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Alkyl Radical Cyclisations of Methylenecyclopropane Derivatives

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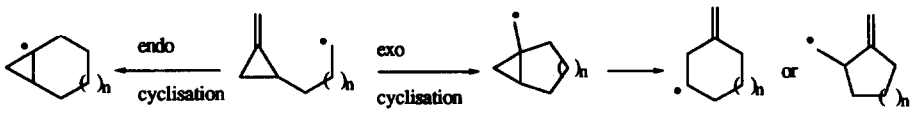
Abstract - Radical cyclisations of various methylenecyclopropane derivatives have been studied. Cyclisation of diphenylsubstituted (methylenecyclopropyl)butyl radical **10** gave the unexpected cyclohexene **5**, *via* a series of radical rearrangements. In further studies, (methylenecyclopropyl)propyl radicals underwent exclusive 5-*exo* cyclisation, while (methylenecyclopropyl)butyl radicals gave mixtures of products resulting from 6-*exo* and 7-*endo* cyclisation. No cyclisation products were detected in attempted cyclisations of (methylenecyclopropyl)-pentyl radicals.

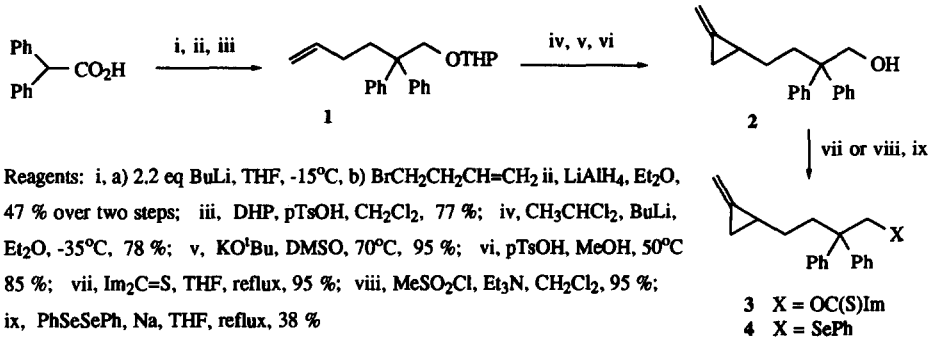
The regioselective 5-*exo* cyclisation of 5-hexen-1-yl radicals, and related systems, has proved to be an extremely versatile and convenient method for the preparation of substituted cyclopentanes, and five-membered ring heterocycles, from acyclic precursors.[1] The analogous cyclisations to give cyclohexanes, or larger ring sytems, are not always as successful, due to lower regioselectivity on cyclisation and competing reaction pathways, including hydrogen atom abstraction to form allyl radicals.[2] In an effort to develop new and efficient approaches to larger ring systems, using radical cyclisation methodology, we have been studying cyclisations of methylenecyclopropyl substituted alkyl radicals. The use of the methylenecyclopropane unit as a radical trap provides a number of intriguing possible pathways for the radical cyclisation.[3]



Initial *endo*-cyclisation might be favoured, due to less steric hindrance encountered in such a pathway, and would lead to a relatively stable cyclopropyl radical. Alternatively, *exo*-cyclisation would lead to an intermediate cyclopropylmethyl radical, which would be expected to open rapidly, to give either the ring expanded methylenecycloalkyl radical or the cycloalkylmethyl radical. In this paper we describe in detail our initial studies on the cyclisations of such systems.[4]

In our first efforts to prepare a methylenecyclopropyl radical precursor we chose to synthesise alcohol **2** (Scheme 1). Thus, diphenyl acetic acid was converted into the protected alcohol **1** which was then reacted

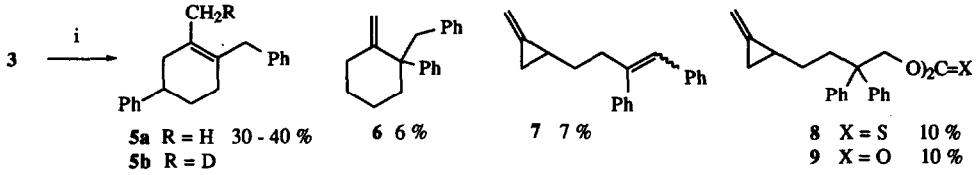
with chloromethylcarbene, followed by a base catalysed elimination, using methodology first outlined by Binger,[5] and used more recently by Motherwell.[6] Deprotection gave the neopentyl alcohol **2**, which we were unable to convert into the corresponding bromide, due to competing phenyl migration. It could, however, be converted into the thioimidazolide **3** or into the phenyl selenide **4** *via* the mesylate (although this transformation was low yielding with large amounts of mesylate being recovered).



Reagents: i, a) 2.2 eq BuLi, THF, -15°C, b) $BrCH_2CH_2CH{=}CH_2$ ii, $LiAlH_4$, Et_2O, 47 % over two steps; iii, DHP, pTsOH, CH_2Cl_2, 77 %; iv, CH_3CHCl_2, BuLi, Et_2O, -35°C, 78 %; v, KO^tBu, DMSO, 70°C, 95 %; vi, pTsOH, MeOH, 50°C 85 %; vii, $Im_2C{=}S$, THF, reflux, 95 %; viii, $MeSO_2Cl$, Et_3N, CH_2Cl_2, 95 %; ix, PhSeSePh, Na, THF, reflux, 38 %

SCHEME 1

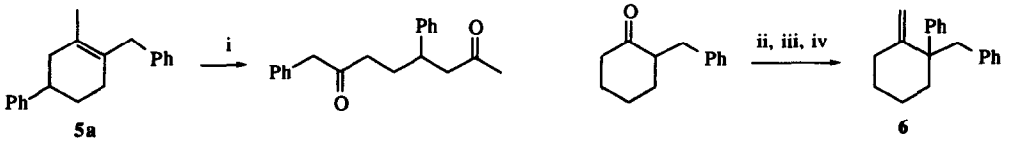
In order to encourage efficient generation of the primary carbon centered radical, from the thioimidazolide **3**, tributyltinhydride and catalytic AIBN were added *via* syringe pump, over 6 hours, to a refluxing 0.014 M solution of **3** in xylene, according to Barton's reported procedure.[7] The reaction gave a mixture of largely unexpected products which were eventually identified as the cyclohexene **5a** (40%), the methylene cyclohexane **6** (6 %), the diene **7** (7%) and the two dimers **8** (10 %) and **9** (10 %) (Scheme 2).



Reagents: i, Bu_3SnH and cat. AIBN (syringe pump addition), xylene, reflux

SCHEME 2

The identification of **5a** was aided by ozonolysis of **5a** to give the corresponding diketone, and identification of **6** was supported by independent synthesis (Scheme 3).

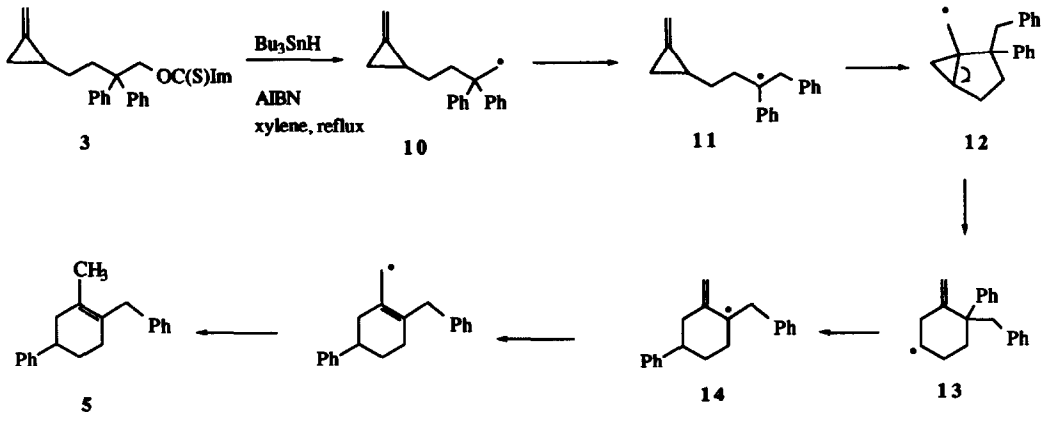


Reagents: i, a) O_3, CH_2Cl_2, b) Me_2S, 32%; ii, $(Me_3Si)_2NH$, CH_2Cl_2, Me_3SiI, 96%; iii, $Ph_2I^+ F^-$, THF, -40°C, 30%; iv, $Ph_3P^+CH_3 I^-$, BuLi, THF, 5%.

SCHEME 3

The diene **7**, generated during the cyclisation (Scheme 2) was presumably formed by a simple eliminative 1,2 phenyl migration and although the mechanism for the formation of the two dimeric compounds **8** and **9** is not entirely clear, we do not believe that it involves the intermediacy of the primary radical **10** which was obviously not formed very readily from the thioimidazolide **3**, even under such high temperature conditions. However, it seems that when this radical was formed, it was converted with reasonable efficiency to the two products **5a** and **6**. This is further supported by the cyclisation of the phenyl selenide **4** with tributyltin hydride and catalytic AIBN (syringe pump addition) in refluxing toluene which gave **5a** (~25 %) and **6** (~25 %) along with recovered starting selenide **4** (33 %).

In order to elucidate the mechanism of formation of **5a** and **6** we repeated the cyclisation of **3** using tributyltin deuteride, which gave the product **5b** in 17 % yield, and identified the final radical intermediate in the reaction. Formation of cyclohexene **5** could therefore occur *via* the sequence of steps outlined in Scheme 4.

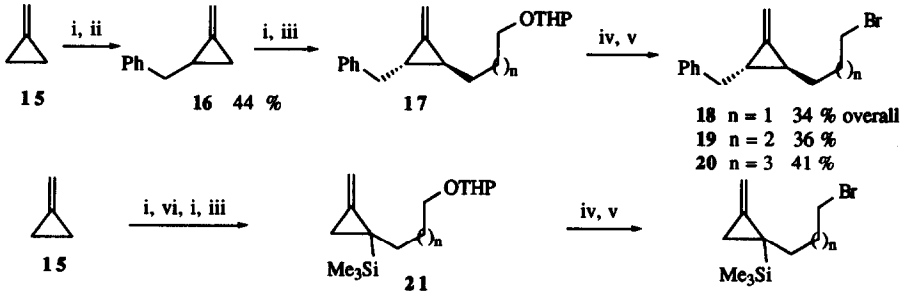


SCHEME 4

Thus, the initially formed primary radical **10** first undergoes a 1,2 phenyl migration to give the more stable benzylic radical **11**. Such migrations are well established in the literature.[8] The radical **11** then cyclises in 5-*exo* fashion, to give an intermediate cyclopropylmethyl radical **12**, which appears to open to give exclusively the methylenecyclohexyl radical **13**. The regioselectivity of the kinetically controlled opening of cyclopropylmethyl radicals has been investigated in some detail,[9] and the reaction is generally deemed to proceed under stereoelectronic control. However, there is no clear stereoelectronic preference which would lead to exclusive '*endo*' opening in our system, so it is probable that, under the high dilution conditions employed here, the opening is reversible and thus under thermodynamic control,[10] to give preferentially the six-membered ring. In any event, radical **13** is either reduced to give small quantities of the methylenecyclohexane **6**, or undergoes a transannular 1,4 phenyl migration, to give the tertiary allylic radical **14**. Such phenyl shifts across cyclohexane rings (*via* a boat transition state) are also documented in the literature,[11] and are particularly favourable when a more stable radical results, the rate constant for such a process being estimated at *ca* 3 x 10^4 sec^{-1} at 150 °C. Finally, radical **14** is reduced, at the sterically more accessible allylic position, to give the major cyclohexene product **5**.

The initial study of radical cyclisation of **3** led to an unusual rearrangement, but indicated that 5-*exo* cyclisation and subsequent opening of the cyclopropyl radical so formed, may be a general process, providing a novel route to methylenecyclohexanes. We next sought to establish this by studying a series of methylenecyclopropylalkyl derivatives, free of functionality that might allow alternative rearrangement pathways.

