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Studies on the catalytic activity of novel hybridized chiral organo-inorganic catalysts for epoxidation and alkylation reactions

O. Lanitou [a,b], D. Dimotikali [a], E. Yannakopoulou [b], K. Papadopoulos [b,*]

[a] *Chemical Engineering Department, National Technical University of Athens, Iroon Polytehniou 9, 15780 Zografou, Athens, Greece*
[b] *Institute of Physical Chemistry, National Centre for Scientific Research "Demokritos", 15310 Ag. Paraskevi Attikis, Athens, Greece*

Abstract

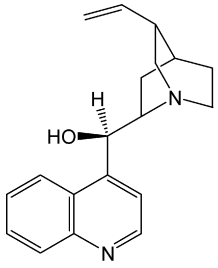
Novel functionalized organo-inorganic chiral catalysts have been prepared in two steps from activated silica gel and chiral organic auxiliaries, such as (+)-cinchonine or (*S*)-(−)-nicotine. These new catalysts have been tested in a solid–liquid–liquid three-phase system for the asymmetric epoxidation of α,β-enones and the asymmetric alkylation reactions of glycine derivatives. The obtained stereoselectivities are negligible for the first case (ee <2%) and appreciable (ee 25–55%) for the second one.

Keywords: Functionalized organo-inorganic chiral catalysts; Solid–liquid–liquid three-phase reactions; Phase-transfer reactions; Epoxidation; Alkylation

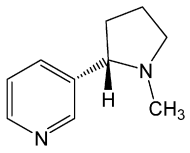
1. Introduction

In recent years, methods for the stereoselective synthesis of epoxides as well as of α-amino acids have attracted widespread attention due to their importance as potential intermediates for the synthesis of natural or pharmaceutical products. Especially, numerous studies for the synthesis of α-amino acids, the "building blocks of life", have been made over the past quarter century [1–4].

The stereoselective formation of the aforementioned compounds has been extensively studied using chiral liquid–liquid phase-transfer catalysts on the basis of cinchona alkaloids [5,6]. These catalysts, however, cause often problems related to their recovery and recycling and the last years are being replaced more and more by hybridized organo-inorganic ones. The big advantage relies in their insolubility in aqueous or organic solvents and therefore in their easily removal from reaction mixtures [7,8]. Soai et al. [9] and Lasperas and co-workers [10,11] were among the first who described the use of such functionalized organo-inorganic chiral catalysts for enantioselective reduction reactions with very promising results. Encouraged by these developments, we decided to prepare similar insoluble silica-functionalized chiral ammonium salts and test them on the asymmetric epoxidation of α,β-enones and asymmetric alkylation reactions of glycine derivatives in a solid–liquid–liquid three-phase system. In the frame of this work we used as substrates for the asymmetric epoxidation and alkylation reactions *trans*-benzylideneacetophenone (*trans*-chalcone) and ethyl-*N*-(diphenylmethylene)-glycinate (O'Donnell's reagent), respectively, while as chiral reagents the aromatic amines (+)-cinchonine and (*S*)-(−)-nicotine. Quaternary ammonium salts of cinchona and nicotinium alkaloids are preferred since one of the tetrahedron faces about the charged bridge nitrogen is totally blocked by the ring system itself.



(+)-cinchonine



(S)-(-)-nicotine

* Corresponding author. Tel.: +30 210 6503647; fax: +30 210 6511766.
E-mail address: kyriakos@chem.demokritos.gr (K. Papadopoulos).

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2. Experimental

2.1. Material/reagents

Silica gel (surface area 500 m^2/g, particle size 63–240 μm, pore size 60 Å) was purchased from Macheray–Nagel and used after activation. Activation was performed in vacuum at temperature about 100 °C. (3-Chloropropyl)-triethoxysilane, *trans*-chalcone, ethyl-*N*-(diphenylmethylene)-glycinate (O'Donnell's reagent), benzyl bromide, (*S*)-(−)-nicotine and (+)-cinchonine were purchased from Aldrich and used without further purification. All reactions were carried out under an argon atmosphere. Toluene, dichloromethane and triethylamine were dried over calcium hydride and distilled prior to use. Double distilled water was used for all phase-transfer reactions.

