# 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.
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## 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 ($16.1 \times 10^{-3}$ mol), dimethyl carbonate (0.19 mol), onium salt ($3.57 \times 10^{-3}$ 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-
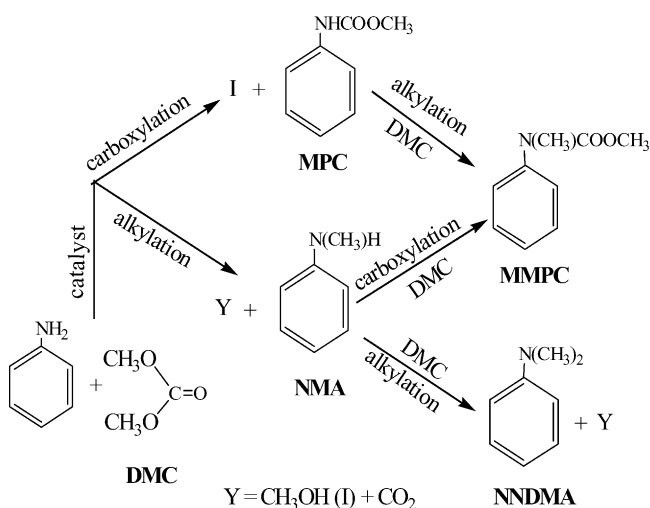


Scheme 1. Synthesis of N,N-dimethyl aniline.

Table 1
Screening of catalysts for *N*-alkylation of aniline[a]

| Serial number | Catalyst (g) | Temperature (K) | Time (h) | Aniline conversion (%) | Yield[b] (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | MPC | NMA | NNDMA |
| 1 | MgO (0.25) | 423 | 2 | Nil | – | – | – |
| 2 | Mg–Al hydrotalcite (0.25) | 423 | 2 | 5 | 0 | 5 | 0 |
| 3 | H-mordenite (1) | 433 | 4 | 26 | 7 | 14 | 12 |
| 4 | K$^+$ silica (1) | 443 | 2 | 14 | 6 | 7 | 1 |
| 5 | K-L (1) | 433 | 4 | 46 | 7 | 28 | 8 |
| 6 | Na-ZSM-5 (Si/Al = 130) (1) | 443 | 2 | 10 | 0 | 8 | 1 |
| 7 | Cs NaX (1) | 423 | 2 | 100 | 0 | 40 | 60 |
| 8 | Cs-Y (1) | 433 | 2 | 100 | 0 | 85 | 15 |
| 9 | Cs-beta (1) | 423 | 2 | 26 | 10 | 12 | 4 |
| 10 | Cs-MCM41 (1) | 423 | 2 | 26 | 13 | 11 | 2 |
| 11 | (*n*-Bu)$_2$SnO (0.45) | 423 | 4 | 100 | 43 | 2 | 5 |
| 12 | (Et)$_4$NBr (1.5) | 423 | 2 | 100 | 8 (16)[c] | – | 76 |
| 13[d] | (Et)$_4$NBr (1.5) | 443 | 2 | 94 | 0 | 16 | 78 |

[a] Reaction conditions: aniline = $16.1 \times 10^{-3}$ mol, DMC = 0.19 mol, stirring speed = 13 Hz and pressure = 34 bar $N_2$.
[b] Yields were determined by GLC and are based on aniline conversion.
[c] Methyl *N*-methyl, *N*-phenyl carbamate (MMPC).
[d] Under biphasic conditions (DMC = 0.1 mol and water 0.56 mol).

mates were not detected (entry 13). However, under biphasic conditions, large amount of DMC was hydrolyzed resulting in a poor selectivity of NNDMA based on DMC conversion. These results are, however, encouraging, since in the presence of water, selectivity to *N*-alkylated product has been improved (yield of NMA, 16% and NNDMA, 78%, entry 13). But under these conditions, complete conversion of aniline is not achieved, however, methyl *N*-phenyl carbamate (MPC) and methyl *N*-methyl-*N*-phenyl carbamate (MMPC) is completely absent. Clearly, water plays a key role in improving selectivity of *N*-alkylated products; therefore the role of water in *N*-alkylation of aniline was also investigated as this effect was thought to be vital for the understanding of *N*-alkylation.

