

Desilylation-acetylation of trimethylsilyl ethers with acetic anhydride catalysed by montmorillonite K-10†

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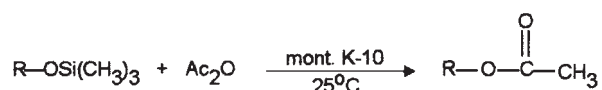
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Two mild and simple one-step desilylation-acetylations of a variety of alkyl- and aryl-trimethylsilyl ethers, Me₃SiOR(Ar), with acetic anhydride in the presence of montmorillonite K-10 clay are described.

Esters are among the most important natural and industrial products.¹ They are usually prepared by esterification of carboxylic acids,^{2,3} transesterification,^{3,4} alkylation of carboxylate anions,⁵ and acylation of alcohols and phenols.^{6–11} These reactions are usually catalysed by acids or bases in either homogeneous or heterogeneous conditions. On the other hand, ethers are also converted to esters by acyl and aroyl halides (including sulfonyl halides) and anhydrides of carboxylic acids in the presence of Lewis acids or of strong proton acids.^{12–14}

Ganem *et al.*¹⁴ reported the possible mechanism of ether-to-acetate transformation for the reaction of a variety of ethers in acetic anhydride in the presence of anhydrous ferric chloride; they proposed a dual mechanism involving O-acylation of the ether followed by dissociation to the more stable carbonium ion or nucleophilic displacement (S_N1 or S_N2) at the oxonium ion by acetate. They also showed only one case of a silylether-to-acetate transformation. Direct conversion of trimethylsilyl (TMS) ethers into the corresponding acetates has also been reported¹⁵ using acetyl chloride and zinc chloride in acetonitrile.

In connection with our ongoing work on montmorillonite clay catalysis,¹⁶ we now wish to report a convenient one-step procedure for deprotection-acetylation of trimethylsilyl TMS ethers with acetic anhydride at room temperature using montmorillonite K-10 as a mild heterogeneous catalyst (Scheme 1). The focal point of this report is on the transformation of a Si–O bond into a new O–CO bond.



Scheme 1

As shown in Table 1, a series of silylated alcohols and phenols are treated with acetic anhydride under catalysis by the solid acid (montmorillonite K-10) under two different conditions; when trimethylsilyl ethers are exposed to the clay in acetic anhydride as solvent (method A, Ac₂O : R-OTMS, mol : mol ratio of 10:1) the acetates are obtained in short period of time. By contrast, a long reaction time is observed for acetylation of the substrates with acetic anhydride in dichloromethane solution (method B, Ac₂O:ROTMS, mol : mol ratio of 2:1) in the presence of the catalyst. It is interesting to note that long reaction times and low yields are observed in the absence of the clay; applying methods A and B to trimethylsilyloxy phenylmethane (entry 3, Table 1) and acetic anhydride without the clay catalyst afforded 42% (reaction time 5h) and 30% (reaction time 48h) yields respectively.

To conclude, montmorillonite K-10 is a good one-pot desilylation-acetylation catalyst for a wide range of silylated alcohols and phenols. The present procedure has the additional advantages of high yield, mild conditions, easy work-up and an inexpensive and environmentally friendly catalyst.

Experimental

General procedure for conversion of trimethylsilyl ethers into the corresponding acetates (method B): To a solution of the trimethylsilyl ether (1 mmol) and acetic anhydride (2 mmol) in dichloromethane (2 ml), montmorillonite K-10 (250 mg) was added and the heterogeneous mixture was stirred at room temperature for 2–24 h. The contents were filtered and the filtrate was extracted with saturated aqueous NaHCO₃ (2 × 6 ml) and water (2 × 6 ml), dried (Na₂SO₄) and evaporated. The residue was purified by column chromatography on silica gel using *n*-hexane: ether (4:1) as eluent.

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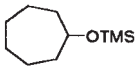
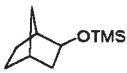
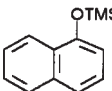
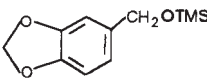
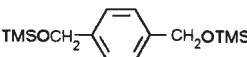
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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Acetylation of trimethylsilyl ethers with acetic anhydride catalysed by Montmorillonite K-10^a

Entry	Substrate	Method A ^b Time (h) (%Yields of acetate) ^d	Method B ^c Time (h)	Ref. ^e
1	<i>p</i> -MeOC ₆ H ₄ CH ₂ OTMS	0.75 (96)	2 (90)	17
2	<i>p</i> -ClC ₆ H ₄ CH ₂ OTMS 1 (54)	2 (63)	18	
3	C ₆ H ₅ CH ₂ OTMS	0.25 (88)	2 (82)	19
4	CH ₃ (CH ₂) ₅ CH ₂ OTMS	0.75 (76)	3 (80)	20
5	CH ₃ (CH ₂) ₄ CH(CH ₃)OTMS	1 (82)	3 (85)	21
6		0.5 (57)	3 (65)	22
7	C ₆ H ₅ CH=CHCH ₂ OTMS	1 (46)	5 (54)	23
8		0.75 (78)	4 (71)	24
9	<i>p</i> -EtC ₆ H ₄ OTMS	0.33 (95)	10 (85)	25
10		24 (32)	24 (61)	26
11		0.5 (82)	3 (87)	27
12		0.25(90)	2 (82)	28

^aAll products were identified by their IR and ¹H NMR spectra and/or by comparison of their bp or mp with authentic samples.

^bAcetic anhydride : substrate (mol : mol) ratio is 10:1. ^cIn CH₂Cl₂, acetic anhydride : substrate (mol : mol) ratio is 2:1. ^dYields of pure isolated products. ^ePublished physical and spectroscopic properties.

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