

# Selective mono-N-methylation of primary aromatic amines by dimethyl carbonate over faujasite X- and Y-type zeolites

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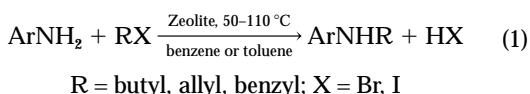
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The reaction of dimethyl carbonate (DMC) with different primary aromatic amines has been investigated under batch conditions (autoclave) in the presence of Y- and X-type zeolites. Operating at 120–150 °C, highly selective mono-N-methylations are observed for anilines even when they are deactivated by either electronic effects or steric hindrance ( $G-C_6H_4NH_2$ ,  $G = p\text{-NO}_2$ ,  $p\text{-CN}$ ,  $o\text{-CO}_2CH_3$  and 2,6-dimethylaniline); typical selectivities for the formation of the corresponding mono-N-methyl derivatives [ $\text{ArNH(CH}_3\text{)}$ ] are in the range 92–98%, at a substrate conversion of 72–93%. A synergic effect between the reactivity of DMC (acting both as a methylating and as a reversible methoxycarbonylating agent) and the dual acid-base properties of zeolites is considered to be responsible for the unusually high selectivity observed; accordingly, a reaction mechanism is discussed, involving carbamates ( $\text{ArNHCO}_2CH_3$ ) and *N*-methylcarbamates [ $\text{ArN(CH}_3\text{)CO}_2CH_3$ ] as intermediates. The reaction is an example of a synthesis with low environmental impact: it couples the use of a non-toxic methylating agent (DMC, in place of the highly toxic methyl halides or dimethyl sulfate) with eco-friendly catalysts (zeolites) in a waste-free process.

## Introduction

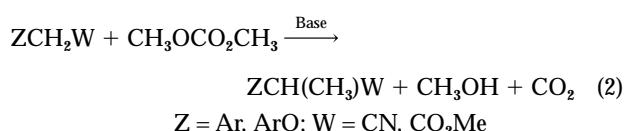
Mono-N-alkylation of primary aromatic amines is a widely used reaction for the synthesis of pharmaceuticals and dyes.<sup>1</sup> However, when common alkylating agents (alkyl halides) are used, the reaction cannot be utilized for synthetic purposes because of its poor selectivity: the high nucleophilicity of the amine nitrogen results in the formation of mixtures of secondary and tertiary amines along with the corresponding ammonium salt.<sup>2</sup>

Very selective mono-N-alkylations of anilines have been reported by using different alkyl halides in the presence of suitable X- and Y-type zeolites under liquid-phase conditions [eqn. (1)].<sup>3–5</sup> Nevertheless, the preparation of mono-*N*-methyl

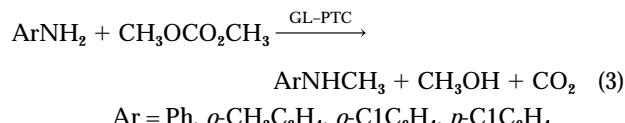


anilines cannot be performed in this way; because of the low steric hindrance of the methyl group, sizeable amounts of *N,N*-dimethyl derivatives are always observed with both a methyl halide or dimethyl sulfate is used as alkylating agent.<sup>3,4</sup> Moreover, as reported for the halogenation of aromatics catalyzed by Y-faujasites, the co-product HX rapidly deactivates the zeolites.<sup>6</sup>

We have extensively reported that dimethyl carbonate (DMC) behaves as a very selective mono-C-methylating agent for a variety of active-methylene compounds [eqn. (2)].<sup>7–11</sup>



