Sequential coupling of the transesterification of cyclic carbonates with the selective *N*-methylation of anilines catalysed by faujasites

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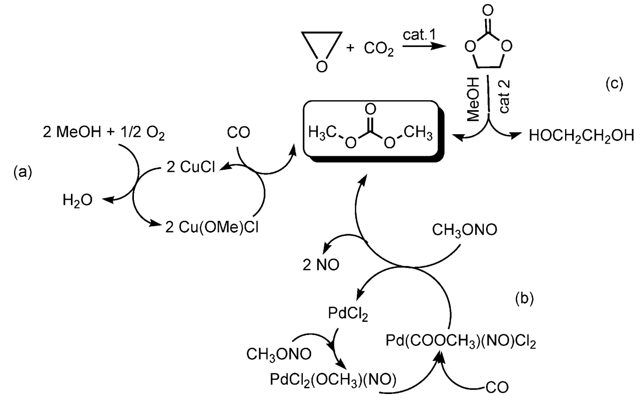
Anilines ($R'C_6H_4NH_2$: R′ = H, *p*-MeO, *p*-Me; *p*-Cl, and *p*-NO_2) react with a mixture of ethylene carbonate and methanol at 180 °C in the presence of alkali metal exchanged faujasites—preferably of the X-type—to give the corresponding *N*,*N*-dimethyl derivatives ($R'C_6H_4NMe_2$) in isolated yields up to 98%. Evidence proves that methanol is not the methylating agent. The reaction instead takes place through two sequential transformations, both catalyzed by faujasites: first transesterification of ethylene carbonate with MeOH to yield dimethyl carbonate, followed by the selective *N*-methylation of anilines by dimethyl carbonate. Propylene carbonate, is less reactive than ethylene carbonate, but it can be used under the same conditions. The overall process is highly chemoselective since the competitive reactions between the anilines and the cyclic carbonates is efficiently ruled out. Ethanol and propanol form the corresponding diethyl- and dipropyl- carbonates in the first step, but these compounds are not successful for the domino alkylation of anilines.

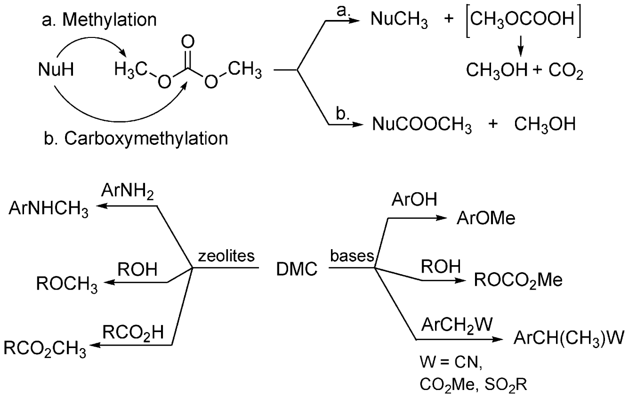
Introduction

The greening of synthetic organic transformations, by the use of eco-friendly reagents has undergone extensive research in the past twenty years.[1] In particular, the alkylation and carbonylation reactions using light organic carbonates in place of the conventional highly noxious alkyl halides, dialkyl sulfates, and phosgene.[2] This is exemplified by the lightest term of the series, *i.e.* dimethyl carbonate ($MeOCO_2Me$, DMC), whose green features include not only its general reactivity and safety, but also its preparation. In fact, the synthesis of DMC is no longer accomplished using phosgene, instead it is carried out by three greener industrial processes: (a) the oxycarbonylation of methanol,[3] (b) the carbonylation of methyl nitrite,[4] and (c) the two-stage process of insertion of CO_2 into an epoxide, followed by a transesterification reaction with MeOH[5] (Scheme 1, eqn a–c).

The feedstocks, catalysts, and conditions, for these three processes prevent hazards and pollution at the source, and they produce DMC free from toxic contaminants.[6] From the reactivity standpoint, both methylation and carboxymethylation reactions of a number of nucleophiles with dimethyl carbonate represent genuine green transformations (Scheme 2, paths a and b) for the following reasons:[7] (a) a safe reagent (DMC) is used, (b) it often acts simultaneously as a solvent, (c) the transformations are catalytic and do not require the use of additional stoichiometric reagents, (d) the only co-products are MeOH (recyclable to the synthesis of DMC) and CO_2, and (e) they are slightly, if at all, exothermic.[8]



Scheme 1 Green synthetic routes for dimethyl carbonate.



Scheme 2 Methyl and carboxymethyl reactivity of DMC.

A more in-depth analysis of the catalytic systems involved in these transformations, shows another potentially valuable aspect: X- and Y-zeolites (alkali metal exchanged faujasites)[9]

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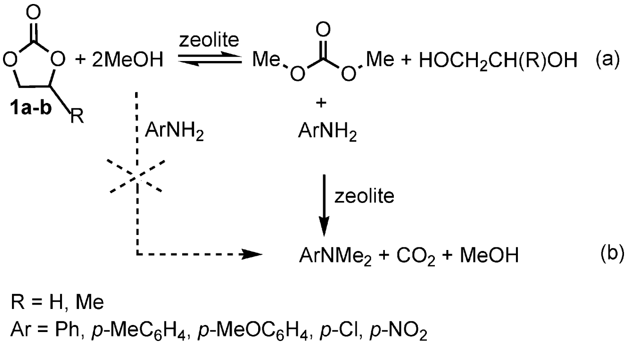
not only catalyze methylation and esterification reactions of nucleophiles with DMC (Scheme 2, bottom left), but they also promote the transesterification of ethylene and propylene carbonates with methanol to yield DMC (Scheme 1, eqn c: cat 2).[10] This dual reactivity of the zeolites can, in principle, be exploited for a sequential reaction, *i.e.* in succession: the synthesis of DMC, followed by its reaction with a nucleophile to yield the methylation and esterification products. This concept is named "green domino" in this paper and employs faujasites, preferably of the X-type, to catalyze the reactions illustrated in Scheme 3.



