



Study of the reaction of 1,1-bis(trimethylsilyl)-2-phenylethylene with some acyl chlorides in the presence of AlCl_3

Kazem D. Safa *, Soleiman Paymard Samani, Shahin Tofangdarzadeh, Akbar Hassanpour

Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran

ARTICLE INFO

Article history:

Received 30 January 2008

Received in revised form 27 February 2008

Accepted 29 February 2008

Available online 5 March 2008

Keywords:

Tris(trimethylsilyl)methane

Peterson olefination

1,1-Bis(trimethylsilyl)-2-phenylethylene

Friedel–Crafts reaction

ABSTRACT

1,1-Bis(trimethylsilyl)-2-phenylethylene (**1**), which has been synthesized from the Peterson reaction between $(\text{Me}_3\text{Si})_3\text{CH}$ and benzaldehyde, reacts with various acyl chlorides (RCOCl , $\text{R} = \text{Me}$, Et , *iso*-Pr, *n*-Bu, *iso*-Bu, *iso*-C₅H₁₁, PhCH₂, PhCH₂CH₂) in the presence of AlCl_3 to give α -silyl- α,β -unsaturated enones **3a–3h** with high *E* stereoselectivity along with *trans*- α,β -unsaturated ketones **4a–4h**. The enones **3** can be partially converted into the ketones **4** with an excess of AlCl_3 . Reaction of **1** with RCOCl , ($\text{R} = \text{Ph}$, $\text{CH}_3\text{CH}=\text{CH}$) afforded only the ketones **4**. Yields were dependent on time and the amounts of AlCl_3 used.

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1. Introduction

Vinylsilanes have recently found extensive use in organic synthesis; notably their electrophilic chemistry has attracted attention. The addition of an electrophile to a vinylsilane results in the build-up of electrophilic character β in the carbon–silicon bond [1–5]. α -Silyl- α,β -unsaturated enones have become important for the synthesis of α -halo- α,β -unsaturated ketones and their derivatives. The preparation of α -silyl- α,β -unsaturated enones by Zr-promoted ene-yne cyclization–carbonylation [6], Pd-catalyzed acylation of α -silylalkenylmetals [7], and the Grignard reaction of vinylsilanes with carbonyl compounds [8], have been studied. However, these methods show poor selectivity and require expensive reagents. Here, we present a convenient and stereoselective route for the synthesis of α -silyl- α,β -unsaturated enones from 1,1-bis(trimethylsilyl)-2-phenylethylene. We have found that the reaction is highly sensitive to time and the amount of AlCl_3 used.

2. Results and discussion

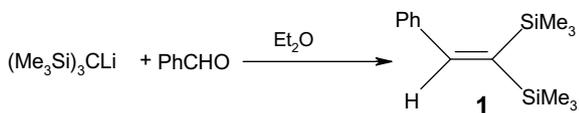
The use of silicon-based reagents to accomplish carbon–carbon bond-forming reactions is a part of our recent research on the development of organosilicon reagents for synthesis [9–14]. We decided to investigate the reaction of 1,1-bis(trimethylsilyl)-2-

phenylethylene (**1**), with various readily available acyl chlorides. This investigation led to a novel route for the synthesis of new α -silyl- α,β -unsaturated enones. The precursor for our work was tris(trimethylsilyl)methane, $(\text{Me}_3\text{Si})_3\text{CH}$, prepared from the reaction between CHCl_3 , Li and Me_3SiCl in THF. The solvated organolithium reagent, $(\text{Me}_3\text{Si})_3\text{CHLi}$, which was obtained by treatment of $(\text{Me}_3\text{Si})_3\text{CH}$ with MeLi under reflux [15], reacts with benzaldehyde in Et₂O to give **1** (Scheme 1) [15,16].

