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Selective *N*,*N*-Dimethylation of Primary Aromatic Amines with Methyl Alkyl Carbonates in the Presence of Phosphonium Salts

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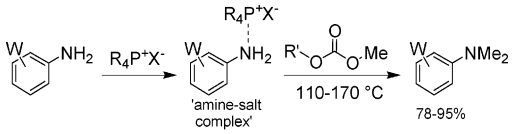


W = H, *p*-Me, *p*-MeO, *p*-Cl, *p*-CO_2Me, *o*-Et, 2,3-Me_2
R' = $MeO(CH_2)_2$; $MeO(CH_2)_2O(CH_2)_2$; $MeO(CH_2)_2O(CH_2)_2O(CH_2)_2$

In the presence of onium salts, at 140−170 °C, methyl alkyl carbonates [**1a**−**c**, $ROCO_2Me$, R = $MeO(CH_2)_2[O(CH_2)_2]_n$; *n* = 2−0, respectively] react with primary aromatic amines ($XC_6H_4NH_2$, X= *p*-OMe, *p*-Me, H, *p*-Cl, *p*-CO_2Me, *o*-Et, and 2,3-$Me_2C_6H_3NH_2$) to yield the corresponding *N*,*N*-dimethyl derivatives ($ArNMe_2$) with high selectivity (up to 96%) and good isolated yields (78−95%). Phosphonium salts (e.g., Ph_3PEtI and *n*-Bu_4PBr) are particularly efficient catalysts. Overall, a solvent-free reaction is coupled with safe methylating agents (**1a**−**c**) made from nontoxic dimethyl carbonate.

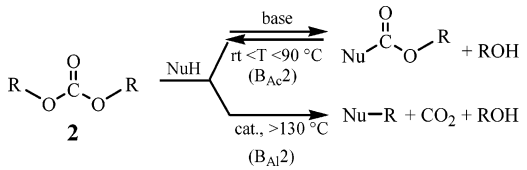
The growing demand for safer reactions has led to intense investigations of new syntheses using ecofriendly reagents and solvents. In this context, dialkyl carbonates ($ROCO_2R$, **2**), obtained by transesterification of the nontoxic dimethyl carbonate (DMC: $MeOCO_2Me$, **2a**), are *green* substitutes for highly noxious alkyl halides, dialkyl sulfates, and phosgene in a variety of reactions.[1] Since carbonates **2** possess two electrophilic carbons (alkyl and carbonyl), they may act as both alkylating and carboxyalkylating agents (Scheme 1).[1]

This reactivity can be often differentiated by the temperature and by the catalyst: below 90 °C, compounds **2** react via a $B_{Ac}2$ mechanism, whereas over 130 °C, both $B_{Ac}2$ and $B_{Al}2$ pathways may coexist, although alkylation predominates due to the reversibility of the carboxyalkylation reaction.

As a part of our interest in dialkyl carbonates,[2] we noticed that the use of unsymmetrical methyl alkyl carbonates ($ROCO_2$-Me, **1**) gave valuable results in methylation reactions. For example, in the presence of a base, compound **1b** [R = $MeO(CH_2)_2O(CH_2)_2$] reacted with phenols to yield anisoles (Scheme 2, path a),[2d] while zeolite-catalyzed reactions of **1b** with primary aromatic amines provided mono-*N*-methylanilines.[2e,h] (Scheme 2, path b). Both processes (a) and (b) proceeded with 99% chemoselectivity and no side-products stemming from $B_{Ac}2$ reactions (Scheme 1) or from competitive alkylations (ArOR, ArNHR) were observed.[3]

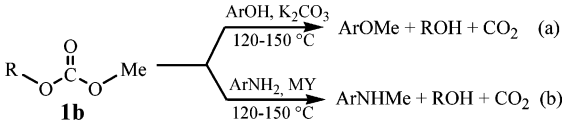
To explore the potential of unsymmetrical methyl alkyl carbonates **1** as new methylating reagents, we decided to investigate the reactivity of representative compounds [**1a,** R =

SCHEME 1. Reactivity of Dialkyl Carbonates 2[a]



[a] NuH is a generic nucleophile.

