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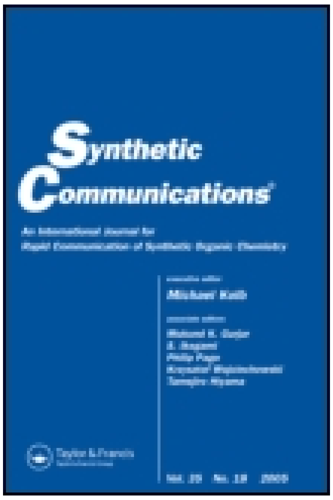

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DIRECT CONVERSION OF SILYL ETHERS OR TETRAHYDROPYRANYL ETHERS INTO THE CORRESPONDING DIPHENYLMETHYL ETHERS

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DIRECT CONVERSION OF SILYL ETHERS OR TETRAHYDROPYRANYL ETHERS INTO THE CORRESPONDING DIPHENYLMETHYL ETHERS

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ABSTRACT

Direct conversion of alcohol silyl ethers into the corresponding diphenylmethyl (DPM) ethers can be easily performed by the reaction with diphenylmethyl formate in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate. By the additional use of triethylsilane, tetrahydropyranyl ethers can be also converted into the corresponding DPM ethers.

Alkyl ethers such as benzyl and substituted benzyl ethers have been widely used as a typical protecting group of the hydroxy function as well as other-type protecting groups, such as silyl ether-, acetal-, and ester-types.[1] The unique ability of benzyl ether and substituted benzyl ethers, such as *p*-methoxybenzyl (PMB), diphenylmethyl (DPM), and triphenylmethyl (Tr) ethers, to be selectively cleaved by simple hydrogenation under mild

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and neutral reaction conditions is the advantage over other-type protecting groups. Generally, protection of alcohols into alkyl ethers is accomplished by reaction with the corresponding alkyl halides under the influence of a base such as sodium hydride,[2] sodium hydroxide,[3] and so on. Direct transformation into alkyl ethers from other-type functional groups, not from a parent alcohol, is very important from the standpoint of green chemistry (efficiency and convenience).

In a series of our studies[4] on the direct transformation of a protecting group of the hydroxy function into another, we have previously demonstrated that direct conversion of aryl trialkylsilyl ethers into the corresponding aryl alkyl ethers can be conveniently carried out by reaction with alkyl bromide under the influence of cesium fluoride.[5] However, this reaction is limited to aryl silyl ethers and does not extend to alkyl silyl ethers. On the other hand, we have found that alcohol tetrahydropyranyl (THP) ethers can be readily converted into the corresponding benzyl ethers in high yields by the reaction with triethylsilane and benzaldehyde catalyzed by trimethylsilyl trifluoromethanesulfonate (TMSOTf) as shown in Scheme 1.[6] However, an attempted direct conversion of THP ether into DPM ether by the use of benzophenone instead of benzaldehyde gave an unsuccessful result, and the corresponding DPM ether was obtained in low yield (Scheme 2).

$$\mathrm{Ph(CH_2)_3OTHP} + \mathrm{PhCHO} \xrightarrow[\mathrm{CH_3CN}\ /\ 0\ ^\circ\mathrm{C}\ /\ 1\ \mathrm{h}]{\mathrm{Et_3SiH\ /\ TMSOTf}} \underset{98\%}{\mathrm{Ph(CH_2)_3OBn}}$$

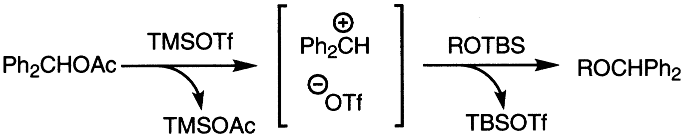
Scheme 1.

$$\mathrm{Ph(CH_2)_3OTHP} + \mathrm{Ph_2CO} \xrightarrow[\mathrm{CH_3CN}\ /\ 0\ ^\circ\mathrm{C}\ /\ 1\ \mathrm{h}]{\mathrm{Et_3SiH\ /\ TMSOTf}} \underset{30\%}{\mathrm{Ph(CH_2)_3ODPM}} \quad \mathrm{DPM = Ph_2CH}$$

Scheme 2.

