

The reaction of glycerol carbonate with primary aromatic amines in the presence of Y- and X-faujasites: the synthesis of *N*-(2,3-dihydroxy)propyl anilines and the reaction mechanism

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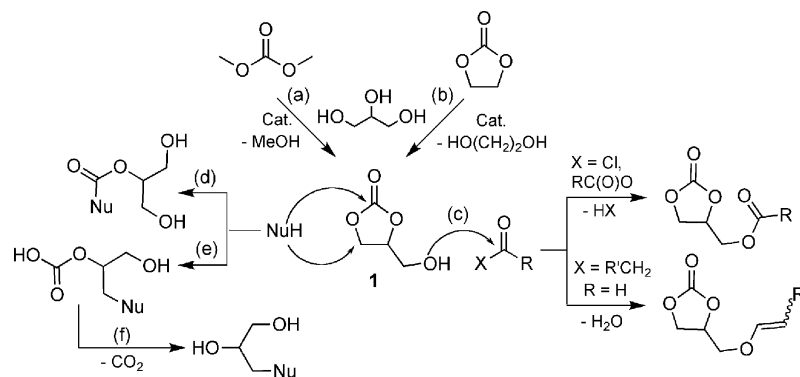
At 140 °C, in the presence of alkali metal exchanged faujasites, preferably NaY, as catalysts, glycerine carbonate (GlyC) is an efficient and green alkylating agent of primary aromatic amines (*p*-XC₆H₄NH₂, X = H, OMe, OH, Cl): the reaction takes place with a high conversion (~90%) and a good selectivity (80–90%) for the formation of *N*-(2,3-dihydroxy)propyl anilines (*p*-XC₆H₄NHCH₂CH(OH)CH₂OH). The alkylation process does not proceed through an exclusive nucleophilic substitution of anilines at the C5 position of GlyC. Evidence proves that a dehydrative condensation of anilines with GlyC produces intermediate species, and both transesterification and hydrolysis reactions are involved to obtain the final *N*-alkyl derivatives. A mechanism is proposed accordingly. Experiments show that faujasites are recyclable catalysts on condition that they are exposed to a mild thermal activation (70 °C, 18 mbar) prior to their re-use. Otherwise, if zeolites are calcined (400 °C, air), both the catalyst activity and the reaction selectivity drop. Isolated yields (60–65%) of *N*-(2,3-dihydroxy)propyl anilines are somewhat limited by the difficult separation of the unreacted GlyC and of the by-product glycerine. Nonetheless, the overall efficiency of the method is comparable to that of alternative routes based on highly toxic reagents (glycidol and aryl halides).

Introduction

In the past two decades, the increasing demand for biofuels, particularly biodiesel, has stimulated a great deal of research devoted to the chemistry of glycerol and, generally speaking, to its conversion to high added value chemicals.¹ Glycerol, in fact, is the major co-product in the industrial production of biodiesel:² according to a recent estimation, the sole European market will receive some additional 1.0 × 10⁶ t y⁻¹ of pure glycerol by 2010.³ This impressive number (almost tripled since 2005)⁴ means there

is an urgent need to discover and develop innovative methods for the use of glycerol itself or of its derivatives.

In this context, due to our long standing interest for eco-friendly reagents and solvents of the class of organic carbonates,⁵ our attention has been caught by glycerol carbonate (GlyC, **1** = 4-hydroxymethyl-1,3-dioxolan-2-one, Scheme 1). This compound is prepared through the transesterification of dimethyl carbonate (DMC) or ethylene carbonate with glycerol (Scheme 1, paths (a) and (b), respectively).^{2,6} In particular, path (a) represents a genuine green synthesis where the reaction of a renewable material (glycerol) and a non toxic compound (DMC)⁷ is performed catalytically and in the absence of added solvents. Methanol is the only co-product. GlyC finds applications in different sectors. It is used as a solvent for varnishes, colours, cosmetics, and pharmaceuticals,^{3,8} while its prominent



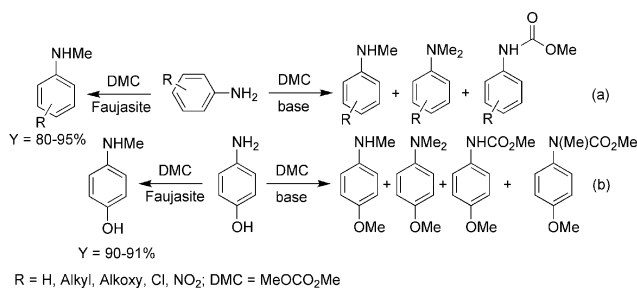
Scheme 1 The synthesis and the multiple reactivity of GlyC.

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role as a reagent is in the fabrication of multi-functional carbonate-based polymers.^{6–9} Paths (c)–(f) of Scheme 1 illustrate the multiple reactivity of GlyC.

The oxygen atom of the hydroxymethyl function of GlyC serves as a nucleophile, while both carbonyl and alkyl carbon atoms (C2 and C5, respectively) show a typical electrophilic character.¹⁰ For example, GlyC reacts with carboxylic acid derivatives or aldehydes (XCOR) to yield the corresponding esters or enol ethers (path (c));¹¹ on the other hand, the reactions of different nucleophiles (NuH: phenols, alcohols, aliphatic amines) with GlyC form both carboxyalkylated and alkylated products (paths (d) and (e), respectively), which, eventually, may lose CO₂ (path (f)).

Although this versatile reactivity opens a variety of synthetic perspectives, it poses the problem of controlling the product distribution. An analogous situation is observed also with light dialkyl carbonates, Scheme 2 exemplifies the case of the reaction of dimethyl carbonate (MeOCO₂Me, DMC) with primary aromatic amines.⁵

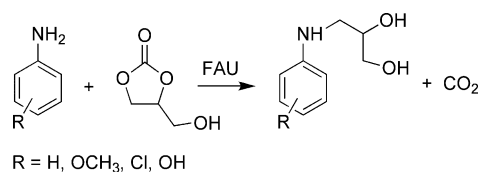


Scheme 2 The product distribution for base- and zeolite-catalysed reactions of DMC with primary aromatic amines.

In the presence of a base catalyst (*e.g.* an alkaline carbonate), anilines react with DMC to produce mixtures of methylanilines and carbamates (path (a), top right). The reaction selectivity is even less satisfactory if an ambident nucleophile, such as *p*-aminophenol, is used (path (b), bottom right): not only do methylation and carboxymethylation take place at the amine function, but the OH group is methylated as well.^{5d} This outcome, however, is dramatically affected by the nature of the catalyst used. When the transformations of Scheme 2 are carried out over alkali metal exchanged faujasites (*e.g.* NaY or NaX, FAU) as catalysts,¹² the exclusive formation of mono-*N*-methylanilines is observed (Scheme 2, paths (a) and (b) top and bottom left, respectively).¹³ Both the alkylation selectivity and the chemoselectivity of the overall process are efficiently controlled by faujasites: neither bis-*N*-methylations nor side-reactions of other nucleophilic terms of ambident amines take place.

These results prompted us to investigate whether NaY and NaX zeolites could be used to exploit the electrophilic reactivity of glycerol carbonate as well. Accordingly, the reaction of GlyC with primary aromatic amines has been investigated in the presence of faujasites as catalysts. This paper reports that these zeolites are not only efficient catalysts for the process, but they are also able to direct the reaction chemoselectivity towards the formation of *N*-alkyl derivatives, namely *N*-(2,3-dihydroxy)propyl anilines (Scheme 3).

The reaction, however, does not proceed exclusively as a direct nucleophilic substitution at the C5 position of GlyC:



Scheme 3

evidence proves that an intermediate species is formed and that both transesterification and hydrolysis reactions are involved to obtain the final product. A mechanism has been proposed to discuss this reactivity scheme.