Under continuous-flow conditions (gas–liquid phase-transfer catalysis) at 180 °C, in the presence of  $\text{K}_2\text{CO}_3$  and poly(ethylene glycol)s as phase-transfer (PT) agents, we also reported that DMC allows selective mono-N-methylation of primary aromatic amines [eqn. (3)].<sup>12</sup> In this case, although no *N,N*-



dialkylated by-products were formed, *N*-methyl-*N*-arylcaramates [ $\text{ArN(CH}_3\text{)CO}_2\text{CH}_3$ ] were observed (3–25% at substrate conversions of 45–90%) under steady-state conditions. In order to avoid this drawback, a two-step procedure was necessary. In fact, a batch synthesis of *N*-methylanilines has been developed based on the formation of *N*-methylurethanes during the reaction of DMC with primary amines in the presence of  $\text{K}_2\text{CO}_3$  and PT agents ('onium salts and crown ethers').<sup>13</sup> Once obtained, *N*-methyl-*N*-arylcaramates were hydrolysed under basic conditions to yield *N*-methylarylamines.

More recently, a continuous flow (CF) reaction of aniline with DMC has also been claimed to proceed with high mono-*N*-methyl selectivity when alkali cation-exchanged zeolites are used as the catalysts, at 180 °C.<sup>14,15</sup>

In light of these results, we have been prompted to investigate the batchwise reaction of DMC with primary aromatic amines carried out in the presence of faujasite-type zeolites. Under such conditions, substrates having low vapour pressure can be reacted whereas CF methods would require harsh conditions; that is, since methylations of aromatic amines with DMC need to be performed at a lower temperature (which is a key factor in inducing high mono-*N*-alkyl selectivity<sup>14</sup>), CF processes cannot be used for high boiling compounds.

Accordingly, this paper reports that very selective mono-*N*-methylations of different anilines are attained with DMC as the alkylating agent, by performing the reactions in an autoclave at temperatures of 120–150 °C and using Y- and X-faujasites.

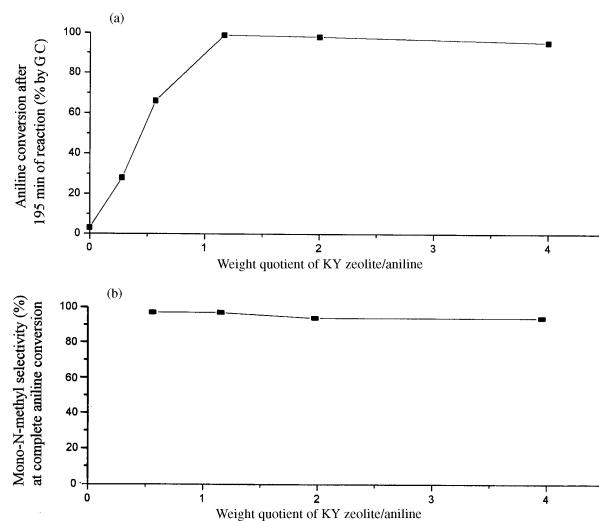
## Results

Preliminary reactions were carried out by using aniline as a test substrate: experiments were run in a stainless steel autoclave at 120–150 °C, by treating a mixture of aniline and DMC (in a 1:74 molar ratio, respectively) in the presence of a zeolite

**Table 1** Reaction of aniline with dimethyl carbonate in the presence of different catalysts<sup>a</sup>

Entry	Catalyst <sup>b</sup>	T/°C	t/min	Weight quotient cat./aniline	Conversion (%) <sup>c</sup>	Selectivity (%) (mono/di) <sup>d</sup>	Products (% by GLC)			
							MA <sup>e</sup>	DMA <sup>f</sup>	PhNHCO <sub>2</sub> CH <sub>3</sub>	PhN(Me)CO <sub>2</sub> CH <sub>3</sub>
1	KY	130	195	1.2	99	96.7	88	3	4	1
		150	165	1.2	96	96.7	89	3	3	1
2	NaY	130	195	1.2	94	97.7	88	2	4	
		130	120	1.2	91	86.9	73	11	3	1
3	13X	120	90	1.2	89	92.8	78	6	3	
		130	120	1.2						
		180	220	1.8	56	86.6	13	2	7	34
4	K <sub>2</sub> CO <sub>3</sub>	130	365	3	8	100	8			
		150	300	1.5	33	100	8	2		23
		180	220	1.8	56	86.6	13	2	7	34