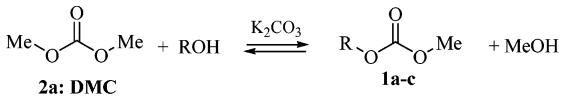
SCHEME 2. Methylating Activity of Carbonate 1b[a]



R = $MeO(CH_2)_2O(CH_2)_2$

[a] MY: alkali metal exchanged. Y: faujasite (M = Na, K).

SCHEME 3. Synthesis of Carbonates 1a−c



1a: R = $MeO(CH_2)_2O(CH_2)_2O(CH_2)_2$;
1b: R = $MeO(CH_2)_2O(CH_2)_2$;
1c: R = $MeO(CH_2)_2$

$MeO(CH_2)_2O(CH_2)_2O(CH_2)_2$; **1b**, R = $MeO(CH_2)_2O(CH_2)_2$; **1c**, R = $MeO(CH_2)_2$] in the presence of moderate Lewis acid catalysts such as onium (both phosphonium and ammonium ions, **3**) and 1,3-dialkylimidazolium salts (**4**).[4] These salts, often referred to as ionic liquids (IL), were already reported to accelerate reactions by dialkyl carbonates, in particular, the N-benzylation of imidazoles, indoles,[5] and aliphatic amines[6] with dibenzyl carbonate (DBnC) and the synthesis of methyl carbamates with DMC.[7]

We wish to report herein that unsymmetrical carbonates **1a**−**c** allow for the rapid and selective *N*,*N*-dimethylation reactions of primary aromatic amines using onium salts, especially phosphonium, as catalysts. In particular, this study shows the general applicability of the procedure to several anilines, even weakly nucleophilic examples. IR spectroscopy is used to account for the effect of compounds **3**.

The synthesis of compounds **1a**−**c** was carried out by the transesterification of dimethyl carbonate catalyzed by K_2CO_3 (Scheme 3).[2,8]

The reaction of *p*-anisidine (**5a**) with the carbonate **1a** was selected for initial investigations.[9] Mixtures of **1a** and **5a** (molar

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(2) (a) Tundo, P.; Selva, M. *Chemtech* **1995**, *25*, 31−35. (b) Selva, M.; Marques, C. A.; Tundo, P. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1889−1893. (c) Selva, M.; Bomben, A.; Tundo, P. *J. Chem. Soc., Perkin Trans 1* **1997**, 1041. (d) Perosa, A.; Selva, M.; Tundo, P.; Zordan, F. *Synlett* **2000**, *1*, 272−274. (e) Selva, M.; Tundo, P.; Perosa, A. *J. Org. Chem.* **2001**, *66*, 677−680. (f) Selva, M.; Tundo, P.; Perosa, A. *J. Org. Chem.* **2002**, *67*, 9238−9247. (g) Selva, M.; Tundo, P.; Perosa, A. *J. Org. Chem.* **2003**, 68, 7374−7378. (h) Selva, M.; Tundo, P.; Foccardi, T. *J. Org. Chem.* **2005**, *70*, 2476−2485. (i) Selva, M.; Tundo, P.; Perosa, A.; Dall'Acqua F. *J. Org. Chem.* **2005**, *70*, 2771−2777.

(3) Methylations with **1b** were carried out at 130−170 °C and at atmospheric pressure.

(4) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2003.

