m), 1350 (m), 1280 (m), 1155 (s), 1080 (m), 1040 (m), 985 (m), 960 (m), 875 (m), 865 (m), 840 (m), 820 (m), 800 (m); δ_H 0.80 - 1.00 (15H, m), 1.22 - 1.69 (12H, m), 1.71 - 2.45 (10H, m), 2.70 - 2.85 (2H, m), 5.12 (1H, dt, *J* 15, 7.5Hz), 5.25 (1H, dt, *J* 15, 7.5Hz), 6.65 (1H, s with ^{119}Sn splitting, J_{Sn-H} 25Hz); δ_C (50.3 MHz, DEPT) C: 132.58, 206.77, CH: 132.23, 133.86, 135.29, CH_2: 10.09, 27.16, 28.34, 29.02, 31.12, 31.72, 33.41, 34.10, 38.08, CH_3: 13.50; *m/z* (D.C.I., NH_3) 455 (MH^+,^{120}Sn, 82%), 414 (13), 397 (100), 308 (70), 291 (72), 221 (20), 203 (15), 165 (40), 147 (97), 91 (18), 58 (8).

Radical reaction of precursor (22)

The vinyl stannane, 2-exomethylene-(E-1'-tributylstannyl)-E-6-methylcyclodec-6-enone (23), was isolated as a colourless oil (80mg, 40%) after sequential purification by flash chromatography/preparative thin layer chromatography (petrol:ether 20:1) following subjection of (22)(0.20g, 0.42mmol) to radical reaction conditions for 96h. (Found: C, 61.50; H, 9.61. $C_{24}H_{44}OSn$ requires C, 61.69; H, 9.49%); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2920 (s), 2880 (s), 1675 (s), 1575 (m), 1470 - 1440 (m), 1420 (m), 1380 (m), 1350 (m), 1280 (m), 1155 (s), 1080 (m), 1040 (m), 985 (m), 960 (m), 875 (m), 865 (m), 840 (m), 820 (m), 800 (m); δ_H 0.85 – 1.02 (15H, m), 1.20 - 1.69 (12H, m), 1.71 (3H, s), 1.80 - 2.43 (10H, m), 2.50 - 2.80 (2H, m), 4.99 - 5.06 (1H,

m), 6.55 (1H, s with ^{119}Sn splitting, J_{Sn-H} 26.5Hz); *m/z* (C.I., NH_3) 469 (MH^+,^{120}Sn, 25%), 411 (100), 308 (98), 291 (60), 161 (50), 136 (10), 95 (40).

Radical reaction of precursor (28)

Subjection of stannane (28)(0.10g, 0.19mmol) to standard radical conditions afforded 2-(4'-pentenyl)-cyclohex-2-enone (29)(26mg, 85%) as a fragrant oil after purification by flash chromatography (petrol : ether 20:1). $\nu_{max.}$ (thin film) 3070 (w), 2920 (s), 2860 (m), 1700 (m), 1670 (s), 1640 (m), 1450 (m), 1430 (m), 1410 (m), 1370 (m), 1250 (m), 1170 (m), 990 (w), 905 (m); δ_H 1.49 (2H, quin., *J* 7.5Hz), 1.92 - 2.11 (4H, m), 2.20 (2H, t, *J* 7.5Hz), 2.27 - 2.46 (4H, m), 4.93 - 5.05 (2H, m), 5.71 - 5.88 (1H, m), 6.62 (1H, t, *J* 4Hz); *m/z* (GCMS, C.I., NH_3) 182 (MNH_4^+, 11%) 165 (MH^+, 100), 149 (5), 135 (3).