Results

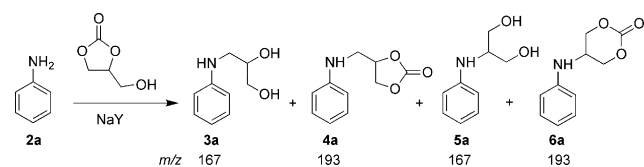
GlyC as an alkylating agent of aniline

The reaction of GlyC with aniline (**2a**) was chosen as a model to begin the study. Four different faujasites (FAU) were used as catalysts; three of them, namely NaY_A, NaY_S and NaX, were commercially available compounds (from Aldrich and Strem, respectively), while the fourth specimen was a LiY zeolite prepared through an ionic exchange reaction from NaY_A.¹⁴ The relative amounts of reactants and of the catalysts were defined according to our previously reported procedures on the alkylation of primary aromatic amines with dialkyl carbonates.⁵ Initially, a mixture of aniline (0.5 g, 5.4 mmol), and GlyC (0.76 g, 6.5 mmol) was set to react at different temperatures (90, 110, 140, and 160 °C) in the presence of the NaY_A faujasite (the weight ratio, $Q = \text{NaY}_A : \mathbf{2a}$ was 1.5). Due to the relatively high viscosity of GlyC, diethyleneglycol dimethylether (MeO(CH₂)₂O(CH₂)₂OMe, diglyme, 2 mL) was used as a co-solvent to allow a uniform stirring of the reacting slurry.¹⁵

Then, at 140 °C, the same procedure was repeated with the other catalysts, NaY_S, LiY, and NaX (the weight ratio, $Q = \text{FAU} : \mathbf{2a}$ was 1.5).

All experiments were run twice, at ambient pressure, in an open vessel.

The reaction mixtures were analysed by GC-MS after 2 and 4 hours, respectively. Four products were observed (**3a–6a**, Scheme 4); the two major derivatives (**3a** and **4a**) were isolated and fully characterised by ¹H and ¹³C NMR, while the structure of minor compounds **5a** and **6a** was assigned from their MS spectra.¹⁶ The results are reported in Table 1.



Scheme 4

In the presence of the NaY_A faujasite, as the temperature was raised from 90 to 160 °C, the reaction conversion increased smoothly up to a substantially quantitative value (96%, entry 6). *N*-(2,3-dihydroxy)propyl aniline (**3a**) was always the main product up to a maximum of 74% at 160 °C (4 h, entry 6). The formation of compound **4a** was also significant: at a moderate conversion (50%), **4a** was present in an amount comparable to

Table 1 The reaction of aniline with GlyC in the presence of different faujasites^a

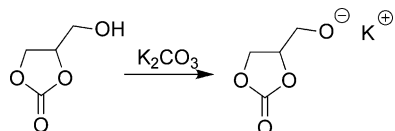
Entry	FAU	$S_A/m^2\text{ g}^{-1b}$	$T/^\circ\text{C}$	t/h	Conv. (%) ^c	Products (% GC) ^c			
						3a	4a	5a	6a
1	NaY _A	748	90	2	18	11	7	—	—
2			110	2	50	23	22	4	1
3			140	2	79	47	31	—	1
4				4	93	64	27	1	1
5			160	2	92	66	24	2	—
6				4	96	74	18	2	2
7	NaY _S	900	140	2	85	45	33	4	3
8				4	89	58	23	4	4
9	LiY	— ^d	140	2	84	51	29	3	1
10				4	94	54	24	6	2
11	NaX	n.a. ^e	140	2	13	—	12	—	—
12				4	22	—	20	—	2

^a All reactions were carried out in the presence of diglyme (2 mL) as solvent. The molar ratio GlyC : **2a** was 1.2, while the weight ratio FAU : **2a** was 1.5. ^b Surface area of faujasites. ^c Each experiment was repeated twice, the values for conversions and amounts of products (% determined by GC) were the average of two runs that did not differ by more than 5–7%. ^d LiY was obtained by an ionic exchange reaction from NaY_A. Entry 10: an unidentified product (8%, GC) was observed. ^e Not available.

that of **3a** (**3a** and **4a**, 23 and 22%, respectively; entry 2). As the reaction proceeded further, the ratio **4a** : **3a** dropped considerably (entries 4–6, **4a** : **3a** = 0.24–0.42). In all cases, the total quantity of compounds **5a** and **6a** was in the range of 1–5% (entries 1–6). At 140 °C, an additional experiment was carried out for 4 h under an inert (N₂) atmosphere, and both the conversion (91%) and the product distribution (**3a**, 62% and **4a**, 27%) were not substantially different to those reported in Table 1 (entry 4).

The activity of other Y zeolites (NaY_S and LiY) was similar to NaY_A: after 4 hours at 140 °C, the range of aniline conversions was 89–94% (entries 8 and 10). These reactions, however, yielded a higher formation of both compounds **5a** and **6a** (8% in total) and, in the case of LiY, of a not identified by-product (8%, footnote d, Table 1). Under the same conditions, the NaX zeolite was much less efficient: the conversion was only 22% and a mixture of **4a** and **6a** (20 and 2%, respectively) was obtained (entry 12).

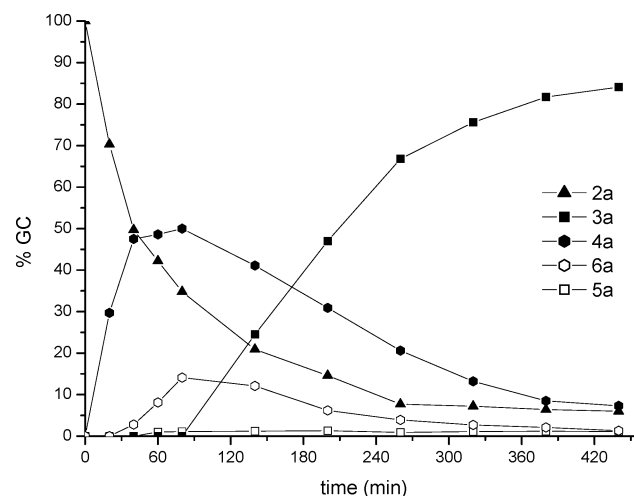
An additional experiment was carried out by using K₂CO₃ as a base catalyst.¹⁷ Under conditions analogous to those reported in entries 3–4 (Table 1), aniline (0.5 g, 5.4 mmol) and GlyC (0.76 g, 6.5 mmol) were set to react at 140 °C in the presence of K₂CO₃ (0.75 g, 5.4 mmol) and diglyme (2 mL). The mixture rapidly turned to a white thick slurry, plausibly due to the precipitation of a GlyC-derived alcoholate (Scheme 5).¹⁸

**Scheme 5**

Then, a very sluggish reaction was observed: after 4 hours, the conversion of aniline was 12% and compound **4a** was the sole product.

The investigation was continued with the use of only NaY_A as a catalyst. In order to clarify the product distribution, an additional reaction was carried out at 140 °C, and it was monitored (by GC-MS) at different time intervals. The conditions were those of entries 3–4 of Table 1, except for the *Q*

ratio (NaY_A : **2a**) which was slightly diminished from 1.5 to 1.¹⁹ Fig. 1 reports the results.

**Fig. 1** The profile of the reaction of aniline with GlyC carried out at 140 °C in the presence of NaY_A as a catalyst (*Q* = 1).

The analysis of the kinetic profile showed three main aspects: (i) a good selectivity (up to 90%) could be achieved towards the alkyl derivative **3a**, the amount of this compound increased progressively with time until it reached a rather constant value (~85%) after 430 min; (ii) products **4a** and **6a** followed a typical intermediate-like behaviour, their concentrations went up to a maximum (**4a**: ~50%, **6a**: 15%) in the first 120 min and then they dropped to less than 10% (**4a**) and 3% (**6a**) as the reaction proceeded further; (iii) the amount of **5a** was always very low (1–3%).

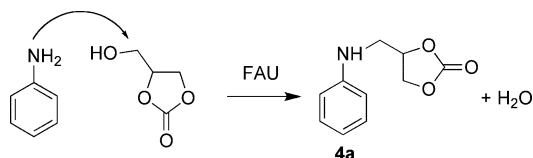
Fig. 1 therefore suggested that the desired product (**3a**) was not obtained through an exclusive nucleophilic substitution of aniline at the C5 position of GlyC. The intriguing feature was the presence of compounds **4a** and **5a**, particularly **4a**, which apparently formed and disappeared in favour of *N*-(2,3-dihydroxy)propyl aniline (**3a**). Accordingly, a set of new experiments was devised to study the reactivity of **4a**, **5a** and

6a as such and of other plausible co-products in the reaction mixture.

