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Acetals by AlFe-Pillared Montmorillonite Catalysis

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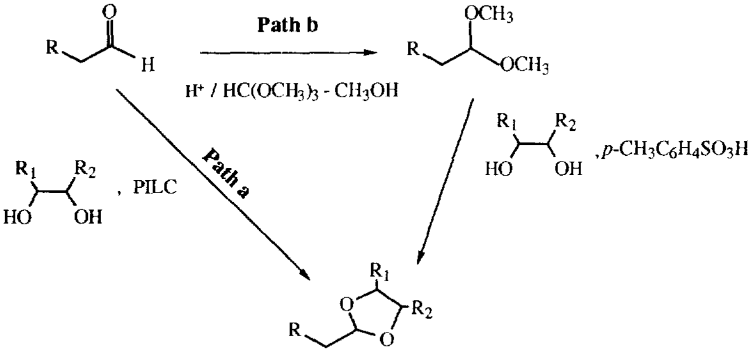
Abstract: AlFe-pillared montmorillonite is an efficient catalyst for acetals preparation in CH_2Cl_2 at room temperature. © 1997 Elsevier Science Ltd.

INTRODUCTION

Clays supported reagents continue to receive great attention in organic synthesis for their selectivity and good efficiency, due to the porous structure and the high surface area, and for the generally mild reaction conditions they require; furthermore they are environmentally friendly alternatives to conventional reagents.[1]

Pillared interlayered clays (PILCs) or simply Pillared clays [2] are microporous materials obtained by ion-exchange of the clay charge-balancing cations with large polyatomic inorganic ones. On calcination, inorganic oxide pillars are formed with a permanent separation between the silicate layers, thus preventing their collapse; by this way a microporous structure with high thermal stability and high surface area is obtained. Both Brønsted and Lewis acids sites are present, the second ones being more numerous. By different types of pillars, a variety of pore dimensions and catalytic activities are obtained; these PILCs are a new group of relatively inexpensive materials with properties similar or complementary to those of zeolites.

On investigating the uses of pillared clays [3], we first applied these catalysts to the preparation (Path a) of 2-alkyl-1,3-dioxolanes, synthetic intermediates of 2,2-dichloroesters (scheme 1); these cyclic acetals have been previously prepared by a two step route (Path b)[4].

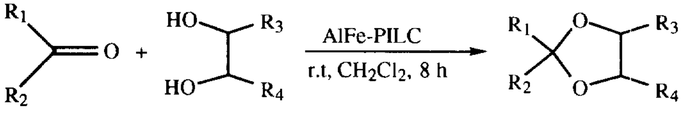


Scheme 1

Usually acetals are prepared from carbonyl compounds and alcohols, diols or orthoesters using acid catalysts like ammonium, zinc(II) or iron(III) chlorides, p-toluensulfonic acid,[5] rare-earth chlorides,[6] Amberlyst 15,[7] N-benzyl- piridinium salts.[8]

Though clays, such as: natural Kaolin,[9] acid-activated montmorillonites like K-10, [10] quaternary ammonium,[11] Al^{3+} or Ce^{3+} exchanged-montmorillonites [12,13] have been used for acid-catalyzed acetalizations, pillared clays have never been tested for these reactions.

Now we report that Al-Fe pillared clay (AlFe-PILC) is an efficient heterogeneous catalyst for acetal preparation in CH_2Cl_2 under mild conditions (scheme 2).



scheme 2

RESULTS AND DISCUSSION

The reaction procedure has been optimised starting from butanal and 1,2-propandiol as substrates (Table 1). The formation of 4-methyl-2-*n*-propyl-1,3-dioxolane is very good by using the CH_2Cl_2, CH_3CN or $C_2H_5OC_2H_5$, whereas completely fails with the basic solvent dimethylformamide (entry 9). A minimum of solvent is necessary; in the absence of any solvent, indeed, lower conversions are observed (entry 4, Table 1). On increasing the amount of catalyst (200 mg) (entry 5) or the temperature (entry 6) the acetalization reaction rate is higher. No reaction at all is instead observed (entry 7) when untreated natural montmorillonite replaces AlFe-PILC.

