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Montmorillonite clay-catalysed synthesis of cyclic allylamines

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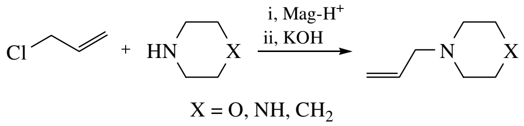
A mild and efficient catalytic method for the synthesis of cyclic *N*-allylamines using an acid-exchanged montmorillonite as a catalyst is described.

Alkylamines are prepared by the condensation of cyclic secondary amines such as piperidine, pyrrolidine and morpholine with carbonyl compounds.[1–7] Traditionally, these reactions involve the use of *p*-toluenesulfonic acid, heat, *etc.*[2] Amides can be N-alkylated in substantial yields under phase-transfer catalytic conditions.[8] Watanable *et al.*[9] reported the N-alkylation of amides with alcohols using ruthenium compounds as catalysts.[9]

The chemical industry is always looking for new substitutes to these classical catalysts. Over the last few decades, selective organic syntheses using inorganic solids have been reported.[10–14] We performed the selective perfluoroalkylation of diethanolamine using montmorilloite clay (H-Maghnite).[15] We are interested in developing a new and efficient method for the preparation of *N*-allylmorpholine, *N*-allylpiperidine and *N*,*N*-diallylpiperazine by the condensation of allyl chloride with morpholine, piperidine and piperazine, respectively, in the presence of acid-exchanged montmorillonite clay called Mag-H$^+$.[16] The advantage of this method is that the acidic clay is inexpensive, stable and non-corrosive. Moreover, work-up procedures are very simple, and the clay can be separated from the reaction mixture by filtration.

The reactions of allyl chloride with amines such as morpholine, piperidine and piperazine without a solvent were carried out at ambient temperature in the presence of Mag-H$^+$ as a catalyst. These amines react with allyl chloride under very mild conditions (Scheme 1).[†]



Scheme 1 Reaction of allyl chloride with secondary amines in the presence of Mag-H$^+$.

The results obtained in these reactions are summarised in Table1.

The acid-treated catalyst (Mag-H$^+$) is highly active in the acid-catalysed reactions of allyl chloride with secondary amines due to the surface acid sites. The importance of the accessibility of active sites in catalysts of this type was illustrated by a series of pillared clays and metal cation-exchanged montmorillonite.[17] The reaction in the pillared clay catalysts was diffusion-controlled, and the superior activity of the Mag-H$^+$ was due to the wider pores and more accessible acid sites in montmorillonite.[18] Although the acid-exchanged catalyst used here exhibits smaller pores than the pillared clays, it is likely that diffusion control is more important in these catalysts than in Mag-H$^+$.

The catalytic activities of ion-exchanged clay minerals in both Brönsted and Lewis acid-catalysed reactions reflect the surface acidities of the catalysts. The Brönsted acidity can be explained in terms of the abilities of the exchangeable cation in the catalyst to polarise the coordinating water molecules and hence to generate protons. Na$^+$MMT and other forms with alkali and alkali earth cations gave very low yields, and no reaction occurred in control experiments without catalysts. The catalysts in these forms show the lowest activity, confirming that the exchangeable cations are indeed the active sites. Experiments with initiating the reaction by adding an allyl chloride to premixed catalyst Mag-H$^+$ plus amine showed no difference in the catalytic activity. The yields obtained with different amines show that the reaction yield depends on the reactivity of the amine molecule, which is connected with its basicity.

The catalytic activity of the prepared material was tested in the preparation of allylamines from amines (morpholine, piperidine and piperazine). The effect of the substitution of amines on the catalysed reaction involved electron-donating forces of the substituting group. Piperazine, in contrast to morpholine and piperidine groups, has more reactivity because of a molecule basicity effect. Therefore, the expected order of reactivity for substituted amines was: piperazine > morpholine > piperidine.

Under reaction conditions, the interlayer spaces are completely filled with reactant and product molecules, and the curvature effects on the external surface of the clay catalyst are likely to promote reagent activation and process selectivity.[18–20]

In order to ascertain the effects of solvents, the N-alkylation of morpholine with allyl chloride was carried out using several solvents (Table 2). The order of the selectivities of N-alkylation is benzene > dioxane > acetonitrile > DMSO.

Table 1 Reactions of amines with allyl chloride catalysed by Mag-H$^+$.

No	Amine	$\varphi^a_{\mathrm{amine}}$/g	$\varphi_{\mathrm{allyl\ chloride}}$/g	*t*/min	Yield (%)
TP1	Morpholine	2.5	2.7	30	78
TP2	Piperazine	2.5	5.4	30	98
TP3	Piperidine	2.5	2.7	30	68

[a] φ is the quantity.

[†] Allyl chloride (Merck) was used without further purification. Morpholine, piperidine and piperazine from Fluka were purified by vacuum distillation. Organic solvents were used without further purification.

The ^{1}H and ^{13}C NMR measurements were carried out on a 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. Tetramethylsilane (TMS) was used as an internal standard.

The IR spectra were measured with a Perkin-Elmer 1600 FT spectrometer.

General procedure. The reactions were carried out in bulk (without solvent). H-Maghnite clay (2 g) was added to a solution of morpholine (2.5 g, 0.028 mol) and an allyl chloride (2.7 g, 0.035 mol), and the mixture was stirred at room temperature. After completion of the reaction, the solution was washed several times with chloroform, the whole mixture was filtered and the clay-free material gave the salt of *N*-allylmorpholinium. After having prepared 100 cm^3 of an aqueous solution of KOH (10%), one added the ammonium salt by small quantities. The mixture was left under stirring overnight. A homogeneous solution was obtained, and the *N*-allylmorpholine was extracted with diethyl ether. Two phases were separated by decantation, diethyl ether was evaporated. The yield of the reaction was 78%.

For *N*-allylmorpholine: ^{1}H NMR, δ: 3.2 (t, 4H), 3.6 (d, 2H), 3.8 (t, 4H), 5.2 (dd, 1H), 5.5 (dd, 1H), 5.8 (m, 1H). ^{13}C NMR, δ: 130 (t, 1C), 125 (d, 1C), 65 (t, 2C), 50 (t, 2C).

For *N*,*N*-diallylpiperazine: ^{1}H NMR, δ: 2.6 (t, 4H), 3.0 (d, 2H), 5.0 (dd, 2H), 5.7 (m, 1H). ^{13}C NMR, δ: 43 (t, 2C), 51 (t, 1C), 120 (t, 1C), 134 (d, 1C).

For *N*-allylpiperidine: ^{1}H NMR, δ: 1.58 (m, 6H), 2.79 (t, 4H), 3.1 (d, 2H), 5.16 (dd, 2H), 5.8 (m, 1H). ^{13}C NMR, δ: 26 (t, 3C), 47 (t, 3C), 120 (t, 1C), 139 (d, 1C). FT-IR (ν/cm^{-1}): 3079 (=C–H), 1680 (C=C), 830 and 950 (out of plane bending vibrations of olefinic C–H groups).

Table 2 N-alkylation of morpholine using Mag-H^+ in several solvents for 2.5 h.

Solvent	Yield (%)
Benzene	52
Dioxane	48
Acetonitrile	41
DMSO	36

Thus, we have developed a mild and efficient catalytic method for the synthesis of *N*-allylmorpholine, *N*-allylpiperidine and *N*,*N*-diallylpiperazine from allyl chloride and morpholine, piperidine and piperazine, respectively, using montmorillonite (Maghnite) as a catalyst.

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