Radical reaction of precursor (30)

Application of general radical conditions for 96hr with regular addition of tributyltin hydride (0.1equiv., 4.8μl)/AIBN(3mg) to (30)(0.10g, 0.18mmol) afforded *trans*-2-methyl-2-(4'-pentenyl)-3-tributylstannylcyclohexanone (31)(60mg, 70%) as a colourless oil after chromatography (petrol : ether 20:1). (Found: C, 60.98; H, 10.10. $C_{24}H_{46}OSn$ requires C, 61.42; H, 9.88%) $\nu_{max.}$ (thin film) 3080 (w), 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1705 (s), 1470 - 1410 (m), 1375 (m), 1070 (w), 910 (m); δ_H 0.79 - 0.98 (15H, m), 1.10 (3H, s), 1.25 - 1.56 (15H, m), 1.80 - 2.13 (8H, m), 2.30 - 2.50 (2H, m), 4.92 - 5.09 (2H, m), 5.70 - 5.91 (1H, m); δ_C (50.3MHz, DEPT) C: 51.80, 215.95, CH: 38.08, 138.82, CH_2: 10.05, 23.49, 25.62, 27.41, 29.09, 30.10, 34.25, 38.43, 38.77, 50.45, CH_3: 13.46, 24.46; *m/z* (E.I.) 413 (M^+-^{n}Bu, ^{120}Sn, 57%), 411(47), 409 (27), 345 (18), 291 (23), 235 (75), 179 (100), 121 (24), 95 (27), 81 (17), 67 (22), 55 (33).

Radical reaction of precursor (33)

Treatment of stannane (33)(0.10g, 0.20mmol) under radical conditions (slow addition of ^{n}Bu$_3$SnH (1.0 equiv.) over 96hr) afforded *trans*-2-allyl-3-tributylstannylcyclohexanone (34)(59mg, 70%) as a colourless oil after purification by flash chromatography (petrol : ether 20:1). (Found: C, 58.88; H, 9.35. $C_{21}H_{40}OSn$ requires C, 59.04; H, 9.44%); $\nu_{max.}$ (thin film) 3080 (w), 2960 (s), 2920 (s), 2865 (s), 1710 (s), 1640 (m), 1470 - 1410 (m), 1375 (m), 1340 (m), 1310 (w), 1070 (m), 1020 (m), 1000 (m), 910 (m), 735 (m); δ_H 0.82 - 0.95 (15H, m), 1.22 - 1.84 (15H, m), 1.87 - 2.22 (4H, m), 2.29 - 2.61 (3H, m), 4.91 - 5.05 (2H, m), 5.71 - 5.95 (1H, m); δ_C (50.3 MHz, DEPT) C: 216.09, CH: 33.49, 54.64, 137.22, CH_2: 9.04, 27.37, 29.08, 30.19, 32.22, 35.41, 42.66, 115.67, CH_3: 13.48; *m/z* (E.I.) 371 (M^+-^{n}Bu, ^{120}Sn, 75), 369 (57), 367 (33), 291 (37), 289 (27), 287 (17), 235 (67), 233 (55), 231 (33), 179 (100), 137 (23), 121 (52), 91 (13), 79 (24), 67 (40), 55 (43).

Radical reaction of precursor (35)

The stannane (35)(0.10g, 0.19mmol) was subjected to general radical reaction conditions with slow addition of ^{n}Bu$_3$SnH (1.0 equiv.) over 72hr affording *trans*-2-methyl-(2-allyl)-3-tributylstannylcyclohexanone (36)(65mg 77%) as a colourless oil after purification by flash chromatography (petrol:ether 20:1). (Found: C, 59.87; H, 9.74. $C_{22}H_{42}OSn$ requires C, 59.73; H, 9.50%); $\nu_{max.}$ (thin film) 3070 (w), 2960 (s), 2920 (s), 2870 (s), 2850 (s), 1705 (s), 1640 (m), 1470 - 1410 (m), 1375 (m), 1330 (m), 1310 (w), 1070 (m), 1020 (m), 1000 (m), 910 (m), 735 (m); δ_H 0.83 - 0.99 (15H, m), 1.10 (3H, s), 1.23 - 1.56 (15H, m), 1.88 - 2.26 (4H, m), 2.30 - 2.54 (2H, m), 4.96 - 5.11 (2H, m), 5.68 - 5.86 (1H, m); δ_C (50.3 MHz, DEPT) C: 51.88, 215.50, CH: 38.07,