The radical precursors, bromides **18-20** and **22-24**, were prepared by successive deprotonation and alkylation, or silylation, of methylenecyclopropane following the work of Binger[12] and Thomas[13] (Scheme 5), followed by conversion of the protected alcohols into the desired bromides. The 1,2 disubstituted methylenecyclopropanes **18**, **19** and **20** were obtained as predominantly the *trans* isomers (> 5 : 1). For the synthesis of **22**, **23**, and **24** the sequence involving deprotonation of methylenecyclopropane, silylation, deprotonation and alkylation could be carried out in one pot.[13]

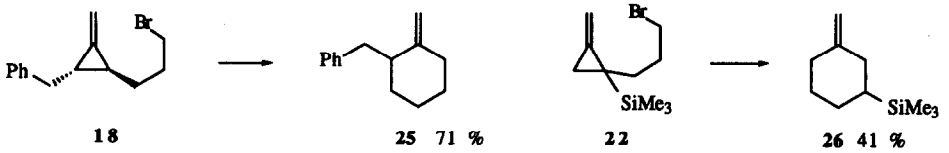


Reagents: i, BuLi, THF, -78 °C; ii, $PhCH_2Br$; iii, $BrCH_2(CH_2)_nCH_2OTHP$; iv, Amberlite IR-120, MeOH; v, CBr_4, Ph_3P; vi, Me_3SiCl

SCHEME 5

(Methylenecyclopropyl)propyl radicals

Cyclisation of bromide **18** (0.015 M in toluene) gave methylenecyclohexane **25** (Scheme 6) as the only identifiable product, in 71 % isolated yield (> 95 % yield by GC analysis) *via* initial 5-*exo* cyclisation followed by ring-opening of the cyclopropylmethyl radical, as for radical **11** (Scheme 3).



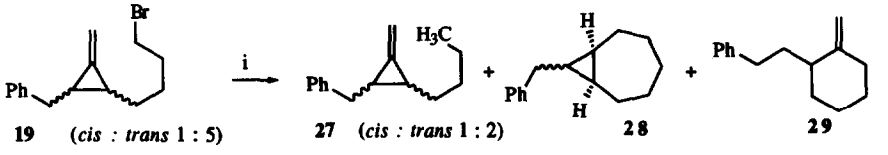
Reagents: i, Bu_3SnH, AIBN, toluene, reflux

SCHEME 6

Cyclisation of bromide **22** (0.028 M in toluene) similarly led to a methylenecyclohexane product **26** in an extremely clean reaction by GC analysis (> 85 % yield), although the volatility of the product made isolation difficult.

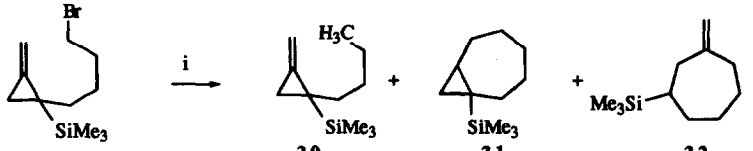
(Methylenecyclopropyl)butyl radicals

Cyclisation of **19** (toluene, syringe pump) (Scheme 7) gave a mixture of products, inseparable by column chromatography, but which were identifiable by NMR and by GC analysis with independently synthesised materials (see below), as a 1:1 mixture of **28** and **29** resulting from initial 7-*endo* or 6-*exo* cyclisation respectively, along with reduced, uncyclised **27**. Carrying out the cyclisation at lower temperature (benzene, 80 °C) merely increased the yield of **27**.



19 (*cis* : *trans* 1 : 5) **27** (*cis* : *trans* 1 : 2) **28** **29**

Ratio **27** : **28** : **29** 2.25 : 1 : 1 (GC analysis) overall isolated yield 45 %



23 **30** **31** **32**

Ratio **30** : **31** : **32** 3.3 : 10.5 : 1 (GC analysis) overall isolated yield 59 %

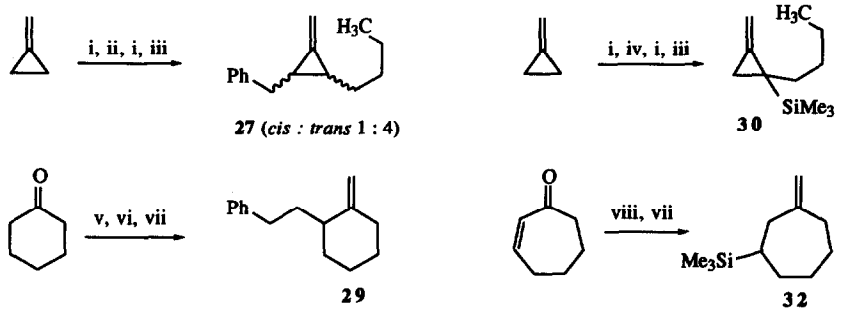
Reagents: Bu_3SnH (syringe pump addition), AIBN, toluene, reflux

SCHEME 7

Cyclisation of **23** (benzene, syringe pump), however, proceeded in predominantly 7-*endo* fashion to give the bicyclo[5.1.0]octane **31**, with small amounts of methylenecycloheptane **32** derived from initial 6-*exo* cyclisation, and reduced product **30**. The trimethylsilyl moiety on **23** may be electronically promoting *endo* attack.[14]

To allow unambiguous identification of the various products formed in the cyclisations of the (methylenecyclopropyl)butyl radicals described above, compounds **27**, **29**, **30**, and **32** were prepared by independent syntheses. Thus the methylenecyclopropane derivatives **27** and **30** were prepared by sequential alkylation of methylenecyclopropane itself. 2-(2-Phenylethyl)methylenecyclohexane **29** was prepared by alkylation of cyclohexanone[15] followed by Wittig methylenation, and 3-trimethylsilylmethylenecycloheptane **32** was prepared by addition of trimethylsilyllithium[16] to cycloheptenone, followed, again, by Wittig methylenation (Scheme 8).

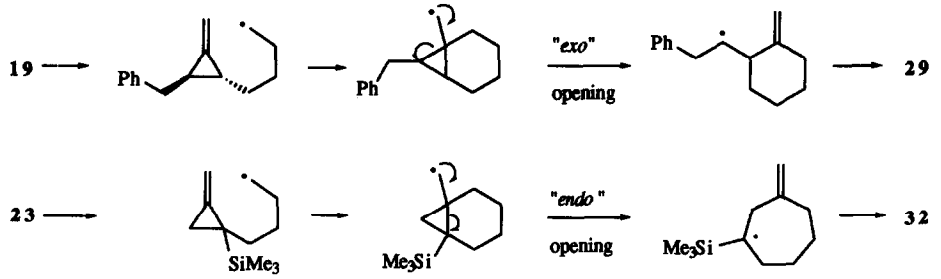
To obtain pure samples of the bicyclo[5.1.0]octane products **28** and **31**, for characterisation, the mixtures of products from the cyclisations were treated with ozone, in order to oxidise the alkene containing components **27** and **29**, or **30** and **32**. Column chromatography of the ozonolysed mixtures then gave clean samples of **28** and **31**.



Reagents: i, BuLi, THF, -78°C; ii, $PhCH_2Br$; iii, $CH_3CH_2CH_2CH_2Br$; iv, Me_3SiCl; v, cyclohexylamine, 4 Å molecular sieves; vi, a) EtMgBr, THF, b) $PhCH_2CH_2Br$; vii, Ph_3PCH_3I, BuLi, THF; viii, $Me_3SiSiMe_3$, MeLi, HMPA.

SCHEME 8

It is noteworthy that the 6-*exo* cyclisation of the radical derived from **19**, was followed by an "*exo*" ring opening of the intermediate cyclopropylmethyl radical (to give **29**), as opposed to the "*endo*" opening found in the case of (methylenecyclopropyl)propyl radicals (Schemes 3 and 6), but in both cases this led to six membered rings as the final products. These observations, and the lack of any conformational restriction on the intermediate cyclopropylmethyl radical,[9] again suggest that this opening is reversible,[10] and under thermodynamic control (Scheme 9).

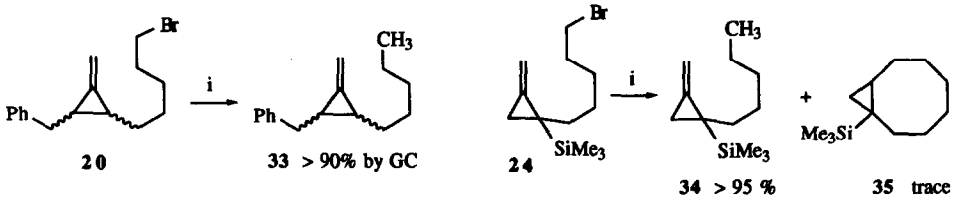


SCHEME 9

The thermodynamic preference for ring opening can be biased by placement of suitable functionality. Thus, the small amount of 6-*exo* cyclised product from **23** leads, *via* an "*endo*" opening of the intermediate cyclopropylmethyl radical, to a seven membered ring **32**, with the final radical intermediate presumably stabilised by the silyl group.[17]

(Methylenecyclopropyl)pentyl radicals

Attempted cyclisation of bromide **20** gave only the reduced methylenecyclopropane derivative **33** (Scheme 10). Similarly, cyclisation of **24** gave largely the reduced methylenecyclopropane derivative **34**, but trace amounts of bicyclo[1.6.0]nonane **35**, from an 8-*endo* cyclisation, could be detected in the ^1H NMR.



20 33 > 90% by GC 24 34 > 95 % 35 trace

Reagents: i, Bu_3SnH (syringe pump addition), AIBN, toluene, reflux

SCHEME 10

Conclusion

The high yielding cyclisations of **18** and **22** suggest that the sequence leading to methylenecyclohexanes is general for (methylenecyclopropyl)propyl radicals. The cyclisation of the homologous (methylenecyclopropyl)butyl radicals, particularly that derived from **23**, provides access to medium sized rings, although reduction, without cyclisation, is a problem, under the conditions described here.

Acknowledgements

We thank Glaxo Research and Development for supporting this work.

Experimental

Thin layer chromatography (tlc) was performed on plastic or aluminium backed sheets (Camlab) coated with silica gel (SiO_2; 0.25 mm), containing fluorescent indicator UV_{254}. Column chromatography was performed on Sorbsil C60, 40-60 mesh silica. All melting points were determined in open capillary tubes using a Gallenkamp Electrothermal Melting Point Apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR machine. Gas Chromatography analyses were carried out at Glaxo, Ware, using a 30 m x 0.32 mmid SPB-1 column with hydrogen carrier at a flow rate of 20 psi., the temperature being held at 50 °C for 10 min then increasing to 250 °C (at 15 °C/min). Quoted percentages from GC analyses refer to area ratio of peaks. NMR spectra were obtained on a JEOL FX 90 Q spectrometer, a JEOL GX 270, a Bruker 250 spectrometer and a Bruker aspect 3000 spectrometer. Microanalytical data were obtained from Glaxo, Ware. Mass spectra were obtained on a VG analytical 70-250-SE normal geometry double focusing mass spectrometer. All EI data were acquired at 70 eV, with the source temperature at 200 °C and with an accelerating voltage of 6 kV. All CI data were obtained using ammonia reagent gas, the source temperature being at 200 °C and with an emission current of 0.5 mA.

2,2-Diphenyl-5-hexen-1-ol. *n*-Butyllithium (2.4 M solution in hexanes, 92 ml, 0.22 mol)was added to a stirred solution of diphenyl acetic acid (23.50 g, 0.11 mol) in dry THF (75 ml) at - 15 °C under nitrogen, the solution was stirred for 45 min. The orange solution was cooled to - 40 °C and 4-bromo-1-butene (15.50 g, 0.11 mol) dissolved in dry THF (20 ml) was added and the temperature was allowed to reach room temperature. The reaction mixture was quenched with a saturated solution of ammonium chloride (100 ml) and the aqueous layer was extracted with diethyl ether (3 x 50 ml). The combined organic extract was dried over sodium sulphate, and the solvent removed under reduced pressure to yield 2,2-diphenyl-5-hexenoic acid as a foam (27.85 g, 95 %) containing residual solvent. Crude 2,2-diphenyl-5-hexenoic acid (26.64 g, 0.1

mol), suspended in diethyl ether (300 ml), was slowly added at room temperature to a stirred suspension of lithium aluminium hydride (11.45 g, 0.3 mol) in diethyl ether (150 ml). After completion of the addition, the mixture was stirred at reflux for 24h and was then quenched by careful addition of water (50 ml) at 0 °C. Ice-cooled 2.5 M sulphuric acid (150 ml) was added until complete dissolution of the aluminium salts. The acidic layer was extracted with diethyl ether (3 x 100 ml), the combined organic extract was washed with a saturated sodium bicarbonate solution (2 x 100 ml) and brine (2 x 100 ml), then dried over sodium sulphate and the solvent removed under reduced pressure. The crude product (24.54 g) was purified by flash column chromatography. Elution with petrol then ethyl acetate/petrol (2/98 to 20/80) yielded *2,2-diphenyl-5-hexen-1-ol* as a colourless oil (11.86 g, 47 %); R_f = 0.60 (20 % ethyl acetate/petrol); ν_{max} (CCl_4) 3453, 2929, 1496, 1445 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.20 (1 H, t, J = 6.8 Hz, OH), 1.90 (2 H, m, C(4)H_2), 2.35 (2 H, m, C(3)H_2), 4.20 (2 H, d, J = 6.8 Hz, C(1)H_2), 5.00 (1 H, d with fine coupling, J = 10 Hz, C(6)H_A), 5.05 (1 H, d with fine coupling, J = 17 Hz, C(6)H_B), 5.86 (1 H, ddt, J = 17, 10, 6.6 Hz, C(5)H), 7.25 ppm (10 H, m, Ph x 2); δ_C (67.94 MHz; $CDCl_3$) 145.55 (arom. C), 138.93 (C-5), 128.44, 128.40, 126.57 (arom. CH), 114.58 (C-6), 68.27 (C-1), 52.13 (C-2), 35.68 (C-3), 28.89 ppm (C-4).