<sup>a</sup> All reactions were carried out in an autoclave by using aniline (0.3 g, 3.2 mmol), DMC (20 ml) and the catalyst (in the reported weight quotient with respect to aniline). Under the conditions of entry 1, starting from 5.0 g of aniline, 4.8 g of N-methylaniline (84%, purity 93% by GLC) were obtained by distillation (bp 52 °C/1.5 mmHg). <sup>b</sup> Before reactions, all catalysts were heated at 500 °C overnight in a muffle, except for K<sub>2</sub>CO<sub>3</sub>. <sup>c</sup> Conversions were determined by GLC. <sup>d</sup> The percentage mono/di selectivity was calculated according to the following expression: {[PhNHCH<sub>3</sub>]/[PhNHCH<sub>3</sub>] + [PhN(CH<sub>3</sub>)<sub>2</sub>] × 100}. <sup>e</sup> MA: N-methylaniline. <sup>f</sup> DMA: N,N-dimethylaniline.



**Fig. 1** The reaction of aniline with DMC in the presence of different amounts of KY zeolite at 130 °C. (a) Aniline conversion (% by GLC) after 195 min of reaction; (b) Mono-N-methyl selectivity {PhNHCH<sub>3</sub>/[PhNHCH<sub>3</sub> + PhN(CH<sub>3</sub>)<sub>2</sub>] × 100}, at complete aniline conversion.

(Y- or X-type faujasite used in a 1.2 weight excess with respect to aniline). DMC was used in a very large excess, acting both as the methylating agent and the solvent. Reactions were also performed using K<sub>2</sub>CO<sub>3</sub> in place of zeolites, according to our previously reported methylation procedure of arylacetonitriles.<sup>8</sup> Table 1 reports the results.

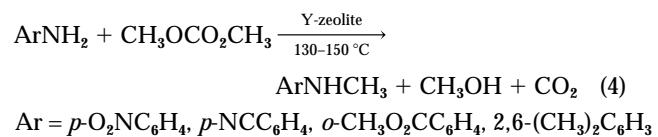
13X zeolite is more active than the NaY or KY catalysts, but these latter compounds improve the selectivity. For instance, operating at 120 °C, a substrate conversion of 89% is reached after 90 min of reaction over 13X while at 130 °C, 99 and 94% conversions, respectively, are reached over KY and NaY after 195 min. However, the selectivity towards the formation of N-methylaniline (MA) is 92.8% for 13X while it increases to 96.7 and 97.7% for KY and NaY, respectively (entries 1–3, Table 1).

When K<sub>2</sub>CO<sub>3</sub> is used in place of faujasites, the reaction is markedly slowed down and is no longer selective towards formation of MA. At 130 °C, only 8% conversion is observed after 365 min reaction, while at higher reaction temperatures (150–180 °C) sizeable amounts of methyl N-methyl-N-phenylcarbamate [PhN(CH<sub>3</sub>)CO<sub>2</sub>Me; 23 and 34% at conversions of 33 and 56%, respectively] are formed (entry 4, Table 1).

Under these conditions, the methylation of aniline by DMC was also investigated using different amounts of KY zeolite. Each experiment was carried out by treating an aniline solution in DMC (20 ml; 0.16 M) and varying the zeolite/aniline (KY/A) weight quotient over the range 0.28–4.0. Figs. 1(a) and 1(b) show the results.

After 195 min of reaction, a *plateau* is reached at an essentially quantitative aniline conversion (95–99%) when the quotient KY/A is ≥ 1.2 [Fig. 1(a)]. Below that value, complete substrate conversion is still attainable but requires longer reaction times; when KY/A is set to 0.58 and 0.28, the observed conversions are 95 and 53% respectively, after 340 min of reaction. In all cases, the selectivity towards N-methylaniline is always high, ranging from 94 to 97% [Fig. 1(b)]. These results underline two points: (i) zeolites (both Y and X) can actually be used in a catalytic amount, and (ii) under given reaction conditions, there exists a peculiar KY/A value [near 1.2 in Fig. 1(a)] at which the substrate is probably no longer saturating all active sites of the zeolite; consequently, over that KY/A value, the reaction cannot be further speeded up.

