Ti(III) Chloride: A Novel Reagent for the Chemoselective Deprotection of Tetrahydropyranyl Ethers

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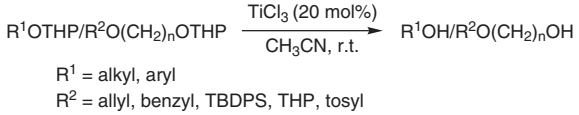
Abstract: Ti(III) chloride was found to be an effective catalyst for the deprotection of tetrahydropyranyl ethers of alcohols and phenols at an ambient temperature. Allyl ether, benzyl ether, *tert*-butyldiphenylsilyl (TBDPS) ether, *p*-toluenesulfonate ester and isomerizable double bond were found to be compatible under the reaction conditions.

Key words: allyl ether, benzyl ether, chemoselectivity, depyranylation, titanium(III) chloride, TBDPS ether, *p*-toluenesulfonate ester

Protection and deprotection of alcohols and phenols play a key role in the synthesis of polyfunctional organic molecules, and a variety of protecting groups have been developed for this purpose.[1] Tetrahydropyranyl (THP) ethers are widely used for the protection of alcohols because of their easy preparation and stability under a variety of reaction conditions involving alkaline media, Grignard reagents, organolithiums, metal hydrides and oxidative reagents.[2] The most common methods for the deprotection of the THP ethers are acid catalyzed hydrolysis in protic solvents.[3] However, these methodologies are inappropriate in the case of acid sensitive molecules. Many other methods have been reported for the deprotection of the THP ethers.[4] More recently, $In(OTf)_3$[5] and $AlCl_3$[6] have been described as efficient reagents for the deprotection of the THP ethers. Many of these procedures have several drawbacks including elevated temperatures, longer reaction times and use of expensive and toxic reagents. Therefore, the developments of new reagents that are more efficient and better yielding are desirable. In this communication, we report an efficient method for the selective removal of the THP ethers using catalytic amount of Ti(III) chloride at an ambient temperature (Scheme 1).

Earlier, several variety of low-valent titanium reagents [Ti(0) and Ti(II), prepared by the reduction of $TiCl_3$/$TiCl_4$ with different reducing metals (Li, K, Mg, Zn) and solvents (THF, DME)] have been developed in our laboratory for the synthesis of alkenes/1,2-diols from carbonyl compounds.[7] We have also demonstrated single electron transfer mediated deprotection of propargyl and allyl ethers and tosylate esters with LVT reagents.[8] Amongst the high valent titanium reagents [Ti(III) and Ti(IV)], Mukaiyama et al. have extensively used $TiCl_4$ as a Lewis acid in directed Aldol condensation.[9] Similarly, aqueous $TiCl_3$ solution has been used for the reductive hydrodimerization of aromatic carbonyl compounds.[10] However, use of anhydrous $TiCl_3$ as a Lewis acid is rather limited.[11,12] A recent report on the hydrolysis of isopropylidene acetals with ytterbium triflate[13] prompted us to investigate the role of anhydrous $TiCl_3$ as a Lewis acid in the deprotection of tetrahydropyranyl ethers.



Scheme 1

In a model reaction, the THP ether **1** of 1-octanol prepared by following the standard procedure [dihydropyran (DHP) and pyridinium *p*-toluenesulfonate (PPTS) in CH_2Cl_2], was exposed to Ti(III) chloride in MeCN at room temperature. The reaction proceeded smoothly (2 h) to afford 1-octanol in 97% yield (Table 1, entry 1). In the above reaction**,** 20 mol% of $TiCl_3$ was required for complete conversion of the substrate**.** Similarly, the THP ethers of 2-octanol and 1-hexadecanol (**2** and **3**, respectively) yielded the corresponding alcohols in good yields (Table 1, entries 2 and 3). The THP ethers **4**–**8** of phenols also underwent facile deprotection in good yields at room temperature (Table 1, entries 4–8). From the results in Table 1, it is clear that with protected phenolic substrates, deprotection was more facile when electron-withdrawing substituents are attached to the aromatic ring. Further, various functional groups such as ketone, ester, nitro, and methylenedioxy were found to be compatible under the reaction conditions.

