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Iron(III) Mediated Transformations of Trimethylsilyloxy Cyclopropyl Ethers Part 2: A New 4-Substituted-2-Cyclohexenone Synthesis

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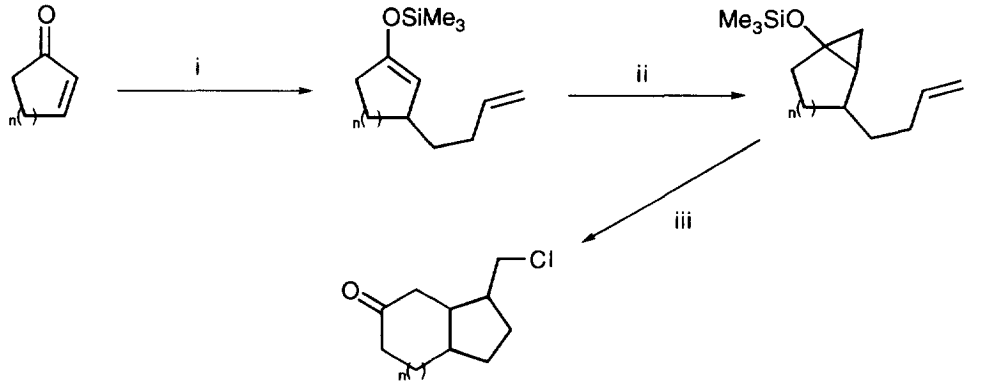
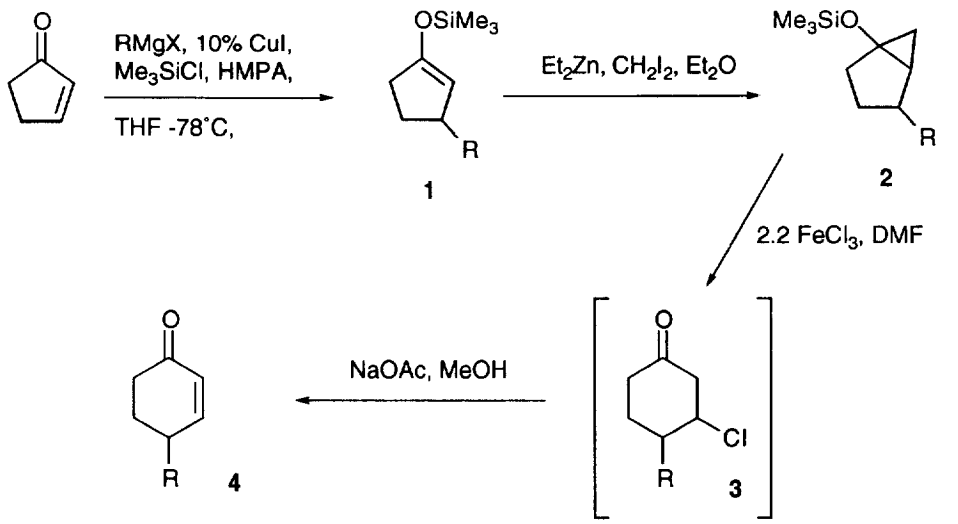
Abstract: Conjugate addition of a variety of Grignard reagents to 2-cyclopentenone gave a number of silyl enol ethers (**1**) which were treated with Et_2Zn/CH_2I_2 to give the corresponding cyclopropyl silyl ethers (**2**) in good yield. Ferric chloride ring expansion followed by base elimination of the resulting β-chloro ketones gave the 4-substituted-2-cyclohexenones (**4**) in moderate to good overall yield. The overall process provides a convenient three step route to these enones from 2-cyclopentenone.

