The Reaction of Carbonyldiimidazole with Alcohols to Form Carbamates and *N*-Alkylimidazoles

Yuanqing Tang, Yuxiang Dong, Jonathan L. Vennerstrom*

College of Pharmacy, University of Nebraska Medical Center, 986025 Nebraska Medical Center, Omaha, NE 68198-6025, USA
Fax +1(402)5599543; E-mail: jvenners@unmc.edu

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Abstract: The reactions of non-benzylic primary and secondary aliphatic alcohols with carbonyldiimidazole (CDI) afford the corresponding carbamates but not *N*-alkylimidazoles. For benzylic primary alcohols, formation of *N*-alkylimidazoles proceeds reasonably at 170 °C in several different solvents and occurs by way of the initially formed carbamate. However, under these rather forcing conditions, or even at lower reaction temperatures, elimination is a significant side reaction for benzylic secondary alcohols with β-hydrogen atoms. With one exception, reactions of six N,N-disubstituted β-aminoalcohols with CDI to form *N*-alkylimidazoles proceed under relatively mild conditions and may occur by way of an aziridinium intermediate.

Keywords: alcohols, alkylations, carbonyldiimidazole (CDI), carbamates, *N*-alkylimidazoles

A number of medicinally important molecules contain an *N*-alkylimidazole moiety,[1] most notably the large family of azole antifungal drugs. This heterocycle is either assembled as one step of a synthetic sequence, or is added preformed, usually by imidazole anion nucleophilic displacement of an alkyl halide[2] or sulfonate.[3] In our plans to incorporate *N*-alkylimidazoles into target molecules, we were attracted by a recent paper in this journal[4] that described high-yield conversions of a large variety of primary and secondary alcohols and phenols into their corresponding *N*-alkylimidazoles and *N*-alkyltriazoles by a facile reaction with carbonyldiimidazole (CDI) or carbonylditriazole at room temperature or in refluxing acetonitrile (MeCN), ethyl acetate, and dichloromethane. When we repeated this reaction for three of these alcohols, we obtained only carbamates for 3,4-dimethylbenzyl alcohol and benzhydrol, and a mixture of the carbamate and *N*-alkylimidazole for 1-indanol. In a similar exploration of Njar's method,[4] Fischer[5] isolated only the corresponding carbamates from 2,6-dimethylphenol and 1-indanol. We also note that Njar[4] reports nearly identical melting point and ^{1}H NMR data for the *N*-alkylimidazole and carbamate reaction products of the secondary alcohol testosterone; the NMR data is consistent with an imidazole carbamate, not an *N*-alkylimidazole (*vide infra*). In order to further clarify the scope of the reaction of alcohols (Figure 1) with CDI to form *N*-alkylimidazoles, we investigated this reaction further and our results are reported herein.

Primary and Secondary Alcohols. Following the procedure of Njar,[4] reaction of primary alcohol **1a** with 1.3 equivalents of CDI in MeCN at room temperature formed carbamate **3a** in quantitative yield (Table 1, entry 1) instead of the expected *N*-alkylimidazole **2a**. The ^{1}H NMR spectrum (Table 2) of **3a** showed one peak at δ 8.14 ppm, typical for the imidazole H-2 in imidazole carbamates, instead of the imidazole H-2 in *N*-alkylimidazoles which is in the range of δ 7.4–7.7 ppm. In addition, the signal at δ

