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Quaternary ammoniums and a cationic sodium complex as supramolecular catalysts in ring-opening of epoxides by amines

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ABSTRACT

Supramolecular ionic organocatalysts and a metal-based catalyst were investigated in the ring-opening of epoxides by amines, without any artifice to enhance conversion (i.e., solvophobic effect, extended reaction time, heating, excess of amine, high catalyst loading). Different β-amino-alcohols were obtained in satisfying conversion (50–80%) in 24 h, under mild conditions.

1. Introduction

The ring-opening reaction of epoxides by amines is a common route to β-amino-alcohols, which are well-known chiral auxiliaries as well as structural components of natural and synthetic bioactive compounds.[1] Moreover, the aminolysis of epoxides still remained a model reaction to evaluate new catalysts as C–O bond activators. The outcome of ring-openings strongly depended on classical electronic and steric effects on reactants. Concerning regioselectivity, the favoured product resulted from the nucleophilic attack on the less hindered epoxide carbon (β-attack), except in the case of styrene oxides where α-attack was the major one. Concerning stereochemistry, under neutral or basic conditions, an SN_2 mechanism was admitted and *trans* β-amino-alcohols were obtained. To better control the formation of products, the enantioselective ring-opening of epoxides was extensively catalyzed by metal-based complexes and enzymes.[2] Additionally, experimental conditions (microwave irradiation,[3] solvent-free[4]) and solvent effects (ionic liquid,[5] hexafluoro-2-propanol,[6] water[7–9]) were also evaluated to improve yields. Current limitations originated from poorly nucleophilic amines (low yields), and other ones were due to protocols that required high temperatures, extensive reaction times, high catalyst loadings or an excess of amine to avoid side-products (mainly bis-adducts).

Over the last decade, research efforts also concentrated on organocatalyzed ring-opening of epoxides, in organic solvents and water.[10] In particular, Hydrogen-bonding catalysis was the most popular strategy. So, Schreiner and Kleiner reported that a thiourea provided with electron-withdrawing groups (TUS, 10 mol %, Scheme 1), catalyzed the aminolysis of epoxides by aliphatic amines in dichloromethane (27–85%) and in water (60–97%), due to hydrophobic effects.[11] Solvent-free conditions at 60 °C were reported for the aminolysis of several epoxides catalyzed by different thioureas (80–100%, 0.2–45 h).[12] A *N*-tosyl urea (10 mol %) catalyzed the addition of anilines to styrene and (*E*)-stilbene oxides in high yields in dichloromethane (75–92%, 3–6 days, one regioisomer).[13] Besides, *N*-formyl-L-proline (10 mol %) was investigated as a catalyst in dichloromethane, towards the ring-opening of styrene oxide by aniline (99% yield, 48 h, 20 °C).[14] In water, the scope of this acid was broader, allowing reactions of anilines in 48 h with several epoxides (44–99%) and their ring-openings by aliphatic amines in 24 h (71–80%). A polystyrene supported poly(amido-amine) dendrimer was also reported to promote the ring-opening of cyclohexene, styrene and 2-butene oxides by anilines in 1,4-dioxane (G3 at 2 mol %, 50 °C, 12–36 h, yield: 85–98%).[15] The catalyst was recycled six times with a limited loss of activity (yield: 98–90%). Finally, chiral amidinium salts (10 mol %) were shown to catalyze the ring-opening of cyclohexene oxide by aniline (2 equiv) in dichloromethane (20 °C, 6 h, yield: 99%).[16] No asymmetric induction was observed on the product. Thus, despite its efficiency in the activation of C=O, $-NO_2$ and C=N bonds, H-bonding