The batchwise conditions were then investigated for the methylation of selected primary aromatic amines. The reactions were carried out at 130–150 °C, in the presence of Na<sup>+</sup>- and K<sup>+</sup>-exchanged Y-faujasites (in a 1.2–6.6 weight excess with respect to the anilines). In particular, poorly reactive amines deactivated by electron-withdrawing groups [*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (**1**), *p*-NCC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (**2**), *o*-CH<sub>3</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (**3**)] and/or steric hindrance [2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> (**4**)] were used [eqn. (4)]. Table 2 reports the results.



In all cases, the mono-N-methylated anilines (ArNHCH<sub>3</sub>) are obtained with a high selectivity (92–97%) at conversions ranging from 72 to 93%. However, deactivated substrates require much longer reaction times with respect to aniline. For instance, when NaY is used at 130 °C, the conversions of substrates **1** and **2** are 79 and 76% after 1260 and 300 min, respectively (entries 1 and 5), while aniline conversion is 94% after only 195 min (entry 2, Table 1).

Moreover, although the data in Table 2 do not suggest a general trend of different activities between NaY and KY, they clearly show how the reactions are dependent on the zeolite/substrate weight quotient (Z/S). Within the examined range (Z/S = 1.2–6.6), an increase of the Z/S value is always followed by a corresponding decrease in reaction time (entries 2, 3, 5, 8 and 9). As expected, the lower nucleophilicity of the investigated amines (with respect to aniline) requires both a higher reaction temperature (150 °C) and a higher Z/S quotient (3.3).

The amines **1–3** also reacted with DMC in the presence of Na<sup>+</sup>-exchanged 13X faujasite. Operating at 130 °C, a satisfactory mono-N-methyl selectivity was observed only in the case of compound **2** (94%, at a conversion of 69% after 210 min reaction; Z/S = 3.3), while for amines **1** and **3** the correspond-

**Table 2** Methylation of primary aromatic amines with dimethyl carbonate in the presence of zeolite catalysts<sup>a</sup>

Entry	Substrate ArNH <sub>2</sub>	Catalyst <sup>b</sup>	T/°C	t/min	Weight quotient cat./substrate	Conversion (%) <sup>c</sup>	Selectivity (%) (mono/di) <sup>d</sup>	Products (% by GLC)		
								Mono	Di	ArNHO <sub>2</sub> CH <sub>3</sub>
1	Ar: <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	NaY	130	840 (1260)	3.3	57 (79)	96.4 (91.9)	53	2	2
2		NaY	150	420	1.2	72	94.3	66	4	2
3		NaY	150	270 (360)	6.6	78 (95)	92.9 (54.9)	65	5	3
4		KY	150	600	3.3	90	92.9	79	6	2
5	Ar: <i>p</i> -NCC <sub>6</sub> H <sub>4</sub>	NaY	130	300 (180)	1.2 (3.3)	76 (87)	90.7 (91.4)	68	7	1
6		NaY	150	120	3.3	89	91.9	80	7	2
7		KY	150	270	3.3	90	97.6	83	2	2
8	Ar: <i>o</i> -CH <sub>3</sub> OCC <sub>6</sub> H <sub>4</sub>	NaY	150	720 (330)	1.2 (3.3)	91 (93)	94.2 (96.6)	81	5	5
9		KY	150	240 (150)	2.0 (3.3)	88 (79)	92.8 (93.2)	77	6	5
10	Ar: 2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	NaY	150	300	3.3	84	93.8	76	5	3

<sup>a</sup> All reactions were carried out in an autoclave by using the amine (0.3 g), DMC (20 ml) and the catalyst (in the reported weight quotient with respect to the amine). <sup>b</sup> Before reaction, all zeolites were heated at 500 °C overnight in a muffle. <sup>c</sup> Conversions were determined by GLC. <sup>d</sup> The % mono/di selectivity was calculated according to the following expression: {[ArNHCH<sub>3</sub>]/[ArNHCH<sub>3</sub>] + [ArN(CH<sub>3</sub>)<sub>2</sub>] × 100}.

ing selectivities were 87 and 54%, at conversions of 54 and 45%, respectively.