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SCHEME 4. Reaction of *p*-Anisidine with 1a

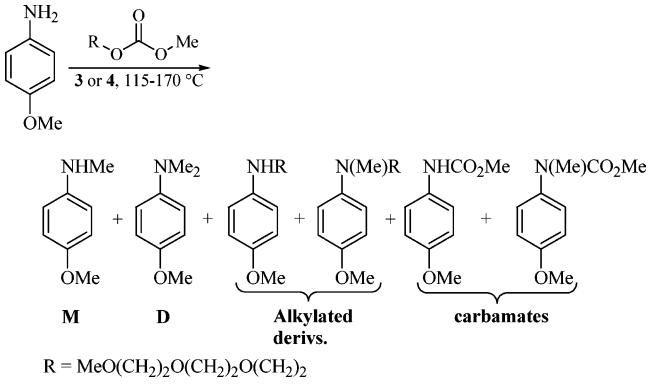


TABLE 1. Reaction of *p*-Anisidine with Carbonate 1a in the Presence of Onium Salts

entry	added salt	molar ratio[a] (salt/**5a**)	*T* (°C)	*t* (min)	convn[b] (%)	products, % GC[c] M	D	C	alkyls	yield[d] (%)
1	none		140	360	8	8				
			170	240	38	18	15		5	
2	Ph_3PEtI(**3a**)	0.5	115	870	97	13	82		2	
3			140	190	96	3	90		3	
4			170	30	100	1	94	1	4	
5		1	170	20	100		96	1	3	89
6	Bu_4PBr(**3b**)	0.5	170	30	96		83	7	6	
7		1		20	100		90	5	5	81
8	$C_{16}H_{33}PBu_3I$ (**3c**)	0.5	170	45	97		87	3	7	
9	Bu_4NBr(**3d**)	1	170	45	100		57[e]	-	3	
10	[Emim]Br(**4a**)	0.5	170	45	91	4	70	<1	15	
11		1		45	95	2	80	1	12	
12[f]	[Bmim]Cl(**4b**)	1	170	45	75	15	53	2	6	

[a] Added salt to *p*-anisidine molar ratio. [b] Reaction conversion (%, by GC). [c] M: $MeOC_6H_4NHMe$; D: $MeOC_6H_4NMe_2$. C: total amount of carbamates [$MeOC_6H_4NHCO_2Me$ and $MeOC_6H_4N(Me)CO_2Me$] by GC. Alkyls: total amount of alkyl derivatives [$MeOC_6H_4NHR$ and $MeOC_6H_4N(Me)R$] by GC. [d] Yield of *N*,*N*-dimethyl derivative (D). [e] $MeOC_6H_4N(Me)Bu$ (40%) was also observed. [f] Reaction did not proceed further than 75% conversion after 45 min.

ratio **1a**/**5a** = 2.2) were reacted at 115−170 °C, in the presence of the onium salts (phosphonium **3a**−**c**; ammonium **3d**; imidazolium **3d**, **4a**, **4b**). Compounds **3** and **4** were added in 0.5−1.0 molar equiv amounts with respect to the amine **5a**. An experiment was also conducted in the absence of added salts. All reactions were monitored by GC: products were identified by GC/MS (Scheme 4) and reported in Table 1.

The *N*,*N*-dimethyl derivative (D) was the major product (up to 96%, by GC; isolated yield: 81−89%, entries 5 and 7). Other alkylated compounds [$MeOC_6H_4NHR$ and $MeOC_6H_4N(Me)R$] and carbamates [$MeOC_6H_4NHCO_2Me$ and $MeOC_6H_4N(Me)CO_2$-Me] were observed in up to 15% and 7% amounts, respectively. When salt **3d** (tetrabutylammonium bromide) was used, a different alkylated product, namely $MeOC_6H_4N(Me)Bu$, was observed in a high quantity (40%, at complete conversion, entry 9): a side reaction of *p*-anisidine with Bu_4NBr accounts for this result. In general, all compounds **3a**−**d** and **4a**,**b** allowed nearly quantitative reactions (91−100%, except for **4b**, entry 12) over 20−45 min, while without added salts, the conversion of **5a** was of 38% after 240 min (entry 1).

Phosphonium salts (**3a**−**c**) gave much better results in terms of the methylation selectivity. To further investigate this effect, the methylation of *p*-anisidine with **1a** (Scheme 4) was conducted using lower quantities of **3a** (ethyltriphenylphosphonium iodide) and **3b** (tetrabutyl phosphonium bromide). A molar ratio **3**/**5a** (*Q* = salt/amine) of 0.1 and 0.25 at 170 °C, was used for each salt.