Investigation of the reaction mechanism

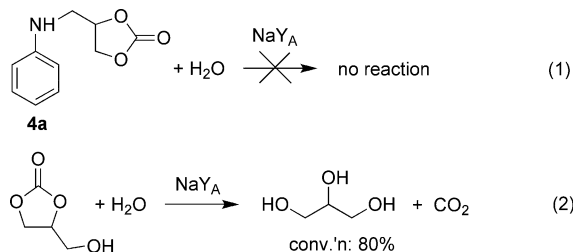
First, compounds **4a**, **5a** and **6a** had to be isolated. Aniline (0.5 g, 5.4 mmol) was set to react with GlyC under the conditions of Fig. 1 (140 °C, $Q = 1$). After 90 min, the reaction was stopped at a 71% conversion, when **4a**, **5a** and **6a** were present in 48, 13 and 4% amounts, respectively. The work up of the mixture was performed by flash column chromatography (FCC) on silica gel using a gradient elution with petroleum ether/ethyl acetate solutions. Compound **4a** (0.42 g, 2.17 mmol) was isolated in a 40% yield. Unfortunately, both **5a** and **6a** were not obtained, not even in trace amounts; all subsequent experiments carried out to separate these derivatives by FCC with eluants of different polarity were always unsuccessful.

Compound **4a** was plausibly formed by the direct condensation of aniline with GlyC (Scheme 6), this hypothesis was corroborated by the fact that very similar reactions were catalysed by alkali metal exchanged faujasites. For example, the dehydration of benzyl alcohol to dibenzyl ether took place at a high temperature (200 °C) over NaY.²⁰ This observation prompted us to examine the role of the co-product water (Scheme 6) to promote hydrolytic processes of carbonate-like derivatives **4a** and **6a**, and of GlyC itself, in the presence of faujasites as catalysts.



Scheme 6

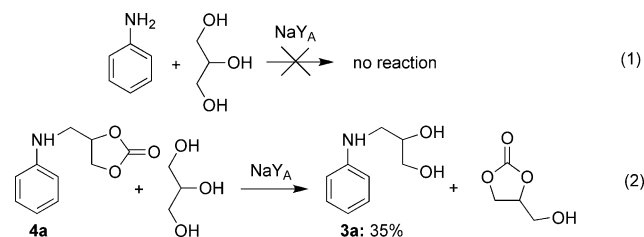
The reactions of both **4a** and GlyC with water were carried out under conditions similar to those reported on entries 3–4 of Table 1. At 140 °C, a mixture of **4a** or GlyC (**4a**: 0.2 g, 1.0 mmol; GlyC: 0.76 g, 6.5 mmol), was set to react with water (20–120 μ L; the molar ratio (W) H_2O : **4a** and H_2O : GlyC was 1), in the presence of NaY_A faujasite (the weight ratio NaY_A : substrate was 1.5), and diglyme (1 mL) as a solvent. Experiments were run for 5 hours. The results are reported in Scheme 7.



Scheme 7

Compound **4a** proved to be quite stable to hydrolysis: the GC-MS analysis of the mixture showed no reaction (eqn (1), Scheme 7). On the contrary, glycerine carbonate was substantially hydrolysed to glycerol (eqn (2), Scheme 7): the ¹H NMR spectrum of the mixture indicated that the reaction proceeded

with a conversion of 80%. This last finding along with Scheme 6 suggested that glycerol was a plausible co-product of the reaction of aniline with GlyC.²¹ If so, the investigation of the direct reactions of glycerol (Gly) with both aniline and **4a** appeared worthwhile. At 140 °C, a mixture of aniline or **4a** (aniline: 0.5 g, 5.4 mmol; **4a**: 0.2 g, 1.0 mmol) was set to react with glycerol (0.58–0.32 g; the molar ratio Gly : aniline and Gly : **4a** was 1.1 and 3.5, respectively) in the presence of NaY_A faujasite (the weight ratio NaY_A : substrate was 1.5) and diglyme (1 mL) as a solvent. Experiments were run for 5 hours. The results are reported in Scheme 8.



Scheme 8

Although the NaY zeolite was plausibly able to catalyse the dehydrative condensation of aniline with GlyC (Scheme 6), the analogous reaction of aniline with glycerol was not allowed and the amine was recovered unaltered (eqn (1), Scheme 7). Instead, compound **4a** gave a clean transesterification reaction to produce *N*-(2,3-dihydroxy)propyl aniline (**3a**) in a 35% yield (eqn (2), Scheme 7). This last result suggested we examine whether an external addition of glycerol affected the overall reaction outcome. Accordingly, at 140 °C, aniline was set to react with GlyC under the conditions of Fig. 1. After 60 min, glycerol (0.25 g, 2.7 mmol; this amount was adjusted to have a Gly : **4a** molar ratio of ~1) was introduced in the reaction mixture. The reaction profile is reported in Fig. 2.

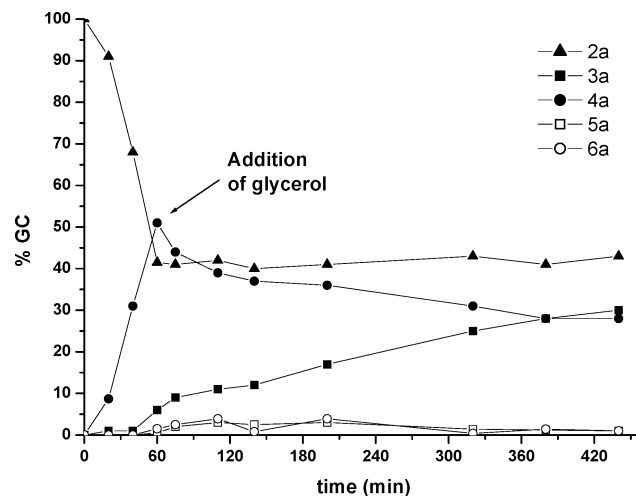


Fig. 2 The reaction of aniline and GlyC with added glycerol.

The addition of glycerol had two significant effects: (i) the conversion of aniline stopped abruptly at ~60%. Aniline did not react anymore even for a prolonged reaction time (7.5 h).²² (ii) The concentration profiles of **3a** and **4a** showed an initial sharp increase and decrease, respectively (between 60 and 120 min).

Then, the further slow consumption of **4a** was the mirror image of the formation of the product **3a**. In other words, once Gly was added, the transesterification of **4a** to **3a** (eqn (2), Scheme 8) was the sole observed process.

Overall, this analysis indicated that faujasites, particularly NaY, were not only effective catalysts for the desired process, but they also addressed the final selectivity by tuning the distribution of products in the reactions of Schemes 5–8.

Loading and recycling of the catalyst

To detail the effect of the catalyst loading, the reaction of aniline with GlyC was examined in the presence of different amounts of NaY_A. Under the conditions of entries 3–4 of Table 1 (140 °C, GlyC : aniline molar ratio $W = 1.2$, diglyme (2 mL) as solvent), the experiments were carried out for 5 hours, by varying the NaY_A : aniline weight ratio (Q) in the range of 0.2–2. The results are reported in Fig. 3, in which the conversion of aniline and the selectivity towards product **3a**,²³ both determined through GC-MS analyses, are plotted *versus* the Q ratio.

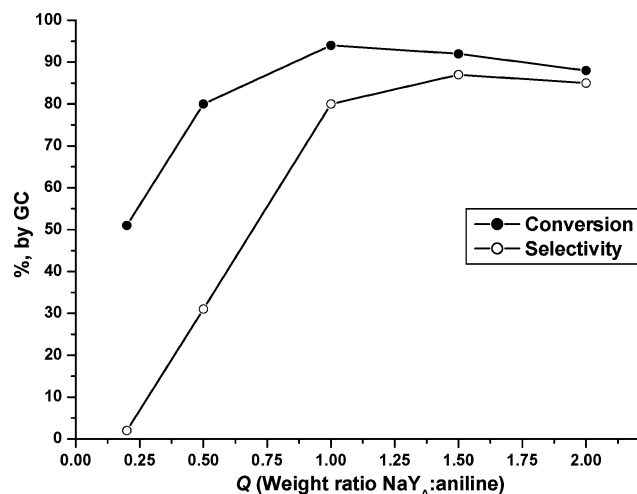


Fig. 3 Trends for conversion and selectivity towards product **3a** in the presence of different amounts of NaY_A catalyst.