Initially we studied the reaction of the bis(trimethylsilyl)alkene **1** with *iso*-butyryl chloride (**2c**) in the presence of AlCl_3 in CH_2Cl_2 at 0 °C to give the related α -silyl- α,β -unsaturated enone **3c** along with the undesired α,β -unsaturated ketone **4c** (Scheme 2). In order to optimize conditions for the formation of **3c**, we decided to investigate the reaction of **2c** (4 mmol) with various amounts of AlCl_3 . When 18 mequiv. of AlCl_3 was used with a reaction time of 1 h, the major product was the α -silyl- α,β -unsaturated enone **3c**, but it was the α,β -unsaturated ketone **4c** when 36 mequiv. of AlCl_3 was used with a reaction time of 3 h. Table 1 shows that the ratio of **4c/3c** increased with prolongation of the reaction time (from 60 min to 150 min). Moreover we found that when the purified product **3c** reacts with AlCl_3 under the same conditions, it is partially converted into **4c** (Scheme 2). Consequently, the present method can also provide a synthesis of α,β -unsaturated ketones.

It has previously been shown that Friedel–Crafts reactions of vinylsilanes often lead to both addition and substitution products [17,18], but in the case of the bis(trimethylsilyl)alkene **1** because of steric hindrance, only substitution products have been obtained.

* Corresponding author. Tel.: +98 411 3393124; fax: +98 411 3340191.
E-mail address: dsafa@tabrizu.ac.ir (K.D. Safa).



Scheme 1. Preparation of 1,1-bis(trimethylsilyl)-2-phenylethylene via Peterson olefination.

The plausible mechanism for this reaction is depicted in **Scheme 3**. The initial step is the coordination of the acyl chloride to the Lewis acid to give complex **5**, which can be served as an electrophile. The carbocation intermediate **6** can be stabilized with Me_3Si groups (Si β -effect). Finally, it loses a SiMe_3Cl to give an alkene **3**.

Following our study on the synthesis of α -silyl- α,β -unsaturated enones (**3**), the optimum conditions (**Table 1**, entry 2, $\text{AlCl}_3/\text{RCOCl} = 1.5$, 60 min and room temperature) have been used for reactions with various acyl chlorides (RCOCl , $\text{R} = \text{Me}$, Et , Bu , iso-Bu , $n\text{-C}_5\text{H}_{11}$, PhCH_2 , PhCH_2CH_2) to give the related α -silyl- α,β -unsaturated enones **3a–3h** along with the undesired α,β -unsaturated ketones **4a–4h** (**Table 2**).

As seen in **Table 2**, the reactions show high stereoselectivity (higher than that reported for alternative methods [6–8]) to provide only *E* stereoisomers. The values of the chemical shifts and coupling constants $^3J_{\text{HH}}$ of the vinylic protons show that all the α,β -unsaturated ketones **4** reported here have *trans* stereochemistry. These results can be explained simply by considering the differences in the size of the various groups that are attached to $\text{C}=\text{C}$ bonds. We also studied the reaction of **1** with benzoyl and crotonyl chloride but all attempts to isolate α -silyl- α,β -unsaturated enones were unsuccessful. Whatever the conditions, only **4i** and **4j** were detected (**Scheme 4**).

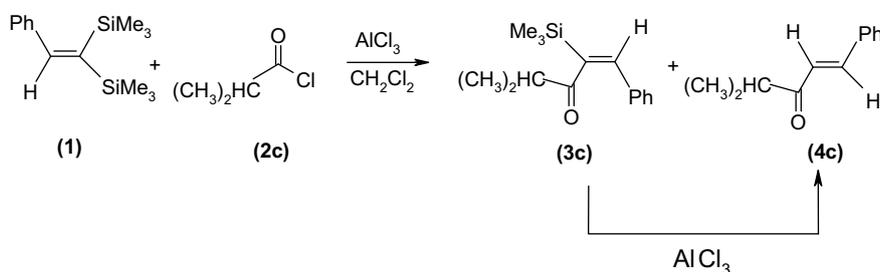
3. Conclusion

Although several methods are available for the preparation of α -silyl- α,β -unsaturated enones, we believe the present method offers considerable advantages in terms of simplicity, high stereoselectivity and mild conditions. Moreover, we found that under suitable conditions, this method provides a route to *trans*- α,β -unsaturated ketones.

4. Experimental

4.1. Solvents and reagents

The reactions were carried out under dry argon. Solvents were dried by standard methods. Substrates for the preparation of tris(trimethylsilyl)methyl lithium, viz. Me_3SiCl (Merck), Li (Merck), CHCl_3 (Merck), and PhCOH (Merck) were used as received. All acyl chlorides were purchased from Merck and distilled before use. AlCl_3 was used after sublimation.



