Chemical Conversions using Sheet Silicates: Novel Intermolecular Elimination of Ammonia from Amines

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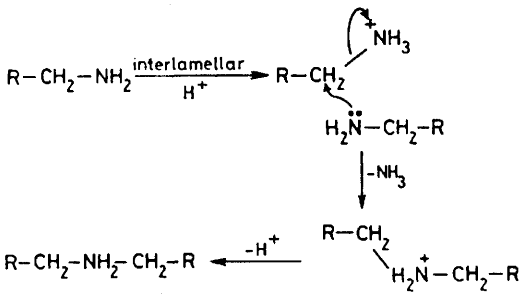
Summary Ammonia is readily eliminated from molecular pairs of intercalated primary amines thereby generating the secondary amines in high yield in a novel proton-mediated reaction; certain cyclic secondary amines produce unusual products by a similar interlamellar reaction.

As an extension of our study of organic reactions catalysed by sheet-silicate intercalates[1,2] we have established[3] that, in the presence of ion-exchanged montmorillonites (*e.g.*, Al^{3+}, Cr^{3+}, or Cu^{2+}) initially hydrated in the interlamellar region, the following primary amines each reacted at *ca.* 200 °C to eliminate ammonia and to form the corresponding secondary amine as essentially the only product: hexan-1-amine, cyclohexylamine, and benzylamine. The products were in each case analysed by g.l.c.–mass spectroscopy and, after collection from the g.l.c. effluent, by n.m.r. spectroscopy; they were unequivocally identified by comparison with authentic or synthetic samples. Studies of initial rates revealed that substantial yields are generated in a few hours.

The reactions have been mainly carried out in small stainless steel pressure vessels (*ca.* 20 cm^3 capacity) and a typical charge would be 1 g of solid catalyst and 5 g of reactant. The pressure vessel was immersed in a liquid thermostat capable of operating up to 220 °C.

It appears that these reactions involve protonic catalysis in the interlamellar space of the sheet silicate as illustrated in Scheme 1.



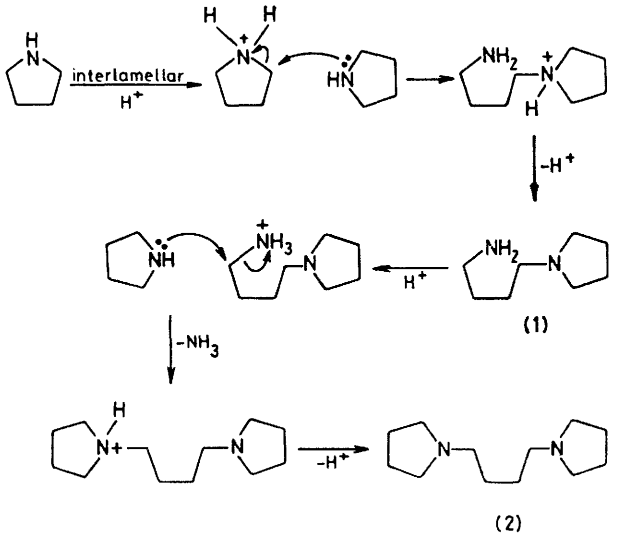
Scheme 1.

The primary amine freely enters the interlamellar region displacing the intercalated water originally present. The amine becomes protonated and combines with a second, unprotonated amine molecule, which reacts by nucleophilic displacement of ammonia to form the protonated secondary amine. Such a reaction scheme is unknown in solution, where all the amino groups would normally be protonated and spatially separated by solvent.

Similar mechanistic considerations could theoretically result in the production of tertiary amines from the secondary aliphatic amine products, but in practice, when the corresponding secondary amines are treated with the sheet silicate, very little reaction takes place and only minute quantities of tertiary amines are produced. Presumably steric considerations are important with secondary aliphatic amines.

When cyclic secondary amines are used,[3] however, interesting products are obtained. Pyrrolidine reacted at *ca.* 200 °C to yield 4-(1-pyrrolidyl)butanamine (**1**) as the principal product, with increasing yields of 1,4-di-(1-pyrrolidyl)butane (**2**) as the reaction progressed [*e.g.*, 52% of pyrrolidine had reacted after 74 h to yield 40% of (**1**) and 10% of (**2**)].

The proposed mechanism of the formation of these cyclic derivatives, as illustrated in Scheme 2, also involves nucleophilic displacement processes but, in this instance, *three* molecules of pyrrolidine are involved in the interlamellar elimination of ammonia.



Scheme 2.

Rate curves for production of (**1**) and (**2**) fully confirm the secondary nature of product (**2**) and the role of (**1**) as its intermediate.

Piperidine reacted very much more slowly (5% conversion after *ca.* 90 h at 200 °C) but, nevertheless, produced two similar compounds, 5-(1-piperidyl)pentanamine and 1,5-di-(1-piperidyl)pentane as the only products. Under the same conditions there was only 2% conversion of morpholine, so a higher temperature is clearly needed.

Primary aromatic amines were totally unaffected when heated with the montmorillonite at 200 °C. This is in line with the proposed mechanistic schemes as these compounds would not undergo the nucleophilic displacement of ammonia.

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[3] Br. P. appl. No. 80/16,384.