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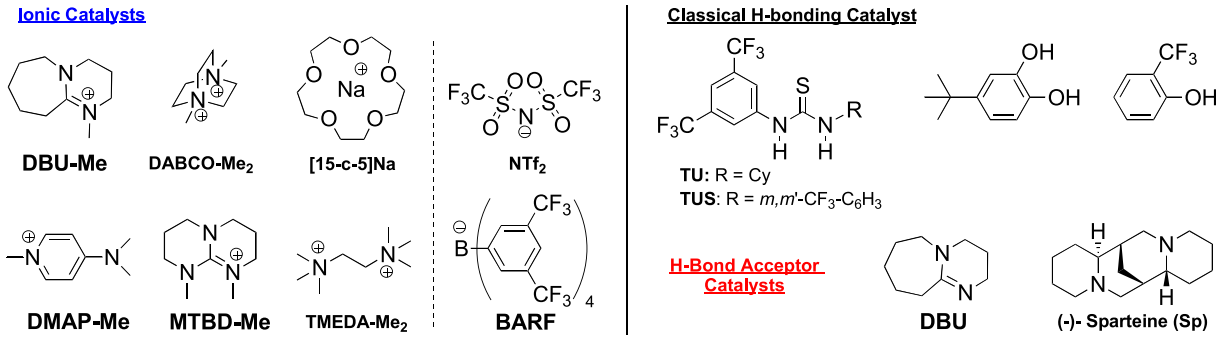


Scheme 1. Structures of supramolecular organocatalysts and a sodium(I)-based catalyst.

catalysis appeared to moderately activate single C–O bonds of epoxides, due to the lower binding abilities of this functional group. Currently, H-bonding catalysts involved in ring-openings by amines could be efficient using protocols that favoured extensive reaction time (>24 h), heating (50–60 °C), high catalyst loading (≥10 mol %) or reactant excess. Moreover the role of water as a solvent was still unclear (i.e., in water or on water).[17]

We proposed to evaluate ionic catalysts towards the C–O bond activation, in dichloromethane to avoid a major solvent effect. Besides, catalyst loadings and reaction times were restricted (5 mol %, 24 h, respectively), temperature was maintained at 20 °C, and reactants were introduced in equimolar quantities. So, a series of new supramolecular catalysts were chosen (Scheme 1): quaternary ammoniums organocatalysts capable of $N^+–CH_3^{\delta+}\cdots O–C$ interactions and a sodium(I) encapsulated in 15-crown-5 ether ([15-c-5]Na) to favour a $Na^+\cdots O–C$ interaction, i.e., a weak coordination bond also called ion–dipole interaction. The discrete cationic sodium complex is solely presented in this study, as the same crown-ether complexes of Li^+ and K^+ are not available. Indeed, the lithium(I) complex is not a well-defined compound as a mixture of (1:1) and (2:1) (15-c-5:Li^+) complexes is obtained. As a consequence, its catalytic activity could not be rationalized. In addition, the discrete potassium(I) complex was prepared with the [18-c-6] macrocycle using NTf_2 and BARF as counterions. The ring-opening of 1,2-epoxyhexane and cyclohexene-oxide by pyrrolidine in presence of this catalyst induced slightly lower conversions (±5%) than in presence of [15-c-5]Na. A detailed investigation of alkali- and alkali-earth crown-ether complexes could shed light on this phenomenon and will be reported in due course.

For a comparison sake, some classical H-bond donors, such as thioureas (TU and Schreiner's Thiourea TUS) and phenol derivatives were also reported. We recently described these ionic and neutral catalysts in the ring-opening polymerization of cyclic esters, based on an efficient activation of C=O bonds.[18] Additionally, the impact of a catalytic system, composed of a donor+an acceptor, using well-known H-bond acceptor catalysts (DBU and (−)-sparteine) were evaluated under the same conditions, as potential activators of nucleophile through H-bonding (N···H-Nu).

