Keith Smith

Controlled bromination with the help of microporous solids

CHCN

At a previous conference on the chemistry of bromine compounds, we reported the development of a new reagent system comprising N-bromosuccinimide and silica. This reagent system was shown to be capable of reacting with electron-rich heterocyclic compounds such as indoles and carbazole. We have investigated the scope of this reagent system further and have noted its limitations. We have also noted an interesting dealkylation reaction on attempted polybromination of N-ethyliminodibenzyl:

Although this reagent system reacts well with heterocycles of the types described above, it is not sufficiently reactive to provide convenient procedures for bromination of less reactive substrates. Even toluene reacts only slowly with the system, while nitrobenzene remains totally unaffected by it. Thus, we have investigated a range of different acidic solid catalysts and a range of different bromine-containing reagents in an attempt to reagent systems with properties appropriate to particular substrates.

Montmorillonite K10 clay is much more acidic than silica and consequently catalyses reactions more readily. Thus, reactions which do not occur in the presence of silica may occur in the presence of K10:

CH, CN

Reactive substrates such as phenols react with many of the brominating agents even in the absence of a solid catalyst. Thus, it is difficult for the solid to influence the reaction at all. However, by use of very unreactive brominating agents the solid can begin to influence the reaction. Ion exchange resins have been found to be particularly appropriate catalysts for some reactions while different selectivity may be achieved in the absence of a solid:

We have also investigated the addition of bromine to carbon-carbon double bonds in the presence of zeolite microporous solids. The zeolite pore structure can be utilized to gain selectivity over the reactions which take place :

These reactions will also be discussed.