# The Reaction of Amines with Benzyl Halides under $CO_2$ Atmosphere

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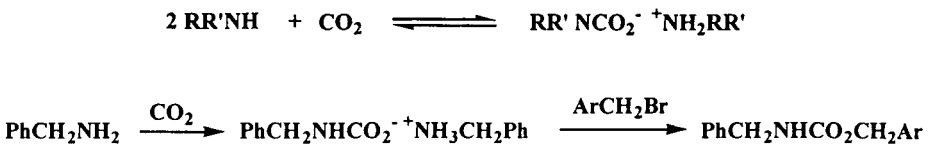
To find a useful, practical, and ecologically safer way to synthesize protected amines, the reactions of amines with benzyl halides under $CO_2$ atmosphere were systematically examined. For primary amines, the $CO_2$-inserted products were obtained in higher yields in the presence of DBU as a base, under a high pressure of $CO_2$, and in a low-polarity solvent (toluene/hexane 1:1). Secondary amines gave only low yields of $CO_2$-inserted products.

**Introduction.** – Organic carbamates exhibit unique physical and chemical properties, accommodating a variety of applications in pharmacology (medicinal drugs), agriculture (pesticides, fungicides, herbicides), and chemical industry (synthetic intermediates) [1]. Their use as protective groups for the $NH_2$ group in amino acids in peptide synthesis is also well-known [2]. So far, the protecting reagent most often used is benzyl carbonochloridate (ZCl), which is prepared from phosgene ($COCl_2$), an extremely hazardous compound used in many syntheses, and benzyl alcohol. Several attempts have been made to employ new methodologies in which the toxic phosgene is replaced with less toxic and less dangerous reagents [3]. One of the many goals of the 'green chemistry movement' intends to replace phosgene by carbon dioxide, a cheap, benign-nature, and abundant reagent [4]. So far, several reports have appeared dealing with the synthesis of carbamate esters from amines, $CO_2$, and alkyl halides [5]. Obviously, this synthetic method can be directly applied to protect amino groups if benzyl carbamates can be produced in high yields. In one of these reports, *Yoshida et al.* found that the reaction of carbamate anions with alkyl halides in the presence of RR′NH as a base gave predominantly *N*-alkylated products (RR′NR″) and only poor yields of carbamate esters ($RR'NCO_2R''$) [5a]. This result may be due to the poor nucleophilicity of the carbamate as compared to the reactivity of the N-atom or to an unfavorable equilibrium concentration of carbamate in solution. Improvements in the yields and selectivities of urethane products over amine products *via* a stabilization of the carbamate anion by DBU as a base were reported by *Hori et al.* [5b]. In this case, however, only reactions with highly reactive electrophiles, *i.e.*, bromides and tosylates, gave acceptable amounts of urethanes. *Calderazzo et al.* have also reported the use of carbamates as nucleophiles in reactions with MeI to give methyl carbamates [6]. These investigations showed that the use of crown ethers and cryptands in combination with carbamate anion/potassium cation systems gave good yields of urethanes. A similar approach has been elucidated by *Aresta* and *Quaranta* in recent reports [7]. Recently, *McGhee et al.* disclosed that, in the reaction of amines, carbon dioxide, and alkyl chlorides, the effect of added base on the yield and selectivity of carbamate

($RNHCO_2R'$) formation was found to be highly important, the use of sterically hindered guanidine bases giving the best results [8]. However, in our own investigation of this reaction, we found that, using DBU as a base, similar yields and selectivities of carbamates ($RNHCO_2R'$) could be obtained as well. In the present paper, we report our results on the synthesis of benzyl carbamates by means of $CO_2$. This reaction is very simple because it is well known that mixing $CO_2$ with amines leads to alkylammonium carbamates. Thus, the key step for the formation of benzyl carbamates is the reaction of alkylammonium carbamates with benzyl halides (*Scheme 1*). One competitive reaction is the direct alkylation of the amine with benzyl halides to give the corresponding secondary or tertiary amine. Thus the selection of solvents and bases, the pressure of $CO_2$, and the nucleophilicity of the amines themselves can drastically affect the reaction.

*Scheme 1*




**Results and Discussion.** – We first examined the reaction of benzylamine with benzyl halides under $CO_2$ atmosphere or in a stainless-steal autoclave with high pressure of $CO_2$ under various reaction conditions. The results, summarized in *Table 1*, show that bases, pressure of $CO_2$, and solvents played a very important role in this reaction. With $Na_2CO_3$ as a base and toluene or MeCN as solvent, no $CO_2$-inserted product could be obtained even under high pressure of $CO_2$ (*Table 1*, *Entries 1–3*) (amine/halide/$Na_2CO_3$ 1:1:1). In the presence of other inorganic bases such as $K_2CO_3$, $Cs_2CO_3$, $Li_2CO_3$, or LiOH in *N*,*N*-dimethylformamide (DMF), the $CO_2$-inserted product **1a** was in general obtained in very low yields (*Entries 4–10*). The tertiary amine **2a** was the major product. The presence of catalytic amounts of phase transfer catalyst and crown ether ([18]crown-6) or high pressure of $CO_2$ did not improve the yields of **1a**. However, with 1.0 equiv. of DBU (=1,8-diazabicyclo[5.4.0]undec-7-ene) as a base, the yields of **1a** could be increased, but the undesired **2a** was still formed, especially with benzyl bromide as an electrophile (*Table 1*, *Entries 11–15*). This result can be explained by the 'hard-and-soft acid/base priciple' (HSAB). As an acid, benzyl chloride is harder than benzyl bromide. As base, $RNHC(O)O^-$ is harder than benzylamine. Thus, **2a** was formed predominantly with benzyl bromide as the electrophile. In low-polarity solvents (toluene or hexane), the reaction yielded *ca.* 20% of **1a**, and the formation of **2a** was reduced (*Table 1*, *Entries 16* and *17*). Moreover, in the mixed solvent toluene/hexane 1:1 at room temperature, the yield of **1a** reached 44% (*Table 1*, *Entries 18* and *19*), and increasing the pressure of $CO_2$ also improved the yield of **1a**. The optimum result, *i.e.* 87% of **1a**, was obtained with 1.0 equiv. of DBU and benzyl chloride as the electrophile at 80° under high pressure of $CO_2$ (*Table 1*, *Entry 21*). The yield of isolated **1a** was very close to that obtained in the