Herein, the ring-opening of four representative epoxides provided with aromatic and aliphatic substituents, were achieved with different nucleophilic amines. So, disubstituted (*E*)-stilbene and cyclohexene oxides, as well as monosubstituted styrene oxide and 1,2-epoxyhexane were chosen to compare reactivity and to evaluate regioselectivity in the latter two cases. Four aliphatic amines were selected according to their nucleophilic parameter in acetonitrile (N):[19] di-isobutylamine (hindered amine), *n*-butylamine (N=15.27) as well as cyclic amines, such as piperidine (N=17.35) and pyrrolidine (N=18.64).[20]

2. Results and discussion

The proposed mechanism is relying on a classical activation between catalysts and reactants through H-bonds (Fig. 1):[11,18] (i) the C–O bond of epoxide can be H-bonded to quaternary ammoniums, phenols or thioureas meanwhile forming a cation–dipole interaction with sodium(I) in [15-c-5]Na, (ii) tertiary amines (DBU or sparteine) can be H-bonded to the nucleophile, then activating its nucleophilicity, (iii) in principle, both catalysts could simultaneously activate the reactants, provided no competitive H-bonds existed in the medium. Indeed, we previously demonstrated that some H-bond donor and acceptor catalysts could preferentially be H-bonded together, and then low conversions were observed.[21] In addition, the products of ring-opening, β-amino-alcohols might also interfere in the mechanism through their alcohol and amine groups as H-bond donors and acceptors.

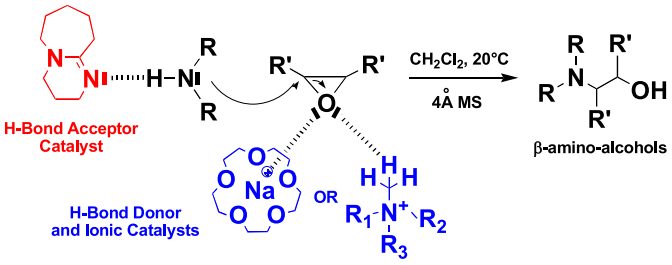


Fig. 1. Non-covalent activation of substrates (epoxide or/and amine) in the aminolysis of epoxides.

To better assess the plausible interactions present in the reaction medium, geometry optimizations at the B3LYP/6-31G* level were achieved on different (1:1) mixtures of H-bonding compounds, in vacuum (Fig. 2). As a model reaction, the ring-opening of 1,2-epoxybutane by piperidine was examined in the presence of two representative H-bonding catalysts (donor and acceptor), i.e., 4-^{t}Bu-catechol and DBU.[22] Even if these simulations were not fully representative of the experimental conditions of ring-opening, they showed the possible supramolecular interactions between the species present in the medium, and their relative strength (see Table S1, Supplementary data).

As proposed in the mechanism, 1,2-epoxybutane is H-bonded to 4-^{t}Bu-catechol ($d_{O1\cdots H1}$=1.99 Å, Fig. 2a) meanwhile DBU is weakly interacting with piperidine ($d_{N1\cdots H1}$=2.54 Å, Fig. 2b). This result suggests that DBU should poorly activate the nucleophile. A possible interaction between two catalysts is highlighted by the formation of an H-bonded complex between 4-^{t}Bu-catechol and DBU ($d_{N1\cdots H1}$=2.07 Å, Fig. 2c). The H-bond donor catalyst 4-^{t}Bu-catechol could also interact with piperidine ($d_{N1\cdots H1}$=2.00 Å, Fig. 2d), with