Table 1- Acetalization reaction between butanal (10 mmol) and 1,2-propandiol (15 mmol) with AlFe-PILC as catalyst

entry	solvent (ml)	catalyst (mg)	temperature °C	reaction time (h)	conversion[a] mol%	acetal yield[b] mol%
1	CH_2Cl_2 (5)	51	25	8	82	99
2	CH_2Cl_2 (1)	51	25	8	97	99
3	CH_2Cl_2 (1)	51	25	5	92	99
4	without solvent	51	25	5	69	99
5	CH_2Cl_2 (1)	200	25	5	99	99
6	CH_2Cl_2 (1)	51	45	5	99	99
7	CH_2Cl_2 (1)	51[c]	25	5	0	0
8	CH_3CN (1)	51	25	8	95	98
9	DMF (1)	51	25	8	0	0
10	$C_2H_5OC_2H_5$ (1)	51	25	8	94	99

[a] Based on the initial amount of carbonyl compound. [b] Yield of isolated product, based on the consumed carbonyl compound.
[c] Untreated natural montmorillonite

Reaction conditions of entry 2 (Table 1) have then been used on a number of diols and carbonyl compounds (Table 2); good to excellents results have been obtained, showing no significative dependence on diol structure.

Table 2. Acetalization of carbonyl compounds by catalysis of Al-Fe pillared montmorillonite

entry	R_1	R_2	R_3	R_4	T °C	conversion[a] mol %	acetal yield[b] mol %
1	$CH_3(CH_2)_2$-	H	H	H	25	92	98
2	$CH_3(CH_2)_2$-	H	CH_3-	H	25	97	99
3	$CH_3(CH_2)_2$-	H	CH_3-	CH_3-	25	94	99
4	$CH_3(CH_2)_2$-	H	$ClCH_2$-	H	25	94	87
5	$CH_3(CH_2)_3$-	H	CH_3-	H	25	82	99
6	$CH_3(CH_2)_6$-	H	CH_3-	H	25	80	98
7	$(CH_3)_2CHCH_2$-	H	CH_3-	H	25	81	99
8	$(CH_3)_2CHCH_2$-	H	CH_3-	CH_3-	25	74	99
9	$(CH_3)_2CHCH_2$-	H	CH_3-	H	60	97	99
10	$(CH_3)_2CHCH_2$-	H	CH_3-	CH_3-	60	99	99
11	$(CH_3CH_2)_2CH$-	H	CH_3-	H	25	48	98
12	$(CH_3CH_2)_2CH$-	H	CH_3-	H	60	86	99
13	C_6H_5-	H	CH_3-	H	25	46	96
14	C_6H_5-	H	CH_3-	CH_3-	25	38	99
15	C_6H_5-	H	CH_3-	H	60	66	99
16	C_6H_5-	H	CH_3-	CH_3-	60	76	99
17	C_6H_5-CH_2-	H	CH_3-	H	25	31	82
18	C_6H_5-$(CH_2)_2$-	H	CH_3-	H	25	30	99
19	C_6H_5-$(CH_2)_2$-	H	CH_3-	CH_3-	25	36	99
20	C_6H_5-$(CH_2)_2$-[c]	H	CH_3-	H	25	30	99
21	C_6H_5-$(CH_2)_2$-	H	CH_3-	H	60	88	99
22	C_6H_5-$(CH_2)_2$-	H	CH_3-	CH_3-	60	92	99
23	$(C_6H_5)(CH_3)CHCH_2$-	H	CH_3-	H	25	27	92
24	*p*-Cl-C_6H_4-	H	CH_3-	H	25	15	100

[a] Based on the initial amount of carbonyl compound, time = 8h. [b] Yield of isolated product, based on the consumed carbonyl compound, time = 8h. [c] Reaction time = 24 h.

As can be seen from Table 2, the catalyst shows a remarkable shape-selectivity towards substrate structures. A 25°C, indeed, conversions of short linear aliphatic aldehydes (entry 1-4) are higher than those of longer chain (entries 5-6) and of C3- and C2- alkyl substituted ones (entries 7 and 11). With these last substrates, however, good conversions can be obtained on increasing thermostation to 60°C (entries 9-10,12,15-16 and 21-22).

