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FACILE CONVERSION OF TRIALKYLSILYL ESTERS TO ALKYL ESTERS MEDIATED BY TETRABUTYLAMMONIUM FLUORIDE TRIHYDRATE

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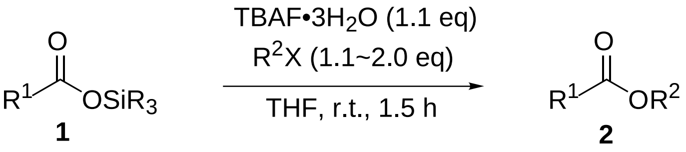
Abstract — Trialkylsilyl esters can be smoothly converted into the corresponding alkyl esters by treatment with tributylammonium fluoride trihydrate (TBAF•3H_2O) and alkyl halides in THF. This direct transformation was found applicable to the formation of lactones through intramolecular alkylations.

(Dedicated to Professor Sho Ito on the occasion of his 77th birthday)

The preparation of esters from carboxylic acids or their derivatives has been viewed one of the most common and fundamental operations in organic synthesis, and an enormous number of methods have been elaborated for this purpose.[1-3] Among them, direct transformation of trialkylsilyl or trialkylstannyl esters into another esters with different properties appears useful and would fulfill a wide spectrum of synthetic demands, though only a limited number of publications have appeared so far.[4-6] Noyori specifically introduced a synthesis of triphenylmethyl esters by the condensation of trimethylsilyl esters and triphenylmethyl fluoride in the presence of catalytic tetrafluorosilane.[7] Recently, Otera reported direct conversion of organotin carboxylates to the corresponding esters using CsF, which unfortunately required a prolonged reaction time.[8] Here we wish to report that trialkylsilyl esters can be cleanly converted to the corresponding alkyl esters by treatment with tetrabutylammonium fluoride trihydrate (TBAF•3H_2O) and alkyl halides in THF through deprotection and alkylation processes (Scheme 1).[9] This approach takes advantage of the high affinity of fluoride ion toward silicon atom and nucleophilicity of the resulting ammonium carboxylates.[10,11]

Scheme 1



Treatment of trimethylsilyl 3-phenylpropionate [**1**; R^1 = $Ph(CH_2)_2$, R_3 = Me_3][12] with $TBAF•3H_2O$ (1.1 equiv) and benzyl bromide (1.1 equiv) in THF at room temperature for 1.5 h gave rise to the corresponding benzyl ester (**2**) (R^1 = $Ph(CH_2)_2$, R^2 = CH_2Ph) quantitatively (Table 1, entry 1).[13] Other selected examples are summarized in Table 1, which clearly demonstrates the efficiency and general applicability of the present method. The reactions with allyl and cinnamyl bromides also proceeded smoothly to furnish the corresponding esters in 86% and 85% yields, respectively (entries 2 and 3) and propargy ester (**2**) (R^1 = $Ph(CH_2)_2$, R^2 = $CH_2C \equiv CH$) was obtained in a similar manner using propargyl bromide (entry 4). The formation of simple *primary* alkyl esters appeared feasible with

Table 1 . TBAF-Mediated Direct Transformation of Trialkylsilyl Esters to Alkyl Esters [a]

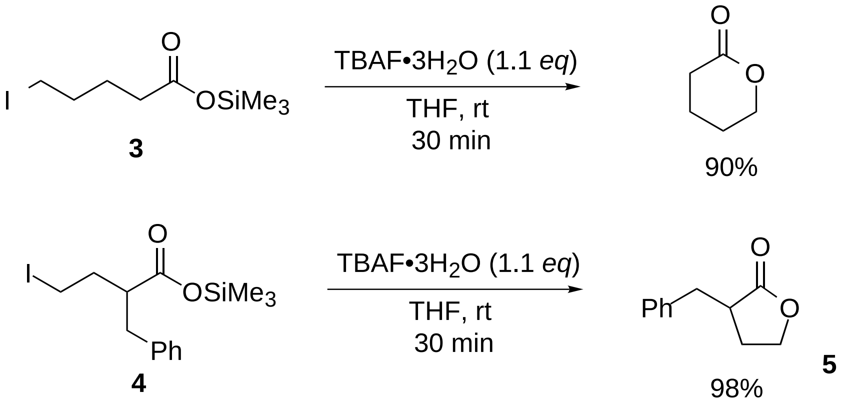
entry	$R^1CO_2SiR_3$, **1**	R^2X	yield (%) of **2** [b]
1	$Ph(CH_2)_2CO_2SiMe_3$	$PhCH_2Br$	96
2		$CH_2{=}CHCH_2Br$	86
3		*trans*-$PhCH{=}CHCH_2Br$	85
4		$CH \equiv CCH_2Br$	85
5		MeI	95
6		EtI	92
7		BuI	86
8		$PhCH(CH_3)Br$	52
9		$CH_3CH_2CH(CH_3)I$	45
10	$Ph(CH_2)_2CO_2SiMe_2Bu^t$	$PhCH_2Br$	91
11		$CH_2{=}CHCH_2Br$	95
12		BuI	91
13	$Ph(CH_2)_2CO_2SiPr^i_3$	$PhCH_2Br$	98
14		BuI	96
15	$Ph(CH_2)_2CO_2SiPh_2Bu^t$	$PhCH_2Br$	87
16		BuI	77
17	$PhCO_2SiMe_3$	$PhCH_2Br$	93
18		$CH_2{=}CHCH_2Br$	86
19		$CH \equiv CCH_2Br$	84
20		BuI	88
21	*trans*-$PhCH{=}CHCO_2SiMe_3$	$PhCH_2Br$	91
22		$CH_2{=}CHCH_2Br$	84
23		BuI	80