2.2. Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Brucker AC 500 MHz spectrometer. Chloroform-*d* ($CDCl_3$) was used for all NMR measurements. Tetramethylsilane was used as internal standard. IR spectra were recorded on a FT-IR Perkin-Elmer 283 spectrometer. Optical rotation measurements were performed at room temperature on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed on a Perkin-Elmer 2400 CHN automatic analyzer.

2.3. Methods

2.3.1. Preparation of functionalized (3-chloropropyl)-silyl silica gel **2**

Functionalized (3-chloropropyl)-silyl silica gel **2** was prepared according to known procedure from dried silica gel [12]. According to this method, 20 g freshly activated silica gel (dried at 100 °C, 2 mmHg, 6 h) and 25 ml of (3-chloropropyl)-triethoxysilane were refluxed in 200 ml toluene for 18 h. The solid was filtered, washed with dichloromethane and dried in vacuum at room temperature. Elemental analysis showed that 1.5 mmol of (3-chloropropyl) silyl reagent was immobilized on 1 g silica gel. Found: C 5.66, H 1.18.

2.3.2. Preparation of functionalized silica ammonium chlorides **3** and **4**

To 10 g of a freshly prepared suspension of functionalized (3-chloropropyl)-silyl silica gel **2** in 150 ml dried toluene were added (+)-cinchonine (13.3 g, 45 mmol) or (*S*)-(−)-nicotine (7.3 g, 45 mmol) and 7.5 ml freshly distilled triethylamine (45 mmol). The reaction mixture was refluxed for 6 h under stirring. The solid was filtered, washed with methanol and dichloromethane and dried under reduced pressure.

Elemental analysis for (+)-cinchoninium derivative **3**, found: C 38.26, H 4.00, N 4.40 (1.54 mmol/g silica). Elemental analysis for (−)-nicotinium derivative **4**, found: C 4.40, H 1.14, N 0.25 (0.1 mmol/g silica).

2.3.3. General procedure for the enantioselective epoxidation of trans-chalcone

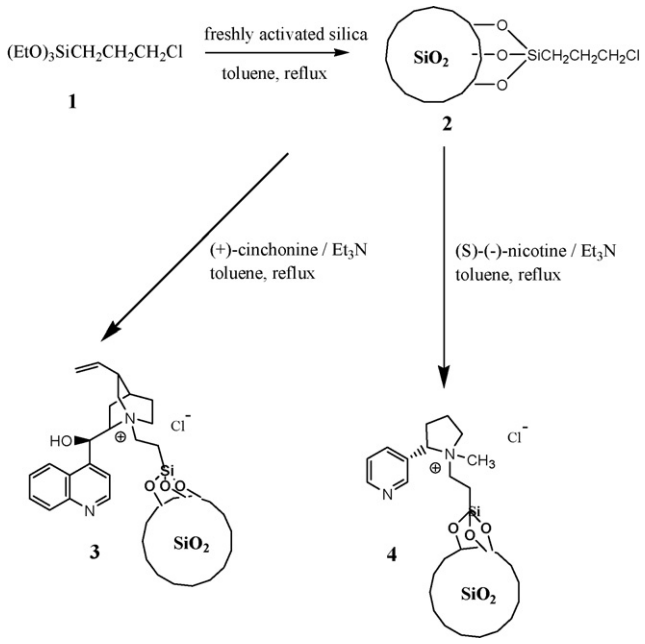
To a mixture of *trans*-chalcone (1.04 g, 5.0 mmol), 0.35 g of functionalized cinconinium chloride **3** or 5 g of functionalized nicotinium chloride **4** and 20 ml organic solvent (toluene or dichloromethane) were added 5 ml hydrogen peroxide (30%) and 0.5 g solid sodium hydroxide (12.5 mmol). The reaction mixture was stirred for 48–100 h. The reaction progress was followed by UV spectroscopy and thin layer chromatography. After this time the solid material (functionalized silica) was removed by simple filtration through a glass filter and the solvents were removed under reduced pressure. To the residue were added 50 ml diethyl ether and 50 ml water. The organic layer was separated from water, dried over $MgSO_4$, removed under reduced pressure and the product purified by column chromatography as a white powder (silica gel, diethyl ether/pentane, 7:1). Chemical yields: 0.62–0.68 g (55–61%). Melting point: 76–77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.93 (2H, m, aromatic protons), 7.67–7.32 (8H, m, aromatic protons), 4.29 (1H, d, J = 7.5 Hz, H-2), 4.06 (1H, d, J = 7.5 Hz, H-3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 135.5, 133.9, 129.0, 128.8, 128.7, 128.3, 125.8, 61.0, 59.3 ppm. $[\alpha]_D = -0.5^\circ$ to -4.0° (c = 1.0, $CHCl_3$).