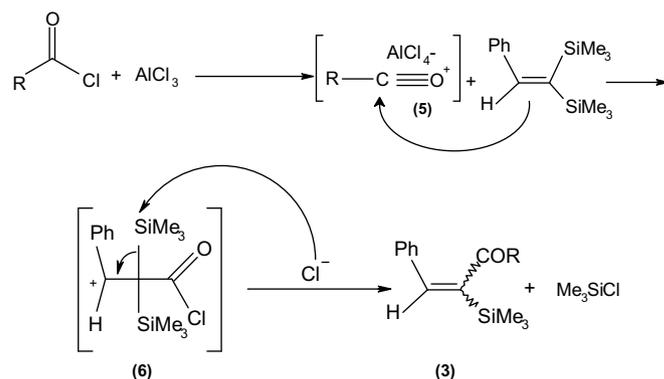
Scheme 2. AlCl_3 mediated reactions of **1** with *iso*-butryl chloride.

Table 1

The effect of time and amount of AlCl_3 on the reaction of 4 mmol **2c** with 4 mmol **1**

Entry	Time (min)	$\text{AlCl}_3/\text{RCOCl}$	3c (%) ^a	4c (%) ^a	Ratio 4c/3c
1	30	1.5	35	20	0.57
		3	45	30	0.67
2	60	1.5	62	30	0.48
		3	50	45	0.9
3	90	1.5	55	40	0.73
		3	45	50	1.1
4	120	1.5	49	47	0.96
		3	40	57	1.43
5	180	1.5	38	58	1.53
		3	30	68	2.27

^a Yields calculated by GC–mass spectrometry.



Scheme 3. Plausible mechanism for the preparation of α -silyl- α,β -unsaturated enones.

4.2. Spectra

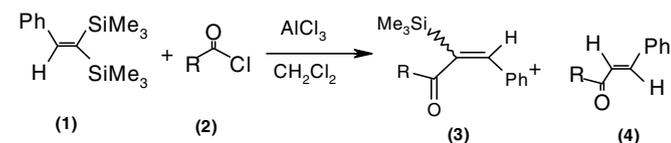
The ^1H NMR and ^{13}C NMR were recorded with a Bruker FT-400 MHz spectrometer at room temperature and CDCl_3 as a solvent. The mass spectra were obtained with a GC-Mass Agilent, quadrupole mode 5973N instrument, operating at 70 eV. The FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with an Elementar vario EL III instrument.

4.3. Preparation of tris(trimethylsilyl)methyl lithium, $(\text{Me}_3\text{Si})_3\text{CLi}$, in THF

The reagent was prepared as described by Eaborn and co-workers [14] and consisted typically of a solution of 5 mmol $(\text{Me}_3\text{Si})_3\text{CLi}$ in 25 ml of THF, with 4 ml of Et_2O always present from the MeLi used in its preparation.

Table 2

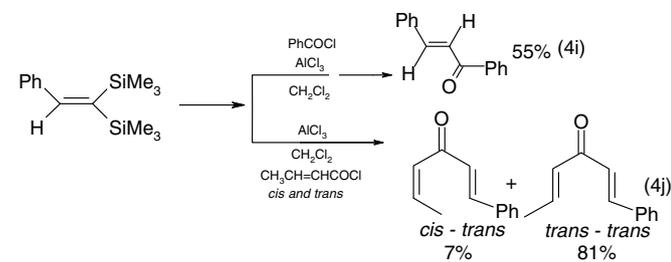
The Friedel–Crafts reaction of 4 mmol **1** with 4 mmol **2b–2h** in the presence of 18 mequiv.^a AlCl₃(AlCl₃/RCOCl = 1.5) during 60 min^b



RCOCl	R	3(%) ^b		4(%)
		E	Z	
2a	Me	61	–	30
2b	Et	50	–	20
2c	iso-Pr	62	–	30
2d	iso-But	53	3	42
2e	n-But	61	–	38
2f	n-Pen	60	4	31
2g	Ph-CH ₂	50	–	20
2h	Ph-CH ₂ -CH ₂	58	–	15

^a mequiv. means milliequivalent.

