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Malonate Radical Cyclisations of Methylenecyclopropane Derivatives

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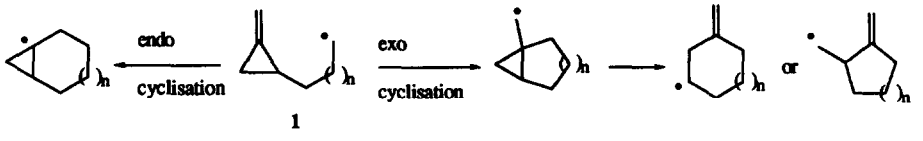
Abstract - Cyclisations of various methylenecyclopropyl substituted malonate radicals have been studied. Radicals derived from malonates **4** and **9** underwent exclusive 5-*exo* cyclisation onto the methylenecyclopropane alkene, followed by opening of the resulting cyclopropylmethyl radical, to give methylenecyclohexane products. Radicals derived from malonates **5** and **10** largely gave bicyclo[1.5.0]octane products, in good yields, as a result of 7-*endo* cyclisation. Cyclisation of the radical derived from malonate **11** gave a bicyclo[1.5.0]nonane derivative in 31% yield, as a result of an 8-*endo* cyclisation.

In the preceding paper[1] we have described studies on the radical cyclisation of methylenecyclopropane derivatives in which we found that (methylenecyclopropyl)propyl radicals **1** (n = 1) cleanly gave methylenecyclohexanes resulting from an initial 5-*exo* cyclisation, and subsequent opening of the intermediate cycloproplymethyl radical (Scheme 1). Cyclisation of (methylenecyclopropyl)butyl radicals **1** (n = 2), however, gave a mixture of products resulting from initial -*exo* and -*endo* cyclisation and from straightforward reduction. Cyclisation of (methylenecyclopropyl)pentyl radicals **1** (n = 3) simply gave the reduced, uncyclised product.



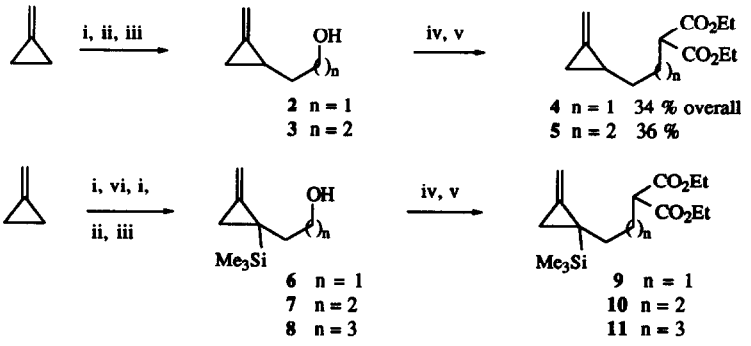
1

SCHEME 1

We therefore decided to look at the cyclisation of the corresponding methylenecyclopropyl derived malonate radicals using the atom transfer methodology which has been considerably developed by Curran in recent years.[2] This should allow relatively slow cyclisations to proceed without the reduction observed for methylenecyclopropylbutyl radicals and methylenecyclopropylpentyl radicals when using tributyltin hydride methodology. In this paper we describe the results of these studies.

Using the methodology already described,[1,3] methylenecyclopropane was converted into alcohols **2**, **3** and **6** - **8**, by deprotonation, alkylation and subequent removal of the THP protecting group. The alcohols

were each converted into the corresponding bromide or mesylate and then reacted with diethylmalonate anion to give the desired diethyl (methylenecyclopropyl)alkylmalonate derivatives **4**, **5** and **9-11** (Scheme 2).



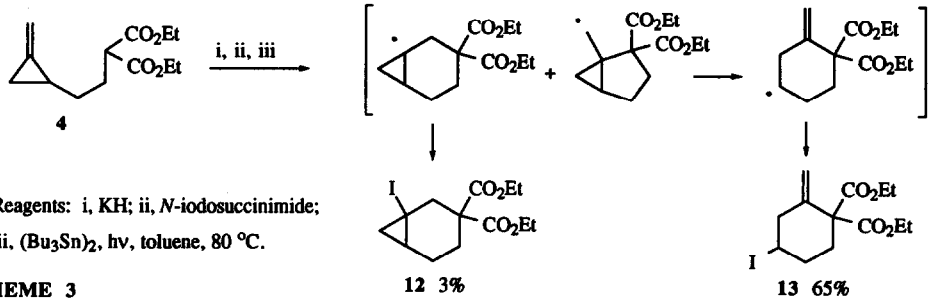
Reagents: i, BuLi, THF, -78 °C; ii, $BrCH_2(CH_2)_2OTHP$; iii, Amberlite IR-120, MeOH; iv, either CBr_4, Ph_3P, or $MeSO_2Cl$, Et_3N; v, $NaCH(CO_2Et)_2$; vi, Me_3SiCl

SCHEME 2

Following Curran's procedure the malonates were treated with potassium hydride followed by *N*-iodosuccinimide.[2c] After passing the reaction mixture through a short silica gel column, the crude iodomalonates so obtained were cyclised without further purification, using 10-20 mol % hexabutylditin in toluene, and irradiating with a 150W lamp.

5-Exo vs. *6*-endo *cyclisations.*

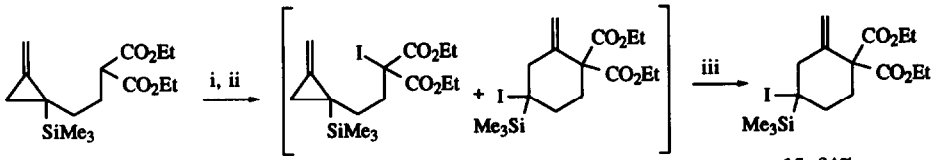
Malonate **4** was converted into the corresponding iodomalonate and cyclised, as described above, to give the anticipated product **13** (65% yield) resulting from initial 5-*exo* cyclisation and opening of the cycloproplymethyl radical (Scheme 3). A small quantity (3%) of **12**, the product of *endo* cyclisation, was also isolated. Subsequent inspection of the ^1H and ^{13}C NMR of the crude iodomalonate used in the cyclisation indicated that a small amount of cyclised product **13** had already formed prior to irradiation.



Reagents: i, KH; ii, *N*-iodosuccinimide; iii, $(Bu_3Sn)_2$, hv, toluene, 80 °C.

SCHEME 3

Treatment of malonate **9** with potassium hydride, followed by *N*-iodosuccinimide, also gave a mixture of the desired iodomalonate **14** and cyclised product **15** in a 2:1 ratio (Scheme 4). Treatment of the mixture, as above, with hexabutylditin gave the methylenecyclohexane **15** in an overall isolated yield of 84%. With this substrate, no product from an initial 6-*endo* cyclisation was detected.