The conversion of aniline (C) and the selectivity for **3a** (S_{3a}) showed a similar trend. Both parameters increased substantially (C from 50 to 92%; S_{3a} from 2 to 80%) as the Q ratio was augmented from 0.2 to 1. Then, a further increase of the catalyst amount ($1.5 < Q < 2$) had only minor effects: the conversion remained rather constant at ~90% and the selectivity slightly increased up to 85%. Apparently, after 5 hours, the rate of consumption of both aniline and compound **4a** (to produce the final product **3a**) were not significantly improved at $Q \geq 1$.

Finally, two sets (A and B) of recycling experiments were carried out. In the first set (A), the reaction of aniline with GlyC was run under the conditions of entries 3–4 of Table 1 (140 °C, $W = 1.2$, $Q = 1.5$) for 4 hours. Then, the catalyst (NaY_A) was filtered, thoroughly washed with MeOH, and dried under vacuum (70 °C, 18 mbar, overnight). The recovered zeolite was re-used under the conditions above described (entry 3, Table 1). The cycle of activation/reaction was repeated once more. In the second set (B), the operating conditions were identical to those of set A, except for the fact that both the fresh and the recycled

faujasite was calcined at 400 °C in an dried air stream before its use. All reaction mixtures were analysed by GC-MS after 4 hours. Fig. 4A and B report the results for the experiments of sets A and B, respectively.

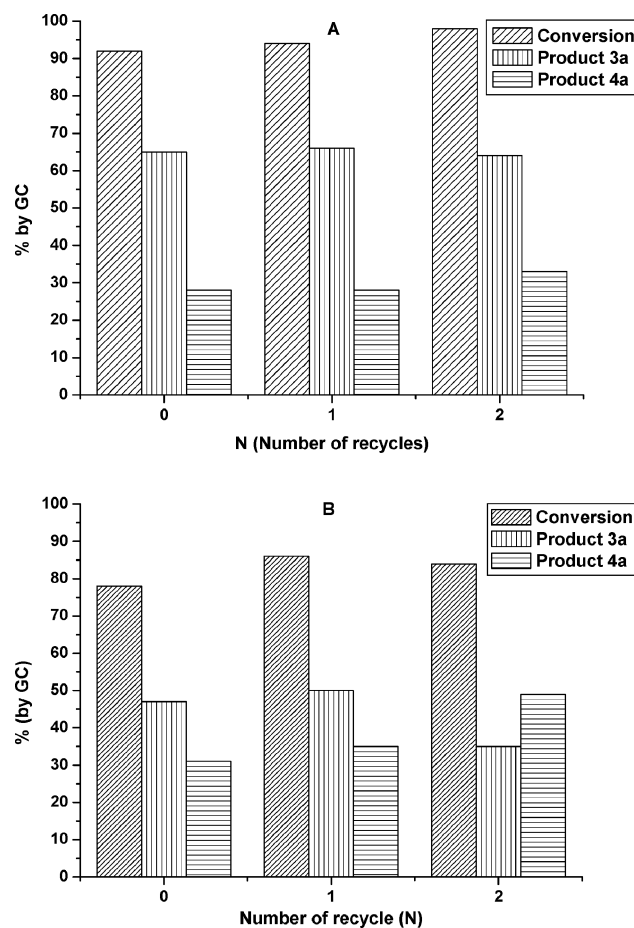


Fig. 4 The recycling of the NaY_A faujasite. (A) Data refer to a not calcined catalyst (set A). (B) Data refer to a calcined catalyst (set B). All reactions were carried out for 4 hours at 140 °C.

The conversion of aniline and the % amounts of the major products (**3a** and **4a**) were plotted against the number of recycles (N). To complete the view, Fig. 3A and B also illustrate the data related to the fresh catalyst ($N = 0$).

The reaction conversion (C) did not change appreciably with the number of recycles, but it was affected by the thermal treatment of the catalyst: the C values ranged between 92–97% and 80–85% for the experiments of the set A (not calcined faujasite, Fig. 4A) and of the set B (calcined faujasite, Fig. 4B), respectively. The product distribution was even more sensitive to the handling of the zeolite before the reaction: the ratio **3a** : **4a** was rather constant (2.0–2.3) during the recycling of the not calcined catalyst (Fig. 4A), while it dropped considerably from 1.5 to 0.6 (with the increase of N) in the case of the calcined zeolite (Fig. 4B). Additional experiments were carried out to further investigate these aspects. Since the calcination was expected to remove large amounts of water adsorbed in the catalyst,²⁴ a gravimetric analysis was carried out on two identical fresh samples of NaY_A (3.0 g). It was found that the water loss (by weight) was 23% and 9% after the solids were calcined

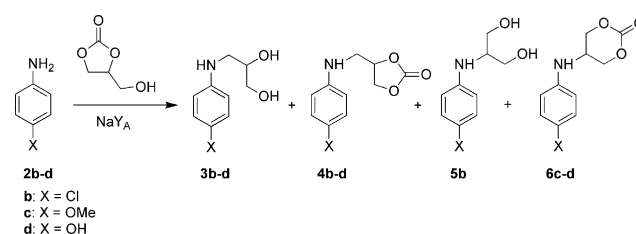
(400 °C, dried air, 4 h, 80 mL min⁻¹) and evacuated at 70 °C (18 mbar, overnight), respectively. The calcined sample was then allowed to stand in the open air (rt, 8 h) until it recovered its original weight. The solid was dried mildly under vacuum (70 °C, 18 mbar, overnight) and, finally, it was re-used to catalyse the reaction of aniline and GlyC under the conditions of entry 3, Table 1. After 4 h at 140 °C, the conversion was 90% and the ratio **3a** : **4a** was 1.9, in line with the results of Fig. 4A. In other words, two facts emerged: (i) the calcination of the faujasite produced a negative effect on both the reaction conversion and on the disappearance of the intermediate compound **4a**; however, (ii) if the calcined solid was allowed to recover its original level of hydration, then the catalytic activity was substantially restored.

Reactivity of other anilines and the isolation of the corresponding *N*-(2,3-dihydroxy)propyl-derivatives

The reaction of GlyC with other primary aromatic amines such as *p*-chloroaniline, *p*-anisidine, and *p*-aminophenol (*p*-XC₆H₄NH₂; **2b**: X = Cl, **2c**: X = MeO, **2d**: X = OH), was examined in the presence of the NaY_A faujasite. The reaction conditions were similar to those used for aniline (Table 1, entry 4), except for the temperature and the reaction time: these parameters were chosen after a preliminary screening of the reactivity of compounds **2b–d**. In addition, to test whether these transformations could be scaled up, all experiments were carried out starting from both ~0.6 and ~2.5 g of each amine. Accordingly, a mixture of the primary amine (5.4 or 21.5 mmol; **2b**: 0.69 or 2.64 g, **2c**: 0.66 or 2.71 g, **2d**: 0.59 or 2.39 g), GlyC (the molar ratio *W* for GlyC : **2** was 1.2), was set to react in the presence of NaY_A (the weight ratio *Q* for NaY_A : **2** was 1.5) and diglyme (2 or 8 mL) as solvent. The temperature was 170, 160, and 140 °C for **2b**, **2c**, and **2d**, respectively. The reaction mixtures were analysed by GC-MS.

Up to three products were observed for each of the reactant substrates (**3–6**, Scheme 9).

Once the reactions on the larger scale (21.5 mmol of **2b–d**) were finished, the major derivatives (**3b–d**) and compound **4c** were isolated by FCC. These products were fully characterised by ¹H and ¹³C NMR. The structure of other compounds **4b**, **5b**, **6c**, **4d**, and **6d** was assigned from their MS spectra.²⁵ To complete this investigation, the reaction of aniline with GlyC was also carried out on a 2.0 g scale (**2a**: 21.5 mmol), at 140 °C. The



Scheme 9

corresponding derivative **3a** was isolated by FCC. The results are reported in Table 2.

All the tested amines gave the corresponding *N*-(2,3-dihydroxy)propyl-derivatives **3a–d**. However, *p*-anisidine (**2b**) and especially *p*-chloroaniline (**2c**) required more severe conditions (entries 1–4): both higher temperatures (160–170 °C) and longer reaction times were necessary with respect to *p*-aminophenol (**2d**) and aniline (**2a**) (entries 3–4). For example, in the reaction of **2b** (5.4 mmol), the conversion was only 69% after 22 hours at 170 °C (entry 1). The reaction time was also dependent upon the starting amount of the amines: regardless of the temperature, the large-scale transformations were considerably longer than the low-scale ones (amines: 21.5 and 5.4 mmoles, respectively; compare entries 1–2, 5–6, and 7–8).