^b As explained in text, this condition was the optimized condition for preparation of **3**.



Scheme 4. Reaction of **1** with benzoyl and crotonyl chloride in the presence of AlCl₃.

4.4. General procedure

A solution of 1,1-bis(trimethylsilyl)-2-phenylethylene (**1**) [16] (1.00 g, 4.03 mmol) in dry CH₂Cl₂ (20 ml) was added during 15 min at 0 °C under argon to a stirred solution of anhydrous aluminum trichloride (0.8 g, 18 mequiv.) in dry CH₂Cl₂ (30 ml) containing acyl chloride (4.03 mmol), and the mixture was stirred at 0 °C for a further 45 min. The reaction was added to water (50 ml) then the organic layer was separated and the aqueous layer was extracted twice with 50 ml Et₂O. The combined extracts were dried over anhydrous sodium sulfate and filtered. The solvent was evaporated from the filtrate and the residue separated by preparative TLC (silica gel) to give the products.

4.4.1. Reaction of **1** with CH₃COCl (**2a**)

For the reaction with **2b** (0.32 g). TLC on silica gel (8:1 *n*-hexane:diethyl ether as eluant) gave **3b** (*R*_f = 0.60) and **4b** (*R*_f = 0.30, m.p. 39 °C). **3b**: FTIR (KBr, cm⁻¹): 3062 (Ar–H), 1676 (C=O), 1676, 1491 (Ph), 1587 (C=C), 1252, 843 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.23 (s, 9H, SiMe₃), 2.06 (s, 3H, CH₃), 6.80 (s, 1H, vinyl), 7.28–7.30 (m, 5H, Ar); ¹³C NMR (CDCl₃): δ –2.6 (SiMe₃), 30.1 (CH₃), 127.0–149.3 (Ph and C=C), 209.6 (C=O); *m/z* (EI): 218 (35%, [M]⁺), 203 (100%, [M–Me]⁺), 145 (6%, [M–SiMe₃]⁺), 129 (41%, [PhC=CCO]⁺), 73 (40%, [SiMe₃]⁺). Anal. Calc. for C₁₃H₁₈SiO: C, 71.5; H, 8.2. Found: C, 71.9; H, 8.5%. **4b**: FTIR (KBr, cm⁻¹): 3033 (Ar–H),

1682 (C=O), 1580 (C=C); ¹H NMR (400 MHz, CDCl₃): δ 2.37 (s, 3H, CH₃), 6.71 (d, 1H, *J* = 16 Hz, PhHC=CH), 7.38–7.59 (m, 6H, PhHC=CH and Ar); ¹³C NMR (CDCl₃): δ 26.5 (CH₃), 126.1–142.4 (Ph and C=C), 197.4 (C=O).

4.4.2. Reaction of **1** with C₂H₅COCl (**2b**)

From the reaction of propionyl chloride (0.38 g) with **1** (1.00 g, 4.03 mmol) TLC on silica gel (4:1 *n*-hexane:diethyl ether) gave products **3c** (*R*_f = 0.54) and **4c** (*R*_f = 0.27, m.p. 38 °C). **3c**: FTIR (KBr, cm⁻¹): 3062 (Ar–H), 1676 (C=O), 1676, 1491 (Ph), 1598 (C=C), 1251, 843 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.22 (s, 9H, Si(CH₃)₃), 0.97 (t, 3H, ³*J*_{HH} = 7 Hz, CH₃), 2.25–2.30 (q, 2H, CH₂), 6.82 (s, 1H, vinyl), 7.24–7.31 (m, 5H, Ar); ¹³C NMR (CDCl₃): δ –2.5 (Si(CH₃)₃), 7.0 (CH₃), 35.4 (CH₂), 127.3–149.2 (Ph, C=C), 212.16 (C=O); *m/z* (EI): 218 (11%, [M–Me]⁺), 203 (100%, [M–Et]⁺), 128 (11%, [PhC=CCO]⁺), 73 (33%, [Si(CH₃)₃]⁺). Anal. Calc. for C₁₄H₂₀SiO: C, 72.4; H, 8.6. Found: C, 72.3; H, 8.6%. **4c**: FTIR (KBr, cm⁻¹): 3032 (Ar–H), 1681 (C=O), 1613, 1490 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 1.17 (t, 3H, ³*J*_{HH} = 7 Hz, CH₃), 2.67–2.71 (q, 2H, CH₂), 6.75 (d, 1H, ³*J*_{HH} = 16 Hz, PhHC=CH), 7.37–7.58 (m, 6H, PhHC=CH and Ar); ¹³C NMR (CDCl₃): δ 7.2 (CH₃), 33.0 (CH₂), 125.0–141.2 (Ph, C=C), 199.9 (C=O).