The synthesis of 4-substituted-2-cyclohexenones is an important goal in organic chemistry as they are valued intermediates and starting materials for a number of synthetic transformations and natural product syntheses. There already exists a number of methods for their preparation which include: the Birch[1] reduction of 4-substituted anisoles followed by hydrolysis and reconjugation; nucleophilic substitution of 2-alkoxy substituted iron tricarbonyl dienyl complexes[2] followed by decomplexation and hydrolysis; Diels-Alder reactions with Danishefsky's diene[3] followed by hydrolysis and Stork's enolate alkylation of 3-alkoxy-2-cyclohexenones followed by reduction and hydrolysis.[4] As part of a program to investigate the synthesis of various [n.3.0] bicyclic ring systems (n=1,2,3) we recently developed[5] a novel tandem ring expansion-cyclisation sequence (scheme 1) based on Saegusa's[6] ferric chloride mediated ring expansion of cyclopropyl silyl ethers.



Scheme 1 *Reagents and conditions:* i, 3-Butenyl magnesium bromide, 10% CuI, HMPA, THF -78°C, Me_3SiCl; ii, Et_2Zn, CH_2I_2, Et_2O; iii, 2.2eq. $FeCl_3$, DMF 0°C

We found that the conjugate addition of butenyl magnesium bromide to a variety of enones followed by a modified Simmons-Smith cyclopropanation proceeded in excellent overall yield for the two steps. We reasoned that application of this conjugate/addition cyclopropanation strategy to 2-cyclopentenone, using a variety of Grignard reagents, would give the corresponding substituted cyclopropanes (**2**). Subjecting these cyclopropanes to Saegusa's ring expansion procedure would give the β-chloro ketones (**3**) which upon base elimination would yield a number of 4-substituted-2-cyclohexenones (**4**). The overall process would provide a simple three step procedure[7] for the conversion of 2-cyclopentenone to substituted cyclohexenones where the only limiting factor would be the availabilty of the starting Grignard reagent (scheme 2).



Scheme 2

Results and Discussion

In general the copper catalysed addition of a variety of Grignard reagents to 2-cyclopentenone proceeded well in all cases using the procedure developed by Matsuzawa[8] to give high yields of conjugate addition products (**1**). The only exceptions were in the case of allyl magnesium bromide and *tert*-butyl magnesium bromide, entries (b) and (c). With *tert*-butyl magnesium bromide a poor yield of (**1**) was obtained and the major product was *tert*-butyltrimethyl silane; this problem was overcome using the cuprate method developed by Johnson.[9] Allyl magnesium bromide gave only the 1,2-addition product, although this was not unexpected as conjugate addition of allyl cuprate reagents is notoriously difficult.[10] This problem was circumvented using the allyl Grignard procedure developed by Lipshutz.[11] For the Matsuzawa procedure all the Grignard reagents, apart from benzyl magnesium chloride, were prepared in THF using magnesium metal activated with a crystal of iodine. The use of commercially available reagents gave much poorer yields. In the case of benzyl magnesium chloride, entry (e), the best results were obtained by preparing the reagent using the activated magnesium procedure developed by Brown.[12] Modified Simmons-Smith cyclopropanation[6] proceeded well in all cases to give the substituted trimethylsilyloxy cyclopropanes (**2**) in good to excellent yield. Ring expansion with ferric chloride followed by

elimination of chloride from the crude β-chloroketones (**3**) with sodium acetate, gave the 4-substituted-2-cyclohexenones (**4**) in moderate to good overall yields. TLC analysis of the crude reaction mixture prior to treatment with sodium acetate showed it to comprise of a mixture of the β-chloroketone (**3**) and the eliminated cyclohexenone (**4**). It is interesting to note the duality of reactivity of the enol ether **2(d)** which contains the butenyl side chain. For example slow addition[5b,c] of ferric chloride to **2(d)** gives rise to ring expansion-cyclisation (Scheme 1) because as the concentration of ferric chloride is low then this allows time for the intermediate carbocyclic radical to cyclise. In the present work **2(d)** is added to a concentrated solution of ferric chloride and therefore, due to the high concentration of available chloride, the ring expanded carbocyclic radical abstracts chlorine before cyclisation can take place. These reactions were run on small scale (2mmol) compared to the original work of Saegusa. However, we found that on scaling up (20mmol) the butenyl example **2(d)** proportionately less solvent could be used and a significantly higher yield was obtained (64%). It would, therefore, appear that the ferric chloride initiated ring expansion step proceeds in higher yields when more concentrated reaction mixtures are used which is in accordance with Saegusa's original published work. These ring expansion reactions would, therefore, appear to benefit from being carried out on large scale (≥20 mmol). The following table summarises our results in this area.