Scheme 3

In particular, when a slurry of a cyclic carbonate (**1a–b**), methanol, a primary aromatic amine ($ArNH_2$), and a solid zeolite is heated to 180 °C in a batch reactor, two sequential reactions occur: a transesterification process (path a) which generates the active methylating agent dimethyl carbonate, followed by the selective methylation of the amine (path b) which forms the corresponding bis-*N*-methyl derivative ($ArNMe_2$) in yields up to 98%. Experimental evidence confirms that methanol is not involved in the alkylation step (Scheme 3: dashed path) and that the transformation is unequivocally mediated by DMC.

Interestingly, it is also highly chemoselective: in fact, the competitive reaction of anilines with cyclic carbonates **1** to yield the *N*-(β-hydroxy)ethyl derivatives ($ArNHCH_2CH_2OH$), is not observed. Overall, the faujasite catalyst significantly intensifies the process since DMC is formed and its alkylating capability exploited *in situ.*

Under the same conditions, the use of higher alcohols (ethanol and *n*-propanol) is not successful to produce the corresponding *N*-alkylamines. In these cases, both diethyl and dipropyl carbonates form, but anilines preferably react with the starting ethylene carbonate, to give the *N*-(β-hydroxy)ethyl derivatives ($ArNHCH_2CH_2OH$) as major products.

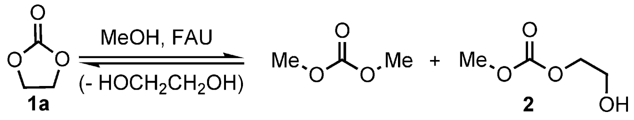
Results

The transesterification of ethylene carbonate with methanol

The initial experiments were carried out to test the activity of faujasites in the transesterification of ethylene carbonate with methanol (Scheme 3, a: R = Me, R′ = H). Five different zeolites, namely MX (M = Li, Na, K) and MY (M = H, Na) were used as catalysts. Four of them were either commercially available (NaX and NaY) or synthesized (LiX and KX) by ion exchange using LiCl or KCl.[11] HY instead, was obtained by calcination of a commercial NH_4Y solid.[12] The main features of these materials are reported in the Experimental section.

The transesterification reactions were performed at temperatures of 110–150 °C, in a stainless steel autoclave (150 mL) charged with ethylene carbonate (**1a**: 2.2 g, 25 mmol), methanol (8–30 mL), and the faujasite catalyst [the weight ratio Q = **1a** : FAU was ranged from 4.8 to 31.4]. After 5 h, the reactor was rapidly cooled to rt and vented, and the reaction mixture was analyzed by GC-MS. Results are reported in Table 1.

In all cases, the major products were dimethyl carbonate and 2-(hydroxy)ethyl methyl carbonate (**2**) (Scheme 4).[13]



Scheme 4

The reaction outcome however, was greatly affected by the nature of the catalysts. At 110 °C (Q = 4.8), alkali metal

Table 1 The transesterification of ethylene carbonate with MeOH in presence of different faujasites[a]

						Products (%, GC)[c]		
Entry	FAU/g	MeOH/mL	**1a** : FA, Q (g : g)[b]	T/°C	Conversion (%)[c]	DMC	**2**	Others[d]
1	NaX (0.45)	30	4.8	110	93	73	12	8
2	LiX (0.45)	30	4.8	110	81	50	26	5
3	KX (0.45)	30	4.8	110	96	80	6	10
4	NaY (0.45)	30	4.8	110	79	17	57	5
5	HY (0.45)	30	4.8	110	26	8	14	4
6	NaX (0.45)	30	4.8	130	97	80	7	10
7	NaX (0.45)	30	4.8	150	96	74	7	15
8	NaX (0.28)	30	7.8	110	96	78	10	8
9	NaX (0.14)	30	15.7	110	96	82	10	4
10	NaX (0.07)	30	31.4	110	86	65	20	1
11	NaX (0.14)	15	15.7	110	83	70	12	1
12	NaX (0.14)	8	15.7	110	71	48	23	—

[a] All reactions lasted 5 h. [b] Q was the weight ratio between ethylene carbonate and faujasite. [c] Both conversion of ethylene carbonate and the product distribution were determined by GC. [d] Others: unidentified products detected by GC/MS analyses.

exchanged faujasites of X-type (MX, M = Li, Na, K) generally afforded both higher conversions (81–97%) and higher yields of dimethyl carbonate (50–80%) with respect to the NaY zeolite (compare entries 1–3 and 4), and to the more acidic HY solid, by far the least effective catalyst (entry 5).

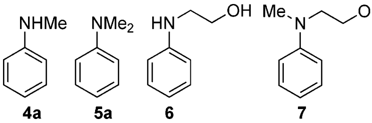
Accordingly, the commercial NaX zeolite was chosen to continue the investigation. Additional experiments were carried out at higher temperatures and with different NaX loadings. At 130 and 150 °C ($Q = 4.8$, entries 6–7), the conversion of ethylene carbonate was substantially quantitative, but the product distribution was not improved. At 110 °C, the zeolite proved to be efficient even at lower loadings: when the Q ratio was increased in the range of 7.8–15.7 (entries 8–9), a conversion of 96% was attained, while the proportion between DMC and compound **2** did not substantially change compared to previous tests. However, a further decrease of the catalyst quantity as well as of the volume of methanol (8–15 mL) resulted in a drop of both conversion and selectivity towards the formation of DMC (entries 10–12).

The *N*-methylation of aniline

The next step of the investigation was to test whether DMC, once prepared through the reaction of Scheme 4, could be used as a methylating agent *in situ*, without isolating it from the mixture. Aniline (**3a**) was chosen as a model nucleophile. Experiments were performed at temperatures of 130–180 °C, in a stainless steel autoclave (150 mL) charged with aniline (**3a**: 0.5 g, 5.4 mmol), ethylene carbonate (**1a**: 2.0–4.0 g, 23–46 mmol), methanol (30–50 mL), and the NaX faujasite catalyst. In particular, four sets of conditions were used:

(i) Molar ratio (W) **1a** : **3a** = 4, methanol 30 mL; (ii) W = 8.5, methanol 30 mL; (iii) W = 4, methanol 50 mL; (iv) W = 8.5, methanol 50 mL. The weight ratio Q' = **3a** : FAU was ranged from 1 to 3. After different time intervals (8–24 h), the reactor was cooled to rt and vented, and the reaction mixture was analyzed by GC-MS. Two additional tests (a–b) were carried out in the absence of (a) ethylene carbonate and of (b) the zeolite.