4.4.3. Reaction of **1** with iso-C₃H₇ (**2c**)

From the reaction of **2a** (0.43 g) with **1** (1.00 g, 4.03 mmol) liquid products **3a** (*R*_f = 0.54) and **4a** (*R*_f = 0.27) were obtained by TLC on silica gel (4:1 *n*-hexane:diethyl ether). **3c**: FTIR (KBr, cm⁻¹): 3139 (Ar–H), 1670 (C=O), 1670, 1457 (Ph), 1581 (C=C), 1251, 842 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.35 (s, 9H, Si(CH₃)₃), 1.08 (d, 6H, ³*J*_{HH} = 7 Hz, CH(CH₃)₂), 2.49–2.60 (m, 1H, CH(CH₃)₂), 7.08 (s, 1H, vinyl), 7.33–7.46 (m, 5H, Ar); ¹³C NMR (CDCl₃): δ –1.9 (Si(CH₃)₃), 17.6 (CH(CH₃)₂), 39.7 (CH(CH₃)₂), 127.0–148.7 (Ph, C=C), 214.9 (C=O); *m/z* (EI): 231 (6%, [M–CH₃]⁺), 203 (100%, [M–CH(CH₃)₂]⁺), 129 (6%, [PhC=CCO]⁺), 73 (41%, [Si(CH₃)₃]⁺). Anal. Calc. for C₁₅H₂₂SiO: C, 73.1; H, 8.9. Found: C, 73.2; H, 8.5%.

4a: FTIR (KBr, cm⁻¹): 3031 (Ar–H), 1680 (C=O), 1612, 1457 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 1.19 (d, 6H, ³*J*_{HH} = 7 Hz, CH(CH₃)₂), 2.89–2.98 (m, 1H, CH(CH₃)₂), 6.82 (d, 1H, ³*J*_{HH} = 16 Hz, PhHC=CH), 7.38–7.63 (m, 6H, PhHC=CH and Ar); ¹³C NMR (CDCl₃): δ 17.5 (CH(CH₃)₂), 38.3 (CH(CH₃)₂), 123.4–141.4 (Ph, C=C), 202.79 (C=O).

4.4.4. Reaction of **1** with C₄H₉COCl (**2d**)

The reaction of **2d** (0.49 g) with **1** (1.00 g, 4.03 mmol) followed by TLC on silica gel (8:1 *n*-hexane:diethyl ether) gave products **3d** (*R*_f = 0.54) and **4d** (*R*_f = 0.27, m.p. 34–36 °C). **3d**: FTIR (KBr, cm⁻¹): 3062, 3018 (Ar–H), 1674 (C=O), 1597, 1482 (Ph), 1251, 843 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.21 (s, 9H, SiMe₃), 0.78 (t, 3H, ³*J*_{HH} = 4 Hz, CH₃), 1.19–1.23 (m, 2H, CH₂–CH₃), 1.44–1.52 (q, 2H, CH₂–CH₂–CH₃), 2.26 (t, 2H, ³*J*_{HH} = 7 Hz, CO–CH₂), 6.82 (s, 1H, PhHC=C), 7.22–7.34 (m, 5H, Ar); ¹³C NMR (CDCl₃): δ –2.5 (Si(CH₃)₃), 12.8 (CH₃), 21.0 (CH₂–CH₃), 24.7 (CH₂–CH₂–CH₃), 41.8 (CO–CH₂), 127.3–149.3 (Ph, C=C), 211.5 (C=O); *m/z* (EI): 260 (5%, [M]⁺), 245 (7.6%, [M–Me]⁺), 203 (100%, [M–(CH₂)₃CH₃]⁺), 128 (7%, [PhC=CCO]⁺), 73 (38%, [Si(CH₃)₃]⁺). Anal. Calc. for C₁₆H₂₄SiO: C, 73.8; H, 9.2. Found: C, 73.5; H, 9.0%. **4d**: FTIR (KBr, cm⁻¹): 3049, 3025 (Ar–H), 1653 (C=O), 1653, 1495 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 0.94 (t, 3H, ³*J*_{HH} = 7 Hz, CH₃), 1.33–1.43 (m, 2H, CH₂–CH₂–CH₃), 1.62–1.70 (q, 2H, CH₂–CH₂–CH₃), 2.66 (t, 2H, ³*J*_{HH} = 8 Hz, CO–CH₂–CH₂), 6.73 (d, 1H, ³*J*_{HH} = 16 Hz, PhHC=CH), 7.36–7.56 (m, 6H, PhHC=CH, Ar); ¹³C NMR (CDCl₃): δ 12.8 (CH₃), 21.4 (CH₂–CH₃), 25.4 (CH₂–CH₂–CH₃), 39.6 (CO–CH₂), 125.1–141.2 (Ph, C=C), 199.6 (C=O).