2.3.4. General procedure for the enantioselective benzylation of O'Donnell's imine

To a mixture of ethyl-*N*-(diphenylmethylene)-glycinate (0.5 g, 1.87 mmol), chiral functionalized (+)-cinchoninium chloride **3** (0.13 g, 0.20 mmol), solid base (4.15 mmol) or aqueous solution of a base (10%) and 20 ml freshly distilled solvent were added 0.34 ml benzyl bromide (2.075 mmol) and the reaction mixture was stirred vigorously at room temperature for 24 h. After this time the solids (base and catalyst) were removed by simple filtration through a glass filter and the solvents removed under reduced pressure. To the residue were added 50 ml diethyl ether and 50 ml water. The organic layer was separated from water, dried over $MgSO_4$, removed under reduced pressure and the product purified with column chromatography as orange viscous oil. Chemical yields: 0.43–0.51 g (65–76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 7.3 Hz, 2H), 7.41–7.30 (m, 8H), 7.21 (t, J = 7.3 Hz, 3H), 7.09 (d, J = 6.8 Hz, 2H), 4.31–4.17 (m, 3H), 3.28 (dd, 2H), 1.29 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.5, 139.3, 137.9, 136.1, 130.1, 129.6, 128.7, 128.2, 128.0, 127.9, 127.6, 126.2, 67.2, 60.9, 39.6, 14.1 ppm. $[\alpha]_D = -27.2^\circ$ to -105.7° (c = 2.0, CH_2Cl_2).

2.3.5. Hydrolysis of the imino-group of the benzylated amino acid ester **7**

In order to determine the absolute configuration and the enantiomeric excess of produced phenylalanine ester, it was necessary to hydrolyze the imine functional group of derivative **7** and compare its optical rotation value with that of a known one. For this purpose, 1 mmol of the imino ester **7** was added to 10 ml ethanolic hydrogen chloride (1N) and stirred vigorously overnight at room temperature. After this time, the solvent was removed under reduced pressure and the product **8** was isolated as white solid powder. Chemical yields: 195–205 mg



Scheme 1. Synthesis of functionalized silica catalysts **3** and **4**.

(85–90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.18 (m, 5H), 4.15 (q, $J_1 = 7.3$ Hz, $J_2 = 6.8$ Hz, 2H), 3.69 (t, $J = 7.3$ Hz, 1H), 2.96 (dd, 2H), 1.50 (s, 3H), 1.23 (t, $J = 7.3$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 137.2, 129.2, 128.3, 126.6, 60.7, 55.7, 41.0, 14.0 ppm. Measured optical rotation values: $[\alpha]_D = -4.8^\circ$ to -18.6° ($c = 2.0$, ethanol).