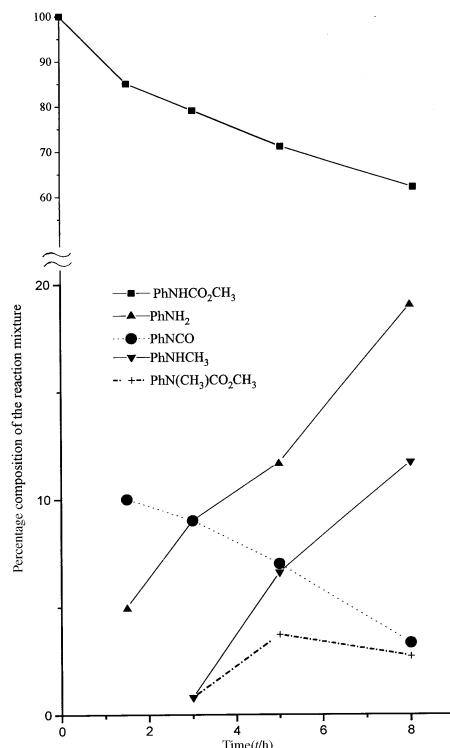
Noteworthy is the environmentally friendly character of the reaction in eqn. (4) which uses the non-toxic DMC and produces no hazardous wastes; in fact, the co-product methanol can be recycled for DMC production,<sup>16</sup> and CO<sub>2</sub> does not involve disposal problems. Conversely, in the methylations with toxic dimethyl sulfate or methyl chloride [eqn. (2)], where a base is used as a reagent, stoichiometric quantities of salts are generated and need to be disposed of.

### Reaction mechanism

We previously reported that the high mono-methyl selectivity observed in the reaction of DMC with arylacetonitriles and methyl arylacetates (ArCH<sub>2</sub>W, W = CN, CO<sub>2</sub>CH<sub>3</sub>) is explicable through the formation of two intermediates, ArCH(CO<sub>2</sub>CH<sub>3</sub>)W and ArC(CH<sub>3</sub>)(CO<sub>2</sub>CH<sub>3</sub>)W, which are both detected during the course of the reaction.<sup>8</sup> In particular, in the presence of a weak base (K<sub>2</sub>CO<sub>3</sub>), two consecutive reactions are considered to take place: (i) the attack of an ArCH<sup>(-)</sup>W anion on the acyl carbon of the dimethyl carbonate (*B*<sub>A2</sub> mechanism) which gives the intermediate ArCH(CO<sub>2</sub>CH<sub>3</sub>)W, and (ii) the attack of the corresponding ArC<sup>(-)</sup>(CO<sub>2</sub>CH<sub>3</sub>)W anion on the alkyl carbon of the dimethyl carbonate (*B*<sub>A1</sub>2 mechanism) which yields ArC(CH<sub>3</sub>)(CO<sub>2</sub>CH<sub>3</sub>)W. This latter compound undergoes a demethoxycarbonylation to the final product ArCH(CH<sub>3</sub>)W.

The reaction of DMC with aromatic amines over Y- and X-zeolites also provides evidence for the formation of the corresponding methoxycarbonylated compounds (carbamates). As reported in Tables 1 and 2, small amounts (1–5%) of methyl arylcarbamates [ArNH(CO<sub>2</sub>CH<sub>3</sub>)] are observed for all the investigated anilines. Moreover, in the case of aniline, the corresponding methyl N-methyl-N-phenylcarbamate [PhN(CH<sub>3</sub>)(CO<sub>2</sub>CH<sub>3</sub>)] is also detected (entries 1–3, Table 1), even though it is formed to a much smaller extent (1%) compared with the reaction carried out in the presence of K<sub>2</sub>CO<sub>3</sub> (23–34%, entry 4, Table 1).