In this communication, we report a highly efficient and convenient method for the direct conversion of alkyl silyl ethers or alkyl THP ethers into the corresponding DPM ethers in a convenient one-pot procedure.

After a screening of various reaction conditions, we found that diphenylmethyl acetate (AcODPM) reacted with alcohol *t*-butyldimethylsilyl (TBS) ether under the influence of TMSOTf, and the desired DPM ether was obtained (Scheme 3). A diphenylmethyl cation generated from AcODPM under Lewis acid conditions was presumed to be an active species, and it reacted with alkyl silyl ether to provide the corresponding alkyl DPM ether. Examination of other DPM alcohol esters in the reaction of TBS ether of 3-phenylpropanol under similar reaction conditions (Table 1, Runs 2–4) indicated that diphenylmethyl formate (HCO_2DPM) is more effective, and the combination with silica gel as an additive gave the best result (Run 5). We have, therefore, tentatively chosen a combination of the TBS ether (0.3 mmol), HCO_2DPM, TMSOTf, (molar ratio; 1 : 1.5 : 0.05), and silica gel (300 mg) as the optimum reaction conditions.



Scheme 3.

Representative examples of a one-pot conversion of alcohol TBS ethers into the corresponding DPM ethers are collected in Table 2.[7] As can be seen, the reaction was successful with TBS ethers of secondary alcohols as well as a primary alcohol (Runs 2 and 3). In the presence of other-type protecting groups, such as a benzyl ether and benzoate, TBS ethers are chemoselectively transformed into the corresponding DPM ethers in high yields (Runs 4 and 5).

Table 1. The Effect of DPM Ester and Silica Gel

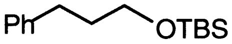
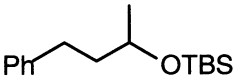
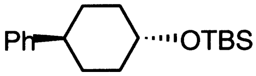
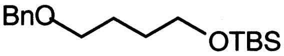
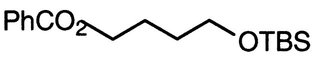
$$\mathrm{Ph(CH_2)_3OTBS} + \overset{1.5\mathrm{eq}}{\mathrm{RCO_2DPM}} \xrightarrow[\mathrm{CH_3CN/0^\circ C/1h}]{\substack{0.05\mathrm{eq}\\ \mathrm{TMSOTf}}} \mathrm{Ph(CH_2)_3ODPM}$$

Run	RCO_2DPM	Additive	Yield (%)[a]
1[b]	AcODPM	–	83
2	AcODPM	–	68
3	$PhCO_2DPM$	–	69
4	HCO_2DPM	–	80
5	HCO_2DPM	silica gel	94

[a] Isolated yield of purified product.
[b] 2.5 equiv. of AcODPM was used. Reaction was carried out at *r.t.* for 12 h.

Table 2. Synthesis of Various DPM Ethers from TBS Ethers[a]

$$\text{ROTBS} + \text{HCO}_2\text{DPM} \xrightarrow[\substack{\text{silica gel/CH}_3\text{CN} \\ 0^\circ\text{C/1 h}}]{\text{TMSOTf}} \text{RODPM}$$

Run	ROTBS	Yield (%)[b]
1		94
2		86
3		84
4		93
5		90

[a] Molar ratio of TBS ether : HCO_2DPM : TMSOTf $= 1 : 1.5 : 0.05$.

[b] Isolated yield of purified product.

Next, we examined the scope of trialkylsilyl ethers (Table 3). The reaction was conducted with various silyl ethers of 3-phenylpropanol using 5 mol% of TMSOTf. Triethylsilyl (TES) ether and triisopropylsilyl (TIPS) ether could also be converted into the DPM ether in high yields (Runs 2 and 3). However, in the case of *t*-butyldiphenylsilyl (TBDPS) ether, the reaction was very slow and the DPM ether was obtained in lower yield (Run 4).