134.99, CH_2: 10.13, 25.85, 27.38, 29.08, 29.27, 38.84, 42.99, 117.39, CH_3: 13.76, 24.35; *m/z* (E.I.) 401 (M^+-C_3H_5, ^{120}Sn, 10%), 385 (39), 383 (30), 381 (18), 291 (38), 289 (30), 287 (17), 235 (75), 179 (100), 135 (22), 121 (41), 79 (26), 67 (28), 55 (45).

Radical reaction of precursor (37)

The precursor (37)(0.20g, 0.38mmol) was subjected to general radical reaction conditions with slow addition of $^nBu_3SnH$ (1.0 equiv.) over 72hr affording an inseparable mixture by flash chromatography (petrol : ether 20:1) of *trans*-2-(3'-butenyl)-3-tributylstannylcyclohexanone (39)(71mg, 42%) and *trans*-2-(2'-butenyl)-3-tributylstannylcyclohexanone (38)(71mg, 42%) as a colourless oil. (Found: C, 59.44; H, 9.90. $C_{22}H_{42}OSn$ requires C, 59.88; H, 9.59%); $\nu_{max.}$ (thin film) 3080 (w), 3030 (w), 2960 (s), 2930 (s), 2870 (s), 2850 (s), 1710 (s), 1640 (w), 1470 - 1410 (m), 1375 (m), 1340 (m), 1165 (m), 1075 (m), 1020 (m), 1000 (m), 970 (m), 960 (m), 910 (w), 875 (w); δ_H (38) 0.80 - 0.99 (15H, m), 1.15 - 1.70 (15H, m), 1.71 - 2.25 (7H, m), 2.25 - 2.60 (3H, m), 5.40 - 5.50 (2H, m); δ_H (39) 0.80 - 0.99 (15H, m), 1.15 - 1.70 (15H, m), 1.71 - 2.25 (6H, m), 2.25 - 2.60 (3H, m), 4.90 - 5.05 (2H, m), 5.70 - 5.90 (1H, m); *m/z* (E.I.) 385 (M^+-^nBu, ^{120}Sn, 77%), 383 (58), 381 (31), 329 (8), 291 (26), 235 (60), 179 (100), 177 (96), 175 (63), 121 (35), 91 (15), 79 (24), 67 (23), 55 (27).

Radical reaction of precursor (40)

The stannane (40)(150mg, 0.27mmol) was subjected to the general radical reaction conditions (45h) leading solely to the formation of 2-butyl-2-cyclopenten-1-one (42) which was afforded as a colourless oil after flash chromatography (20:1 petrol : ether)(31mg, 83%). $\nu_{max.}$ (thin film) 3040 (w), 2960 (m), 2930 (s), 2860 (m), 1705 (m), 1635 (w), 1470 - 1430 (m), 1380 (w), 1050 (w), 1005 (m), 790 (m), 740 (m); δ_H 0.89 (3H, t, *J* 7Hz), 1.15 - 1.68 (4H, m), 2.17 (2H, td, *J* 7, 2.5Hz), 2.34 - 2.45 (2H, m), 2.50 - 2.63 (2H, m), 7.25 - 7.35 (1H, m); *m/z* (E.I.) 138 (M^+, 56%), 123 (32), 109 (53), 96 (100), 81 (31), 79 (25), 77 (12), 67 (51), 65 (19), 55 (21), 53 (39).