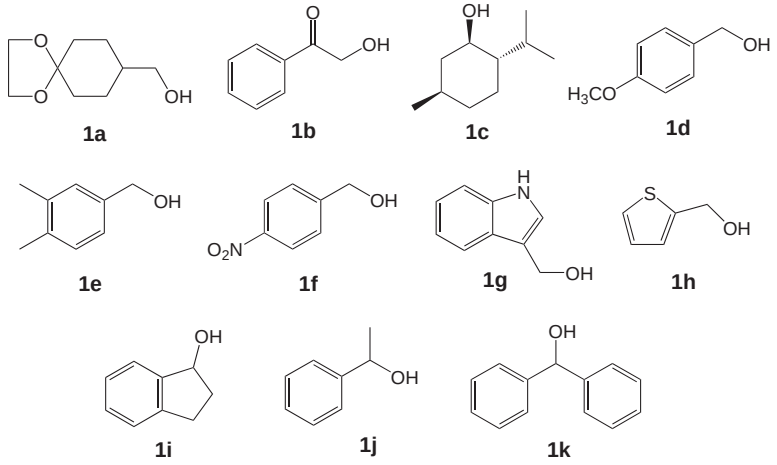

Figure 1 Structures of alcohols **1**

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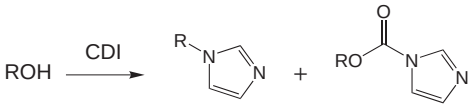
Table 1 Reactions of CDI with Alcohols



1 **2** **3**

Entry	Alcohol	Conditions	Products, yield [%][a]
1	**1a**	MeCN, r.t., 2 h	**3a**, 100
2	**1a**	NMP, 170 °C, 5 h	**3a**, 92
3	**1c**	NMP, 170 °C, 24 h	**3c**, 90
4	**1d**	NMP, 170 °C, 1 h	**2d**, 80
5	**1e**	NMP, 170 °C, 1 h	**2e**, 70
6	**1f**	NMP, 170 °C, 1 h	**2f**, 82
7	**1f**	diglyme, 170 °C, 1 h	**2f**, 92; **3f**, 8
8	**1f**	diglyme, 170 °C, 18 h	**2f**, 94
9	**1f**	xylene, 170 °C, 1 h	**2f**, 65; **3f**, 35
10	**1f**	xylene, 170 °C, 18 h	**2f**, 74
11	**1f**	decane, 170 °C, 18 h	**2f**, 10
12	**1g**	THF, reflux, 5 h	**2g**, 60
13	**1g**	MeCN, r.t., 4 h	**2g**, 50
14	**1h**	EtOAc, r.t., 7 h	**3h**, 99
15	**1h**	EtOAc, reflux, 7 h	**2h**, 25; **3h**, 70
16	**1h**	MeCN, reflux, 24 h	**2h**, 70
17	**1i**	MeCN, reflux, 5 h	**2i**, 30; **3i**, 10; indene, 30
18	**1j**	EtOAc, reflux, 18 h	**3j**, 94
19	**1j**	NMP, 170 °C, 1 h	**2j**, 55; **3j**, 5; styrene, 20
20	**1j**	NMP, 170 °C, 5 h	**2j**, 55; styrene, 5
21	**1k**	MeCN, r.t., 2 h	**3k**, 80
22	**1k**	NMP, 170 °C, 1 h	**2k**, 80

[a] Isolated yields except for entries 7, 9, 15, 17, 19 and 20. For those entries, estimated yields are based on integration of ^{1}H NMR spectra. In each case, all signals could be assigned.

4.27 (J = 6.3 Hz, 2 H) indicated a –CH_2O– rather than –CH_2N–. More important, a signal at δ 148.7 ppm in the ^{13}C NMR spectrum of **3a** unambiguously pointed to the carbamate carbonyl group. In order to confirm this, **2a** was independently prepared in a reaction between imidazole sodium salt (NaH in DMF) and the mesylate of **1a**. The ^{1}H NMR spectrum of **2a** showed signals at δ 3.80 (d, J = 6.8 Hz, 2 H) and 6.88 (s, 1 H), 7.05 (s, 1 H), 7.43 (s, 1 H) consistent with –CH_2N– and imidazole substructures. The reaction of **1a** and CDI in hot NMP also yielded only **3a** (Table 1, entry 2). Similarly, 2-hydroxyacetophenone (**1b**) and S–(–)-menthol (**1c**) formed only the corresponding carbamates (Table 1, entry 3) regardless of the solvent (MeCN, NMP) or reaction temperature.