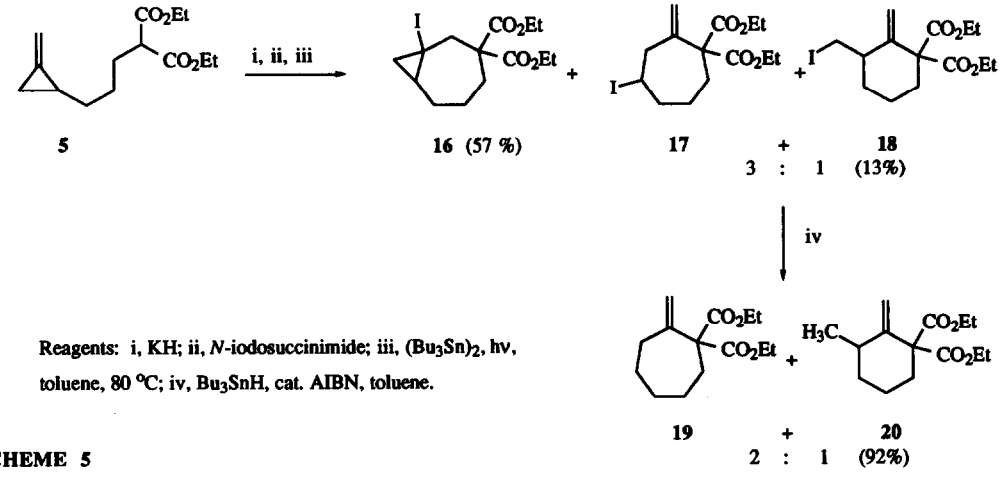
9 **14** **15** **15** 84%

Reagents: i, KH; ii, *N*-iodosuccinimide; iii, $(Bu_3Sn)_2$, hv, toluene, 80 °C.

SCHEME 4

6-Exo vs. *7*-endo *cyclisations.*

The malonates **5** and **10** were converted into the corresponding iodomalonates without any concommitant cyclisation, and were then irradiated in the presence of hexabutylditin, as above. Using this procedure, malonate **5** gave predominantly **16** (57% isolated yield), the product of a 7-*endo* cyclisation, along with an inseparable mixture of two compounds which were identified, on the basis of ^1H and ^{13}C NMR, as a 3:1 mixture of **17** and **18** (13% isolated yield), resulting from initial 6-*exo* cyclisation (Scheme 5). Treatment of this mixture with tributyltin hydride/AIBN in refluxing toluene gave a 2:1 mixture of the corresponding reduced compounds **19** and **20**, in 92% yield.[4]



5 **16** (57 %) **17** + **18**

3 : 1 (13%)

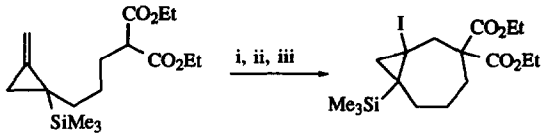
19 + **20**

2 : 1 (92%)

Reagents: i, KH; ii, *N*-iodosuccinimide; iii, $(Bu_3Sn)_2$, hv, toluene, 80 °C; iv, Bu_3SnH, cat. AIBN, toluene.

SCHEME 5

Cyclisation of the iodomalonate derived from **10**, however, gave the bicyclo[5.1.0]nonane **21**, the product of a 7-*endo* cyclisation as the only isolated product in 86% yield (Scheme 6).



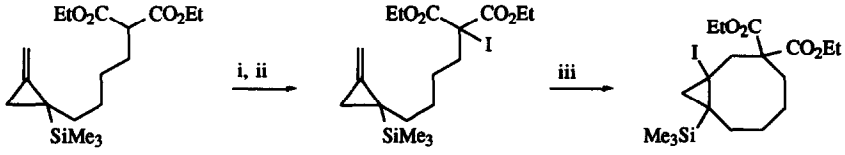
10 **21** (86 %)

Reagents: i, KH; ii, *N*-iodosuccinimide; iii, $(Bu_3Sn)_2$, hv, toluene, 80 °C.

SCHEME 6

7-Exo vs. 8-endo *cyclisations.*

Malonate **11** was converted into the corresponding iodomalonate **22**, free of any cyclised products, and irradiation in the usual way, in the presence of hexabutylditin gave **23**, the product of an 8-*endo* cyclisation, in 31% isolated yield (Scheme 7).



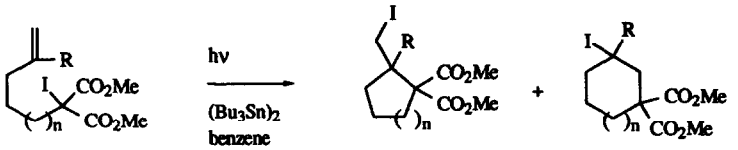
11 **22** **23** (31 %)

Reagents: i, KH; ii, *N*-iodosuccinimide; iii, $(Bu_3Sn)_2$, hv, toluene, 80 °C.

SCHEME 7

Discussion.

Malonate radicals derived from **4** and **9** gave almost exclusively methylenecyclohexane products as a result of initial 5-*exo* cyclisation. This result was expected in the light of earlier work with methylenecyclopropylalkyl radicals, but contrasts with the reported exclusive 6-*endo* cyclisation of closely related iodomalonate **24** (Scheme 8).[2c] Curran found that the 6-*endo* cyclisation of **24** was under kinetic control, and that kinetic products could generally be obtained from atom transfer cyclisations, if irradiation was terminated soon after consumption of starting iodomalonate, and before relatively slow equilibration of the iodide products began. For the malonate radicals derived from **4** and **9** we stopped the irradiation before consumption of the starting iodomalonates was complete, but in the resulting product mixtures we could not find any products resulting from 6-*endo* cyclisation, indicating that in this case the kinetic preference appears to be for 5-*exo* cyclisation, rather than 6-*endo* cyclisation.[5] The formation of cyclised products during the preparation of the iodomalonates from **4** and **9**, prior to irradiation, is precedented by observations by Curran[2c] and Beckwith,[6] when sodium hydride/iodine, or lithium diisopropylamide/iodine, were used as reagents to prepare the iodomalonates. In Curran's work,[2c] however, the use of potassium hydride and *N*-iodosuccinimide, as reagents, avoided the formation of cyclic products. The failure of these reagents, when used with malonates **4** and **9**, to completely suppress cyclisation may be attributed to the particluar reactivity of the methylenecyclopropane system.



	exo cyclisation	*endo* cyclisation
24 n = 1, R = Me	-	>84%
25 n = 2, R = Me	-	>71%
26 n = 3, R = H	unidentified products and starting material	

SCHEME 8

Malonate radicals derived from **5** and **10** gave largely bicyclo[1.5.0]octane products *via* a 7-*endo* cyclisation, and starting with malonate **10** this was a particularly clean and high yielding reaction. The latter result again demonstrates, in line with earlier observations,[1] that the silyl group appears to promote *endo* cyclisation over *exo* cyclisation in these systems. Compared with cyclisation of the corresponding primary (methylenecyclopropyl)butyl radicals, described in the preceding paper,[1] the atom transfer methodology has also greatly improved the yield and regioselectivity of these cyclisations. The complete reversal of regioselectivity for the cyclisations of **5** and **10** (7-*endo*) compared to clean 5-*exo* for **4** and **9** is also noteworthy, although the 7-*endo* selectivity for the former pair is now in line with Curran's observation[2c] that iodomalonate **25** also gave exclusive 7-*endo* cyclisation (Scheme 8).

The atom transfer methodology has also allowed the preparation of a bicylco[1.6.0]nonane *via* the 8-*endo* cyclisation of iodomalonate **22**, albeit in low yield. Reports of 8-*endo* radical cyclisations are rare in the literature,[7] and it is noteworthy that Curran found that attempted cyclisation of **26** gave no identifiable cyclised products (Scheme 8).[2c] Presumably the relatively successful cyclisation of iodomalonate **22** can be attributed to the higher reactivity of the strained methylenecyclopropane, compared to the relatively unstrained alkene in **26**, and to the reduced conformational flexibility of the methylenecyclopropane derivatives.