Radical reaction of precursor (43)

The stannane (43)(0.20g, 0.35mmol) was refluxed in benzene with the catalytic addition of tributyltin hydride/AIBN every 12h according to the general protocol for 96h, however periodic ^1H NMR detected no ring expansion product and the starting precursor was eventually consumed giving the directly reduced adduct (44). The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography (petrol : ether 20:1) to afford 2-methyl-(2-butyl)-3-tributylstannylcyclopentanone (44)(148mg, 95%) as a colourless oil. (Found: C, 59.16; H, 10.20. $C_{22}H_{44}OSn$ requires C, 59.61; H, 10.00%); $\nu_{max.}$ (thin film) 2960 (s), 2939 (s), 2880 (s), 2860 (s), 1740 (s), 1465 (m), 1420 (w), 1410 (w), 1380 (m), 1290 (w), 1180 (w), 1080 (m), 960 (w); δ_H 0.87 - 0.97 (18H, m), 1.01 (3H, s), 1.18 - 1.68 (19H, m), 1.87 - 2.40 (4H, m); *m/z* (C.I., NH_3) 462 (MNH_4^+, ^{120}Sn, 5%), 387 (26), 331 (5), 312 (17), 308 (100), 291 (60), 252 (10), 235 (13), 196 (10), 137 (42), 121 (13), 69 (15), 55 (14).

Radical reaction of precursor (45)

A solution of (45)(0.15g, 0.26mmol) in benzene required 16h at reflux for completion of reaction using the general protocol. The reaction mixture was concentrated *in vacuo* and purification by flash chromatography

afforded an unseparable mixture of E(?)-cycloundec-6-enone (46) (26mg, 60%) and 2-butyl-2-cyclohepten-1-one (47)(8.5mg, 20%). Spectral data for (46) and (47); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2929 (s), 2860 (s), 1710 (s), 1695 (s), 1665 (s), 1450 (s), 1375 (m), 1245 (w), 1180 (w), 1120 (w), 1070 (w), 975 (m), 920 (w), 850 (w), 730 (m); (47) δ_H 0.86 (3H, t, *J* 7.5 Hz), 1.42 - 1.56 (4H, m), 1.70 - 1.75 (2H, m), 1.91 - 1.98 (2H, m), 2.20 (2H, t, *J* 7.5Hz), 2.31 - 2.36 (2H, m), 2.52 - 2.59 (2H, m), 6.42 (1H, t, *J* 6Hz); (46) δ_H 1.22 - 1.35 (8H, m), 1.66 - 1.75 (4H, m), 2.31 - 2.36 (4H, m), 5.13 - 5.27 (2H, m); *m/z* (GCMS, C.I., NH_3) 167 (MH^+, 50%), 166 (M^+, 30), 137 (30), 123 (40), 109 (24), 95 (70), 79 (48), 67 (100), 55 (68).

Radical reaction of precursor (48)

A solution of (48)(0.20g, 0.35mmol) in benzene required 19h at reflux for completion of reaction using general radical reaction conditions. The reaction mixture was concentrated *in vacuo* and purification by flash chromatography (petrol:ether 20:1) afforded an inseparable mixture (35mg, 66%) of E-cyclodec-5-enone (49)(33%) and 2-propyl-2-cyclohepten-1-one (50)(33%). For (49) and (50) $\nu_{max.}$ (thin film) 3030 (w), 2920 (s), 2860 (s), 1705 (s), 1680 (s), 1610 (m), 1440 (m), 1420 (m), 1270 (m), 1140 (m), 985 (m); for (49) δ_H 1.65 - 1.99 (6H, m), 2.23 (4H, brm), 2.40 - 2.61 (4H, m), 5.16 (1H, dt, *J* 15, 7.5Hz), 5.36 (1H, dt, *J* 15, 7.5Hz); for (50) δ_H 0.94 (3H, t, *J* 7.5Hz), 1.48 (2H, sextet, *J* 7.5Hz), 1.60 - 1.92 (6H, m), 2.09 (2H, td, *J* 7.5Hz, 1.5Hz), 2.40 - 2.61 (2H, m), 6.64 (1H, td, *J* 7.5, 1.5Hz); *m/z* (GCMS, C.I., NH_3) 170 (MNH_4^+, 18%), 153 (MH^+, 40), 135 (100), 109 (2), 95 (2), 80 (2), 67 (1), 58 (2).