[a] The reaction was carried out in dry THF (0.5 M) with 1.1 equiv of $TBAF•3H_2O$ and 1.1~2.0 equiv of alkyl halides at room temperature for 1.5 h. [b] Isolated yield.

various alkyl iodides (entries 5-7), though the yield was unfortunately lowered in the reaction with *secondary* alkyl halides (entries 8 and 9). Notably, *t*-butyldimethylsilyl 3-phenylpropionate [**1**; R^1 = $Ph(CH_2)_2$, R_3 = Me_2Bu^t], upon exposure to the representative reaction conditions with benzyl bromide as an alkyl halide, resulted in clean formation of the desired benzyl ester (**2**) (R^1 = $Ph(CH_2)_2$, R^2 = CH_2Ph) in 91% yield (entry 10). Moreover, in addition to the commonly used *t*-butyldimethylsilyl group,[2] more stable triisopropylsilyl and *t*-butyldiphenylsilyl groups were found to be employable. Interestingly, triisopropylsilyl group is quite appropriate to increase the stability of the ester against simple hydrolysis, while still being able to react with fluoride ion smoothly (entries 13 and 14). In this respect, slightly diminished chemical yields observed in the reactions of *t*-butyldiphenylsilyl 3-phenylpropionate [**1**; R^1 = $Ph(CH_2)_2$, R_3 = Ph_2Bu^t] seem to be in accord with its lower susceptibility toward TBAF-mediated O-Si bond cleavage (entries 15 and 16).[2] Aromatic as well as *α,β*-unsaturated silyl esters turned out to be good candidates for the present system (entries 17-23).

Furthermore, this direct transformation of silyl esters to alkyl esters was successfully applied to the formation of lactones *via* intramolecular alkylations. For instance, treatment of trimethylsilyl 5-iodopentanoate (**3**) with TBAF•$3H_2O$ (1.1 equiv) in THF at room temperature for 30 min afforded *δ*-valerolactone in 90% isolated yield (Scheme 2). Similarly, silyl ester (**4**) can be rapidly converted to the corresponding five-membered lactone (**5**) almost quantitatively as also illustrated in Scheme 2.

Scheme 2



A typical experimental procedure is as follows. Tetrabutylammonium fluoride trihydrate (174 mg, 0.55 mmol) was placed in a dry two-neck flask with a stirring bar under argon, and freshly distilled THF (1 mL) was introduced. To this solution were added benzyl bromide (65 μL, 0.55 mmol) and trimethylsilyl 3-phenylpropionate [**1**; R^1 = $Ph(CH_2)_2$, R_3 = Me_3] (111 mg, 0.5 mmol) sequentially at room temperature. After being stirred for 1.5 h at room temperature, the resulting reaction mixture was poured into water (5 mL) and extracted with ether (10 mL x 3). The combined organic extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (hexane/ether = 10:1 as eluant) gave pure benzyl ester (**2**) (R^1 = $Ph(CH_2)_2$, R^2 = CH_2Ph) (116 mg, 96% yield) as a colorless oil (entry 1 in Table 1).

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12. For the convenient preparation of trimethylsilyl esters, see: C. Palomo, *Synthesis*, 1981, 809.
13. Commercially available TBAF•3H_2O was simply dried *in vacuo* (0.6 mmHg) for 10 min before use. Use of commercially available 1 M THF solution of TBAF generally brought about 10~20% decrease of the chemical yield.