### 3.2. Screening of onium salts as catalyst

Several onium salts as catalysts were screened and the results are presented in Table 2. It was observed that 100% aniline conversion is achieved in all the cases with >95% selectivity for the dialkylated products. In order to ascertain the activity trend in onium salts, conversions and yields were also monitored at short contact time of 0.5 h (see Table 2). The variation in selectivity with different onium salts, as catalyst was only marginal, while tetra-methyl and ethyl ammonium bromides favour the most selective formation of NNDMA with selectivity close to 100%. Phosphonium salts are only marginally improving the yields of NNDMA over ammonium salts (entries 4 and 7) and can be alternative substitutes for ammonium salts. It was further observed that hindered onium salt, e.g. hexaethyl gaunidinium bromide shows excellent activity towards *N*-alkylation (entry 5). It may be noted that at short contact time of 0.5 h, the selectivity to *N*-alkylated products is in the range of 50–60%. The lower selectivity of products in the initial period was found to be due to reaction of

aniline with onium salt forming an activated intermediate of quaternized aniline.[1] However, at the end of 2 h of reaction aniline is completely converted into *N*-alkylated products. However, due to the complications of substrate interactions with catalyst to form activated adduct in the initial period (0.5 h) a direct comparison of catalyst activities of quaternary salts is difficult under the experimental conditions investigated in this work. In homologous series of quaternary ammonium bromides, the formation of carbamate as a side product increases from methyl to butyl (entries 1–4). This effect is probably due to the fact that [(*n*-C$_4$H$_9$)$_4$N]Br is more lipophilic than either methyl or ethyl quaternary ammonium bromides [19] and hence not as efficient in hydrolysing carbamates (which essentially proceeds in hydrophilic media) to amines, thus decreasing selectivity of *N*-alkylated products.

### 3.3. Effect of substrate

Several substituted anilines such as toluidine, chloro anilines, nitro aniline and anisidine were investigated to see the reactivity of substrates towards *N*-alkylation by DMC (see Table 3). Excellent yields of dialkylated products are obtained except *p*-nitro and *o*-chloro anilines, in which case poor yields of dialkylated products were realized (entries 5 and 7). Since the *N*-alkylated products are formed by the nucleophilic substitution of anilines on DMC, electron donating or withdrawing substituents on aniline is expected to increase or decrease the nucleophilic character of aniline, respectively. Although substituted anilines follow the expected reactivity pattern (see Table 3) that is based on the nucleophilicity of

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[1] An experiment was carried out with (Et)$_4$NBr as catalyst, toluene as a solvent, and contact time of 0.5 h but without DMC and keeping other reaction conditions similar to that mentioned in Table 2, showed ~18% conversion of aniline and no *N*-alkylated products were detected.

Table 2
Reaction of aniline with dimethyl carbonate in the presence of different onium salts[a]

| Serial number | Onium salt | Aniline conversion (0.5 h) (%) | NNDMA (0.5 h) | | NMA (0.5 h) | | Side products[c] (0.5 h) (%) |
|---|---|---|---|---|---|---|---|
| | | | Selectivity (%) | Yield[b] (%) | Selectivity (%) | Yield[b] (%) | |
| 1 | $(Me)_4NBr$ | 100 (82) | 98.8 (39.6) | 98.8 (32.2) | 1.2 (31.9) | 1.2 (26) | Nil (nil) |
| 2 | $(Et)_4NBr$ | 100 (97.1) | 99.8 (53) | 99.8 (51.4) | 0.2 (5.5) | 0.2 (5.3) | Nil (nil) |
| 3 | $(n\text{-}Pr)_4NBr$ | 100 (98.0) | 98 (55.5) | 98 (54.2) | 0.5 (3.9) | 0.5 (3.8) | 1.5 (nil) |
| 4 | $(n\text{-}Bu)_4NBr$ | 100 (98.1) | 96 (49.5) | 96 (48.6) | 0.2 (4) | 0.2 (3.9) | 4.0 (0.5) |
| 5 | $HgBr^d$ | 100 (97.5) | 96.8 (47.6) | 96.8 (46.2) | 0.2 (5.9) | 0.2 (5.7) | 3.0 (1.0) |
| 6 | $(Et)_4NI$ | 100 (100) | 98 (57.2) | 98 (57.4) | 0.2 (nil) | 0.2 (nil) | 1.8 (0.8) |
| 7 | $(n\text{-}Bu)_4PBr$ | 100 (97.4) | 97.8 (51.1) | 97.8 (49.8) | 0.3 (4.9) | 0.3 (4.8) | 1.9 (0.6) |

