A New Vanadium-pillared Montmorillonite Catalyst for the Regioselective Epoxidation of Allylic Alcohols

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Unusual regioselectivity towards internal allylic double bonds in preference to terminal allylic double bonds is displayed using the newly synthesized vanadium-pillared montmorillonite catalyst.

The preparation of a new class of catalysts by intercalating clay minerals of the smectite type with various pillaring agents is of current interest. Al, Zr, Cr, Ti, Nb, Ta, *etc.* have been used as pillaring materials.[1—5] Hitherto, the evaluation of these pillared clays has been focused mainly on shape-selective studies, invariably of vapour phase reactions,[1b] and very few reports on liquid phase reactions have been cited recently.[4b,6] Herein, we decribe the synthesis and characterisation of the vanadium-pillared montmorillonite catalyst (V-PILC) and its application in epoxidation reactions. A novel feature of this catalyst is the display of unusual regioselectivity towards internal allylic double bonds over terminal ones in the epoxidation reactions (Table 1).

V-PILC was synthesised by refluxing $VOCl_3$ (0.5 ml) in dry benzene (70 ml) with H-Montmorillonite[7] (5 g) under nitrogen atmosphere until the solid clay suspension turned a deep bottle green colour (within approximately 6 h). The solid was filtered under nitrogen atmosphere, washed repeatedly with dry benzene, and moist air was passed over. It was oven dried at 110 °C for 6 h and analysed. The clay was thus intercalated with 14% by weight of vanadium according to a plasma analysis for metal atoms. The FT-IR spectrum showed characteristic bands due to V=O and V–O–V stretching vibrations in the ranges 1050—920 and 830—820 cm^{-1} respectively. Bands in the range 600—400 cm^{-1} can be assigned to the V–O–V rocking vibrations and a weak band at 910 cm^{-1} indicates the V–O–Si fragment.[8] An *X*-ray diffraction study of V-PILC showed (001) spacing of 22.9 Å giving an expansion from 9.6 Å of anhydrous montmorillonite. This expansion is due to the intercalation of polymeric vanadia species. Using the Brunauer–Emmett–Teller (BET) method, the surface area was calculated as 47.58 $m^2\ g^{-1}$. The ESR spectrum of V-PILC showed a well-resolved hyperfine splitting due to ^{51}V ($I = 7/2$) with $g_\perp = 2.040$ and $g_\parallel = 1.970$ which is due to the dispersed V^{4+} species formed in the pillar.[9] Thus, greater loading and higher c-spacing is achieved using this methodology than that reported by us previously using a different method of preparation and a different pillaring agent.[6]

$VO(acac)_2$ has been widely used in epoxidation reactions under homogeneous reaction conditions.[10—12] Separation of the homogeneous catalyst is difficult after the reaction, but the use of V-PILC provides easy separation by simple filtration and recycling. The reactions in entries 1—5 of Table 1 proceed

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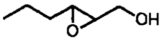
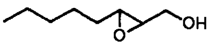
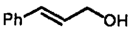
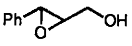
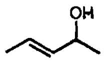
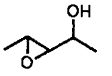
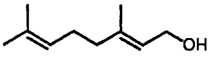
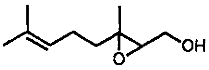
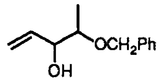
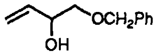
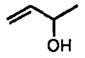
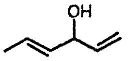
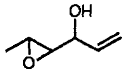
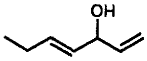
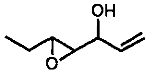
Table 1. Regioselective epoxidation of allylic alcohols using V-PILC.[a]

Entry	Substrate	Product[b,c]	Isolated yield/%	Time/h
1			96	5
2			89	5
3			92	7
4			94	2.5
5			88	7.5
6		No reaction	—	15
7		No reaction	—	15
8		No reaction	—	15
9			91	7
10			95	7

[a] All reactions were performed on 7 mmol allylic alcohols in 15 ml dry benzene using 42 mg of V-PILC (containing 0.1 mmol of vanadium) and 1.3 ml of azeotropically dried hydroperoxide (*ca.* 3.1 M in toluene) at room temperature under nitrogen atmosphere. [b] Purified by column chromatography or distillation. [c] Characterised by IR and ^{1}H NMR spectroscopy.

at rates comparable with those achieved using $VO(acac)_2$. The reaction is limited to the allylic double bonds as evidenced in entry 5 (Table 1), giving exclusively monoepoxide. However, V-PILC is passive towards terminal allylic alcohols as shown in entries 6—8 (Table 1), despite the extended reaction times. This property has been successfully exploited in selective epoxidation of internal allylic double bonds in the presence of terminal allylic double bonds in specially designed substrates, entries 9 and 10 (Table 1), to give exclusively monoepoxides leaving the terminal allylic double bond intact. This remarkable regioselectivity has not been observed in vanadium catalysed epoxidations reported previously.[10] A recent report described the selective epoxidation of backbone double bonds in a polybutadiene system catalysed by MoO_2Cl_2–[3-(diethoxyphosphinyl)camphor], but it lacks generality for other substrates.[13]

In conclusion, a simple procedure for the regioselective epoxidation of allylic alcohols with successful recycling of V-PILC is demonstrated. The scope and utility of the pillared catalyst should be extendable to other reactions as a heterogenised catalyst.

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