Table 2 Characteristic ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm) Data of Imidazole Carbamates (**3** or **7**) and *N*-Alkylimidazoles (**2**, **8** or **10**)

3 or **7**	^{1}H (δ, ppm)	**2**, **8** or **10**	^{1}H (δ, ppm)
3a	8.14, 7.43, 7.07 (Im)[a], 4.27 (α)	**2a**	7.43, 7.05, 6.88 (Im), 3.80 (α)
3e	8.14, 7.42, 7.05 (Im), 5.35 (α)	**2e**	7.52, 7.06, 6.88 (Im), 5.03 (α)
3h	8.13, 7.42, 7.05 (Im), 5.57 (α)	**2h**	7.54, 7.05, 6.95 (Im), 5.26 (α)
3i	8.10, 7.40, 7.04 (Im), 6.41 (α)	**2i**	7.41, 7.05, 6.81 (Im), 5.65 (α)
3k	8.22, 7.50, 7.09 (Im), 7.05 (α)	**2k**	7.39, 7.08, 6.84 (Im), 6.51 (α)
7a	8.14, 7.43, 7.07 (Im), 4.46 (α)	**8a**	7.59, 7.03, 6.96 (Im), 3.97 (α)
7b	8.34, 7.42, 7.06 (Im), 5.19 (α)	**8b**	7.51, 7.01, 6.92 (Im), 4.15 (α)
7c	8.18, 7.46, 7.07 (Im), 6.15 (α)	**8c**	7.66, 7.04, 6.96 (Im), 5.22 (α)
7d	8.15, 7.44, 7.08 (Im), 4.45 (α)	**8d**	7.59, 7.03, 6.93 (Im), 3.88 (α)
7e	8.15, 7.44, 7.06 (Im), 5.08 (α)	**8e**	Not formed
7f	8.13, 7.43, 7.05 (Im), 4.96 (α)	**8f**	7.46, 7.01, 6.90 (Im), 3.86 (α)
		10b	7.49, 7.02, 6.94 (Im), 3.94, 3.72 (α)
		10c	7.64, 6.94, 6.77 (Im), 4.40, 4.13 (α)

[a] Im = imidazole.

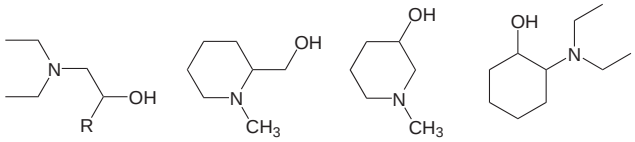
Benzylic Primary Alcohols. The reaction of benzylic primary alcohols with CDI was dependent both on alcohol structure and reaction conditions. In refluxing MeCN or ethyl acetate, benzyl alcohols **1d**–**1f** afforded only the corresponding carbamates (data not shown). In contrast, in NMP at 170 °C, the three benzyl alcohols gave good yields of *N*-alkylimidazoles **2d**,[6] **2e**,[6] and **2f**[6] (Table 1, entries 4–6). At the same temperature, the conversion of **1f** to **2f** also proceeded readily in less polar solvents such as diglyme and xylene (Table 1, entries 7–10), but in decane, the yield dropped to 10% even with an 18 h reaction time (Table 1, entry 11). Consistent with the results of Le Borgne,[7] indole carbinol **1g** readily formed *N*-alkylimidazole **2g** in either refluxing THF or in MeCN at room temperature (Table 1, entries 12 and 13). In ethyl acetate at room temperature (Table 1, entry 14) thiophene carbinol

1h formed only carbamate **3h**, whereas in refluxing ethyl acetate or MeCN, *N*-alkylimidazole **2h**[8] was obtained in 25% and 70% yields, respectively (Table 1, entries 15 and 16). These data suggest that formation of *N*-alkylimidazoles occurs more easily for electron-rich benzylic systems.

Benzylic Secondary Alcohols. In refluxing MeCN, indanol (**1i**) gave a modest yield of *N*-alkylimidazole **2i** along with carbamate **3i**[4,5] and indene, the dehydration product (Table 1, entry 17). In refluxing ethyl acetate, 1-phenylethanol (**1j**) formed carbamate **3j**[9] in high yield (Table 1, entry 18), whereas in hot NMP, *N*-alkylimidazole **2j**[10] was formed in moderate yield along with carbamate **3j** and styrene, the dehydration product (Table 1, Entry 19). With prolonged reaction times (Table 1, entry 20), the yield of **2j** remained the same, and the yield of styrene decreased, most likely due to polymerization. In MeCN at room temperature, benzhydrol (**1k**) afforded only carbamate **3k**[11] (Table 1, entry 21), whereas in hot NMP, *N*-alkylimidazole **2k**[11] was obtained (Table 1, entry 22).

