Hydrogen transfer reduction of ketones catalyzed by Fluka K-10 montmorillonite

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Abstract

K-10 montmorillonite (Fluka) catalyzes the reduction of aliphatic and aromatic ketones by H-transfer in isopropanol under basic conditions (0.06 M KOH). © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Reduction; Hydrogen transfer; Ketones; Montmorillonite

1. Introduction

An attractive strategy for the conversion of ketones to alcohols is by transfer hydrogenation, using different organic hydrogen donors and catalytic systems [1–12]. In recent years, new catalysts have been discovered, which allow the transfer hydrogenation reaction to occur rapidly under mild conditions and also extend the applicability of this method to new substrates. The heterogenization of homogeneous transition metal complexes as catalysts, by anchoring the complexes to insoluble supports, is another area of considerable interest [13–15].

We envisaged clay–metal complexes as potential catalysts for the hydrogen transfer reaction. We now wish to report that montmorillonite itself, or a ruthenium complex of the clay, is effective for the hydrogen transfer reduction of ketones.

2. Results and discussion

One of us previously showed that rhodium intercalated on clay is a useful catalyst for the hydroformylation of vinylsilanes [16] and allyl acetates [17]. Several soluble rhodium complexes have been used for the hydrogen transfer reduction of ketones [1–12,18]. Attempted reaction of acetophenone with Rh-clay **1** (prepared by intercalation of $[Rh(COD)Cl]_2$ into montmorillonite) and KOH in isopropanol, at 95°C, for 24 h (nitrogen atmosphere), gave recovered starting material. Recently we initiated an investigation of the preparation and catalytic activity of ruthenium bound to montmorillonite (Ru-clay). The latter is useful for the hydrogenation of functionalized olefins. [1] Two Ru-clays were prepared, and anchored to montmorillonite by means of bipyridyl (bpy-**2**), and siloxypro-
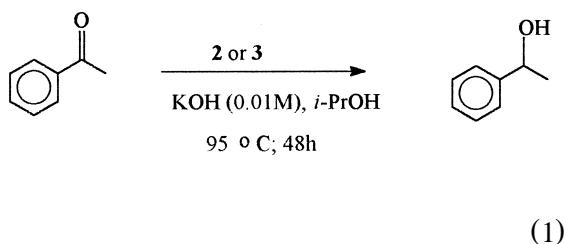
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[1] R. Aldea, H. Alper, unpublished results.

Table 1
Reduction of acetophenone with Ru containing catalysts

No.	Catalyst	Ru content (mmol/100 mg catalyst)	Yield (% 1-phenyl ethanol)
1	Clay-(bpy)-RuCl$_3$ (**2**)	0.018	70
2	Clay-(OSi(OMe)$_2$(CH$_2$)$_3$PPh$_2$)-RuCl$_3$ (**3**)	0.017	10

Reaction conditions: 2 mmol acetophenone, 30 mg catalyst (0.005 mmol Ru), [KOH] = 0.01 M in isopropanol, 95°C, 48 h.

pyldiphenylphosphine (OSi(OMe)$_2$(CH$_2$)$_3$PPh$_2$-**3**) units. When acetophenone was subjected to transfer hydrogenation (Eq. (1)) using an approximately 100:1 ratio of reactant to

$$(1)$$

catalyst, 1-phenyethanol was isolated in 10–70% yield (Table 1). The yield of the alcohol was good using **2**, while **3** was a poor catalyst for the reaction.

When the hydrogen transfer reaction of acetophenone was run under homogeneous conditions using ruthenium trichloride as the catalyst, the substrate was recovered unchanged. The same inertness was found using montmorillonite and 0.01 M KOH but no bound ruthenium. However, reduction of acetophenone does proceed at 0.06 M KOH for the clay system (no ruthenium) in 52–64% yield depending on the time the clay is pretreated with isopropanol and the temperature for such pretreatment (Table 2).