Finally, the isolated yields of compounds **3a–d** did not exceed 65% (entries 2, 4, 6, and 8). During the flash column chromatography (gradient elution: petroleum ether/ethyl acetate from 9 : 1 to 1.9 v/v), the desired products were partly co-eluted with the residual GlyC and glycerine. Experimental conditions were not further investigated to improve the separation technique.

Discussion

Comparison of different catalysts

Table 1 and Fig. 1 clearly indicate that alkali metal exchanged faujasites, especially of the Y type, are good catalysts for the investigated reaction. To our knowledge, this is the first ever reported case in which zeolites are claimed to promote the *N*-alkylation reaction of aromatic amines with glycerol carbonate. Faujasites are often described as amphoteric solids whose acid–base features are tuned by both the Lewis acid character

Table 2 The reaction of GlyC with different amines **1a–d** catalysed by the faujasite NaY_A^a

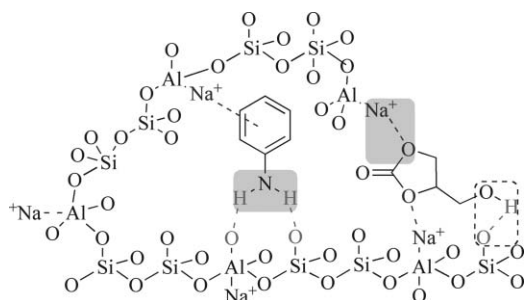
Entry	Substrate		<i>T</i> /°C	<i>t</i> /h	Conv. (%) ^b	Products (% , CG)				Yield (3 , %) ^c
	<i>p</i> -XC ₆ H ₄ NH ₂	Initial amount/mmol				3	4	5	6	
1	2b : X = Cl	5.4	170	22	69	65	3	1	—	—
2		21.5	170	72	45	34	9	—	—	13
3	2c : X = OMe	5.4	160	6	90	73	10	—	7	—
4		21.5	170	7	86	64	22	—	—	61
5 ^d	2d : X = OH	5.4	140	5	88	75	8	—	1	—
6 ^d		21.5	140	22	78	65	7	—	1	61
7 ^e	2a : X = H	5.4	140	7	93	84	6	1	—	—
8		21.5	140	16	88	80	8	—	—	65

^a All reactions were carried out in the presence of diglyme (2 mL: entries 1, 3, and 5; 8 mL: entries 2, 4, and 6) as solvent. The molar ratio GlyC : **2a–d** was 1.2, while the weight ratio NaY_A : **2a–d** was 1.5. ^b The reaction conversion was determined by GC-MS analyses. ^c The isolated yields of crude products **3a–d** were evaluated after the FCC separation. ^d Entries 5 and 6, 4 and 5% of unidentified by-products, respectively. ^e Data taken from Fig. 1.

of their metal ions (often Na^+ , Li^+ , K^+ , and Cs^+) and the basic nature of the oxygen atoms of the aluminosilicate framework.²⁶ In particular, the basicity of oxygen atoms is controlled by the Si/Al ratio (ranging from 1.0–1.5 to 1.5–3.0 for X and Y type, respectively) of the solid: in the presence of the same cation, X-faujasites are more basic than the Y- ones. This behaviour plausibly accounts for the striking diversity shown in Table 1, where NaY is, by far, more active than NaX (entries 3–4 and 11–12).²⁷ The trend seems further substantiated by the use of K_2CO_3 : this base catalyst is even less efficient than NaX (Scheme 5).²⁸ Finally, the minor differences observed between the Y-type zeolites (NaY_A , NaY_S , and LiY : entries 3–4, 7–8, and 9–10) may be attributed to a slight variation of both the Lewis acidity and the surface area (748–900 $\text{m}^2 \text{g}^{-1}$) of the solids.

The reaction mechanism

Anilines and dialkyl carbonates diffuse within the polar cages (supercavities) of zeolites and are there adsorbed primarily through two modes of interaction: (i) H-bonds between NH_2 groups and oxygen atoms of the lattice, and (ii) acid–base reactions of the metal cations on the surface of the solid with both the aromatic rings of amines and the carbonate fragments of dialkyl carbonates.²⁹ In a similar fashion, also the OH functions of alcohols undergo H-bonds with faujasites to form alcoholate-like species.³⁰ Scheme 10 depicts the overall pattern of adsorption for the model case of aniline and glycerine carbonate on a Na-faujasite: both H-bonds and acid–base reactions are highlighted.³¹



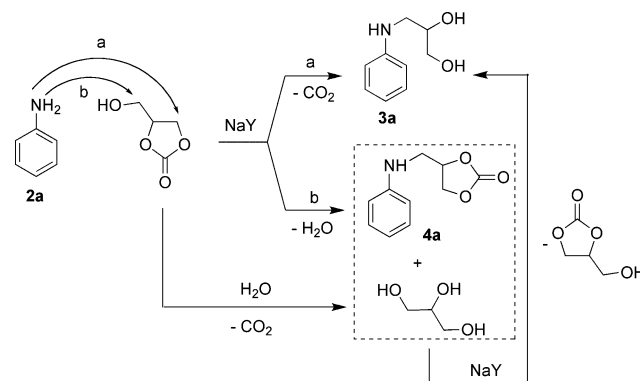
Scheme 10 Pictorial view of the adsorption of aniline and glycerine carbonate over a Na-faujasite.

This complex network of interactions implies that the aromatic amine and GlyC experience a nucleophilic (shaded section, left) and an electrophilic (shaded section, right) activation, respectively. Accordingly, two reactions are favoured: (i) the NH_2 group is assisted to attack GlyC through a $\text{S}_{\text{N}}2$ reaction occurring preferably at the less hindered C5 position of the cyclic carbonate.³² Compound **3a** and CO_2 are directly produced (Scheme 3); (ii) water, co-adsorbed on the faujasite,³³ initiates the hydrolysis of GlyC at its C2 position (carbonyl carbon) to form glycerol (eqn (2), Scheme 7). The difference in the size and possibly in the requisites of adsorption of aniline and water mostly account for the fact that the reaction of aromatic amines at the carbonyl carbon of GlyC is forbidden. This reflects an even more general trend observed in the reactions of anilines with dialkyl carbonates catalysed by faujasites: these transformations never produce carbamates (ArNHCO_2R).^{5,34}

Water entrapped in the catalyst can play a further role: it may allow the protonation of the alcoholate-like moiety derived from GlyC (dashed section, Scheme 10) to favour the $\text{S}_{\text{N}}2$ process for the formation of compound **4a** (Scheme 6). This compound (**4a**) in turn displays a peculiar reactivity: (i) despite a carbonate structure, its hydrolytic cleavage does not occur in contrast to what observed for GlyC (Scheme 7: compare eqn (1) and (2)). This behaviour has presently no clear reasons, though different modes of adsorption of the two carbonates (**4a** and GlyC) at the catalyst surface might be considered. (ii) Compound **4a** acts as a typical intermediate species: once formed, it is consumed through its reaction with glycerol to produce *N*-(2,3-dihydroxy)propyl aniline (**3a**) as the final derivative (eqn (2), Scheme 8). It should be noted here that faujasites are catalysts for transesterification processes even when bulky electrophiles (*i.e.* triglycerides) and different alcohols including glycerol are used.³⁵ Nonetheless, Fig. 2 clearly indicates that the direct addition of glycerol to the reacting mixture of aniline and GlyC does not help the overall process. The competitive adsorption of glycerol at the polar surface of the faujasite catalyst³⁶ inhibits the conversion of aniline.

Finally, the lack of direct condensation between aniline and glycerol (eqn (1), Scheme 8) is plausibly due to relatively modest reaction temperature: in the presence of zeolites or acid solids as catalysts, the dehydration of glycerol usually takes place at $T \geq 250$ °C, preferably over 300 °C.³⁷

The reaction mechanism of Scheme 11 sums up all these considerations.



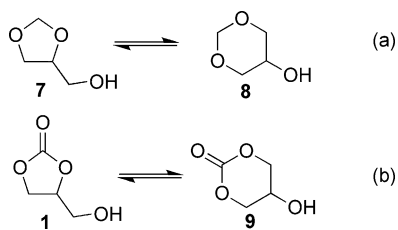
Scheme 11 The reaction mechanism.