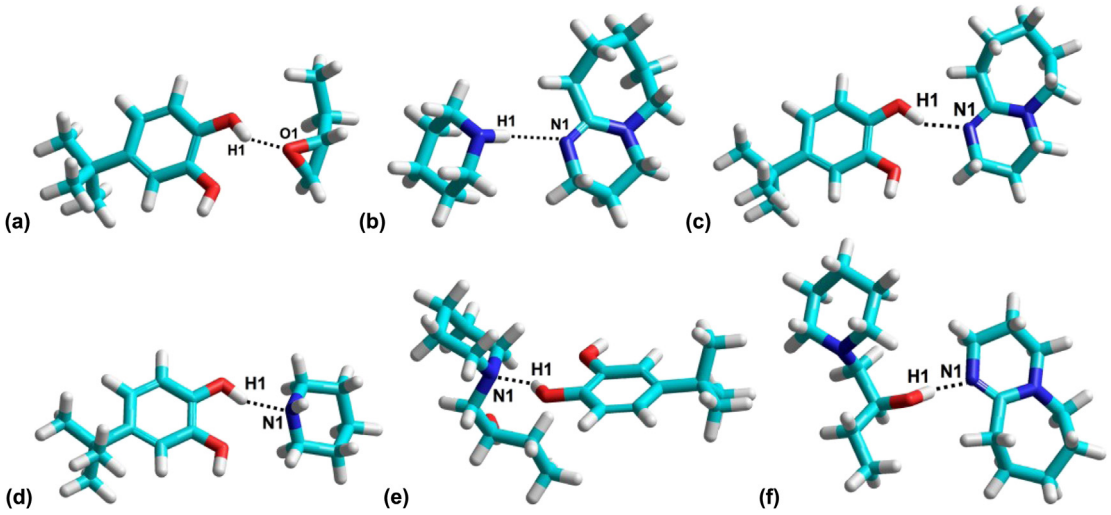


Fig. 2. Minimum-energy structures of possible complexes involved in the catalyzed ring-opening of 1,2-epoxybutane by piperidine, optimized at B3LYP/6-31G* level: (a) 4-^{t}Bu-catechol/epoxide, (b) DBU/piperidine, (c) DBU/4-^{t}Bu-catechol, (d) 4-^{t}Bu-catechol/piperidine, (e) 1-*n*-butyl-2-pyrrolidinyl ethan-1-ol/4-^{t}Bu-catechol, (f) 1-*n*-butyl-2-pyrrolidinyl ethan-1-ol:/DBU.

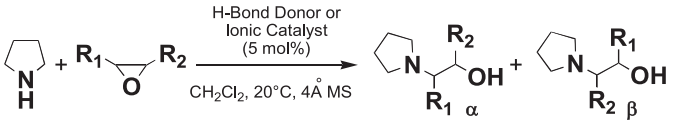
a similar strength as in the (4-^{t}Bu-catechol:epoxide) complex. Thus, the expected interaction of 4-^{t}Bu-catechol towards epoxide could be disturbed by the nucleophile. Finally, the product of the reaction could also be H-bonded to 4-^{t}Bu-catechol and DBU catalysts (respectively, $d_{O1\cdots H1}$=2.13 Å, Fig. 2e and $d_{N1\cdots H1}$=2.03 Å, Fig. 2f). So, the catalytic activity of both catalysts could be reduced by the presence of the product, especially at high conversion. In summary, molecular modelling indicates that H-bonding catalysis in epoxide ring-openings is complex to control as C–O activation could occur, meanwhile inhibition of H-bonding catalysis could also exist, due to the presence of product or two catalysts. Experimentally, the outcome of the reaction will be driven by the overall H-bonding equilibriums.

At first, the ring-opening of four representative epoxides (stilbene, styrene, cyclohexene oxides and 1,2-epoxyhexane) by the most nucleophilic amine (pyrrolidine) was studied in dichloromethane (Table 1), in presence of H-bond donor or [15-c-5]Na catalysts. The percentage of conversion and regioselectivity (when appropriate) was determined by ^{1}H NMR and gas chromatography (see Supplementary data). In all cases, β-amino-alcohols were the unique products as no bis-adduct was detected.

Stilbene oxide is ring-opened by pyrrolidine up to 40% conv. in the presence of TU meanwhile the best conversions are reached when TMEDA-Me$_2$·2NTf$_2$ (43%) and DABCO-Me$_2$·2NTf$_2$ (47%) di-ionic catalysts are employed. Only racemic *trans* β-amino-alcohols are obtained. Then, styrene oxide, a more reactive compound than stilbene oxide is evaluated. As expected,[2] the product resulting from the α-attack is favoured and the (α/β) ratio is 2:1. DBU-Me·NTf$_2$, [15-c-5]Na·NTf$_2$ and 4-^{t}Bu-catechol moderately catalyze the reaction (56, 57 and 63% conv., respectively) compared to TU, TUS, TMEDA-Me$_2$·2NTf$_2$ and DABCO-Me$_2$·2NTf$_2$ that induce higher conversions (69–72%). Concerning 1,2-epoxyhexane, all catalysts allow a similar conversion (68–73%, unique β-attack). Finally, cyclohexene oxide is converted at 71–81%, with the best results noticed for TU (81%), TMEDA-Me$_2$·2NTf$_2$ (77%) and DABCO-Me$_2$·2NTf$_2$ (77%).