Mechanistic Considerations. The following experiment provided some clues to the mechanism of the reaction of alcohols with CDI to form *N*-alkylimidazoles (Scheme 1). Preformed carbamate **3e**[4] in hot NMP afforded a mixture of alcohol **1e**, *N*-alkylimidazole **2e**, and carbonate **4e**. Using the same reaction conditions, the reaction of **3e** in the presence of 1, 2, and 5 equivalents of 2-methylimidazole afforded *N*-alkylimidazole **2e** in progressively decreasing yields and *N*-alkyl-2-methylimidazole **5e** in progressively increasing yields. This outcome is inconsistent with the S_Ni pathway postulated by Njar.[4] Instead, the reaction appears to proceed by entropy-driven decarboxylation of the initially formed imidazole carbamate.

N,N-Disubstituted β-Aminoalcohols. Intrigued by reports that treatment of a *N*,*N*-dimethyl-β-aminoalcohol with CDI and excess imidazole afforded the corresponding *N*-alkylimidazole,[12] and that treatment of N-substituted β-aminoalcohols with CDI forms oxazolidine-2-ones, and in some cases, aziridines,[13] we investigated the reaction of N,N-disubstituted β-aminoalcohols **6** with CDI in refluxing ethyl acetate (Figure 2, Table 3). Primary alcohols **6a** and **6d** formed, along with carbamate **7d** and carbonates **9a** and **9d**, *N*-alkylimidazoles **8a**[14] and **8d** (Table 3, entries 23 and 26), whereas secondary alcohols **6b** and **6c** formed *N*-alkylimidazoles **8b** and **8c** along with the regioisomeric *N*-alkylimidazoles **10b** and **10c**, respectively (Table 3, entries 24 and 25, Figure 3). Interestingly, carbamate **7b** was quite unstable, and when treated with H_2O–EtOAc, it was partially converted to carbonate **9b** along with alcohol **6b** (data not shown). Formation of **10b** and **10c** suggest that the imidazole alkylations occurred via aziridinium intermediates.[15,16] The failure of **6e** to form *N*-alkylimidazole **8e** (Table 3, entry 27), and the low conversion of **6d** and **6f** to their corresponding *N*-alkylimidazoles **8d** and **8f** (Table 3, entries 26 and 28), may reflect the diminished tendency to form their more strained and sterically hindered bicyclic aziridium intermediates. Indeed, treatment of the *N*,*N*-dimethyl analog of **6f** with 2.1 equivalents of CDI in refluxing THF (3.5 h) formed only the corresponding carbamate.[17]

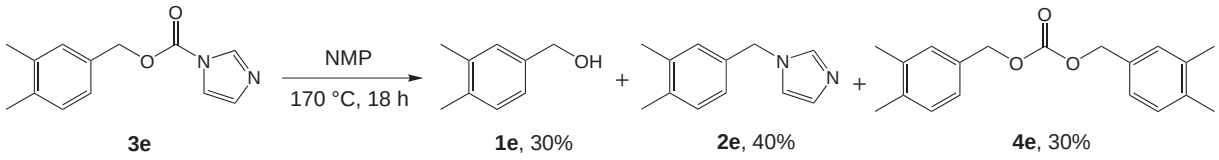


6a R = H
6b R = Me
6c R = Ph

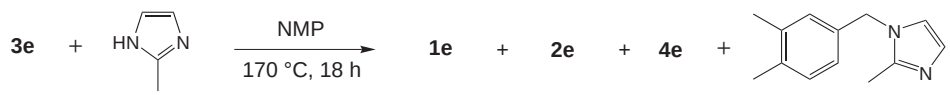
6d **6e** **6f**

Figure 2 Structures of N,N-disubstituted β-aminoalcohols **6**

In summary, the reaction to form *N*-alkylimidazoles from alcohols appears to proceed by entropy-driven decarboxylation of the initially formed imidazole carbamate. For benzylic primary alcohols with both electron-donating (**1d**) and electron-withdrawing (**1f**) substituents, forma-