This hypothesis should also assume that the rates for the formation and the consumption of glycerol are balanced to avoid its accumulation in the reaction mixture. Otherwise, the conversion of aniline would stop (Fig. 2).

Other reaction intermediates/products

The structure of compounds **5a** and **6a** has been proposed from the analysis of the MS spectra (Scheme 4 and Fig. 1). A further support to the formation of these products can be offered by the behaviour of glycerol formal (GlyF). It is well known that GlyF exists in an equilibrium mixture of two cyclic acetal alcohols, such as 4-hydroxymethyl-1,3-dioxolane and 5-hydroxy-1,3-dioxane (**7** and **8**, respectively) (Scheme 12a).³⁸

The similarity between the structures of GlyF and GlyC suggests the occurrence of an analogous equilibrium, also for



Scheme 12

the case of GlyC, involving a six-membered cyclic isomer of **1** (compound **9**, Scheme 12b). If so, the reaction of such a carbonate (**9**) with aniline would substantiate the presence of both products **5a** and **6a**. A more in-depth NMR investigation of commercial samples of GlyC is currently under progress to corroborate this hypothesis.³⁹ Once the structures of **5a** and **6a** will be confirmed, their reactivity, particularly the unexpected intermediate-like behaviour of **5a** (Fig. 1), will be examined.

The catalytic activity and the recycling of the faujasite

In the presence of NaY_A, Fig. 3 shows that the conversion of aniline (**C**) and the selectivity for compound **3a** (*S*_{3a}) reach rather constant values (~90% and ~80%, respectively), once the weight ratio (*Q*) NaY_A : aniline is ≥ 1. One may conclude that at *Q* ≥ 1, the reactants no longer saturate all active sites of the zeolite and, consequently, both the decay of aniline and the reactions involving other species (Scheme 11) plausibly proceed at the maximum rate allowed by the reaction conditions. Hence, the conversion and the product distribution (selectivity) must level off.

The comparison of Fig. 4A and B clearly indicates that the NaY_A faujasite can be re-used after a mild thermal treatment (heating at 70 °C, under vacuum, Fig. 4A), but the activity of the zeolite drops if it is recycled after calcination at 400 °C (Fig. 4B). All faujasites are rather thermally stable materials; therefore, no morphological-structural variations are induced by thermal treatments below or at 400 °C.⁴⁰ In addition, experimental evidence proves that the efficiency of the calcined catalyst is significantly restored once the solid is allowed to recover its original level of hydration.⁴¹ These observations give a further support to the mechanism proposed in Scheme 11: the extensive removal of water from the catalyst (calcination) affects both the hydrolytic cleavage of GlyC and the formation of the intermediate **4a**, so that the overall process is disfavoured.

Doetschman *et al.*⁴⁰ have observed a similar behaviour also in the hydrolytic decomposition of phosphonate esters catalysed by a NaX faujasite. In this case, an increase of the catalytic activity was obtained once a controlled amount of water was available at the zeolite surface.

Other anilines

Three major aspects emerge from Table 2. (i) The reactivity trend shown by aniline and *p*-substituted primary aromatic amines (*p*-Cl << *p*-OMe << H ~ *p*-OH) does not follow the nucleophilicity scale (*p*-Cl < H < *p*-OMe < *p*-OH) expected by the electronic properties of the aromatic substituents. Although the electron-withdrawal effect of the Cl group may account for the slowest reaction of *p*-chloroaniline, steric reasons offer a

good explanation for the faster alkylation of aniline with respect to *p*-anisidine:⁴² the bulkier the substituent (OMe vs. H), the more difficult the diffusion of the amine within the catalytic pores and, consequently, the lower the reaction rate. A similar behaviour was observed by us also in the methylation of primary aromatic amines with methyl alkyl carbonates in the presence of faujasite catalysts.^{5c} Finally, the adsorption modes of reactants should be considered: in the case of *p*-aminophenol (**2d**), despite the moderate steric hindrance of the *p*-OH group, the capability of the hydroxyl substituent to form extra H-bonds over the catalytic surface (Scheme 10) along with its strong electron-donating character, may account for the comparable reactivity of **2d** and aniline. (ii) Multi-gram scale processes (entries 2, 4, 6, and 8) require a significantly longer reaction time with respect to small-scale reactions (entries 1, 3, 5, and 7). The high viscosity of GlyC and the physical nature of the catalyst (fine powder) are the most plausible reasons for this behaviour: on the larger scale, the reaction mixtures are thick slurries whose difficult stirring may favour the onset of mixed chemical- and diffusion-controlled regimes. (iii) The moderate yields of products **3a–d** suffer from the difficult separation of the unreacted GlyC and of the by-product glycerine. It should be noted, however, that alternative routes for the synthesis of compounds **3** are not always more efficient (average yields: 36–90%) and, most of all, compared to the safe glycerine carbonate,⁴³ they are based on the use of very toxic and carcinogenic reagents such as glycidol [(oxiran-2-yl)methanol] and aryl halides.⁴⁴

Conclusions

The catalytic reaction of primary aromatic amines with GlyC offers a genuine green route for the synthesis of *N*-(2,3-dihydroxy)propyl anilines (**3**), in which the use of a glycerol-derived and innocuous alkylating agent such as glycerine carbonate is coupled to eco-safe solid catalysts such as alkali metal exchanged faujasites. Among the investigated zeolites, NaY has been the most efficient catalyst. Although NaY must be used in a relatively high amount, it allows a fine control of the selectivity towards the desired compounds **3**, and it can be recovered and recycled without any loss of its performance. Experimental evidence suggests that at least two consecutive reactions account for the formation of *N*-(2,3-dihydroxy)propyl anilines. Accordingly, a mechanistic hypothesis has been formulated through four major steps catalysed by the faujasite: (i) the nucleophilic attack of anilines at the C5 position of GlyC, followed by a decarboxylation process which yields directly compounds **3**; (ii) the dehydrative condensation of anilines with GlyC, which generates water and carbonate-like species (compounds **4**) as intermediates; (iii) the hydrolysis of GlyC to glycerine and CO₂, and (iv) the transesterification of compounds **4** with glycerine, which also ends up in the formation of compounds **3**. The recycling experiments corroborate the role of water adsorbed over the polar catalytic surface: faujasites can be re-used without any loss of activity and/or selectivity, only if they are activated under mild conditions (70 °C, 18 mbar) which avoids an extensive removal of water from the catalysts.

The nucleophilicity scale of the investigated anilines (*p*-Cl < H < *p*-OMe < *p*-OH) does not account for the observed trend of reactivity (*p*-Cl << *p*-OMe << H ~ *p*-OH). This is

better explained through the combined effects of both electronic and steric properties of the substituents, which alter not only the amine nucleophilicity, but also the diffusion/adsorption of reagents within the catalytic pores of the faujasites.

Although these alkylation reactions are rather energy intensive, an added value is the possibility to scale the processes up to multi-gram preparations with isolated yields (~65%) of compounds **3** comparable to those reported for more conventional methods based on highly toxic starting materials (glycidol and aryl halides).

Future studies will be devoted to a more in-depth investigation of other by-products/intermediates, in particular compounds **5** and **6** (Schemes 4 and 8), whose isolation and structural definition will possibly improve the mechanistic interpretation.

Experimental

General

Anilines **2a–d** (*p*-XC₆H₄NH₂, **2a**: X = H; **2b**: X = Cl; **2c**: X = OMe; **2d**: X = OH), glycerine carbonate (GlyC), glycerine (Gly) and diglyme (diethylene glycol dimethyl ether) were of ACS grade and were employed without further purification. Wherever used, water was of milli-Q grade. Zeolites were all of the faujasite (FAU) type: NaY_A and NaX were from Aldrich, while NaY_S was from Strem. Zeolite LiY was synthesized from NaY_A by an ionic exchange reaction using LiCl.¹⁴ Unless otherwise stated, the zeolites were dried under vacuum (70 °C, 18 mbar, overnight) before each reaction. GC-MS (EI, 70 eV) analysis were run using a HP5/MS capillary column (30 m). ¹H NMR were recorded at 400 MHz, ¹³C NMR spectra at 100 MHz. Chemical shifts were reported in δ values downfield from TMS; CDCl₃ or CD₃OD were used as solvents.