In these ring-openings, ionic compounds, thioureas and phenols induce 50–80% conversion under mild conditions. Facing a general moderate epoxide activation, the catalysts have a similar impact (±20% range). Remarkably, no major inhibition due to side H-bond interactions is noticed, as fair conversions are reached. So, the modelled interactions between the reaction components (H-bond donor, epoxide and β-amino-alcohol) are in accordance with the experimental results. The main advantage of the catalysts is the possibility of reaching good conversions (72–81%, except for low reactive stilbene oxide: 47%) in β-pyrrolidino-alcohols under mild conditions (CH_2Cl_2, 1 equiv amine, cheap catalyst, 20 °C, 24 h) that can also be useful for sensitive or expensive reactants.

Table 1
Ring opening of epoxides by pyrrolidine, in presence of H-bond donor or ionic catalysts[a]

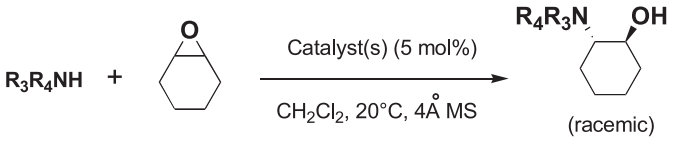


Epoxides	Catalyst (NTf$_2$)[b]	% Conv.	(α/β)
Stilbene oxide (trans)	DBU-Me·X	23	
	[15-c-5]Na·X	29	
	DABCO-Me$_2$·2X	47	
	TMEDA-Me$_2$·2X	43	
	TU	40	
	TUS	29	
	4-^{t}Bu-catechol	27	
Styrene oxide	DBU-Me·X	56	(2:1)[c]
	[15-c-5]Na·X	57	(2:1)
	DABCO-Me$_2$·2X	72	(2:1)
	TMEDA-Me$_2$·2X	69	(2:1)
	TU	71	(2:1)
	TUS	70	(2:1)
	4-^{t}Bu-catechol	63	(2:1)
1,2-Epoxyhexane	DBU-Me·X	70	(0:100)[d]
	[15-c-5]Na·X	73	(0:100)
	DABCO-Me$_2$·2X	68	(0:100)
	TMEDA-Me$_2$·2X	69	(0:100)
	TU	73	(0:100)
	TUS	69	(0:100)
	4-^{t}Bu-catechol	69	(0:100)
Cyclohexene-oxide	DBU-Me·X	71	
	[15-c-5]Na·X	78	
	DABCO-Me$_2$·2X	77	
	TMEDA-Me$_2$·2X	77	
	TU	81	
	TUS	74	
	4-^{t}Bu-catechol	76	

[a] Conditions: oxirane (4 M in CH_2Cl_2), 20 °C, 1 equiv nucleophile, 5 mol % catalyst, 20 °C, 4 Å MS. Reactions monitored by ^{1}H NMR and confirmed by GC.
[b] X=NTf$_2$.
[c] Major regioisomer (α-attack): 2-phenyl-2-pyrrolidinyl-ethanol.
[d] Unique regioisomer (β-attack): 1-*n*-butyl-2-pyrrolidinyl ethanol.

To explore the scope of amines, several ring-openings of cyclohexene oxide were undertaken under the same conditions (Table 2, % conv. Cat.). Reactions were carried out in the presence of four different amines, following their increasing nucleophilicity:[19,20] di-isobutylamine (hindered amine), *n*-butylamine, piperidine and pyrrolidine. Additionally, a catalytic system composed of H-bond donor+acceptor (DBU or Sp i.e., (−)-sparteine) was evaluated (Table 2, % conv. Cat.+DBU or Cat.+Sp). The effect of counterion (X: NTf_2, BARF) in ionic catalysts was also reported in the ring-opening of cyclohexene oxide by pyrrolidine.

