# *Notes*

## A New Version of the Peterson Olefination

Moncef Bellassoued* and Nicolas Ozanne

*Laboratoire de Synthèse Organométallique associé au CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, Tour 45, 75252 Paris, Cedex 05, France*

*Received April 25, 1995*

One of the most frequently used methods for the conversion of carbonyl compounds into olefins is the Peterson olefination.[1] Conceptually, it involves the reaction of an α-lithio silane with a carbonyl compound to form a β-hydroxy silane, followed by a basic or acidic elimination to give the corresponding alkene (Scheme 1).

We[2] and others[3] have reported on a modification of this olefination reaction using bis(trimethylsilyl) methyl derivatives and fluoride ion or zinc bromide as catalysts in THF or methylene chloride. Recently,[4] we have shown that CsF−DMSO combination was very efficient for one-pot conversion of aldehydes into (2*E*,4*E*) dienals using γ-trimethylsilyl crotonaldimine.

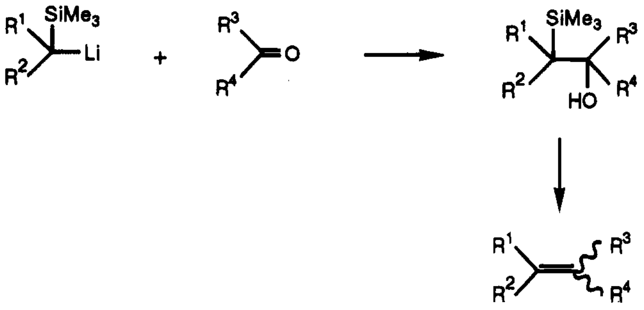
We thought that this combination could be utilized for a new simplified version of the Peterson olefination; the monosilylated reagent **1** would be added to aldehyde in the presence of a catalytic amount of CsF in DMSO to give the adduct **2** (step 1). Subsequent elimination of "$Me_3SiOH$" would give the corresponding alkene **3** (step 2) (Scheme 2).

With this idea in mind, α-(trimethylsilyl)acetate **1a** was added to benzaldehyde in the presence of catalytic CsF (10%) in DMSO at room temperature. After 35 min, β-siloxyacetate **2a** was isolated in 91% yield.[5] Heating **2a** with the same catalyst at 100 °C for 1 h led to the formation of the cinnamic ester **3a** in 93% yield with excellent (*E*) stereoselectivity (>98%) ( Scheme 3).

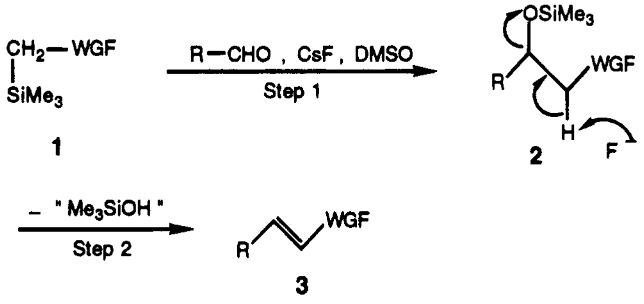
It is noteworthy that the nature of the solvent and the source of the fluoride were essential for this condensation−elimination process. Thus, for example, the formation of compound **2** was very slow in THF; furthermore, no product resulting from elimination was detected even after several hours at reflux. In sharp contrast to these latter results, the reaction was very rapid (5 min) and exothermic (20 °C → 65 °C) with tetrabutylammonium fluoride (TBAF) in DMSO. Unfortunately, a mixture of cinnamic ester and β-hydroxyacetate was obtained. The solution of TBAF (1.0 M in THF, available from Aldrich Chemical Co. Ltd.) contained water, which probably accounted for the formation of the hydroxy ester which could not undergo subsequent elimination of "$Me_3SiOH$". CsF in DMF also gave good results.

Prompted by the excellent results obtained with **1a**, we have examined the generalization of this new olefination method to other monosilylated derivatives. The results are summarized in Table 1.