General procedure for the reaction of GlyC with anilines **2a–d** (Table 1; Table 2: entries 1, 3, 5, and 7)

A glass reactor (7 mL) shaped as a test tube and equipped with a side screw-capped neck for the withdrawal of samples and a condenser was charged with the chosen substrate (**2a–d**, 5.4 mmol; **2a**: 0.50 g, **2b**: 0.69 g, **2c**: 0.66 g, **2d**: 0.59 g), GlyC (0.76 g, 6.5 mmol, molar ratio GlyC : **2** was 1.2), diglyme (2 mL) and the faujasite NaY_A as a catalyst (the weight ratio FAU : **2** was 1.5). The reactor was then immersed in an oil bath thermostated at the desired temperature (90–170 °C, see Tables 1–2 and Fig. 1–3 for details) and the mixture was kept under magnetic stirring throughout the reaction. At intervals, samples of the reaction mixture were withdrawn and analysed by GC-MS.

The same procedure was used to run a single experiment under an inert atmosphere. In this case, once the mixture was charged in the reactor, air was carefully removed by 3 vacuum/N₂ cycles. The system was then equipped with a N₂-filled rubber reservoir (2 L) and kept under a static inert atmosphere throughout the reaction.

The above described procedure was adapted for the following experiments, (i) and (ii).

(i) Reactions with different catalyst loadings (Fig. 3): being all other conditions unaltered, the weight ratio $Q = \text{NaY}_A : \mathbf{2a}$ was set to 0.2, 0.5, 1, 1.5, and 2, respectively (NaY_A = 0.1, 0.25, 0.5, 0.75 and 1 g).

(ii) Scale-up of the reactions (Table 2, entries 2, 4, 6 and 8): a round-bottomed glass flask (50 mL) equipped with a condenser and a side screw-capped neck for the withdrawal of samples was charged with the chosen substrate (**2a–d**, 21.5 mmol; **2a**: 2.00 g, **2b**: 2.64 g, **2c**: 2.71 g, **2d**: 2.39 g), GlyC (3.04 g, 25.8 mmol, molar ratio GlyC : **2** was 1.2), diglyme (8 mL) and the faujasite NaY_A as a catalyst (the weight ratio FAU : **2** was 1.5). The reactor was then thermostated (oil bath) at the desired temperature (140–170 °C) with magnetic stirring. At intervals, samples of the reaction mixture were withdrawn and analysed by GC-MS.

Reaction of water with 4-[(phenylamino)methyl]-1,3-dioxolan-2one (**4a**) and with glycerine carbonate (Scheme 7 eqn (1) and (2), respectively)

A cylindrical glass reactor (7 mL) equipped with a condenser was charged with compound **4a** (0.20 g, 1.0 mmol), diglyme (1 mL) and dried faujasite NaY_A (0.3 g; the weight ratio FAU : **4a** was 1.5). The reactor was immersed in an oil bath thermostated at 140 °C, and the slurry was kept under magnetic stirring. Water (20 μ L; the molar ratio H₂O : **4a** was 1) was added at once, with a microsyringe, to the mixture. After 5 hours, compound **4a** was recovered unaltered. An analogous procedure was used for the reaction of water with GlyC: a mixture of GlyC (0.76 g, 6.5 mmol), water (120 μ L; the molar ratio H₂O : GlyC was 1), NaY_A faujasite (1.15 g; the weight ratio NaY_A : GlyC was 1.5), and diglyme (1 mL) was set to react at 140 °C. After 5 hours, GlyC was substantially hydrolysed to glycerine (conversion 80%, by ¹H NMR).

Reaction of glycerol with aniline or with 4-[(phenylamino)methyl]-1,3-dioxolan-2one (Scheme 8 eqn (1) and (2), respectively)

A cylindrical glass reactor (7 mL) equipped with a condenser was charged with aniline (0.5 g, 5.4 mmol), glycerol (0.58 g, 6.3 mmol; the molar ratio Gly : aniline was 1.1), diglyme (1 mL), and dried faujasite NaY_A (0.75 g; the weight ratio FAU : aniline was 1.5). The reactor was immersed in an oil bath thermostated at 140 °C, and the slurry was kept under magnetic stirring. After 5 hours, the mixture was analysed by GC-MS: no reaction took place. An analogous procedure was used for the reaction of glycerol with compound **4a**: a mixture of **4a** (0.2 g, 1.0 mmol), glycerol (0.32 g, 3.5 mmol; the molar ratio Gly : aniline was 3.5), NaY_A faujasite (0.3 g; the weight ratio NaY_A : **4a** was 1.5), and diglyme (1 mL) was set to react at 140 °C. After 5 hours, the transesterification of **4a** with glycerol produced *N*-(2,3-dihydroxy)propyl aniline (**3a**) in a 35% yield (by GC-MS).

Recycling of the catalyst

Two sets (A and B) of recycling experiments were carried out by using the same catalyst (NaY_A) for three subsequent reactions (Fig. 3A and B, respectively). At the end of each reaction, the catalyst was filtered, thoroughly washed with methanol (100 mL) and then reactivated. In the first set (A), NaY_A was re-activated by drying it at 70 °C under vacuum (18 mbar) overnight. In the second set (B), NaY_A was first dried overnight at room temperature. Then, the solid was placed in a tubular quartz reactor and calcined in a stream of dried air (~80 mL min⁻¹).

Table 3 Synopsis of MS spectra of non isolated products

Compound	GC-MS (relative intensity, 70 eV)
5a	<i>m/z</i> : 167 (M ⁺ , 22%), 136 (M ⁺ – CH ₂ OH, 99), 119 (13), 118 (M ⁺ – CH ₂ OH – H ₂ O, 100), 117 (29), 106 (24), 93 (52), 91 (48), 77 (35), 65 (17), 51 (22)
6a	<i>m/z</i> : 193 (M ⁺ , 63%), 148 (M ⁺ – CO ₂ – H, 7), 132 (11), 130 (19), 120 (13), 119 (18), 118 (M ⁺ – CH ₂ OCO ₂ , 31), 117 (11), 106 (68), 105 (34), 104 ([PhN≡CH] ⁺ , 75), 93 (41), 91 (38), 78 (15), 77 (100), 51 (38)
4b	<i>m/z</i> : 227 (M ⁺ , 10%), 142 (32), 140 ([ClC ₆ H ₄ NH=CH ₂] ⁺ , 100), 111 (10), 77 (11)
5b	<i>m/z</i> : 201 (M ⁺ , 25%), 172 (25), 170 (M ⁺ – CH ₂ OH, 25), 154 (16), 152 (M ⁺ – CH ₂ OH – H ₂ O, 29), 140 (43), 127 (48), 125 (18), 118 (13), 117 (M ⁺ – CH ₂ OH – H ₂ O – Cl, 100), 111 (23), 77 (17), 76 (10), 51 (13)
5c	<i>m/z</i> : 197 (M ⁺ , 4%), 193 (10), 148 (M ⁺ – CH ₂ OH – H ₂ O, 3) 136 (35), 106 (100), 77 (26), 51 (12)
6c	<i>m/z</i> : 223 (M ⁺ , 100%), 150 (12), 149 (22), 148 (M ⁺ – CH ₂ OCO ₂ , 14), 146 (12), 137 (10), 136 (54), 135 (36), 134 ([MeOC ₆ H ₄ NH=CH] ⁺ , 90), 133 (18), 123 (15), 122 (14), 121 (37), 120 (56), 117 (11), 108 (41), 107 (36), 92 (29), 78 (22), 77 (39), 65 (24), 64 (25), 63 (22), 52 (20), 51 (23)
4d	<i>m/z</i> : 209 (M ⁺ , 10%), 122 ([HOC ₆ H ₄ NH=CH ₂] ⁺ , 100), 94 (13), 65 (15)
6d	<i>m/z</i> : 209 (M ⁺ , 72%), 164 (M ⁺ – CO ₂ – H, 4), 146 (19), 136 (13), 135 (22), 134 (M ⁺ – CH ₂ OCO ₂ , 23), 122 (63), 121 (56), 120 ([OHC ₆ H ₄ NH=CH] ⁺ , 100), 109 (33), 107 (39), 94 (18), 93 (44), 65 (48), 53 (17), 52 (26)

The final calcination temperature (400 °C) was reached through a ramp of 10 °C min⁻¹, and it was kept constant for 3.5 hours. The catalyst was cooled to room temperature and directly used.