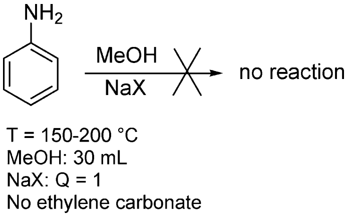
Four main products were identified: their structure was assigned by GC-MS and by comparison to authentic samples (Scheme 5).



Scheme 5

Results are reported in Table 2.

At 150 °C, aniline was recovered unaltered in the absence of faujasite (entry 1). By contrast, in presence of NaX (Q' = 1) conversions of 65 and 82% were measured after 8 h, at 150 and 180 °C, respectively (entries 3–4). Under these conditions, a moderate conversion was observed even at 120 °C (entry 2: conv. 43%, 20 h). The formation of both compounds **4a** and **5a** (*N*-methylaniline and *N*,*N*-dimethylaniline) proved that a methylation process occurred in all cases. By using methanol in the absence of ethylene carbonate at 150–200 °C for the methylation of aniline in the presence of the faujasite, no conversion was observed, thereby confirming that DMC was the active methylating agent (Scheme 6).[14]



Scheme 6

However, under the conditions of entries 2–4, the selectivity was never satisfactory: the presence of sizeable amounts (17–26%) of products **6–7** indicated that competitive methylation and (β-hydroxy) ethylation reactions, mediated by DMC and ethylene carbonate respectively, took place to comparable extents. A higher loading of ethylene carbonate [conditions (ii): W = 8.5],

Table 2 The reaction of aniline (**3a**) with ethylene carbonate and methanol, catalyzed by NaX zeolite

							Products (%, GC)[d]				
Entry	MeOH/mL	**3a** : FAU, Q' (g : g)[a]	**1a** : **3a**, W (mol : mol)[b]	T/°C	t/h	Conversion (%)[c]	**4a**	**5a**	**6**	**7**	Others
1	30	—[e]	4	150	8	—					
2	30	1	4	120	20	43	18	5	16	4	
3	30	1	4	150	8	65	17	22	11	15	
4	30	1	4	180	8	82	26	36	7	10	3
5	30	1	8.5	165	8	88	21	44	7	15	
6	30	1	8.5	180	8	97	8	64	3	19	3
7	30	2	4	180	8	96	5	40	26	20	5
8	30	3	4	180	8	99	9	13	35	30	11
9	50	1	4	150	8	24	20	4			
10	50	1	4	180	8	64	35	29			
11	50	1	4	180	24	88	24	64			
12	50	1	8.5	180	8	82	21	61			
13	50	1	8.5	180	16	99	5	89		5	

[a] Q' was the weight ratio between aniline and the NaX faujasite. [b] Molar ratio between ethylene carbonate and aniline. [c] Conversion of aniline. [d] The structure of products **4–7** was assigned by GC-MS and by comparison to authentic samples of **4a**, **5a** and **6**. Others were unidentified compounds detected by GC/MS analyses. [e] In the absence of faujasite.

improved aniline conversion (88–97%, entries 5–6), but it did not produce significant changes of the methylation selectivity: the total of methylamines (**4a** + **5a** = 65–72%) remained less than three times the amount of **6** and **7** (22–23%). The formation of the latter compounds was in fact favored by the use of higher catalyst loadings ($Q' = 2$–3, entries 7–8; **6** + **7** = 46–65%).

Although methanol did not take part in the alkylation reaction (Scheme 5) it played a crucial role on the reaction outcome: the increase of its volume (from 30 to 50 mL), had two effects: (a) it decreased the conversion (compare entries 4 and 10, and 6 and 12[15]); and (b) it greatly improved the selectivity towards the exclusive formation of methylamines (entries 9–13). Under these conditions, when the molar ratio ethylene carbonate/aniline (W) was augmented from 4 to 8.5, the reaction became faster and the bis-methylation process predominated (entries 9–11 and 12–13). At 180 °C, over a NaX zeolite catalyst, the green domino of Scheme 3, produced dimethylaniline (**5a**) in very high selectivity and yield (89%, 16 h: entry 13). Compound **5a** was purified by FCC (petroleum ether/diethyl ether, 95 : 5 v/v), and it was isolated in a 85% yield.

The *N*-methylation of primary aromatic amines with alkylene carbonates

To extend the scope of the green domino procedure, different anilines ($R'C_6H_4NH_2$: 0.5 g; **3b**: R′ = *p*-MeO; **3c**: R′ = *p*-Me; **3d**: R′ = *p*-Cl; **3e**: R′ = *p*-NO_2) were set to react with both ethylene and propylene carbonates (**1a** and **1b**, respectively). Experiments were run under conditions (iii) and (iv) previously described for aniline ($W = 4$–8.5, $Q' = 1$, $T = 180$–200 °C, MeOH = 50 mL). In all cases, the structures of products were assigned by GC-MS and by comparison to authentic samples.

The reaction of aniline (**3a**) with propylene carbonate was also investigated.

Finally, two further experiments were aimed at improving the overall mass index of the green domino.[16] The reactions of aniline and *p*-anisidine, were performed by decreasing the amounts of both the catalyst and ethylene carbonate: Q' and W ratios were set to 0.1 and 3, respectively. In these cases, the temperature was increased to 190 °C.

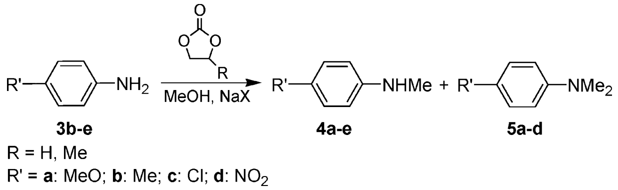
Results are reported in Table 3.

Five main features emerged from this investigation:

(a) No competitive formation of *N*-(β-hydroxy)ethyl derivatives due to the reaction of ethylene or propylene carbonates with the amine was observed. The *N*-methylation reaction promoted by DMC was the sole observed process for each of the tested amines.