[a] Reaction conditions: aniline $= 16.1 \times 10^{-3}$ mol, DMC $= 0.19$ mol, catalyst $= 3.57 \times 10^{-3}$ mol, $H_2O = 0.11$ mol, temperature $= 443$ K, time $= 2$ h, stirring speed $= 13$ Hz and pressure $= 34$ bar $N_2$.
[b] Yields were determined by GLC and are based on aniline conversion.
[c] Methyl N-phenyl carbamate, methyl N-methyl N-phenyl carbamate.
[d] Hexaethyl gaunidinium bromide.

Table 3
Methylation of primary anilines with dimethyl carbonate in the presence of TEAB as a catalyst[a]

| Serial number | Substrate | Dialkyl yield[b] (%) | Monoalkyl yield (%) | Side product yield[c] (%) |
|---|---|---|---|---|
| 1 | $C_6H_5NH_2$ | 99.8 | 0.2 | 0 |
| 2 | $p\text{-}CH_3C_6H_4NH_2$ | 99.5 | 0 | 0.5 |
| 3 | $p\text{-}ClC_6H_4NH_2$ | 98.5 | 0.3 | 1.2 |
| 4 | $m\text{-}ClC_6H_4NH_2$ | 98.5 | 0.4 | 1.1 |
| 5 | $o\text{-}ClC_6H_4NH_2$ | 62.6 | 30.2 | 0.8 |
| 6 | $p\text{-}CH_3OC_6H_4NH_2$ | 99.6 | 0 | 0.4 |
| 7 | $p\text{-}NO_2C_6H_4NH_2$ | 35.9 | 27 | 7 |
| 8 | $p\text{-}NH_2C_6H_4NH_2$ | 98.0 | 0 | 2 |

[a] Reaction conditions: substrate $= 16.1 \times 10^{-3}$ mol, DMC $= 0.19$ mol, TEAB $= 3.57 \times 10^{-3}$ mol, $H_2O = 0.11$ mol, temperature $= 443$ K, time $= 2$ h, stirring speed $= 13$ Hz and pressure $= 34$ bar $N_2$.
[b] Yields were determined by GLC and are based on substrate conversion.
[c] N-Carbamates.

anilines, the effect is not very pronounced for electron donating substituents but at the same time steric hindrance of these substituents to $NH_2$ group is dominating the reactivity of anilines, e.g. o-Cl aniline showed lower conversion and poor selectivity to respective dialkylated product (entry 5). In p-nitro aniline, nitro is very strong electron withdrawing group and having $-R$ effect which decreases nucleophilic character of aniline, showing poor conversion and selectivity to dialkylated product (see entry 7). The alkylated product of 1,4-phenylene diamine (entry 8) has a special importance as a reagent and excellent yield of $N,N,N',N'$-teramethyl-1,4-phenylene diamine is obtained.

### 3.4. Solvent effect

Five different solvents were screened with wide range of variation in their dielectric constants ($\varepsilon$) to see the effect of solvent on catalyst activity and selectivity to N-alkylated products. These results are presented in Fig. 1. The results on solvent screening indicate that as dielectric constant ($\varepsilon$) of a solvent increases, conversion and yield of NNDMA go through an optimum value for $\varepsilon$. The shape of a graph (for activity and yield) shows that a maximum of 78% yield of NNDMA is obtained which corresponds to a value of dielectric constant ($\varepsilon^{25}$) $= 7.2$ (using triglyme as solvent) and at two extremes of this graph lie xylene having $\varepsilon^{25} = 2.25$ and