3e **1e**, 30% **2e**, 40% **4e**, 30%

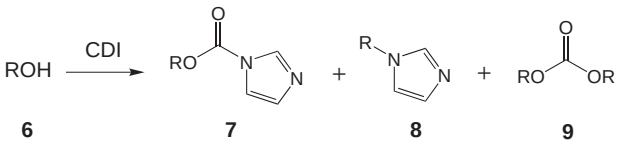


5e

1 equiv	25%	26%	10%	39%
2 equiv	21%	24%	0%	55%
5 equiv	10%	12%	0%	78%

Scheme 1

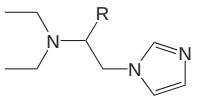
Table 3 Reactions of CDI with N,N-Disubstituted β-Aminoalcohols



6 **7** **8** **9**

Entry	Alcohol	Products, yield [%][a]
23	**6a**	**8a**, 90; **9a**, 10
24	**6b**	**8b**, 25; **10b**,[b] 75
25	**6c**	**8c**, 82; **10c**,[b] 8
26	**6d**	**7d**, 37; **8d**, 6; **9d**, 57
27	**6e**	**7e**, 65; **9e**, 35
28	**6f**	**7f**, 62; **8f**, 21

[a] Estimated yields are based on integration of ^{1}H NMR spectra. In each case, all signals could be assigned.
[b] Rearranged *N*-alkylimidazole products (see Figure 3).



10b R = Me
10c R = Ph

Figure 3 Structures of *N*-alkylimidazoles **10b** and **10c**

tion of *N*-alkylimidazoles works reasonably well at elevated reaction temperatures. However, under these rather forcing conditions, or even at lower reaction temperatures, elimination is a significant side reaction for benzylic secondary alcohols with β-hydrogen atoms such as **1i** and **1j**. Only for indole and thiophene carbinols **1g** and **1h**, did we obtain the corresponding *N*-alkylimidazoles under relatively mild conditions, a result consistent with previous data.[7] Several reports[2b,17,18] disclose that in refluxing dichloromethane or THF, several substituted benzhydrols form the corresponding *N*-alkylimidazoles in low to excellent yields, but we observed that benzhydrol formed the corresponding *N*-alkylimidazole only at elevated reaction temperatures. It is apparent from this data that reaction of alcohols with CDI to form *N*-alkylimidazoles is not a generally applicable synthetic method, although the corresponding reaction of N,N-disubstituted β-aminoalcohols proceeded under relatively mild conditions and may have occurred by way of aziridinium intermediates. Finally, ^{1}H NMR and ^{13}C NMR spectra unambiguously differentiate *N*-alkylimidazoles and the corresponding carbamates.

The melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer using $CDCl_3$ as solvent. All chemical shifts are reported in ppm and are relative to internal TMS for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C NMR. FAB-HRMS spectra were obtained using a Kratos MS-50 spectrometer.

Reaction of Alcohols with CDI to Form Carbamates 3; Typical Procedure

1,4-Dioxaspiro[4,5]dec-8-ylmethyl 1*H*-Imidazole-1-carboxylate (3a, Table 1, Entry 1)

A mixture of **1a** (172 mg, 1 mmol), CDI (210 mg, 1.3 mmol) and MeCN (15 mL) was stirred at r.t. for 2 h before quenching with cold H_2O (50 mL). The reaction mixture was extracted with $CHCl_3$ and the organic extract was washed with H_2O and brine, dried over $MgSO_4$, filtered and dried in vacuo to afford **3a** as a colorless solid (266 mg, 100%).

Mp 48–50 °C.