(b) Different aryl substituents on the anilines affected the final outcome. A reactivity scale was clearly evident: *p*-anisidine > *p*-toluidine ≥ aniline > *p*-chloroaniline >> *p*-nitroaniline. For example, after 8 h at 180 °C ($W = 8.5$), in the presence of ethylene carbonate, the reactions of *p*-anisidine (**3b**) and *p*-toluidine (**3c**) showed comparable conversions (100 and 95%, respectively); though, *N*,*N*-dimethyl *p*-anisidine **5b** was obtained in a 100% yield (entry 2), while **3c** gave a mixture of mono- and bis-*N*-methyl derivatives (**4c** + **5c**) in 8 and 83%, amounts (entry 5). Under the same conditions, the reaction of *p*-chloroaniline (**3d**) required a considerably longer time: a conversion of 91% was reached after 28 h (entry 7). The corresponding products of mono- and di-methylation (**4c** + **5c**) were observed in 9 and 90% quantities, respectively. Finally, *p*-nitroaniline reacted only at 200 °C: after 24 h, notwithstanding the high temperature, a modest conversion of 16% was attained (entry 9).

Table 3 The reaction of different anilines (**3a–e**) with alkylene (ethylene and propylene) carbonates, and methanol, catalyzed by NaX zeolite[a]



Entry	Alkyl carbonate	$R'C_6H_4NH_2$ R′:	**3** : NaX, Q'	**1** : **3**, W (mol : mol)[b]	T/°C	t/h	Conversion (%)[c]	Products (%, GC)[d] 4	5	Others	Yield (%)[e]
1	**1a**	**3b**: *p*-MeO	1	4	180	16	95	9	86		
2	**1a**	**3b**: *p*-MeO	1	8.5	180	8	100		100		98
3	**1b**	**3b**: *p*-MeO	1	8.5	180	8	96	9	87		
4	**1a**	**3c**: *p*-Me	1	4	180	24	92	12	80		
5	**1a**	**3c**: *p*-Me	1	8.5	180	8	95	8	83	4	78
6	**1b**	**3c**: *p*-Me	1	8.5	180	8	90	12	78		
7	**1a**	**3d**: *p*-Cl	1	8.5	180	28	99	9	90		87
8	**1b**	**3d**: *p*-Cl	1	8.5	180	28	91	23	68		
9	**1a**	**3e**: *p*-NO_2	1	8.5	200	24	16	16			
10	**1b**	**3a**: H	1	8.5	180	24	97	8	86	3	
11	**1a**	**3a**: H	0.1	3	190	24	81	25	51	5	
12	**1a**	**3b**: *p*-MeO	0.1	3	190	24	87	18	69		

[a] All reactions were carried out using 0.5 g of the substrate (**3a–e**), and 50 mL of MeOH. Q' ratio was in the range of 0.1–1. [b] Molar ratio between alkylene carbonate and aniline. [c] Conversion of the substrate. [d] The structure of products ArNHMe and $ArNMe_2$ was assigned by GC-MS and by comparison to authentic samples. Others were unidentified compounds detected by GC-MS analyses. [e] Isolated yields of compounds **5b**, **5c**, and **5d**.

(c) As in the case of aniline, the increase of the W ratio from 4 to 8.5 improved the methylation rate for both *p*-anisidine and *p*-toluidine (compare entries 1–2, and 4–5).

(d) Both ethylene- and propylene-carbonate (**1a** and **1b**) could be used to produce DMC and to finally methylate amines **3a–e**. However, the use of **1a** allowed faster reactions with respect to **1b**. For example, after 8 h at 180 °C, compound **5b** (p-$MeOC_6H_4NMe_2$) was obtained in 100 and 87% yields using **1a** and **1b**, respectively (entries 2 and 3). Likewise, in the case of *p*-toluidine and *p*-chloroaniline, the amounts of products **5c** and **5d** (p-$MeC_6H_4NMe_2$ and p-$ClC_6H_4NMe_2$) were higher with **1a** than with **1b** (compare entries 5–6 and 7–8). A similar behavior held also for aniline, whose reaction with propylene carbonate (entry 10, Table 3: conv. 97%, 24 h) was slower than that with ethylene carbonate (entry 13, Table 2: conv. 99%, 16 h).

(e) The green domino proceeded even when NaX was used in a catalytic amount ($Q' = 0.1$) and ethylene carbonate was slightly over the stiochiometric quantity ($W = 3$) (entries 11 and 12). Although a tenperature of 190 °C was necessary to allow sufficiently rapid conversions of both aniline and *p*-anisidine, these results proved not only the catalytic role of the faujasite, but also that the overall flow of materials involved in the process, could be improved to make the transformation more green and economic. However, further optimization of the conditions/parameters is the object of future studies.

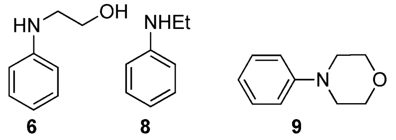
Once reactions of entries 2, 5 and 7 were completed, *N*,*N*-dimethyl-*p*-anisidine, *p*-toluidine and *p*-chloroaniline were purified by FCC (petroleum ether/diethyl ether, 95 : 5 v/v): they were isolated in 98%, 78%, and 87% yields, respectively.

The reaction of aniline with ethylene carbonate and light alcohols (ethanol and *n*-propanol)

The reaction of aniline and ethylene carbonate (Scheme 3) was carried out also with ethanol and *n*-propanol in place of methanol. Experiments were performed at 180 and 200 °C under the conditions of Table 3 ($W = 8.5$, $Q' = 1$).

Three products were identified by GC-MS and by comparison to authentic samples (Scheme 7).[17] Results are reported in Table 4.

In the presence of ethanol, the conversion was good (89–96% after 15 h), but the selectivity was elusive: mixtures of **6** and **9** (total of 77–81%) were always obtained along with minor amounts of **8** (2–4%) and other unidentified by-products (8–17%) (entries 1–4). A larger volume of ethyl alcohol (from 50 to 110 mL) did not substantially improve the product distribution. Products **6** and **9** were observed also in the presence of *n*-propanol (entry 5): in this case, not even a trace of *N*-propylaniline (PhNHPr) was detected.