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 or Merk, Kieselgel 60 mesh 230 ASTM, for dry flash chromatography. 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. 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.
The preparation of alcohols **7** and **8** and the corresponding bromides, has already been described.[1]

2-(Methylenecyclopropyl)ethan-1-ol (**2**). *n*-Butyllithium (2.4 M solution in hexanes, 63 ml, 0.151 mol) was added to a stirred solution of methylenecyclopropane[8] (10 ml, 8.0 g, 0.148 mol) in dry THF (200 ml) under nitrogen at - 30 °C. The reaction was warmed to 0 °C over 30 min and kept at this temperature for an additional 30 min, the temperature was then lowered to - 60 °C and ethylene oxide (20 ml, 17.6 g, 0.400 mol) added. The reaction mixture was stirred overnight at room temperature, and then quenched with a saturated solution of ammonium chloride (150 ml) and the aqueous layer was extracted with diethyl ether (3 x 150 ml). The combined organic extract was washed with water, dried over sodium sulphate and concentrated under reduced pressure. The crude product (14.75 g) was purified by flash column chromatography. Elution with diethyl ether/petrol (20/80 and 40/60) gave *2-(methylenecyclopropyl)ethan-1-ol* (**2**) (6.16 g, 42 %) as a colourless oil; R_f = 0.48 (60 % diethyl ether/petrol); spectroscopic data in accordance with literature.[9]

2-[(3'-Methylenecyclopropyl)propoxy]tetrahydropyran was prepared, using the same alkylation procedure described above, using *n*-BuLi (2.5 M solution in hexanes, 18 ml, 45.0 mmol), methylenecyclopropane (**36**) (6 ml, 4.8 g, 89 mmol) and 2-(3'-bromopropoxy)-tetrahydropyran (10.04 g, 45.0 mmol) to give *2-[(3'-methylenecyclopropyl) propoxy]tetrahydropyran* (4.88 g, 55 %) as a colourless oil; R_f = 0.53 (5 % ethyl acetate/ 95 % petrol); ν_{max} (liq. film) 2940 (s), 2869 (s), 1442 (m), 1352 (m), 1200 (m), 1122 (m), 1035 (m), 884 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.75 (1 H, m, cyclopropyl CH), 1.20 (1 H,m, cyclopropyl CH), 1.25-1.95 (11 H, br m, C(3)H_2, C(4)H_2, C(5)H_2, C(2')H_2, C(3')H_2, cyclopropyl CH), 3.38-3.84 (4 H, 2 x m, C(1')H_2, C(6)H_2), 4.58 (1 H, t, J = 3.5 Hz, C(2)H), 5.33 (1 H, m, =CH), 5.40 (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 139.98 (C-2"), 102.67 (=CH_2), 98.94 (C-2), 67.31, 62.43 (C-1', C-6), 30.90, 29.87, 29.66, 25.63, 19.78 (C-3, C-4, C-5, C-2', C-3'), 15.58 (C-1"), 9.53 (C-3").

3-Methylenecyclopropylpropan-1-ol (**3**). 2-[(3'-Methylenecyclopropyl) propoxy]tetrahydropyran (1.50 g, 4.22 mmol) was stirred with Amberlite IR-120 (+) resin (1.56 g) in methanol (75 ml) under nitrogen at 60 °C for 2 days. The reaction mixture was cooled, filtered and concentrated under reduced pressure. The crude mixture (0.99 g) was purified by flash column chromatography. Elution with diethyl ether/petrol (25/75 and 50/50) gave *3-methylenecyclopropylpropan-1-ol* (**3**) (0.71 g,82%) as a colourless oil; R_f = 0.45 (30 % ethyl acetate/petrol); ν_{max} (liq. film) 3328 (br m), 2927 (s), 2855 (m), 1053 (m), 885 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.72 (1 H, m, cyclopropyl CH), 1.16-1.72 (6 H, br m, cyclopropyl CH x 2, C(2)H_2, C(3)H_2), 2.50 (1 H, br s, OH), 3.62 (2 H, t, J = 6.6 Hz, C(1)H_2), 5.31 (1 H, m with very fine splitting, =CH), 5.37 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 139.88 (C-2"), 102.70 (=CH_2), 62.40 (C-1), 32.44, 29.35 (C-2, C-3), 15.42 (C-1'), 9.46 (C-3').

2-(1'-Trimethylsilylmethylenecyclopropyl)ethan-1-ol (**6**). *n*-Butyllithium (2.5 M solution in hexanes, 20 ml, 50 mmol) was added to a stirred solution of methylenecyclopropane (4 ml, 3.2 g, 59 mmol) in dry THF (70 ml) under nitrogen at - 30 °C. The reaction was warmed to 0 °C over 40 min and kept at this temperature

for an additional 40 min. The temperature was lowered to -55 °C and chlorotrimethylsilane (6.4 ml, 5.48 g, 50 mmol) was added and the warming procedure repeated. The temperature was lowered again to - 55 °C, *n*-butyllithium (2.5 M solution in hexanes, 20 ml, 50 mmol) added and the warming procedure repeated. The reaction was cooled to -60 °C and ethylene oxide (5 ml, 4.4 g, 100 mmol) was added. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with saturated ammonium chloride solution (100 ml) and the aqueous layer was extracted with diethyl ether (3 x 100 ml). The combined organic extract was washed with brine, dried over sodium sulphate and concentrated under reduced pressure. The crude product (9.62 g) was purified by flash dry column chromatography. Elution with petrol, then ethyl acetate/petrol (5/95) gave *2-(1'-trimethylsilylmethylenecyclopropyl)ethan-1-ol* (**6**) (6.10 g, 72 %) as a colourless oil; R_f = 0.40 (20 % ethyl acetate/petrol); ν_{max} (liq. film) 3340 (br s), 2956 (s), 1733 (m), 1408 (m), 1250 (s), 1040 (s), 838 (s) cm^{-1}; δ_H (270 MHz; $CDCl_3$) - 0.02 (9 H, s, $Si(CH_3)_3$), 0.91 (1 H, ddd, J = 1.7, 2.1 and 7.7 Hz, C(3')H_A), 1.08 (1 H, ddd, J = 1.4, 2.1 and 7.7 Hz, C(3')H_B), 1.75 (2 H, m, C(2)H_2), 3.62 (2 H, m, C(1)H_2), 5.23 (1 H, dt, J = 1.0 and 2.1 Hz, =CH), 5.30 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz, $CDCl_3$) 139.49 (C-2'), 101.06 (=CH_2), 62.02 (C-1), 38.02 (C-2), 12.65 (C-3'), 11.43 (C-1'), - 2.54 ($Si(CH_3)_3$); *m/z* 188 ($(M + NH_4)^+$, 4 %), 171 ($(M + H)^+$, 20), 155 (30), 81 (78), 73 (100).

1-Bromo-3-methylenecyclopropylpropane. Triphenylphosphine (3.22 g, 12.3 mmol) was added portionwise over 1 h to a stirred solution of 3-methylenecyclopropylpropan-1-ol (**3**) (0.69 g, 6.15 mmol) and carbon tetrabromide (2.55 g, 7.69 mmol) in dichloromethane (20 ml) under nitrogen at 0 °C. The mixture was stirred overnight at room temperature, then concentrated under reduced pressure, and the crude mixture (6.46 g) purified by flash column chromatography. Elution with petrol afforded *1-bromo-3-methylenecyclopropylpropane* (0.90 g, 83 %) as a colourless oil; R_f = 0.53 (petrol); ν_{max} (liq. film) 2972 (s), 2933 (s), 2853 (m), 1439 (m), 1248 (m), 888 (s), 657 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.78 (1 H, m, C(3')H_A), 1.25 (1 H, tt, J = 2 and 8.6 Hz, C(1')H), 1.34-1.62 (3 H, m, C(3')H_B, C(3)H_2), 2.00 (2 H, quintet, J = 6.9 Hz, C(2)H_2), 3.44 (1 H, dt, J = 9.9 and 6.9 Hz, C(1)H_A), 3.49 (1 H, dt, J = 9.9 and 6.9 Hz, C(1)H_B), 5.37 (1 H, br s, =CH), 5.41 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 136.26 (C-2"), 103.15 (=CH_2), 33.63, 32.77, 31.62 (C-1, C-2, C-3), 14.84 (C-1'), 9.56 (C-3').

