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Biomimetic reductive amination under the continuous-flow reaction conditions

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Dedicated to the memory of Professor L. M. Yagupolskii, the founder of Fluorine Chemistry in Ukraine.

ABSTRACT

This study present a full account of continuous-flow reaction conditions for biomimetic reductive amination of fluorinated carbonyl compounds to corresponding amines and amino acids of biomedical importance. We demonstrate that simple silica-adsorbed DBU can be used as efficient catalysts for on-column 1,3-proton shift reaction, a key transformation in the biomimetic reductive amination process. This new on-column process features operationally convenient conditions, higher chemical yields, enantioselectivity and purity of the corresponding products as compared with traditional in-flask reactions. Moreover the removal of base-catalyst, the most delicate problem of the in-flask reactions, is not an issue in the on-column process, as the silica-adsorbed DBU or polymer-bound guanidine remains on the column and can be reused. This feature renders the overall process substantially more economical and synthetically efficient, in particular, for large-scale synthesis of the corresponding fluorinated amines and amino acids target.

The development of bio-inspired synthetic methodology is currently considered as the most promising direction in modern organic chemistry [1]. The overall advantage of the biomimetic reactions over traditional chemical methods is that this approach offers a "greener", environmentally benign and operationally convenient [2] methodological option for preparation of target organic compounds. Among various biological processes, the enzymatic cofactor pyridoxal 5′-phosphate-catalyzed transamination [3] (Scheme 1) and related reactions inspired many organic chemists to investigate its mechanistic role [4] and develop the corresponding chemical models for practical synthetic applications [5].

The key step in chemical adaptation of the biological transamination is the control over the equilibrium between imines **3** and **4**. However, it is well known that this type of azomethine–azomethine isomerization (1,3-proton shift), due to the usually low C–H acidity of aliphatic imines, requires application of relatively strong base-catalyst under impractically harsh reaction conditions [5k,l]. From the theoretical stand point, the required isomerization as well as the position of the equilibrium can be facilitated and controlled by the designed combination of highly electrophilic carbonyl compound **2** and nucleophilic amine **1** or, vice versa, electrophilic amine **1** and nucleophilic carbonyl compound **2**. Since the latter combination is rather a curiosity, the practical synthetic models mimicking the biological transamination has been achieved with application of highly electrophilic carbonyl compounds **2** for oxidative deamination of amino compounds **1**. Professor Corey's group was first use this biomimetic principle for oxidative deamination, as a key reaction step in several reported by them total syntheses of natural products [6]. Other groups have developed and introduced a series of truly efficient reagents for practical and generalized transformation of amines to the corresponding carbonyl compounds via this biomimetic intramolecular oxidation–reduction reaction [7]. The opposite transformation, the biomimetic reductive amination of carbonyl compounds, turned out to be more difficult to realize, as in this case the increasing nucleophilicity of potential amine-reagent is mirrored by the decreasing C–H acidity, thus requiring stronger base-catalysts and harsher reaction conditions. Nevertheless, a number of successful examples have been reported [8], in particular

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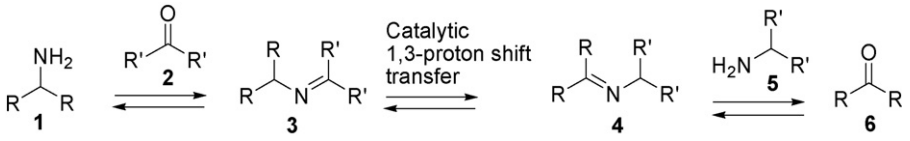


Scheme 1. Biomimetic oxidative deamination (from 1 to 6) and reductive amination (from 6 to 1).

for asymmetric transamination of α-keto to α-amino acids [5a,b,i,j,9].