methanol having $\varepsilon^{25} = 32.6$ with NNDMA yield of 11.7 and 45, respectively, and other solvents fall in between these two extremes. Aromatic solvents such as p-xylene and toluene having low dielectric constants behave similar to the solvents
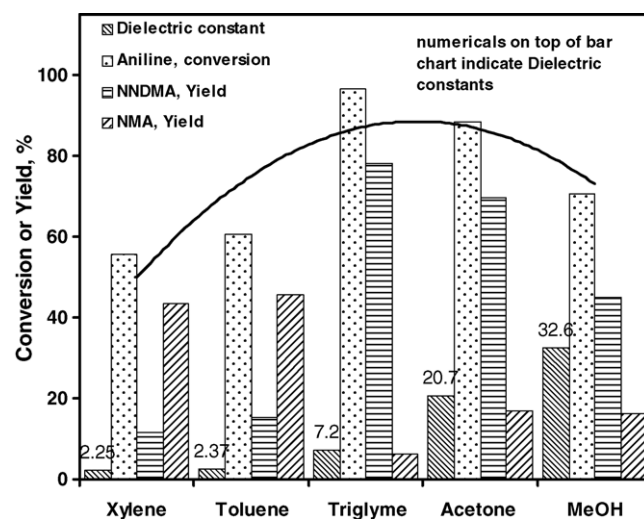


Fig. 1. Effect of solvent. Reaction conditions: aniline $= 10.7 \times 10^{-3}$ mol, DMC $= 32.2 \times 10^{-3}$ mol, $H_2O = 0.11$ mol, TEAB $= 2.38 \times 10^{-3}$ mol, solvent $= 14$ ml, temperature $= 443$ K, time $= 2$ h, stirring speed $= 13$ Hz and pressure $= 34$ bar of $N_2$.

having high dielectric constants, e.g. acetone and methanol (see Fig. 1). It was observed that solvents such as *p*-xylene and toluene form a biphasic system in the presence of water and TEAB catalyst is partitioned into two phases decreasing the availability of catalyst in the organic phase. The depletion of catalyst concentration in the organic phase lowers *N*-alkylation rates. The results obtained for triglyme, as a solvent deserves some comments. The *N*-alkylation reaction depends on the nucleophilicity of amines. Factors that increase the nucleophilicity of amines, e.g. electron donating groups attached to a ring or nucleophilic environment such as that generated by solvents having basic groups or atoms such as N or O, help increase its reactivity. Triglyme has an open chain polyether structure with basic oxygen atoms, and is a perfect solvent capable of inducing nucleophilic environment around hydrogen of amine thus generating reactive ArNH−, which on further reaction with DMC produces *N*-methylated products. This is a probable explanation, however, similar effects have been observed earlier [20,21]. The results clearly show that the solvent plays an important role in activation (or deactivation) of substrates, but dielectric constant alone does not explain this effect. The effect of DMC, as a solvent ($\varepsilon^{25} = 3.1$) could not be compared, as DMC is also one of the reactants, however, DMC works as an excellent solvent and due to its benign nature was selected for further studies.