Table 2
Ring opening of cyclohexene oxide by amines, in presence of supramolecular catalysts[a]



Nucleophile	Catalysts X: NTf_2, BARF	% Conversion Cat.[b]	Cat.+DBU (Cat.+Sp)
i-Bu_2NH	DBU-Me·NTf_2	1	1
	[15-c-5]Na·NTf_2	3	3
	DABCO-Me_2·$2NTf_2$	1	1
n-$BuNH_2$	DBU-Me·NTf_2	22	27
	[15-c-5]Na·NTf_2	29	34
	DABCO-Me_2·$2NTf_2$	36	39
	TU	51	54
	TUS	25	29
	4-^{t}Bu-catechol	31	37
Piperidine	DBU-Me·NTf_2	33	59 (57)
	[15-c-5]Na·NTf_2	45	68 (45)
	DABCO-Me_2·$2NTf_2$	50	61(61)
	TU	63	62 (70)
	TUS	39	61 (60)
	4-^{t}Bu-catechol	49	66 (50)
	2-CF_3-phenol	40	61 (44)
	Pyrogallol	41	72 (70)
Pyrrolidine	DBU-Me·X	71, 82[c]	78, 82[c]
	[15-c-5]Na·X	78, 82[c]	80, 82[c]
	DABCO-Me_2·2X	77, 81[c]	78, 80[c]
	MTBD-Me·X	74, 81[c]	78, 80[c]
	DMAP-Me·X	76, 81[c]	78, 81[c]
	TMEDA-Me_2·2X	77, 83[c]	78, 81[c]
	TU	81	81
	TUS	74	77
	4-^{t}Bu-catechol	76	78
	2-CF_3-phenol	77	80
	Pyrogallol	76	78

[a] Conditions: cyclohexene oxide (4 M in CH_2Cl_2), 20 °C, nucleophile (1 equiv) and catalyst(s) (5 mol %). Reaction monitored by ^{1}H NMR and confirmed by GC.
[b] Cat.: H-bond donor or ionic catalyst.
[c] % conv. when X=NTf_2, BARF, respectively.

As anticipated by the poor nucleophilicity of di-isobutylamine, catalyzed ring-opening of cyclohexene oxide is almost null whatever the catalysts (1–3% conv.). Ring-openings by *n*-butylamine catalyzed by H-bond donor give fair results: TU triggers 51% conv., whereas DABCO-Me_2·$2NTf_2$ reaches 36% conv. The catalytic systems (H-bond donor+DBU) induce slightly higher conversions (27–54%) than the H-bond donors alone (22–51%). The moderate conversions could be attributed to the poor nucleophilicity of *n*-butylamine, regardless of the catalyst combination, and possibly to side-interactions between catalysts that moderate their individual impacts, as anticipated by modelling the H-bonded complex between 4-^{t}Bu-catechol and DBU (Fig. 2c).

Concerning the ring-openings by piperidine, a more nucleophilic amine than the two previous ones, H-bond donor catalysis is efficient and the best results are obtained in the presence of 4-^{t}Bu-catechol (49% conv.), DABCO-Me_2·$2NTf_2$ (50% conv.) and TU (63% conv.). Percentages of conversion are ever higher in the presence of (H-bond donor+DBU) catalysts, ranging between 59 and 72%. This effect was remarkable upon poor H-bonding catalysts, such as DBU-Me·NTf_2 (59% vs 33% alone) and pyrogallol (72% vs 41% alone). Here, the beneficial effect of a dual H-bonding catalytic system upon conversion could be rationalized by a combined effect when two catalysts could activate both reactants (as seen in the ring-opening polymerization).[21] This effect is not observed in the previous reactions due to the poor reactivity of the reactants. It was also noticed that, in the case of TU, conversion is similar in absence or presence of co-catalyst DBU (62% vs 63% alone). In the latter case, H-bonding between TU and DBU could limit their action towards the reactants and thus leads to a moderate conversion. The catalytic systems based on (−)-sparteine (Sp) have a similar effect on conversion than those with DBU. Compared to H-bond donor catalysts, increased conversions are observed for the following catalytic systems, due to the combined effects of both catalysts upon each reactant: DBU-Me·NTf_2+Sp (57% vs 33%), DABCO-Me_2·$2NTf_2$+Sp (61% vs 50%), TU+Sp (70% vs 63%), TUS+Sp (60% vs 39%), pyrogallol+Sp (70% vs 41%). No or little effect is seen upon conversion when [15-c-5]Na·NTf_2+Sp (45% in both cases), 4-^{t}Bu-catechol+Sp (~50% in both cases) and 2-CF_3-phenol+Sp (44% vs 40%) are employed. In latter cases, a side-interaction involving both catalysts could be suspected. Additionally, the looser interaction between TU and Sp compared to TUS (more acidic) and Sp could account for the higher conversion observed with the first catalytic system (70% vs 60%).