Water loss from the catalyst

Two samples, A and B (3.00 g each), of NaY_A were weighed as received on an analytical balance: A was placed in a quartz reactor and calcined in dried air (400 °C, 4 h, 80 mL min⁻¹), while B was dried at 70 °C, under vacuum (18 mbar), overnight. After the thermal treatment, both samples were cooled to room temperature (in dried air and under vacuum, respectively), and rapidly re-weighed three times in 1.0 min. The final weight values for both A and B were the average of the three measures.

Isolation and characterization of the products

All products **3a–d**, **4a–d**, **5a–c**, **6a** and **6c,d** were characterized by GC-MS. Compounds **3a–d**, **4a** and **4c** were isolated by flash column chromatography (eluant: petroleum ether (PE) and ethyl acetate (EA), gradient elution: initial PE : EA = 9 : 1 v/v, final PE : EA = 1 : 9 v/v) and further characterized by ¹H and ¹³C NMR. Table 3 summarizes MS spectra of compounds **5a–6a**, **4b–5b**, **5c–6c**, **4d** and **6d** which were not isolated.

N-(2,3-Dihydroxy)propyl aniline, 3a. Pale yellow solid.⁴⁵ ¹H NMR (400 MHz, CDCl₃) δ 3.10 (dd, 1H, *J*₁ = 7.6 Hz, *J*₂ = 12.9 Hz), 3.21 (dd, 1H, *J*₁ = 4.1 Hz, *J*₂ = 12.9 Hz), 3.58 (dd, 1H, *J*₁ = 6.3 Hz, *J*₂ = 11.4 Hz), 3.71 (dd, 1H, *J*₁ = 3.2 Hz, *J*₂ = 11.4 Hz), 3.88–3.95 (m, 1H), 6.63 (d, 2H, *J* = 8.3 Hz), 6.75 (t, 1H, *J* = 7.3 Hz), 7.17 (t, 2H, *J* = 7.7). ¹³C NMR (100 MHz, CDCl₃) δ 46.6, 48.8, 70.4, 113.4, 118.2, 129.3, 147.9. MS (EI), *m/z* (relative int.): 167 (M⁺, 12%), 136 (M⁺ – CH₂OH, 3), 106 (M⁺ – CH(CH₂OH)OH, 100), 77 (20).

4-[(Phenylamino)methyl]-1,3-dioxolan-2-one, 4a. Brown solid. ¹H NMR (400 MHz, CDCl₃) δ 3.45 (dt, 1H, *J*₁ = 5.2 Hz, *J*₂ = 14.2 Hz), 3.56 (dt, 1H, *J*₁ = 4.5 Hz, *J*₂ = 14.4 Hz), 3.95 (brs, 1H), 4.30 (dd, 1H, *J*₁ = 6.8 Hz, *J*₂ = 8.5 Hz), 4.57 (t, 1H, *J* = 8.3 Hz), 4.91–4.98 (m, 1H), 6.64–6.67 (m, 2H), 6.77–6.83 (m, 1H), 7.19–7.24 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 45.9, 67.0, 75.1, 113.3, 119.0, 129.5, 146.8, 154.6. MS (EI), *m/z* (relative int.): 193 (M⁺, 10%), 106 ([PhNH=CH₂]⁺, 100), 77 (21).

p-Chloro[N-(2,3-dihydroxy)propyl]aniline, 3b⁴⁶. Light brown oil. ¹H NMR (400 MHz, CDCl₃) δ 3.15 (dd, 1H, *J*₁ = 7.5 Hz, *J*₂ = 12.9 Hz), 3.25 (dd, 1H, *J*₁ = 4.1 Hz, *J*₂ = 12.9 Hz), 3.64 (dd, 1H, *J*₁ = 6.0 Hz, *J*₂ = 11.2 Hz), 3.78 (dd, 1H, *J*₁ = 3.5 Hz, *J*₂ = 11.2 Hz), 3.92–3.99 (m, 1H), 6.55–6.60 and 7.10–7.15 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 46.6, 64.7, 70.4, 114.4, 122.6, 129.1, 146.6. MS (EI), *m/z* (relative int.): 201 (M⁺, 11%), 170 (M⁺ – CH₂OH, 3), 142 (32), 141 (10), 140 (M⁺ – CH(CH₂OH)OH, 100), 77 (12), 75 (11).

p-Methoxy[N-(2,3-dihydroxy)propyl]aniline, 3c. Dark brown solid.⁴⁷ ¹H NMR (400 MHz, CD₃OD) δ 2.99 (dd, 1H, *J*₁ = 7.4 Hz, *J*₂ = 12.7 Hz), 3.24 (dd, 1H, *J*₁ = 4.5 Hz, *J*₂ = 12.7 Hz), 3.53–3.62 (m, 2H), 3.71 (s, 3H), 3.78–3.84 (m, 1H), 6.65–6.70 and 6.74–6.79 (m, 4H). ¹³C NMR (100 MHz, CD₃OD) δ 48.9, 56.2, 65.7, 71.7, 115.8, 116.0, 144.1, 153.9. MS (EI), *m/z* (relative int.): 197 (M⁺, 11%), 166 (M⁺ – CH₂OH, 3), 136 (M⁺ – CH(CH₂OH)OH, 100), 121 (10), 108 (13).

4-[(4'-Methoxyphenyl-amino)methyl]-1,3-dioxolan-2-one, 4c. Brown solid. ¹H NMR (400 MHz, CDCl₃) δ 3.37 (dd, 1H, *J*₁ = 5.6 Hz, *J*₂ = 14.1 Hz), 3.49 (dd, 1H, *J*₁ = 4.0 Hz, *J*₂ = 14.1 Hz), 3.75 (s, 3H), 4.30 (dd, 1H, *J*₁ = 6.8 Hz, *J*₂ = 8.5 Hz), 4.55 (t, 1H, *J* = 8.3), 4.89–4.96 (m, 1H), 6.60–6.66 and 6.77–6.82 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 47.1, 55.7, 67.0, 75.3, 114.9, 115.0, 140.8, 153.2, 154.6. MS (EI), *m/z* (relative int.): 223 (M⁺, 14%), 136 ([MeOC₆H₄NH=CH₂]⁺, 100), 121 (10).

p-Hydroxy[N-(2,3-dihydroxy)propyl]aniline, 3d. Dark brown solid.^{44b} ¹H NMR (400 MHz, CD₃OD) δ 2.97 (dd, 1H, *J*₁ = 7.5 Hz, *J*₂ = 12.7 Hz), 3.21 (dd, 1H, *J*₁ = 4.5 Hz, *J*₂ = 12.7 Hz), 3.52–3.61 (m, 2H), 3.76–3.84 (m, 1H), 6.59–6.67 (m, 4H). ¹³C NMR (100 MHz, CD₃OD) δ 49.6, 65.7, 71.7, 116.6, 116.9, 143.0, 150.7. MS (EI), *m/z* (relative int.): 183 (M⁺, 12%), 152 (M⁺ – CH₂OH, 3), 122 (M⁺ – CH(CH₂OH)OH, 100), 94 (13).

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- FCC was used to purify the final reaction mixtures. Efforts to isolate both compounds **5a** and **6a** were always unsuccessful: these products were eluted together with a mixture of glycerol and (unreacted) glycerol carbonate.
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- Under the conditions of Fig. 1, an additional experiment was also carried out by adding glycerol (0.25 g, 2.7 mmol) at the very beginning of the reaction: after 120 min, no reaction took place.
- The selectivity towards compound **3a** was calculated through the expression: [(**3a**) / ∑(all products)] × 100, where (**3a**) and ∑ (all products) were the % amount, determined by GC, of compound **3a** and of all reaction products, respectively.
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- Alkali metal exchanged Y- and X-faujasites are a class of zeolites in which the negative charge of the aluminosilicate framework is counterbalanced by an alkali metal cation. For example, NaY and NaX faujasites possess the same 3D-structure, but they differ for the Si/Al content. Their general formulas are Na₃₆[(AlO₂)₅₆(SiO₂)₁₃₆]·250H₂O and Na₈₆[(AlO₂)₈₆(SiO₂)₁₀₆]·264H₂O, respectively. For morphological details and other properties, see: (a) F. Schwochow and L. Puppe, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 620; (b) G. C. Bond, in *Heterogeneous Catalysis Principles and Applications*, Oxford University Press, New York, USA, 2nd edn, 1987, pp. 104–110; (c) D. Barthomeuf, *J. Phys. Chem.*, 1984, **88**, 42–45.
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