### 3.5. Role of water

The effect of water on conversion of aniline and yields of *N*-alkylated products (NNDMA, NMA) and carbamate (MMPC) is shown in Fig. 2. In the absence of any water the yield of NNDMA obtained is 85% and appreciable amount
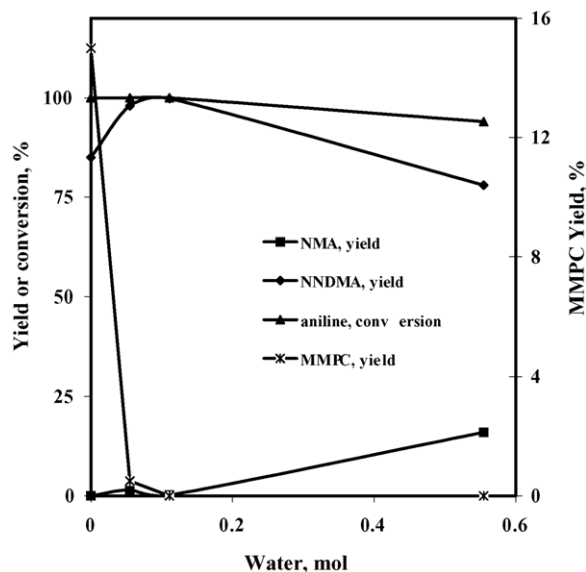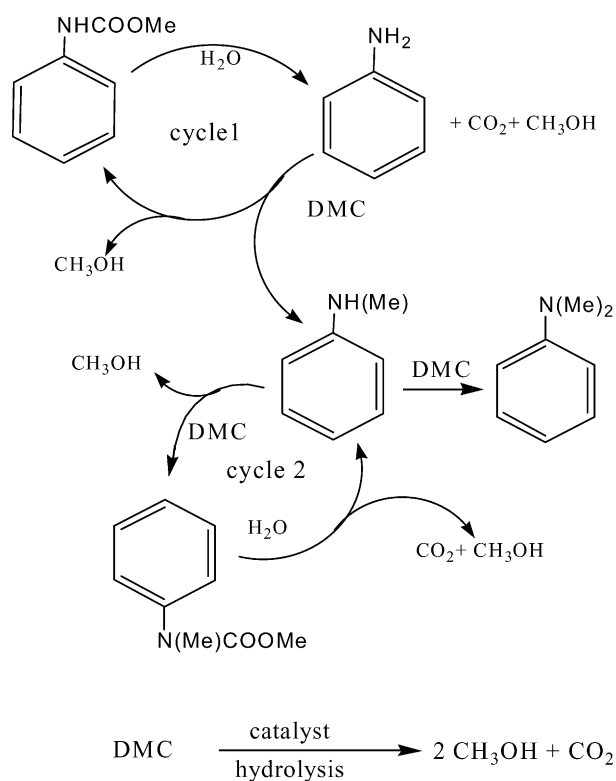
of MMPC is formed (15%). Addition of water to the system drastically improves the yield of NNDMA to almost 99.8% with traces of NMA (0.2%, yield) while MMPC is completely absent (see Fig. 2). At higher concentration of water, the biphasic conditions are approached decreasing the yield of NNDMA (also discussed in preliminary experimental section). Thus, there exists an optimum quantity of water to be added to the system in order to maximize the selectivity to *N*-alkylated products. Therefore, experiments were carried out by adding pre-calculated water to the system. Water plays a key role in the selective synthesis of *N*,*N*-dimethylaniline and in hydrolysis of carbamates and carbonate. For example hydrolysis of DMC, methyl *N*-phenyl carbamate (MPC) and methyl *N*-methyl *N*-phenyl carbamate (MMPC) are known to give methanol, $CO_2$, aniline and *N*-methyl aniline (see also Scheme 2). In a blank experiment carried out without aniline but otherwise under standard reaction conditions, it was observed that 50% of DMC was hydrolyzed to methanol and $CO_2$. Hydrolysis of DMC is an unwanted reaction as it reduces DMC based selectivity of NNDMA. While, hydrolysis of both MPC and MMPC to aniline and to *N*-methyl aniline, respectively, is a welcome reaction as it helps increase the selectivity of *N*-alkylation (see Scheme 2, cycles 1 and 2). Particularly, hydrolysis of MMPC to NMA is important since it was observed earlier that in the absence of water this carbamate decreases the selectivity of *N*-alkylated products (also discussed later). Once *N*-methyl aniline is produced further alkylation by DMC gives NNDMA (see Scheme 1). It



Fig. 2. Effect of water addition on selectivity of *N*-alkylation. Reaction conditions: aniline = $16.1 \times 10^{-3}$ mol, DMC = make-up to 20 ml, TEAB = $3.57 \times 10^{-3}$ mol, temperature = 443 K, time = 2 h, stirring speed = 13 Hz and pressure = 34 bar of $N_2$.



Scheme 2. Reaction networking of NNDMA synthesis (for the sake of convenience formation of $CO_2$ and methanol is not shown for some reactions).

is believed that at higher temperatures aniline carboxylation is negligible [10] and hence only small amount of water is required to convert carbamates formed via this step to amine or alkylated amine derivative.