3. Results and discussion

3.1. Synthesis and characterization of functionalized chiral catalysts *3* and *4*

The novel functionalized organo-inorganic chiral catalysts have been synthesized in two steps as shown in Scheme 1. In the first step, 3-chloropropyl-triethoxysilane **1** was bound on freshly activated silica gel (pore diameter 6.0 nm) by simple refluxing in toluene. In the second step, the isolated functionalized silica **2** was refluxed again in toluene with the chiral auxiliaries (+)-cinchonine or (*S*)-(−)-nicotine resulting in the functionalized chiral catalysts **3** and **4**. Elemental analysis measurements showed that 0.1 mmol of (*S*)-(−)-nicotine and 1.54 mmol of (+)-cinchonine were bound per gram of catalyst. The existence of organic material on silica was also verified by infrared spectroscopy (Fig. 1). In the infrared spectrum of cinchoninium functionalized catalyst **3** (spectrum B) the characteristic bands of the aliphatic protons (2850, 2950 cm^{-1}) as well as and those of the aromatic ones (3000–3150 cm^{-1}) are observed. No aliphatic or aromatic bands are present on the spectrum of pure silica gel (spectrum A). The novel hybridized organo-inorganic catalysts **3** and **4** were tested on the catalytic asymmetric epoxidation of *trans*-chalcone and on the asymmetric benzylation of O'Donnell's imine. These organic substrates have been chosen because of the satisfactory stereochemical results obtained in liquid–liquid phase-transfer-catalysis reactions and for comparison reasons because of the known stereochemistry of their products.

3.2. Stereoselective epoxidation of trans-chalcone

Asymmetric epoxidation reactions of *trans*-chalcone in homogeneous or heterogeneous liquid–liquid PTC reactions have been often used in the last years with appreciable to very good chemical and stereochemical yields [13–21]. In the present work we tried, for the first time, the asymmetric epoxidation of *trans*-chalcone in a solid–liquid–liquid three-phase system using cinchonine and nicotine hybridized catalysts. The functionalized organo-inorganic chiral catalysts constitute the solid phase, while the organic solvents and water the liquid ones. In the organic phase there is the organic substrate, e.g. *trans*-chalcone, while in aqueous phase, the oxidizing reagent and the base. The extent of the stereoselectivities (de, ee) as well as the absolute configuration of epoxide **5** (Scheme 2) was determined by proton NMR spectroscopy and optical rotation measurements. In the proton NMR spectrum of the epoxide **5** the characteristic aliphatic peaks belonging to the *trans*-diastereomer (4.29 and 4.06 ppm) are observed. No peaks of the *syn*-diastereomer could be observed. The absolute configuration (±) and enantiomeric excess (ee, %) of product **5** were determined by comparing their measured optical rotation values with a known one [22]. The

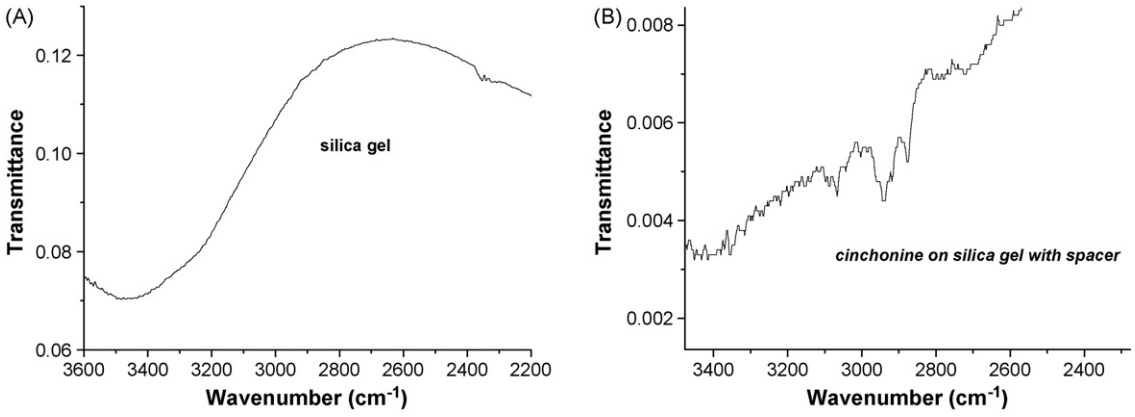
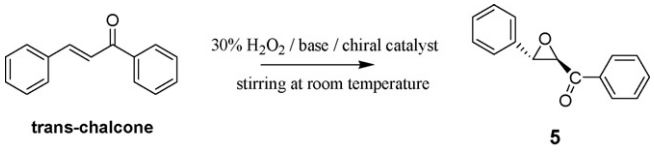