^{1}H NMR ($CDCl_3$): δ = 1.38–1.45 (m, 2 H), 1.52–1.61 (m, 2 H), 1.78–1.90 (m, 5 H), 3.94–4.00 (m, 4 H), 4.27 (d, *J* = 6.3 Hz, 2 H), 7.07 (s, 1 H), 7.43 (s, 1 H), 8.14 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 26.6, 33.9, 35.9, 64.30, 64.33, 72.3, 108.4, 117.1, 130.7, 137.1, 148.7.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{19}N_2O_4$: 267.1345; found: 267.1354.

2-Oxo-2-phenylethyl 1*H*-Imidazole-1-carboxylate (3b)

Brown solid (207 mg, 90%); mp 62–65 °C.

^{1}H NMR ($CDCl_3$): δ = 5.63 (s, 2 H), 7.09 (s, 1 H), 7.49 (s, 1 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 7.64 (t, *J* = 7.3 Hz, 1 H), 7.92 (d, *J* = 7.4 Hz, 2 H), 8.21 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 68.3, 117.1, 127.5, 128.8, 130.5, 133.3, 134.2, 137.1, 148.2, 190.2.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{11}N_2O_3$: 231.0770; found: 231.0772.

Menthyl 1*H*-Imidazole-1-carboxylate (3c, Table 1, Entry 3)

Colorless oil (yield 90%).

^{1}H NMR ($CDCl_3$): δ = 0.82 (d, *J* = 7.3 Hz, 3 H), 0.93 (d, *J* = 7.3 Hz, 3 H), 0.95 (d, *J* = 7.0 Hz, 3 H), 1.14–1.20 (m, 2 H), 1.50–1.60 (m, 2 H), 1.71–1.79 (m, 2 H), 1.84–1.88 (m, 1 H), 2.14–2.20 (m, 1 H), 4.86–4.92 (m, 1 H), 7.07 (s, 1 H), 7.42 (s, 1 H), 8.13 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 16.4, 20.6, 21.9, 23.5, 26.5, 31.4, 33.9, 40.5, 47.0, 79.3, 117.1, 130.5, 137.0, 148.3.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{23}N_2O_2$: 251.1760; found: 251.1762.

1-(1,4-Dioxaspiro[4,5]dec-8-ylmethyl-1*H*-imidazole (2a)

A solution of methanesulfonyl chloride (1.38 g, 12 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a mixture of **1a** (1.38 g, 8 mmol), Et_3N (1.52 g, 15 mmol) and CH_2Cl_2 (20 mL). Upon completion of the addition, the reaction mixture was stirred for 1 h at r.t., and washed successively with 0.5 M HCl, H_2O and brine, dried over $MgSO_4$, filtered and dried in vacuo to afford the mesylate as a colorless oil (2.0 g, 100%).

^{1}H NMR ($CDCl_3$): δ = 1.30–1.40 (m, 2 H), 1.50–1.60 (m, 2 H), 1.76–1.86 (m, 5 H), 3.00 (s, 3 H), 3.90–4.00 (m, 4 H), 4.06 (d, *J* = 6.3 Hz, 2 H).

To a suspension of 60% NaH (0.08 g, 2 mmol) in DMF (4 mL) under nitrogen at 0 °C was added a solution of imidazole (0.14 g, 2 mmol) in DMF (4 mL). The mixture was stirred for 30 min before a solution of the above mesylate (0.25 g, 1 mmol) in DMF (4 mL) was added dropwise. The mixture was heated at 60 °C for 2 h before being quenched with H_2O (40 mL) and then extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine (3 × 30 mL), dried over $MgSO_4$, filtered, and concentrated to afford **2a** (0.20 g, 90%) as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 1.22–1.36 (m, 2 H), 1.48–1.56 (m, 2 H), 1.62 (d, *J* = 5.6 Hz, 2 H), 1.70–1.80 (m, 3 H), 3.80 (d, *J* = 6.8 Hz, 2 H), 3.90–3.97 (m, 4 H), 6.88 (s, 1 H), 7.05 (s, 1 H), 7.43 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 27.6, 33.9, 38.0, 52.5, 64.2, 64.3, 108.4, 119.2, 129.4, 137.4.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{19}N_2O_2$: 223.1446; found: 223.1434.