**Scheme 1**

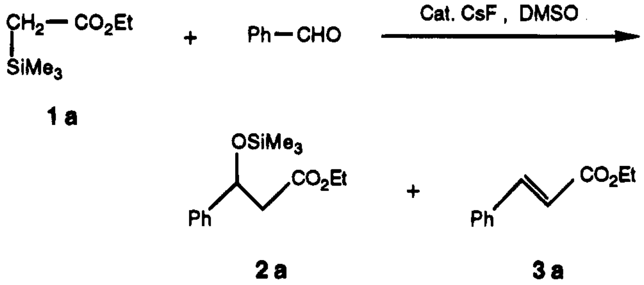


**Scheme 2**



WGF : Withdrawing General Function

**Scheme 3**



| | 2 a | 3 a |
|---|---|---|
| rt , 35 min | 91 % | traces |
| rt, 35 min then 100°C, 1h | 0 % | 93 % |

The above results illustrate the efficacy of the reaction with aromatic and heteroaromatic as well as α,β-unsaturated aldehydes. Interestingly, trimethyl acetaldehyde (entry 3) gave the corresponding alkene in fairly good yield (65%). Unfortunately, with enolizable aldehydes, the alkenes were obtained, accompanied by the self-condensation compounds (entry 6).

In conclusion, anhydrous CsF in DMSO has proven to be the catalyst of choice for the addition−elimination reaction of monosilylated reagents to nonenolizable aldehydes. Starting from trimethylsilyl *N*-*tert*-butylimines, this new simplified version of the Peterson olefination could successfully be applied to the aromatic polyenals synthesis.

---

[1] Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. For reviews, see: Ager, D. J. *Synthesis* **1984**, 384; *Org. React.* **1990**, *38*, 1.

[2] (a) Gaudemar, M.; Bellassoued, M. *Tetrahedron Lett.* **1990**, *31*, 349. (b) Bellassoued, M.; Majidi, A. *J. Org. Chem.* **1993**, *58*, 2517.

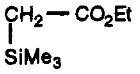
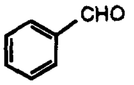
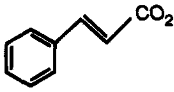
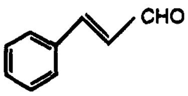
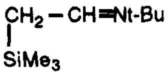
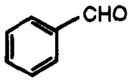
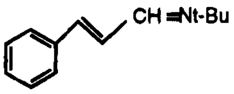
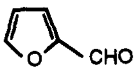
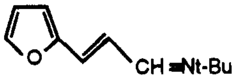
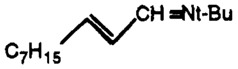
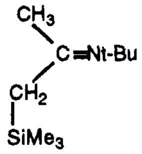
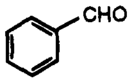
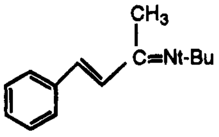
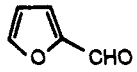
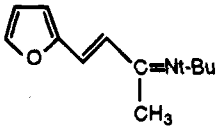
[3] Palomo, C.; Aizpurua, J. M.; Garcia, J. M.; Ganboa, I.; Cossio, F. P.; Lecea, B.; Lôpez, C. *J. Org. Chem.* **1990**, *55*, 2498.

[4] Bellassoued, M.; Salemkour, M. *Tetrahedron Lett.* **1993**, *34*, 5281.

[5] In THF with TBAF at rt (3 h), Kuwajima has reported the formation of the β-trimethylsiloxy ester **2a** in 76% yield: *Tetrahedron Lett.* **1976**, 1699.