### 3.6. Efficiency of carbonates

The activity of carbonates as alkylating or arylating agents has been examined for aniline as a substrate (see Fig. 3). DMC as alkylating agent shows the highest activity followed by ethyl and butyl carbonates, diphenyl carbonate, as an arylating agent shows no activity. The results are in complete agreement with the steric hindrance experienced by reacting alkyl cation of the carbonate (see Table 2 for conditions), e.g. DMC having $H_3C+$ as methylating cation is the least bulkier amongst cations, and hence shows the highest reactivity. From the point of view of electronic effects as well, the observed trend of carbonate reactivity is in agreement with the expectation that, the methyl cation which is the most electrophilic, shows the highest reactivity towards *N*-alkylation. Reaction of aniline and diphenyl carbonate leads to only carbonate hydrolysis forming phenol and carbon dioxide.

### 3.7. Synthesis of N,N-dimethyl aniline (NNDMA)

The effect of reaction conditions was investigated on the most important diamine, *N,N*-dimethyl aniline. For this purpose, *N*-alkylation of aniline was considered for synthesis of NNDMA and the effect of different parameters on conversion, selectivity and yield is discussed below:

Experiments were carried out to determine product distribution and material balance in the alkylation of aniline with DMC. Since, DMC is acting as a solvent as well as alkylating agent, aniline is considered as the limiting reactant and on the basis of moles of aniline reacted, NMA and NNDMA
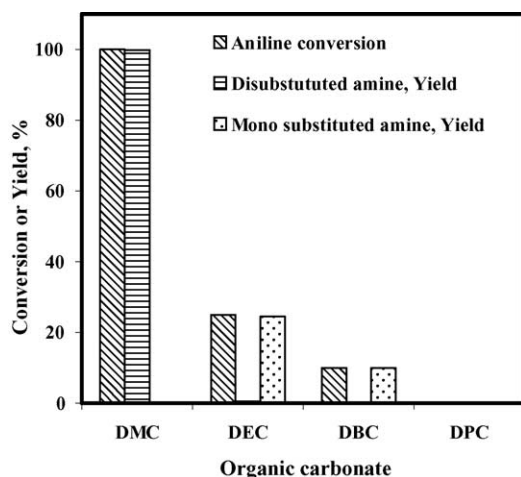
formation and DMC consumed were tallied. A complete conversion of aniline was achieved with concurrent formation of *N*-alkylated products and correspondingly DMC was also consumed although in about 20% excess than the stoichiometric quantities that is required based on aniline consumption, indicating that DMC based selectivity is reduced due to the formation of side products arising from hydrolysis of DMC. In a typical experiment (see Table 2, entry 2), aniline conversion of 100% with 99.8% selectivity of NNDMA and 0.2% selectivity for NMA formation on the basis of aniline converted and 83.6% selectivity of NNDMA and 0.16% selectivity for NMA on the basis of DMC converted was observed at the end of 2 h of reaction time. In the present case, both the reactants (amine and carbonate) are infinitely soluble under reaction conditions offering a homogeneous liquid phase and therefore no liquid side mass transfer resistance is expected. However, experiments were carried out at different agitation speed, which confirmed that beyond 8.33 Hz conversion of aniline remained unaffected.

Several other reaction parameters such as catalyst loading, temperature, recycle of catalyst, etc. were varied, the results of which are discussed below.

#### 3.7.1. Effect of catalyst loading

The effect of catalyst loading on conversion of aniline and selectivity of NMA and NNDMA is shown in Fig. 4. Both conversion of aniline and yield of NNDMA increased with increase in TEAB loading while the yield of intermediate NMA decreased. It can be seen from this plot that higher catalyst concentration is required for the selective formation of NNDMA this, however, lowers the TON. In the present case, the product NNDMA is formed via an intermediate NMA and the catalyst is involved in both the steps and hence a linear dependency of conversion with catalyst loading is not observed.
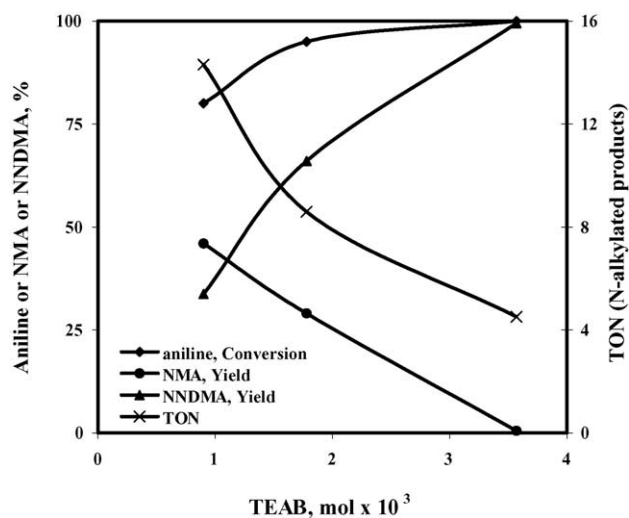