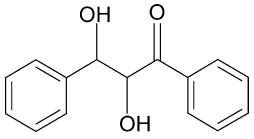
Fig. 1. Infrared spectra of silica gel (A) and functionalized silica with cinchoninine (B).



Scheme 2. Catalytic asymmetric epoxidation of *trans*-chalcone.

measured optical values for epoxide **5** (−0.5 to −4.0) correspond to enantioselectivities between 0.01 and 1.8%. In the literature, the (−) sign is attributed to the absolute configuration (2*R*, 3*S*). Although the first enantioselectivities of epoxide **5** are disappointing, the very good diastereoselectivity (de > 96%) and the relative good chemical yields (65–76%) encourage us to search this reaction further. At this point it should be noted that in our work, only hydrogen peroxide has been used as oxidizing agent. We believe that by using other oxidizing reagents, such as organic peroxides, peracids, potassium persulfate or sodium periodate, the so-called single oxygen donors, the chemical and stereochemical yields may be improved. Such observations have been made by other authors as well [23].

The low chemical yields of epoxide **5** can be attributed partly to its slow decomposition in strong alkaline solutions during the long reaction times needed (sometimes up to 100 h). In one case we were able to isolate and characterize one of these products, namely 2,3-dihydroxy-3-phenylpropiophenone **6.**



This product was isolated by column chromatography and characterized by proton and carbon NMR spectroscopy. The aliphatic protons bound to the carbons C-2 and C-3 appear in proton NMR spectrum at $\delta = 3.35$ and 3.92 ppm as pure duplets indicating the higher diastereoselectivity of this product, while the carbons C-2 and C-3 in carbon NMR spectrum appear at 37.1 and 44.9 ppm, respectively.

As far as the mechanism of this complicated reaction is concerned, it is very difficult to propose a plausible explanation without kinetic or spectroscopic data. However, it is our feeling that this reaction follows a similar mechanism proposed by Yaozhong for solid–liquid–liquid three-phase reactions [24]. All reactions, with exception of the first one, proceed at the aqueous–solid interphase. We suppose that in the beginning of the reaction, hydrogen peroxide and the base which are in the aqueous phase react to give the peroxide anion (reaction (1)).

$$MOH + H_2O_2/H_2O \;\text{======}\; M^+HO_2^- \quad (1)$$

$$M^+HO_2^- + SiO_2{\sim}NR_4^+Cl^- \;\text{======}\; SiO_2{\sim}NR_4^+HO_2^- + MCl \quad (2)$$

$$SiO_2{\sim}NR_4^+HO_2^- + \text{chalcone} \;\text{======}\; SiO_2{\sim}NR_4^+\text{ChalOOH}^- \quad (3)$$

$$SiO_2{\sim}NR_4^+\text{ChalOOH}^- \;\text{======}\; \text{epoxide} + SiO_2{\sim}NR_4^+OH^- \quad (4)$$

$$SiO_2{\sim}NR_4^+OH^- + H_2O_2 \;\text{======}\; SiO_2{\sim}NR_4^+OH^- + H_2O \quad (5)$$

