Supplementary data for *Chem. Commun.*

‘Bismesitylmagnesium: a thermally stable and non-nucleophilic carbon-centred base reagent for the efficient preparation of silyl enol ethers’

William J. Kerr,*[a] Allan J. B Watson[a] and Douglas Hayes[b]

[a]Department of Pure and Applied Chemistry, WESTChem, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, UK

[b]GlaxoSmithKline, Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire, SG1 2NY, UK.

Supporting Information

1. General

1.1. Purification of Reagents

THF and 1,4-dioxane were dried by heating to reflux over sodium wire using benzophenone ketyl as indicator, and then distilled under N_2. Diethyl ether and light petroleum were used as purchased from suppliers without further purification. Light petroleum refers to the fraction of b.p. 30-40^{o}C.

2-Mesitylmagnesium bromide,[1] obtained as a 1 M solution in THF, *n*-butyllithium, obtained as a 2.5 M solution in hexanes, and *tert*-butyllithium, obtained as a 1.7 M solution in pentane, were standardised using salicaldehyde phenylhydrazone as indicator.[2]

Di*iso*propylamine was dried by heating to reflux over calcium hydride and distilling under nitrogen.

Cyclohexanone **1a**, cyclopentanone **1b**, cycloheptanone **1c**, 2-methylcyclohexanone **1d**, 2,6-dimethylcyclohexanone **1e**, 4-methylcyclohexanone **1f**, 4-*n*-propylcyclohexanone **1g**, α-tetralone **1j**, 4-chlorobutyrophenone **1k**, and propiophenone **1l** were dried by heating to reflux over calcium chloride and distilled either under reduced pressure or under nitrogen and stored over 4 Å molecular sieves.

4-*t*-Butylcyclohexanone **1h** and 4-phenylcyclohexanone **1i** were recrystallised twice from dry hexane at 4^{o}C and stored under N_2.

Chlorotrimethylsilane was distilled under N_2 and stored over 4 Å molecular sieves.

1.2. Purification and Analysis of Products

Thin layer chromatography was carried out using Camlab silica plates coated with indicator UV_{254}. These were analysed using a Mineralight UVGL-25 lamp or developed using vanillin. Flash column chromatography was carried out using Prolabo silica gel (230-400 mesh).

Gas chromatography was carried out using a Hewlett Packard 5890 Series 2 Gas Chromatograph fitted with a Varian WCOT Fused Silica Column containing a CP-SIL 19CB coating and using H_2 as carrier gas.

IR spectra were obtained on a Perkin Elmer Spectrum One machine.

^1H and ^{13}C spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in ppm. Coupling constants are reported in Hz and refer to $^3J_{H-H}$ interactions unless otherwise specified.

High resolution mass spectra was obtained using a JEOL JMS-700 high resolution mass spectrometer. The ionization method used was Electron Impact (EI) with PFK perfluorokerosene (PFK) as the reference compound.

2. Experimental Procedures

All reactions were air sensitive and, as such, were carried out using flame dried Schlenk apparatus. Purging refers to an evacuation/nitrogen refilling procedure carried out 3 times.

2.1 Preparation of Bismesitylmagnesium, Mes_2Mg[3,4]

To a solution of MesMgBr (1 M in THF, 100 mmol, 100 mL) under N_2 at room temperature was added 1,4-dioxane (105 mmol, 9.25 g, 8.95 mL) steadily over 5 minutes. The mixture was stirred vigorously for 3 hours before discontinuation of the stirring. The mixture (now a yellow solution with a fine white precipitate) was then left to settle for 72 h. After this time, the precipitate had settled to a thick white layer at the bottom of the Schlenk tube allowing removal of the yellow Mes_2Mg solution *via* cannula to a previously flame-dried and purged pear-shaped flask. Care was taken to avoid withdrawing any of the precipitate. The Mes_2Mg solution was standardised using salicaldehyde phenylhydrazone as indicator before use.[2] The molarity of the Mes_2Mg solution was typically 0.5 M (100% conversion of MesMgBr to Mes_2Mg, yield typically ~90 mL, ~90%).

