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Direct Conversion of Trimethylsilyl and Tetrahydropyranyl Ethers into Esters with Acid Chlorides in the Presence of Montmorillonite K-10

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ABSTRACT

A simple method is described for an efficient conversion of variety of trimethylsilyl (TMS) and tetrahydropyranyl (THP) ethers into their corresponding esters with acid chlorides in the presence of montmorillonite K-10.

Esters are common intermediates in natural product chemistry due to their stability and accessibility for easy interconversion. The traditional preparations^[1] use acid and alcohol in the presence of classic acids

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which are corrosive in nature. Further modifications use alcohols and acid chlorides.^[2–6] Other routes such as transesterification,^[7] alkylation of carboxylate anions,^[8] and cleavage of ethers^[9] have also been used. However, just a few reports are available dealing with the conversion of trimethylsilyl and tetrahydropyranyl ethers into the corresponding esters.^[10] In a recent report, a variety of TMS and THP ethers were converted to the corresponding acetates and benzoates with acetic and benzoic anhydrides in the presence of Bi(III) salts in refluxing acetonitrile.^[10b]

Montmorillonite clays, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for a wide variety of organic reactions.^[11] Recently, we introduced two convenient one-step procedures for the deprotection -acetylation of TMS ethers with acetic anhydride using montmorillonite K-10.^[10d] In view of environmental, practical, and economical demands and to explore the generality and scope of montmorillonite K-10 catalyzed esterification, this article describes a simple, efficient, and mild one-pot method to transform different classes of TMS and THP ethers to the corresponding esters with acid chlorides at room temperature using montmorillonite K-10 as a mild heterogeneous catalyst (Sch. 1).

The reactions were performed with equimolar amounts of the ethers and acid chlorides in the presence of the clay in chloroform at room temperature. The representative examples illustrating the conversion of TMS ethers into the corresponding esters are listed in Table 1. The results clearly show the need for longer reaction times for silylated phenols, giving the esters also with lower yield.

Table 2 shows the results obtained for THP ethers. The reaction of the THP ether of benzyl alcohol with acetyl and propionyl chlorides gave the corresponding esters in 0.5 h, whereas the reaction of the same ether with benzoyl chloride was rather slow (3 h). THP ethers of primary and secondary alcohols gave the esters with much better results than the THP ether of *tert*-butanol (Table 2, Entry 14).

In summary, the present method describes a simple, mild, and efficient procedure for one-pot transformation of TMS and THP ethers to the corresponding esters in high yield. In addition, easy work-up, availability, and nontoxicity of the catalyst are notable advantages of this method.

Scheme 1.

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Conversion of TMS and THP Ethers

	Table 1. Conversion of TMS ether	s to their corresponding	esters in the pi	esence of montr	norillonite K-10.
			Time	Yield ^a	M.P. (°C)(obs.)/M.P.
No.	TMS ether	Acid chloride	(h)	(%)	or B.P.(°C/mm)(lit.) ^{ref}
-	PhCH ₂ OTMS	CH ₃ COCI	0.3	66	$(212)/214^{[12]}$
7	PhCH ₂ OTMS	PhCOCI		85	$(oil)/323^{[14]}$
ю	PhCH ₂ OTMS	CH ₃ CH ₂ COCI	0.3	88	$(220)/222^{[13]}$
4	$CH_3(CH_2)_{10}CH_2OTMS$	CH ₃ COCI	0.4	84	$(148)/151^{[14]}$
5	$CH_3(CH_2)_{10}CH_2OTMS$	CH ₃ CH ₂ COCI	0.5	80	$(oil)/166-8, 20 \mathrm{mm}^{[13]}$
9	CH ₃ (CH ₂) ₆ CH ₂ OTMS	CH ₃ COCI	0.3	81	$(207)/210^{[14]}$
Г	CH ₃ (CH ₂) ₆ CH ₂ OTMS	PhCOCI	1.5	75	$(oil)/305-6^{[13]}$
8	CH ₃ (CH ₂) ₅ CH(CH ₃)OTMS	CH ₃ COCI	0.4	62	$(195)/84, 15 \mathrm{mm}^{[13]}$
6	CH ₃ (CH ₂) ₅ CH(CH ₃)OTMS	PhCOCI	2	72	$(oil)/175, 2-5 mm^{[13]}$
10	CH ₃ (CH ₂) ₅ CH(CH ₃)OTMS	CH ₃ CH ₂ COCI	0.5	76	$(222)/96, 15 \mathrm{mm}^{[13]}$
11	PhOTMS	CH ₃ COCI	18	61	$(192)/196^{[14]}$
12	PhOTMS	PhCOCI	22	50	$(67-68)/71^{[14]}$
^a Isolated	yields.				