Table: Synthesis of 4-substituted-2-cyclohexenones

Entry	R	1 (Yield %)	2 (Yield %)	4 (Yield %)[a]
a	*n*-Bu	99	93	54
b	*t*-Bu	Ref.9	70	48
c		76	76	45
d		Ref. 5(c)	Ref. 5(c)	42 (64)[b]
e	Ph	95	80	53
f	$PhCH_2$	92	87	61

[a] Reactions carried out on a 2 mmol scale; [b] Reaction carried out on a 20 mmol scale

In conclusion this methodology provides access to 4-substituted-2-cyclohexenones from 2-cyclopentenone *via* a convenient three step procedure involving conjugate addition of Grignard reagents, cyclopropanation of the resulting enol ethers and subsequent ferric chloride mediated ring expansion.

Acknowledgements

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Experimental

B.p.s refer to Kugelrohr oven temperature during distillation. All manipulations involving anhydrous ferric chloride (Aldrich) were carried out in a glove bag under an atmosphere of argon or nitrogen. DMF was dried by distillation from calcium hydride immediately before use. IR spectra were run neat as thin films on a Perkin-Elmer 1720 X FT spectrometer. ^{1}H and ^{13}C spectra were recorded on a Bruker AC 300 or a Jeol EX 270 FT

spectrometer in either deuteriochloroform or deuteriobenzene. Chemical shifts are referenced to tetramethylsilane, or in the case of any of the trimethylsilyl compounds to the residual $CHCl_3$ or C_6H_6 signals. Mass spectra were recorded at low resolution on a Finnigan 4500 instrument and at high resolution on a Kratos Concept 1-S instrument. Mass spectra were recorded under electron-impact (EI) conditions, or chemical ionisation (CI) conditions using ammonia. Pet. ether refers to the fraction of petroleum ether boiling at 40-60°C. TLC was performed using Camlab Polygram® SIL G/UV_{254} plastic plates, visualized by the combination of a UV lamp and subsequent staining with acidified potassium permanganate solution followed by heating. Flash chromatography was performed using Merck silica gel 60 (particle sizes 40-60m).

General procedure for the formation of 1-(trimethylsilyloxy)-3-substituted cyclopent-1-enes (1): To a stirred suspension of magnesium metal (0.365g 15mmol, activated by heating with a crystal of I_2, under Ar) in dry THF (20cm^3), under an Ar atmosphere, was added the appropriate bromide (15mmol). After the initial exotherm had subsided the reaction mixture was stirred for 1 hr after which HMPA (5mL, 30 mmol) was added and the mixture cooled to -78°C. Copper iodide (0.23g, 1.21mmol) was added and the resulting mixture stirred for 10min before a mixture of 2-cyclopentenone (1g, 11.9 mmol) and TMSCl (3mL, 23.6 mmol) in 10mL THF were added dropwise over 10-20min. The resulting white suspension was stirred for 1hr, before the addition of Et_3N(3cm^3) and allowing to warm to RT. The resulting suspension was poured onto pet. ether (200cm^3), washed with water (3 x 200cm^3), dried over $MgSO_4$ and the solvent evaporated to give the crude products which were purified by Kugelrohr distillation.