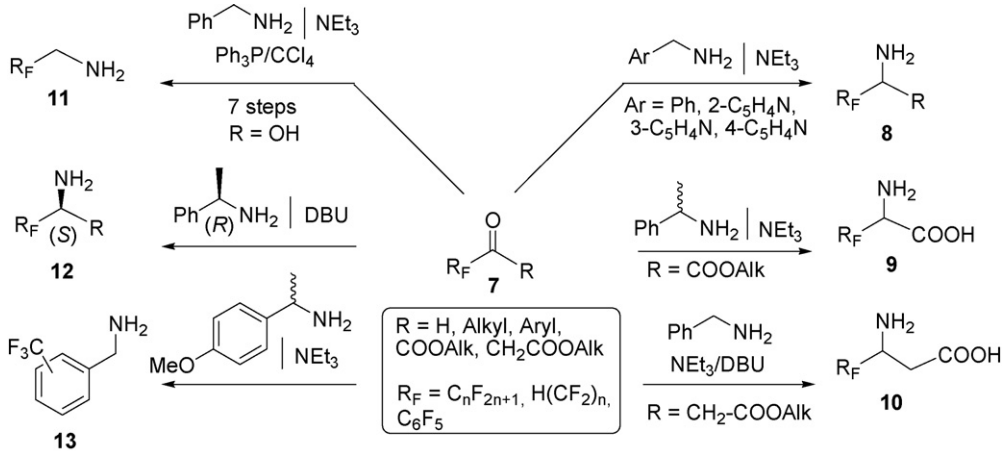
Due to the strong electron-withdrawing nature of fluorine, fluorinated carbonyl compounds are generally highly electrophilic derivatives and therefore, one would envision that their biomimetic reductive amination with alkyl amines might hold promising synthetic potential. In 1988 [10], our group in Kiev, led by Professors V. P. Kukhar and Y. L. Yagupolskii, was first to demonstrate the practicality and generality of this approach for preparation of various fluorinated amino compounds of biomedical importance. Scheme 2 shows the up-to-date synthetic scope of the biomimetic reductive amination of fluorinated carbonyl compounds. Thus, the most straightforward application of this methodology is preparation of fluoroalkylamines **8** by transamination of the corresponding aldehydes and ketones with benzylamine or picolinamines in the presence of triethylamine (TEA) [11]. Application of benzylamine for transamination of perfluoroalkyl α-keto carboxylic esters was found to be complicated due to substantial haloform reaction-type decomposition of the starting keto esters [12]. On the other hand, more sterically bulky *rac*-α-(phenyl)ethylamine allowed preparation of α-amino acids **9** in good isolated yields [13]. Synthesis of β-amino acids **10**, via transamination with benzylamine can be cleanly conducted at elevated temperatures and in the presence of stronger than TEA bases, such as DBU or guanidine [14]. Of particular interest is a unique example of double biomimetic transamination of fluorinated carboxylic acids to α,α-dihydroperfluoroalkylamines **11**. In this case both α-protons of starting benzylamine are used as "reducing reagents". Taking into account that the whole one-pot procedure takes seven separate steps, the obtained yields of >90% were simply remarkable [15]. Asymmetric version of this methodology was developed using inexpensive enantiomers of α-(phenyl)ethylamine, as transaminating reagent. In most cases, due to the lower C–H acidity of the chiral amine as compared with that of benzylamine, application of DBU was required [16]. It is interesting to mention that this reductive amination represent a quite rare case of highly (>90% ee) stereoselective proton transfer from a more to a less configurationally stable stereogenic center [17]. Catalytic asymmetric synthesis of amines **12** using cinchonidine derived bases was also demonstrated [18].

It should be noted that this methodology is not limited to the transamination of carbonyl compounds containing fluoroalkyl group directly bonded to the carbonyl function. Its potential for preparation of benzylamines **13** containing, for instance, trifluoromethyl groups of the phenyl ring has been recently demonstrated [19].

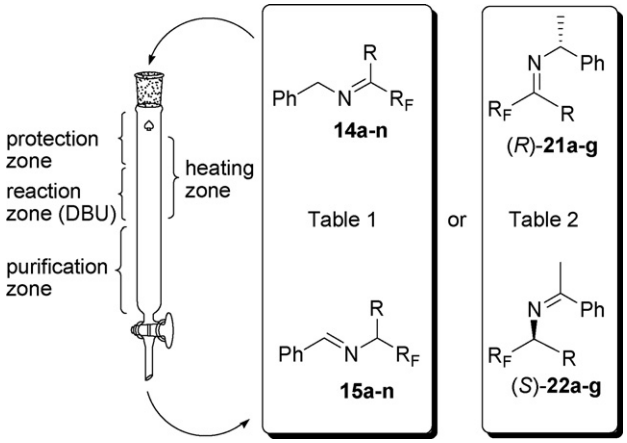
While the high practical value of this biomimetic reductive amination methodology for preparation of fluorinated amines and amino acids, was appreciated by the synthetic community [20] its major advantage over the conventional reduction amination methods, the intramolecular reduction/oxidation process, has never been synthetically explored. We have envisioned that since this biomimetic process does not require the use any external reducing reagents; a conceptually new continuous-flow, on-column, reductive amination process can be realized. Here we report a full account [21] of our studies on the development of continuous-flow reaction conditions for biomimetic reductive amination of fluorinated carbonyl compounds.