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	Table 2. Conversion of THP ether	s to their corresponding es	sters in the pre-	sence of montn	norillonite K-10.
			Time	Yield ^a	M.P. ($^{\circ}$ C)(obs.)/M.P.
No.	1 HP ether	Acid chloride	(u)	(0%)	or B.P.(C/mm)(lit.)
1	CH ₃ (CH ₂) ₆ CH ₂ OTHP	CH ₃ COCI	0.5	78	$(207)/210^{[14]}$
7	$CH_3(CH_2)_4CH_2OTHP$	CH ₃ COCI	0.5	77	$(168)/172^{[14]}$
С	CH ₃ (CH ₂) ₅ CH ₂ OTHP	CH ₃ COCI	0.5	75	$(191)/192^{[14]}$
4	$CH_3(CH_2)_{10}CH_2OTHP$	CH ₃ CH ₂ COCI	0.75	76	$(oil)/166-8, 20 \mathrm{mm}^{[13]}$
5	$CH_3(CH_2)_{10}CH_2OTHP$	CH ₃ CH ₂ CH ₂ COCI	0.75	74	$(oil)/194.5, 30 \mathrm{mm}^{[13]}$
9	CH ₃ (CH ₂) ₆ CH ₂ OTHP	PhCOCI	С	70	$(oil)/305-6^{[13]}$
7	CH ₃ (CH ₂) ₅ CH(CH ₃)OTHP	CH ₃ COCI	0.5	77	$(195)/84, 15 \mathrm{mm}^{[13]}$
8	CH ₃ (CH ₂) ₅ CH(CH ₃)OTHP	CH ₃ CH ₂ COCI	1	75	$(222)/96, 15 \mathrm{mm}^{[13]}$
6	CH ₃ (CH ₂) ₅ CH(CH ₃)OTHP	CH ₃ CH ₂ CH ₂ COCI	1	73	$(oil)/115, 18 \mathrm{mm}^{[13]}$
10	cyclo-C ₆ H ₁₁ OTHP	PhCOCI	9	68	(oil)/285 ^[14]
11	PhCH ₂ OTHP	CH ₃ COCI	0.5	90	$(212)/214^{[12]}$
12	PhCH ₂ OTHP	CH ₃ CH ₂ COCI	0.5	87	$(220)/222^{[13]}$
13	PhCH ₂ OTHP	PhCOCI	3	85	$(oil)/323^{[14]}$
14	(CH ₃) ₃ COTHP	CH ₃ COCI	0.3	10	$(95-7)/97-8^{[14]}$
^a Isolated	yields.				

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Conversion of TMS and THP Ethers

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EXPERIMENTAL

Infrared spectra were obtained using a Shimadzu IR-408 instrument. ¹H NMR spectra were recorded on a Jeol JNM-EX90A. Products were characterized by comparison of their physical data, IR, and NMR spectra with those reported in the literature.

General Procedure for the Conversion of TMS Ethers into Their Corresponding Esters

To a stirred suspension of TMS ether (1 mmol), dry chloroform (6 mL), and montmorillonite K-10 (250 mg), acid chloride (1.2 mmol) was added dropwise. The mixture was stirred at room temperature for the length of time indicated in Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by filteration and the filtrate was evaporated. The resulting crude product was purified by preparative TLC (silica gel; eluent, dichloromethane/petroleum ether, 5:1) to afford the ester.

General Procedure for the Conversion of THP Ethers into Their Corresponding Esters

To a stirred solution of THP ether (1 mmol) in dry chloroform (6 mL), montmorillonite K-10 (250 mg) was added. Acid chloride (1.2 mmol) was added to the heterogeneous mixture and stirring at room temperature continued for the appropriate time (Table 2). The contents were filtered and the filtrate was evaporated. The resulting crude product was purified by preparative TLC (silica gel; eluent, dichloromethane/petroleum ether, 5:1 or *n*-hexane/ethyl acetate, 5:1) to obtain the ester.

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