3-(n-Butyl)-1-trimethylsilyloxylcyclopent-1-ene 1(a): As above using n-butyl bromide with twice the molar quantities of reagents gave the title compound as a clear colourless liquid. b.p.150°C @ 15mmHg (4.98g, 99%). ν_{max}/cm^{-1} 2957, 1645; δ^1H (300MHz; C_6D_6) 0.18 (9H, s, TMS), 0.89 (3H, t, CH_3-4'), 1.27 (6H, m, CH_2), 1.37 (1H, m, CH_2-4), 1.97 (1H, m, CH_2-4), 2.35 (2H, m, CH_2-5), 2.62 (1H, m, CH-3), 4.75 (1H, d, J=1.8Hz, CH-2); $\delta^{13}C$ (75.47MHz) 0.03 (TMS), 14.4 (CH_3-4'), 23.4 (CH_2), 28.6 (CH_2), 30.3 (CH_2), 33.8 (CH_2), 37.6 (CH_2), 42.4 (C-3), 106.8 (C-2), 155.2 (C-1); *m/z* (EI), Found $[M]^+$ 212.1597, $C_{12}H_{24}24OSi$ requires 212.1596

3-Phenyl-1-trimethylsilyloxylcyclopent-1-ene 1(e): As above using bromobenzene gave the title compound as a clear yellow liquid. b.p.180-190°C @ 15 mmHg (2.65g,95%). ν_{max}/cm^{-1} 2959, 1642; δ^1H (300MHz; C_6D_6) 0.16 (9H,s,TMS), 1.6-1.8 (1H, m), 2.3 (3H, m), 3.80 (1H, m, CH-3), 4.76 (1H, d, J=1.7Hz, CH-2), 7.0-7.3 (5H, m, Ph); $\delta^{13}C$ (75.47MHz) 0.0 (TMS), 32.4 (C-4), 34.0 (C-5), 48.3 (C-3), 106.1 (C-2), 126-129 (arom), 156.7 (C-1), 148.2 (arom); *m/z* (EI), Found$[M]^+$ 232.1283, $C_{14}H_{20}OSi$ requires 232.1283.

3-Benzyl-1-trimethylsilyloxylcyclopent-1-ene 1(f): As above but using magnesium (5 equivalents) activated by the method of Brown[12] and benzyl chloride gave the title compound as a clear liquid. b.p.150°C @ 15 mm (2.7g, 92%). ν_{max}/cm^{-1} 2957, 1644; δ^1H (300MHz; C_6D_6) 0.14 (9H, m, TMS), 1.44 (1H, m), 1.80-1.95 (2H, m), 2.28 (1H, m), 2.52 (1H, dd, J_{vic}=5.67Hz, $J=_{gem}$13.15Hz, benzyl CH_2), 2.56 (1H, dd, J_{vic}=7.31Hz, J_{gem}=13.07Hz, benzyl CH_2), 2.89 (1H, m, CH-3), 4.67 (1H, d, J=1.7Hz, CH-2), 7.0-7.3 (5H,

m, Ph); $\delta^{13}C$ (75.47MHz) 0.1 (TMS), 28.1 (C-4), 33.7 (C-5), 44.0 (benzyl CH_2), 44.3 (C-3), 106.2 (C-2), 127-130 (arom.CH), 141.8 (arom.C); *m/z* (EI), Found[M]$^+$246.1442, $C_{15}H_{22}OSi$ requires 246.1440.