Fig. 3. Efficiency of carbonates as dialkylating and arylating agent. Reaction conditions: aniline $= 16.1 \times 10^{-3}$ mol, carbonate $= 0.19$ mol, TEAB $= 3.57 \times 10^{-3}$ mol, temperature $= 443$ K, time $= 2$ h, stirring speed $= 13$ Hz and pressure $= 34$ bar of $N_2$.



Fig. 4. Effect of catalyst loading. Reaction conditions: aniline $= 16.1 \times 10^{-3}$ mol, DMC $= 0.19$ mol, temperature $= 443$ K, time $= 2$ h, stirring speed $= 13$ Hz and pressure $= 34$ bar of $N_2$.
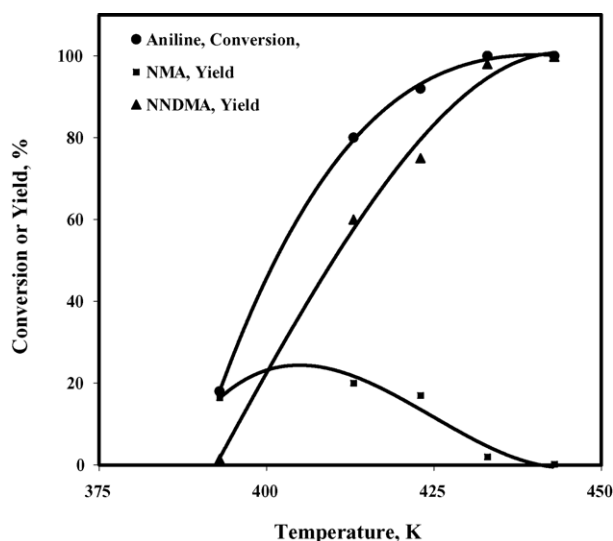
Fig. 5. Effect of temperature on NNDMA and NMA yield. Reaction conditions: aniline = $16.1 \times 10^{-3}$ mol, DMC = 0.19 mol, TEAB = $3.57 \times 10^{-3}$ mol, time = 2 h, stirring speed = 13 Hz and pressure = 34 bar of $N_2$.

### 3.7.2. Effect of temperature

The temperature effect was investigated in the range of 393–443 K and the results are shown in Fig. 5 as a graph of aniline conversion and yield of alkylated products at different temperatures. The conversion of aniline and NNDMA yield increases sharply with increase in temperature, while NMA yield diminishes with increase in temperature. Temperature plays an important role in alkylation of amines when organic carbonates are used as alkylating agents. Both carboxylation and alkylation of amine is possible depending on the temperature of the reaction. Usually, temperature in the range of 423–473 K is required to selectively form alkylated products [10]. Side products arising from aromatic ring bromination or alkyl group bromination were not detected even at 443 K. Note that even at lower temperature (393 K) carboxylation products are not present (see Fig. 5).

### 3.7.3. Catalyst recycling

The catalyst recycling was studied by diluting the concentrated reaction crude (free from low boilers such as DMC and methanol) in chloroform and extracting it three times in minimum amount of water (~5 ml), the aqueous phase is then concentrated by evaporating water to a required amount and recycling it with the fresh charge of the substrate aniline and alkylating agent (DMC). The results on catalyst recycle experiments show very good recycling ability of the catalyst. The yields of NNDMA obtained drops only slightly from 99.8% for a fresh catalyst to ~98% at the end of fifth recycle, indicating that almost complete conversions are obtained with the recycled catalyst under the experimental conditions employed in this work. The recycling efficiency of the catalyst also confirms that catalyst degradation arising from brominated products (brominated amines, alkyl bromides, etc.) is absent.