2.2 Deprotonation of Cyclohexanone (1a) Using Mes_2Mg with an Amine Additive

A flame-dried Schlenk tube was charged with Mes_2Mg (0.5 M solution in THF, 1.1 mmol, 2.2 mL), THF (7.8 mL) and di*iso*propylamine (0.2 mmol, 20 mg, 28 μl). The mixture was stirred for 30 minutes at room temperature before cooling to 0^oC. TMSCl (4 mmol, 435 mg, 0.5 mL) was added and the mixture was stirred for 5 minutes before addition of cyclohexanone (1 mmol, 98 mg, 0.1 mL) as a solution in THF (2 mL) over 1 h *via* syringe pump. The reaction mixture was stirred at 0^oC under N_2 for 16 h before quenching with sat. $NaHCO_3$ aq. solution (10 mL). The mixture was allowed to warm to room temperature before extracting with Et_2O ((1 x 40 mL) + (2 x 25 mL)). The combined organic extracts were dried (Na_2SO_4) and a representative sample was analysed by G.C. to obtain the ketone to silyl enol ether conversion. The solution was then filtered and concentrated *in vacuo* to afford a residue which was purified by column chromatography eluting with 1% Et_2O/petrol to afford 1-trimethylsilyloxycyclohexene **2a** as a colourless oil.

2.3 Deprotonation of Cyclohexanone (1a) Using Mes_2Mg without an Amine Additive

A flame-dried Schlenk tube was charged with Mes_2Mg (0.5 M solution in THF, 1.1 mmol, 2.2 mL) and THF (7.8 mL). The mixture was stirred for 30 minutes at room temperature before cooling to 0^oC. TMSCl (4 mmol, 435 mg, 0.5 mL) was added and the mixture was stirred for 5 minutes before addition of cyclohexanone (1 mmol, 98 mg, 0.1 mL) as a solution in THF (2 mL) over 1 h *via* syringe pump. The reaction mixture was stirred at 0^oC under N_2 for 16 h before quenching with sat. $NaHCO_3$ aq. solution (10 mL). The mixture was allowed to warm to room temperature before extracting with Et_2O ((1 x 40 mL) + (2 x 25 mL)). The combined organic extracts were dried (Na_2SO_4) and a representative sample was analysed by G.C. to obtain the ketone to silyl enol ether conversion. The solution was then filtered and concentrated *in vacuo* to afford a residue which was purified by column chromatography eluting with 1% Et_2O/petrol to afford 1-trimethylsilyloxycyclohexene **2a** as a colourless oil.

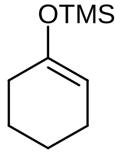
2.4 Deprotonation of Ketones Using Optimised Mes_2Mg Conditions

A Schlenk tube was charged with LiCl (2 mmol, 85 mg) and flame-dried under vacuum. The tube was purged three times with N_2 before cooling to room temperature and charging with Mes_2Mg (0.5 M solution in THF, 0.5 mmol, 1 mL) and THF (9 mL). The mixture was stirred for 15 minutes at room temperature before cooling to 0^oC. TMSCl (1 mmol, 108.64 mg, 0.13 mL) was added and the mixture was stirred for 5 minutes before addition of the ketone (1 mmol) as a solution in THF (2 mL) over 1 h *via* syringe pump. The reaction mixture was stirred at 0^oC under N_2 for 8 h before quenching with sat. $NaHCO_3$ aq. solution (10 mL). The mixture was allowed to warm to room temperature before extracting with Et_2O ((1 x 40 mL) + (2 x 25 mL)). The combined organic extracts were dried (Na_2SO_4) and a representative sample was analysed by G.C. to obtain the ketone to silyl enol ether conversion. The solution was then filtered and concentrated *in vacuo* to afford a residue which was purified by column chromatography eluting with 1% Et_2O/petrol to afford the silyl enol ether product.

3. Product Data

IR and ^1H NMR data for known compounds **2a-2k** followed by IR, ^1H NMR, ^{13}C NMR, and HRMS data for novel compound **2l** are provided.

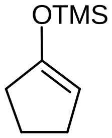
2a: 1-Trimethylsilyloxycyclohexene[5,6,7a,8]



ν_{max} (DCM): 1668 cm^{-1}.

