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Selective synthesis of *N*,*N*-dimethyl aniline derivatives using dimethyl carbonate as a methylating agent and onium salt as a catalyst

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Abstract

N-Alkylation of anilines by dimethyl carbonate (DMC) catalyzed by onium salts has been demonstrated. The work presented here shows that a simple catalytic system consisting of onium salts in the presence of a small amount of water is extremely effective in enhancing the DMC mediated *N*-alkylation of anilines to dialkylated products. The effect of reaction conditions, on the synthesis of *N*,*N*-dimethyl aniline (NNDMA) from aniline and DMC has been investigated. Under the optimized conditions highest yield of NNDMA obtained was 99.8%, which is the best reported for liquid phase *N*-alkylation of aniline using DMC. The role of water in enhancing the yield of NNDMA is explained and a reaction-networking scheme is constructed, which summarizes the chemistry behind liquid phase *N*-alkylation of anilines by DMC. The catalyst has been shown to recycle up to five times and at the end of fifth recycle almost 98% of NNDMA yields were obtained.

Keywords: *N*-Alkylation; Methylation; Onium salts; *N*,*N*-Dimethyl aniline; Aniline; Dimethyl carbonate

1. Introduction

The increasing demands of environmental legislations have been prompting the chemical industry to minimize, or preferably eliminate synthetic routes producing waste materials such as salts, acid slurries, etc. *N*-Alkylated anilines represent examples, where conventional Friedel–Crafts [1] or mineral acid [2] (sulphuric acid) catalysts are used or alkylating reagents such as dimethyl sulphate, methyl halides are used in stoichiometric amounts producing salts in large quantities. These lead to problems of corrosion, high toxicity and cause pollution to environment due to neutralization of the acids and undesired by products.

N,*N*-Dimethyl anilines are useful intermediates in the synthesis of dyestuffs, pharmaceuticals and agrochemicals as well as fine chemicals such as Vanillin, Michler's ketone, etc. They are also used as solvents and additives in the production of synthetic rubber [3]. *N*,*N*,*N*′,*N*′-Teramethyl-1,4-phenylene diamine is used in the bio-medical field as a reagent known as Wurster's blue [4].

Although in the last decade attempts were made to develop alternative processes based on environmentally acceptable starting materials such as methanol as the alkylating agent and solid acid as recyclable catalysts [1], the process still require high temperatures typically in the range 573–623 K and the yield of dialkylated product is very low (in the range of 12–40%) [5–7]. A vapour phase continuous process for the production of *N*,*N*-dimethyl aniline (NNDMA) from aniline and methanol has been described using alumina based solid acid catalyst, wherein ∼86% yield of dimethyl aniline has been claimed [8].

The use of DMC as a methylating agent has become popular ever since Enichem-Ravenna, in Italy started the commercial production of dimethyl carbonate (DMC) by oxidative carbonylation route; thus making available DMC by environmentally benign process. DMC has now been recognised as a green reagent and its application in chemical industry is also growing steadily [9,10].

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The vapour phase *N*-alkylation of aniline using DMC as alkylating agent was investigated extensively [11–13]. In particular Fu and Ono reported high yield of *N*-methyl aniline (NMA) with selectivity ∼92% using Faujasite NaX as a catalyst at 423 K, while at 513 K temperature NNDMA is produced with selectivity >95% [11].

Liquid phase *N*-methylation of anilines has been reported by Tundo and coworkers [14–16] using DMC as an alkylating agent and Faujasite X or Y zeolite as a catalyst. Their results indicate that at a temperature of 403–453 K, mono-methyl aniline is produced selectively in 96% yield with only traces of dimethyl derivative. Dehmlow et al. [17] examined the *N*-alkylation of anilines by alkyl halides under PTC conditions (onium salt and alkali hydroxide), but the maximum yield of dialkylated product obtained was only in the range of 20–22%.

Thus, previous reports on synthesis of *N*,*N*-dialkylated anilines suffer from several techno-ecological problems. The results on *N*-alkylation of anilines with organic carbonates indicate that, while mono-alkylated products are formed selectively in the liquid phase alkylation, dialkylated products are difficult to synthesize selectively. Only in vapour phase alkylation, dialkylated anilines are formed selectively but requires high temperature >513 K. Also, it is extremely difficult to separate aniline and *N*-alkylated anilines into pure components by distillation. Therefore, it is most desirable to produce selectively NNDMA in high yield.

