



Short Communication

Iron oxide-pillared clay catalyzed the synthesis of acetonides from epoxides

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ABSTRACT

FeO_x-pillared clays (FeO_x-pillared bentonite, FeO_x-pillared hectorite and FeO_x-pillared taeniolite) were synthesized by the intercalation of FeCl₃ into clay interlayers and calcination. The synthesized catalysts were exploited for conversion of epoxides furnishing acetonides in good to quantitative yields with short time under mild conditions. The catalysts could be recovered and reused up to five times without appreciable loss of activity.

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1. Introduction

The protection of a carbonyl functional group from nucleophilic attack is still a challenging task. One of the most useful protecting methods for carbonyl compounds (aldehydes and ketones) include acetalization, thioacetalization and ketalization [1]. 1,3-Dioxolanes are widely used to protect aldehydes and ketones. Epoxides are attractive intermediates due to their wide range of regio-, chemo- and stereoselective transformations with concomitant ring opening. The direct transformation of epoxides to acetonides was previously reported using several Lewis acid catalysts such as anhydrous CuSO₄ [2], BF₃·OEt₂ [3], CH₃ReO₃ [4], RuCl₃ [5], TiO(TFA)₂ and TiCl₃(OTf) [6], Fe(TFA)₃ [7], K₅CoW₁₂O₄₀·3H₂O [8], Bi(TFA)₃ [9], TABCO [10], SnCl₂ [11], Sn(tpp)(OTf)₂ [12], Er(OTf)₃ [13], and LiBF₄ [14]. Some reported methods suffered from air- and moisture-sensitive catalysts, expensive and toxic catalysts, high refluxing temperature, long reaction time, difficulty in separation and recovery, less selectivity or yields and functional group intolerance. In recent years, inorganic solid acids catalyzed organic reactions have gained importance due to the proven advantage of heterogeneous catalysts such as simplified product isolation, easy work-up, mild reaction conditions, shorter reaction time, easy recovery and reusability of catalysts, better yield and a large reduction in the generation of wasteful products [15].

Previously, certain clays such as K10-montmorillonite [16] and natural kaolinitic clay [17] have been reported as an efficient catalyst in the synthesis of acetonides from epoxides. Nonetheless, no report on the utilization of FeO_x-pillared clays as catalysts has been addressed. Herein, we

report a new and efficient procedure for the preparation of acetonides from epoxides by pillared clay catalysts under mild conditions.

2. Experimental

2.1. General

Two types of the 2:1 layered clays were used as starting materials. Hectorite (Volclay Siam Limited), with typical chemical analysis of (wt.%): SiO₂ 61.78, Al₂O₃ 1.58, MgO 20.32, Fe₂O₃ 1.23, CaO 10.07, Na₂O 2.80, and K₂O 0.33, was used as received. Bentonite clay (Cernic International Co., LTD) with typical chemical analysis of (wt.%): SiO₂ 63.60, Al₂O₃ 17.60, Fe₂O₃ 3.10, CaO 3.00, Na₂O 3.40, and K₂O 0.50, was purified by fractionated centrifugation in order to remove quartz and other dense impurities. De-ionized water was used throughout the study. For preparation of catalysts, FeCl₃·6H₂O (Riedel-de Haën) and NaOH (Merck) were of laboratory reagent grade. De-ionized water was used throughout the study. For catalytic study, all organic solvents were purified using standard distillation techniques. All reactants were purchased from Fluka as a laboratory reagent grade.

2.2. General preparation of acetonides

The mixture of epoxide 1 mmol and acetone (3 mL) was added to a round bottle flask with 10 wt.% of catalyst to epoxide. The solution was continuously stirred for desired time and temperature. After the specific time or the reaction was finished, the catalyst was filtered out of the mixture, and washed the product out with EtOAc. The solvent was evaporated to dryness under reduced pressure to afford the product. The