4.5.5. Reaction of **1** with iso-C₄H₉COCl (**2e**)

The reaction between **2e** (0.49 g) and **1** (1.00 g, 4.03 mmol) gave liquid products **3e** ($R_f = 0.54$) and **4e** ($R_f = 0.27$), separated by TLC on silica gel (8:1 *n*-hexane:diethylether). **3e**: FTIR (KBr, cm⁻¹): 3062, 3020 (C–H Ar), 1674 (C=O), 1674, 1458 (Ph), 1251, 842 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.22 (s, 9H, Si(CH₃)₃), 0.81 (d, H, ³J_{HH} = 6 Hz, CH(CH₃)₂), 2.06–2.12 (m, 1H, CH₂CH(CH₃)₂), 2.17 (d, 2H, ³J_{HH} = 6 Hz, COCH₂CH(CH₃)₂), 6.81 (s, 1H, PhHC=C), 7.23–7.35 (m, 5H, Ar); ¹³C NMR (CDCl₃): δ –2.4 (Si(CH₃)₃), 21.6 (CH(CH₃)₂), 22.3 (CH(CH₃)₂), 50.6 (CH₂CH(CH₃)₂), 127.3–149.3 (Ph, C=C), 210.5 (C=O); *m/z* (EI): 260 (23%, [M]⁺), 245 (69%, [M–Me]⁺), 218 (38%, [M–CH(CH₃)₂]⁺), 203 (100%, [M–CH₂CH(CH₃)₂]⁺), 128 (20%, [PhC=CO]⁺), 73 (92%, [SiMe₃]⁺). Anal. Calc. for C₁₆H₂₄SiO: C, 73.8; H, 9.2. Found: 73.6; H, 8.9%. **4e**: FTIR (KBr, cm⁻¹): 3032 (C–H Ar), 1682 (C=O), 1659, 1494 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 0.98 (d, 6H, ³J_{HH} = 7 Hz, CH(CH₃)₂), 2.20–2.27 (m, 1H, CH₂CH(CH₃)₂), 2.53 (d, 2H, ³J_{HH} = 7 Hz, CH₂CH(CH₃)₂), 6.73 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH), 7.37–7.56 (m, 6H, PhHC=CH, Ar); ¹³C NMR (CDCl₃): δ 21.6 (CH(CH₃)₂), 24.1 (CH(CH₃)₂), 48.8 (CH₂CH(CH₃)₂), 125.5–141.3 (Ph, C=C), 199.3 (C=O).

