

# SYNLETT Spotlight 32

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## Montmorillonite<sup>#</sup>

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Aayesha nasreen received her B. Sc (Bachelor's degree) in 1993 from Kakatiya University, Warangal, A.P. India. She did her post graduation in organic chemistry with specialization as medicinal chemistry in 1995 from Osmania University, Hyderabad, A.P. India. She then joined Indian Institute of Chemical Technology (IICT) Hyderabad, as research trainee. She is working under the supervision of Dr. Adapa Srinivas Rao, as SRF (Senior Research Fellow) for her Ph. D. Currently she is working in the area of organic chemistry particularly asymmetric synthesis catalyzed by metal salts.



### Introduction

Montmorillonite clay's are layered silicates and are among the numerous inorganic supports for reagents used in organic synthesis. They can be used as an efficient and versatile catalyst for various organic reactions. In Montmorillonite clay one octahedral aluminate layer is sandwiched between two octahedral silicate layers.<sup>1</sup> These are non-toxic, non-corrosive, economical and recyclable. In Montmorillonite clay both Brønsted and Lewis acidic catalytic sites are available, hence its natural occurrence as well as its ion exchange properties allow it to function efficiently as a catalyst. The interlayer cations are exchangeable, thus allowing alteration of the acidic nature of the material by simple ion-exchange procedure.<sup>2</sup> In recent years Montmorillonite particularly Montmorillonite K-10 emerges as an efficient acidic catalyst in organic chemistry. This can be prepared by calcination of Montmorillonite. Montmorillonites are modified by simple cation

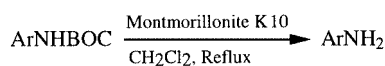
exchange process to give more effective Montmorillonites such as Fe<sup>+</sup> Montmorillonite, clayfen, claycop.<sup>3</sup> Most of the nitrates are deposited on K 10, i.e. Iron (II) nitrate-K 10, Montmorillonite clay and copper (II) nitrate K 10 Bentonite clay. These are used in oxidation and nitration reactions. K 10 is some times misunderstood by name or its uses with other clay based acidic catalysts (KSF, K10F, H<sup>+</sup>-exchanged Montmorillonite, clay).

The activation<sup>4</sup> of K 10 clay is carried out by thermal activation. Its acidic character is enhanced by cation exchange i.e by Fe (II)<sup>5</sup>, Zn (II)<sup>6</sup> or by deposition of Lewis acids such as Zn (II)<sup>7</sup> or Iron (III)<sup>8</sup> chlorides.

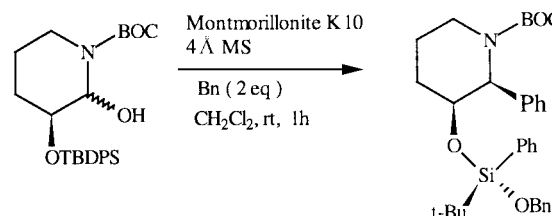
Recent reports on K 10 focus on some important reaction and various transformations. K 10 is used as catalyst in the synthesis of dimethyl acetals,<sup>9</sup> enamines,<sup>10</sup>  $\gamma$ -lactones,<sup>11</sup> enolthioethers,<sup>12</sup>  $\alpha,\beta$ -unsaturated aldehydes<sup>13</sup> and porphyrin synthesis<sup>14</sup> etc

### Abstracts

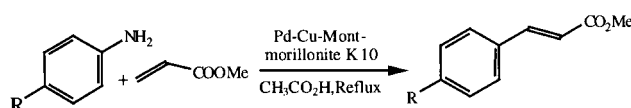
A) Montmorillonite K 10 is used as catalyst for the selective deprotection of N-BOC group. The N-BOC group of aromatic amines selectively deprotected without effecting the aliphatic N-BOC protected amines.<sup>15</sup>



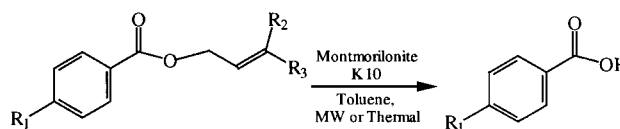
(B) Montmorillonite K 10 is utilized in a novel aryl migration from silicon to carbon which forms an efficient approach to the asymmetric synthesis of  $\alpha$ -aryl  $\beta$ -hydroxycyclic amines and silanols.<sup>16</sup>



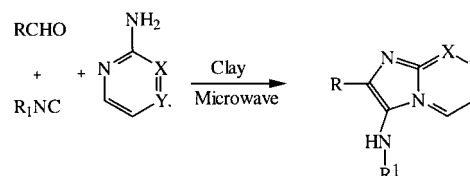
(C) Waterlot et al. reported direct synthesis of methyl cinnamates by Heck vinylation reaction of anilines with vinylacetate catalyzed palladium chloride and copper nitrate intercalated Montmorillonite K 10 as catalyst. The substituted methyl cinnamates were obtained in excellent yield without stilbene by product formation.<sup>17</sup>



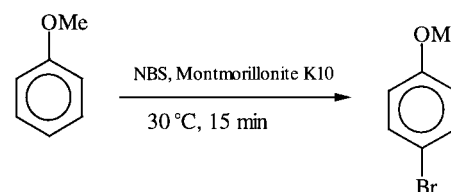
(D) The allyl esters are selectively deprotected under mild and solvent free conditions to yield carboxylic acids in good yields with excellent chemoselectivity. The method provides almost 100 fold reduction of reaction time under microwave irradiation and reaction was performed under ecofriendly conditions.<sup>18</sup>



(E) Varma et al. reported one pot synthesis of imidazo [1,2-a] annulated pyrazines and pyrimidines via the condensation of aldehydes, amines and isocyanides catalyzed by Montmorillonite K 10 under microwave irradiation in solvent free conditions. The method is an easy route for the synthesis of multisubstituted imidazo [1,2-a] pyridines, imidazo [1,2-a] pyrazines and imidazo [1,2-a] pyrimidines.<sup>19</sup>



(F) Reaction of methoxybenzenes and naphthalenes with N-bromosuccinimide in presence of Montmorillonite K 10 affords excellent yields of regioselectively brominated product in solvent free condition.<sup>20</sup>



## References and Notes

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