Investigations were also carried out with the THP ethers of allylic alcohols, which are vulnerable to isomerization. To our satisfaction, the THP ethers **9** and **10** of the Baylis–Hillman adducts also underwent smooth deprotection to yield the corresponding allylic alcohols in moderate yields (Table 1, entries 9 and 10) without any isomerization.

In presence of other hydroxyl protecting functionalities, chemoselectivity for the depyranylation reaction using anhydrous $TiCl_3$ was also investigated. It was observed that the reaction proceeded smoothly even in the presence of sensitive functional groups such as TBDPS and tosyl (Table 1, entries 11 and 12). The *O*-allyl and *O*-benzyl groups, which get cleaved with the LVT reagents, were

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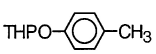
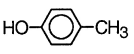
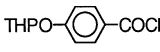
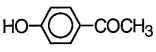
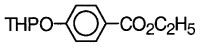
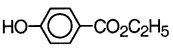
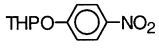
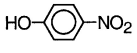
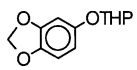
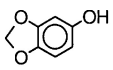
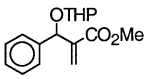
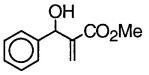
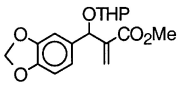
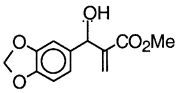
Table 1 Ti(III) Chloride-Induced Deprotection of Tetrahydropyranyl Ether of Alcohols/Phenols

Entry	Substrate		Product	Time (h)	Yield (%)
1	$CH_3(CH_2)_7OTHP$	(**1**)	$CH_3(CH_2)_7OH$	2	97
2	$CH_3(CH_2)_5CH(OTHP)CH_3$	(**2**)	$CH_3(CH_2)_5CH(OH)CH_3$	3	96
3	$CH_3(CH_2)_{15}OTHP$	(**3**)	$CH_3(CH_2)_{15}OH$	16	85
4		(**4**)		16	82
5		(**5**)		3	72
6		(**6**)		2.5	88
7		(**7**)		1	69
8		(**8**)		24	81
9		(**9**)		6	46
10		(**10**)		7	66
11	$CH_3CH(OTBDPS)(CH_2)_9OTHP$	(**11**)	$CH_3CH(OTBDPS)(CH_2)_9OH$ (**12**)	6	63
12	$TsO(CH_2)_8OTHP$	(**13**)	$TsO(CH_2)_8OH$	6	80
13	$AllylO(CH_2)_8OTHP$	(**14**)	$AllylO(CH_2)_8OH$	4	91
14	$BnO(CH_2)_8OTHP$	(**15**)	$BnO(CH_2)_8OH$	6	84
15	$CH_3CH(OTHP)(CH_2)_9OTHP$	(**16**)	$CH_3CH(OH)(CH_2)_9OH$ (**17**)	5	91

also unaffected by $TiCl_3$ (Table 1, entries 13 and 14). However, the reagent did not show any selectivity between the THP protected primary and secondary carbinol functionalities. For example, the substrate **16** furnished the diol **17** in excellent yield (Table 1, entry 15).

In conclusion, Ti(III) chloride-mediated depyranylation of alcohols and phenols has been demonstrated for the first time. Chemoselective deprotection of the THP ethers even in the presence of TBDPS ether, *p*-toluenesulfonate ester, allyl ether and benzyl ether, was also observed. Thus, the present protocol offers several advantages including compatibility with various sensitive and hydroxyl protecting functional groups, use of catalytic amount of the reagent, high yields and experimental simplicity, which makes it a useful addition to the existing synthetic methodologies.