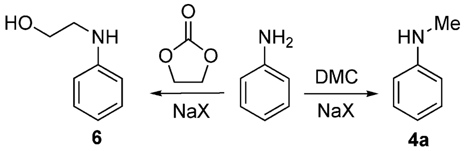


Scheme 7

The relative reactivity of dialkyl carbonates

The results of Tables 2 and 3 showed that when methanol was present in a relatively large amount, the competition between DMC and ethylene carbonate as methylating and hydroxyethylating agents of primary aromatic amines was suppressed, and the *N*-methylation reaction proceeded with a selectivity up to 100%. By contrast, the corresponding reactions carried out with ethanol and propanol, took place with the exclusive formation of products derived from ethylene carbonate (Table 4). To investigate these aspects, the relative reactivity of DMC and ethylene carbonate was tested in competitive reactions with aniline. Two sets of experiments were performed at 90 °C (refluxing temperature of DMC) and at 140 °C, respectively. In both cases, a mixture of aniline (0.5 g, 5.4 mmol), DMC (10 g, 111 mmol), and NaX (0.5 g, $Q' = 1$), was set to react with different amounts of ethylene carbonate (**1a**). In particular, the molar ratio DMC : **1a** was increased from 1 to 5, 10, 20, and 40, respectively.

GC-MS analyses showed that major products were mono-*N*-methylaniline (**4a**) and mono-*N*-(β-hydroxy)ethylaniline (**6**) (Scheme 8),[18] whose total amount (**4a** + **6**) corresponded to 97–99% of all the observed products.



Scheme 8

Results are reported in Fig. 1, where the ratio of anilines **6** : **4a** (GC amounts) is plotted against the molar ratio DMC : **1a**.

Table 4 The reaction of aniline (**3a**) with ethylene carbonate, in the presence of ethanol or *n*-propanol, and NaX zeolite catalyst[a]

					Products			
Entry	Alcohol/mL	T/°C	t/h	Conversion (%)[b]	**8**	**6**	**9**	Others
1	EtOH (50)	180	15	93	2	80	11	
2	EtOH (70)	200	15	96	2	39	38	17
3	EtOH (90)	200	15	94	3	50	11	10
4	EtOH (110)	200	15	89	4	43	34	8
5	*n*-PrOH (90)	200	15	92		55	32	5

[a] All reactions were carried out using 0.5 g of the aniline, 0.5 g of NaX ($Q' = 1$), and 4.0 g of ethylene carbonate ($W = 8.5$). Different volumes of EtOH were used (entries 1–4: 50 to 110 mL). Entry 5:90 mL of *n*-PrOH. [b] Conversion of aniline. [c] The structure of products **6**, **8** and **9** was assigned by GC-MS and by comparison to authentic samples. Others were unidentified compounds detected by GC-MS analyses.

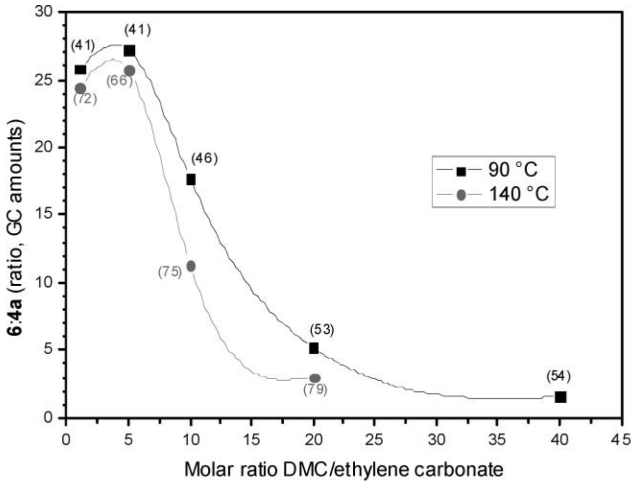


Fig. 1 Ratio of N-(β-hydroxy)ethylaniline (**6**)/N-methylaniline (**4a**) as a function of the DMC : **1a** molar ratio. Conversions of aniline are shown in parethesis. ■: reactions at 90 °C; ●: reactions at 140 °C.

For a coherent evaluation, each set of data was calculated at comparable conversions.

At 90 °C, in the range of conversions of 41–54%, N-(β-hydroxy)ethylaniline (**6**) was always the main product even though ethylene carbonate (**1a**) was used in a considerably lower amount with respect to DMC (black curve). The ratio **6** : **4a**, decreased smoothly from ~27 to 5 while the molar ratio DMC : **1a** increased from 5 to 20. Remarkably, the quantity of **6** was 1.5 higher than that of N-methyl aniline, even when DMC was present in a 40 molar excess over ethylene carbonate: under these conditions, ethylene carbonate was understoichiometric to aniline.

An analogous behavior was observed at 140 °C. In the range of conversions of 66–79%, the ratio **6** : **4a** varied between 3 and 26 (grey curve). Apparently, the reaction temperature had a limited effect on the relative rates of hydroxyethylation and methylation of aniline. Ethylene carbonate was, by far, more reactive than DMC, and the formation of **6** was favored at all times, with respect to **4a**.

Other experiments were run at 140 °C, in the presence of co-solvents of different polarity: cyclohexane, 1,2-dimethoxy ethane, and N,N-DMF. A mixture of aniline (0.5 g, 5.4 mmol) dimethylcarbonate (13.11 g, 111 mmol), ethylene carbonate (0.97 g, 11.1 mmol) (molar ratio DMC : **1a** = 10), and NaX (0.5 g), was set to react in presence of these solvents (20–40 mL).[19]

Results are reported in Table 5. For a convenient comparison, the table also includes the reaction carried out without added solvents.

Despite the excess of DMC used in all reactions, β-hydroxyethyl aniline (**6**) was always the preferred product, in particular in the presence of the apolar cyclohexane (40 mL) where **6** was the only observed product (entry 3). In the more polar DME and DMF (20 mL), the ratio **6** : **4a** was ~15 (entries 4–5), comparable to that reported using only DMC as a solvent (11.5, entry 1). A larger volume of DMF (40 mL) resulted in a considerable decrease of the ratio **6** : **4a** to 5.1 (entry 6). Higher dilution also caused longer reaction times for both cyclohexane and DMF: conversions of ~60% were reached after 2 and 3 h, respectively (entries 3 and 6).

Finally, at 140 °C, a mixture of aniline (0.5 g, 5.4 mmol), diethylcarbonate (13.11 g, 111 mmol) and ethylene carbonate (0.48 g, 5.4 mmol) (molar ratio DEC : **1a** = 20), was set to react in the presence of NaX (0.5 g). After 2 h, the conversion was of 60%, and N-(β-hydroxy)ethyl aniline (**8**) was the sole product. No competition was observed between ethylene carbonate and diethyl carbonate.