0022-3263/95/1960-6582$09.00/0

**Table 1. Reaction of Monosilylated Reagents 1 with Some Aldehydes**

| Entry | Monosilylated Reagent 1 | Aldehydes | Reaction Conditions | Alkenes 3 Obtained[a] | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  $\underset{\mathrm{SiMe_3}}{\mathrm{CH_2}}\mathrm{-CO_2Et}$<br>**1a** |  | rt,35 min;<br>100°C,1h |  | 93 |
| 2 | |  | rt,40 min;<br>100°C,0.5h |  | 65 |
| 3 | | t-Bu — CHO | rt,40min;<br>120°C,2.5h |  | 65 |
| 4 |  $\underset{\mathrm{SiMe_3}}{\mathrm{CH_2}}\mathrm{-CH{=}Nt\text{-}Bu}$<br>**1b** |  | rt,2h;<br>60°C,0.5h |  | 94 |
| 5 | |  | rt, 30min;<br>85°C,1h |  | 78 |
| 6 | | $C_7H_{15}$—CHO | rt,2h;<br>60°C,0.5h |  | 36[b] |
| 7 | <br>**1c** |  | rt,1.5h;<br>75°C,0.5h |  | 89 |
| 8 | |  | rt,25 min;<br>50°C,1h |  | 71[b] |

[a] The isomeric purity (*E*) for each product was confirmed to be >98% by $^1$H NMR. [b] Yield of the hydrolyzed imine.

## Experimental Section

All commercially available compounds used in this work were purchased from Aldrich and were used without further purification unless otherwise specified. Trimethylsilyl chloride was distilled from $CaH_2$ and stored over molecular sieves. Tetrahydrofuran and diethyl ether were distilled over sodium and benzophenone. Lithium diisopropylamide (LDA) was prepared in situ from diisopropylamine and *n*-butyllithium (1.6 M solution in hexane) at −60 °C. *tert*-Butylimines were easily prepared from the corresponding carbonyl compounds and *tert*-butylamine in pentane following the usual way.[6] Reactions requiring anhydrous conditions were performed in flame-dried glassware under a nitrogen atmosphere.

Proton nuclear magnetic resonance spectra were recorded at 200 or 400 MHz. All chemical shifts were reported as $\delta$ values (ppm) relative to internal tetramethylsilane. Flash column chromatography was done on Merck grade 60 silica gel (230–400 mesh) with a mixture of cyclohexane/AcOEt as eluent.

**Preparation of α-Trimethylsilyl Reagents.** Ethyl α-(trimethylsilyl)acetate (**1a**) was prepared from ethyl bromoacetate, chlorotrimethylsilane, and zinc according to the method of Fessenden.[7] α-Trimethylsilyl *N-tert*-butylimines **1b** and **1c** were obtained from *N-tert*-butylimines, LDA, and chlorotrimethylsilane at −60 °C in THF.[8]

**Representative Procedure for the Synthesis of Unsaturated Esters.** Ethyl α-(trimethylsilyl)acetate (**1a**) (1.6 g, 10 mmol) in DMSO (2 mL) was added over 5 min to benzaldehyde (0.9 g, 8.5 mmol) in the presence of catalytic CsF (0.15 g, 1 mmol) in DMSO (2 mL) under nitrogen at room temperature. After being stirred for 35 min at the same temperature, the yellow reaction mixture was heated at 100 °C for 1 h. The dark solution then obtained was diluted with 50 mL of ether, washed with water, dried over $MgSO_4$, and concentrated in vacuo to give crude olefin **3a** in almost quantitative yield. The yellow oil was submitted to Kugelrohr distillation (GKR-51, BÜCHI) to afford 1.39 g (93%) of pure ethyl (*E*)-cinnamate which can be also purified by flash chromatography. The ethyl cinnamate is a

---

(6) Campbell, K. N.; Sommers, H.; Campbell, B. K. J. *J. Am. Chem. Soc.* **1944**, *66*, 82.

(7) Fessenden, R. J.; Fessenden, J. S. *J. Org. Chem.* **1967**, *32*, 3535.

(8) Corey, E. J.; Enders, D.; Bock, M. G. *Tetrahedron Lett.* **1967**, 7.

known compound and was easily characterized by comparison with an authentic sample. However, spectral and analytical data of the two other esters are given below.

**Ethyl 5-phenyl-2(*E*),4(*E*)-pentadienoate:** $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.22 (t, 3H, $J$ = 7.15 Hz), 4.15 (q, 2H, $J$ = 7.15 Hz), 5.90 (d, 1H, $J$ = 16 Hz), 6.78 (m, 2H), 6.98 (d, 1H, $J$ = 16.1 Hz), 7.15−7.42 (m, 5H); IR (KBr) 1728 cm$^{-1}$ (C=O). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.29; H, 6.99. Found: C, 77.73; H, 6.94.

