

## FeCl<sub>3</sub>-adsorbed on montmorillonite K-10: An efficient catalyst for one-pot dealkylation–acetylation of ethers<sup>†</sup>

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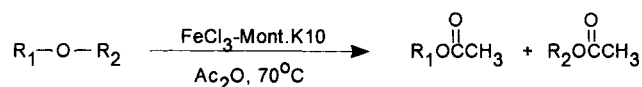
Direct conversion of ethers into acetates is achieved by treatment of ethers with acetic anhydride in the presence of FeCl<sub>3</sub>-adsorbed on montmorillonite K-10.

**Keywords:** FeCl<sub>3</sub>, montmorillonite K-10

Esters are among the most important industrial products<sup>1</sup> and well-established in hydroxyl group protection.<sup>2</sup> They are usually synthesized by one of the three main methods: (i) direct esterification of carboxylic acids or their derivatives,<sup>3</sup> (ii) transesterification of methyl or ethyl esters,<sup>4</sup> and (iii) alkylation of carboxylate anions.<sup>5</sup> The first two methods have been widely studied, and a variety of acetylation procedures have been developed.<sup>6</sup> Some of these procedures are highly acidic and suffer from unfavorable side reactions (*e.g.* dehydration), bulk requirement of solid support, and unavailability of the catalyst.

On the other hand, ethers have extensively been used for protection of hydroxyl groups;<sup>7</sup> although they are easily accessible by simple nucleophilic substitution reactions, their widespread use as protecting groups still await satisfactory methods for their convenient cleavage to the parent alcohols. The various methods described either use too drastic conditions<sup>7</sup> which might break-up sensitive parts of the molecules, or do not lead to the desired alcohols.<sup>8</sup> A combination of Lewis acids with carboxylic acid chlorides and anhydrides has been examined for the ether-to-acetate transformation.<sup>9</sup>

Montmorillonite clays have been extensively employed as efficient catalysts for variety of organic reactions.<sup>10</sup> In connection with our ongoing work on montmorillonite K-10,<sup>11</sup> we now wish to report a convenient and efficient method for one-pot acetylation of ethers using FeCl<sub>3</sub>-adsorbed on montmorillonite K-10 as a heterogeneous catalyst and acetic anhydride (Scheme 1).



**Scheme 1**

In order to have a background knowledge of the activity of the extensively used montmorillonite clays, dibenzyl ether was treated with acetic anhydride under different conditions (Table 1). It is found that FeCl<sub>3</sub> supported montmorillonite K 10 is conspicuously effective among the clays for the dealkylation–acetylation of ethers. The capacity of the reagent determined by the atomic absorption technique was 0.25 mmol/g of solid catalyst. Using dibenzyl ether, the amount of catalyst was optimized and an ether to clay ratio of 1: 0.063 was taken. The catalyst can be recovered and reused after activation at 280 °C. In this study, a variety of dialkyl and aryl–alkyl ethers were treated with acetic anhydride in the

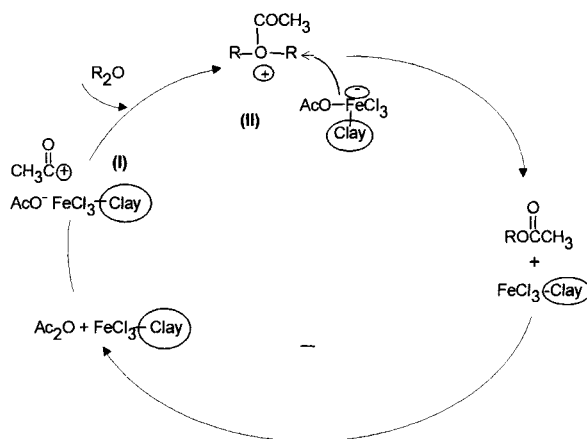
**Table 1** Dealkylation-acetylation of dibenzyl ether using different montmorillonite clay catalysts and acetic anhydride<sup>a</sup>

Clay catalyst	Amount/g	Time/h	Yield/%
Montmorillonite K 10	0.25	24	0
Montmorillonite K 10	0.5	24	<5
Montmorillonite KSF	0.5	24	0
Fe <sup>3+</sup> montmorillonite K 10	0.5	24	<5
FeCl <sub>3</sub> -montmorillonite K 10	0.25	22	94
FeCl <sub>3</sub> -montmorillonite K 10	0.5	12	95

<sup>a</sup>Progress of the reactions monitored by GC.

presence of a catalytic amount of FeCl<sub>3</sub>-montmorillonite K-10 and the corresponding acetates were obtained in moderate to high yields. It is worth noting that convenient demethylations of aryl and alkyl ethers were also performed, and the corresponding acetates were obtained as the sole cleavage products in reasonable yields (entries 8–11, Table 2). It is also pertinent to note that the carbon–carbon double bond remains unaffected (entry 9, Table 2) and no elimination product is observed (entries 3 and 4, Table 2). As expected, diphenyl ether was not acetylated. The results are generally better than those of existing methods, specially in terms of the amount of required catalyst, reaction period and yields. Such advantages along with its simplicity and versatility make this system a worthwhile alternative route for ether-to-acetate conversion.