In the present study, we report an environmentally benign catalytic route to synthesize selectively *N*,*N*-disubstituted alkyl anilines in high yields and almost free from side products such as mono-alkylated anilines, carbamates and alkyl toluidines using DMC as methylating agent and onium salts as catalysts.

2. Experimental

Aniline and various substituted aromatic amines, organic carbonates were purchased from M/S S.D. fine chemicals, India. *n*-Dibutyl carbonate was prepared by transesterification of dimethyl carbonate and *n*-butanol [18]. Various quaternary salts like: tetramethylammonium bromide, tetraethylammonium bromide, tetraethylammonium iodide, tetrapropylammonium bromide, tetrabutylammonium bromide, tetrabutylphosphonium bromide, etc. were purchased from Aldrich Chemicals, USA. Amines were freshly distilled prior to use.

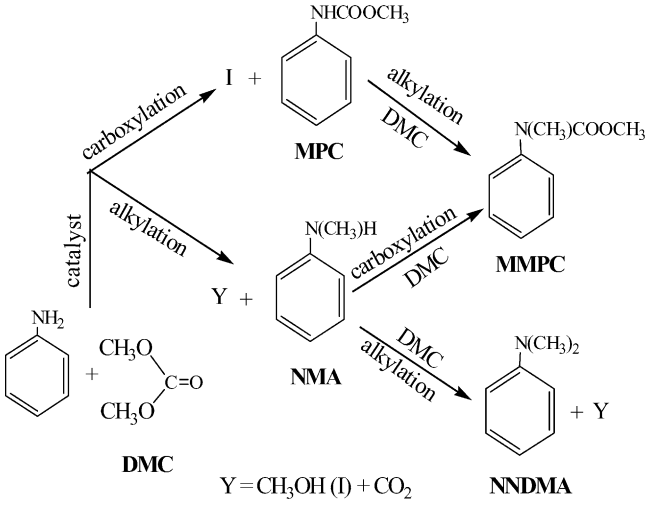
In a typical experimental procedure, amine (16.1×10^{-3} mol), dimethyl carbonate (0.19 mol), onium salt (3.57×10^{-3} mol) and water (0.11 mol) measuring total reaction volume of ∼20 ml, was charged into a 50 ml Hast 'C', high pressure reactor (supplied by Parr Instrument Co., USA). The whole system was flushed with nitrogen and the reaction was carried out at 443 K under 34 bar N_2 for 2 h under stirring at 13 Hz. After cooling the reaction mixture, the gases were analysed and vented off. Liquid phase was quantitatively analysed using gas chromatography on a HP-5 capillary column of 30 m lengths. Products were confirmed by GC–MS. Catalyst screening and alkylation of various amines were carried out with the same experimental procedure.

3. Result and discussion

In order to investigate *N*-alkylation of anilines to dialkylated products using onium salts as catalysts, several experiments were carried out first to screen the onium salts, solvents, substrates, carbonates, etc. Further, the effect of temperature, catalyst loading, recycle of catalyst was also investigated for *N*,*N*-dimethyl aniline synthesis. The results reported here demonstrate that in the presence of onium salts such as tetra-methyl and tetra-ethyl ammonium bromides as catalysts, dialkylation of aniline and its derivatives can be carried out selectively (yield >99.8%). However, the use of DMC as an alkylating agent also produces carbamate as a side product via carboxylation (see Scheme 1). The complexities arsing in the reaction for selective synthesis of *N*,*N*-dimethyl aniline has been investigated.

3.1. Preliminary experiments

Preliminary experiments carried out on the reaction between aniline and DMC in the presence of solid base catalysts such as MgO, hydrotalcite, zeolites, clay, etc. showed that NNDMA was not obtained selectively (see Table 1) in most cases. Use of homogeneous base catalysts, e.g. dibutyl tin oxide (DBTO) resulted in poor yield of NNDMA (Table 1, entry 11). Interestingly, with tetraethyl ammonium bromide (TEAB) as a catalyst, substantially higher yield of NNDMA was obtained (entry 12). On the other hand, alkylation under biphasic (organic/aqueous) conditions with TEAB catalyst selectively produced only *N*-alkylated amines, while carba-



Scheme 1. Synthesis of *N*,*N*-dimethyl aniline.