δ_H (400 MHz, $CDCl_3$): 0.18 (s, 9H, $Si(CH_3)_3$), 1.48-1.54 (m, 2H, CH_2), 1.63-1.69 (m, 2H, CH_2), 1.97-2.03 (m, 4H, 2xCH_2), 4.86-4.88 (m, 1H, CH).

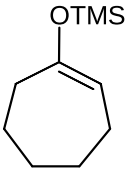
2b: 1-Trimethylsiloxycyclopentene[5,6,7b,9]



ν_{max} (DCM): 1645 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.20 (s, 9H, Si(CH_3)$_3$), 1.82-1.90 (m, 2H, CH_2), 2.24-2.29 (m, 4H, 2xCH_2), 4.62-4.63 (m, 1H, C*H*).

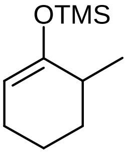
2c: 1-Trimethylsilyloxycycloheptene[10]



ν_{max} (DCM): 1660 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.18 (s, 9H, Si(CH_3)$_3$), 1.50-1.59 (m, 4H, 2xCH_2), 1.66-1.70 (m, 2H, CH_2), 1.97-2.01 (m, 2H, CH_2), 2.22-2.24 (m, 2H, CH_2), 4.86-4.88 (m, 1H, C*H*).

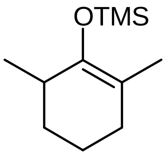
2d: 6-Methyl-1-trimethylsilyloxy-1-cyclohexene[5,6,8]



ν_{max} (DCM): 1660 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.19 (s, 9H, Si(CH_3)$_3$), 1.04 (d, 3H, CH_3, J=7.0 Hz), 1.36-1.41 (m, 1H, C*H*), 1.45-1.49 (m, 1H, C*H*), 1.57-1.59 (m, 1H, C*H*), 1.78-1.82 (m, 1H, C*H*), 1.98-2.02 (m, 2H, CH_2), 2.14-2.15 (m, 1H, C*H*), 4.81 (td, 1H, C*H*, J=3.95, 1.2 Hz).

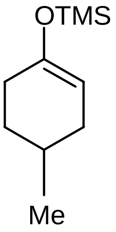
2e: 2,6-Dimethyl-1-trimethylsilyloxy-1-cyclohexene[11-16]



ν_{max} (DCM): 1678 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.19 (s, 9H, Si(CH_3)$_3$), 1.04 (d, 3H, CH_3, J=6.9 Hz), 1.35-1.41 (m, 1H, C*H*), 1.43-1.49 (m, 1H, C*H*), 1.56 (s, 3H, CH_3), 1.58-1.65 (m, 1H, C*H*), 1.75-1.82 (m, 1H, C*H*), 1.95 (t, 2H, C*H*, J=6.2), 2.12-2.14 (m, 1H, C*H*).

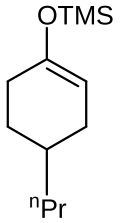
2f: 4-Methyl-1-trimethylsilyloxy-1-cyclohexene[16-18]



ν_{max} (DCM): 1669 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.18 (s, 9H, Si(CH_3)$_3$), 0.95 (d, 3H, CH_3, J=6.3 Hz), 1.29-1.34 (m, 1H, C*H*), 1.62-1.73 (m, 3H, C*H*+CH_2), 1.93-2.00 (m, 1H, C*H*), 2.05-2.09 (m, 2H, CH_2), 4.82-4.83 (m, 1H, C*H*).

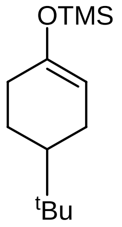
2g: 4-*n*-Propyl-1-trimethylsilyloxy-1-cyclohexene[16]



ν_{max} (DCM): 1670 cm^{-1}.

δ_H (400 MHz, $CDCl_3$): 0.18 (s, 9H, Si(CH_3)$_3$), 0.90 (t, 3H, CH_3, J=7.2 Hz), 1.21-1.37 (m, 5H, C*H*+2xCH_2), 1.44-1.49 (m, 1H, C*H*), 1.63-1.69 (m, 1H, C*H*), 1.72-1.78 (m, 1H, C*H*), 1.93-2.00 (m, 1H, C*H*), 2.05-2.12 (m, 2H, CH_2), 4.82-4.84 (m, 1H, C*H*).