The FT-IR spectra were scanned with a Nicolet FT-IR spectrophotometer (model 410). The ^1H NMR spectra were recorded with a Bruker AC 200 (200 MHz) spectrometer. Mass spectra were recorded with a Fisons MD 800 mass spectrometer. Microanalyses were performed with a Carlo Erba elemental analyzer (model 1110). All reactions were carried out under an Ar atmosphere. MeCN and CH_2Cl_2 were distilled over P_2O_5. Ti(III) chloride and 3,4-dihydro-2*H*-pyran (DHP) were purchased from Aldrich Chemical Co. and used as such. The Baylis–Hillman adducts were prepared following the literature procedure.[14]

Preparation of the THP Ethers; General Procedure

A solution of the alcohol/phenol (30 mmol), PPTS (1.51 g, 20 mol%) and DHP (2.945 g, 35 mmol) in anhyd CH_2Cl_2 (100 mL) was stirred at r.t. till the reaction was complete (monitored by TLC). Then the reaction mixture was washed with aq 10% $NaHCO_3$, the organic layer separated and washed with water and brine, and dried (Na_2SO_4). Removal of solvent followed by column chromatography (silica gel) of the crude product using EtOAc–petroleum ether (bp 60–80 °C) as the eluent yielded the respective THP ethers in 54–84% yields. The THP ethers **1**–**9**, **13** and **15** were characterized from their known spectral data.

1-(2-Tetrahydropyranyloxy)octane (1)[15a]

Yield: 74%; colorless viscous oil.

IR (neat): 2927, 2870, 1466, 869, 815 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.86 (t, *J* = 6.6 Hz, 3 H), 1.09–1.97 (m, 18 H), 3.25–3.97 (m, 4 H), 4.56 (br s, 1 H).

2-(2-Tetrahydropyranyloxy)octane (2)[15a]

Yield: 75%; colorless viscous oil.

IR (neat): 2930, 2857, 1466, 870, 814 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.85 (t, *J* = 6.6 Hz, 3 H), 1.08–1.98 (m, 18 H), 3.25–3.93 (m, 4 H), 4.55 (br s, 1 H).

1-(2-Tetrahydropyranyloxy)hexadecane (3)[15b]

Yield: 80%; colorless viscous oil.

IR (neat): 2925, 2853, 1466, 869, 816 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.6 Hz, 3 H), 1.24 (br s, 28 H), 1.44–1.94 (m, 6 H), 3.30–3.56 (m, 2 H), 3.62–3.94 (m, 2 H), 4.57 (br s, 1 H).

4-(2-Tetrahydropyranyloxy)toluene (4)[15c]
Yield: 79%; colorless viscous oil.

IR (neat): 2944, 2873, 970, 921, 872, 818 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.54–2.16 (m, 6 H), 2.34 (s, 3 H), 3.52–3.70 (m, 1 H), 3.88–4.08 (m, 1 H), 5.43 (br s, 1 H), 6.80–7.18 (m, 4 H).

4-(2-Tetrahydropyranyloxy)acetophenone (5)[15d]
Yield: 81%; low-melting solid.

IR ($CHCl_3$): 2948, 2871, 1714, 916, 841 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.46–2.07 (m, 6 H), 2.55 (s, 3 H), 3.50–3.68 (m, 1 H), 3.75–3.91 (m, 1 H), 5.51 (br s, 1 H), 7.07 (d, *J* = 8.8 Hz, 2 H), 7.91 (d, *J* = 8.8 Hz, 2 H).

Ethyl 4-(2-Tetrahydropyranyloxy)benzoate (6)[15e]
Yield: 80%; colorless viscous oil.

IR ($CHCl_3$): 2950, 1694, 1608, 852, 773 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.37 (t, *J* = 7.1 Hz, 3 H), 1.50–2.11 (m, 6 H), 3.25–3.68 (m, 1 H), 3.75–3.95 (m, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 5.49 (br s, 1 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 7.98 (d, *J* = 8.8 Hz, 2 H).

4-(2-Tetrahydropyranyloxy)nitrobenzene (7)[15a]
Yield: 65%; low melting solid.

IR ($CHCl_3$): 2948, 1495, 1173, 849, 823 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.42–2.12 (m, 6 H), 3.44–3.94 (m, 2 H), 5.52 (br s, 1 H), 7.11 (d, *J* = 9.3 Hz, 2 H), 8.17 (d, *J* = 9.3 Hz, 2 H).