4.5.6. Reaction of **1** with C₅H₁₁COCl (**2f**)

The reaction of **1** (1.00 g, 4.03 mmol) with 0.54 g of **2f** followed by TLC on silica gel (4:1 *n*-hexane:diethyl ether) gave products **3f** ($R_f = 0.54$) and **4f** ($R_f = 0.27$, m.p. 36–38 °C). **3f**: FTIR (KBr, cm⁻¹): 3054 (Ar–H), 1657 (C=O), 1650, 1490 (Ph), 1251, 843 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.21 (s, 9H, Si(CH₃)₃), 0.81 (t, 3H, ³J_{HH} = 7 Hz, CH₂CH₃), 1.11–1.22 (m, 4H, CH₂CH₂CH₃), 1.46–1.53 (q, 2H, COCH₂CH₂CH₃), 2.25 (t, 2H, ³J_{HH} = 8 Hz, COCH₂CH₂), 6.816 (s, 1H, vinyl), 7.24–7.30 (m, 5H, Ar); ¹³C NMR (CDCl₃): δ –2.5 (Si(CH₃)₃), 12.8 (CH₂CH₃), 21.3 (CH₂–CH₃), 30.1 (CH₂–CH₂–CH₃), 42.0 (COCH₂CH₂), 52.4 (CO–CH₂), 127.0–149.3 (Ph, C=C), 211.6 (C=O); *m/z* (EI): 274 (5%, [M]⁺), 259 (8%, [M–Me]⁺), 218 (6%, [M–(CH₂)₃CH₃]⁺), 203 (100%, [M–(CH₂)₄CH₃]⁺), 73 (30%, [SiMe₃]⁺). Anal. Calc. for C₁₇H₂₆SiO: C, 74.4; H, 9.4. Found: C, 74.8; H, 9.0%. **4f**: FTIR (KBr, cm⁻¹): 3054, 3024 (Ar–H), 1657 (C=O), 1657, 1496 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 0.90 (t, 3H, ³J_{HH} = 7 Hz, CH₂CH₃), 1.31–1.38 (m, 4H, CH₂CH₂CH₃), 1.65–1.72 (q, 2H, COCH₂CH₂CH₃), 2.66 (t, 2H, ³J_{HH} = 8 Hz, COCH₂CH₂), 6.74 (d, 1H, ³J_{HH} = 16 Hz, PhHC=C), 7.37–7.57 (m, 6H, PhHC=CH, Ar); ¹³C NMR (CDCl₃): δ 12.9 (CH₃), 21.5 (CH₂–CH₃), 23.0 (CH₂–CH₂–CH₃), 30.5 (COCH₂CH₂), 39.9 (CO–CH₂), 125.2–141.2 (Ph, C=C), 199.7 (C=O).

4.5.7. Reaction of **1** with PhCH₂COCl (**2g**)

The reaction **1** (1.00 g, 4.03 mmol) with **2g** (0.62 g) followed by TLC on silica gel (4:1 *n*-hexane:diethyl ether) gave products **3g** ($R_f = 0.6$) and **4g** ($R_f = 0.3$, m.p. 68–71 °C). Spectroscopic data for **3g**: FTIR (KBr, cm⁻¹): 3063, 3029 (Ar–H), 1677 (C=O), 1677, 1493 (Ph), 1254, 843 (Si–Me₃); ¹H NMR (400 MHz, CDCl₃): δ 0.12 (s, 9H, Si(CH₃)₃), 3.55 (s, 2H, CH₂), 6.96 (s, 1H, vinyl), 7.01–7.37 (m, 10H, Ar); ¹³C NMR (CDCl₃): δ –2.6 (Si(CH₃)₃), 49.1 (CH₂), 125.7–148.8 (Ph, C=C), 207.9 (C=O); *m/z* (EI): 294 (7%, [M]⁺), 279 (8%, [M–CH₃]⁺), 203 (100%, [M–CH₂Ph]⁺), 73 (50%, [Si(Me)₃]⁺). Anal. Calc. for C₁₉H₂₂SiO: C, 77.5; H, 7.4. Found: C, 77.3; H, 7.5%.

4g: FTIR (KBr, cm⁻¹): 3023 (Ar–H), 1659 (C=O), 1659, 1488 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 3.95 (s, 2H, CH₂), 6.79 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH), 7.27–7.53 (m, 10H, Ar), 7.64 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH); ¹³C NMR (CDCl₃): δ 47.37 (CH₂), 124.1–149.4 (Ph, C=C), 196.3 (C=O).

