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MONTMORILLONITE CATALYZED DEHYDRATION OF TERTIARY ALCOHOLS TO OLEFINS

M. Lakshmi Kantam*, P. Lakshmi Santhi and M. Fyyazuddin Siddiqui

Homogeneous Catalysis Discipline
Indian Institute of Chemical Technology, Hyderabad 500 007, India

Abstract : H-montmorillonite is shown to be an effective catalyst for easy conversion of tertiary alcohols to the corresponding olefins in excellent yields. The catalyst is recycled almost quantitatively.

Acid catalysts[1] have been used on an industrial scale or in the laboratory for several decades for dehydration of alcohols but there is a need for environmentally friendly catalysts that would work under mild conditions.

Interlamellar silicate sheets of montmorillonite are the versatile hosts for Bronsted and Lewis acid catalyzed diverse organic reactions[2,3] such as protonation of alkenes, esterification, Diels-Alder, Friedel-Crafts reactions etc. Earlier ion-exchanged montmorillonites were used for elimination reactions[4] of alcohols and amines at elevated temperatures (200°C). Recently we have reported[5] Molybdenyl (VI) acetylacetonate catalyzed dehydration of tertiary alcohols to olefins. Herein this letter, we present the successful dehydrations of alcohols to olefins in excellent yields at moderate temperatures catalyzed by specifically designed H-montmorillonite with enhanced acidic sites (Table 1). In addition to this the reusability of the catalyst with consistant activity for several recycles has been demonstrated.

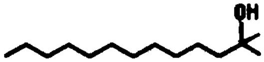
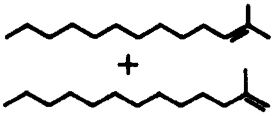
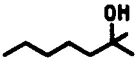
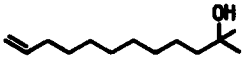
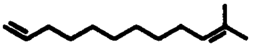
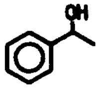
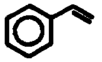
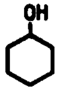
General Procedure

H-montmorillonite was prepared[6] ($H_0 = -5.6$ to -8.2) from commercial montmorillonite K_{10} (Fluka). To a solution of 0.428 g (2 mmol) of tertiary alcohol (Table 1, entry 1) in 25ml of absolute air-free dioxane, 0.200 g of vacuum dried H-montmorillonite was added. The mixture was heated under reflux and argon with stirring. After 6 h, the mixture was then cooled to room temperature, filtered and most of the dioxane removed under reduced pressure. The residue was diluted with 30 ml of ether, washed with saturated sodium chloride solution, water and dried over Na_2SO_4. After evaporation, a clear colourless oil was obtained, yield (0.356 g, 91%).

The activity of H-montmorillonite decreases with humidity because the acidity decreases with increase of water content. Thus, H-montmorillonite with its increased interlayer acidity than the metal ion exchanged montmorillonite is able to induce dehydration of the alcohols at moderate temperatures. However, poor conversions are obtained for sterically hindered alcohols.

The present methodology envisages the following advantages. 1. Preparation of olefins

TABLE-1 MONTMORILLONITE CATALYZED DEHYDRATION OF TERTIARY ALCOHOLS TO OLEFINS

Entry	Substrate	Products	% yield^a	(Ratio of products)
1			91	(81 : 19)
	2nd cycle	″	90	(80 : 20)
	7th cycle	″	86	(78 : 22)
2			89	(78 : 22)
3			90	(80 : 20)
4			85	(76 : 24)
5			85	
6			75^{b,c}	
7	 HO		78^c	
8			89^c	

a) Characterized by NMR and Mass

b) Reaction completed in 4h, Total polymerization on prolonged reaction.

c) G.C. analysis of the product.

in excellent yields under mild conditions. 2. The reactions are clean and regioselective. 3. Montmorillonite is readily available and cheap. 4. The easy and almost quantitative recycling of H-montmorillonite.

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