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# Pinacol-Pinacolone Rearrangement on FeCl<sub>3</sub> Modified Montmorillonite K10

Ajit B. Shinde<sup>a</sup>, Nilesh B. Shrigadi<sup>a</sup>, Ramakrishna P. Bhat<sup>a</sup> & Shriniwas D. Samant<sup>a</sup> <sup>a</sup> Organic Chemistry Research Laboratory, Institute of Chemical Technology, University of Mumbai, N. M. Parekh Road, Matunga, Mumbai, 400 019, India Published online: 18 Oct 2011.

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## **Pinacol-Pinacolone Rearrangement on FeCl<sub>3</sub> Modified Montmorillonite K10**

#### Ajit B. Shinde, Nilesh B. Shrigadi, Ramakrishna P. Bhat, and Shriniwas D. Samant\*

Organic Chemistry Research Laboratory, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai, India

#### ABSTRACT

Pinacol-pinacolone rearrangement was investigated over Fe-modified montmorillonite K10 catalysts in liquid phase. Exceptional activity was found to be associated with FeCl<sub>3</sub> impregnated on K10 through its acetonitrile solution. 100% conversion of benzopinacol was observed in 10 minutes. The catalysts are recyclable.

*Key Words:* Pinacol-pinacolone rearrangement; Montmorillonite K10; FeCl<sub>3</sub>.

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<sup>\*</sup>Correspondence: Shriniwas D. Samant, Organic Chemistry Research Laboratory, Institute of Chemical Technology, University of Mumbai, N. M. Parekh Road, Matunga, Mumbai-400 019, India; Fax: 91 22 414 5614; E-mail: ssd@udct.ernet.in.

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#### INTRODUCTION

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The pinacol-pinacolone rearrangement is an acid catalyzed rearrangement of vicinal diols, which involves internal rearrangement with transformation and reduction in functionality.<sup>[1]</sup> Besides producing crowded ketones, the reaction poses mechanistic challenges. To effect the rearrangement strong Brönsted acids such as H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> or Lewis acids like AlCl<sub>3</sub> are commonly used; generally in large quantities.<sup>[2]</sup> In a recent drive to replace hazardous stoichiometric catalysts by cleaner and environmentally benign catalysts, various heterogeneous solid acidic catalysts viz. alumina, clays, zeolites, ion-exchange resins, heteropoly acids have been tested for this transformation.<sup>[3]</sup> Among the ion-exchanged clays  $Cr^{3+}$  and  $Al^{3+}$  exchanged clays were found to be active.<sup>[4]</sup> Recently, Hsien has observed that Fesubstituted molecular sieves to be very active catalyst in this rearrangement.<sup>[5]</sup> In our previous study we noticed that Fe modified K10 catalysts activated at a low temperature have significant Brönsted acidity, which coupled with reducible nature of  $Fe^{3+}$  cation could serve as a promising catalyst for Friedel–Crafts benzylation<sup>[6]</sup> and Beckmann rearrangement.<sup>[7]</sup> Beckmann rearrangement involves protonation of hydroxyl group of oximes in which Brönsted acids have a special role to play. This prompted us to employ FeCl<sub>3</sub> modified montmorillonite K10 for pinacol-pinacolone rearrangement (Sch. 1).

#### **RESULTS AND DISCUSSION**

Montmorillonite K10 was treated with anhydrous  $FeCl_3$  in its acetonitrile (K10-Fe-O) and aqueous (K10-Fe-A) solutions. These two catalysts were used after drying at 80° and 120°C (K10-Fe-O-80/120 and K10-Fe-A-80/120). The preparation and characterization of these catalysts have already been reported.<sup>[6]</sup> We have already noticed that as the temperature of calcination was increased beyond 120°C the Brönsted acidity decreased. Hence catalysts were activated at 80°C and 120°C.





#### **Pinacol-Pinacolone Rearrangement**

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*Table 1.* The rearrangement of benzopinacol (1a) in the presence of different K10 catalysts.

Catalyst	Yield of benzopinacolone (2a) (	
K10	58	
K10-120	43	
K10-Fe-O-80	97	
K10-Fe-O-120	62	
K10-Fe-A-80	70	
K10-Fe-A-120	53	

*Notes:* Benzopinacol = 1 mmol, Catalyst = 0.1 g, Time = 1 h, Temp. =  $80^{\circ}$ C, Toluene = 5 mL.