3-Allyl-1-trimethylsilyloxylcyclopent-1-ene 1(c): Anhydrous CuI (5.9g, 31mmol) and LiBr (2.7g, 31mmol) were stirred together under Ar after which THF (50mL) was added to give a yellow solution. This was cooled to -78°C after which commercially available allyl magnesium bromide (27.6mL, 1.0 M solution in ether) was added to give a black solution. Chlorotrimethylsilane (3.9mL, 31mmol) was added followed immediately by 2-cyclopentenone (0.82mL, 9.8mmol), the mixture was stirred for 40min before the addition of NEt_3 (3mL). The reaction mixture was then poured onto pet. ether (200mL), washed with water (2x150mL), dried and the solvent evaporated. Kugelrohr distillation (100-120°C @ 15mmHg) gave the product as a clear pale brown liquid (1.46g, 76%). ν_{max}/cm^{-1} 2957, 1641 (weak); δ^1H (300MHz; C_6D_6) 0.16 (9H, s, TMS) 1.41 (1H, m), 1.91 (1H, m), 2.04 (3H, m), 2.30 (2H, brt, J=7Hz, CH_2), 4.70 (1H, s, CH-2), 5.02 (2H, m, CH_2-3'), 5.78 (1H, m, CH-2'); $\delta^{13}C$ (75.47MHz) 0.03 (TMS), 27.8 (C-4), 33.7 (C-5), 41.95 (C-3 + C-1'), 106.1 (C-2), 115.6 (C-3'), 137.7 (C-2'), 155.5 (C-1); *m/z* (CI, NH_3), Found[M+H]$^+$197.1364, $C_{11}H_{21}OSi$ requires 197.1362.

General cyclopropanation procedure: 4-butyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane 2(a) The enol ether **1(a)** (2.0g, 9.43 mmol) was weighed into a dry apparatus under Ar before the addition of dry diethyl ether (30 mL), diethylzinc (11.5mL, 11.5mmol, 1M solution in hexane) and diiodomethane (0.91mL, 11.3 mmol). The solution was heated at reflux for 2 hr to give a cloudy solution which was allowed to cool and then quenched by the dropwise addition of pyridine (3mL), after which the resulting precipitate was washed into a conical flask with pet. ether (250mL). The resulting white suspension was filtered, and the solvent evaporated to give a yellow liquid. Kugelrohr distillation (b.p.140-150°C) gave the title compound as a clear colourless liquid (2.0g, 93%). ν_{max}/cm^{-1} 2957; δ^1H (300MHz; C_6D_6) 0.16 (9H, s, TMS), 0.49 (1H, brt, J=5Hz, endo-H), 0.87 (4H, m, CH_3/exo-H), 1.1-1.4 (10H, m, CH_2), 1.84 (1H, m), 2.01 (1H, m); $\delta^{13}C$ (75.47MHz) 1.2 (TMS), 14.3 (C-4'), 16.1 (C-6), 23.2 (CH_2), 27.3 (CH_2), 28.9 (C-5), 30.5 (CH_2), 32.1 (CH_2), 35.6 (CH_2), 40.0 (C-4), 65.0 (C-1); *m/z* (EI), Found[M]$^+$ 226.1755, $C_{13}H_{26}OSi$ requires 226.1753.

4-*t* -Butyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane 2(b): As in **2(a)** above using 1g of **1(b)** gave the title compound as a clear colourless oil (0.74g, 70%) after Kugelrohr distillation (b.p.130°C @ 15 mmHg). ν_{max}/cm^{-1} 2959; δ^1H (300MHz; C_6D_6) 0.16 (9H, s, TMS), 0.35 (1H, t, J=4.5Hz, endo-H), 0.76 (1H, brt, J=3Hz, exo-H), 0.89 (9H, s, *t*-Bu), 1.0-1.1 (1H, m, CH-5), 1.4-1.5 (3H, m, CH_2), 1.8-2.0 (2H, m, CH_2); $\delta^{13}C$ (75.47MHz) 1.25 (TMS), 17.5 (C-6), 23.4 (C-3), 27.5 (C-5), 28.1 (CH_3,*t* -Bu), 33.2 (C-*t* -Bu), 34.4 (C-2), 51.7 (C-4), 66.2 (C-1); *m/z* (EI), Found[M]$^+$ 226.1755, $C_{13}H_{26}OSi$ requires 226.1753.