2-(2',2'-Diphenyl-5'-hexenyloxy)tetrahydropyran (**1**). 2,2-Diphenyl-5-hexen-1-ol (11.80 g, 0.047 mol) dissolved in dichloromethane (15 ml) was added dropwise to a refluxing solution of 3,4-dihydro-2 H-pyran (5.12 g, 0.061 mol) and *p*-TsOH (0.30 g) in dichloromethane (5 ml), the condenser being fitted with a drying tube. The reaction was stirred at reflux for 12 hours, more 3,4-dihydro-2 H-pyran (1.10 g, 0.013 mol) was added and the reaction was stirred at reflux for one more day. After cooling the reaction mixture to room temperature, sodium bicarbonate (0.20 g) was added and the reaction was stirred for two hours. The mixture was filtered and concentrated under reduced pressure. The crude mixture (17.22 g) was purified by flash column chromatography. Elution with petrol then ethyl acetate/petrol (1/99 and 2/98) yielded *2-(2',2'-diphenyl-5'-hexenyloxy)tetrahydropyran* (**1**) (12.20 g, 77 %) as an oil; R_f = 0.48 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2942, 2870, 1496, 1445 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.50 (6 H, br m, C(3)H_2, C(4)H_2, C(5)H_2), 1.90 (2 H, m, C(4')H_2), 2.39 (2 H, m,C(3')H_2), 3.35 (2 H, m, C(6)H_2), 3.90 (1 H, d, J = 9.5 Hz, C(1')H_A), 4.35 (1 H, d, J = 9.5 Hz, C(1')H_B), 4.5 (1 H, br s, C(2)H), 4.8 (1 H, d with fine coupling, J = 10 Hz, C(6')H_A), 5.05 (1 H, d with fine coupling, J = 17.2 Hz, C(6')H_B), 5.84 (1 H, ddt, J= 17.2, 10, 6.5 Hz, C(5')H), 7.25 ppm (10 H, m, Ph x 2); δ_C (22.49 MHz; $CDCl_3$) 147 (arom. C), 139.29 (C-5'), 128.39, 127.91, 126.01 (arom. CH), 114.27 (C-6'), 98.77 (C-2), 72.85 (C-1'), 61.53 (C-6), 50.68 (C-2'), 36.14 (C-3'), 30.60, 29.17, 25.65, 19.04 ppm (C-3, C-4, C-5, C-4').

2-[2',2'-diphenyl-4'-(2"-chloro-2"-methylcyclopropyl)butoxy]tetrahydropyran. Following Motherwell's procedure,[6] *n*-butyllithium (2.35 M solution in hexanes, 50 ml , 0.117 mol) was added dropwise over six hours, by means of a syringe pump, to 2-(2', 2'-diphenyl -5'-hexenyloxy) tetrahydropyran (12.00 g, 0.035 mol) and 1,1-dichloroethane (4.00 g, 0.040 mol) in diethyl ether (120 ml) at - 35 °C under nitrogen. Three further portions of 1,1-dichloroethane (1.00 g, 0.010 mol) were added at hourly intervals. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was recooled to - 35 °C, the above sequence of additions of *n*-butyllithium followed by 1,1 dichloroethane was repeated, and the solution was then warmed to room temperature. This operation was repeated several times, until tlc showed no starting material (total *n*-butyllithium used in reaction = 85 ml, 0.199 mol, total CH_3CHCl_2 used in reaction = 25 g, 0.252 mol). The reaction mixture was quenched with water (100 ml), and extracted with

diethyl ether (3 x 50 ml), the combined organic extract was dried over sodium sulphate and the solvent removed under reduced pressure. The crude mixture (17 g) was purified by flash column chromatography. Elution with petrol and ethyl acetate/petrol (from 1/99 to 5/95) yielded *2-[2',2'-diphenyl-4'-(2"-chloro-2"-methylcyclopropyl)-butoxy]tetrahydropyran* (11.17 g, 78 %) as an oil and a mixture of diastereomers; R_f = 0.42 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2941, 2870, 1496, 1444, 1352, 1260, 909, 815 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.80-1.60 (11 H, br m, C(1")H, C(3")H_2, C(3)H_2, C(4)H_2, C(5)H_2, C(4')H_2), 1.65 (3 H, s, CH_3), 2.40 (2 H, m, C(3')H_2), 3.35 (2 H, m, C(6)H_2), 3.90 (1 H, 2 x d, J = 9 Hz, C(1')H_A), 4.33 (1 H, 2 x d, J = 9 Hz, C(1')H_B), 4.52 (1 H, br s, C(2)H), 7.25 ppm (10 H, m, Ph x 2); δ_C (22.65 MHz; $CDCl_3$) 146.80, 146.57 (arom. C), 128.33, 127.73, 125.89 (arom. CH), 98.65 (C-2), 72.73, 72.49 (C-1'), 61.23 (C-6), 50.56 (C-2'), 45.74 (C-2"), 36.44, 36.26 (C-3'), 30.54 (CH_2) , 29.05 (CH_3), 26.37 (C-1"), 26.07 (CH_2), 25.53 (CH_2), 21.90 (CH_2),18.92 ppm (CH_2); *m/z* 416 ($(M + NH_4)^+$, 70 %), 282 (58), 102 (100), 85 ($C_5H_9O^+$, 51).

2-[2',2'-Diphenyl-4'-(methylenecyclopropyl)butoxy]tetrahydropyran. 2-[2',2'-Diphenyl-4'-(2"-chloro-2"-methylcyclopropyl)butoxy]tetrahydropyran (4.20 g, 0.0105 mol) in dry DMSO (20 ml) was added to a stirred solution of potassium *tert*-butoxide(2.35 g, 0.021 mol) in dry DMSO (10 ml) at 70 °C over 2 hours, the mixture was stirred one hour at 70 °C and cooled to room temperature. The reaction mixture was poured into ice-cooled water (30 ml) and extracted with diethyl ether (4 x 30 ml). The combined organic extract was washed with water (3 x 30 ml), dried over sodium sulphate and the solvent removed under reduced pressure. The crude product (3.94 g) was purified by flash column chromatography. Elution with petrol then ethyl acetate/petrol (2/98 and 5/95) yielded *2-[2',2'-diphenyl-4'-(methylenecyclopropyl)butoxy]tetrahydropyran* (3.60 g, 95 %) as an oil; R_f = 0.45 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2940, 1742, 1599, 1496, 1444, 1385 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.65 (1 H, m, C(3")H_A), 1.30 (10 H, br m, C(1")H, C(3")H_B, C(3)H_2, C(4)H_2, C(5)H_2, C(4')H_2,), 2.40 (2H, m, C(3')H_2), 3.35 (2 H, m, C(6)H_2), 3.85 (1 H, dd, J = 2.5 and 9.5 Hz, C(1')H_A), 4.29 (1 H, dd, J = 2.5 and 9.5 Hz, C(1')H_B), 4.49 (1 H, br s, C(2)H_2), 5.33 (1 H, br s, =CH), 5.42 (1 H, br s, =CH), 7.30 ppm (10 H, m, Ph x 2); δ_C (22.65 MHz, $CDCl_3$) 146.92 (arom. C), 137.09 (C-2"), 128.33, 127.85, 125.95 (arom. CH), 102.65 (=CH_2), 98.71 (C-2), 72.79 (C-1'), 61.41 (C-6), 50.50 (C-2'), 36.56 (C-3'), 30.60, 28.28, 25.65, 19.04 (C-3, C-4, C-5, C-4'), 16.36 (C-1"), 9.51 ppm (C-3"); *m/z* 380 ($(M + NH_4)^+$, 80 %) , 296 (12), 102 (100), 85 ($C_5H_9O^+$, 35).

2,2-Diphenyl-4-methylenecyclopropylbutan-1-ol (2). 2-[2',2'-Diphenyl-4'-(methylenecyclopropyl)butoxy]-tetrahydropyran (4.70 g, 12.9 mmol) and *p*-TsOH (0.02 g, 0.1 mmol) were stirred in methanol (100 ml) at 50 °C for 3 hours. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product (3.96 g) was purified by flash column chromatography. Elution with petrol then diethyl ether/petrol (5/95 to 20/80) yielded *2,2-diphenyl-4-methylenecyclopropylbutan-1-ol* (2) (3.05 g, 85 %) as a viscous oil; R_f = 0.31 (20 % diethyl ether/petrol); ν_{max} (liq. film) 3425, 2938, 1599, 1496 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.70 (1 H, m, C(3')H_A), 1.30 (5 H, m, C(1')H, C(3')H_B, C(4)H_2, OH), 2.36 (2 H, t, J = 7.9 Hz, C(3)H_2), 4.18 (2 H, d, J = 6 Hz, C(1)H_2), 5.37 (1 H, br s, =CH), 5.46 (1 H, t, J = 1 Hz, =CH), 7.25 ppm (10 H, m, Ph x 2); δ_C (22.65 MHz, $CDCl_3$) 145.61 (arom. C), 136.79 (C-2'), 128.27, 126.36 (arom. CH), 102.71 (=CH_2), 68.32 (C-1), 51.87 (C-2), 36.08 (C-3), 27.97 (C-4), 16.12 (C-1'), 9.45 ppm (C-3'); *m/z* 260 ($(M - H_2O)^+$, 5 %), 247 (68), 205 (35), 169 (75), 143 (33), 129 (25), 105 (45), 91

($C_7H_7^+$, 100), 77 (23), 41 (20), 28 (7); found: C, 85.92; H, 8.06 %. $C_{20}H_{22}O$ (278.395) requires C, 86.29; H, 7.97 %.

(2,2-Diphenyl-4-methylenecyclopropyl)butyl methanesulphonate. Methanesulphonyl chloride (0.1 ml, 1.3 mmol) was added slowly to 2,2-diphenyl-4-methylenecyclopropylbutan-1-ol (**2**) (0.26 g, 0.9 mmol) and triethyl amine (0.2 ml, 1.4 mmol) in dichloromethane (4 ml) at - 15 °C under nitrogen. The reaction mixture was stirred between - 15 °C and 0 °C during one hour. The mixture was poured into a saturated sodium bicarbonate solution (10 ml), and extracted with dichloromethane (4 x 5 ml), the combined organic extract was washed with brine (2 x 10 ml), dried over sodium sulphate and the solvent removed under reduced pressure to give *(2,2-diphenyl-4-methylenecyclopropyl)butyl methanesulphonate* (0.37 g, 100 %) as yellow oil; R_f = 0.65 (dichoromethane); ν_{max} (liq. film) 2971, 1495, 1445, 1357, 1175, 962 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.70 (1 H, br m, cyclopropyl CH), 1.10-1.40 (4 H, br m, cyclopropyl CH x 2, C(4)H_2), 2.39 (2 H, t, J = 8.4 Hz, C(3)H_2), 2.45 (3 H, s, SO_2CH_3), 4.75 (2 H, s, C(1)H_2), 5.33 (1 H, s, =CH), 5.41 (1 H, s, =CH), 7.25 ppm (10 H, m, Ph x 2); δ_C (67.94 MHz; $CDCl_3$) 144.46 (arom. C), 136.44 (C-2'), 128.40, 127.98, 126.86 (arom. CH), 102.99 (=CH_2), 74.82 (C-1), 49.96 (C-2), 36.67 (SO_2CH_3), 36.06 (C-3), 27.77 (C-4), 15.83 (C-1'), 9.47 ppm (C-3').