Radical reaction of precursor (51)

A degassed solution of (51)(0.10g, 0.17mmol) in benzene containing catalytic amounts of tributyltin hydride (5μl) and AIBN (5mg) required 72hrs at reflux using the general radical conditions with regular additions of initiator for complete consumption of starting iodide.The solvent was removed *in vacuo* and the residual oil was purified by flash chromatography employing petrol : ether 20:1 as the eluting solvent. The ring expanded compound E(?)-6-methylcycloundec-6-enone (52) was afforded as a fragrant oil (21.6mg, 72%).$\nu_{max.}$ (thin film) 3030 (m), 2940 (s), 2860 (s), 1705 (s), 1605 (w), 1450 (s), 1420 (m), 1405 (w), 1375 - 1320 (m), 1235 - 1200 (m), 1120 (w), 1070 (w), 840 (w); δ_H (300MHz) 1.60 (3H, s), 1.58 - 1.78 (8H, m), 1.99 - 2.03 (4H, m), 2.29 - 2.38 (4H, m), 5.00 (1H, t, *J* 8Hz); *m/z* (GCMS, C.I., NH_3) 198 (MNH_4^+, 12%), 182 (15), 181 (MH^+, 100), 179 (13), 165 (22), 163 (78), 161 (7), 58 (10).

Radical reaction of precursor (53)

Application of the general radical conditions to (53)(0.20g, 0.31mmol) with regular additions of catalytic quantities of AIBN/tributyltin hydride (0.1 equiv.), up to one complete equivalent over 96h produced the stannane adduct (54) as a colourless oil (128mg, 80%). (Found: C, 58.66; H, 9.67. $C_{25}H_{48}O_3Sn$ requires C, 58.27; 9.39%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1730 (s), 1700 (s), 1465 - 1430 (m), 1380 (w), 1225 (m), 1160 (m), 1070 (m), 910 (m); δ_H 0.83 - 0.95 (18H, m), 1.20 - 1.63 (21H, m), 1.81 - 1.96 (4H, m), 2.40 - 2.49 (1H, m), 2.65 - 2.76 (1H, m), 3.73 (3H, s); δ_C (50.3MHz, DEPT) C: 53.05, 175.33, 216.55, CH: 34.82, CH_2: 10.41, 23.29, 25.10, 27.41, 27.54, 29.23, 32.53, 34.82, 38.42, 41.28, CH_3: 13.65, 15.23, 51.79; *m/z* (D.C.I., NH_3) 517 (MH^+, ^{120}Sn, 26%), 485 (2), 459 (100), 403 (5), 345 (5), 308 (8), 291 (20), 250 (5), 235 (6), 209 (7), 138 (7), 67 (2), 55 (3).

Radical reaction of precursor (55)