Although the yield of 1-phenylethanol was similar using 0.06 M KOH-clay (56–64%) and 0.01 M KOH-Ru clay (70%), the fact that no metal is necessary led us to examine the scope of the H-transfer reduction process with 0.06 M KOH-montmorillonite. The results are presented in Table 3. Methyl aryl ketones are converted to the corresponding alcohols in good yields (Table 3, entries 1–3). The diaryl ketone, benzophenone, also reacts but the yield of the alcohol is appreciably lower (Table 3, entry 4). Dialkylketones such as 4-phenyl-2-butanone, 4-*t*-butycyclohexanone, 2-decalone, and 5α-cholestan-3-one (Table 3, entries 5–8) gave the alcohols in excellent yield. The ratio of *trans/cis* 4-*t*-butylcyclohexanol was 56/44, and that for 3β/3α-dihydrocholesterol was 63/37, indicating low stereoselectivity. In contrast zeolite BEA was reported [19] to afford a high selectivity for *cis-t*-butyl-cyclohexanol, due to the more bulkier transition state, required by the *trans*-alcohol, which can not be accommodated within the straight channels of BEA. In the case of the zeolite it is proposed that the active site is the

Table 2
Catalytic activity of the commercial clay (Fluka montmorillonite)

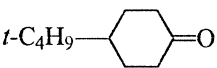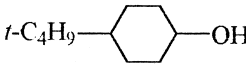| Conditions	[KOH] (mol/1)	Reaction time (h)	Yield (%)[b]
Without activation	0.06	48	52
Activation at 100°C[a]	0.06	24	56
Activation at 100°C[a]	0.01	24	0
Activation at room temperature (24 h)[c]	0.06	24	60
Activation at room temperature (1 h)[c]	0.06	24	64

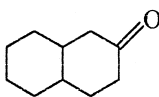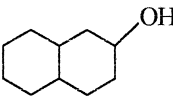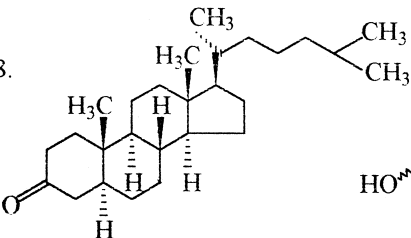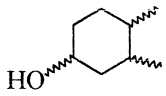Reaction conditions: 2 mmol acetophenone, 30 mg clay, 95°C.
[a] Clay pretreated with isopropanol for 24 h in a Soxhlet.
[b] Yield determined by ^{1}H NMR using an internal standard.
[c] Clay stirred in isopropanol at room temperature.

Table 3
Hydrogen transfer reduction of ketones using Fluka K-10 montmorillonite as catalyst[a]

No.	Substrate	Product	Conversion[b] (Isolated Yield) (%)
1.	$PhCOCH_3$	$PhCH(OH)CH_3$	64 (51)
2.	$p\text{-}C_2H_5C_6H_4COCH_3$	$p\text{-}C_2H_5C_6H_4CH(OH)CH_3$	58
3.	$p\text{-}CH_3OC_6H_4COCH_3$	$p\text{-}CH_3OC_6H_4CH(OH)CH_3$	87
4.	$PhCOPh$	$PhCH(OH)Ph$	52 (27)
5.	$PhCH_2CH_2COCH_3$	$PhCH_2CH_2CH(OH)CH_3$	85
6.	$t\text{-}C_4H_9$—⬡=O	$t\text{-}C_4H_9$—⬡—OH	100 (72)[c]
7.			100 (85)
8.			94 (88)[d]

[a]Reaction conditions: 2 mmol (entries 1–6) or 1 mmol (entries 7–8), 30 mg Fluka K-10 montmorillonite, 0.06 M KOH solution in isopropanol, 95°C, 24 h.
[b]Conversion determined by ^{1}H NMR using internal standard.
[c]56:44 *trans/cis*.
[d]63:37/3β:3α dihydrocholesterol.

octahedrally coordinated aluminum formed during activation of the catalyst. The octahedrally coordinated aluminum is a component of montmorillonite. Also, 2-decalone afforded a *cis/trans* mixture of alcohol [20]. Santonin did not undergo conversion to the alcohol, with the α,β-unsaturated ketone, resulting from the hydrogenation of the C_4–C_5 double bond, formed instead. Interestingly, α,β-unsaturated carbonyls such as cholest-4-en-3-one and testos-

terone do not react with 0.06 M KOH-montmorillonite.

The catalytic activity of the clay (K-10 montmorillonite) is not surprising for the H-transfer reduction of ketones. The classical Meerwein–Ponndorf–Verley reduction takes place in the presence of aluminum isopropoxide [21] and, in a variation of this reaction, aldehydes are selectively reduced by isopropyl alcohol or diisopropylcarbinol on dehydrated alumina [22]. Chlorinated γ-Al_2O_3 in combination with a small amount of $Al(Oi-Pr)_3$ catalyses the reduction of acetophenone by isopropanol [1–12]. On the other hand, montmorillonite, the clay used in this work, contains aluminium and oxygen atoms. It has, as building elements, a central sheet made of aluminium or magnesium, octahedrally coordinated to oxygens and hydroxyls linked to two tetrahedral sheets, one on each side, made of silicon and oxygen [23].