[(2',2'-Diphenyl-4'-methylenecyclopropyl)butoxythiocarbonyl]-1-imidazole (**3**). Following the method of Barton[6] 2,2-diphenyl-4-methylenecyclopropylbutan-1-ol (**2**) (0.28 g, 1 mmol) and 1,1'-thiocarbonyl-diimidazole (0.50 g, 2.3 mmol) were stirred at reflux in THF (5 ml) under nitrogen for two hours, the reaction mixture was then cooled and the solvent was removed under reduced pressure. The crude mixture (0.85 g) was purified by flash column chromatography. Elution with ethyl acetate/petrol (10/90) yielded *[(2',2'-diphenyl-4'-methylenecyclopropyl)butoxythiocarbonyl]-1-imidazole* (**3**) (0.37 g, 95 %) as an oil; R_f = 0.35 (10 % ethyl acetate/petrol); ν_{max} (liq. film) =2970, 1764, 1601, 1496, 1327, 1104, cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.65-1.20 (5 H, m, C(1")H, C(3")H_2, C(4')H_2), 2.40 (2 H, m, C(3')H_2), 5.20 (2 H, s, C(1')H_2), 5.30 (1 H, s, =CH), 5.40 (1 H, s, =CH), 6.95 (1 H, s, C(4)H), 7.25 (11 H, m, C(5)H, Ph x 2), 8.05 ppm (1 H, s, C(2)H); δ_C (67.94 MHz, $CDCl_3$) 183.92 (OC(S)N), 144.57, 144.53 (arom. C), 136.52, 136.25 (C-2, C-2"), 130.83 (C-4 or C-5), 128.50, 127.72, 126.89 (arom. CH), 117.92 (C-4 or C-5), 103.02 (=CH_2), 78.34 (C-1'), 49.96 (C-2'), 37.09 (C-3'), 28.03 (C-4'), 15.76 (C-1"), 9.47 ppm (C-3"); *m/z* 388 ($M^{+\cdot}$, 1 %), 297 (11), 205 (38), 194 (21), 178 (48), 169 (77), 141 (23), 129 (29), 115 (36), 103 (25), 91 ($C_7H_7^+$, 100), 41 (31).

Radical cyclisation of [(2',2'-diphenyl-4'-methylenecyclopropyl)butoxythiocarbonyl]-1-imidazole (**3**). Tributyltin hydride (1.55 ml, 1.68 g, 5.76 mmol) and AIBN (0.085 g, 0.52 mmol) dissolved in dry xylene (10 ml) were added *via* syringe pump over 6 h to a refluxing solution of [(2',2'-diphenyl-4'-methylenecyclopropyl)butoxythiocarbonyl]-1-imidazole (**3**) (2.00 g, 5.15 mmol) in dry xylene (350 ml) under nitrogen. The reaction mixture was stirred at reflux for 12 h, cooled and the xylene removed under reduced pressure. The crude product (3.86 g) was purified by flash column chromatography. Elution with petrol then ethyl acetate/petrol (1/99 to 20/80) gave the following products:
Starting material (**3**) (0.26 g, 13 % recovery) and *1-methyl-2-benzyl-5-phenylcyclohexene* (**5a**) (0.04 g, 40 %) as a colourless oil; R_f = 0.62 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2923, 1601, 1494, 1452 cm^{-1};

δ_H (360 MHz; $CDCl_3$) 1.65 (1 H, m, C(4)H_A), 1.75 (3 H, s, Me), 1.85 (1 H, m, C(4)H_B), 2.00 (2 H, m, C(3)H_2), 2.20 (2 H, d with very fine splitting, J = 6.6 Hz, C(6)H_2), 2.75 (1 H, m, C(5)H), 3.33 (1 H, d, J = 14.9 Hz, C(1')H_A), 3.42 (1 H, d, J = 14.9 Hz, C(1')H_B), 7.25 ppm (10 H, m, Ph x 2); δ_C (90.56 MHz, $CDCl_3$) 147.32 (arom. C), 141.04 (arom. C), 128.76, 128.59, 128.47, 128.41 (arom. CH), 127.66 (C-1 or C-2), 126.99 (arom. CH), 126.73 (C-1 or C-2), 126.06, 125.85 (arom. CH), 40.93 (C-5), 40.38 (C-6), 39.01 (C-1'), 30.43 (C-4), 30.22 (C-3), 19.54 ppm (Me); *m/z* 262 ($M^{+\cdot}$, 93 %), 171 (42), 158 (32), 143 (74), 129 (52), 115 (33), 104 (56), 91 ($C_7H_7^+$, 100); found: *m/z* 262.1721. $C_{20}H_{22}$ requires *m/z*, 262.1722;

2-Benzyl-2-phenylmethylenecyclohexane (**6**) (0.08 g, 6 %) as a colourless liquid; R_f = 0.72 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2932, 1636, 1602, 1494, 891 cm^{-1}; δ_H (360 MHz; $CDCl_3$) 1.39 - 1.52 (3 H, m, C(4)H_A, C(5)H_A, C(3)H_A), 1.58 (1 H, m, C(4)H_B), 1.70 (1 H, m, C(5)H_B), 1.91 (1 H, m, C(6)H_A), 2.20 (1 H, m, C(6)H_B), 2.31 (1 H, m, C(3)H_B), 2.95 (1 H, d, J = 12.4 Hz, C(1')H_A), 3.01 (1 H, d, J = 12.4 Hz, C(1')H_B), 5.10 (1 H, t, J = 1.6 Hz, =CH), 5.15 (1 H, t, J = 1.1 Hz, =CH), 6.45 (1 H, m, arom. CH), 6.46 (1 H, m, arom. CH), 7.15 ppm (8 H, m, 8 x arom. CH); δ_C (67.94 MHz; $CDCl_3$) 155.82, 142.87, 137.98 (2 x arom. C, C-1), 131.17, 128.31, 127.97, 127.18, 125.94, 125.91 (arom. CH), 107.96 (=CH_2), 49.57 (C-1'), 49.09 (C-2), 35.04 (C-3), 34.73 (C-6), 29.20 (C-5), 22.36 ppm (C-4); *m/z* 262 ($M^{+\cdot}$, 32 %), 171 (100), 129 (62), 91 ($C_7H_7^+$, 50); found: *m/z* 262.1728. $C_{20}H_{22}$ requires *m/z*, 262.1722 and identical with material prepared by an alternative procedure - see Scheme 3 in text;

1,2-Diphenyl-4-methylenecyclopropyl-1-butene (**7**) (0.10 g, 7 %) as an oil; R_f = 0.69 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2971, 1598, 1494, 1444, cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.65-1.50 (5 H, 3 x m, C(1')H, C(3')H_2, C(4)H_2), 2.85 (2 H, t, J = 7.7 Hz, C(3)H_2), 5.30 (2 H, br s, =CH_2), 6.70 (1 H, s, C(1)H), 7.25 ppm (10 H, m, Ph x 2); δ_C (67.94 MHz; $CDCl_3$) 142.97, 142.68 (arom. C), 138.36 (C-2), 136.72 (C-2'), 129.15, 128.99, 128.70, 128.56, 128.40, 128.30, 127.98, 127.83, 126.76 (arom. CH, C-1), 102.91 (=CH_2), 32.29 (C-3), 30.07 (C-4), 15.78 (C-1'), 9.60 ppm (C-3'); *m/z* 278 ($(M + NH_4)^+$, 97 %), 261 ($(M + H)^+$, 100), 232 (41), 205 (28), 183 (73), 169 (67), 157 (33), 115 (27), 91 ($C_7H_7^+$, 28);

Di-(2,2-diphenyl-4-methylenecyclopropylbutyl)thiocarbonate (**8**) (0.15 g, 10 %) as a very viscous oil; R_f = 0.55 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2928, 1714, 1600, 1495, cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.60 (1 H, m, cyclopropyl CH), 1.10 (4 H, br m, 2 x cyclopropyl CH, C(4)H_2), 2.22 (2 H, t, J = 8.2 Hz, C(3)H_2), 4.72 (2 H, s, C(1)H_2), 5.20 (1 H, br s, =CH), 5.30 (1 H, br s, =CH), 7.15 ppm (10 H, m, Ph x 2); δ_C (67.94 MHz; $CDCl_3$) 194.86 (thiocarbonate C), 144.94, 144.86 (arom. C), 136.46 (C-2'), 128.01, 127.85, 126.33 (arom. CH), 102.69 (=CH_2), 76.52 (C-1), 49.64 (C-2), 36.45 (C-3), 27.87 (C-4), 15.81 (C-1'), 9.30 ppm (C-3'); *m/z* 616 ($(M + NH_4)^+$, 9 %), 296 (88), 261 ($C_{20}H_{21}^+$, 100), 183 (78), 91 ($C_7H_7^+$, 16); found: *m/z* 616.3249. $C_{41}H_{46}NO_2S$ [$(M + NH_4)^+$] requires *m/z*, 616.3249;

Di-(2',2'-diphenyl-4'-methylenecyclopropylbutyl)carbonate (**9**) (0.14 g, 10 %) as a very viscous oil; R_f = 0.45 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2928, 1748, 1600, 1495 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.61 (1 H, m, cyclopropyl CH), 0.90-1.30 (4 H, br m, 2 x cyclopropyl CH, C(4)H_2), 2.26 (2 H, t, J = 8.3 Hz, C(3)H_2), 4.55 (2 H, s, C(1)H_2), 5.30 (1 H, br s, =CH), 5.35 (1 H, br s, =CH), 7.15 ppm (10 H, m, Ph x 2); δ_C (67.94 MHz; $CDCl_3$) 154.89 (carbonate C), 145.19, 145.15 (arom. C), 136.69 (C-2'), 128.14, 128.04, 126.44 (arom. CH), 102.84 (=CH_2), 72.25 (C-1), 49.74 (C-2), 36.29 (C-3), 27.96 (C-4), 15.99 (C-1'), 9.47 ppm (C-3'); *m/z* 600 ($(M + NH_4)^+$, 21 %), 261 ($C_{20}H_{21}^+$, 89), 183 (75), 169 (76), 91

($C_7H_7^+$, 100); found: *m/z* 600.3466. $C_{41}H_{46}NO_3$ [$(M + NH_4)^+$] requires *m/z*, 600.3478.

Radical cyclisation of [(2',2'-diphenyl-4'-methylenecyclopropyl)butoxythio carbonyl]-1-imidazole (**3**) *with tributyltin deuteride* yielded (**5b**) (0.04g, 17 %); same spectra as for (**5a**) except for the methyl group signals which were replaced by : δ_H (270 MHz; $CDCl_3$) 1.75 (2 H, br s, CH_2D); δ_C (67.94 MHz; $CDCl_3$) 19.32 (t, J = 19 Hz, CH_2D).

(2,2-Diphenyl-4-methylenecyclopropyl)butyl phenyl selenide (**4**). To a solution of diphenyldiselenide (0.310 g, 0.99 mmol) in dry THF (0.8 ml) was added sodium metal pieces (0.050 g, 2.17 mmol), the mixture was stirred at reflux under nitrogen for 2.5 h.[18] After allowing to cool to room temperature, the flask was sequentially charged with HMPA (0.017 ml, 0.018 g, 0.1 mmol) and (2,2-diphenyl-4-methylenecyclopropyl)butyl methanesulphonate (0.50 g, 1.40 mmol) in dry THF (1 ml). The reaction mixture was stirred at reflux for 2 days, methanol (1 ml) was then added, the mixture was poured into water (2 ml) and extracted with diethyl ether (4 x 5 ml). The combined organic extract was washed with water, dried over sodium sulphate and concentrated under reduced pressure. The crude mixture (0.60 g) was purified by flash column chromatography. Elution with petrol, then petrol/diethyl ether (9/1) gave *(2,2-diphenyl-4-methylenecyclopropyl)butyl phenyl selenide* (**4**) (0.22 g, 38 %) as a pale yellow oil; R_f = 0.48 (5 % ethyl acetate/petrol); ν_{max} (liq. film) 2970, 1597, 1578, 1494, 1476, 1443 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.60 (1 H, m, cyclopropyl CH), 0.95 -1.34 (4 H, br m, cyclopropyl CH x 2, C(4)H_2), 2.48 (2 H, t, J = 8.3 Hz, C(3)H_2), 3.76 (2 H, s, C(1)H_2), 5.32 (1 H, br s, =CH), 5.40 (1 H, br s, =CH), 7.20 ppm (15 H, m, Ph x 3); δ_C (67.94 MHz; $CDCl_3$) 147.25 (arom. C), 136.82 (C-2'), 133.44, 129.03, 128.08, 128.00, 127.02, 126.33 (arom. CH), 102.83 (=CH_2), 49.99 (C-2), 40.74 (C-1), 38.28 (C-3), 28.04 (C-4), 15.96 (C-1'), 9.49 ppm (C-3'); *m/z* 419 ($(M + H)^+$, 4 %), 261 (25), 167 (28), 91 ($C_7H_7^+$, 100); found: *m/z* 418.1181. $C_{26}H_{26}Se$ requires *m/z*, 418.1200.

Cyclisation of (2,2-diphenyl-4-methylenecyclopropyl)butyl phenyl selenide (**4**): Tributyltin hydride (0.17 ml, 0.18 g, 0.63 mmol) and AIBN (0.012 g, 0.07 mmol) dissolved in dry toluene (10 ml) were added *via* syringe pump over 6 h to a refluxing solution of selenide (**4**) (0.21 g, 0.50 mmol) in dry toluene (20 ml) under nitrogen. The reaction mixture was stirred at reflux for 12 h, cooled and the toluene was removed under reduced pressure. The crude product (0.46 g) was purified by flash column chromatography. Elution with petrol then ethyl acetate/petrol (1/9) yielded recovered selenide (**4**) (0.07 g, 33 % recovery), *1-methyl-2-benzyl-5-phenylcyclohexene* (**5**) (0.03 g, 23 %) and *2-benzyl-2-phenylmethylenecyclohexane* (**6**) (0.03 g, 23 %) with spectral data as reported previously.