3,4-Methylenedioxy-1-(2-tetrahydropyranyloxy)benzene (8)[15f]
Yield: 60%; colorless viscous oil.

IR ($CHCl_3$): 2945, 2875, 967, 931, 872, 819 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.44–2.10 (m, 6 H), 3.46–3.70 (m, 1 H), 3.78–4.04 (m, 1 H), 5.25 (br s, 1 H), 5.99 (s, 2 H), 6.41–6.78 (m, 3 H).

Methyl 2-Methylene-3-phenyl-3-(2-tetrahydropyranyloxy)propanoate (9)[15g]
Yield: 75%; colorless viscous oil.

IR (neat): 2949, 2871, 1727, 1352, 911, 870, 817 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.37–1.97 (m, 6 H), 3.34–3.94 (m, 5 H), 4.51 (m, 0.5 H), 4.77 (m, 0.5 H), 5.63 (m, 1 H), 5.97 (br s, 0.5 H), 6.09 (br s, 0.5 H), 6.32 (s, 0.5 H), 6.39 (s, 0.5 H), 7.16–7.50 (m, 5 H).

Methyl 2-Methylene-3-(3,4-methylenedioxyphenyl)-3-(2-tetrahydropyranyloxy)propanoate (10)
Yield: 54%; colorless viscous oil.

IR (neat): 2948, 2872, 1725, 1641, 996, 938, 896, 822 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.34–1.96 (m, 6 H), 3.39–3.92 (m, 5 H), 4.52 (m, 0.5 H), 4.71 (m, 0.5 H), 5.53 (m, 1 H), 5.92 (m, 2.5 H), 6.09 (br s, 0.5 H), 6.30 (s, 0.5 H), 6.37 (s, 0.5 H), 6.64–6.96 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 18.4, 24.6, 29.7, 50.9, 61.2, 62.1, 72.8, 74.4, 93.7, 96.2, 100.3, 107.2, 121.4, 123.5, 124.1, 132.3, 133.5, 140.2, 140.9, 146.3, 146.6, 146.8, 146.9, 165.4, 165.5.

EI–MS: 320 [M^+].

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.72; H, 6.30. Found: C, 63.54; H, 6.28.

10-[(1,1-Dimethylethyl)diphenylsilyloxy]-1-(2-tetrahydropyranyloxy)undecane (11)
Yield: 84%; colorless viscous oil.

IR (neat): 3070, 2930, 2856, 1472, 1430, 1114, 1035 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.99–1.08 (m, 12 H), 1.12–1.75 (m, 22 H), 3.25–3.54 (m, 2 H), 3.62–3.90 (m, 3 H), 4.57 (m, 1 H), 7.35–7.41 (m, 6 H), 7.65–7.69 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 19.1, 19.6, 23.1, 25.1, 25.4, 26.2, 26.9, 29.4, 29.7, 30.7, 39.3, 62.1, 67.5, 69.5, 98.6, 127.3, 129.3, 134.5, 134.8, 135.8.

EI–MS: 510 [M^+].

Anal. Calcd for $C_{32}H_{50}O_3Si$: C, 75.22; H, 9.87. Found: C, 75.09; H, 9.85.

1-(4-Methylphenylsulfonyloxy)-8-(2-tetrahydropyranyloxy)octane (13)[8c]
Yield: 78%; colorless viscous oil.

IR (neat): 2938, 2858, 1363, 1177, 1033, 966, 815 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.12–1.33 (m, 8 H), 1.41–1.92 (m, 10 H), 2.42 (s, 3 H), 3.23–3.53 (m, 2 H), 3.65–3.89 (m, 2 H), 3.98 (t, *J* = 6.5 Hz, 2 H), 4.54 (br s, 0.8 H), 4.93 (br s, 0.2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.76 (d, *J* = 8.3 Hz, 2 H).

1-Allyloxy-8-(2-tetrahydropyranyloxy)octane (14)
Yield: 81%; colorless viscous oil.