Set-up of a suitable process for a continuous-flow reaction using the principle of biomimetic transamination is very simple (Scheme 3) and can be readily assembled and used in any organic chemistry laboratory.

The only issues which can be determined by experiments are the relative proportions between the obviously needed three zones designed for protection, reaction and purification (to remove completely any trace of the base-catalyst). To this end, a conventional Pyrex-glass column was packed about 3/4 of height with a regular silica gel (hexanes), followed by addition, on top of the column, of the calculated amount of DBU (0.25 wt% of the whole amount of silica gel) in a solution of dichloromethane. This step should be done carefully, allowing the solution of DBU to slowly percolate down to the surface and thus generate the reaction zone. An additional amount (1/4 of the whole amount) of silica gel should be charged carefully onto the column, as protection zone. According to experimental data, the DBU penetrates into the silica gel to occupy about 1/4–1/5 of the



Scheme 2. Synthetic scope of biomimetic reductive amination of fluorinated carbonyl compounds.



Scheme 3. Continuous-flow reaction conditions for biomimetic reductive amination using DBU as a base.

Table 1
Yields for isomerization of **14a–n** to **15a–n** under the conditions of continuous-flow reaction.

14	R	R_F	Yield of **15**	
			On-column	In-flask (lit. data)
a	H	CF_3	>98	87
b	H	C_3F_7	95	86
c	H	C_4F_9	96	89
d	H	$H(CF_2)_2$	94	89
e	H	$H(CF_2)_4$	92	89
f	H	$H(CF_2)_6$	95	90
g	Ph	CF_3	>98	93
h	Me	CF_3	93	90
i	Et	CF_3	97	91
j	H	C_6F_5	>98	95
k	Me	C_6F_5	82	73
l	Ph—	CF_3	>98	90
m	*n*-Oct—	CF_3	>98	94
n	n-Hex—	CF_3	>98	93

whole silica gel column volume. Thus assembled column should have the following optimal relative ratios between the three functional parts: protection zone (about 1/4 of the volume), reaction zone (1/4) and purification zone (1/2). A series of various fluorine-containing imines **14a–n**, prepared by standard procedures [11b], were eluted through the column using a mixture of hexanes/acetonitrile (4/1) as a solvent. Expectedly, the rate of the desired isomerization of imines **14a–n** to products **15a–n** was found to depend heavily on concentration of the starting compounds, amount of DBU and rate of the elution. Optimization of these parameters indicated that for a given amount of the catalyst (see Section 1) the imine concentration of about 10 mol% and the elution rate about 1 drop a second from the column tip, generally provide for complete isomerization of starting imines **14a–n** to products **15a–n**. The structure and purity of the products **15a–n**, conveniently collected from the column's tip, were determined by NMR.

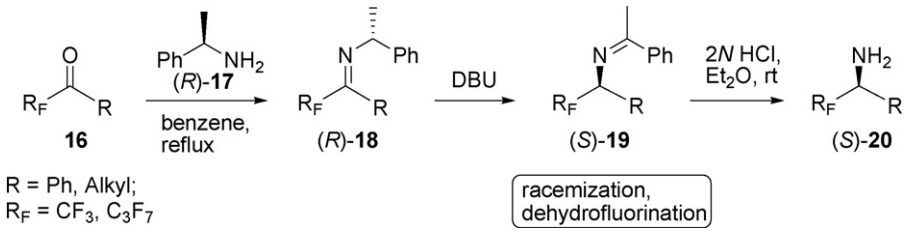
Taking into account that the nature of starting imine **14a–n** has a significant effect on the isomerization rate, the practical rate of the elution and/or the imine **14a–n** concentration should be experimentally adjusted for each particular case. However, there are some useful generalizations can be used as, for instance, the group of fluoroalkyl aldehydes **14a–f** and ketones **14l–n** derived imines showed similar reactivity and therefore can be successfully isomerized under the same set of reaction conditions. Another group of compounds with similar reactivity are ketones derived imines **14g–i,k** and imine **14j**, prepared from perfluorobenzaldehyde. Their isomerization to the corresponding Schiff bases **15g–k** is relatively slow, therefore lower elution rate/lower concentration/longer reaction zone should be used. Experimentally it was found that the twice lower, as compared with the group of **14a–f**, **14l–n** imines, elution rate is generally sufficient to provide complete transformation of **14g–k** to the compounds **15g–k**. The structure and purity of the products **15a–n** were confirmed by NMR and compared with the literature data [11,12,14].