2-(Methylenecyclopropyl)ethyl methanesulphonate. Methanesulphonyl chloride (1.67 g, 14.58 mmol) was added over 5 min to 2-(methylenecyclopropyl)ethan-1-ol (**2**) (1.19 g, 12.13 mmol) and triethyl amine (2.7 ml, 1.96 g, 19.40 mmol) in dry dichloromethane (55 ml) at - 10 °C under nitrogen. The reaction mixture was stirred between - 10 °C and 0 °C for two hours, and washed with ice-water (25 ml), 2 M HCl (25 ml), saturated sodium bicarbonate solution (25 ml) and brine (25 ml), then dried over sodium sulphate and concentrated under reduced pressure to give *2-(methylenecyclopropyl)ethyl methanesulphonate* (**2**) (1.99 g, 93 %) as yellow oil; R_f = 0.50 (35 % ethyl acetate/petrol); δ_H (270 MHz; $CDCl_3$) 0.82 (1 H, m, cyclopropyl CH), 1.28-1.46 (2 H, m, cyclopropyl CH), 1.78 (2 H, m, C(2)H_2), 2.98 (3 H, s, SO_2CH_3), 4.26 (2 H, t, J = 6.5 Hz, C(1)H_2), 5.37 (1 H, m with very fine splitting, =CH), 5.43 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 134.64 (C-2'), 103.91 (=CH_2), 69.86 (C-1), 37.32 (SO_2CH_3), 32.55 (C-2), 11.83 (C-1'), 9.34 (C-3').

2-(1'-Trimethylsilylmethylenecyclopropyl)ethyl methanesulphonate was prepared according to the above procedure. 2-(1'-Trimethylsilylmethylenecyclopropyl)ethan-1-ol (**6**) (2.55 g, 15.0 mmol), triethylamine (3.3 ml, 2.40 g, 23.7 mmol) and methanesulphonyl chloride (2.06 g, 18.0 mmol) gave 2-(1'-trimethylsilylmethylenecyclopropyl)ethyl methanesulphonate (3.72 g, 100 %) as a yellow oil; R_f = 0.44 (20 % ethyl acetate/petrol); δ_H (270 MHz; $CDCl_3$) 0.01 (9 H, s, $Si(CH_3)_3$), 0.93 (1 H, ddd, J = 1.7, 2.1 and 7.7 Hz, C(3')H_A), 1.15 (1 H, ddd, J = 1.4, 2.1 and 7.7 Hz, C(3')H_B), 1.92 (2 H, m, C(2)H_2), 2.99 (3 H, s, SO_2CH_3), 4.20 (2 H, m, C(1)H_2), 5.27 (1 H, dt, J = 1.0 and 2.1 Hz, =CH), 5.34 (1 H, br s, =CH); δ_C (67.94 MHz, $CDCl_3$) 137.80 (C-2'), 101.92 (=CH_2), 68.88 (C-1), 37.66 (SO_2CH_3), 34.39 (C-2), 13.00 (C-3'), 10.68 (C-1'), -2.64 ($Si(CH_3)_3$).

Diethyl 3-(methylenecyclopropyl)propane-1,1-dicarboxylate. Sodium hydride (60 % dispersion in mineral oil, 0.54 g, 0.32 g NaH, 13.55 mmol) was washed several times with petrol and the remaining solvent was removed under reduced pressure. Dry THF (60 ml) was added and the suspension cooled to 0 °C under nitrogen. Diethyl malonate (1.81 g, 11.30 mmol) was added dropwise, the reaction was stirred for 5 min at 0 °C, then 1.5 h at room temperature. The reaction was cooled to 0 °C and 2-(methylenecyclopropyl)ethyl methanesulphonate (1.99 g, 11.29 mmol) in dry THF (15 ml) was added. The reaction was refluxed for 26 h, cooled and quenched with water (60 ml) and extracted with diethyl ether (3 x 60 ml). The combined organic extract was dried over sodium sulphate and concentrated under reduced pressure. The crude mixture (2.29 g) was purified by flash column chromatography. Elution with ethyl acetate/petrol (5/95) gave *diethyl 3-(methylenecyclopropyl)propane-1,1-dicarboxylate* (**4**) (1.36 g, 50 %) as a colourless oil; R_f = 0.45 (10 % ethyl acetate/petrol); δ_{max} (liq. film) 2982 (m), 2938 (m), 1732 (s), 1448 (m), 1370 (m), 1253 (s), 1175 (s), 1029 (m), 888 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.70 (1 H, m, cyclopropyl CH), 1.21 (6 H, t, J = 7.2 Hz, CH_3), 1.20-1.40 (4 H, m, cyclopropyl CH x 2, C(3)H_2), 1.95 (2 H, m, C(2)H_2), 3.33 (1 H, t, J = 7.5 Hz, C(1)H), 4.14 (4 H, q, J = 7.2 Hz, CO_2CH_2), 5.29 (1 H, br s, =CH), 5.38 (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 169.42 (CO_2), 135.96 (C-2'), 103.00 (=CH_2), 61.29 (CO_2CH_2), 51.57 (C-1), 30.69, 28.55 (C-2, C-3), 15.03 (C-1'), 14.09 (CH_3), 9.40 (C-3'); *m/z* 258 ($(M + NH_4)^+$, 100 %), 241 ($(M + H)^+$, 80); found *m/z* 258.1704. $C_{13}H_{24}NO_4$ ($(M + NH_4)^+$) requires *m/z* 258.1705.

Diethyl 3-(1'-trimethylsilylmethylenecyclopropyl)propane-1,1-dicarboxylate (**9**) was prepared according to the above procedure, using sodium hydride (0.48 g, 20.0 mmol), diethyl malonate (2.40 g, 15.0 mmol) and 2-(1'-trimethylsilylethylenecyclopropyl)ethyl methanesulphonate (3.66 g, 14.73 mmol) to give malonate (**9**) (2.27 g, 49 %) as a colourless oil; R_f= 0.55 (10 % ethyl acetate/petrol); δ_{max} (liq. film) 2983 (m), 2958 (m), 1734 (s), 1369 (m), 1250 (s), 1177 (s), 1029 (m), 839 (s) cm^{-1}; δ_H (270 MHz; $CDCl_3$) - 0.02 (9 H, s, $Si(CH_3)_3$), 0.81 (1 H, ddd, J = 1.7, 2.1 and 7.7 Hz, C(3')H_A), 1.05 (1 H, ddd, J = 1.5, 2.1 and 7.7 Hz, C(3')H_B), 1.24 (6 H, t, J = 7.2 Hz, CH_3), 1.45 (2 H, m, C(3)H_2), 1.90 (2 H, m, C(2)H_2), 3.23 (1 H, t, J = 7.4 Hz, C(1)H), 4.18 (4 H, 2 overlapping q, J = 7.2 Hz, CO_2CH_2), 5.20 (1 H, dt, J = 1.0 and 2.3 Hz, =CH), 5.24 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 169.47 (CO_2), 139.34 (C-2'), 100.68 (=CH_2), 61.39 (CO_2CH_2), 52.26 (C-1), 33.43, 27.68 (C-2, C-3), 14.21 (CH_3), 13.57 (C-1'),

12.65 (C-3'), - 2.48 ($Si(CH_3)_3$); *m/z* 330 ($(M+NH_4)^+$, 75 %), 313 ($(M + H)^+$, 100), 90 (35); found *m/z* 330.2104. $C_{16}H_{32}NO_4Si$ ($(M + NH_4)^+$) requires *m/z* 330.2101.

