

SHAPE-SELECTIVE ISOMERISATION OF α -ACETYLENIC ALCOHOLS TO α,β -ETHYLENIC CARBONYL COMPOUNDS BY VANADIUM-PILLARED MONTMORILLONITE CATALYST[†]

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Abstract : A very simple, convenient method for an efficient shape-selective isomerisation of acyclic and aromatic α -acetylenic alcohols only, to the corresponding α,β -ethylenic carbonyl compounds, leaving the cyclic ones unreacted using catalytic amounts of vanadium-pillared montmorillonite catalyst, having $-Si-O-V=O$ groups with successful reusability is described.

The isomerisation of α -acetylenic alcohols into α,β -ethylenic carbonyl compounds, versatile organic intermediates in the manufacture of fragrances¹, carotenoids² etc. has been studied extensively. Many acidic catalysts³ and derivatives of metals such as Mo, Ti, V, W⁴ etc. have been successfully employed for the isomerisation of α -acetylenic alcohols. However, they often lead to complex mixtures of products and unselective rearrangements⁵. Recently, it was reported by us that smectite clays pillared with transition metal oxides are very efficient catalysts for selective organic transformations in liquid phase reactions⁶. Here in, we report a very simple and convenient method for an efficient shape-selective isomerisation of acyclic and aromatic α -acetylenic alcohols only to the corresponding α,β -ethylenic carbonyl derivatives (Scheme 1) leaving the cyclic ones unreacted (Scheme 2) using catalytic amounts of vanadium-pillared montmorillonite catalyst^{6a} (V-PILC) with the advantage of reusability.

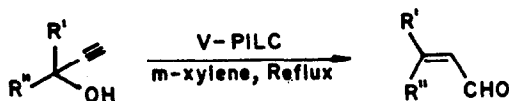
The isomerisation was performed by stirring V-PILC (42 mgs, contains 0.1 mmol of vanadium) initially in m-xylene under nitrogen atmosphere for 15 mins, followed by the addition of α -acetylenic alcohol (7 mmol). The overall contents were refluxed and the reaction was monitored by TLC. After the completion of the reaction, the solid catalyst was filtered, and the filtrate was spin dried and subjected to column chromatography. All the products were characterised by IR, NMR and Mass Spectra. It was observed that acyclic and aromatic α -acetylenic alcohols were readily isomerised by V-PILC, to afford α,β -ethylenic carbonyl compounds (Scheme 1) and no side reactions were observed.

Cyclic propargyl alcohols such as 1-ethynylcyclopentanol (Scheme 2) were totally inert under the same experimental conditions. On prolonged reaction times also no reaction was observed and since the α -acetylenic alcohols are sensitive to heating⁷, are getting converted to unidentified polymeric products.

The activity and unusual shape-selectivity of V-PILC has been retained during the recycling (3 cycles were tested). The fact that cyclic propargyl alcohols were inert can be explained

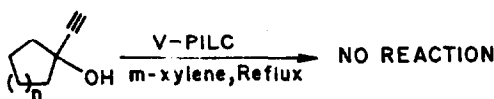
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in terms of space restriction imposed due to the pillaring of the interlayers of montmorillonite. Thus, the alignment of the cyclic propargyl alcohols for the complexation with the vanadium atom may not be possible, thus leading to their inertness^{6b}.



Scheme 1

R'	R''	Time (hrs.)	Isolated yields
CH ₃	CH ₃	1.0	82
CH ₃	C ₂ H ₅	1.5	84
C ₂ H ₅	C ₂ H ₅	1.5	78
H	n-C ₆ H ₁₃	2.0	91
H	n-C ₅ H ₁₁	2.0	88
H	Ph	2.5	86



n = 1, 2, 4

Scheme 2

In conclusion, the use of pillared clay (V-PILC) having $-\text{Si}-\text{O}-\text{V}=\text{O}$ groups, intercalated in the interlayers of montmorillonite leads to highly efficient shape-selective isomerisation of acyclic and aromatic α -acetylenic alcohols leaving the cyclic ones unreacted. The V-PILC is acidic in nature and thermally very stable is not easily hydrolyzed like other vanadic esters⁴. With these advantages combined with reusability, the present solid catalyst becomes a practical alternative to other catalysts reported earlier³⁻⁵.

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