1,5-Diphenyl-2,7-octanedione. Ozone was bubbled through a solution of 1-methyl-2-benzyl-5-phenylcyclohexene (**5**) (0.14 g, 0.5 mmol) in dichloromethane (10 ml) at - 70 °C, for one hour to give a persistent blue colour. The solution was then purged for 15 mins with nitrogen and treated with dimethylsulphide (0.20 ml, 2.7 mmol) and the reaction mixture was stirred overnight, the temperature being allowed to warm to 10 °C. The excess of dimethylsulphide and the solvent were evaporated under reduced pressure. The residue was diluted in dichloromethane and washed with water. The organic layer was dried over sodium sulphate and concentrated under reduced pressure. The crude mixture (0.16 g) was purified by

flash column chromatography. Elution with ethyl acetate/petrol (5/95 and 20/80) afforded *1,5-diphenyl-2,7-octanedione* (0.05 g, 32 %) as an oil; R_f = 0.30 (20 % ethyl acetate/petrol); ν_{max} (liq. film) 2929, 1759, 1714, 1602, 1495, 1453, 1161 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.70-1.95 (2 H, m, C(4)H_2), 2.00 (3 H, s, C(8)H_3), 2.28 (2 H, br m, C(3)H_2), 2.65 (1 H, dd, J = 7.3 and 16.4 Hz, C(6)H_A), 2.73 (1 H, dd, J = 7.0 and 16.4 Hz, C(6)H_B), 3.05 (1 H, m, C(5)H), 3.55 (2 H, s, C(1)H_2), 7.25 (10 H, m, Ph x 2); δ_C (67.94 MHz; $CDCl_3$) 208.07, 207.64 (C-2, C-7), 143.46, 134.25 (arom. C), 129.52, 128.82, 128.24, 127.65, 127.12, 126.85 (arom. CH), 51.00 (C-6), 50.17 (C-1), 40.46 (C-5), 39.95 (C-3), 30.68 (C-8), 29.99 ppm (C-4); *m/z* 294 ($M^{+\cdot}$, 17 %), 203 (17), 185 (67), 167 (48), 160 (30), 145 (100), 117 (37), 105 (22), 91 ($C_7H_7^+$, 72); found: *m/z* 294.1620. $C_{20}H_{22}O_2$ requires *m/z* 294.1620.

Benzylmethylenecyclopropane (**16**). Methylenecyclopropane[22] (**15**) (25 ml, 0.39 mol) was added to a stirred solution of *n*-butyl lithium (2.3 M solution in hexanes, 109 ml, 0.25 mol) in dry THF (80 ml) under nitrogen at - 15 °C. The reaction was warmed to 10 °C over one hour and kept at this temperature for an additional hour. The temperature was then lowered to - 70 °C and benzyl bromide (44.22 g, 0.26 mol) in dry THF (20 ml) was added. The reaction mixture was stirred overnight, the temperature being allowed to warm to room temperature. The reaction was quenched with a saturated solution of ammonium chloride (100 ml) and the aqueous layer was extracted with diethyl ether (4 x 50 ml). The combined organic extract was dried over sodium sulphate and concentrated under reduced pressure. The crude product (39.04 g) was distilled under reduced pressure to yield *benzylmethylenecyclopropane* (**16**) (16.13 g, 44 %); b.p. 92 °C/12 mm of Hg; R_f = 0.50 (petrol); ν_{max} (liq. film) 2989, 1604, 1496, 1453, 1030 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.88 (1 H, m, C(3)H_A), 1.30 (1 H, m, C(1)H), 1.67 (1 H, m, C(3)H_B), 2.66 (2 H, d, J = 7 Hz, C(1')H_2), 5.40 (1 H, br s, =CH), 5.45 (1 H, m with fine splitting, =CH), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz, $CDCl_3$) 141.52 (arom. C), 136.26 (C-2), 128.50, 126.20 (arom. CH), 103.55 (=CH_2), 39.07 (C-1'), 16.64 (C-1), 9.76 ppm (C-3); Found: C, 91.58; H, 8.41. $C_{11}H_{12}$ requires C, 91.61; H, 8.39 %.

2-[3'-(3''-Benzyl-2''-methylenecyclopropyl)propan-1-ol. *n*-Butyl lithium (1.45 M solution in hexanes, 5.5 ml, 7.98 mmol) was added to a stirred solution of benzylmethylenecyclopropane (**16**) (1.16 g, 8.04 mmol) in dry THF (20 ml) at - 40 °C under nitrogen. The reaction mixture was allowed to warm to 0 °C over 30 min and kept at 0 °C for 1h. After cooling to - 60 °C, 2-(3'-bromopropoxy)tetrahydropyran (0.90 g, 4.03 mmol) was added to the deep red solution. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solution was quenched with a saturated ammonium chloride solution (3 ml), and the aqueous phase was extracted with diethyl ether (3 x 3 ml). The combined organic extract was dried over sodium sulphate and concentrated under reduced pressure. The crude mixture was stirred with Amberlite IR-120 (+) resin (0.9 g) in methanol (50 ml) under nitrogen at 50 °C for 20 h. The reaction mixture was cooled, filtered and concentrated under reduced pressure and the crude mixture was purified by flash column chromatography. Elution with ethyl acetate/petrol (10/90 to 30/70) gave *3-(3'-benzyl-2'-methylenecyclopropyl)propan-1-ol* (0.67 g, 45 %) as a pale yellow oil and as a mixture of *cis/trans* isomers (*trans* assumed to be major); R_f = 0.40 (20 % Ethyl acetate/Petrol); ν_{max} (liq. film) 3346, 2929, 1602, 1495, 1453, 1057 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.20-1.80 (7 H, br m, OH, C(1')H, C(3')H, C(2)H_2, C(3)H_2), 2.68 (2H, m, C(1'')H_2), 3.62 (2 H, 2 x t, J = 6.4 Hz, *trans/cis* C(1)H_2), 5.40 (2 H, br s, =CH_2), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 141.83, 141.56 (arom. C and C-2'), 128.43, 128.37,

126.04, 125.95 (arom CH), 103.10 (=CH_2 *trans*), 102.18 (=CH_2 *cis*), 62.51 (C-1 *cis*), 62.36 (C-1 *trans*), 38.63 (C-1"), 33.01 (CH_2 *cis*), 32.41 (C-2 *trans*), 28.81 (C-3 *trans*), 24.03 (CH_2 *cis*), 23.54, 22.44 (C-1', C-3' *trans*), 20.37, 19.72 ppm (C-1', C-3' *cis*); *m/z* 184 ($(M - H_2O)^+$, 3 %), 143 (86), 129 (75), 111 (29), 104 (68), 91 ($C_7H_7^+$, 100).

4-(3'-Benzylmethylenecyclopropyl)butan-1-ol was prepared according to the procedure described above, using benzylmethylenecyclopropane (**16**) (0.71 g, 4.92 mmol) and 2-(4'-chlorobutoxy)tetrahydropyran (0.95 g, 4.93 mmol), to give recovered benzylmethylenecyclopropane (**16**) (0.20 g, 28 % recovery) and *4-(3'-benzylmethylenecyclopropyl)butan-1-ol* (0.44 g, 42 %) as a colourless oil and as a mixture of *cis/trans* isomers (*trans* assumed to be major); R_f = 0.40 (20 % ethyl acetate/petrol); ν_{max} (liq. film) 3348, 2931, 1602, 1496, 1453, 1059 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.20-2.00 (9 H, br m, C(1')H, C(3')H, C(2)H_2, C(3)H_2, C(4)H_2, OH), 2.65 (2 H, m, C(1")H_2), 3.60 (2 H, m, C(1)H_2), 5.40 (2 H, br s, =CH_2), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 142.08, 141.72 (arom C and C-2'), 128.85, 128.46, 128.40, 126.04 (arom CH), 102.92 (=CH_2 *trans*), 102.02 (=CH_2 *cis*), 62.97 (C-1 *trans*), 62.05 (C-1 *cis*), 38.73 (C-1"), 33.52, 32.67 (CH_2 *cis*), 32.42 (CH_2 *trans*), 32.38 (CH_2 *trans*), 27.61, 26.29 (CH_2 *cis*), 25.65 (CH_2 *trans*), 23.60, 22.79 (C-1' and C-3' *trans*), 20.34, 20.02 ppm (C-1' and C-3' *cis*).

5-(3'-Benzylmethylenecyclopropyl)pentan-1-ol was prepared according to the procedure described above, using benzylmethylene cyclopropane (**16**) (0.65 g, 4.51 mmol) and 2-(5'-chloropentyloxy)tetrahydropyran (1.00 g, 4.84 mmol), to give recovered benzylmethylenecyclopropane (**16**) (0.07 g, 11 % recovery) and *5-(3'-benzyl methylenecyclopropyl)pentan-1-ol* (0.51 g, 49 %) as a yellow oil and as a mixture of *cis/trans* isomers, (*trans* assumed to be major); R_f = 0.45 (30 % ethyl acetate/cyclohexane); ν_{max} (liq. film) 3337, 2928, 1604, 1456, 1054 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.20-1.70 (10 H, br m, C(1')H, C(3')H, C(2)H_2, C(3)H_2, C(4)H_2 , C(5)H_2), 2.70 (2 H, m, C(1")H_2), 3.62 (2 H, m, C(1)H_2), 5.40 (2 H, br s, =CH_2), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 142.32, 142.02, 141.81 (arom. C and C-2' *cis/trans*), 128.50, 128.44, 126.10, 126.00 (arom. CH), 102.86 (=CH_2 *trans*), 101.97 (=CH_2 *cis*), 63.16 (C-1), 38.83 (C-1"), 33.57 (CH_2 *cis*), 32.91 (CH_2 *trans*), 32.65 (CH_2 *trans*), 29.99 (CH_2 *cis*), 29.35 (CH_2 *trans*), 27.81 (CH_2 *cis*), 25.77 (CH_2 *cis*), 25.50 (CH_2 *trans*), 23.64, 22.93 (C-1' and C-3' *trans*), 20.41, 20.11 ppm (C-1' and C-3' *cis*). Found: C, 83.14; H, 9.29. $C_{16}H_{22}O$ requires C, 83.43; H, 9.63 %.

1-Bromo-3-(3'-benzylmethylenecyclopropyl)propane (**18**). Triphenylphosphine (2.31 g , 8.8 mmol) was added portionwise over 1h to a stirred solution of 3-(3'-benzyl-2'-methylenecyclopropyl)propan-1-ol (0.89 g, 4.4 mmol) and carbon tetrabromide (1.82 g, 5.5 mmol), in dichloromethane (15 ml), under nitrogen at 0 °C. The mixture was stirred for 3 h and was concentrated under reduced pressure and purified by flash column chromatography. Elution with dichloromethane/petrol (2/98 to 10/90) afforded *1-bromo-3-(3'-benzylmethylenecyclopropyl)propane* (**18**) (0.89 g, 76 %) as an oil and as a mixture of *cis/trans* isomers in ~ 1:4 ratio (*trans* assumed to be major); R_f = 0.50 (5 % dichloromethane/petrol); ν_{max} (liq. film) 2924, 2851, 1602, 1496, 1246, cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.19 (1 H, m, C(1')H), 1.35 (1 H, m, C(3')H), 1.50 (2 H, m, C(3)H_2), 1.90 (2 H, m, C(2)H_2), 2.68 (2 H, m, C(1")H_2), 3.33 (1.6 H, t, J = 6.8 Hz, C(1)H_2 *trans*), 3.44 (0.4 H, t, J = 6.8 Hz, C(1)H_2 *cis*), 5.40 (2 H, br s, =CH_2), 7.25 ppm (5 H, m, Ph);

δ_C (67.94 MHz; $CDCl_3$) 141.58, 141.37, 141.19, 140.91 (arom. C, C-2' *cis/trans*), 128.75, 128.44, 128.37, 126.14, 126.03 (arom. CH), 103.41 (=CH_2 *trans*), 102.50 (=CH_2 *cis*), 38.61 (C-1"), 33.57, 33.17 (CH_2 *cis*), 33.44, 32.59, 30.95 (C-1, C-2, C-3 *trans*), 26.39 (CH_2 *cis*), 23.64, 21.68 (C-1', C-3' *trans*), 20.37, 19.03 ppm (C-1', C-3' *cis*); *m/z* 284, 282 ($(M + NH_4)^+$, 30, 33 %), 266 (30), 264 (28), 185 (17), 157 (26), 143 (100), 130 (30), 104 (57), 91 ($C_7H_7^+$, 60). Found: *m/z* 282.0839. $C_{14}H_{21}BrN$ ($M + NH_4$) requires *m/z* 282.0857.