A stronger evidence of AlFe-PILC shape-selectivity is observed starting from an equimolar mixture of butanal and 2-ethylbutanal. By stopping the reaction after 5h, a high conversion difference (91% and 17%, respectively) is observed. Accordingly, acetalization of linear and cyclic ketones gives poor results in any case.

AlFe-PILC catalyses through its acid sites: on adding, indeed, pyridine (25% mol/mol, with respect to the carbonyl compound) the reaction quite stops, as observed by using dimethylaminobenzaldehyde as substrate or dimethylformammide as solvent.

Removal of water produced in the reaction is not necessary, because the porous catalyst acts as a molecular sieve.

AlFe-PILC can be reused without loss of activity, after dehydration-activation at 120°C.

By the same reaction conditions, methanol[14] give rises to acetalization in satisfactory yields (Table 3).

Table 3-Acetalization of carbonyl compounds with methanol

entry	R_1	R_2	conversion[a] mol%	acetal yield[b] mol %
1	$CH_3(CH_2)_2$-	H	89	99
2	$CH_3(CH_2)_3$-	H	77	99
3	$(CH_3)_2CHCH_2$-	H	65	98
4	$(CH_3CH_2)_2CH$-	H	47	99
5	C_6H_5-	H	49	99

[a]Based on the initial amount of the carbonyl compound, time = 5h. [b]Yield of isolated product, based on the consumed carbonyl compound.

It can be pointed out that recently too, Uemura and co-workers[13] obtained poor results in the acetalization of linear aliphatic aldehydes with methanol under cation-exchanged montmorillonite (Ce^{3+}-Mont).

On considering the easy reaction procedure, the low amount of solvent needed, the high conversions and yields, the reuse and the low costs of raw materials, AlFe-PILC is a very good tool for the preparation of cyclic and acyclic acetals.

EXPERIMENTAL

Reagents and solvents were standard grade commercial products and used without further purification. CH_2Cl_2 was dried over three batches of 4Å molecular sieves (5% w/v, 12h). Mass spectra were obtained on a combined HP 5890GC-HP 5989A MS Engine. ^{1}H-NMR spectra were recorded on a Brucker DPX 200.

Preparation of Al/Fe-PILC

Pillared Clay has been prepared by reaction of an aqueous suspension of Ca^{2+}-montmorillonite with base-hydrolysed solution of $Al(NO_3)_3$ and $Fe(NO_3)_3$ (Al/Fe (9:1)) with 0.1 M NaOH ($OH^-/(Fe+Al)$ (1.2:1)). The product was then separated from the solution and air-dried. Calcination was carried out in air at 350° for 3 hours.

Acetalization Procedure at 25°C

To a stirred solution of the carbonyl compound (10 mmol) and diol (15 mmol) (or alcohol (30 mmol)) in dry CH_2Cl_2 (1 ml), the catalyst (51 mg, 0.054 mmol Al^{3+}, 0.024 mmol Fe^{3+}) was added at room temperature. After 8 h, the catalyst was removed by filtration and washed with CH_2Cl_2 (3 x 2 ml). The CH_2Cl_2 phases were collected, washed with 5 % NaOH solution (5 ml) and dried ($MgSO_4$). The crude product was isolated by distillation and give consistent GC-MS and ^{1}H-NMR spectra.

Acetalization Procedure at 60°C

In a schlenk tube containing a solution of carbonyl compound (10 mmol) and diol (15 mmol) in dry CH_2Cl_2 the catalyst (51 mg) was added. The stirred mixture was thermostatted at 60°C for 8h. After being cooled to room temperature, the catalyst was removed by filtration and washed with CH_2Cl_2 (3 x 2 ml). The CH_2Cl_2 phases were collected, washed with 5 % NaOH solution (5 ml) and dried ($MgSO_4$). The crude product was isolated by distillation and gave consistent GC-MS and ^{1}H-NMR spectra.

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14. By replacing the solvent (CH_2Cl_2) with methanol higher conversions and excellent yields of aldehydes to dimethyl-acetals are obtained (butanal: 98% conversion, yield 99%; benzaldehyde: 65% and 99% ; t=5h).

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