The data collected (Table 1) clearly demonstrates that the isomerization of ket- and aldimines **14a–n** to the products **15a–n**, under the continuous-flow reaction conditions (on-column process) is generally more synthetically efficient, as compared with a conventional (in-solution) reactions. Remarkably, in all cases studied the Schiff bases **15a–n** were obtained in higher yields and of sufficient purity, allowing their further hydrolysis to the target amines without any additional purification. Furthermore, the overall experimental procedure is also significantly more operationally convenient. The durability of the catalyst (SiO_2-absorbed DBU) used in this continuous-flow reaction procedure is high and can be estimated as 5 mol% for about preparation of 1 mol of the products. For repeated use of the same column the elution rate should be slowed by 10% for each 15 mol% of product. The decrease of catalytic activity is most probably the result of CO_2 intake form the air as well as some partial (<1%) dehydrofluorination after products 15 formation. No attempts have been made to regenerate the activity of the catalyst.

With these results in hand we explored next the asymmetric biomimetic reductive amination under continuous-flow reaction conditions. As shown in Scheme 4, the conventional procedure [16,17] for asymmetric biomimetic transamination includes condensation of ketones **16** with chiral amine **17** to form imines **18** followed by their DBU-catalyzed isomerization to Schiff bases **19**, which can be easily hydrolyzed to the target amines **20** and acetophenone as a byproduct.

The key step of this process, the base-catalyzed isomerization of **18** to **19**, is notably stereoselective (up to 97% ee) regardless that the products **19** are substantially less configurationally stable as compared with starting compounds **18**. However, the relative configurational instability of products **19** creates a few problems in the conventional in-flask process. Thus, compounds **19** can undergo some racemization, especially in the presence of relatively strong base, like DBU. For example, in the isomerization of **18** (R = Ph, C_F = CF_3) to highly C–H acidic product **19**, the stereochemical outcome can range from 50 to 87% ee [17]. In principle, the partial racemization problem cannot be solved under the conventional "in-flask" conditions as the products must be exposed to the action of base until the reaction completion. On the other hand, the continuous-flow reaction conditions could offer a unique technical solution to this synthetic complication as the corresponding products can be gradually removed from the reaction zone virtually immediately upon their formation.

To realize the asymmetric reductive amination process under the continuous-flow reaction condition, the same design (Scheme 3) can be used. The only difference in this case is a necessity to run the process under elevated temperature as the isomerization of chiral derivatives **21a–g** to imines **22a–g** takes place under relatively forced reaction conditions. Therefore, we need to add the "heating zone" unit, which can be easily implemented using a usual heating spiral or a mantle (set at 50 °C), covering completely the "reaction zone" and about half of the "protection zone". Imines **21a–g** were charged onto top of the column as described above for the achiral process. The rate of elution vs. completion of the isomerization (^{19}F NMR) was the key issue to limit, to the very minimum possible, the time of the products **22a–g** exposure to the DBU in the "reaction zone". After some experimentations we found



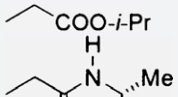
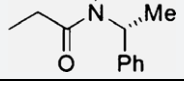
Scheme 4. General scheme for in-flask asymmetric biomimetic reductive amination of fluorinated carbonyl compounds.

that, for the indicated above amount of DBU and the imines **21a–e** concentration, the elution rate about 1 drop per three seconds provided for >95% conversion of starting compounds **21a–e** to the imines **22a–e**. For isomerization of β-amino acid derivatives **21f,g** the same elution rate can be used, however the temperature in the "heating zone" should be raised to 70 °C. The structure and purity of the products **22a–g** were confirmed by NMR and compared with the literature data [16,17]. Taking into account that fluorine-containing compounds have a tendency for high magnitude of the self-disproportionation of enantiomers via ap-chromatography [22] of evaporation/sublimation [23] the enantiomeric composition of products **22a–g** was determined directly on the samples collected from the column before even evaporation of the solvent, using SUMICHIRAL OA-4500; eluent: *n*-hexane/dichloromethane/ethanol = 60/30/10.