In conclusion the reduction of ketones by the system 0.06 M KOH/isopropanol and montmorillonite is of value for the hydrogen transfer reduction to alcohols.

3. Experimental section

3.1. General

The substrates were purchased from Aldrich Chemical, and were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 and Varian XL 300; Bomem MB 100-C15 (FT-IR) was used for IR and Varian 3400 for GC analyses.

3.2. General procedure for H-transfer reduction using Fluka K-10 montmorillonite

Fluka K-10 montmorillonite (30 mg) was suspended in isopropanol containing 0.06 M KOH (15 ml). The montmorillonite used was initially stirred in isopropanol for 1 h (1 g clay in 20 ml isopropanol), filtered, and then was dried in vacuo. The ketone (2 mmol) was added, and the mixture was heated (95°C), under N_2,

for 24 h. The reaction mixture was filtered through Celite and the solvent was evaporated. To the crude product was added ether (10 ml) and the suspension formed was washed with 2 N HCl solution. The aqueous layer was extracted three times with ether (15 ml). The combined organic layers were dried ($MgSO_4$). When the conversion was not complete, the remaining substrate was removed by column chromatography or distillation.

3.3. General procedure for H-transfer reduction using **2**–**3** as catalysts

Ru-clay (30 mg, 0.005 mmol Ru) was suspended in KOH (0.01 M) in isopropanol (12 ml). Acetophenone (2 mmol) was added and the mixture was heated (95°C) under N_2 for 48 h. The reaction mixture was filtered through Celite and the solvent was evaporated. The crude mixture was analyzed by ^{1}H NMR using an internal standard for the determination of the yield of the alcohol.

3.3.1. Rh-clay **1**
The Rh-Clay **1** was prepared by following a literature procedure [16].

3.3.2. Preparation of Ru-clays: clay **2**
H-montmorillonite was prepared from montmorillonite K-10 (Fluka) by treatment with saturated NaCl solution followed by 0.1 N HCl solution. It was dried in air and then in vacuo. 7 g H-montmorillonite was suspended in dry benzene (50 ml) and reacted with $SOCl_2$ (10 ml, 0.13 mol) under reflux for 24 h [24]. The chloromontmorillonite obtained was filtered and dried in vacuo and then 2 g of chloromontmorillonite was reacted with excess *n*-butyllithium (3.5 ml, 5.6 mmol, 1.6 M in hexane) at −78°C in dry THF. The solution was then stirred at 0°C for 4 h and allowed to warm to room temperature and stirred for one more hour. Bipyridine (1.185 g, 7.6 mmol) was added and the mixture was brought to reflux for 4 h [24]. The reaction mixture, which turned purple during refluxing, was then cooled at room temperature and air

was bubbled through the solution until it had become yellow. The montmorillonite was washed with THF, ethyl acetate and benzene followed by Soxhlet extraction with THF for 24 h. Finally 41.5 mg $RuCl_3 \cdot H_2O$ (0.2 mmol) was added to 2g of dry bipyridine-montmorillonite, suspended in THF, and stirred for 8 h under N_2. The resulting Ru-clay was thoroughly washed with water and THF to remove the excess $RuCl_3$ and dried in vacuo (Ru: 0.18 mmol g^{-1}).

3.3.3. Clay 3

H-montmorillonite (4 g), which was prepared as in the case of **2**, was suspended in benzene (40 ml), $(MeO)_3SiCH_2CH_2CH_2$ Cl (5 ml, 0.027 mol) was added and the mixture was refluxed for 12 h. The clay was then extracted with toluene for 24 h in a Soxhlet and dried [25]. The resultant clay (2.5 g) was suspended in dry THF. $KPPh_2$ (4 mmol, 8 ml, 0.5 M solution in THF) was added dropwise and the mixture was brought to reflux overnight [25]. The excess $KPPh_2$ was quenched with methanol and the clay was subjected to extraction with methanol for 24 h and then with toluene for 24 h. Finally it was dried in vacuo. 0.8 g of the obtained montmorillonite was suspended in THF and 20.7 mg (0.1 mmol) $RuCl_3 \cdot H_2O$ was added. It was stirred for 8 h, under N_2, and then washed with water and THF. It was dried under vacuo (Ru: 0.17 mmol g^{-1}).

Acknowledgements

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