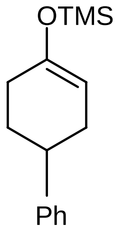
2h: 4-*t*-Butyl-1-trimethylsilyloxy-1-cyclohexene[11,16,18]



ν_{max} (DCM): 1672 cm^{-1}.

δ_H (400 MHz, $CDCl_3$): 0.19 (s, 9H, Si(CH_3)$_3$), 0.90 (s, 9H, 3xCH_3), 1.21-1.29 (m, 2H, CH_2), 1.78-1.85 (m, 2H, CH_2), 1.98-2.09 (m, 3H, C*H*+CH_2), 4.84-4.86 (m, 1H, C*H*).

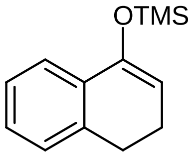
2i: 4-Phenyl-1-trimethylsilyloxy-1-cyclohexene[17,18]



ν_{max} (DCM): 1669 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.24 (s, 9H, Si(CH_3)$_3$), 1.86-1.93 (m, 1H, CH), 1.96-1.99 (m, 1H, CH), 2.06-2.11 (m, 1H, CH), 2.19-2.34 (m, 3H, CH+CH_2), 2.76-2.78 (m, 1H, CH), 4.97-4.98 (m, 1H, CH), 7.19-7.34 (m, 5H, C$_6H_5$).

2j: (3,4-Dihydro-1-naphthyloxy)trimethylsilane[7c,10]

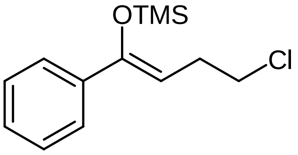


ν_{max} (DCM): 1638 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): 0.38 (s, 9H, Si(CH_3)$_3$), 2.42-2.47 (m, 2H, CH_2), 2.89 (t, 2H, CH_2, J=7.8 Hz), 5.32 (t, 1H, CH, J=4.6 Hz), 7.21-7.36 (m, 3H, 3xArCH), 7.54 (d, 1H, ArCH, J=7.4).

2k: *Z*-4-Chloro-1-phenyl-1-trimethylsilyloxybut-1-ene

Single isomer, tentatively assigned as *Z* on comparison to the spectrum for **2l** (below) and from comparison to references 5, 9, 19, and 20.



ν_{max} (DCM): 1649 cm^{-1}.

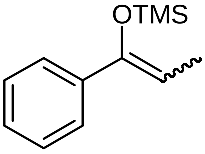
δ_H (400 MHz, CDCl$_3$): 0.15 (s, 9H, Si(C*H*$_3$)$_3$), 2.68 (q, 2H, C*H*$_2$, J=7.1 Hz), 3.59 (t, 2H, C*H*$_2$, J=7.15 Hz), 5.27 (t, 1H, C*H*, J=7.1 Hz), 7.26-7.34 (m, 3H, 3xArC*H*), 7.47 (dd, 2H, 2xAr*H*, J= 6.8, 1.5 Hz).

δ_C (100 MHz, CDCl$_3$): 0.8, 29.9, 44.4, 106.6, 125.8, 128.1, 128.3, 138.9, 151.6.

HRMS: *m/z* calculated for $C_{13}H_{19}ClOSi$: ^{35}Cl 254.0894 ^{37}Cl 256.0864

Found: ^{35}Cl 254.0890 ^{37}Cl 256.0839

2l: 1-Phenyl-1-silyloxyprop-1-ene[5,9,19,20]



ν_{max} (DCM): 1686, 1652 cm^{-1}.

δ_H (400 MHz, CDCl$_3$): *Z*-isomer: 0.17 (s, 9H, Si(C*H*$_3$)$_3$), 1.76 (d, 3H, C*H*$_3$, J=6.9 Hz), 5.35 (q, 1H, C*H*, J=6.9 Hz), 7.23-7.49 (m, 5H, 5xArC*H*); *E*-isomer: 0.15 (s, 9H, Si(C*H*$_3$)$_3$), 1.73 (d, 3H, C*H*$_3$, J=7.3 Hz), 5.13 (q, 1H, C*H*, J=7.3 Hz), 7.23-7.49 (m, 5H, 5xArC*H*).

4. References

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