

Lithium Perchlorate Diethyl Ether/Methyl Triflate Catalyzed Transfer of Silicon from Oxygen to Carbon in Silyl Ketene (Thio) Acetals

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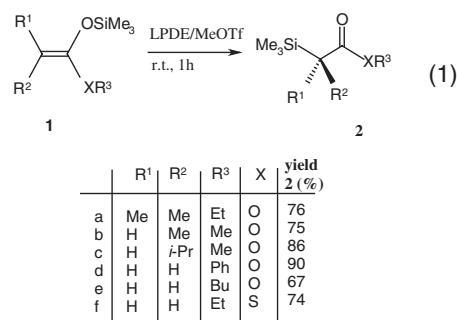
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Migration of a trimethylsilyl group from oxygen to the α -carbon (retro- [1,3]-Brook rearrangement) in silyl ketene acetals is catalyzed by LPDE/methyl triflate under mild conditions.

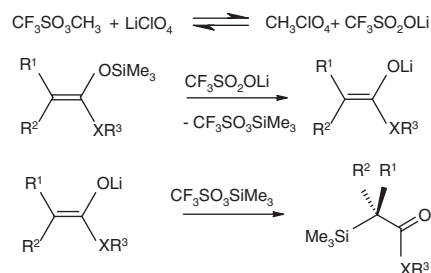
The synthetic utility of α -silylated esters has been amply demonstrated.¹ Although these systems have been generated in a variety of ways, the majority of these preparations suffer from less than readily available starting materials and/or a lack of generality.² The most general route to these interesting systems involves reactions of trimethylsilyl triflates with esters to give the α -trimethylsilyl esters in moderate to good yield with some contamination from the O-silylated and bis-silylated products.³ All reports to date on the silylation of ester enolates have shown that the predominant product is that of O-silylation. The two exceptions to this general observation are *tert*-butyl acetates and esters of cyclopropane carboxylic acid. No good example of C-silylation of an enolates of an α -substituted ester has been reported to date. The thermal migration of a trialkylsilyl group from carbon to oxygen in α -silyl ketones by an intramolecular concerted four-center mechanism has been well established.⁴ The reverse process has been also observed in silylketene acetals,⁵ but less is common because of competitive decomposition to ketenes and trialkylsilyl ethers.⁶ In addition, thermal, high pressure⁷ and Lewis acid catalyzed migration of the silyl group from O to the α -C has been documented using mercury (II) iodide at 70 °C,⁸ [Cp₂Zr(*Ot*-Bu)THF][BPh₄],⁹ organoaluminum compounds¹⁰ and lanthanoid trifluoromethanesulfonates (trimethylsilyl ketene acetals derived from ethyl isobutyrate, methyl phenylacetate and methyl 3-phenylbutyrate were decomposed to the corresponding esters quantitatively and no α -silylated products were obtained).¹¹ Nevertheless, in the presence of TiCl₄ silyl ketene acetals are oxidatively dimerized to succinates.¹²

In recent years, lithium perchlorate in diethyl ether (LPDE) has gained importance as a versatile reaction medium for effecting various organic transformations such as Diels–Alder reactions;^{13a} 1,3-Claisen rearrangements;^{13b} Hetero Diels–Alder reactions;^{13c} substitution reactions of allylic acetates and allylic alcohols;^{13d} chelation controlled addition of allylstannanes to aldehydes;^{13e} [2+2] cycloadditions;^{13f} selective carbonyl protection;^{13g} selective deoxygenation of allylic alcohols and acetates;^{13h} ene reactions;¹³ⁱ ionization of C7 methoxy group in rapamycin;^{13j} [2+3] addition of *p*-benzoquinone with alkenes;^{13k} selective rearrangement of epoxides;^{13l} cationic [5+2] cycloaddition reactions;^{13m} tetrahydropyranlation of alcohols;¹³ⁿ Baylis–Hilman reactions;^{13o} α -aminoalkylation;^{13p} α -aminocyanation;^{13q} α -cyanohydroxylamination;^{13r} and *N*-trimethylsilyloxy- α -aminophosphonation.^{13s} In an attempt to prepare α -methylesters by reaction of O-silyl ketene acetals and methyl trifluoromethanesulfonate in 5 M LPDE, we observed instead the

formation of α -trimethylsilyl esters,¹⁴ as exemplified by Eq 1.



Though the behavior of LiClO₄ is not clear, it seems that LiClO₄ interacts with the methyl triflate to generate an active anionic species, which accelerates the reaction. The reaction may proceed via the trimethylsilyltriflate and it should be noted that stoichiometric amounts of methyl triflate is needed to complete the reaction.¹⁵ The reaction of trimethylsilyl ketene acetal **1b** was monitored by ¹³C NMR in LPDE (CDCl₃ as internal standard). Carbon absorptions of the trimethylsilyl group and α -C atom of **1b** appeared at –0.15 and 153 ppm respectively. Addition of stoichiometric amount of MeOTf in the reaction mixture gave new signals at 179 and –4 ppm, after 15 min. These peaks correspond to (C=O) and trimethylsilyl group of **2b**. These results suggest that the migration of the silyl group proceeds via initial generation of lithium enolate (not detected by ¹³C NMR under conditions used), and TMSOTf, followed by C-silylation of enolate. Such C-silylation by trimethylsilyl triflate in the presence of trimethylamine has already been reported.³



In conclusion, we have described an LPDE/MeOTf mediated retro [1,3]-Brook rearrangement, which provides silylated esters directly from keteneacetals.

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- 14 **A typical experimental procedure.** To a mixture of ketene acetal (2 mmol) in 5 M LPDE (4 ml) was added methyl triflate (2.2 mmol) at room temperature. The mixture was stirred for 1 h and the product was extracted with CH₂Cl₂. The organic phase was collected, dried (Na₂SO₄) and evaporated to afford the crude product. The product was purified by preparative gas chromatography OV-101, 150 °C isotherm. ¹H NMR, ¹³C NMR, IR and MS spectra were entirely consistent with the assigned structures. Selected data as follow: **2a** (R¹ = R² = Me, R³ = Et, X = O): ¹H NMR (500 MHz, CDCl₃) δ 3.5 (q, 2H), 1.2 (t, 3H), 1.15 (s, 3H), 1.1 (s, 3H), 0.1 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 180.5 (C=O), 61.99 (OCH₂), 53.41 (C), 18.5 (CH₃), 14.3 (CH₃), 13.6 (CH₃), -0.7 (SiMe₃); **2C** (R¹ = H, R² = iso-propyl, R³ = Me, X = O): ¹H NMR (400 MHz, CDCl₃) δ 3.5 (s, 3H), 2.1 (m, 1H), 1.7 (d, 1H), 0.9 (d, 3H), 0.8 (d, 3H), 0.1 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 175 (C=O), 50.6 (OCH₃), 46.3 (CH), 28.2 (CH), 23.5 (CH₃), 22.7 (CH₃), -0.7 (SiMe₃); **2d** (R¹ = R² = H, R³ = Ph, X = O): ¹H NMR (400 MHz, CDCl₃) δ 7.3-7.0 (m, 5H), 2.1 (s, 2H), 0.1 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.3 (C=O), 151 (C), 129.3 (CH), 125.5 (CH), 121.7 (CH), 27 (CH₂), -1.3 (SiMe₃).
- 15 The solution of silyl ketene acetals and methyl triflate in diethyl ether remains unchange after 3 h at room temperature. In addition the solution of silyl ketene acetals in LPDE remains unchange after 3 h at room temperature.