The application of the general radical reaction conditions to stannane (55)(0.20g, 0.36mmol) afforded a separable mixture of E(?)-2-methylcycloundec-6-enone (56)(49mg, 52%) and 2-pentyl-2-cyclohepten-1-one (57)(16mg, 17%) by chromatography (20:1 petrol : ether) after 24hours at reflux in benzene with three additions of catalytic amounts of AIBN/$^{n}Bu_3SnH$. Data for (56); $\nu_{max.}$ (thin film) 3040 (w), 2960 (s), 2930 (s), 2870 (s), 2860 (s), 1710 (s), 1465 - 1435 (m), 1375 (m), 975 (m); δ_H 1.00 (3H, d, *J* 7Hz)), 1.40 - 1.70 (8H, m), 1.71 - 2.15 (4H, m), 2.45 - 2.75 (3H, m), 5.18 - 5.40 (2H, m); *m/z* (GCMS, C.I., NH_3) 181 (MH^+, 22%), 151 (45), 133 (23), 123 (34), 112 (60), 109 (29), 95 (75), 90 (25), 86 (53), 84 (85), 67 (100), 55 (57). Data for (57); $\nu_{max.}$ (thin film) 3030 (w), 2960 (s), 2930 (s), 2880 (s), 2860 (s), 1700 (s), 1670 (s), 1470 - 1440 (m), 1380 (m), 1250 (w), 1075 (w), 860 (w); δ_H 0.88 (3H, t, *J* 6.5Hz), 1.22 - 1.43 (6H, m), 1.62 - 1.81 (4H, m), 2.22 (2H, t, *J* 7Hz), 2.33 - 2.40 (2H, m), 2.50 - 2.61 (2H, m), 6.47 (1H, t, *J* 6.5Hz); *m/z* (GCMS, E.I.) 180 (M^+, 12%), 151 (33), 123 (18), 112 (35), 95 (100), 81 (55), 67 (90), 55 (35).

Radical reaction of precursor (58)

The application of the general radical reaction conditions to precursor (58)(0.10g, 0.18mmol) afforded 2-methyl-2-pentyl-3-tributylstannylcycloheptanone (59)(65mg, 75%) as a colourless oil after purification by chromatography (petrol : ether 15:1). (Found: C, 61.54; H, 10.61. $C_{25}H_{50}OSn$ requires C, 61.87; H, 10.38%); $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2870 (s), 2860 (s), 1700 (s), 1470 - 1430 (m), 1375 (m), 1345 (m), 1135 (m), 1080 (m), 1020 (w), 865 (w); δ_H 0.80 - 0.98 (21H, m), 1.13 - 1.55 (24H, m), 1.80 - 1.95 (3H, m), 2.10 - 2.24 (1H, m), 2.85 - 3.00 (1H, m); δ_C (50.3 MHz, DEPT) C: 54.37, 217.88, CH: 38.04, CH_2: 10.27, 22.17, 23.85, 26.72, 27.41, 28.98, 29.36, 32.18, 32.61, 38.43, 41.27, CH_3: 13.44, 13.76, 21.68; *m/z* (E.I.) 429 (M^+-^{n}Bu, ^{120}Sn, 46%), 427 (36), 425 (21), 359 (12), 291 (25), 235 (37), 179 (51), 121 (27), 98 (28), 81 (30), 71 (60), 55 (100),

Radical reaction of lactone (63)

Application of general radical reaction conditions to stannane (63)(0.20g, 0.35mmol) with catalytic quantities of $^{n}Bu_3SnH$ (5mg) and AIBN (5mg) required a period of 12hours for completion. The solvent was removed *in vacuo* and the resultant oil purified by flash chromatography (gradient elution, 20:1 petrol : ether to 3:1 petrol : ether) to afford 5,6-dihydro-3-butyl-2H-pyran-2-one (64)(48mg, 90%) as a colourless oil. $\nu_{max.}$ (thin film) 2960 (s), 2940 (s), 2870 (m), 1725 (s), 1650 (w), 1470 (m), 1430 (s), 1400 (s), 1280 (s), 1190 (m), 1130 (s), 1100 (m), 1080 (m), 1060 (m), 990 (m), 860 (m); δ_H 0.92 (3H, t, *J* 7Hz), 1.29 - 1.51 (4H, m), 2.31 (2H, t, *J* 7.5Hz), 2.43 (2H, ca., q, *J* 6Hz), 4.37 (2H, t, *J* 6Hz), 6.61 (1H, t, J 4Hz); *m/z* (GCMS, C.I., NH_3) 172 (MNH_4^+, 57%), 155 (MH^+, 100), 139 (2), 125 (3), 81 (4).