4-Allyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane 2(c): As in **2(a)** above using 0.87g of **1(c)** gave the title compound as a clear colourless oil (0.7g, 76%) after Kugelrohr distillation (b.p.130°C @ 15 mmHg). ν_{max}/cm^{-1} 2956, 1641 (weak); δ^1H (300MHz; C_6D_6) 0.18 (9H, s, TMS), 0.49 (1H, t, J=5Hz, endo-H), 0.90 (1H, m, exo-H), 1.10 (1H, m, CH-5), 1.32 (2H, m, CH_2), 1.72 (1H, q, J=7Hz, CH_2), 1.85 (1H, dd, J=8Hz,

J=10Hz, CH_2), 2.05 (3H, m), 5.02 (2H, m, CH_2-3'), 5.76 (1H, m, CH_2-2'); $\delta^{13}C$ (75.47MHz) 1.2 (TMS), 16.0 (C-6), 26.6 (CH_2), 28.6 (C-5), 31.9 (CH_2), 39.55 (C-4), 40.1 (C-1'), 65.05 (C-1), 115.7 (C-3'), 137.8 (C-2'); *m/z* (EI), Found[M]$^+$ 210.1443, $C_{12}H_{22}OSi$ requires 210.1440.

4-Phenyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane 2(e): As in **2(a)** above using 2.5g of **1(d)** gave the title compound as a clear colourless oil (2.13g, 80%) after Kugelrohr distillation (b.p.150°C @ 14 mmHg). ν_{max}/cm^{-1} 2957, 1603 (weak); δ^1H (300MHz; C_6D_6) 0.16 (9H, s, TMS), 0.53 (1H, t, J=5Hz, endo-H), 0.97 (1H, m, exo-H), 1.38 (2H, m), 1.54 (1H, m), 1.78 (1H, dd, J=7.4Hz, J=12.0Hz, CH_2-2), 2.16 (1H, m, CH_2-2), 2.87 (1H, d, J=7.5, CH-4), 7.1-7.3 (5H, m, Ph); $\delta^{13}C$ (75.47MHz) 1.15 (TMS), 16.45 (C-6), 29.5 (C-5), 31.1 (C-3), 32.1 (C-2), 45.4 (C-4), 65.9 (C-1), 127-9 (arom. CH), 147.4 (arom.C; *m/z* (CI,NH_3), Found[M+NH_4]$^+$ 264.1784, $C_{15}H_{26}ONSi$ requires 264.1784.

4-Benzyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane 2(f): As in **2(a)** above using 2g of **1(f)** gave the title compound as a clear colourless oil (1.83g, 87%) after Kugelrohr distillation (b.p.160°C @ 14 mmHg). ν_{max}/cm^{-1} 2955, 1603 (weak), 1454; δ^1H (300MHz; C_6D_6) 0.17 (9H, m, TMS), 0.45 (1H, t, J=5, endo-H), 0.83 (1H, m, exo-H), 0.98 (1H, m, CH-5), 1.30 (2H, m), 1.82-1.94 (2H, m, CH_2-2), 2.06 (1H, m, CH-4), 2.50 (1H, dd, J_{vic}=8.17Hz, J_{gem}=13.55Hz, benzyl-CH_2), 2.62 (1H, dd, J_{vic}=7.49Hz, J_{gem}=13.52Hz, benzyl-CH_2), 7.0-7.3 (5H, m, Ph); $\delta^{13}C$ (75.47MHz) 1.2 (TMS), 15.9 (C-6), 26.3 (C-3), 28.7 (C-5), 31.8 (C-2), 41.65 (C-4), 41.75 (benzyl-CH_2), 65.0 (C-1), 126-129 (arom. C-H), 141.4 (arom. C); *m/z* (EI), Found[M]$^+$ 260.1593, $C_{16}H_{24}OSi$ requires 260.1596.