1-Bromo-4-(3'-benzylmethylenecyclopropyl)butane (**19**) was prepared according to the procedure described above, using triphenylphosphine (0.46 g, 1.76 mmol), 4-(3'-benzylmethylenecyclopropyl)butan-1-ol (0.19 g, 0.88 mmol) and carbon tetrabromide (0.36 g, 1.09 mmol), to give *1-bromo-4-(3'-benzylmethylenecyclopropyl)butane* (**19**) (0.25 g, 100 %) as an oil and as a mixture of *cis/trans* isomers in ~ 1:4 ratio (*trans* assumed to be major); R_f = 0.50 (5 % dichloromethane/petrol); ν_{max} (liq. film) 2932, 1602, 1496, 1453 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.20-1.95 (8 H, br m, C(1')H, C(3')H, C(4)H_2, C(3)H_2, C(2)H_2), 2.70 (2 H, m, C(1")H_2), 3.37 (1.4 H, t, J = 6.8 Hz, C(1)H_2 *trans*), 3.44 (0.6 H, t, J = 6.8 Hz, C(1)H_2 *cis*), 5.35 (2 H, br s, =CH_2), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 141.81, 141.59, 141.52 (arom. C and C-2' *cis/trans*), 128.83, 128.49, 128.43, 126.11, 126.01 (arom. CH), 103.12 (=CH_2 *trans*), 102.22 (=CH_2 *cis*), 38.70 (C-1"), 33.96, 32.44, 31.73, 28.10 (C-1, C-2, C-3, C-4 *trans*), 33.53, 32.68, 28.66, 26.96 (C-1, C-2, C-3, C-4 *cis*), 23.65, 22.56 (C-1', C-3' *trans*), 20.37, 19.81 ppm (C-1', C-3' *cis*); *m/z* 280 and 278 ($M^{+\cdot}$, 8 %), 157 (31), 144 (26), 143 (100), 130 (36), 129 (85), 128 (35), 115 (27), 104 (79), 91.($C_7H_7^+$, 95). Found: *m/z* 278.0664. $C_{15}H_{19}Br$ requires *m/z* 278.0670.

1-Bromo-5-(3'-benzylmethylenecyclopropyl)pentane (**20**) was prepared according to the procedure described above, using triphenylphosphine (1.05 g, 4.00 mmol), 4-(3'-benzylmethylenecyclopropyl)pentan-1-ol (0.46 g, 1.99 mmol) and carbon tetrabromide (0.82 g, 2.47 mmol), to give bromide (**20**) (0.50 g, 85 %) as a colourless oil and as a mixture of *cis/trans* isomers (*trans* assumed to be major); R_f = 0.63 (10 % dichloromethane/petrol); ν_{max} (liq. film) 2927, 1496, 888, 699 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.19-1.90 (10 H, br m, C(1')H, C(3')H, C(2)H_2, C(3)H_2, C(4)H_2, C(5)H_2), 2.75 (2 H, m, C(1")H_2), 3.4 (2 H, 2 overlapping t, J = 6.8 Hz, C(1)H_2 *cis/trans*), 5.35 (2 H, br s, =CH_2), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 142.17, 141.88, 141.75 (arom. C and C-2' *cis/trans*), 128.50, 128.46, 126.11, 126.03 (arom. CH), 102.96 (=CH_2 *trans*), 102.07 (=CH_2 *cis*), 38.80 (C-1"), 34.12 (CH_2 *trans*), 33.57 (CH_2 *cis*), 32.94 (CH_2 *trans*), 32.46 (CH_2 *trans*), 29.34 (CH_2 *cis*), 28.72 (CH_2 *trans*), 28.20 (CH_2 *cis*), 27.93 CH_2 *trans*), 27.67 (CH_2 *cis*), 27.09 (CH_2 *cis*), 23.70, 22.82 (C-1', C-3' *trans*), 20.41, 20.02 ppm (C-1', C-3' *cis*); *m/z* 292 and 294 ($M^{+\cdot}$,1 %), 129 (64), 104 (55), 91.($C_7H_7^+$, 100). Found: *m/z* 292.0813. $C_{16}H_{21}Br$ requires *m/z* 292.0827.

3-(1'-Trimethylsilylmethylenecyclopropyl)propan-1-ol. *n*-Butyllithium (2.17 M solution in hexanes, 12 ml, 26.0 mmol) was added to a stirred solution of methylenecyclopropane (**15**) (2.5 ml, 2 g, 37 mmol) in dry THF (50 ml) at - 40 °C under nitrogen. The reaction mixture was warmed to 0 °C over 30 min and stirred at 0 °C for 40 min, then cooled to - 70 °C. Chlorotrimethyl silane (3.4 ml, 2.91 g, 26.8 mmol) was added and the reaction mixture was warmed to 0 °C over 30 min and stirred at 0 °C for 30 min, then cooled again to - 70 °C. *n*-butyllithium (2.17 M solution in hexanes, 12 ml, 26.0 mmol) was added and the warming procedure

repeated before addition at - 70 °C of 2-(3'-bromopropoxy)tetrahydropyran (5.80 g, 26.0 mmol) in dry THF (3 ml). The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The solution was quenched with saturated ammonium chloride solution (50 ml), and the aqueous phase was extracted with diethyl ether (4 x 25 ml). The combined organic extracts were washed with brine (3 x 50 ml), dried over sodium sulphate and concentrated under reduced pressure. The crude mixture was stirred with Amberlite IR-120 (+) resin (7 g) in methanol (350 ml) under nitrogen at 50 °C for 6 h, then at room temperature overnight. The reaction mixture was filtered, concentrated under reduced pressure and purified by flash column chromatography. Elution with ethyl acetate/petrol (0/100 to 10/90) gave *3-(1'-trimethylsilyl-methylenecyclopropyl)propan-1-ol* (1.90 g, 40 % overall) as a colourless oil; $R_f = 0.40$ (20 % ethyl acetate/cyclohexane); ν_{max} ($CHBr_3$) 3609, 2951, 1728, 1248 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, $Si(CH_3)_3$), 0.81 (1 H, dt, J = 7.5 and 1.9 Hz, C(3')H_A), 1.05 (1 H, dt, J = 7.5 and 1.7 Hz, C(3')H_B), 1.60 (5 H, m, OH, C(2)H_2, C(3)H_2), 3.60 (2 H, t, J = 6 Hz, C(1)H_2), 5.21 (1 H, br s, =CH), 5.26 ppm (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 139.95 (C-2'), 100.47 (=CH_2), 63.21 (C-1), 31.74, 31.50 (C-2, C-3), 13.63 (C-1'), 12.61 (C-3'), - 2.44 ppm ($Si(CH_3)_3$); found: C, 64.86; H, 11.17. $C_{10}H_{20}OSi$ requires C, 65.15; H, 10.94 %.

4-(1'-Trimethylsilylmethylenecyclopropyl)butan-1-ol was prepared according to the procedure described above, to give 4-(1'-trimethylsilylmethylenecyclopropyl)butan-1-ol (57% overall) as a colourless oil; R_f = 0.40 (20 % ethyl acetate/cyclohexane); ν_{max} ($CHBr_3$) 3607, 2935, 1728, 1248 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, Si(CH3)3), 0.81 (1 H, ddd, J = 1.7, 2.3 and 7.5 Hz, C(3')H_A), 1.04 (1 H, ddd, J = 1.5, 2.3 and 7.5 Hz, C(3')H_B), 1.45 (7 H, m, OH, C(2)H_2, C(3)H_2, C(4)H_2), 3.62 (2 H, t, J = 6.4 Hz, C(1)H_2), 5.19 (1 H, dt, J = 1.2 and 2.3 Hz, =CH_X), 5.25 ppm (1 H, br q, J = 1.5 Hz, =$CH_{X'}$); δ_C (67.94 MHz; $CDCl_3$) 140.08 (C-2'), 100.22 (=CH_2), 62.87 (C-1), 35.56, 33.18, 24.56 (C-2, C-3, C-4), 14.06 (C-1'), 12.57 (C-3'), - 2.44 ppm ($Si(CH_3)_3$); found: C, 66.54; H, 10.84. $C_{11}H_{22}OSi$ requires C, 66.60; H, 11.18 %.

5-(1'-Trimethylsilylmethylenecyclopropyl)pentan-1-ol was prepared according to the procedure described above, to give 5-(1'-trimethylsilylmethylenecyclopropyl)pentan-1-ol (43% overall) as a colourless oil; R_f = 0.42 (20 % ethyl acetate/cyclohexane); ν_{max} (liq. film) 3342, 2928, 1728, 1249 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.00 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, dt, J = 7.5 and 1.9 Hz, C(3')H_A), 1.05 (1 H, dt, J = 7.5 and 1.7 Hz, C(3')H_B), 1.40 (9 H, br m, OH, C(2)H_2, C(3)H_2, C(4)H_2, C(5)H_2), 3.65 (2 H, m, C(1)H_2), 5.20 (1 H, m with very fine splitting, =CH), 5.26 ppm (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 140.25 (C-2'), 100.11 (=CH_2), 63.06 (C-1), 35.79, 32.80, 28.25, 26.23 (C-2, C-3, C-4, C-5), 14.09 (C-1'), 12.62 (C-3'), - 2.39 ppm ($Si(CH_3)_3$); found: C, 68.03; H, 11.20. $C_{12}H_{24}OSi$ requires C, 67.86; H, 11.39 %.

1-Bromo-3-(1'-trimethylsilylmethylenecyclopropyl)propane (**22**) was prepared according to the bromination procedure described above, to give *1-bromo-3-(1'-trimethylsilylmethylenecyclopropyl)propane* (**22**) (87 %) as a colourless oil; $R_f = 0.66$ (petrol); ν_{max} ($CHBr_3$) 2922, 1728, 1249, 877 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, $Si(CH_3)_3$), 0.83 (1 H, dt, J = 7.5 and 1.9 Hz, C(3')H_A), 1.08 (1 H, ddd, J = 1.5, 2.1 and 7.5 Hz, C(3')H_B), 1.59 (2 H, m, C(3)H_2), 1.88 (2 H, m, C(2)H_2), 3.35 (1 H, dt, J = 11.4 and 6.8 Hz, C(1)H_A), 3.39 (1 H, dt, J = 11.4 and 6.8 Hz, C(1)H_B), 5.22 (1 H, dt , J = 1.0 and 2.1 Hz, =CH), 5.29

ppm (1 H, br s, =CH); δ_C (62.90 MHz; $CDCl_3$) 139.27 (C-2'), 100.57 (=CH_2), 34.05, 33.83, 31.61 (C-1, C-2, C-3), 13.16 (C-1'), 12.52 (C-3'), - 2.64 ppm ($Si(CH_3)_3$); found: C, 48.73; H, 7.79; Br, 31.27. $C_{10}H_{19}BrSi$ requires C, 48.58; H, 7.75; Br, 32.32 %.

1-Bromo-4-(1'-trimethylsilylmethylenecyclopropyl)butane (**23**) was prepared according to the procedure described above, to give bromide (**23**) (90 %) as a colourless oil; R_f = 0.65 (petrol); ν_{max} ($CHBr_3$) 2956, 1456, 1250, 877 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, ddd, J = 1.7, 2.3 and 7.5 Hz, C(3')H_A), 1.06 (1 H, ddd, J = 1.4, 2.3 and 7.5 Hz, C(3')H_B), 1.50 (4 H, m, C(3)H_2, C(4)H_2), 1.82 (2 H, quintet, J = 7.0 Hz, C(2)H_2), 3.40 (2 H, t, J = 7.0 Hz, C(1)H_2), 5.21 (1 H, dt, J = 1.2 and 2.3 Hz, =CH), 5.27 ppm (1 H, br q, J = 1.4 Hz, =CH); δ_C (67.94 MHz; $CDCl_3$) 139.93 (C-2'), 100.44 (=CH_2), 34.97, 33.92, 33.18, 27.05 (C-1, C-2, C-3, C-4), 13.95 (C-1'), 12.74 (C-3'), - 2.37 ppm ($Si(CH_3)_3$); *m/z* 280 and 278 ($(M + NH_4)^+$, 10 %), 263 and 261 ($(M + H)^+$, 45), 109 (97), 90 (100). Found: C, 50.91; H, 8.45; Br, 30.45. $C_{11}H_{21}BrSi$ requires C, 50.57; H, 8.10; Br, 30.58 %.