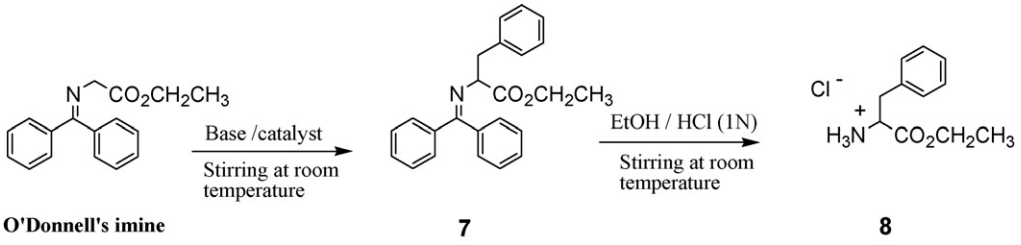
Where: M metal; NR_4^+ cinconinium or nicotinium; ChalOOH^-, 3-peroxy-2.3-dihydrochalcone.

Scheme 3. Possible reactions steps for the epoxidation of *trans*-chalcone.

This species is then quickly adsorbed on the solid surface and build a complex with the ammonium moiety bound on silica surface (reaction (2)). By rapid stirring, the organic substrate (*trans*-chalcone) is also adsorbed on the surface of the solid, reacts with the peroxide anion and gives a new complex (reaction (3)). This complex is of high importance for the stereoselectivity of the new product. It is believed that the conformations of the enolate anion of chalcone in this complex will be stabilized in such a way that the formation of one of possible stereoisomers will be in excess. The linear chalcone-peroxide formed in reaction (3) reacts further via an intra-molecular way to the end product (epoxide, reaction (4)) which is quickly transferred to the organic phase. Finally, the functionalized solid ammonium hydroxide, built in the reaction (4), reacts with hydrogen peroxide to give the functionalized ammonium hydrogen peroxide (reaction (5)). The last species begins a new cycle of reactions (3), (4) and (5) until all the organic substrate (*trans*-chalcone) is consumed. Scheme 3 shows all the possible reactions steps for the epoxidation of *trans*-chalcone.

3.3. Alkylation of glycine derivatives

In benzylation reactions of ethyl-*N*-(diphenylmethylene)-glycinate (O'Donnell's imine) (Scheme 4), the (+)-cinchonine derived functionalized inorganic catalyst **3** leads to good overall chemical yields (65–85%) and moderate enantiomeric excess (25–55%), while no reaction was observed by using the nicotine catalyst **4**, even after 100 h reaction time. This is a very surprising result and cannot be explained at this stage of our research. The only plausible explanation is the very small amounts of nicotine bound on the surface of inorganic material (0.1 mmol nicotine per gram silica gel) which are not enough for catalysis. The extent of the enantiomeric excess (ee) and the absolute configuration (*R*) were determined by comparing the measured optical rotation values of product **8** with that of a known one ($[\alpha]_D = +33.7$, $c = 2$, ethanol) [25]. According to literature data,



Scheme 4. Catalytic asymmetric synthesis of (*R*)-(−)-phenylalanine ethyl ester hydrochloride.

Table 1
Chemical and stereochemical yields of (*R*)-(−)-phenylalanine ethyl ester hydrochloride **8** obtained by using the novel chiral catalyst **3** (10 mol%)

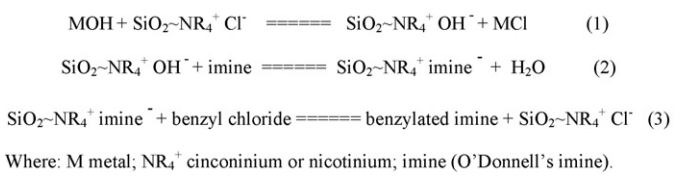
Solvent	Base	Chemical yield[a] (%)	Optical rotation[b] $[\alpha]_D^{25}$	Enantiomeric excess[c] (ee, %)	Absolute configuration[c]
CH_2Cl_2	KOH/K_2CO_3	53	−8.7	25.80	*R*
CH_2Cl_2	$CsOH{\cdot}H_2O$	55	−18.6	55.25	*R*
MeOH	$CsOH{\cdot}H_2O$	65[d]	–	–	–
CH_2Cl_2	NaH	45	−4.8	14.24	*R*
Toluene/CH_2Cl_2 7:3	aq. NaOH (10%)	50	−12.1	35.94	*R*