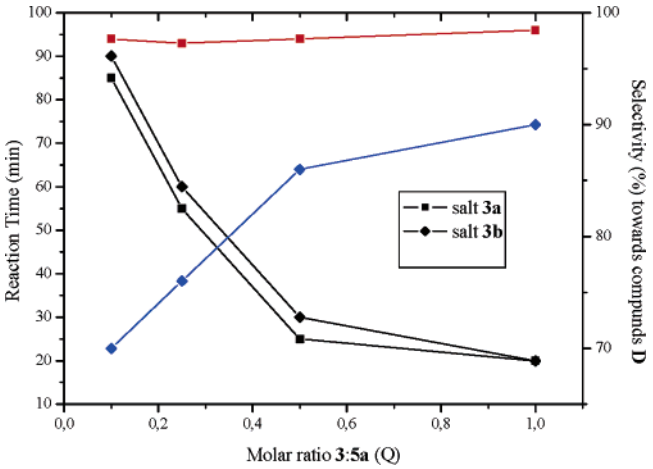


FIGURE 1. Black curves: reaction time (left to right) for substantially quantitative conversion of **5a** vs the molar ratio (Q) **3**/**5a**. Red and blue curves: selectivity (right to left; red, salt **3a**; blue, salt **3b**) toward the formation of $MeOC_6H_4NMe_2$ vs the molar ratio **3**/**5a**.

Results are reported in Figure 1 where, for a more comprehensive picture, results of entries 4−5 and 5−6 of Table 1 (*Q* = 0.5 and 1, respectively) are included.

Phosphonium salts allowed a quantitative conversion (95−100%, black profiles) even when they were used in 0.1 molar equiv amounts with respect to the amine. Compound **3a**, however, was a superior catalyst than **3b**: for all molar ratios **3**/**5a**, the selectivity toward the dimethyl derivative D remained constant (S_D = 93−96%, red curve) with **3a**, while it dropped to 70−75% in the presence of lower amounts of **3b** (Q = 0.1−0.25, blue curve).[10] Under these conditions, the behavior of **3b** was due not only to the formation of carbamates and alkyl derivatives (Scheme 4; up to 8 and 9%, respectively) but also to the incomplete methylation reaction: at quantitative conversions of *p*-anisidine, the corresponding mono-*N*-methylamine (M) was still present in a 10−12% amount.

Based on results of Table 1 and Figure 1, several anilines (4.0 mmol; $XC_6H_4NH_2$, **5b**, X = *p*-Me; **5c**, X = H; **5d**, X = *p*-Cl; **5e**, X = *p*-CO_2Me; **5f**, X = *o*-Et; **5g**, X = *o*-CO_2Me, and $X_2C_6H_3NH_2$, **6a**, X_2 = 2,3-Me_2; **6b**, ×2 = 2,6-Me_2) were made to react at 170 °C, with the carbonate **1a**, in the presence of the salt **3a** as a catalyst. The molar ratios **1a**:**5** and **1a**:**6** were of 2.2, while compound **3a** was added in the range of 0.25−1 molar equiv. with respect to amines **5** and **6**. All reactions were monitored by GC: the representative products were identified by GC/MS (Scheme 5) and reported in Table 2.

Triphenylphosphonium iodide (**3a**) was an efficient catalyst for the reaction. For *p*-substituted amines and aniline (**5b**−**e**), the methylation rate followed the scale of the electron-donating ability of the substituents (Me > H > Cl > CO_2Me): for example, at 170 °C, *p*-toluidine and methyl 4-aminobenzoate showed quantitative conversions after 30 and 120 min, respectively (entries 1−4). The corresponding *N*,*N*-dimethyl derivatives (Dx) were the major products (85−94%, by GC; entries 1−6) isolated in good to excellent yields (84−95%).