4.5.8. Reaction of **1** with PhCH₂CH₂Cl (**2h**)

The reaction of **2h** (0.68 g) with **1** (1.00 g, 4.03 mmol) gave after TLC on silica gel (3:2 *n*-hexane:diethyl ether) **3h** ($R_f = 0.6$) and **4h** ($R_f = 0.35$). **3h**: FTIR (KBr, cm⁻¹): 3063, 3029 (Ar–H), 1679 (C=O),

1679, 1493 (Ph), 1252, 843 (Si–CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.13 (s, 9H, Si(CH₃)₃), 2.54 (t, 2H, ³J_{HH} = 7 Hz, CH₂CH₂Ph), 3.55 (t, 2H, ³J_{HH} = 7 Hz, CH₂CH₂Ph), 6.97 (s, 1H, vinyl), 7.01–7.36 (m, 10H, Ar); ¹³C NMR (CDCl₃): δ –2.6 (Si(CH₃)₃), 29.1 (CH₂Ph), 41.4 (CH₂CH₂Ph), 125.1–141.7 (Ph, C=C), 198.3 (C=O); *m/z* (EI): 307 (7.7%, [M–1]⁺), 231 (100%, [M–Ph]⁺), 158 (55%, [PhHC=CCOCH₂CH₂]⁺), 73 (84%, [SiMe₃]⁺). Anal. Calc. for C₂₀H₂₄SiO: C, 77.9; H, 7.7. Found: C, 77.9; H, 7.7%. **4h**: FTIR (KBr, cm⁻¹): 3065, 3036 (Ar–H), 1712 (C=O), 1602, 1465 (Ph); ¹H NMR (400 MHz, CDCl₃): 2.67 (t, 2H, ³J_{HH} = 7 Hz, CH₂CH₂Ph), 3.13 (t, 2H, ³J_{HH} = 7 Hz, CH₂CH₂Ph), 6.79 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH), 7.27–7.53 (m, 10H, Ar), 7.63 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH); ¹³C NMR (CDCl₃): δ 24.7 (CH₂Ph), 35.1 (CH₂CH₂Ph), 124.1–149.3 (Ph, C=C), 196.2 (C=O).

4.5.9. Reaction of **1** with benzoyl chloride (**2i**)

The reaction of **2i** (0.56 g) with **1** (1.00 g, 4.03 mmol) gave a single solid product **4i** (m.p. 56–57 °C) isolated by preparative TLC (silica gel; 3:2 *n*-hexane:diethyl ether, $R_f = 0.4$), FTIR (KBr, cm⁻¹): 3060 (Ar–H), 1661 (C=O), 1605, 1495 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 7.39–8.04 (m, 12H, Ar and vinyl); ¹³C NMR (CDCl₃): δ 121.1–143.8 (Ph, C=C), 191.1 (C=O).

4.5.10. Reaction of **1** with PhCH₂CH₂COCl (**2j**)

To a stirred mixture of **2j** (0.42 g) and AlCl₃ (0.8 g) was added drop wise **1** (1.00 g, 4.03 mmol) according to the general procedure A yellow product **4j** was obtained by TLC (silica gel; 4:1 *n*-hexane:diethyl ether, $R_f = 0.6$). FTIR (KBr, cm⁻¹): 3031 (Ar–H), 1666 (C=O), 1624, 1494 (Ph), 1605 (C=C); ¹H NMR (400 MHz, CDCl₃): δ 1.96–1.98 (dd, 3H, ³J_{HH} = 7, 1 Hz, CH₃), 6.44–6.49 (qq, 1H, ³J_{HH} = 16 Hz, CH₃HC=CH), 6.97 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH), 6.98–7.07 (m, 1H, CH₃HC=CH), 7.37–7.59 (m, 5H, Ph), 7.63 (d, 1H, ³J_{HH} = 16 Hz, PhHC=CH); ¹³C NMR (CDCl₃): δ 17.4 (CH₃), 123.7–142.4 (Ph, C=C), 188.1 (C=O). GC–mass spectrometric analysis of the crude product indicated that both *trans–trans* and *cis–trans* stereoisomer were formed, but only *trans–trans* isomer was isolated by TLC.

Acknowledgement

We thank Dr. J. D. Smith for his helpful comments.

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