In the light of this analogy between the methylations of acidic-methylene compounds and amines, the reaction of methyl phenylcarbamate (PhNHCO<sub>2</sub>CH<sub>3</sub>, 5) with DMC in the presence of KY faujasite was investigated in order to study the reaction mechanism [eqn. (5)]. Thus, compound 5 was treated



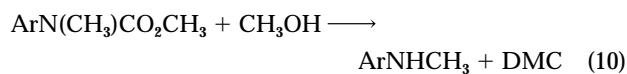
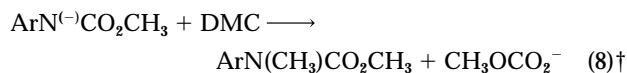
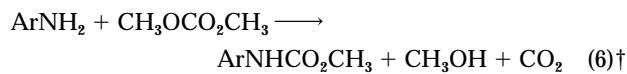
**Fig. 2** The reaction of methyl phenylcarbamate 5 with DMC over 13X zeolite in refluxing DMF solvent

under the same conditions as for aniline. In an autoclave at 130 °C (KY/5 = 1.2 w/w), the carbamate underwent slow demethoxycarbonylation with simultaneous methylation; after 240 min, the conversion was 58% and aniline, phenyl isocyanate and methyl N-methyl-N-phenylcarbamate were formed (24, 10 and 14% yield, respectively, as determined by GLC and GLC-MS), along with an unidentified high boiling product (10%).

The reaction of compound 5 with DMC was also performed at atmospheric pressure. Because DMC acts as a methylating agent only at temperatures ( $\geq$ 120 °C) well over its boiling point (90 °C),<sup>7–11</sup> it was necessary to use a high boiling solvent. Dimethylformamide (DMF) was chosen. Accordingly, the urethane was dissolved in DMF in the presence of 13X zeolite; once the mixture had been heated at the reflux temperature (155 °C), small aliquots of DMC (~one-tenth of the reaction volume) were added dropwise at 1 h intervals (see Experimental section for details). The reaction proceeded slowly due

to the small amount of DMC which could remain dissolved in the DMF. Also in this case, the carbamate **5** yielded aniline, *N*-methylaniline, phenyl isocyanate, and methyl *N*-methyl-*N*-phenylcarbamate derived from both demethoxycarbonylation and methylation reactions. Fig. 2 depicts the result.

On this basis, the same mechanism reported for the DMC monomethylation of active-methylene compounds<sup>8</sup> might be considered to operate also for primary aromatic amines [eqns. (6)–(10)]. In this case, the mono-*N*-methylation can be assisted by the zeolite cages. The mono-*N*-alkylation of anilines



with either classical alkylating agents or DMC over zeolites is usually considered to occur within the intracrystalline pores, whereas the selectivity arises mainly from the steric bulkiness of the *N*-alkyl group of the product.<sup>4,5,14,15</sup> However, this hardly explains our results: it is difficult to justify why bulky primary amines such as *o*-CH<sub>3</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> or 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> undergo methylation (entries 8–10, Table 2) while the less hindered PhNHCH<sub>3</sub> does not, being preserved by a further methylation.

Nevertheless, some reagent selectivity is surely present in the reaction of aromatic amines with DMC, as shown by the behaviour of zeolites fitting different ranges of molecular size. The monomethylation of aniline proceeds successfully only when Y, X, EMT or β-zeolites are used, while smaller pore molecular sieves (*e.g.*, 3 or 4 Å) are completely ineffective.<sup>3,14</sup> Also, we observed (not reported in Table 2) that the large and hindered 2-aminobiphenyl can in no way be selectively methylated using either Y- or X-faujasites; even at low conversions (15–25%; a very slow reaction occurs), the selectivity ranges from 65 to 70% probably because the high steric hindrance does not allow the reagent to fit properly into the pores of the zeolite.