Reaction of Benzylic Alcohols with CDI to Form *N*-Alkylimidazoles 2; Typical Procedure

1-Benzhydryl-1*H*-imidazole (2k)

A mixture of **1k** (184 mg, 1 mmol), CDI (210 mg, 1.3 mmol) and NMP (10 mL) was heated at 170 °C for 1 h. After cooling to r.t., the reaction mixture was diluted with EtOAc (30 mL) and washed with H_2O (2 × 20 mL), brine (20 mL) and dried over $MgSO_4$. Filtration and removal of solvents in vacuo afford **2k**[11] as a colorless solid (178 mg, 80%).

Reaction of 3,4-Dimethylbenzyl 1*H*-Imidazole-1-carboxylate with 2-Methylimidazole

1-(3,4-Dimethylbenzyl)-2-methyl-1*H*-imidazole (5e)

A mixture of 3,4-dimethylbenzyl 1*H*-imidazole-1-carboxylate (**3e**) (230 mg, 1 mmol), 2-methylimidazole (420 mg, 5 mmol) and NMP (10 mL) was heated at 170 °C for 16 h. After cooling to r.t., the reaction mixture was diluted with EtOAc (30 mL) and washed with H_2O (2 × 20 mL), brine (20 mL) and dried over $MgSO_4$. Filtration and removal of solvents in vacuo afford a mixture of **2e**[6] and **5e** (1:4).

For 5e

^{1}H NMR ($CDCl_3$): δ = 2.22 (s, 3 H), 2.23 (s, 3 H), 2.33 (s, 3 H), 4.95 (s, 2 H), 6.78 (d, *J* = 7.8 Hz, 1 H), 6.81 (s, 1 H), 6.83 (s, 1 H), 6.92 (s, 1 H), 7.08 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.9, 19.2, 19.6, 49.3, 119.7, 124.0, 126.9, 133.5, 136.1, 144.6.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{17}N_2$: 201.1392; found: 201.1390.

Reaction of N,N-Disubstituted β-Aminoalcohols with CDI; Typical Procedure

***N*,*N*-Diethyl-2-(1*H*-imidazol-1-yl)propan-1-amine (8b) and *N*,*N*-Diethyl-1-(1*H*-imidazol-1-yl)propan-2-amine (10b)**

A mixture of **6b** (400 mg, 3 mmol), CDI (582 mg, 3.6 mmol) and EtOAc (20 mL) was refluxed overnight. After cooling to r.t., the reaction mixture was washed with H_2O (2 × 20 mL), brine (20 mL) and dried over $MgSO_4$. Filtration and removal of solvents in vacuo afford a 1:3 mixture of **8b** and **10b**.

For 8b

^{1}H NMR ($CDCl_3$): δ = 0.92 (t, *J* = 6.8 Hz, 3 H), 0.94 (t, *J* = 6.8 Hz, 3 H), 1.47 (d, *J* = 6.8 Hz, 3 H), 2.39 (q, *J* = 6.8 Hz, 2 H), 2.43–2.47 (m, 1 H), 2.53 (q, *J* = 6.8 Hz, 2 H), 2.55–2.59 (m, 1 H), 4.13–4.17 (m, 1 H), 6.95 (s, 1 H), 7.04 (s, 1 H), 7.54 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.0, 19.2, 47.8, 53.0, 60.5, 116.6, 128.9, 136.1.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{20}N_3$: 182.1657; found: 182.1655.

For 10b

^{1}H NMR ($CDCl_3$): δ = 0.96 (t, *J* = 7.2 Hz, 3 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 2.41 (q, *J* = 7.2 Hz, 2 H) 2.56 (q, *J* = 7.2 Hz, 2 H), 3.05 (m, 1 H), 3.72 (dd, *J* = 4.3, 13.7 Hz, 1 H), 3.94 (dd, *J* = 7.6, 13.7 Hz, 1 H), 6.94 (s, 1 H), 7.02 (s, 1 H), 7.49 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.2, 14.1, 43.2, 50.7, 56.2, 119.3, 128.9, 137.6.

HRMS–FAB: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{20}N_3$: 182.1657; found: 182.1655.

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