1-Bromo-5-(1'-trimethylsilylmethylenecyclopropyl)pentane (**24**) was prepared according to the procedure described above, to give bromide (**24**) (83 %) as a colourless oil; R_f = 0.66 (petrol); ν_{max} ($CHBr_3$) 2931, 1248, 839 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, ddd, J = 1.7, 2.1 and 7.5 Hz, C(3')H_A), 1.04 (1 H, ddd, J = 1.5, 2.1 and 7.5 Hz, C(3')H_B), 1.40 (6 H, m, C(3)H_2, C(4)H_2, C(5)H_2, 1.82 (2 H, quintet, J = 6.8 Hz, C(2)H_2), 3.39 (2 H, t, J = 6.8 Hz, C(1)H_2), 5.20 (1 H, br s, =CH), 5.25 ppm (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 140.08 (C-2'), 100.25 (=CH_2), 35.63, 34.06, 32.88, 28.69, 27.63 (C-1, C-2, C-3, C-4, C-5), 14.05 (C-1'), 12.65 (C-3'), - 2.38 ppm ($Si(CH_3)_3$); *m/z* 294 and 292 ($(M + NH_4)^+$, 7 %), 277 and 275 ($(M + H)^+$, 47), 123 (60), 90 (100). Found: C, 52.64; H, 8.35; Br, 28.62. $C_{12}H_{23}BrSi$ requires C, 52.35; H, 8.42; Br, 29.02 %.

Radical cyclisation of 1-bromo-3-(3'-benzylmethylenecyclopropyl) propane (**18**). Tributyltin hydride (0.90 ml, 0.97 g, 3.34 mmol) and AIBN (0.050 g, 0.30 mmol) were added to a refluxing solution of bromide (**18**) (0.80 g, 3.02 mmol) in dry toluene (200 ml) under nitrogen. After 12 h at reflux, the reaction mixture was cooled, concentrated under reduced pressure and purified by flash column chromatography. Elution with petrol afforded *2-benzylmethylenecyclohexane* (**25**) (0.40 g, 71 %) as a colourless oil; R_f = 0.60 (petrol); ν_{max} (liq. film) 2929, 1644, 1602, 1495 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.10-1.70 (6 H, m, C(4)H_2, C(5)H_2, 2 x CH), 2.06 (1 H, m, CH), 2.3 (2 H, m, 2 x CH), 2.52 (1 H, dd, J = 9.3 and 13.3 Hz, C(1')H_A), 2.97 (1 H, dd, J = 5.4 and 13.3 Hz, C(1')H_B), 4.60 (1 H, s, =CH), 4.68 (1 H, s, =CH), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 152.99 (C-1), 141.45 (arom. C), 129.24, 128.29, 125.84 (arom. CH), 105.74 (=CH_2), 44.80 (C-2), 39.13 (C-1'), 35.70, 33.11, 28.95, 24.96 (C-3, C-4, C-5, C-6); *m/z* 186 ($M^{+\cdot}$, 65 %), 95 (100). Found: C, 89.95; H, 9.87. $C_{14}H_{18}$ requires C, 90.26; H, 9.74 %.

Radical cyclisation of 1-bromo-3-(1'-trimethylsilylmethylenecyclopropyl)propane (**22**) . 1-Bromo-3-(1'-trimethylsilyl methylenecyclopropyl)propane (**22**) (0.68 g, 2.75 mmol), tributyltin hydride (0.82 ml, 0.89 g, 3.05 mmol) and AIBN (0.075 g, 0.45 mmol) in dry, degassed toluene (100 ml) under argon were heated in a pre-heated oil bath at 90 °C. After stirring at 90 °C overnight, the reaction mixture was cooled and most of the

toluene was removed under reduced pressure. Diethyl ether (30 ml) was added to the crude mixture, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 0.7 ml, 0.71 g, 4.68 mmol) was added and the solution stirred for 10 min. A solution of iodine (0.2 M in diethyl ether) was added dropwise until the iodine colour persisted.[23] The reaction was passed through a short silica gel column eluting with diethyl ether. After concentration under reduced pressure, the crude product (0.65 g) was purified by flash column chromatography. Elution with pentane gave *3-(trimethylsilyl)methylene cyclohexane* (**26**) (0.19 g, 41 %) as a colourless oil; $R_f = 0.70$ (pentane); ν_{max} (liq. film) 2954, 1648, 1443, 1247 cm^{-1} (which is consistent with the reported data, lit.[24]); δ_H (360 MHz; $CDCl_3$) 0.00 (9 H, br s, $Si(CH_3)_3$), 0.70 (1 H, tt, J = 3 and 13 Hz, $C(3)H_{ax}$), 1.22 (1 H, dq, J = 3 and 13 Hz, $C(4)H_{ax}$), 1.35 (1 H, tq, J = 4 and 13 Hz, $C(5)H_{ax}$), 1.75 (1H, dddd, J = 1.6, 3, 4.6 and 13 Hz, $C(4)H_{eq}$), 1.85 (1 H, ddt, J = 1.4, 3 and 13 Hz, $C(2)H_{ax}$), 1.91 (1 H, m, $C(5)H_{eq}$), 2.00 (1 H, dddt, J = 1.6, 3, 4.5 and 13 Hz, $C(6)H_{ax}$), 2.26 (1 H, ddt, J = 1.8, 3 and 13 Hz, $C(2)H_{eq}$), 2.33 (1 H, ddt, J = 1.8, 4 and 13 Hz, $C(6)H_{eq}$), 4.58 ppm (2 H, m with very fine splitting, $=CH_2$); δ_C (67.94 MHz; $CDCl_3$) 151.16 (C-1), 105.85 ($=CH_2$), 36.04, 35.65, 30.26, 27.18 (C-2, C-3, C-4, C-5, C-6), 28.45 (C-3), - 3.37 ppm ($Si(CH_3)_3$); found: C, 71.13; H, 12.05. $C_{10}H_{20}Si$ requires C,71.34; H, 11.97 %.

3-Benzyl-1-butylmethylenecyclopropane (**27**) was prepared according to the procedure described above for the alkylation of benzyl methylenecyclopropane, using iodobutane as alkylating agent, to give *3-benzyl-1-butylmethylene cyclopropane* (**27**) as a colourless oil and as a mixture of *cis/ trans* isomers in a ratio of 1:4 by GC analysis (assuming *trans* major); $R_f = 0.50$ (*n*-hexane); ν_{max} (liq. film) 2926, 1601, 1496, 1450, 886 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.90-1.55 (11 H, m, C(1)H, C(3)H, $(CH_2)_3CH_3$), 2.68 (2 H, m, $C(1")H_2$), 5.38 (2 H, m, $=CH_2$), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 142.51, 141.83 (arom. C, C-2), 129.26, 128.49, 128.43, 128.22, 126.05, 125.97 (arom. CH), 102.74 ($=CH_2$ *trans*), 101.85 ($=CH_2$ *cis*), 38.84 (C-1"), 33.60 (CH_2 *cis*), 32.46 (CH_2 *trans*), 32.42 (CH_2 *cis*), 31.79 (CH_2 *trans*), 27.58 (CH_2 *cis*), 23.57, 23.08 (C-1, C-3 *trans*), 22.73 (CH_2 *cis*), 22.52 (CH_2 *trans*), 20.44, 20.21 (C-1, C-3 *cis*), 14.28, 14.24 ppm (CH_3 *cis /trans*); *m/z* 200 ($M^{+\cdot}$, 7 %), 143 (58), 129 (86), 104 (61), 91 ($C_7H_7^+$, 100).

2-(2'-Phenylethyl)cyclohexanone was prepared according to the method of Stork and Dowd.[15] *N*-cyclohexylidene cyclohexylamine[25] (1.50 g) was added to ethylmagnesium bromide (1 M solution in THF, 15 ml, 15 mmol) in dry THF (35 ml) and stirred at reflux under nitrogen for one hour. After cooling to room temperature, (2-bromoethyl)benzene (2.1 ml, 2.85 g, 15.38 mmol) was added. The reaction mixture was stirred at reflux overnight, 2 N HCl (20 ml, 40 mmol) was added and the mixture stirred at reflux for a further 90 min. The reaction was cooled and the aqueous phase was extracted with diethyl ether (3 x 25 ml). The combined organic extract was washed with brine (3 x 40 ml), dried over sodium sulphate and concentrated under reduced pressure. The crude mixture (3.52 g) was purified by flash column chromatography. Elution with cyclohexane, then ethyl acetate/cyclohexane (5/95 and 10/90) gave *2-(2'-phenylethyl)cyclohexanone* (1.09 g, ~ 66 %) as an oil; $R_f = 0.50$ (10 % ethyl acetate/cyclohexane); ν_{max} (liq. film) 2930, 2850, 1710, 700 (m) cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.40-2.45 (11 H, br m, $C(2)H$, $C(3)H_2$, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(1')H_2$), 2.63 (2 H, t, J = 8 Hz, $C(2')H_2$), 7.25 ppm (5 H, m, Ph); found: C, 83.14; H, 8.93. $C_{14}H_{18}O$ requires: C, 83.12; H, 8.97 %.

2-(2'-Phenylethyl)methylenecyclohexane (**29**) was prepared from 2-(2'-phenylethyl)cyclohexanone (0.92 g, 4.55 mmol) using the same procedure described for the preparation of 2-benzyl-2-phenylmethylene-cyclohexane (**6**), to give *2-(2'-phenylethyl)methylenecyclohexane* (**29**) (0.79 g, 87 %) as a colourless oil; R_f = 0.53 (cyclohexane); ν_{max} (liq. film) 2929, 1650, 1490, 740 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.25-2.30 (11 H, br m, C(2)H, C(3)H_2, C(4)H_2, C(5)H_2, C(6)H_2, C(1')H_2), 2.63 (2 H, t, J = 8 Hz, C(2')H_2),.4.62 (1 H, br s, =CH), 4.70 (1 H, br s, =CH), 7.25 ppm (5 H, m, Ph); δ_C (62.90 MHz; $CDCl_3$) 152.59 (C-1), 142.96 (arom. C), 128.38, 128.26, 125.58 (arom. CH), 105.85 (=CH_2), 42.77 (C-2), 34.67, 34.08, 33.91, 33.77, 28.83, 24.14 ppm (C-1', C-2',.C-3, C-4, C-5, C-6); found: C, 90.32; H, 10.34. $C_{15}H_{20}$ requires C, 89.94; H, 10.06 %.

Radical cyclisation of 1-bromo-4-(3'-benzylmethylenecyclopropyl)butane (**19**). Tributyltin hydride (0.48 ml, 0.52 g, 1.77 mmol) and AIBN (0.027 g, 0.16 mmol) dissolved in dry toluene (10 ml) were added *via* syringe pump over 6 h to a refluxing solution of 1-bromo-4-(3'-benzylmethylenecyclopropyl)butane (**19**) (0.45 g, 1.61 mmol) in dry toluene (50 ml) under nitrogen. The reaction mixture was stirred at reflux for a further 5 h, cooled, and the toluene removed under reduced pressure. The crude product was purified by flash column chromatography. Elution with petrol, then dichloromethane/petrol (5/95) yielded recovered bromide (**19**) (0.19 g, 42 % recovery) and a mixture of four different compounds (0.11 g, 44 %) which were identified by GC analysis as: *3-benzyl-1-butylmethylenecyclopropane* (**27**) (*trans* (16 %) and *cis* (8 %)), *2-(2'-phenylethyl) methylenecyclohexane* (**29**) (11 %), and *8-benzylbicyclo[5.1.0]octane* (**28**) (11 %), the last of which was identified from the following ozonolysis experiment.

8-Benzylbicyclo[5.1.0]octane (**28**). A solution of the mixture isolated from the above reaction (0.057 g, 0.28 mmol) was treated with ozone following the procedure described for the preparation of 1,5-diphenyl-2,7-octanedione, to give *8-benzylbicyclo[5.1.0]octane* (**28**) (0.01 g) as a colourless oil and as a single isomer; R_f = 0.68 (petrol); δ_H (360 MHz; $CDCl_3$) 0.72-0.78 (3 H, m, C(1)H, C(7)H, C(8)H), 0.85-1.05 (2 H, m, C(2)H_A, C(6)$_A$), 1.15 (1 H, m, C(4)H_A), 1.28-1.40 (2 H, C(3)H_A, C(5)H_A), 1.67-1.77 (2 H, C(3)H_B, C(5)H_B), 1.82 (1 H, m, C(4)H_B), 2.15-2.22 (2 H, m, C(2)H_B, C(6)$_B$), 2.59 (2 H, d, J = 6.1 Hz, C(1')H_2), 7.30 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 142.71 (arom. C), 128.39, 128.34, 125.79 (arom. CH), 39.84 (C-1'), 32.94 (C-4), 30.90 (C-2, C-6), 30.09 (C-3, C-5), 29.63 (C-8), 24.44 ppm (C-1, C-7); *m/z* 218 ($(M + NH_4)^+$, 45 %), 200 ($M^{+\cdot}$, 100), 104 (68), 91 ($C_7H_7^+$, 32), 52 (55). Found: *m/z* 200.1562. $C_{15}H_{20}$ requires *m/z* 200.1565.