We think that two different reaction mechanisms operate: the first occurring with classical alkylating agents through an *S<sub>N</sub>2* displacement and the second taking place with DMC through a more complicated reaction pathway. Both mechanisms are controlled by the shape of the zeolites, but in a different manner. In the first case, zeolites allow selectivity when relatively hindered alkyl groups are involved (*e.g.*, allyl, butyl, benzyl),<sup>3,4</sup> this being a clear effect of product selectivity.

Instead, in the case of DMC, the results reported herein seem to be better described through an intermediate selectivity rather than a reagent or a product one.<sup>17</sup> Accordingly, once the reacting amine is held into the zeolite cages, the corresponding urethane may readily form inside the same cavities [eqn. (6)] and, due to its polarity, it can be retained there and forced to undergo both methylation and demethoxycarbonylation reactions before it exits [eqns. (8) and (10)]. The carbamate formation represents a crucial step in the overall mono-*N*-methylation process: while preserving it from a double methylation, the presence of the methoxycarbonyl group in ArNHCO<sub>2</sub>CH<sub>3</sub>

increases the acidity of the remaining proton thus favouring the formation of the anion and the subsequent methylation step [eqns. (7) and (8)]. The demethoxycarbonylation reaction [eqn. (10)] could be favoured by weakly Lewis acidic sites on the zeolite which seem to be required for the reaction to proceed.<sup>15</sup> In turn, this agrees well with the observation that, when K<sub>2</sub>CO<sub>3</sub> is used, the *N*-methyl-*N*-arylcaramate forms and accumulates in solution under both batchwise (autoclave) and CF conditions.

The basicity of amines is also a critical factor in discriminating between the two considered mechanisms; an increased basicity results in the lack of selectivity. For instance, in the reaction of benzylamine (PhCH<sub>2</sub>NH<sub>2</sub>) with DMC over Y- and X-zeolites (conditions of entries 5 and 6, Table 2), the ratio of mono-*N*-methyl to *N,N*-dimethyl derivatives was ≈1:1, even at a conversion of 10%. When compared with aniline, this result is not attributable merely to molecular size but rather to a different basicity: the more basic aliphatic amine can react with DMC via a direct *B<sub>A1</sub>2* displacement (yielding both mono- and di-methylated products), while the aromatic amine is forced to react through eqns. (6)–(10).

## Conclusions

The reported reaction represents a valuable one-pot procedure for the preparation of mono-*N*-methylanilines even when starting from weakly nucleophilic anilines.

Although the reaction mechanism needs further investigation, preliminary results suggest that the unusual mono-*N*-alkyl selectivity observed is likely to be attributable to a synergic effect between the double reactivity of DMC (acting both as a methylation and as a reversible methoxycarbonylating agent) and the dual acid-base properties of zeolites along with the steric demand by their cavities.

Besides the high selectivity which allows high-purity mono-*N*-methylanilines to be prepared, the reaction also has remarkable environmentally benign features: it uses the non-toxic DMC, no inorganic wastes are produced, and no solvents are required.

## Experimental

All the compounds used were ACS grade and were employed without further purification. NaY and 13X zeolites were from Aldrich; KY was prepared by a conventional ion-exchange method using aq. KCl (0.5 M).<sup>3</sup> Before use, all the zeolites were dried at 500 °C, in a muffle overnight. <sup>1</sup>H NMR Spectra were recorded on a Varian Unity 400 (400 MHz) spectrometer using CDCl<sub>3</sub> with tetramethylsilane as the internal standard. GLC Analyses were performed on a Varian GC 3400CX using a 30 m, DB5 capillary column. GC-MS Analyses were performed on an HP 5971 mass detector at 70 eV coupled to an HP 5890-Series II gas chromatograph fitted with a 30 m, DB5 capillary column.