**Ethyl 4,4-dimethyl-(*E*)-pentenoate:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.07 (s, 9H), 1.23 (t, 3H, $J$ = 7.05 Hz), 4.18 (q, 2H, $J$ = 7.05 Hz), 4.68 (d, 1H, $J$ = 16.5 Hz), 6.95 (d, 1H, $J$ = 16.5 Hz); IR (KBr) 1721 cm$^{-1}$ (C=O). Anal. Calcd for $C_9H_{16}O_2$: C, 69.74; H, 10.34. Found: C, 69.83; H, 10.24.

**General Procedure for the Reaction of α-Silylated Imine with Aldehydes.** To a solution of the corresponding aldehyde (10 mmol) and CsF (1 mmol) in DMSO (10 mL) was added dropwise at room temperature a solution of **1b** or **1c** (11 mmol) in DMSO (5 mL). The resulting reaction mixture was heated as indicated in Table 1, the reaction quenched with water (10 mL), and the mixture extracted with pentane (3 × 40 mL). The organic layer was dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded crude *N-tert*-butyl-unsaturated imine, which was submitted to Kugelrohr distillation. Some imines were thus isolated and are described below, designated by their entries in Table 1. The crude imines were also hydrolyzed under very mild conditions by the addition of an aqueous solution of $ZnCl_2$ (2 g in 20 mL of water) and ether (25 mL), and the solution was stirred for 1 h at room temperature. The precipitate was filtered through a pad of Celite. The aqueous layer was extracted with ether (2 × 25 mL), and the organic extracts were washed with water (10 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The reaction crude was purified by flash chromatography to give the corresponding pure carbonyl compound.

**4:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.23 (s, 9H), 6.93 (d, 2H, $J$ = 4.9 Hz), 7.29−7.47 (m, 5H), 8.01 (d, 1H, $J$ = 4.8 Hz). Anal. Calcd for $C_{13}H_{17}N$: C, 83.49; H, 9.16; N, 7.49. Found: C, 83.22; H, 9.12; N, 7.39.

**5:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.12 (s, 9H), 6.41 (m, 2H), 6.78 (m, 2H), 7.40 (d, 1H, $J$ = 3.5 Hz), 8.0 (m, 1H). Anal. Calcd for $C_{11}H_{15}ON$: C, 74.64; H, 8.54; N, 7.91. Found: C, 74.52; H, 8.47; N, 7.81.

**6:** $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.21 (m, 15H), 6.06 (ddt, 1H, $J$ = 16.0, 8.0, 2.0 Hz), 6.81 (td, 1H, $J$ = 16.0, 8.0 Hz), 9.42 (d, 1H, $J$ = 8.0 Hz); IR (KBr) 1690 cm$^{-1}$ (C=O). Anal. Calcd for $C_{10}H_{18}O$: C, 77.99; H, 11.78. Found: C, 77.73; H, 11.74.

**7:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.30 (s, 9H), 2.22 (s, 3H), 6.78 (d, 1H, $J$ = 15.7 Hz), 6.92 (d, 1H, $J$ = 15.7 Hz), 7.24−7.45 (m, 5H). Anal. Calcd for $C_{14}H_{19}N$: C, 83.65; H, 9.53; N, 6.97. Found: C, 83.50; H, 9.64; N, 6.87.

**8:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.27 (s, 3H), 6.48 (d, 1H, $J$ = 16.9 Hz), 7.42 (d, 1H, $J$ = 16.9 Hz), 6.65 (dd, 1H, $J$ = 3.5, 1.8 Hz), 6.97 (d, 1H, $J$ = 3.5 Hz), 7.87 (m, 1H); IR (KBr) 1680 cm$^{-1}$ (C=O). Anal. Calcd for $C_8H_8O_2$: C, 70.65; H, 7.93. Found: C, 70.82; H, 7.91.

JO950773J