Shape-selective Synthesis of Substituted Pyridine on Zeolite-hosted Monovalent Cobalt

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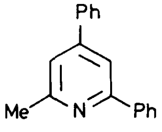
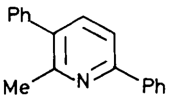
The synthesis of diphenyl methyl pyridine *via* the cotrimerization of phenyl acetylene and acetonitrile using a novel monovalent cobalt catalyst generated reductively in zeolitic media is described.

Alkylpyridines have been synthesized in homogeneous media using monovalent cobalt complexes.[1] Ample evidence has been provided as to the monovalent nature of the active cobalt complex. Along with a number of well defined cobalt(I) complexes, numerous cobalt(II) salt precursors have been used to generate reductively the active moiety within the reaction mixture.

Little information is available concerning the separation and analysis of the products. However, it is expected that, at least, separation of the soluble catalyst from the product



(I)



(II)

mixture would involve tedious and lengthy steps. In this respect, zeolites have been shown, over the years, to be effective solid solvents for various complexes and suitable media for reactions catalysed by co-ordinated transition metal complexes. However, there is no mention in the literature of the generation of monovalent cobalt species in zeolitic media, although a few zerovalent complexes have been reported to be stablized or formed in zeolite matrices.[2,3]

We report here the generation and catalytic use of monovalent cobalt species in the synthesis of diphenyl methyl pyridine *via* the cotrimerizaton of phenyl acetylene and acetonitrile within synthetic zeolites (NaY from Linde Division Union Carbide and NaZ from Norton). Cobalt(II) ions were introduced *via* the conventional ion-exchange procedure. The final sodium and cobalt contents were determined by flame photometry. All prepared samples exhibited high crystallinity to *X*-rays and the cobalt content was 3%

The Co^{II} zeolite (300 mg Co) was dried at 100 °C in an oven and introduced into a flask containing the reaction mixture including 30 ml of phenyl acetylene and a large excess of acetonitrile (50 ml). Constant stirring was established and the reducing agent (0.5 g $NaBH_4$) was admitted into the flask. From pink the zeolite turned to green then progressively to brown. A temperature increase was observed. The reaction mixture was refluxed for 48 h and finally cooled down to room temperature. The zeolite was then filtered off.

The pyridines produced were precipitated from the reaction mixture by hydrochloric acid. The precipitate was subsequently dissolved using 0.1 M aqueous sodium hydroxide solution. The organic product was extracted using chloroform which was finally removed by simple evacuation. The white, slightly fluorescent mixture was then analysed by g.l.c. using an 1/8 inch (diameter) × 1 m long column packed with 15% OV 101 on Chromosorb G/HT maintained at 150 °C. Individual isomers were separated using t.l.c. and were identified by ^1H and ^{13}C n.m.r. spectroscopy using a CAMECA 350 n.m.r. spectrometer. The assignment of structures (I) and (II) to the resulting isomers was thus confirmed. Both g.l.c. and ^1H n.m.r. spectroscopy (Me resonances) gave identical isomer ratios, which varied with the nature of the catalytic medium: while the $CoCl_2$ based catalyst gave 80% of isomer (I),[1] NaCoY and NaCoZ precursor catalysts yelded 70% and 60% of isomer (I) respectively. These significant variations of the (I)/(II) ratio are indicative of the constraints imposed by the zeolite matrix on the active monovalent cobalt centre. This suggests that the produced monovalent cobalt is strongly held within the zeolite matrix possibly *via* co-ordination to the framework oxide ions during the catalytic process.

Confirmation of this stems from blank experiments: after all the reactants had been introduced the zeolite was filtered off under an argon atmosphere. The homogeneous solution was then allowed to reflux for 48 h. No alkylpyridine was formed under these conditions indicating that the monovalent cobalt complex *was not* eluted from the zeolite matrix. On the other hand the much lower activity rate observed in zeolitic media confirms that the reaction does not occur in solution. However it is not clear as yet whether the catalytic reaction occurred at the pore mouths or well inside individual microcrystals. The selectivity shift towards isomer (II) as the pore dimensions decreased is not drastic enough to favour unambiguously bulk *vs.* surface reactions. It is our intention to use various substituted acetylenes and nitriles in order to probe these steric aspects. Shape-selective reactions may well produce particular substituted pyridines selectively.

Received, 14th November 1985; Com. 1581

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