Radical reaction of lactone (66)

Precursor (66)(0.20g, 0.34mmol) was subjected to general radical conditions and after a total period of 72hours at reflux with regular addition of initiator/hydride (up to one complete equivalent) only the directly reduced adduct 3-butyl-4-tributylstannyl-5,6-2H-pyran-2-one (67)(133mg, 85%) was afforded as a colourless oil following chromatography (5:1 petrol:ether). (Found: C, 57.45; H, 9.94. $C_{22}H_{44}O_2Sn$ requires C, 57.53; H, 9.66%); $\nu_{max.}$ (thin film) 2960 (s), 2920 (s), 2870 (s), 2860 (s), 1730 (s), 1465 (s), 1430 (m), 1400 (s), 1380 (s), 1270 (s), 1140 (s), 1075 (s), 1040 (s); δ_H 0.82 - 0.98 (18H, m), 1.18 - 1.60 (21H, m), 1.73 - 2.11 (3H, m), 4.17 -

4.43 (2H, m); δ_C (DEPT, 50.3 MHz) CH_3: 13.30, 13.70, 20.60, CH_2: 9.72, 22.01, 25.07, 27.13, 27.31, 29.00, 40.70, 72.30, CH: 20.27, C: 46.98, 176.71; *m/z* (C.I.) 461 (MH^+, ^{120}Sn, 75%), 403 (31), 308 (18), 291 (47), 235 (22), 153 (100), 138 (36), 113 (20), 83 (12), 69 (15), 55 (12).

Hydrogenation of (11)

A solution of (11)(30mg, 0.20mmol) in ethyl acetate (3ml) with a catalytic amount of 5% palladium on activated carbon (5mg) was evacuated and hydrogen gas introduced *via* balloon. The resultant mixture was stirred overnight at room temperature, then filtered over celite, and the solvent was removed *in vacuo* to afford (±)-2-methylcyclononanone (13)(30mg, 100%) as a colourless oil without the need for further purification. $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2870 (s), 1710 (s), 1465 - 1445 (m), 1375 (w), 1240 -1210 (w), 1150 (w); δ_H 1.00 (3H, d, J 7.5Hz), 1.20 - 1.95 (12H, m), 2.30 - 2.75 (3H, m); *m/z* (GCMS, C.I., NH_3) 172 (MNH_4^+, 100%), 155 (MH^+, 77), 112 (5), 98 (4), 58 (6).

Hydrogenation of (56)

The procedure described above for the hydrogenation of (11) was used to reduce E(?)-2-methylcycloundec-6-enone (56)(20mg, 0.11mmol) to the saturated ketone (60). The crude product required minor purification by p.l.c. to yield pure 2-methylcycloundec-1-one (60) (18.6mg, 92%). $\nu_{max.}$ (thin film) 2930 (s), 2860 (s), 1705 (s), 1470 - 1410 (m); 1375 (w), 1240 - 1200 (w), 1150 (w); δ_H 1.00 (3H, d, *J* 7.5Hz), 1.21 - 1.95 (16H, m), 2.30 - 2.80 (3H, m); *m/z* (GCMS, C.I., NH_3) 200 (MNH_4^+, 53%), 183 (MH^+, 100), 112 (32).

Oxidation of (13)

To a solution of (13)(20mg, 0.13mmol) in anhydrous dichloromethane(5ml) was added *m*-CPBA (1.1equiv., 25mg), and the resultant mixture stirred for 10 days at room temperature. Solid was removed by filtration, washed with petrol (25ml) and the filtrate washed with 10% $NaHCO_3$, water (20ml) and then brine (20ml). The organic layer after drying and filtration was concentrated *in vacuo* to afford a fragrant oil. The crude oil was purified by preparative thin layer chromatography (CH_2Cl_2) to afford (±)-phoracantholide[3a] ((±)-decan-9-olide)(19.9mg, 90%). $\nu_{max.}$ (thin film) 2960 (s), 2930 (s), 2860 (s), 1720 (s), 1470 - 1420 (m), 1250 (m), 1025 (s); δ_H 1.27 (3H, d, *J* 6.5Hz), 1.40 - 2.56 (14H, m), 4.97 - 5.05 (1H, m); *m/z* (GCMS, C.I., NH_3) 188 (MNH_4^+, 62%), 171 (MH^+, 100), 153 (11), 98 (10).