Finally, the ring-opening of cyclohexene by pyrrolidine leads to the best results with TU (81% conv.) and ionic catalysts provided with BARF anion, due to a looser ionic pair and a better solubility (81–83% conv.). The dual (H-bond donor+DBU) catalytic systems give similar or slightly higher results than H-bond donor catalysts themselves (77–82% conv.). Thus, no additive effect on catalysis is observed in this ring-opening, possibly due to side-interaction between catalysts and possibly between the catalyst and product, present in a large portion at the highest conversions.

So, organocatalyzed ring-opening of epoxides by ionic catalysts and phenols is shown to reach 50–80% conversion, in dichloromethane, in 24 h using different amines and epoxides. Interestingly, several new H-bond donor catalysts (TMEDA-Me_2·$2NTf_2$, DABCO-Me_2·$2NTf_2$, [15-c-5]Na·NTf_2, 4-^{t}Bu-catechol) and TU prove to be efficient. In the case of ring-opening by piperidine, the (H-bond donor+DBU) catalytic systems are shown to lead to the highest conversions. In comparison with organocatalysts employed in dichloromethane,[11–14,16] our results are satisfying in terms of catalyst loading (5% mol), conversion (50–80% in 24 h, 20 °C), economic impact (commercially available or cheap catalysts) and regioselectivity followed the general rules.

3. Conclusion

Organocatalyzed ring-opening of epoxides by quaternary ammoniums, Na^+@[15-c-5] and phenols in dichloromethane were demonstrated to lead to 50–80% conversions under mild conditions (5 mol % catalyst loading, 24 h, 20 °C, 1 equiv amine, cheap catalysts). When nucleophilic amines were employed, the catalytic systems composed of H-bond donor+acceptor can be the most efficient, provided that no side-interactions disturbed their action. Bifunctional catalysts are currently investigated to overcome this issue.

4. Experimental part

4.1. Material

Dichloromethane and amines were dried over calcium hydride and distilled. Commercially available epoxides and phenols were

used as received. Ionic catalysts[18a] and thioureas[23] were prepared according to known procedures.

4.2. General procedure for ring-opening of epoxides

Epoxide (4 mmol), H-bonding or ionic catalyst (5 mol %) and 4 Å molecular sieves were introduced in a dry Schlenk under nitrogen. A solution of amine (4 mmol) and co-catalyst if necessary (DBU or Sp, 5 mol %) in dry dichloromethane (1 mL) was added. The reaction was stirred at 20 °C for 24 h and quenched with benzoic acid when a co-catalyst was employed. The mixture was filtered and concentrated under reduced pressure. The percentage of conversion and the regioselectivity was determined by ^{1}H NMR ($CDCl_3$) and GC, by comparison with the pure product samples.

4.3. Molecular modelling

The molecular structures of the catalysts, reactants and product were submitted to a geometry optimization in vacuum at the B3LYP/6-31+G* level, as implemented in HyperChem release 8 software package. Then (1:1) mixtures were subjected to the same process. Calculations were conducted on (1*R*)-1-*n*-butyl-2-piperidinyl ethan-1-ol.

Acknowledgements

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Supplementary data

Monitoring of ring-opening reactions, intermolecular distances, cartesian coordinates and energy of modelled complexes. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.01.018.

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