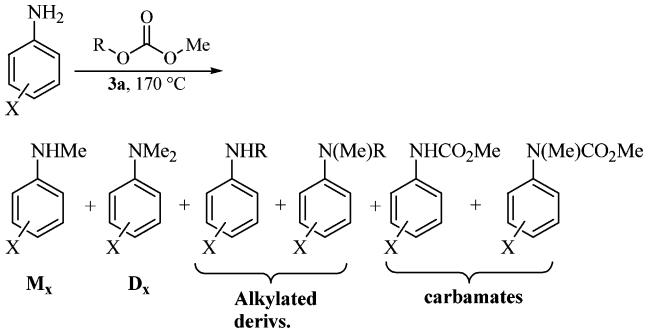
As expected, *o*-substituted amines such as *o*-ethyl- and 2,3-dimethylaniline (**5f** and **6a**) underwent slower reactions with respect to *p*-toluidine (entries 1, 5, and 6), although the *N*,*N*-dimethylation selectivity (S_{Dx}) was still very high (86−89%). The reactions of methyl *o*-aminobenzoate and 2,6-dimethyla-

(8) (a) Shaik, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951−976, (b) Veldhurthy, B.; Clacens, J.-M.; Figueras, F. *Eur. J. Org. Chem.* **2005**, 1972−1976, (c) Selva, M.; Trotta, F. Tundo, P. *J. Chem. Soc., Perkin Trans. 2* **1992**, *4*, 519−522.

(9) **2a** and **5a** could be easily analyzed by GC, and the *N*-methylation and the *N*-methoxycarbonylation products of the amine **5a** could be discriminated by GC/MS.

(10) Selectivity was referred to the reaction times of Figure 1 required for complete conversion of **5a**.

SCHEME 5. Reaction of Anilines 5b−g and 6a,b with 1a



R = $MeO(CH_2)_2O(CH_2)_2O(CH_2)_2$

X= **5b**: *p*-Me, **5c**: H, **5d**: *p*-Cl, **5e**: *p*-CO_2Me, **5f**: *o*-Et, **5g**: *o*-CO_2Me
6a: 2,3-Me_2, **6b**: 2,6-Me_2

TABLE 2. Reaction of Anilines 5b−g and 6a,b with Carbonate 1a in the Presence of Ph_3PEtI at 170 °C

entry	$XC_6H_4NH_2$ X	molar ratio (**3a**/sub)[a]	*t* (min)	convn[b] (%)	products, % GC[c] Mx	Dx	alkyls	C	yield[d] (%)
1	**5b**: *p*-Me	0.25	30	100		94	5	1	95
2	**5c**: H	0.25	60	99		89	6	4	85
3	**5d**: *p*-Cl	0.25	75	100	2	90	5	3	88
4a	**5e**: *p*-CO_2Me	0.25	120	100	7	85	5	3	
4b		1	30	100	3	89	7	1	84
5	**5f**: *o*-Et	0.25	75	99	6	89	2	2	78
6	**6a**: 2,3-$(Me)_2$-$C_6H_3NH_2$	0.25	60	97	6	86	4	1	82
7a	**6b**: 2,6-$(Me)_2$-$C_6H_3NH_2$	0.25	45	99	13	56	6	24	
7b		0.5	30	100		73	4	23	
7c		1	15	100	3	72	5	20	
8a	**5g**: *o*-CO_2Me	0.25	110	100	27	35	34	4	
8b		1	45	100	28	39	28	5	

[a] Molar ratio between **3a** and amines **5** or **6**. [b] Reaction conversion (%, by GC). [c] Mx: XC_6H_4NHMe. Dx: $XC_6H_4NMe_2$. Alkyls = the total amount of alkyl derivatives [XC_6H_4NHR and $XC_6H_4N(Me)R$, structures assigned by GC/MS] observed by GC. C = the total amount of carbamates [$XC_6H_4NHCO_2Me$ and $XC_6H_4N(Me)CO_2Me$, structures assigned by GC/MS] observed by GC. [d] Yield of *N*,*N*-dimethyl derivatives (Dx).