Diethyl 4-methylenecyclopropylbutane-1,1-dicarboxylate (**5**) was prepared according to the above procedure from sodium hydride (0.056 g, 2.33 mmol), diethyl malonate (0.31 g, 1.94 mmol) and 1-bromo-3-methylenecyclopropylpropane (0.34 g, 1.94 mmol) to give malonate (**5**) (0.24 g, 59 %) as a colourless oil; R_f = 0.50 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2980 (m), 2929 (m), 1733 (s), 1369 (m), 1153 (m), 1031 (m), 887 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.78 (1 H, m, C(3')H_A), 1.22-1.50 (12 H, overlapping t, J = 7.2 Hz, 2 x CH_3, and m, C(3')H_B, C(1')H, C(3)H_2, C(4)H_2), 1.93 (2 H, m, C(2)H_2), 3.31 (1 H, t, J = 7.6 Hz, C(1)H), 4.18 (4 H, q, J = 7.2 Hz, 2 x CO_2CH_2), 5.33 (1 H, br s, =CH), 5.39 (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 169.67 (CO_2), 136.78 (C-2'), 102.77 (=CH_2), 61.42 (CO_2CH_2), 52.12 (C-1), 32.74, 28.51, 27.27 (C-2, C-3, C-4), 15.45 (C-1'), 14.22 (CH_3), 9.53 (C-3'); *m/z* 272 ($(M + NH_4)^+$, 100 %), 255 ($(M + H)^+$, 92), 209 (17), 95 (26); found *m/z* 272.1875. $C_{14}H_{26}NO_4$ ($(M + NH_4)^+$) requires *m/z* 272.1862.

Diethyl 4-(1'-trimethylsilylmethylenecyclopropyl)butane-1,1-dicarboxylate (**10**) was prepared according to the above procedure, from sodium hydride (0.072 g, 3.00 mmol), diethyl malonate (0.39 g, 2.46 mmol) and 1-bromo-3-(1'-trimethylsilyl methylenecyclopropyl)-propane (0.67 g, 2.71 mmol) gave malonate (**10**) (0.51 g, 64 %) as a colourless oil; R_f = 0.53 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2957 (m), 1734 (s), 1250 (m), 1153 (m), 1035 (m), 839 (s) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.0 (9 H, s, $Si(CH_3)_3$), 0.78 (1 H, ddd, J = 1.7, 2.1 and 7.5 Hz, C(3')H_A), 1.02 (1 H, ddd, J = 1.5, 2.1 and 7.5 Hz, C(3')H_B), 1.26 (6 H, t, J = 7.2 Hz, 2 x CH_3), 1.30-1.50 (4 H, br m, C(3)H_2, C(4)H_2), 1.83 (2 H, m, C(2)H_2), 3.29 (1 H, t, J = 7.6 Hz, C(1)H), 4.17 (4 H, q, J = 7.2 Hz, 2 x CO_2CH_2), 5.17 (1 H, dt, J = 1.1, 2.1 Hz, =CH), 5.23 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 169.51 (CO_2), 139.66 (C-2'), 100.32 (=CH_2), 61.29 (CO_2CH_2), 51.90 (C-1), 35.23, 29.05, 26.06 (C-2, C-3, C-4), 14.15 (CH_3), 13.76 (C-1'), 12.55 (C-3'), - 2.55 ($Si(CH_3)_3$); *m/z* 344 ($(M + NH_4)^+$, 32 %), 327 ($(M + H)^+$, 100), 90 (42); found *m/z* 344.2257. $C_{17}H_{34}NO_4Si$ ($(M + NH_4)^+$) requires *m/z* 344.2257.

Diethyl 5-(1'-trimethylsilylmethylenecyclopropyl)pentane-1,1-dicarboxylate (**11**) was prepared according to the above procedure, from sodium hydride (0.072 g, 3.00 mmol), diethyl malonate (0.40 g, 2.50 mmol) and 1-bromo-4-(1'-trimethylsilylmethylene cyclopropyl)butane (0.72 g, 2.75 mmol) to give malonate (**11**) (0.61 g, 72 %) as a colourless oil; R_f = 0.53 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2956 (m), 2931 (m), 1753 (s),1735 (s), 1249 (s), 1152 (m), 838 (s) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.0 (9 H, s, $Si(CH_3)_3$), 0.77 (1 H, ddd, J = 1.7, 2.1 and 7.5 Hz, C(3')H_A), 1.02 (1 H, ddd, J = 1.5, 2.1 and 7.5 Hz, C(3')H_B), 1.23-1.50 (6 H,2 overlapping t, J = 7.2 Hz, 2 x CH_3, and 6 H, m, C(3)H_2, C(4)H_2, C(5)H_2), 1.85 (2 H, q, J = 7.5 Hz, C(2)H_2), 3.28 (1 H, t, J = 7.5 Hz, C(1)H), 4.18 (4 H, q, J = 7.2 Hz, 2 x CO_2CH_2), 5.16 (1 H, dt, J = 1.2 and 2.1 Hz, =CH), 5.22 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 169.70 (CO_2), 140.06 (C-2'), 100.21 (=CH_2), 61.41 (CO_2CH_2), 52.18 (C-1), 35.55, 28.82, 28.10, 27.86 (C-2, C-3, C-4, C-5), 14.24 (CH_3), 14.01 (C-1'), 12.61 (C-3'), - 2.42 ($Si(CH_3)_3$); found: C, 63.51; H, 9.63.

$C_{18}H_{32}O_4Si$ requires C, 63.49; H, 9.47 %.

Procedure for the preparation of iodomalonates.[2c]

Diethyl 1-iodo-3-(methylenecyclopropyl)propane-1,1-dicarboxylate. Potassium hydride (35 % wt suspension in mineral oil, 0.326 g) was washed several times with petrol under nitrogen, the remaining solvent was removed under reduced pressure and the flask weighed again (KH, 0.123 g, 3.07 mmol). Dry THF (17 ml) was added and the suspension cooled to 0 °C under nitrogen. Malonate (**9**) (0.508 g, 2.11 mmol) in dry THF (2 ml) was added dropwise, and the reaction was stirred at room temperature for 1.5 h. The pale yellow solution was cooled to - 78 °C and the flask was wrapped in aluminium foil. A solution of *N*-iodosuccinimide (0.515 g, 2.29 mmol) in dry THF (2 ml) was added to the stirred reaction mixture, and the reaction was allowed to warm to -60 °C over 40 min. The crude reaction mixture was filtered through a short silica gel column eluting with diethyl ether to give *diethyl 1-iodo-3-(methylenecyclopropyl) propane-1,1-dicarboxylate* contaminated with some 5-*exo* cyclised product (**13**) (0.78 g, 100 % overall) as a yellow oil; R_f= 0.50 (10 % ethyl acetate/petrol); δ_H (270 MHz; $CDCl_3$) 0.75 (1 H, m, cyclopropyl CH), 1.21 (6 H, t, J = 7.2 Hz, CH_3 x 2), 1.20-1.40 (4 H, m, cyclopropyl CH x 2, C(3)H_2), 2.22 (2 H, m, C(2)H_2), 4.10 (4 H, q, J = 7.2 Hz, CO_2CH_2), 5.28 (1 H, br s, =CH), 5.38 (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 168.13 (CO_2), 168.04 (CO_2), 135.79 (C-2'), 103.20 (=CH_2), 62.99 ($CO_2\underline{C}H_2$), 44.95 (C-1), 39.71, 31.37 (C-2, C-3), 14.80 (C-1'), 13.83 (CH_3), 9.47 ppm (C-3').