Methyl phenylcarbamate **5** was prepared by the reaction of aniline with methyl chloroformate, according to established procedures.<sup>18</sup>

### Reactions carried out in an autoclave. General procedure (Tables 1 and 2)

All methylation reactions by DMC were carried out in a stainless-steel (AISI 316) autoclave (internal volume 250 ml), equipped with a purging valve, through which, at room temperature, air was removed before each reaction by purging with a stream of N<sub>2</sub>. A magnetically stirred mixture of dimethyl carbonate, the aromatic amine and the zeolite in the reported weight proportions (see Tables) was heated in the autoclave, itself heated in an electric oven; the reaction temperature (120–150 °C) was checked by a thermocouple fixed onto the autoclave head. Under the same conditions, methyl *N*-phenylcarbamate was treated with DMC at 130 °C.

<sup>†</sup> Eqns. (6) and (8): *B<sub>A1</sub>2* and *B<sub>A1</sub>2* mechanisms, respectively.

<sup>‡</sup> Z is a basic site of the zeolite.

The reaction of urethane **5** with DMC was also performed at atmospheric pressure according to the following procedure. A 3-necked, round-bottomed flask (50 ml) was loaded with a solution of PhNHCO<sub>2</sub>CH<sub>3</sub> (0.31 g, 2.0 mmol) in DMF (7.0 ml) and 13X zeolite (0.35 g). The flask was equipped with a condenser, a dropping funnel charged with DMC (10 ml) and a glass screw-capped tube (fitted with a rubber silicon septum) used for sample withdrawal. Before heating, air was removed under vacuum, N<sub>2</sub> was inlet (by a rubber reservoir placed at the top of the condenser) and kept for the whole course of the reaction. The mixture was then heated and subjected to magnetic stirring at the reflux temperature (155 °C) in an oil-bath. At intervals (1 h), small aliquots of DMC ( $\approx$ 1 ml) were added dropwise to the reaction mixture which was analysed by GLC.

*N*-Methylaniline and *N*-methylamines **1a** (*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCH<sub>3</sub>) and **3a** (*o*-CH<sub>3</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>NHCH<sub>3</sub>) were characterized by comparison with authentic samples commercially available. Spectral data for amines **2a** (*p*-NCC<sub>6</sub>H<sub>4</sub>NHCH<sub>3</sub>), **4a** [2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHCH<sub>3</sub>] and methyl phenylcarbamate **5** were in agreement with those reported in the literature.<sup>19-24</sup>

Methyl arylcarbamates reported in Tables 1–2 were identified by GC-MS spectra which are reported below.

**PhN(CH<sub>3</sub>)CO<sub>2</sub>CH<sub>3</sub>** (entries 1 and 3–4, Table 1): m/z 166 (11); M<sup>+</sup>, 99%), 165 (M<sup>+</sup>, 99%), 134 (12), 120 (32), 119 (10), 108 (14), 107 (51), 106 (100), 105 (31), 104 (32), 79 (31), 78 (17), 77 (71), 72 (19), 59 (15) and 51 (17).

**p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCO<sub>2</sub>CH<sub>3</sub>** (entries 1–4, Table 2): m/z 196 (M<sup>+</sup>, 14%), 152 (100), 138 (31), 122 (48), 108 (13), 106 (22), 105 (21), 92 (16), 79 (27), 78 (17), 77 (43), 65 (43) and 63 (16).

**p-NCC<sub>6</sub>H<sub>4</sub>NHCO<sub>2</sub>CH<sub>3</sub>** (entries 5–7, Table 2): m/z 176 (M<sup>+</sup>, 9%), 144 (12), 132 (62), 131 (100), 118 (22) and 102 (13).

**o-CH<sub>3</sub>O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>NHCO<sub>2</sub>CH<sub>3</sub>** (entries 8–9, Table 2): m/z 209 (M<sup>+</sup>, 32%), 177 (42), 146 (100), 105 (11), 104 (12), 92 (11) and 90 (18).

**2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHCO<sub>2</sub>CH<sub>3</sub>** (entry 10, Table 2): m/z 179 (M<sup>+</sup>, 63%), 148 (11), 147 (60), 146 (11), 121 (14), 120 (100), 119 (33), 118 (18), 105 (10), 91 (19) and 77 (18).

Also, dimethyl derivatives [ArN(CH<sub>3</sub>)<sub>2</sub>] were identified through GLC-MS analysis.

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