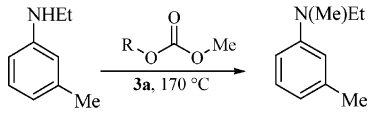
niline (**5g** and **6b**) were more complex: they not only proceeded slowly, but with a significant drop of the selectivity (S_{Dx} of 60−70%, entries 7a and 8a), which could not be compensated by using a higher amount of catalyst (entries 7b,c and 8b). In particular, the reaction of **5g** showed the formation of alkylated derivatives [ArN(R)Me and ArNHR], in 28−34% GC yields, while compound **6b** yielded up to 24% of carbamates [$ArNHCO_2$-Me and $ArN(Me)CO_2Me$, entry 7]. No clear reasons could account for this behavior.

At 170 °C, in the presence of ethyltriphenylphosphonium iodide (**3a**) as the catalyst, also *N*-ethyl *m*-toluidine (**7a**, 0.5 g), was reacted with the carbonate **1a**. In two subsequent experiments, the molar ratio **7a**/**1a**/**3a** was set to 1:2.2:0.25 (conditions i, same as entry 1 in Table 2) and to 1: 1.1: 0.1 (conditions ii), respectively. The two reactions showed the expected different rates (15 and 45 min, for conditions i and ii, respectively); in both cases however, the formation of *N*-ethyl-*N*-methyl-*m*-toluidine (**7b**) was observed in 88−90% amount (by GC) (Scheme 6). The *N*,*N*-dimethylation selectivity was still very high despite the steric hindrance around the secondary NH group of *N*-ethyl-*m*-toluidine. This also suggested that the different behavior observed for amines **5g** and **6b** (entries 7 and 8, Table 2) was due to *ortho effects* between the 2,6-Me_2 and *o*-CO_2Me substituents and the NH_2 function.

Unsymmetrical carbonates **1b**,**c** were tested as possible methylating agents of primary aromatic amines. In particular, the reactions of anilines **5a**−**c** (4.0 mmol) with compounds **1b**,**c** were investigated at 170 °C, in the presence of Ph_3PEtI (**3a**) as a catalyst (molar ratio **5**/**2**/**3a** = 1:2.2:0.25).

Table 3 discloses the results. For a more complete comparison, the table also includes data related to the reactions of amines **5a**−**c** with the carbonate **1a**.

SCHEME 6. *N*-Methylation of *N*-Ethyl-*m*-toluidine with Carbonate 1a



7a **7b**

2a: R = $MeO(CH_2)_2O(CH_2)_2O(CH_2)_2$

	7a:**2a**:**3a** (molar ratio)	t (min)	**7b** (Y%, GC)
i)	1: 2.2: 0.25	15	90
ii)	1: 1.1: 0.1	45	88

TABLE 3. Reaction of Aromatic Amines 1a−c with Unsymmetrical Carbonates 1a,b in the Presence of Ph_3PEtI[a]

entry	$XC_6H_4NH_2$ X =	$ROCO_2Me$[b]	*t* (min)	convn[c] (%)	products, % GC[d] Mx	Dx	alkyls	C
1	**5a**: *p*-MeO	**1a**	30	98		92	5	1
2		**1b**	35	100		91	7	2
3		**1c**	45	97	6	83	7	1
4	**5b**: *p*-Me	**1a**	30	100		94	5	1
5		**1b**	30	100	5	83	10	2
6		**1c**	85	99	7	79	8	5
7	**5c**: H	**1a**	60	99		89	6	4
8		**1b**	60	97	8	80	5	4
9		**1c**	100	97	7	77	5	8

[a] The molar ratio carbonate/substrate/Ph_3PEtI was 1:2.2:0.25. [b] **1a**: R = $MeO(CH_2)_2O(CH_2)_2O(CH_2)_2$. **1b**: R = $MeO(CH_2)_2O(CH_2)_2$. **1c**: R = $MeO(CH_2)_2$. [c] See footnote c of Table 2. [d] See footnote d of Table 2.