Procedure for irradiation of iodomalonates.[2c]

Crude iodomalonate (0.440 g, 1.20 mmol) and hexabutyl ditin (0.12 ml, 0.140 g, 0.24 mmol) in dry, degassed toluene (4 ml, 0.3 M) were placed in front of a 150 W lamp. The solution was irradiated for 2h, raising the temperature to 80 °C. The reaction was cooled, diluted with diethyl ether (10 ml) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.060 g, 0.39 mmol) was added. The solution was stirred for 5 min, followed by the addition of a solution of iodine (0.1 M in ether) until the iodine colour persisted. The reaction was filtered through a short silica gel column eluting with diethyl ether, and the crude product was purified by flash column chromatography. Elution with ethyl acetate/petrol (2.5/97.5) gave *diethyl 3-iodomethylenecyclohexane-6,6-dicarboxylate* (**13**) (0.285 g, 65 % overall from malonate **4**) as a pale yellow oil; R_f = 0.45 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2980 (s), 1735 (s), 1647 (m), 1443 (s), 1298 (s), 1243 (s), 1144 (s), 1076 (s), 1049 (s), 910 (m), 855 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.26 (6 H, 2 superimposed t, J = 7.0 Hz, CH_3), 1.90-2.18 (3 H, m, C(4)H_2, C(5)H_A), 2.40 (1 H, m, C(5)H_B), 2.84 (1 H, dd, J = 9.4 and 14.1 Hz, C(2)H_A), 2.94 (1 H, dd, J = 4.7 and 14.1 Hz, C(2)H_B), 4.23 (5 H, m, C(3)H, CO_2CH_2), 4.75 (1 H, s, =CH), 5.03 (1 H, s, =CH); δ_C (67.94 MHz; $CDCl_3$) 170.23, 169.72 (2 x CO2), 142.80 (C-1), 113.99 (=CH_2), 61.90, 61.85 (CO_2CH_2), 61.62 (C-6), 46.59 (C-2), 35.34 (C-4), 33.80 (C-5), 27.67 (C-3), 14.15 (CH_3); m/z 384 ($(M + NH_4)^+$, 15 %), 367 ($(M + H)^+$, 100), 293 (58), 239 (70), 165 (51); found m/z 367.0400. $C_{13}H_{20}IO_4$ ($(M + H)^+$) requires m/z 367.0406; found C, 42.74; H, 5.52. $C_{13}H_{19}IO_4$ requires C, 42.64; H, 5.23 %;

and *diethyl 1-iodobicyclo[4.1.0]heptane 3,3-dicarboxylate* (**12**) (0.015 g, 3 % overall from malonate **4**) as a pale yellow oil; R_f = 0.50 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2979 (m), 2935 (m), 1729 (s), 1446 (m), 1366 (m), 1257 (s), 1179 (s), 1100 (s), 1065 (m), 1027 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.86 (1 H,

dd, J = 5.8 and 8.3 Hz, C(7)H_A), 1.03 (1 H, dd, J = 5.8 and 6.0 Hz, C(7)H_B), 1.29 (3 H, t, J = 7.2 Hz, CH_3), 1.30 (3 H, t, J = 7.2 Hz, CH_3), 1.60-2.22 (5 H, m, C(4)H_2, C(5)H_2, C(6)H), 3.80 (2 H, s, C(2)H_2), 4.25 (4 H, m, CO_2CH_2); δ_C (67.94 MHz; $CDCl_3$) 171.06, 170.95 (2 x CO_2), 61.85, 61.54 (2 x CO_2CH_2), 60.96 (C-3), 34.03 (C-1), 32.02 (C-6), 31.64, 26.33, 19.32, 13.20 (C-2, C-4, C-5, C-7), 14.22, 14.14 (2 x CH_3); *m/z* 384 ($(M + NH_4)^+$, 75 %), 367 ($(M+H)^+$, 100), 239 (34); found *m/z* 367.0416. $C_{13}H_{20}IO_4$ ($(M + H)^+$) requires *m/z* 367.0406.

Diethyl 1-iodo-3-(1'-trimethylsilylmethylenecyclopropyl)propane-1,1-dicarboxylate (**14**) was prepared according to the above procedure for the preparation of iodomalonates. Malonate (**9**).(0.800 g, 2.56 mmol), potassium hydride (0.152 g, 3.79 mmol) and *N*-iodosuccinimide (0.634 g, 2.82 mmol) gave a mixture of *iodomalonate* (**14**) and *diethyl 3-iodo-3-trimethylsilylmethylene cyclohexane-6,6-dicarboxylate* (**15**) ((**14**):(**15**) in a 2:1 ratio from ^1H NMR, 1.096 g, 100 % overall) as a yellow oil. This mixture was used directly in the next reaction.

Diethyl 3-iodo-3-trimethylsilylmethylenecyclohexane-6,6-dicarboxylate (**15**). Irradiation of crude iodomalonate (**14**) (1.096 g, 2.5 mmol) with hexabutyl ditin (0.25 ml, 0.29 g, 0.50 mmol) in dry, degassed toluene (8 ml, 0.3 M) at 80 °C for 2.5 h according to the above procedure for the irradiation of iodomalonates gave *diethyl 3-iodo-3-trimethylsilylmethylenecyclohexane-6,6-dicarboxylate* (**15**) (0.885 g, 84 % overall from malonate (**9**) as a pale yellow oil; R_f= 0.50 (10 % ethyl acetate/petrol); δ_{max} (liq. film) 2954 (m), 2900 (m), 1732 (s), 1646 (m), 1435 (m), 1250 (s), 1231 (s), 1174 (m), 1067 (m), 901 (m), 841 (s) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.16 (9 H, s, $Si(CH_3)_3$), 1.25 (1 H, m, C(4)H_A), 1.26 (3 H, t, J = 7.1 Hz, CH_3), 1.29 (3 H, t, J = 7.1 Hz, CH_3), 1.99 (1 H, br dt, J = 15.3 and 3.5 Hz, C(4)H_B), 2.37 (1 H, dt, J = 13.7 and 3.3 Hz, C(5)H_A), 2.58 (2 H, s, C(2)H_2), 2.64 (1 H, dt, J = 3.7 and 13.7 Hz, C(5)H_B), 4.24 (4 H, m, CO_2CH_2), 4.88 (1 H, s, =CH), 4.98 (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 170.20, 169.85 (2 x CO_2), 140.67 (C-1), 114.62 (=CH_2), 61.87 (C-6), 61.65 (CO_2CH_2), 50.72 (C-3), 44.95 (C-2), 32.88 (C-4), 31.69 (C-5), 14.16 (CH_3), - 3.10 ($Si(CH_3)_3$); *m/z* 456 ($(M + NH_4)^+$, 97 %), 439 ($(M + H)^+$, 55), 313 (70), 90 (66); found *m/z* 456.1065. $C_{16}H_{31}INO_4Si$ ($(M + NH_4)^+$) requires *m/z* 456.1067.