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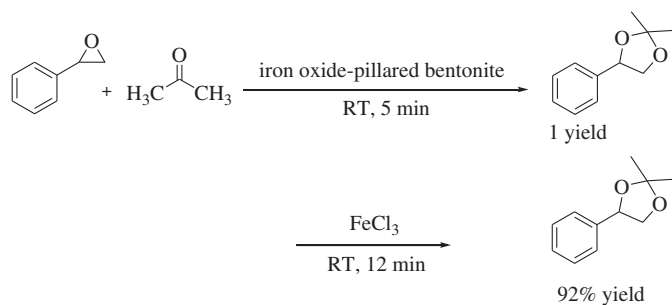


Fig. 1. Synthesis of acetone from epoxides.

reactions were monitored by TLC aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF₂₅₄). Products of acetone from epoxides were monitored by Shimadzu GC 14-B (FID, HP-5 column) and Shimadzu QP-5000 GCMS. The ¹H NMR spectra were obtained in CDCl₃ and determined by Mercury plus 400 NMR spectrometer operated at 399.84 MHz. All products were identified by ¹H NMR.

2,2-Dimethyl-4-phenyl-1,3-dioxolane; ¹H NMR (CDCl₃) δ (ppm): 1.48 (³H, s), 1.52 (³H, s), 3.67 (¹H, t), 4.27 (¹H, dd, J = 8.6, 6.4 Hz), 5.05 (¹H, dd, J = 8.6 Hz), 7.31 (⁵H, m).

2,2-Dimethyl-hexahydro-benzo[1,3]dioxole; ¹H NMR (CDCl₃) δ (ppm): 1.24–1.00 (⁴H, m), 1.35 (⁶H, s), 2.58–2.07 (⁴H, m), 4.34–4.05 (²H, m).

4-Decyl-2,2-dimethyl-1,3-dioxolane; ¹H NMR (CDCl₃) δ (ppm): 0.81 (³H, t), 1.14 (¹⁶H, m), 1.29 (³H, s), 1.34 (³H, s), 1.56 (²H, m), 3.42 (¹H, dd, J = 8.8, 7.2 Hz), 4.00 (²H, m).

4-(Butoxymethyl)-2,2-dimethyl-1,3-dioxolane; ¹H NMR (CDCl₃) δ (ppm): 0.84 (³H, t), 1.30 (³H, s), 1.34 (³H, s), 1.48 (⁴H, m), 3.49 (³H, m), 3.67 (²H, m), 3.99 (¹H, dd, J = 8.0, 6.8 Hz), 4.20 (¹H, quin).

4-(tert-Butoxymethyl)-2,2-dimethyl-1,3-dioxolane; ¹H NMR (CDCl₃) δ (ppm): 1.13 (⁹H, s), 1.31 (³H, s), 1.38 (³H, s), 3.25 (¹H, dd, J = 9.0, 6.4 Hz), 3.41 (¹H, dd, J = 9.0, 5.6 Hz), 3.68 (¹H, dd, J = 8.0, 5.6 Hz), 4.01 (¹H, dd, J = 8.0, 6.4 Hz), 4.13 (¹H, quin).

4-(Isopropoxymethyl)-2,2-dimethyl-1,3-dioxolane; ¹H NMR (CDCl₃) δ (ppm): 1.09 (⁶H, d), 1.28 (³H, s), 1.34 (³H, s), 3.31 (¹H, dd, J = 9.6, 6.0 Hz), 3.44 (¹H, dd, J = 9.0, 6.4 Hz), 3.53 (¹H, septet), 3.65 (¹H, dd, J = 8.0, 6.2 Hz), 3.98 (¹H, dd, J = 8.0, 6.4 Hz), 4.16 (¹H, quin).

2,2-Dimethyl-4-(phenoxymethyl)-1,3-dioxolane; ¹H NMR (CDCl₃) δ (ppm): 1.38 (³H, s), 1.45 (³H, s), 3.89 (²H, ddd, J = 5.0, 9.2, 15.2 Hz), 4.01 (¹H, dd, J = 9.0, 4.6 Hz), 4.12 (¹H, dd, J = 14.4, 8.0 Hz), 4.45 (¹H, quin), 6.91 (³H, m), 7.25 (²H, t).