### 3.7.4. Networking of N-alkylation reaction

*N*-Alkylation of aniline by DMC as an alkylating agent produces carbamates and alkylated products depending on the reaction conditions (temperature, water and methanol content, etc.). Carbamates such as methyl *N*-phenyl carbamate and methyl *N*-methyl *N*-phenyl carbamate can form via two routes (Scheme 1) and their inter convertibility into amines via hydrolysis is possible (see Scheme 2, cycles 1 and 2). Moreover, possibility of methanol as an alkylating agent producing NMA and DMC via hydrogen transfer reaction between MMPC and methanol cannot be ruled out under our experimental conditions. To clarify these issues, diagnostic experiments were carried out and these results are presented in Table 4. Reaction of MPC with DMC in the absence of water yields only MMPC (Table 4, entry 1), while in the presence of water, a similar experiment showed 50% conversion of MPC to NNDMA (50% yield, entry 2), indicating that hydrolysis of MMPC produces NNDMA via NMA alkylation (Scheme 2, cycle 2). In the absence of water, MMPC accumulates in the system, as it does not have active hydrogen atom for further reaction with DMC. Similar reaction car-

Table 4
*N*-Alkylation of substrates showing networking of reaction scheme[a]

| Serial number | Substrate | Water | Methylating agent | Substrate conversion (%) | Product yield[b] (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | MPC | MMPC | NMA | NNDMA |
| 1 | MPC | Nil | DMC | 90 | – | 90 | – | – |
| 2 | MPC | Yes | DMC | 50 | – | – | – | 50 |
| 3 | NMA | Nil | DMC | 100 | Nil | 18 | – | 82 |
| 4 | NMA | Yes | DMC | 100 | Nil | Nil | – | 99.8 |
| 5 | Aniline | Nil | DMC | 100 | Nil | 15 | Nil | 85 |
| 6 | Aniline | Yes | DMC | 100 | Nil | Nil | 0.2 | 99.8 |
| 7 | Aniline | Yes | MeOH | Nil | Nil | Nil | Nil | Nil |
| 8 | MMPC | Nil | MeOH | Nil | – | – | Nil | Nil |
| 9 | MMPC | Nil | DMC | Nil | – | – | Nil | Nil |

[a] Reaction conditions: substrate = $16.1 \times 10^{-3}$ mol, DMC = 0.19 mol, TEAB = $3.57 \times 10^{-3}$ mol, $H_2O$ = 0.11 mol, temperature = 443 K, time = 2 h, stirring speed = 13 Hz and pressure = 34 bar $N_2$.
[b] Yields were determined by GLC and are based on substrate conversion.

ried out either with NMA or aniline as a substrate with DMC gave NNDMA and MMPC in the absence of water and the same reaction in the presence of water gave selectively only NNDMA (entries 3–6). Reaction of aniline or MMPC with methanol under the experimental conditions does not yield alkylated anilines indicating that alkylation using methanol is not facile (entries 7 and 8). Similarly reaction of MMPC and DMC does not give alkylated products (entry 9). These experiments conclusively show that MMPC hydrolysis to NMA is the key reaction in increasing the selectivity of NNDMA in the present case.

## 4. Conclusion

Aniline and its derivatives can be *N*-alkylated by DMC to yield dialkylated products. The investigations show that onium salts in the presence of a small amount of water are excellent catalysts for selective *N*-alkylation. Side products such as carbamates formed during this reaction are hydrolyzed to *N*-alkylated anilines thereby increasing the selectivity for alkylated products. The results on the effect of reaction conditions indicated that solvents capable of inducing nucleophilic environment around hydrogen of amine enhance *N*-alkylation of amines. *N*-Alkylation of substituted anilines show that steric hindrance and electronic effects of substituents shows the expected trends on amine reactivity; similarly, carbonate reactivity also follows the same pattern, expected on the basis of the steric hindrance of alkylating moiety. Diagnostic experiments carried out to understand the hydrolysis and methanolysis of carbamates showed that hydrolysis is a facile reaction under experimental conditions leading to *N*-alkylated products, but the methanolysis or *N*-alkylation of carbamate (by methanol) does not take place under these conditions. The possibility of *N*-alkylation of aniline by methanol was also explored and was found not feasible. Based on these experiments, a reaction network has been proposed which explains the chemistry of *N*-alkylation by DMC. The reusability of catalyst has been demonstrated.

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