Diethyl 1-iodo-4-(methylenecyclopropyl)butane-1,1-dicarboxylate was prepared according to the above procedure for the preparation of iodomalonates. Potassium hydride (0.111 g, 2.78 mmol), malonate (**5**) (0.482 g, 1.90 mmol), and *N*-iodosuccinimide (0.470 g, 2.09 mmol) gave diethyl 1-iodo-4-(methylenecyclopropyl)butane-1,1-dicarboxylate (0.661g, 92 %) as a yellow oil; R_f = 0.58 (10 % ethyl acetate/petrol); δ_H (270 MHz; $CDCl_3$) 0.72 (1 H, m, cyclopropyl CH), 1.24-1.55 (6 H, 2 overlapping t, J = 7.2 Hz, 2 x CH_3, and 6 H, m, cyclopropyl CH x 2, C(3)H_2, C(4)H_2), 2.17 (2 H, m, C(2)H_2), 4.25 (4 H, q, J = 7.2 Hz, 2 x CO_2CH_2), 5.33 (1 H, m with very fine splitting, =CH), 5.39 (1 H, m with very fine splitting, =CH); δ_C (67.94 MHz; $CDCl_3$) 168.33, 168.30 (CO_2), 136.58 (C-2'), 102.96 (=CH_2), 63.09 (CO_2CH_2), 45.77 (C-1), 39.69, 32.61, 27.71 (C-2, C-3, C-4), 15.40 (C-1'), 13.95 (CH_3), 9.60 (C-3').

Irradiation of diethyl 1-iodo-4-(methylenecyclopropyl)butane-1,1-dicarboxylate. Irradiation of diethyl 1-iodo-4-(methylenecyclopropyl)butane-1,1-dicarboxylate (0.200 g, 0.53 mmol) with hexabutyl ditin (0.026 ml, 0.030 g, 0.05 mmol) in dry, degassed toluene (18 ml, 0.03 M) at 75 °C for 4 h according to the above procedure gave *diethyl 1-iodobicyclo[5.1.0]octane 3,3-dicarboxylate* (**16**) (0.113 g, 57 %) as a colourless oil ; R_f = 0.50 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2980 (m), 2937 (m), 1729 (s), 1294 (m), 1249 (s), 1210 (s), 1181 (s), 1133 (m), 1055 (m) cm^{-1}; δ_H (360 MHz; $CDCl_3$) 0.74 (1 H, t, J = 5.8 Hz, $C(8)H_A$), 1.04 (1 H, m, $C(6)H_A$), 1.23 (3 H, t, J = 7.1 Hz, CH_3), 1.29 (3 H, t, J = 7.1 Hz, CH_3 and 1 H, m, $C(8)H_B$), 1.46 (2 H, m, $C(5)H_A$, C(7)H), 1.94 (2 H, m, $C(5)H_B$, $C(6)H_B$), 2.04 (1 H, dt, J = 14.6 and 4.2 Hz,$C(4)H_A$), 2.38 (1 H, d, J = 16.8 Hz,$C(2)H_A$), 2.62 (1 H, ddd, J = 4.2, 12.3, 14.6 Hz,$C(4)H_B$), 3.07 (1 H, d, J = 16.8 Hz,$C(2)H_B$), 4.20 (4 H, m, 2 x CO_2CH_2); δ_C (90.56 MHz; $CDCl_3$) 171.77, 171.51 (CO_2), 61.66, 61.50 (CO_2CH_2), 57.38 (C-3), 43.69 (C-2), 31.22 (C-4), 27.99 (C-6), 27.91 (C-8), 27.07 (C-7), 22.76 (C-5), 14.13, 14.07 (CH_3), 2.51 (C-1); *m/z* 398 ($(M + NH_4)^+$, 100 %), 381 ($(M + H)^+$, 42), 272 (31), 255 (45), 35 (75);

and a mixture of 6-*exo* cyclised products: *diethyl 6-iodomethylenecycloheptane-2,2-dicarboxylate* (**17**) and *diethyl 6-(iodomethyl)methylenecyclohexane-2,2-dicarboxylate* (**18**) (3:1 mixture (from ^1H NMR), 0.026 g, 13 %) as a pale yellow oil; R_f = 0.40 (10 % ethyl acetate/petrol); individual representative data taken from the spectra of the mixture are given below;

for (**17**): δ_H (270 MHz; $CDCl_3$) 5.15 (1 H, s, =CH), 5.33 (1 H, s, =CH); δ_C (67.94 MHz; $CDCl_3$) 144.69 (C-1), 120.42 ($=CH_2$), 61.77 (CO_2CH_2), 47.83, 44.83, 33.96 (C-3, C-5, C-7), 32.59 (C-6), 25.63 (C-4), 14.18 (CH_3);

for (**18**): δ_H (270 MHz; $CDCl_3$) 4.80 (1 H, s, =CH), 5.00 (1 H, s, =CH); δ_C (67.94 MHz; $CDCl_3$) 110.59 ($=CH_2$), 61.65 (CO_2CH_2), 43.03 (C-6), 34.60, 34.38, 22.39 (CH_2), 14.18 (CH_3), 9.70 (CH_2).

Reduction of mixture of (**17**) *and* (**18**) *with tributyltin hydride.* A mixture of iodides (**17**) and (**18**) (0.056 g, 0.15 mmol) was stirred at reflux with tributyltin hydride (0.055 ml, 0.060 g, 0.20 mmol) and AIBN (0.005 g, 0.03 mmol) in dry, degassed toluene (0.7 ml) for five hours. The reaction was cooled and diluted with diethyl ether (5 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.05 g, 0.33 mmol) was added, followed by the addition of a solution of iodine (0.1 M in ether) until the iodine colour persisted. The reaction was filtered through a short silica gel column eluting with diethyl ether, and the crude product (0.066 g) purified by flash column chromatography. Elution with ethyl acetate/petrol (2.5/97.5) gave a mixture of *diethyl methylenecycloheptane-2,2-dicarboxylate* (**19**) and *diethyl 6-(methyl)methylenecyclohexane-2,2-dicarboxylate* (**20**) (2:1 mixture from ^1H NMR, 0.034 g, 92 %) as a colourless oil; R_f = 0.48 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2937 (m), 2858 (m), 1731 (s), 1458 (m), 1448 (m), 1245 (s), 1149 (m), 1035 (m) cm^{-1};

for (**19**): δ_H (270 MHz; $CDCl_3$) 4.99 (1 H, s, =CH), 5.18 (1 H, s, =CH); δ_C (67.94 MHz; $CDCl_3$) 147.46 (C-1), 116.75 ($=CH_2$);

for (**20**): δ_H (270 MHz; $CDCl_3$) 1.09 (3 H, d, J = 6.6 Hz, CH_3), 4.68 (1 H, s, =CH), 4.99 (1 H, s, =CH); δ_C (67.94 MHz; $CDCl_3$) 150.10 (C-1), 108.83 ($=CH_2$), 35.63 (C-6), 18.96 (CH_3).

Diethyl 1-iodo-4-(1'-trimethylsilylmethylenecyclopropyl) butane-1,1-dicarboxylate was prepared according to the above procedure for the preparation of iodomalonates. Potassium hydride (0.034 g, 0.85 mmol), malonate (**10**) (0.200 g, 0.61 mmol) and *N*-iodosuccinimide (0.152 g, 0.67 mmol) gave, after column chromatography on silica gel eluting with diethyl ether/petrol (5/95), diethyl 1-iodo-4-(1'-trimethylsilylmethylenecyclopropyl) butane-1,1-dicarboxylate (0.224 g, 81 %) as a pale yellow oil; R_f = 0.58 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2955 (m), 1735 (s), 1247 (s), 1185 (m), 837 (s) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.0 (9 H, s, $Si(CH_3)_3$), 0.79 (1 H, ddd, J = 1.7, 2.1 and 7.5 Hz, C(3')H_A), 1.03 (1 H, ddd, J = 1.5, 2.1 and 7.5 Hz, C(3')H_B), 1.26 (6 H, t, J = 7.2 Hz, 2 x CH_3), 1.30-1.50 (4 H, br m, 2 x CH_2), 2.08 (2 H, m, CH_2), 4.23 (4 H, q, J = 7.2 Hz, 2 x CO_2CH_2), 5.18 (1 H, dt, J = 1.2, 2.1 Hz, =CH), 5.23 (1 H, br q, J = 1.4 Hz, =CH); δ_C (67.94 MHz; $CDCl_3$) 168.27 (CO_2), 139.62 (C-2'), 100.53 (=CH_2), 63.06 (CO_2CH_2), 45.62 (C-1), 40.36, 35.29, 26.76 (C-2, C-3, C-4), 13.93 (CH_3), 13.86 (C-1'), 12.74 (C-3'), - 2.44 ($Si(CH_3)_3$).