Discussion

The catalytic activity of faujasites

Alkali metal exchanged faujasites are often described as amphoteric solids[20] due to the simultaneous presence of Lewis acidic metal cations (Li^+, Na^+, K^+, and Cs^+), and basic oxygen atoms in the zeolite framework. In particular, by following the acid–base scale proposed by Barthomeuf,[21] Table 1 shows that more basic MX systems (entries 1–3) offer better performances than NaY and HY zeolites (entries 4–5) in the transesterification of ethylene carbonate with methanol. Even more specifically, a comparison among X-type faujasites indicates that KX (entry 3) is more active than NaX and LiX (entries 1 and 2, respectively), thanks to the milder acidic character of K^+ with respect to Na^+ and Li^+. These results match those observed by other authors[10] in the study of the transesterification of cyclic carbonates over zeolites. In general, this reaction is reported to be rather sensitive to the basic properties of the catalysts involved.[5,22]

Table 5 The reaction of aniline with ethylene carbonate and DMC, in the presence of NaX and different co-solvents[a]

							Products			
Entry	Solvent/mL	ε[b]	DMC : **1a** (mol : mol)[c]	T/°C	t/h	Conversion (%)[d]	**4a**	**6**	Others	Ratio **6** : **4a**
1	DMC (10)	3.08	10	140	1	75	6	69		11.5
2	CyH (20)	2.02	10	140	1	56	2	54		27
3	CyH (40)		10	140	2	61		61		∞
4	DME (20)	7.2	10	140	1	68	4	61	3	15.3
5	DMF (20)	38.3	10	140	1	60	3	47	10	15.6
6	DMF (40)		10	140	3	59	8	41	10	5.1

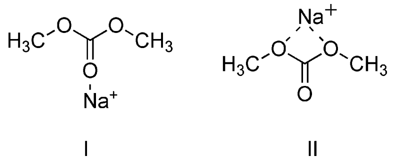
[a] All reactions were carried out using aniline (0.5 g, 5.4 mmol), NaX (0.5 g, $Q' = 1$), DMC (10 g, 111 mmol), ethylene carbonate (0.98 g, 10.8 mmol), and the solvent (20 or 40 mL of cyclohexane, of 1,2-dimethoxyethane, and of N,N-DMF in entries 2–6, respectively). [b] Dielectric constants were taken from ref. 18. [c] Molar ratio between DMC and ethylene carbonate. [d] Conversion of aniline. [e] The structure of products **4a** and **6** was assigned by GC-MS and by comparison to authentic samples. Others were unidentified compounds detected by GC-MS analyses.

The "green domino"

The results of Table 2 show that in presence of the NaX faujasite catalyst a mixture of aniline, ethylene carbonate, and methanol react to produce mono-*N*- and bis-*N*-methyl anilines (**4a** and **5a**) as major products. In addition, in the absence of ethylene carbonate aniline is recovered fully unreacted (Scheme 5). This is evidence of the fact that methanol does not act itself as the methylating agent of the amine. The most plausible explanation for the occurrence of compounds **4a**–**5a**, is through two sequential processes: the transesterification of ethylene carbonate to yield dimethyl carbonate, which in turn methylates aniline (Scheme 3). This domino reaction may suffer from the competition between the two organic carbonates for the nucleophile (Scheme 8), and the formation of *N*-(β-hydroxy)ethyl anilines (**6** and **7**) is described accordingly.[23] Yet, 100% methylation selectivity can be achieved by increasing the volume of methanol from 30 to 50 mL (Table 2, entries 4 and 11). This beneficial effect is not likely to be due to the shift in the transesterification equilibrium of ethylene carbonate towards the formation of DMC due to MeOH (Scheme 3, path a). In fact, the ratio of the equilibrium concentrations does not vary significantly between the lowest MeOH : **1a** molar ratio (= 27.0) calculated with 50 mL of methanol, and the highest MeOH : **1a** molar ratio (= 34.5) calculated with 30 mL of methanol (Table 6).

Why then the exclusive formation of methyl anilines **4a** and **5a** with respect to hydroxyethyl amines **6** and **7**? A further consequence of the increase of methanol is the reduction of the reaction rate (for instance, compare entries 6 and 13 of Table 2). This result parallels the behavior reported for several liquid-phase processes catalyzed by faujasites:[15] in general, the more polar the solvent is, the more it competes with organic reagents for the adsorption on active sites of the polar surface of zeolites, and consequently, the lower the reaction rates are. In our case however, a strong MeOH/faujasite interaction may also play a further role on the adsorption of dialkyl carbonates over the catalytic surface. In fact, IR and Raman investigations demonstrate that DMC (and likely ethylene carbonate as well) is adsorbed over the zeolites through the formation of acid–base complexes (I and II) with weak Lewis acidic sites (*e.g.* Na^+ cations) of the framework of the aluminosilicate (Scheme 9).[24]

These modes of adsorption of dialkyl carbonates are plausibly altered when methanol is itself co-adsorbed over the catalytic surface. Although the nature (and entity) of such a perturbation is not presently clear, its effect may modify the relative reactivity of DMC and ethylene carbonate, favoring the former (DMC). This behavior becomes unpredictable if the two organic carbonates are compared in the competitive alkylation of aniline catalyzed by NaX (Fig. 1): in the formation of *N*-(β-hydroxy)ethyl anilines (**6** and **7**, Scheme 5), the relief of some ring strain in ethylene carbonate likely accounts for its higher reactivity with respect to DMC.[25] Under these conditions however, a moderate, but visible, effect on the reaction selectivity, is observed if co-solvents are used (Table 5). In polar solvating media such as DMF, the methylation of aniline is less disfavored than in apolar cyclohexane, where the reaction may not take place at all. This evidence further corroborates the results above discussed: a large excess of polar MeOH alters the reaction environment to the point that the *N*-methylation of aniline occurs on an exclusive basis.



Scheme 9 Interactions of DMC with Na^+ of faujasites.

