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Metal Cation-Exchanged Montmorillonite (M^{n+}-Mont)-Catalyzed Friedel–Crafts Acylation of 1-Methyl-1-cyclohexene and 1-Trimethylsilyl-1-alkynes

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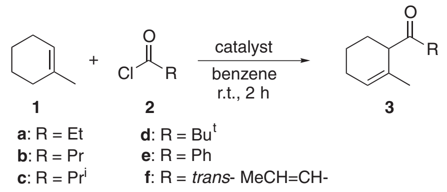
The acylation of 1-methyl-1-cyclohexene and 1-trimethylsilyl-1-alkynes with acyl chlorides has been investigated in the presence of a variety of metal cation-exchanged montmorillonites (abbreviated as M^{n+}-monts), where the catalysts are recyclable for several times after simple washing.

Organic transformation in the presence of a variety of solid catalysts is of recent interest and many useful synthetic methods have been developed.[1] Currently we have been much interested in the use of clay minerals as the solid catalysts, since they are known as environmentally-friendly materials and might work as the substitutes for several homogeneous catalysts.[2,3] Here we describe the result of our attempts for Friedel–Crafts acylation of 1-methyl-1-cyclohexene and 1-trimethylsilyl-1-alkynes with various acyl chlorides in the presence of cation-exchanged montmorillonites (abbreviated as M^{n+}-monts), a kind of clay mineral. Although aromatic Friedel–Crafts reactions have so far been investigated using various M^{n+}-monts as catalysts,[4] there are no examples of aliphatic acylation in the presence of M^{n+}-monts to the best of our knowledge.



Scheme 1.

Table 1. Acylation of **1** with **2b** in the Presence of M^{n+}-Mont

Entry	M^{n+}-mont	(mmol)[a)]	Isolated yield of **3b**[b)]/%	TON[c)]
1	Fe^{3+}	0.105	45	13
2	In^{3+}	0.059	25	13
3	Zr^{4+}	0.220	9	1
4	La^{3+}	0.060	Trace	0
5	Al^{3+}	0.159	0	0
6	Ce^{3+}	0.042	0	0
7	Yb^{3+}	0.097	0	0
8	Dy^{3+}	0.018	0	0
9[d)]	—	—	0	0

Reaction conditions: **1** (6.0 mmol), **2b** (3.0 mmol), M^{n+}-mont (300 mg), benzene (8 cm^3), rt, 2 h. a) The amount of acid sites of M^{n+}-mont was estimated by NH_3-TPD analysis. b) Mol of **3b**/mol of acid sites. c) Based on the mol of acid sites. d) 24 h.

First, we examined Friedel–Crafts acylation of 1-methyl-1-cyclohexene (**1**) (2 molar amounts) with butyryl chloride (**2b**) (1 molar amount) in the presence of several M^{n+}-monts ($2–7 \times 10^{-2}$ molar amounts) (Scheme 1, Table 1). Fe^{3+} and In^{3+}-monts were revealed to be effective for this reaction (entries 1 and 2), the TON (turnover number) being 13 in both cases. The catalytic activity of Zr^{4+} and La^{3+}-monts was lower (entries 3 and 4). On the other hand, Al^{3+}, Ce^{3+}, Yb^{3+}, and Dy^{3+}-monts did not show any catalytic activity (entries 5–8). No reaction proceeded in the absence of M^{n+}-mont (entry 9). The amount of Fe^{3+}-mont slightly affected the product yield and we found that the use of 0.012 molar amounts of Fe^{3+}-mont (100 mg) gave the best result, a larger and a smaller amount of it resulting in a decrease of the product yield.

Thus, Fe^{3+} and In^{3+}-monts were applied to the reaction of **1** with a variety of acyl chlorides **2a–2f** (Scheme 1, Table 2). As a result, the corresponding 6-acyl-1-methyl-1-cyclohexene was obtained in up to 58% yield, but some unidentified isomeric compounds were detected by GC–MS analysis.

The recovered Fe^{3+}-mont was successfully reused in the reaction of **1** with **2b** to afford **3b** at least three times after washing it with 50% aqueous acetone and drying at 120 °C for 24 h (1st use, 45%: 2nd use, 40%: 3rd use, 40%).

Separately, we confirmed that the acylation of **1** with **2b** proceeded even in the presence of a catalytic amount of $FeCl_3$ and $InCl_3$, but the catalytic activity of these Lewis acids was not as high as that of Fe^{3+} and In^{3+}-monts in terms of the isolated yields of **3b** (15–31%).

Next, we investigated the reaction of several 1-trimethylsilyl-1-alkynes **4** with **2b** (Scheme 2, Table 3). Treatment of **4** with **2b** in the presence of Fe^{3+} and In^{3+}-monts at room temperature for 2 h produced the corresponding acyl compounds in moderate yields by replacing a trimethylsilyl group with an acyl group; the yield was up to 64% (entry 2). Even when an excess amount of **2b** to **4a** was employed, only a monosubstituted product **5a** was obtained without any formation of a disubstituted product.