N,*N*-Dimethyl derivatives (Dx: $XC_6H_4NMe_2$, X = *p*-MeO, *p*-Me, and H) were the main products in all cases. Reaction rates were still sensitive to the electron-donating ability of the amine substituents (*p*-MeO ≥ *p*-Me > H). Though, the performance of carbonates **1b**,**c** was less satisfactory with respect to **1a**: both lower selectivities toward Dx (79−86%, entries 3, 5, 6, 8, and 9), and slower reactions (entries 3, 6, and 9) were observed, especially when 2-(methoxy)ethyl methyl carbonate (**1c**) was used. No obvious reasons could account for this behavior, but the different vapor pressures of compounds **1a**−**c** (see the Experimental Section) might play a role. At 170 °C, a vigorous refluxing was observed only when methylation reactions were carried out with the carbonate **1c**.

To examine possible interactions between the reactant amines and onium salts, IR spectra of pure *p*-anisidine and *p*-toluidine (**5a**,**b**) of salts Ph_3PEtI and *n*-Bu_4PBr (**3a**,**b**) and of equimolar mixtures of **5a** and **3a**, **5b** and **3a**, and **5b** and **3b**, were recorded at ambient temperature, on KBR pellets. Figure 2a,b shows only **5b** (black curve), **3a** (red curve), and the related mixture (blue curve). (Results for other systems are available in the Supporting Information).

Two regions of the IR spectra were enlarged to consider particularly the bands of asymmetric and symmetric N−H stretching modes (3417−3295 cm^{-1}) and of the C−NH_2 stretching modes (1280−1263 cm^{-1}) of *p*-toluidine.[11] In the first (N−H stretching modes, Figure 2a), the pure amine showed four major adsorption peaks at 3417, 3372, 3335, 3220 cm^{-1} (black curve); four signals were also present in the IR spectrum of the mixture **5b**/**3a**, but they appeared shifted to the right (at 3407, 3364, 3305, 3193 cm^{-1}) (blue profile) and with rather different shapes and intensities with respect to *p*-toluidine. A similar situation was already reported by us in the IR analysis of mixtures of benzylamine and onium salts.[9]

In the second region (C−NH_2 stretching modes, 1300−1250 cm^{-1}, Figure 2b), the pure amine showed two neat adsorption bands (at 1280 and 1263 cm^{-1}, black curve), while the mixture **5b**/**3a** displayed only a single peak (at 1283 cm^{-1}, blue profile).

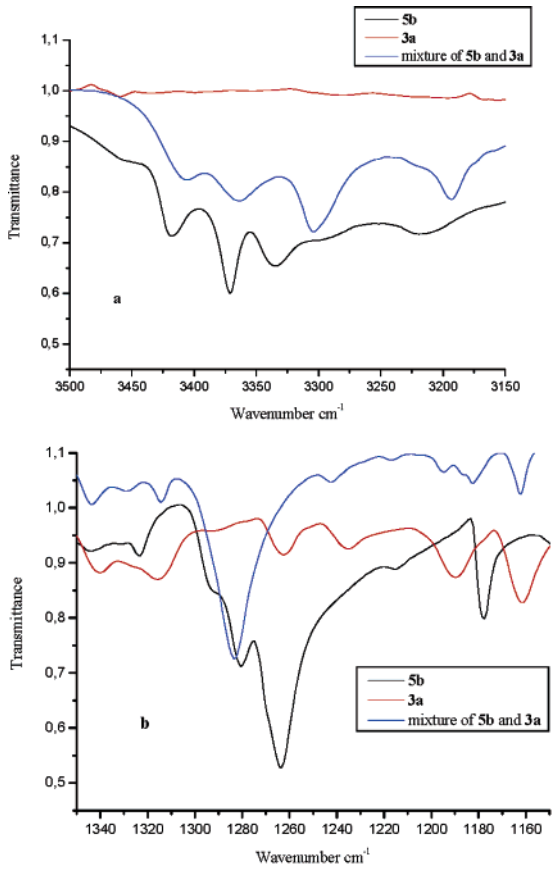


FIGURE 2. Overlap of IR spectra of pure *p*-toluidine (**5b**, black), pure Ph_3PEtI (**3a**, red), and a mixture of **5b** and **3a** (blue), recorded at room temperature: (a) enlargement between 3500 and 3150 cm^{-1}; (b) enlargement between 1350 and 1150 cm^{-1}.