General ring expansion procedure: 4-(1'-but-3'-enyl)cyclohex-2-en-1-one 4(d)

Method 1: A solution of **2(d)** (0.448g, 2.0mmol) in dry, degassed DMF (5mL) was added rapidly to a stirred solution of ferric chloride (0.714g, 4.4mmol) in dry, degassed DMF (10mL) at 0°C under Ar. After stirring for a further 1hr the mixture was allowed to warm to RT and poured onto water (400mL). Following extraction with EtOAc (4x150mL), the organic layer was washed with water (2x100mL), dried over $MgSO_4$ and the solvent evaporated to give the crude β-chloroketone as a brown liquid. This was heated in MeOH (5mL) containing NaOAc (0.5g) for 3hr, after which it was poured onto water (200mL), extracted with EtOAc (3x100mL), dried and the solvent evaporated. Flash chromatography (15% ether in pet. ether) gave the title compound as a yellow oil (0.125g, 42%).

Method 2: A solution of **2(d)** (4.48g, 20mmol) in dry degassed DMF (5mL) was added over 20min to a stirred solution of ferric chloride (7.14g, 44mmol) in dry degassed DMF (10mL) at 0°C under Ar. Work up as in method 1 above gave a pale brown liquid. This was heated at reflux in saturated methanolic NaOAc (20mL) for 3 hr, after which it was poured onto water (200mL), extracted with EtOAc (3x100mL), dried and the solvent evaporated to give the crude product. Flash chromatography (15% ether in pet. ether) gave the title compound as a yellow oil (1.91g, 64%). ν_{max}/cm^{-1} 2923, 1680 (C=O); δ^1H (300MHz; $CDCl_3$) 1.4-1.6 (3H, m), 2.0-2.2 (3H, m), 2.3-2.5 (3H, m, CH_2-6 + CH-4), 4.95 (2H, brt), 5.73 (1H, m, CH-3'), 5.90 (1H, dd, J=2.4Hz, J=10Hz, CH-2), 6.79 (1H, dt, J=1Hz, J=10Hz, CH-3); $\delta^{13}C$ (75.47MHz) 28.3 (CH_2), 30.8 (CH_2), 33.4

(CH_2), 35.1 (C-4), 36.7 (CH_2), 115.2 (C-4'), 128.8 (C-2), 137.6 (C-3'), 154.7 (C-3), 197.65 (C=0); *m/z* (CI, NH_3), Found$[M+NH_4]^+$ 168.1392, $C_{10}H_{18}NO$ requires 168.1388.

4-(*n*-Butyl)-2-cyclohexen-1-one 4(a): Method 1 gave the title compound as a colourless oil (0.164, 44%). ν_{max}/cm^{-1} 2930, 1684; δ^1H (300MHz; C_6D_6) 0.84 (3H, t, J=7Hz, CH_3), 1.30 (6H, m, CH_2), 1.61 (1H, m), 2.04 (1H, m), 2.25-2.42 (3H, m), 5.88 (1H, dd, J=10.1Hz, J=2.2, CH-2), 6.79 (1H, dd, J=10.1Hz, J=2.3Hz, CH-3); $\delta^{13}C$ (75.47MHz) 11.7 (CH_3), 20.4 (C-3'), 26.3 (C-2'), 26.8 (C-1') 32.0 (C-5), 33.8 (C-4), 34.7 (C-6), 126.6 (C-2), 153.1 (C-3), 197.65 (C=O); *m/z* (CI, NH_3), Found$[M+NH_4]^+$ 170.1540, $C_{10}H_{20}ON$ requires 170.1545

4-(*t*-Butyl)-2-cyclohexen-1-one 4(b): Method 1 gave the title compound as a clear colourless oil (0.145g, 48%). ν_{max}/cm^{-1} 2961, 1690, 1471; δ^1H (300MHz; $CDCl_3$) 0.91 (9H, m, tBu), 1.69 (1H, m), 2.0-2.35 (3H, m), 2.45 (1H, m, CH-4), 5.97 (1H, dt, J =10.4Hz, J=1.7Hz), 6.96 (1H, dt, J=10.4Hz, J=1.4Hz, CH-3); $\delta^{13}C$ (75.47MHz) 24.2 (C-5), 27.2 (tBu-CH_3), 32.8 (tBu-C), 37.7 (C-6), 46.7 (C-4), 129.8 (C-2), 152.8 (C-3), 199.9 (C=O); *m/z* (CI,NH_3), Found$[M+NH_4]^+$ 170.1555, $C_{10}H_{20}ON$ requires 170.1545.