2.3. General preparation of FeO_x-pillared clay catalysts

FeO_x-pillared clays were synthesized by intercalation of iron precursors, followed by calcinations at high temperature. Na-clays were dispersed in de-ionized water (10wt.%) by vigorous stirring for 1 day at

Table 1

Conversion of styrene oxide to **1** catalyzed by different FeO_x-pillared clay catalysts.

Entry	Catalysts	Yield (%)
1	FeO _x -pillared bentonite	Quant ^a
2	FeO _x -pillared hectorite	83 ^b
3	FeO _x -pillared taeniolite	77 ^b
4	Bentonite	Trace ^c
5	Hectorite	Trace ^c
6	Taeniolite	Trace ^c
7	None	0 ^c

Reaction conditions: styrene oxide (1 mmol), acetone (3 mL), catalyst 10 wt.% to styrene oxide at 30 °C.

^a 5 min.

^b 30 min.

^c 24 h.

Table 2

The amount of acidity and surface area.

Entry	Catalysts	Wt.% Fe content	Surface area (m ² /g)	Acidity (mmol/g)		Total amount of acidity (mmol/g)
				Weak acid sites	Strong acid sites	
1	FeO _x -pillared bentonite	10.14	155.52	0.62	3.11	3.73
2	FeO _x -pillared hectorite	9.54	122.30	0.73	1.43	2.16
3	FeO _x -pillared taeniolite	4.22	20.33	0.61	0.91	1.52
4	Bentonite	3.49	65.05	0.14	1.12	1.26
5	Hectorite	0.95	57.11	0.04	0.51	0.55
6	Taeniolite	0.35	3.53	0.43	–	0.43

RT. Then 1 M FeCl₃ · 6H₂O was slowly added in the suspended Na-clay under stirring for 24 h at RT. The products were collected by centrifugation, and washed with de-ionized water until chloride ions were eliminated. The as-synthesized products, Fe-intercalated clays were dried followed by calcination at 300 °C.

2.4. The characterization of FeO_x-pillared clay catalysts

The prepared catalysts were characterized by XRD, surface area analyzer and NH₃-TPD [18]. The XRD of raw clays and synthesized FeO_x-pillared clays were measured by a Rigaku, Dmax 2200/ultima + X-ray powder diffractometer (40 Kv, 30 mA) with a monochromator and Cu K_α radiation. The 2θ was ranged from 2 to 30° with the scan speed of 3°/min and the scan step of 0.02°. The BET specific surface area of raw clays and synthesized FeO_x-pillared clays was obtained from surface area analysis using the Quantachrome Autosorb-1 nitrogen adsorptometer. Acidity of all catalysts was measured by temperature-programmed desorption (TPD). Spectra of ammonia were recorded by Quantachrome Autosorb-1-C equipped with thermal conductivity detector.

Sample preparation for ICP: The 0.0400 g of a calcined catalyst, placed in a 100 mL Teflon beaker, was soaked with 10 mL concentrated HCl and subsequently with 10 mL of 48% HF in order to remove silica in the form of volatile SiF₄ species. The mixture was heated but not boiled to dryness on a hot plate. The removal of silica was repeated three times. Then, 10 mL of 6 M HCl: 6 M HNO₃ mixtures in the ratio of 1:3 was added and further heated to dryness. 5 mL of 6 M HCl was added and the mixture was warmed for 5 min to complete dissolution. The solution was transferred to 50 mL polypropylene volumetric flask and made up its volume by adding deionized water. If the sample was not analyzed immediately, the solution was then transferred into a plastic bottle with a treated cap underlined with a polypropylene seal.

3. Results and discussion

3.1. Catalytic activities of FeO_x-pillared clay catalysts

A mild and efficient method for the direct conversion of epoxides to acetone using FeO_x-pillared clays at RT in acetone was disclosed. A synthesis of **1** from styrene oxide with acetone is displayed in Fig. 1.

Table 3

Effect of the amount of iron oxide-pillared bentonite.

Entry	Fe-pillared bentonite (wt.%)	% Yield	% Styrene oxide (recovered)
1	2	83	17
2	5	91	8
3	10	94	0
4	30	95	0

Reaction conditions: styrene oxide 1 mmol, acetone in excess (3 mL), iron oxide-pillared bentonite varied at RT (30 °C) for 5 min.

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