It should be noted that the salt **3a** did not substantially adsorb between 3500 and 3150 cm^{-1} and between 1300 and 1220 cm^{-1} (Figure 2a,b, red profiles). The IR spectra of mixtures of **1a** and salts **3a** and **3b** were merely the overlap of those of the pure components.

This IR investigation indicated that vibrational modes of amines were perturbed by the onium salts. A similar situation was also reported by different authors for the adsorption of anilines over Lewis acidic materials such as aluminum halides.[11b,d] More recent NMR and UV investigations also demonstrated that an acid−base equilibrium can be detected between ionic liquids of the imidazolium type (e.g., [BMIM][BF_4]) and aliphatic amines.[12] An interaction between weak Lewis-acidic phosphonium salts and anilines, could account for these results, and for the selectivity observed in the reaction. Coordination of the bulky onium cation with the amine group of anilines, could increase the steric hindrance around the NH_2 and make the nucleophilic attack of the amine easier on the methyl rather than on the carbonyl carbon of the carbonate.[13]

To sum up, a general procedure is described for the *N*,*N*-dimethylation of aromatic amines, even deactivated by both steric or electronic effects, with methyl alkyl carbonates, catalyzed by phosphonium salts. The high methylation selectivity (S_{Dx} up to 96%) openly contrasts the behavior claimed for other methyl carbonates such as DMC and MPC (methyl phenyl carbonate), whose reactions with amines and Lewis-acidic catalysts, proceed with the exclusive formation of methyl carbamates ($RNHCO_2Me$, R = alkyl, aryl).[8,14]

The *green* features of the procedure should also be highlighted: although the reaction is quite energy intensive, it is a catalytic and a solventless process which shows an atom economy (AE) of 44% and a mass index (MI) of 4.8.[15] Both metrics are better than those of conventional methylating agents such as dimethyl sulfate (AE: 28%, MI: 18.5,[16]) and methyl iodide (AE: 41%, MI: 8.3,[17]).

Experimental Section

Carbonates **1a**−**c** were prepared following our previous procedures:[2d,e,h,8] transesterification of DMC (350 mL, 4.15 mol) was carried out with triethylene glycol, diethylene glycol, and ethylene glycol monomethyl ether in the presence of K_2CO_3 (DMC/alcohol/K_2CO_3 in a 7:1:1.5 molar ratio).

***N,N*-Dimethylation of Anilines.** In a 10 mL glass reactor equipped with condenser, a mixture of the amine (**5a**−**g**, **6a**,**b**, and **7a**: 4.0 mmol), the methyl alkyl carbonate (8.8 mmol; **1a**; 1.95 g; **1b**: 1.56 g; **1c**: 1.18 g), and an onium- or imidazolium-type salt (**3a**−**d** and **4a,b**; 0.1−1 molar equiv with respect to the reactant amine; Tables 1−3, Figure 1, and Scheme 6) was set to react at 115−170 °C, with stirring. At intervals, samples of the mixture were analyzed by GC and GC/MS. *N*,*N*-Dimethylanilines (compounds Dx of Tables 1−3) were then isolated by FCC.

Physical and spectroscopic properties of carbonates **1a**−**c** and of amines Dx are reproted in the Supporting Information. IR spectra (Figure 2) were recorded at room temperature on KBr disks.

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Supporting Information Available: ^1H and ^{13}C NMR of carbonates **1a**−**c**, ^1H NMR of *N*,*N*-dimethylanilines (Tables 1 and 2), and GC/MS spectrum of *N*-ethyl-*N*-methyl-*m*-toluidine. This material is available free of charge via the Internet at http://pubs.acs.org.

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