As it follows from the data presented in Table 2, the stereochemical outcome of the isomerization reactions conducted under the continuous-flow conditions, was generally higher as compared with that of in-flask reactions [16,17]. For example, in the case of preparation of the most C–H acidic product **22a**, the enantioselectivity was improved from 77 (in-flask) to 93% ee. In the case of derivative **22b**, trifluoromethyl and containing benzyl groups, the yield and enantioselectivity were both improved. In the case of the most unstable (prone to dehydrofluorination) product **22e** noticeable increase in chemical yield was observed (from 74 to 87%). β-Amino acid derivatives **21f,g** were also isomerized to products **22f,g** with a bit better chemical yields and stereoselectivity.

In summary, the results presented here clearly demonstrate that the continuous-flow conditions (on-column) for biomimetic transamination have noticeable advantage of the conventional in-flask procedure in terms of chemical yield, stereochemical outcome and operational convenience. In particular, this new approach may be recommended for repeating, large-scale synthesis of biologically important fluorinated amines and amino acids. As the next step in the further development of continuous-flow methodology application of polymer-bound bases, such as 1,5,7-Triazabicyclo[4.4.0]dec-1-ene (TBD) [24] can be recommended to study.

Table 2
Yields and stereochemical outcome for isomerization of **21a–g** to **22a–g** under the conditions of continuous-flow reaction.

21	R	R_F	22	
			On-column yield (%)/% ee	In-flask (lit. data) yield (%)/% ee
a	Ph	CF_3	95/93	98/77
b	Bn	CF_3	93/91	86/88
c	Me	CF_3	95/93	94/93
d	Et	CF_3	92/91	87/87
e	Me	C_3F_7	87/95	74/97
f		CF_3	92/90	90/85
g		CF_3	91/95	98/93

1. Experimental part

The structure and purity of the products **15a–n** [11,12,14] and **22a–g** [16,17] were confirmed by NMR and compared with the literature data. The enantiomeric composition of compounds **22a–g** was determined using SUMICHIRAL OA-4500; eluent: *n*-hexane/dichloromethane/ethanol = 60/30/10.

General procedure for isomerization of **14a–n** to **15a–n**. In typical experiment, a glass column (3 cm × 80 cm) was charged with 200 g of silica gel (hexanes). While leaving about 1 cm of the solvent on top of silica gel, a suspension of 100 g of silica gel in dichloromethane containing 1 g of DBU was charged onto the top and allowed to percolate down to the surface of silica gel. Finally, additional 100 g of silica gel (hexanes) was added on the top of the column allowing the solvent to percolate down to the surface of silica gel completely. Using thus prepared column, a solution [10 mol% in hexanes/acetonitrile (4/1)] of fluorinated imine **14a–n** was eluted through the column at the rate of 1 drop per second. UV-active fractions (detection by TLC) were collected and evaporated to afford products **15a–n** (for yields, see Table 1).

General procedure for isomerization of **21a–g** to **22a–g**. Typical set-up of the column and experiment: a glass column (3.9 cm × 104 cm) was charged with 260 g of silica gel (hexanes). While leaving about 1 cm of the solvent on top of silica gel, a suspension of 130 g of silica gel in dichloromethane containing 1.3 g of DBU was charged onto the top and allowed to percolate down to the surface of silica gel. Finally, additional 150 g of silica gel (hexanes) was added on the top of the column allowing the solvent to percolate down to the surface of silica gel completely. A heating mantle was attached to the column covering fully the corresponding "reaction zone" and about half of the "protection zone"; the temperature was set at 50 °C. Using thus prepared column, a solution [10 mol% in hexanes/acetonitrile (4/1)] of fluorinated imine **21a–g** was eluted through the column at the rate of 1 drop per second. UV-active fractions (detection by TLC) were collected and evaporated to afford products **22a–g** (for yields and enantioselectivity, see Table 2).

Acknowledgements

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