Selective Organic Reactions in Sheet-silicate Intercalates: Conversion of 4,4'-Diamino-*trans*-stilbene into Aniline

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Summary. Aniline is produced in good (*ca.* 45%) yield when the intercalate of montmorillonite and 4,4'-diamino-*trans*-stilbene is heated, *in vacuo*, to *ca.* 300 °C.

Highly selective molecular conversions in caged and other restrictive environments have aroused interest partly because of the quest for 'biomimetic functionalization'[1] and partly because of the efficiency, as catalysts for NH_3 and CH_4 synthesis, of certain mixed inter-lamellar compounds of graphite.[2] Weiss and his co-workers[3] have also shown the versatility of some sheet-silicate frameworks as media for a wide range of organic reactions, and the recently discovered unusual electronic properties of novel transition-metal chalcogenide derivatives[4] has focussed fresh attention on the properties of intercalates.

In a study[5] of the intercalate chemistry of the clay mineral montmorillonite, we have discovered an easy conversion which occurs in the solid state of the 4,4'-diaminostilbene intercalate of montmorillonite, the structure of which is outlined in the Figure. The intercalate was formed by addition of excess of aqueous 4,4'-diaminostilbene dihydrochloride to aqueous colloidal suspensions of purified sodium-exchanged Wyoming montmorillonite. This results in the flocculation of the clay, the green precipitate turning brown when left. Potentiometric titration established that 35 mmol of the diamine hydrochloride was adsorbed per 100 g of the air-dried clay. As the cation exchange capacity of the montmorillonite had been determined to be 70 meq/100 g it follows that the amine is taken up by a cation exchange mechanism as a doubly charged diprotonated species. The formula of the intercalate, which on heating forms aniline, is approximately

$$(H_3NC_6H_4\text{—}CH{=}CH\text{—}C_6H_4NH_3)[(OH)_4Si_8Al_{3.5}Mg_{0.5}O_{20}]_4$$

Aniline, identified by mass spectrometry and g.l.c., is obtained in yields close to 45% (of the parent diamine)

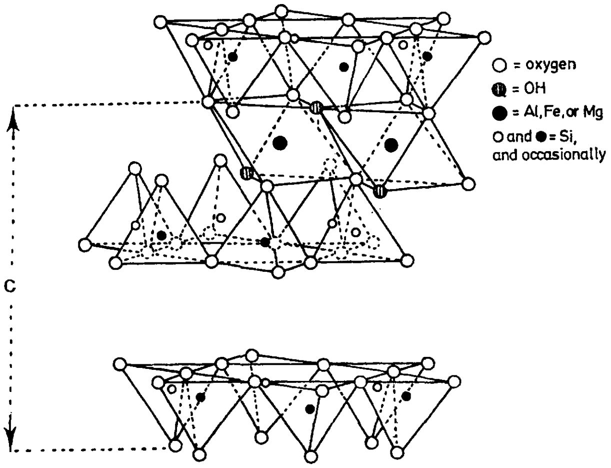

Figure. Schematic structure of montmorillonite. The *c* spacing of the 4,4'-diaminostilbene intercalate is 14·5 Å compared with 9·8 Å for montmorillonite dried at 110 °C.

when the intercalate is heated *in vacuo* to *ca.* 300 °C for 30 min. The mass-spectrometric cracking patterns of the unprotonated and diprotonated 4,4′-diamino-*trans*-stilbene are very different from those of their intercalated analogues, the dominant fraction for the parent organic molecules alone being the molecular ion. The pyrolysis products of the intercalate formed by heating *in vacuo* were collected in a cold trap and taken up in a standard solution of *o*-xylene in ether. The sole gaseous product detected was aniline, which was determined quantitatively by comparison of peak areas for aniline and *o*-xylene (used as a calibration standard).

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