1-(1'-Trimethylsilylmethylenecyclopropyl)butane (**30**) was prepared according to the procedure described above for the silylation and alkylation of methylenecyclopropane, using iodobutane as alkylating agent, to give*1-(1'-trimethylsilylmethylenecyclopropyl) butane* (**30**) (64 %) as a colourless oil; R_f = 0.88 (petrol); ν_{max} (liq. film) 2957, 1249, 872 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, Si$(CH_3)_3$), 0.80 (1 H, dt, J = 7.3 and 1.9 Hz, C(3')H_A), 0.88 (3 H, t, J = 6.6 Hz, C(4)H_3), 1.04 (1 H, dt, J = 7.3 and 1.7 Hz, C(3')H_B), 1.30 (6 H, m, C(1)H_2, C(2)H_2, C(3)H_2), 5.19 (1 H, m with very fine splitting, =CH), 5.24 ppm (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 140.41 (C-2'), 100.09 (=CH_2), 35.79, 30.88, 23.35 (C-1, C-2, C-3), 14.28 (C-4, C-1'), 12.72 (C-3'), - 2.31 ppm (Si$(CH_3)_3$); *m/z* 200 ($(M + NH_4)^+$, 14 %), 183 ($(M + H)^+$, 76), 90 (100).

(3-Trimethylsilyl)cycloheptanone. A solution of hexadimethyldisilane (0.5 ml, 0.36 g, 2.5 mmol) in dry HMPA (2 ml) was cooled to 0 °C under nitrogen. Methyllithium (1.4 M in ether, 1.5 ml, 2.1 mmol) was added and the resulting deep red solution was stirred for 15 min to complete the preparation of trimethylsilyllithium.[16] Dry THF (10 ml) was added and the solution was immediately cooled to - 78 °C. A solution of 2-cycloheptenone (0.17 g, 1.5 mmol) in dry THF (1 ml) was added dropwise. After stirring for an additional 10 min, methanol (1 ml) was added and the reaction mixture was allowed to warm slowly to 10 °C. The reaction mixture was poured into pentane (50 ml), washed with water (2 x 25 ml), dried over sodium sulphate and concentrated under reduced pressure. The crude mixture (0.20 g) was purified by flash column chromatography. Elution with ether/petrol (10/90 and 20/80) gave *(3-trimethylsilyl)cycloheptanone* (**32**) (0.07 g, 25 %) as a colourless oil; R_f = 0.38 (10 % ether/petrol); ν_{max} (liq. film) 2953, 1700, 1445, 1249 cm^{-1}; δ_H (270 MHz; $CDCl_3$) - 0.01 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, m, CH), 1.20 (2 H, m, CH x 2), 1.50 (1 H, m, CH), 1.92 (3 H, m, CH x 3), 2.41 (4 H, m, 4 x CH); δ_C (67.94 MHz; $CDCl_3$) 215.70 (C-1), 44.60, 43.55 (C-2, C-7), 32.02, 31.23, 24.53 (C-4, C-5, C-6), 23.81 (C-3), - 3.43 ppm ($Si(CH_3)_3$).

(3-Trimethylsilyl)methylenecycloheptane (**32**) was prepared from (3-trimethylsilyl)cycloheptanone (0.06 g, 0.32 mmol) using the same procedure described for the preparation of 2-benzyl-2-phenylmethylenecyclohexane (**6**), to give *(3-trimethylsilyl)methylenecycloheptane* (**32**) (0.02 g, 33 %) as a colourless oil; R_f = 0.88 (petrol); ν_{max} (liq. film) 2954, 1638, 1248, 856 cm^{-1}; δ_H (270 MHz; $CDCl_3$) - 0.01 (9 H, s, $Si(CH_3)_3$), 0.66 (1 H, ddt, J = 2.5, 3.6 and 11 5 Hz, C(3)H), 1.05-2.45 (10 H, br m, $C(2)H_2$, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(7)H_2$), 4.67 ppm (2 H, s, $=CH_2$); δ_C (67.94 MHz; $CDCl_3$) 153.77 (C-1), 109.97 ($=CH_2$), 37.16, 36.15 (C-2, C-7), 31.51, 29.96, 28.82 (C-4, C-5, C-6), 27.41 (C-3), - 3.20 ppm ($Si(CH_3)_3$); *m/z* 200 ($(M + NH_4)^+$, 4 %), 183 ($(M + H)^+$, 70), 90 (100).

Radical cyclisation of 1-bromo-4-(1'-trimethysilylmethylenecyclopropyl)butane (**23**). Tributyltin hydride (0.29 ml, 0.31 g, 1.05 mmol) and AIBN (0.016 g, 0.10 mmol) in dry benzene (3 ml) were added *via* syringe pump over 7 h to a refluxing solution of 1-bromo-4-(1'-trimethysilylmethylenecyclopropyl)butane (**23**) (0.25 g, 0.96 mmol) in dry, degassed benzene (30 ml, 32 mM) under nitrogen. The reaction mixture was stirred at reflux for 24 h, cooled and the benzene removed by distillation. DBU/iodine work-up,[23] as previously described, gave the crude product which was purified by flash column chromatography. Elution with pentane yielded a mixture of products (0.10 g, 59 % overall) assigned by GC analysis as: *1-(1'-trimethylsilylmethylenecyclo propyl)butane* (**30**) (13 %), *(3-trimethylsilyl)methylenecycloheptane* (**32**) (4 %) and*bicyclo[5.1.0]oct-1-yl trimethylsilane* (**31**) (42 %) which was identified from the following ozonolysis experiment.

Bicyclo[5.1.0]oct-1-yl trimethylsilane (**31**). A solution of the mixture isolated from the above reaction (0.18 g, 0.98 mmol) was treated with ozone following the procedure described for the preparation of 1,5-diphenyl-2,7-octanedione, to give*bicyclo[5.1.0]oct-1-yl trimethylsilane* (**31**) (0.03 g) as a colourless oil; R_f = 0.89 (pentane); ν_{max} (liq. film) 2954, 1247, 850 cm^{-1}; δ_H (360 MHz; $CDCl_3$) -0.05 (9 H, s, $Si(CH_3)_3$), 0.19 (1 H, t, J = 4.3 Hz, $C(8)H_A$), 0.63 (1 H, dd, J = 3.8 and 7.7 Hz, $C(8)H_B$), 0.85 (1 H, m, C(7)H), 1.03-1.21 (3 H, m, $C(2)H_A$, $C(6)H_A$, $C(4)H_A$), 1.27-1.46 (2 H, m, $C(5)H_A$, $C(3)H_A$), 1.60-1.83 (3 H, m, $C(3)H_B$, $C(5)H_B$, $C(4)H_B$), 2.11-2.23 ppm (2 H, m, $C(2)H_B$, $C(6)H_B$); δ_C (67.94 MHz; $CDCl_3$) 33.44 (C-2), 33.18 (C-4), 31.77 (C-6), 29.86 (C-5), 29.44 (C-3), 21.22 (C-7), 20.85 (C-8), 11.40 (C-1), -

2.16 ppm ($Si(CH_3)_3$); *m/z* 200 ($(M + NH_4)^+$, 8 %), 183 ($(M + H)^+$, 37), 90 (100); found *m/z* 183.1567. $C_{11}H_{23}Si$ (M + H) requires *m/z* 183.1569.

Attempted radical cyclisation of 1-bromo-5-(3'-benzylmethylenecyclopropyl)pentane (**20**). Tributyltin hydride (0.15 ml, 0.16 g, 0.56 mmol) and AIBN (0.008 g, 0.05 mmol) in dry benzene (2 ml) were added *via* syringe pump over 7 h to a refluxing solution of 1-bromo-5-(3'-benzylmethylenecyclopropyl)pentane (**20**) (0.15 g, 0.51 mmol) in dry and degassed benzene (20 ml, 26 mM) under nitrogen. The reaction mixture was stirred at reflux for 7 h, cooled and concentrated under reduced pressure. The crude product (0.44 g) was purified by flash column chromatography. Elution with petrol yielded, *3-benzyl-1-pentylmethylene-cyclopropane* (**33**), as a mixture of *cis/trans* isomers in a 1:4 ratio from GC analysis (assuming *trans* major) (0.05 g, 45 %); R_f = 0.72 (petrol); ν_{max} (liq. film) 2957, 1496, 1454 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.92 (3 H, m, C(5')H_3), 1.35 (10 H, m, C(1)H, C(3)H, $(CH_2)_4$), 2.75 (2 H, m, C(1")H_2), 5.42 (2 H, m with fine splitting, $=CH_2$), 7.25 ppm (5 H, m, Ph); δ_C (67.94 MHz; $CDCl_3$) 142.53, 142.22, 141.83 (arom. C, C-2 *cis/trans*), 128.49, 128.43, 126.07, 125.97 (arom. CH), 102.73 ($=CH_2$ *trans*), 101.85 ($=CH_2$ *cis*), 38.86 (C-1"), 33.60 (CH_2 *cis*), 32.74 (CH_2 *trans*), 31.90 (CH_2 *cis*), 31.67 (CH_2 *trans*), 29.90 (CH_2 *cis*), 29.28 (CH_2 *trans*), 27.86 (CH_2 *cis*), 23.58, 23.12 (C-1, C-3 *trans*), 22.82 (CH_2 *trans*), 20.44, 20.26 (C-1, C-3 *cis*), 14.28 (CH_3 *cis*), 14.25 (CH_3 *trans*); *m/z* 232 ($(M + NH_4)^+$, 16 %), 215 ($(M + H)^+$, 99), 143 (62), 123 (52), 104 (73), 91 ($C_7H_7^+$, 100). All properties were identical to those of a sample prepared by alkylation of methylenecyclopropane with 1-bromopentane, using the alkylation procedure used for the preparation of 3-(3'-benzyl-2'-methylenecyclopropyl)propan-1-ol.

Attempted radical cyclisation of 1-bromo-5-(1'-trimethysilylmethylenecyclopropyl)pentane (**24**). Tributyltin hydride (0.18 ml, 0.19 g, 0.68 mmol) and AIBN (0.010 g, 0.06 mmol) in dry benzene (2.5 ml) were added *via* syringe pump over 7 h to a refluxing solution of 1-bromo-5-(1'-trimethysilylmethylenecyclopropyl)-pentane (**24**) (0.17 g, 0.62 mmol) in dry and degassed benzene (20 ml, 31 mM) under nitrogen. The reaction mixture was stirred at reflux for 24 h, cooled and concentrated under reduced pressure. The crude product (0.49 g) was purified by column chromatography. Elution with petrol yielded a colourless oil (0.12 g, 100 %) containing mainly the reduced product *1-(1'-trimethylsilylmethylenecyclopropyl) pentane* (**34**) with traces of *bicyclo[6.1.0]non-1-yltrimethylsilane* (**35**) based upon the reported ^1H NMR data[26] of (**35**); R_f = 0.88 (petrol); representative data for (**35**): δ_H (270 MHz; $CDCl_3$) 0.51 (1 H, dd, J = 4 and 8 Hz), 2.10 ppm (2 H, m).

A sample of 1-(1'-trimethylsilylmethylenecyclopropyl)pentane (**34**) was alternatively prepared according to the procedure described above for the silylation and alkylation of methylenecyclopropane, using iodopentane as alkylating agent, to give *1-(1'-trimethylsilylmethylenecyclopropyl)pentane* (**34**) (0.70 g, 64 %) as a colourless oil ; R_f = 0.88 (petrol); ν_{max} (liq. film) 2957, 1248 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.00 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, dt, J = 7.3 and 1.9 Hz, C(3')H_A), 0.89 (3 H, t, J = 7.4 Hz, C(5)H_3), 1.04 (1 H, dt, J = 7.3 and 2.1 Hz, C(3')H_B), 1.30 (8 H, br m, C(1)H_2, C(2)H_2, C(3)H_2, C(4)H_2), 5.19 (1 H, br s, =CH), 5.24 ppm (1 H, br s, =CH); δ_C (90.56 MHz; $CDCl_3$) 140.44 (C-2'), 99.96 ($=CH_2$), 35.93, 32.41, 28.18, 22.73 (C-1, C-2, C-3, C-4), 14.28 (C-1'), 14.22 (C-5), 12.65 (C-3'), - 2.38 ppm ($Si(CH_3)_3$); found: C, 73.12; H, 12.41. $C_{12}H_{24}Si$ requires C, 73.38; H, 12.32 %.

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