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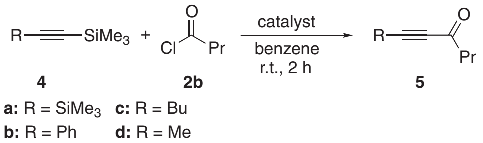
Table 2. Acylation of **1** with **2** in the Presence of Fe^{3+} and In^{3+}-Mont

Entry	**2**	M^{n+}-mont	Isolated yield of **3**/%	TON[a)]
1	**2a**	Fe^{3+}-mont	49	42
2	**2b**	Fe^{3+}-mont	58	50
3	**2c**	Fe^{3+}-mont	38	33
4	**2d**	Fe^{3+}-mont	19	16
5	**2e**	Fe^{3+}-mont	16	14
6	**2f**	Fe^{3+}-mont	20	17
7	**2a**	In^{3+}-mont	45	69
8	**2b**	In^{3+}-mont	58	89
9	**2c**	In^{3+}-mont	34	52
10	**2d**	In^{3+}-mont	34	52
11	**2e**	In^{3+}-mont	23	35
12	**2f**	In^{3+}-mont	27	42

Reaction conditions: **1** (6.0 mmol), **2** (3.0 mmol), M^{n+}-mont (100 mg; Fe^{3+}-mont, 0.0349 mmol, 0.012 mol amt, In^{3+}-mont, 0.0197 mmol, 0.0066 mol amt), benzene (8 cm^3), rt, 2 h. a) Mol of **3**/mol of acid sites.



Scheme 2.

Table 3. Acylation of **4** with **2a** or **2b** in the Presence of M^{n+}-Mont

Entry	R	M^{n+}-mont	Isolated yield of **5**/%	TON[a)]
1	$SiMe_3$	Fe^{3+}-mont	54	46
2	Ph	Fe^{3+}-mont	64	55
3	Bu	Fe^{3+}-mont	36	31
4	Me	Fe^{3+}-mont	9	8
5	$SiMe_3$	In^{3+}-mont	31	48
6	Ph	In^{3+}-mont	51	78
7	Bu	In^{3+}-mont	31	48
8	Me	In^{3+}-mont	9	14

Reaction conditions: **4** (6.0 mmol), **2b** (3.0 mmol), M^{n+}-mont (100 mg; Fe^{3+}-mont, 0.0349 mmol, 0.012 mol amt, In^{3+}-mont, 0.020 mmol, 0.0066 mol amt), benzene (8 cm^3), rt, 2 h. a) Mol of **5**/mol of acid sites.

We have applied this reaction to many other substrates, such as cyclohexene, α-pinene, norbornene, trimethyl(vinyl)silane, and allyltrimethylsilane, but all reactions resulted in a formation of many unidentified products unfortunately. The treatment of 2-phenylpropene produced only the corresponding dimer.[2e]

Experimental

General Procedures. All commercially available organic and inorganic compounds were used without further purification.

In^{3+}-mont was newly prepared from Kunipia® G (<100 mesh, 6 g) and $In(NO_3)_3 \cdot 3H_2O$ (21.3 g, 60 mmol).[2a] The amount of acid sites (Brønsted and Lewis acid sites) was estimated by the temperature-programmed desorption of ammonia gas (NH_3-TPD) analysis to be 0.195 mmol g^{-1}. The basal spacing (d_{001}) of In^{3+}-mont was estimated by a sharp peak obtained on XRD analysis to be 15.4 Å, showing that the compound has an interlayer structure.

The acyl compounds **3a**–**3f** and **5a**–**5d** are known and were characterized by their spectral data after their isolation.[5–13]

General Procedure for M^{n+}-Mont-Catalyzed Friedel–Crafts Acylation of 1-Methyl-1-cyclohexene (1) with Acyl Chloride 2. To a mixture of acyl chloride **2** (3 mmol) and benzene (8 cm^3) was added Fe^{3+}-mont (100 mg, 0.0349 mmol as acid sites estimated by NH_3-TPD) in one portion at room temperature with magnetic stirring. After the mixture was stirred at the temperature for a few minutes, 1-methyl-1-cyclohexene (**1**) (0.71 mL, 6 mmol) was added to it and the mixture was stirred vigorously at room temperature for 2 h. The catalyst was filtered off and rinsed with Et_2O (50 cm^3). The solvent in a mixture of the filtrate and the ethereal washings was removed under the reduced pressure to leave an oil, which was subjected to silica gel column chromatography (eluent, hexane:diethyl ether = 10:1) to give the corresponding 6-acyl-1-methyl-1-cyclohexene **3**.

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