Based on our observations, we suggest that this conversion may proceed through the formation of the acylium ion (I) by clay-assisted cleavage of the anhydride, which is followed by activation of ethers to produce the oxonium ion (II). Finally, O-acetylation of the ether, dissociation of the more stable carbonium ion or nucleophilic attack of oxonium ion by acetate anion of FeCl<sub>3</sub>-montmorillonite K-10 clay species will follow (Scheme 2).





**Scheme 2**

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

**Table 2** Ethers deblocking-acetylation with Ac<sub>2</sub>O in the presence of FeCl<sub>3</sub>-montmorillonite K-10<sup>a</sup>

Entry	R <sub>1</sub>	R <sub>2</sub>	Time/h	Product	Yield/%
1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	22	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OAc <sup>b</sup>	90
2	PhCH <sub>2</sub>	PhCH <sub>2</sub>	22	PhCH <sub>2</sub> OAc <sup>c</sup>	94
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	24	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OAc <sup>b</sup>	83
4	PhCH <sub>2</sub>	<i>n</i> -Pr-CH(Me)	17	PhCH <sub>2</sub> OAc <i>n</i> -Pr-CH(Me)OAc	70 <sup>d</sup> 22 <sup>d</sup>
5	PhCH <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> C	14	PhCH <sub>2</sub> OAc (Me) <sub>3</sub> COAc	45 <sup>d</sup> 50 <sup>d</sup>
6	PhCH <sub>2</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	22	PhCH <sub>2</sub> OAc CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OAc	41 <sup>d</sup> 46 <sup>d</sup>
7	Ph	Ph	40	no reaction	0
8	Ph	CH <sub>3</sub>	36	PhOAc <sup>b</sup>	45
9	CH <sub>2</sub> =CHCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	36	CH <sub>2</sub> =CHCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -OAc <sup>b</sup>	61
10	4-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	36	4-ClC <sub>6</sub> H <sub>4</sub> OAc <sup>b</sup>	66
11	α-naphthyl	CH <sub>3</sub>	38	α-naphthyl acetate <sup>c</sup>	69
12	PhCH <sub>2</sub>	CH <sub>3</sub>	29	PhCH <sub>2</sub> OAc <sup>c</sup>	68
13	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	26	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OAc <sup>c</sup>	63
14	ClCH <sub>2</sub> CH <sub>2</sub>	ClCH <sub>2</sub> CH <sub>2</sub>	30	ClCH <sub>2</sub> CH <sub>2</sub> OAc <sup>c</sup>	57
15	PhCH <sub>2</sub>		28	 O Ac PhCH <sub>2</sub> O Ac	49 <sup>d</sup> 31 <sup>d</sup>

<sup>a</sup>Reactions are carried out at 70 °C using 0.063 mole of FeCl<sub>3</sub> on montmorillonite K-10.

<sup>b</sup>Products were identified by their IR spectra and by comparison with authentic samples.

<sup>c</sup>Products were characterised by their IR and NMR spectra.

<sup>d</sup>Yields refer to isolated mixture of products which determined by GC and <sup>1</sup>H NMR (200 MHz).

## Experimental

Ethers were either synthesised according to general procedures<sup>12</sup> or purchased from the Fluka company. The montmorillonite K-10 was purchased from the Fluka company and the FeCl<sub>3</sub>-montmorillonite K-10 was prepared by the procedure reported by Pai *et al.*<sup>13</sup> The IR spectra were run on a Shimadzu IR 470 instrument. <sup>1</sup>H NMR spectra were recorded on a Jeol JNM-PMX 60SI and a Bruker 200 MHz spectrometer. The progress of the reactions was monitored by TLC or gas chromatography (Shimadzu, GC-8A). All products were identified by comparison of their spectral data based on those of authentic samples.

**General procedure for conversion of ethers into the corresponding acetates:** To the stirred solution of ether (1.0 mmol) and acetic anhydride (10 mmol) in a round bottomed flask equipped with a condenser, FeCl<sub>3</sub>-montmorillonite K-10 (250 mg, containing 0.063 mmole of FeCl<sub>3</sub>) was added. The mixture was heated at 70 °C for the time as specified in Table 2. Progress of the reaction was monitored by TLC (eluent, *n*-hexane: ether, 5:1); on completion, after cooling, dichloromethane (10 ml) was added and stirred for 15 minutes at room temperature. The solution was filtered and the filtrate was washed with saturated sodium bicarbonate. Evaporation of the organic layer afforded the desired esters in 22–94% yields.

**Spectroscopic data for compound 11:** m.p. 48–49 °C (Lit. 49 °C)<sup>12</sup>; IR (neat) v/cm<sup>-1</sup> 2900–3100 (m), 1760 (s), 1595 (s), 1500 (s), 1460 (s), 1410 (w), 1395 (s), 1365 (s); <sup>1</sup>H NMR (CCl<sub>4</sub>), δ (ppm) : 7.1–7.9 (m, 7H), 2.4 (s, 3H).<sup>14</sup>

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