IR (neat): 2939, 2867, 1441, 1125, 1075, 1035, 967 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.17–1.92 (m, 18 H), 3.25–3.58 (m, 4 H), 3.65–4.01 (m, 4 H), 4.55 (br s, 0.2 H), 4.93 (br s, 0.8 H), 5.08–5.33 (m, 2 H), 5.75–6.01 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 19.2, 25.1, 25.8, 29.0, 29.3, 30.2, 61.6, 62.2, 67.1, 69.9, 71.3, 93.9, 98.2, 116.0, 134.6.

EI–MS: 270 [M^+].

Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.05; H, 11.19. Found: C, 70.92; H, 11.17.

1-Benzyloxy-8-(2-tetrahydropyranyloxy)octane (15)[15h]
Yield: 76%; colorless viscous oil.

IR (neat): 2937, 2855, 1454, 1123, 1034, 968 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.08–1.30 (m, 8 H), 1.32–1.77 (m, 10 H), 3.26–3.85 (m, 6 H), 4.47 (s, 2 H), 4.55 (br s, 0.7 H), 4.94 (br s, 0.3 H), 7.19–7.36 (m, 5 H).

1,10-Bis(2-tetrahydropyranyloxy)undecane (16)
Yield: 75%; colorless viscous oil.

IR (neat): 2934, 2854, 1441, 1354, 1200, 1123, 1035 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.01–1.92 (m, 31 H), 3.29–3.56 (m, 3 H), 3.62–3.92 (m, 4 H), 4.52–4.73 (m, 1.4 H), 4.95 (br s, 0.6 H).

^{13}C NMR ($CDCl_3$): δ = 18.6, 19.3, 19.7, 21.2, 25.2, 25.9, 29.2, 30.4, 30.9, 36.2, 37.2, 61.7, 61.9, 62.3, 67.2, 70.6, 73.5, 94.0, 95.1, 98.2, 98.3.

EI–MS: 356 [M^+].

Anal. Calcd for $C_{21}H_{40}O_4$: C, 70.72; H, 11.32. Found: C, 70.61; H, 11.31.

Depyranylation; General Procedure
To a solution of the THP ethers (2 mmol) in anhyd MeCN (10 mL), anhyd $TiCl_3$ (0.062 g, 20 mol%) was added and the mixture stirred at r.t. for the time specified in Table 1. Then the reaction mixture was concentrated in vacuo, taken in Et_2O and the extract was successively washed with 10% aq $NaHCO_3$, water and brine, and dried

(Na_2SO_4). Removal of solvent followed by column chromatography (silica gel) of the crude product using EtOAc–petroleum ether (bp 60–80 °C) as the eluent afforded the respective alcohols/phenols in 46–97% yields. The products obtained from the substrates **1**–**10** and **13**–**15** were characterized from their known spectral data.

10-[(1,1-Dimethylethyl)diphenylsilyloxy]undecan-1-ol (12)
Yield: 63%; colorless viscous oil.

IR (neat): 3365, 3070, 2929, 2855, 1463, 1427, 1111, 1059 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.01–1.07 (m, 12 H), 1.12–1.75 (m, 16 H), 1.94 (br s, 1 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 3.75–3.90 (m, 1 H), 7.26–7.49 (m, 6 H), 7.65–7.78 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 19.2, 23.3, 25.1, 25.7, 26.9, 27.1, 29.5, 32.7, 39.4, 62.8, 69.5, 127.3, 129.3, 134.5, 134.9, 135.9.

EI–MS: 426 [M^+].

Anal. Calcd for $C_{27}H_{42}O_2Si$: C, 75.98; H, 9.93. Found: C, 75.75; H, 9.90.

1,10-Dihydroxyundecane (17)
Yield: 91%; colorless viscous oil.

IR (neat): 3364, 2927, 2854, 1455, 1075 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.01–1.82 (m, 19 H), 2.74 (br s, 1 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 3.59–3.77 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 23.1, 23.3, 25.5, 29.3, 32.5, 39.1, 62.6, 67.9.

EI–MS: 188 [M^+].

Anal. Calcd for $C_{11}H_{24}O_2$: C, 70.14; H, 12.86. Found: C, 70.01; H, 12.83.

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