Diethyl 1-iodo-7-trimethylsilylbicyclo[5.1.0]octane 3,3-dicarboxylate (**21**) was prepared according to the above procedure for irradiation of iodomalonates. Irradiation of diethyl 1-iodo-4-(1'-trimethylsilylmethylenecyclopropyl) butane-1,1-dicarboxylate (0.220 g, 0.49 mmol) for 2 h in the presence of hexabutyl ditin (0.25 ml, 0.29 g, 0.50 mmol) in dry, degassed toluene (16 ml, 0.031 M) gave *diethyl 1-iodo-7-trimethylsilylbicyclo[5.1.0]octane 3,3-dicarboxylate* (**21**) (0.188 g, 86 %) as an oil; R_f = 0.53 (10 % ethyl acetate/petrol); ν_{max} (liq. film) 2955 (m), 1732 (s), 1250 (s), 1207 (m), 1179 (m), 1059 (m), 838 (m) cm^{-1}; δ_H (360 MHz; $CDCl_3$) 0.16 (9 H, s, $Si(CH_3)_3$), 0.78 (1 H, d, J = 5.4 Hz, C(8)H_A), 1.12-1.32 (8 H, m + 2 x t, J = 7.2 Hz, C(6)H_A + 2 x CH_3, C(8)H_B), 1.40 (1 H, m, C(5)H_A), 1.77 (1 H, m, C(5)H_B), 1.95 (1 H, dd, J = 7.7 and 14.8 Hz, C(6)H_B), 2.15 (1 H, dt, J = 14.5 and 3.5 Hz, C(4)H_A), 2.53 (1 H, dt, J = 4.9 and 14.5 Hz, C(4)H_B), 2.87 (1 H, d, J = 17.0 Hz, C(2)H_A), 3.25 (1 H, d, J = 17.0 Hz, C(2)H_B), 4.20 (4 H, m, 2 x CO_2CH_2); δ_C (67.94 MHz; $CDCl_3$) 172.07, 171.37 (CO_2), 61.75, 61.56 (CO_2CH_2), 57.11 (C-3), 47.27 (C-2), 31.46 (C-8), 31.08 (C-6), 29.23 (C-4), 22.77 (C-5), 18.22 (C-1), 14.48 (CH_3), 13.82 (C-7), - 0.54 ($Si(CH_3)_3$), *m/z* 470 ($(M + NH_4)^+$, 100 %), 453 ($(M + H)^+$, 63), 327 (51), 253 (59), 90 (66), 35 (56); Found *m/z* 453.0957. $C_{17}H_{30}IO_4Si$ ($(M + H)^+$) requires *m/z* 453.0958.

Diethyl 1-iodo-5-(1'-trimethylsilylmethylenecyclopropyl)pentane-1,1-dicarboxylate (**22**) was prepared according to the above procedure for the preparation of iodomalonates. Potassium hydride (0.068 g, 1.70 mmol), malonate (**11**) (0.413 g, 1.21 mmol) and *N*-iodosuccinimide (0.300 g, 1.33 mmol) gave iodomalonate (**22**) (0.533 g, 95 %) as a yellow oil; R_f = 0.58 (10 % ethyl acetate/petrol); δ_H (270 MHz; $CDCl_3$) - 0.03 (9 H, s, $Si(CH_3)_3$), 0.78 (1 H, ddd, J = 1.7, 2.1 and 7.5 Hz, C(3')H_A), 1.03 (1 H, ddd, J = 1.5, 2.1 and 7.5 Hz, C(3')H_B), 1.27 (6 H, 2 overlapping t, J = 7.2 Hz, 2 x CH_3 and 6 H, m, C(3)H_2, C(4)H_2, C(5)H_2), 2.12 (2 H, m, C(2)H_2), 4.24 (4 H, q, J = 7.2 Hz, 2 x CO_2CH_2), 5.18 (1 H, dt, J = 1.2, 2.1 Hz, =CH), 5.24 (1 H, br s, =CH); δ_C (67.94 MHz; $CDCl_3$) 168.37 (CO_2), 139.93 (C-2'), 100.38 (=CH_2), 63.10 (CO_2CH_2), 45.75 (C-1), 40.05, 35.49, 28.22, 27.97 (C-2, C-3, C-4, C-5), 14.01 (C-1'), 13.96 (CH_3), 12.62 (C-3'), -2.41 ($Si(CH_3)_3$).

Diethyl 1-iodo-8-trimethylsilylbicyclo[6.1.0]nonane 3,3-dicarboxylate (**23**) was prepared according to the above procedure for irradiation of iodomalonates. Iodomalonate (**22**) (0.104 g, 0.22 mmol) and hexabutyl ditin (0.02 ml, 0.023 g, 0.02 mmol) in dry, degassed toluene (2 ml, 0.11 M) gave *diethyl 1-iodo-8-trimethylsilylbicyclo[6.1.0]nonane 3,3-dicarboxylate* (**23**) (0.032 g, 31 %) as a pale yellow solid; m.p. = 82-84 °C; R_f = 0.53 (10 % ethyl acetate/petrol); ν_{max} (liq. film in CCl_4) 2923 (s), 1731 (m), 1453 (m) cm^{-1}; δ_H (270 MHz; $CDCl_3$) 0.16 (9 H, s, $Si(CH_3)_3$), 0.78 (1 H, d, J = 5.5 Hz, $C(9)H_A$), 0.95 (2 H, m, 2 x CH), 1.21 (3 H, t, J = 7.2 Hz, CH_3), 1.30 (3 H, t, J = 7.2 Hz, CH_3), 1.32 (1 H, d, J = 5.5 Hz, $C(9)H_B$), 1.40-1.60 (2 H, m, 2 x CH), 1.85 (1 H, m, CH), 2.15 (2 H, m, CH, $C(4)H_A$), 2.40 (1 H, d, J = 16.5 Hz, $C(2)H_A$), 2.51 (1 H, m, $C(4)H_B$), 3.26 (1 H, d, J = 16.5 Hz, $C(2)H_B$), 4.20 (4 H, m, 2 x CO_2CH_2); δ_C (67.94 MHz; $CDCl_3$) 171.80, 171.45 (CO_2), 61.75, 61.65 (CO_2CH_2), 59.14 (C-3), 42.86 (C-2), 35.03, 31.08, 29.07, 27.93, 23.87 (C-4, C-5, C-6, C-7, C9), 21.31, 16.27 (C-1, C-8), 14.24, 14.01 (CH_3), 0.69 ($Si(CH_3)_3$); *m/z* 484 ($(M + NH_4)^+$, 100 %), 467 ($(M + H)^+$, 36), 341 (58), 267 (25), 90 (40); found *m/z* 484.1404. $C_{18}H_{35}INO_4Si$ ($(M + NH_4)^+$) requires *m/z* 484.1380.

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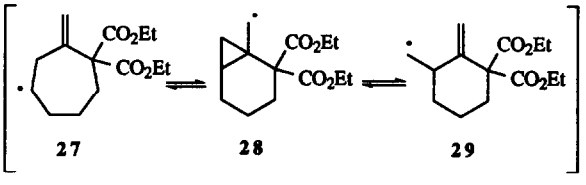

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