Table 6 The excess of methyl alcohol over ethylene carbonate

Entry	Methanol/mL	**1a** : **3a** (mol : mol)[a]	MeOH : **1a**
1	30	4	34.5
2	30	8.5	16.2
3	50	4	57.4
4	50	8.5	27.0

[a] Molar ratio between ethylene carbonate (**1a**) and aniline (**3a**). [b] Molar ratio between methanol and ethylene carbonate.

The outcome of reactions carried out with ethanol and *n*-propanol (Table 4), is also explained through the competitive reactivity of dialkyl carbonates. The alkylation rate of several nucleophiles, drops of 1–2 orders of magnitude by simply substituting DMC with diethyl carbonate (DEC).[7,26] Accordingly, both diethyl- and dipropyl-carbonates, which form under the conditions of Table 4,[27] cannot vie with the more reactive ethylene carbonate.

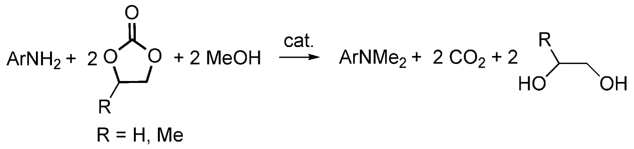
Different anilines and different cyclic carbonates

Table 3 shows that the green domino is effective for different primary aromatic amines. The reactivity scale of these compounds leaves few doubts about the effect of aryl substituents: the *N*-methylation reaction is accelerated by electron-donating groups, while it becomes difficult with scantily nucleophilic amines such as *p*-chloro- and particularly, *p*-nitro-aniline. This closely follows a result previously described by us, for the alkylation of aromatic amines with DMC catalyzed by faujasites.[7]

Table 3 indicates that also propylene carbonate (**1b**) promotes the selective methylation of different anilines; though, the overall reaction rate drops with respect to the use of ethylene carbonate (**1a**). A plausible explanation comes from the study of the transesterification of cyclic carbonates with methanol: Arai *et al.*,[5] have reported that when ethylene carbonate is replaced with propylene carbonate, the different steric hindrance of the two carbonates accounts for a sharp decrease of reactivity. For the same reason, the availability of DMC and consequently, the *N*-methylation rates decrease in the green domino promoted by **1b**.

Conclusions

An innovative and selective synthesis of bis-*N*-methyl anilines is described through the reaction of aromatic amines, methanol and a cyclic carbonate. Although in the formal stoichiometry of the process, methanol is the alkylating agent (Scheme 10), the overall transformation proceeds *via* the coupling of two sequential processes, both catalysed by alkali metal exchanged faujasites.



Scheme 10

In particular, ethylene or propylene carbonate react preferably in the presence of a NaX zeolite, with methanol, to produce dimethyl carbonate (DMC) which *in situ*, acts as an efficient methylating agent of anilines. This green domino sequence, offers an original approach from both synthetic and environmental standpoints: in fact, the transesterification of cyclic carbonates with MeOH is the preferred eco-friendly solution for the production of the non-toxic DMC, that itself possesses much better and greener alkylation performances than methanol. *N*,*N*-dimethylanilines can be isolated in good to excellent yields (78–98%), starting from *p*-substituted amines with both electron-donating and -withdrawing groups; though, the more nucleophilic the substrates (*e.g. p*-anisidine and *p*-toluidine), the faster the reaction. In addition, steric reasons likely account for the higher reactivity of ethylene carbonate with respect to propylene carbonate.

The study of competitive reactions of aniline with mixtures of ethylene carbonate and DMC, unequivocally proves that the cyclic carbonate is the better *N*-alkylating agent. Notwithstanding, under the *green domino* conditions, a methylation selectivity up to 99%, is achieved. This intriguing and unpredictable result is explained mainly by the presence of MeOH as a reagent/solvent, whose polar protic features alter the modes of adsorption (and the reactivity) of dialkyl carbonates over the surface of the faujasites catalysts. The effects observed in the presence of other polar and apolar co-solvents (DMF, DME and cyclohexane) further support these considerations.

Experimental

Anilines ($R'C_6H_4NH_2$; **3a**: R′ = H, **3b**: R′ = *p*-MeO, **3c**: R’ = *p*-Me, **3d**: R′ = *p*-Cl, **3e**: R′ = *p*-NO_2), cyclic carbonates (**1a**: ethylene-; **1b**: propylene-carbonate), and dimethyl carbonate were ACS grade and were employed without further purification. Zeolites NaY and NaX were from Aldrich. The metal content of MX (M = Li, Na, K) and NaY catalysts was determined according to a procedure previously reported by us.[15] Table 7 summarizes the composition of these solids.

Before each reaction, all the faujasites were dried by heating at 65 °C, under vacuum (10 mmHg) overnight.

Table 7 Faujasite catalysts

Starting zeolite (Na,%)[a]	Product	Ionic exchange (%)[b]
NaX (7.5)	LiX	71
NaX (7.5)	KX	92
NaY (8.1)		

[a] The Na content was evaluated through atomic adsorption (AA). [b] Percentage of ionic exchange (from NaX) was evaluated by AA (K) and emission (Li).

MS (EI, 70 eV) analyses were run using HP5/MS capillary columns (30 m), respectively. ^1H NMR spectra were recorded on a 300 MHz spectrometer, using $CDCl_3$ as solvent.

Reactions carried out in autoclave (Tables 1, 2, 3, 4, and 5). General

A stainless-steel autoclave (150 mL of internal volume) equipped with a pressure gauge, a thermocouple, and two needle valves, was charged with the mixture of reagents and the catalyst. At room temperature and before each reaction, air was purged with a N_2 stream. The autoclave was then heated by an electric oven, while the reaction mixture was kept under magnetic stirring. After the desired time interval, the autoclave was cooled to rt, vented and opened. The reaction mixture was analysed by GC-MS.

The transesterification of ethylene carbonate with methanol (Table 1). A mixture of ethylene carbonate (**1a**: 2.2 g, 25 mmol), methanol (the volume ranged from 8 to 30 mL), and the catalyst (MX; M = Li, Na. K; NaY, and HY; the weight ratio **1a** : faujasite ranged from 4.8 to 15.7), was set to react at different temperatures (110–150 °C) for 5 h. Major products were dimethyl carbonate and 2-(hydroxy)ethyl methyl carbonate (**2**). Both compounds were not isolated: they were identified by GC-MS. 2-(Hydroxy)ethyl methyl carbonate (**2**): MS (EI), *m/z* (relative int.) 120 (M^+, 1%), 89 ($M^+ - OCH_3$, 14), 59 ($M^+ - O(CH_2)_2OH$, 100), 58 (51). The structure of DMC was confirmed also by comparison to an authentic sample.