As mentioned above, we recently reported that THP ethers can be readily converted into the corresponding benzyl ethers by the reaction with triethylsilane, benzaldehyde catalyzed by TMSOTf (Scheme 1). This reaction proceeded via a formation of the corresponding TES ether as an intermediate.[6] This result suggested that using HCO_2DPM in place of benzaldehyde under the influence of silica gel would afford the corresponding DPM ethers from THP ethers. We tested the direct conversion of THP ethers into DPM ethers. As can be seen from Table 4, DPM ethers of primary and secondary alcohols were obtained in good yields as well as a conversion from silyl ethers (Runs 1–6). The reaction was compatible with the aromatic ketone (Run 7) which is reducible by exposure to triethylsilane under acidic conditions.[8]

Table 3. Synthesis of DPM Ethers from Various Silyl Ethers[a]

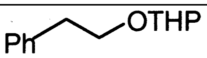
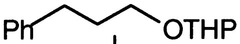
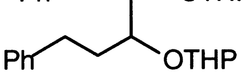
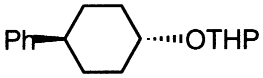
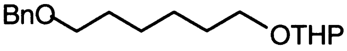
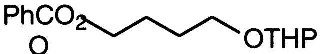
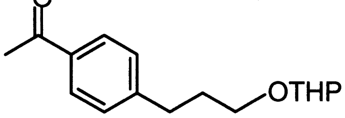
$$\mathrm{Ph(CH_2)_3O}\mathit{Si} + \mathrm{HCO_2DPM} \xrightarrow[\substack{\text{silica gel/CH}_3\text{CN} \\ 0^\circ\text{C/1 h}}]{\text{TMSOTf}} \mathrm{Ph(CH_2)_3ODPM}$$

Run	*Si*	Yield (%)[b]
1	*t*-BuMe$_2$Si (TBS)	94
2	Et$_3$Si (TES)	90
3	*i*-Pr$_3$Si (TIPS)	91
4	*t*-BuPh$_2$Si (TBDPS)	47

[a] Molar ratio of silyl ether : HCO$_2$DPM : TMSOTf = 1 : 1.5 : 0.05.
[b] Isolated yield of purified product.

Table 4. Synthesis of Various DPM Ethers from THP Ethers[a]

$$\mathrm{ROTHP} + \mathrm{HCO_2DPM} \xrightarrow[\substack{\text{silica gel/CH}_3\text{CN} \\ 0^\circ\text{C/0.5–1 h}}]{\text{Et}_3\text{SiH/TMSOTf}} \mathrm{RODPM}$$

Run	ROTHP	Yield (%)[b]
1		90
2		89
3		83
4		80
5		78
6		89
7		79

[a] Molar ratio of THP ether : HCO$_2$DPM : Et$_3$SiH : TMSOTf = 1 : 1.5 : 1.1 : 0.05.
[b] Isolated yield of purified product.

In a series of our investigations on the one-step conversion between typical protecting groups of the hydroxy function, we have added new direct transformation of silyl ethers into the DPM ethers, and THP ethers into the DPM ethers.

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5. Oriyama, T.; Noda, K.; Yatabe, K. Synlett **1997**, 701.
6. Suzuki, T.; Ohashi, K.; Oriyama, T. Synthesis **1999**, 1561.
7. A typical experimental procedure for the direct conversion of alcohol TBS ethers into the corresponding DPM ethers is as follows: To a suspension of silica gel (300 mg), 2-*t*-butyldimethylsilyloxy-3-phenylpropane (75.1 mg, 0.300 mmol) and diphenylmethyl formate (95.5 mg, 0.450 mmol) in CH_3CN (2 mL) was added a solution TMSOTf (3.3 mg, 0.015 mmol) in CH_3CN (0.5 mL) at 0°C under argon atmosphere. The reaction mixture was stirred for 1 h at 0°C and quenched with saturated aqueous sodium hydrogen carbonate. The organic materials were extracted with Et_2O and dried over anhydrous magnesium sulfate. The solvent was evaporated and 1-diphenylmethyloxy-3-phenylpropane (85.2 mg, 94%) was isolated by thin-layer chromatography on silica gel (ether : hexane = 1 : 10).
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