Oxidation of (60)

The exact protocol described for the oxidation of (13) was used to oxidize compound (60)(20mg, 0.11mmol) to the natural product (±)-dihydrorecifeiolide[3e] ((±)-dodecan-11-olide)(61)(19.6mg, 92%). $\nu_{max.}$ (thin film) 2930 (s), 2870 (s), 1725 (s), 1250 (s); δ_H 1.25 (3H, d, *J* 6.5Hz), 1.90 - 1.10 (16H, m), 2.10 - 2.57 (2H, m), 5.00 - 5.24 (1H, m); *m/z* (E.I.) 198 (M^+, 10%), 180 (23), 111 (60), 58 (100).

Destannylation of vinyl stannane (19)

To a solution of (19)(20mg, 0.044mmol) in anhydrous THF(2ml) was added tosic acid (1.0 equiv., 8.38mg) as a solution in THF(3ml) over a 3h period. The progress of the reaction was followed by tlc analysis and was essentially completed in 5h. The solvent was removed *in vacuo* and the crude product was purified by preparative thin layer chromatograph. The compound 2-exomethylene-E-cyclodec-6-enone (20) was afforded as a fragrant oil

(6.8mg, 95%); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2930 (s), 2860 (s), 1680 (s), 1625 (m), 1440 (m), 1360 (m), 1170 (m), 1150 (m), 1100 (m), 1060 (m), 985 (m), 965 (m), 935 (w), 920 (w), 800 (w); δ_H (300 MHz) 1.43 - 1.56 (2H, m), 1.79 - 2.01 (4H, m), 2.14 - 2.36 (4H, m), 2.54 (1H, ca., t, *J* 12.5Hz), 2.76 (1H, ca., t, *J* 12.5Hz), 5.17 (1H, dt, *J* 15, 7.5Hz), 5.30 (1H, dt, *J* 15, 7.5Hz), 5.47 (1H, s), 5.65 (1H, s); δ_C (125 MHz, DEPT) CH: 132.77, 133.23, CH_2: 28.72, 29.48, 31.30, 33.56, 34.16, 38.15, 119.09; *m/z* (GCMS, C.I., NH_3) 182 (MNH_4^+, 13%), 165 (MH^+, 100), 147 (60), 135 (7), 131 (7), 121 (7), 108 (8), 93 (8), 81 (11), 67 (6), 58 (7).

Destannylation of vinyl stannane (23)

The procedure described above for the destannylation of stannane (19) was used exactly for the destannylation of derivative (23)(15mg, 0.032mmol). The compound 2-exomethylene-6-methyl-E-cyclodec-6-enone (24) was afforded as a fragrant oil (5.1mg, 89%); $\nu_{max.}$ (thin film) 3020 (w), 2960 (s), 2930 (s), 2860 (s), 1680 (s), 1625 (m), 1440 (m), 1360 (m), 1170 (m), 1150 (m), 1100 (m), 1060 (m), 985 (m), 965 (m), 920 (w), 815 (w), 765 (w); δ_H 1.43 - 1.56 (2H, m), 1.71 (3H, s), 1.80 - 2.01 (4H, m), 2.14 - 2.40 (4H, m), 2.54 (1H, ca., t, *J* 12.5Hz), 2.76 (1H, ca., t, *J* 12.5Hz), 4.90 - 5.03 (1H, m), 5.48 (1H, s), 5.55 (1H, s); *m/z* (GCMS, C.I., NH_3) 196 (MNH_4^+, 8%), 179 (MH^+, 100), 163 (38), 137 (10), 121 (7), 107 (5), 91 (6), 80 (7), 67 (4), 58 (5).

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