The rearrangement of benzopinacol (1a) was attempted using different K10 catalysts (Table 1). With K10-Fe-O-80, 97% of benzopinacolone (2a) was obtained in 10 minutes. With all other catalysts, we could achieve maximum of 70% product even after continuing for 1 h. Among the ion-exchanged catalysts also, the activity of catalyst activated at  $80^{\circ}$ C was found be higher than that activated at  $120^{\circ}$ C. This observation is in consonance with the fact that the higher the activation temperature lower is the Brönsted acidity. Moreover, in the Beckmann rearrangement, we have noticed that impregnated catalysts are more active than the ion-exchanged catalysts.

Using K10-Fe-O-80 catalyst, a series of symmetrical benzopinacols (1a-e) were rearranged (Table 2). As the reaction can lead to the formation of two pinacolones 2 and 3 (Scheme 2), a modified Bachmann procedure was employed to find out the composition of the product mixture.<sup>[8]</sup> Thus, a

*Table 2.* The Pinacol rearrangement of substituted benzopinacols in the presence of K10-Fe-O-80.

Entry	Reactant		Selectivity (%)	
	1	Ar	2(a-e)	3(a-e)
1	1a	Ph-	(10	)0) <sup>a</sup>
2	1b	4-Me-Ph-	56	44
3	1c	4-MeO-Ph-	70	30
4	1d	4-Cl-Ph-	26	74
5	1e	4-Br-Ph-	21	79

*Notes:* Benzopinacol = 1 mmol, Catalyst = 0.1 g, Time = 10 min, Temp. =  $80^{\circ}$ C, Toluene = 5 mL, Coversion of 1 = 100%. <sup>a</sup>Single product.

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mixture of the pinacolones was cleaved into triarylmethanes (5 and 7) and acids (4 and 6) (Sch. 2). The acids formed were then esterified (8 and 9) and from the ratio of the esters (GC), the relative amount of pinacolones formed was calculated.

From Table 2, we can see that the presence of electron-donating substituents at the *para* position increases the migratory aptitude of the aryl group. The catalyst K10-Fe-O-80 was found to be recyclable. There was no significant change in the activity of the catalyst even after 5 cycles.

#### **EXPERIMENTAL**

Montmorillonite K10 was obtained from Aldrich (Manufactured by M/s Sud-Chemie AG). Prior to any further treatment, the clay was dried overnight





#### **Pinacol-Pinacolone Rearrangement**

at  $120^{\circ}$ C. The catalysts were prepared as per the reported procedure.<sup>[6]</sup> Benzopinacols 1,2,4,5<sup>[9]</sup> and 3<sup>[10]</sup> were prepared by following the reported procedures.

#### **Pinacol Rearrangement**

The rearrangement was carried out in a 25 mL round bottom flask fitted with a reflux condenser. A solution of benzopinacol (1) (1 mmol) in toluene (5 mL) along with catalyst (0.1 g) was heated at 80°C. Reaction was monitored by TLC. After completion of the reaction, toluene was removed by distillation to get a mixture of benzopinacolones (2 and 3).

#### General Procedure for the Analysis of the Mixture of 2 and 3

To the pinacolone mixture (2.0 g), a solution of KOH (10 g) in methanol (40 mL) was added. Benzene (10 mL) was used to aid the dissolution of the pinacolones. The solution was refluxed till the splitting of the pinacolone was complete (about 3 days). The alcohol and benzene were distilled and water (ca. 30 mL) was added to dissolve the potassium salt of the acids, while the triarylmethanes precipitated. The aqueous solution was acidified with hydrochloric acid and extracted with solvent ether in order to get the acids. The mixture of acids was esterified by the reported procedure<sup>[11]</sup> and analysed by gas chromatograph.

#### CONCLUSIONS

Pinacol-pinacolone rearrangement of benzopinacols can be effected using  $FeCl_3$  modified montmorillonite K10 catalysts prepared from acetonitrile solution and activated at a low temperature 80°C (K10-Fe-O-80). 100% conversion of benzopinacol was achieved in 10 minutes. A normal migratory aptitude was observed in all the cases. The catalyst is recyclable.

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