[a] Overall yields.
[b] Measured in ethanol ($c = 1.0$, EtOH).
[c] Determined by comparison of the measured optical rotation values of product **8** with that given in the literature [15].
[d] Dialkylated product.

the (+)-sign of amino acid ester hydrochloride **8** corresponds to the absolute (*S*)-configuration. Thus, the functionalized cinchoninium catalyst **3** produces the *R*-configured phenylalanine hydrochloride. All chemical and stereochemical data of these reactions are shown in Table 1.

Table 1 shows that all chemical and stereochemical results depend strongly on the solvents and bases used. The best results obtained in dichloromethane and its mixtures with toluene. In protic solvents, such as methanol, only the dialkylated product could be obtained. The best stereochemical results were obtained by using solid caesium hydroxide as a base (ee = 55%). Comparing these results with those published in the international literature for the asymmetric synthesis of amino acids in liquid–liquid PTC reactions, it can be seen that our results produced in three-phase reactions, solid–liquid–liquid (catalyst–aqueous base–organic solvent) or solid–liquid (catalyst, base-organic solvent) are about 20–30% lower than the published ones [4,26–28]. Optimizing further this reaction and testing it for the synthesis of other amino acids, the chemical and stereochemical yields may reach those of literature and even higher.

Regarding the mechanism of the asymmetric benzylation of O'Donnell's imine by using the functionalized chiral silica catalysts **3** and **4** it can be said that this is similar to that proposed earlier for the epoxidation reactions with some differences. Firstly, by using anhydrous solid bases in benzylation reactions, the reaction environment constitutes a solid–liquid two-phase system. Secondly, two reactions less is needed for the alkylation of the imine than for epoxidation reactions and the functionalized catalyst are truly regenerated (in the chloride form). This is not the case in epoxidation reactions where the catalyst obtained at the end of the reaction is not an ammonium halide but an ammonium hydroxide. All possible reactions steps for the benzylation of O'Donnell's imine are given in Scheme 5. At the beginning, the base is adsorbed to the surface of catalyst and an anion exchange process begins leading to a silica-ammonium complex (reaction (1)). This species abstracts then a proton from adsorbed imine and leads to a new complex containing the imine in anionic form (reaction (2)). Finally, the last complex (reaction (3)) reacts further with alkylated reagent giving the end product and the functionalized catalyst in the initial form.



Scheme 5. Possible reactions steps for the benzylation of O'Donnell's imine.

It should be noted, however, that the novel hybridized catalysts are partially decomposed to silica gel and the corresponding ammonium salts. The decomposition is lesser by using anhydrous bases. This has been confirmed by proton NMR and ultra-violet spectroscopy. With this in mind, we expect that the optical and chemical yields of the final products are the result of reactions happened in a three-phase system as well as in that of a liquid–liquid phase-transfer catalysis system. The organic species (cinchoninium or nicotinium salts) leached into the aqueous phase act as true liquid–liquid phase-transfer catalysts. After exchanging their chloride ions with hydroxide in the aqueous phase, they proceed as ammonium hydroxides to the organic phase, starting the alkylation reactions, going back to the aqueous phase as ammonium chlorides and starting again a new cycle of reactions.

4. Conclusions

Although the first stereochemical results of the novel hybridized chiral organo-inorganic catalysts on the asymmetric epoxidation of *trans*-chalcone are disappointing, the good chemical and stereochemical yields produced on the benzylation of ethyl-*N*-(diphenylmethylene)-glycinate (O'Donnell's reagent) by using the functionalized cinchoninium catalyst **3** show that the last reaction may be improved further by optimization experiments using various other alkyl halides.

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