4-Allyl-2-cyclohexen-1-one 4(c): Method 1 gave the title compound as a clear oil (0.121g, 45%). ν_{max}/cm^{-1} 2922, 1685 (C=O); δ^1H (300MHz; $CDCl_3$) 1.72 (1H,m), 2.08 (1H,m), 2.19 (2H, t, J=7.2Hz, CH_2-6), 2.35 (1H, m, CH-4), 2.45 (2H, m, CH_2-1'), 5.07 (2H, brd, CH_2-3'), 5.76 (1H, m, CH-2'), 5.94 (1H, brd, J=10.2Hz, CH-2), 6.83 (1H, dd, J=10.2Hz, J=1.4Hz, CH-3); $\delta^{13}C$ (75.47MHz) 28.5 (C-5), 35.7 (C-4), 36.85 (C-1'), 38.8 (C-6), 117.4 (C-3'), 129.2 (C-2), 135.2 (C-2'), 154.05 (C-3), 199.65 (C-1). *m/z* (CI,NH_3), Found$[M+H]^+$ 137.0968, $C_9H_{13}O$ requires 137.0966.

4-Phenyl-2-cyclohexen-1-one 4(e): As for Method 1 except 1g (4.07mmol) of **2(e)** was used to give the title compound as a clear yellow oil (0.37g, 53%). ν_{max}/cm^{-1} 2951, 1685 (C=O); δ^1H (300MHz; $CDCl_3$) 2.05 (1H, m, CH_2-5), 2.36 (1H, m, CH_2-5), 2.54 (2H, m, CH_2-6), 3.72 (1H, m, CH-4), 6.15 (1H, dd, J=10.2Hz, J=2.5Hz, CH-2), 6.97 (1H, dd, J =10Hz, J=2.9Hz, CH-3), 7.19-7.37 (5H, m, Ph); $\delta^{13}C$ (75.47MHz) 32.4 (C-5), 36.9 (C-6), 42.5 (C-4), 127.0, 127.5, 128.8, 129.9 (Ph-H+C-2), 142.7 (C-Ph), 153.0 (CH-3), 199.3 (C=O); *m/z* (CI, NH_3), Found$[M+H]^+$ 173.0961, $C_{12}H_{13}O$ requires 173.0966.

4-Benzyl-2-cyclohexen-1-one 4(f): As for Method 1 except 1.04g (4mmol) of **2(f)** was used to give the title compound as a pale brown oil. (0.456g, 61%). ν_{max}/cm^{-1} 2920, 1679 (C=O), 1495; δ^1H (300MHz; $CDCl_3$) 1.72 (1H, m, CH_2-5), 2.06 (1H, m, CH_2-5), 2.34 (1H, m, CH_2-6), 2.48 (1H, m, CH_2-6), 2.72 (3H, m, benzyl-CH_2+CH-4), 5.96 (1H, dd, J=10Hz, J=1Hz, CH-2), 6.82 (1H, d, J=10.1Hz, CH-3), 7.1-7.3 (5H, m, Ph); $\delta^{13}C$ (75.47MHz) 28.5 (C-5), 36.7 (C-6), 37.9 (C-4), 40.8 (benzyl-CH_2), 126.45, 128.5, 129.0, 129.2 (Ph-H+CH-2), 138.9 (C-Ph), 153.7 (CH-3), 199.6 (C=O). *m/z* (CI, NH_3), Found$[M+NH_3]^+$ 204.1387, $C_{13}H_{18}ON$ requires 204.1388.

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