The methylation of aniline (Table 2). A mixture of aniline (**3a**: 0.5 g, 5.4 mmol), ethylene carbonate (**1a**: the weight amount ranged from 2.0 to 4.0 g; 23–46 mmol), methanol (the volume ranged from 30 to 50 mL), and NaX (the weight ratio **3a** : NaX ranged from 1 to 3), was set to react at temperatures of 130–180 °C, for different time intervals (4–24 h). Two additional tests were carried out in the absence of: (a) ethylene carbonate; (b) the zeolite. Products **4a** (mono-*N*-methyl aniline), **6** [*N*-(2-hydroxyethyl)aniline], and **7** [*N*-(2-hydroxyethyl),*N*-methylaniline] were not isolated: they were identified by GC-MS and by comparison to authentic samples (only for **4a** and **6**). Product **5a** (bis-*N*-methylaniline) was isolated as reported below.

The methylation of primary aromatic amines (Table 3). A mixture of a primary amine ($R'C_6H_4NH_2$: 0.5 g; **3b**: R′ = *p*-MeO; **3c**: R′ = *p*-Me; **3d**: R′ = *p*-Cl; **3e**: R′ = *p*-NO_2), ethylene carbonate (1.4–3.5 g; the molar ratio **1a** : **3** ranged from 4 to 8.5), methanol (50 mL), and NaX (0.5 g), was set to react at temperatures of 180–200 °C, for different time intervals (8–28 h). Under the same conditions, reactions of *p*-anisidine, *p*-toluidine, *p*-chloroaniline, and aniline were carried out using propylene carbonate (**1b**: 3.5–4.0 g; the molar ratio **1b** : **3** was 8.5) in place of ethylene carbonate.

At 190 °C, the reaction of aniline and *p*-anisidine (0.5 g, 5.4 and 4.1 mmol, respectively) were also performed by decreasing the amounts of both NaX (0.1 g) and ethylene carbonate (1.1–1.4 g; the molar ratio **1a** : **3** was 3).

Isolation and characterization of *N*,*N*-dimethyl anilines ($R'C_6H_4NMe_2$: R′ = H, *p*-MeO, *p*-Me, *p*-Cl). Under the conditions of entry 13 in Table 2, and of entries 2, 5, 7 in Table 3, once reactions were completed (8–28 h), final mixtures were filtered, and methanol was removed by rotary evaporation. The viscous residues were purified by flash-chromatography on silica gel (F60; eluant: petroleum ether/diethyl ether, 95 : 5 v/v). *N*,*N*-dimethyl- aniline, *p*-anisidine, *p*-toluidine, and *p*-chloroaniline, were obtained in isolated yields of 85% (0.55 g), 98% (0.60 g), 78% (0.49 g), and 87% (0.53 g), respectively.

All *N*,*N*-dimethyl anilines were known products, whose characterization was carried out by ^{1}H NMR and GC-MS, and by comparison to commercial authentic samples. The spectroscopic/physical properties were in full agreement to those reported in the literature.[28]

The reaction of aniline with ethylene carbonate in presence of ethanol or of *n*-propanol (Table 4). A mixture of aniline (**3a**: 0.5 g, 5.4 mmol), ethylene carbonate (4.0 g; 45.5 mmol), ethanol or *n*-propanol (the volume ranged from 50 to 110 mL), and NaX (0.5 g), was set to react at temperatures of 180–200 °C, for 15 h. Products **8** (mono-*N*-ethylaniline), **6** [*N*-(2-hydroxyethyl)aniline], and **9** (*N*-phenylmorpholine) were not isolated: they were identified by GC-MS and by comparison to authentic commercial samples.

The competitive reactions of aniline with ethylene carbonate and dimethyl carbonate (Fig. 1). Two sets of experiments were performed at 90 °C and at 140 °C, respectively. At 90 °C (refluxing temperature of DMC; method A), reactions were carried out using standard laboratory glassware. At 140 °C (method B), reactions were run in an autoclave.

Method A. A two-necked, round-bottomed, 50 mL flask fitted with a reflux condenser, a magnetic stirring bar, and an adapter for the withdrawal of samples, was charged with a mixture of aniline (0.5 g, 5.4 mmol), DMC (10 g, 111 mmol), NaX (0.5 g), and ethylene carbonate (9.7 g, 111 mmol). The mixture was placed under a nitrogen atmosphere at room temperature, and then heated in an oil bath at 90 °C. At intervals, aliquots (0.2 mL) of the mixture were analyzed by GC-MS, and products **4a** (mono-*N*-methylaniline) and **6** [*N*-(2-hydroxyethyl)aniline] were identified accordingly. Four subsequent experiments were carried out with the same procedure: since other conditions were unaltered, the amount of ethylene carbonate was decreased to 1.9, 0.97, 0.48, and 0.24 g (21.6, 11.0, 5.5, and 2.7 mmol), respectively.

Method B. A stainless steel autoclave (45 mL) was charged with a mixture of aniline (0.5 g), DMC (10 g), NaX (0.5 g), and ethylene carbonate (whose amount ranged from 9.7, 1.9, 0.97, and 0.48 g). Before, each reaction, at room temperature, the autoclave was degassed under a moderate vacuum (20 mm), and purged with a N_2 stream. The reactor was electrically heated at 140 °C, while the mixture was kept under a magnetic stirring throughout the reaction. After the desired time interval, the autoclave was cooled to rt and opened. The mixture was analysed by GC-MS.

The competitive reactions of aniline with ethylene carbonate and dimethyl carbonate, in presence of different co-solvents (Table 5). The experiments were performed according to the procedure described for method B. A 45 mL autoclave was charged with aniline (0.5 g,), DMC (10 g), NaX (0.5 g), and ethylene carbonate (0.97 g), in presence of a co-solvent. In particular, cyclohexane (20 and 40 mL), dimethoxyethane (20 mL), and *N*,*N*-DMF (20 and 40 mL) were used in five subsequent tests carried out at 140 °C.

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