Table 1. *The Reaction of Benzylamine with Benzyl Halides under $CO_2$ Atmosphere at Room Temperature*

$$PhCH_2NH_2 + PhCH_2X \xrightarrow[\text{base, solvent}]{CO_2} PhCH_2NHCO_2CH_2Ph + PhCH_2N(CH_2Ph)_2$$

| *Entry* | $PhCH_2X$ | Base | Pressure, $CO_2$/kg/cm$^2$ | Solvent | Yield/% [a]) | |
|---|---|---|---|---|---|---|
| | | | | | **1a** | **2a** |
| *1* | Cl | $Na_2CO_3$ | 1 | toluene | – | 30 |
| *2* | Cl | $Na_2CO_3$ | 1 | MeCN | – | 40 |
| *3* | Cl | $Na_2CO_3$ | 50 | MeCN | – | 35 |
| *4* | Cl | $K_2CO_3$ | 1 | DMF[b]) | trace | 40 |
| *5* | Cl | $Cs_2CO_3$ | 1 | DMF | 8 | 50 |
| *6* | Cl | $Cs_2CO_3$ | 50 | DMF | 13 | 60 |
| *7* | Cl | $Cs_2CO_3$ | 50 | DMF[c]) | 13 | 60 |
| *8* | Cl | $Cs_2CO_3$ | 50 | DMF[d]) | 10 | 50 |
| *9* | Br | $Li_2CO_3$ | 1 | DMF | 3 | 46 |
| *10* | Br | LiOH | 1 | DMF | – | – |
| *11* | Cl | DBU | 1 | DMF | 10 | trace |
| *12* | Br | DBU | 1 | $H_2O$ | 6 | 60 |
| *13* | Br | DBU | 1 | DMF/$H_2O$ | 32 | 34 |
| *14* | Br | DBU | 1 | DMF | 37 | 30 |
| *15* | Cl | DBU | 1 | DMF | 32 | 12 |
| *16* | Br | DBU | 1 | toluene | 19 | 10 |
| *17* | Br | DBU | 1 | hexane | 24 | 1 |
| *18* | Br | DBU | 1 | toluene/hexane | 44 | 12 |
| *19* | Cl | DBU | 1 | toluene/hexane | 43 | 14 |
| *20* | Br | DBU | 50 | toluene/hexane | 55 | 13 |
| *21* | Cl | DBU | 50 | toluene/hexane[e]) | 87 | 7 |

[a]) Yield of isolated product. [b]) In the presence of [18]crown-6 (0.1 equiv.). [c]) In the presence of DBU (0.1 equiv.). [d]) In the presence of $(Bu_4N)Br$ (5 mol-%) as phase-transfer catalyst. [e]) The reaction was carried out at 80°.

presence of sterically hindered guanidine as base [8]. We believe that DBU in this reaction acted both as a $CO_2$ carrier and a base (*Scheme 1*) [9][1]).

To clarify the substituent effect on the benzyl chlorides on the reaction, we studied other benzyl chlorides $C_6H_4CH_2Cl$ (R = F, $CF_3$, or Me) and $MeO_2C_6H_4CH_2Cl$ under the optimized reaction conditions (*Scheme 2*, *Table 2*). For benzyl chlorides having electron-withdrawing groups (F or $CF_3$) or a weak electron-donating group (Me) at the phenyl ring, $CO_2$-inserted products were isolated in similar yields as with benzyl chloride, along with small amounts of the corresponding secondary amines **3** or tertiary amines **2** (*Table 2*). However, in the case of $(MeO)_2C_6H_3CH_2Cl$, only the corresponding tertiary amine **2e** was obtained in low yield because the two strong electron-donating MeO groups disfavor the nucleophilic attack of benzylammonium carbamates and benzylamine to benzyl halides. These results suggest that the substituents at the phenyl ring do not affect the electron density at the benzyl $CH_2$ moiety, which is connected to chloride and is attacked by alkylammonium carbamates

[1]) We also found that **1a** was formed in a very low yield even under the conditions reported by *Butcher*, with $Cs_2CO_3$ as a base [10a]; the major product was the tertiary amine **2a**. A careful examination of this reaction revealed that no so called 'cesium ionic effect' could be reproduced under the same conditions. According to a detailed report by *Jung* and co-workers [10c], both 3 equiv. of $Cs_2CO_3$ and 3 equiv. of $Bu_4N$ are required to give a high yield of **1a** in DMF under $CO_2$ atmosphere with bubbling.

*Scheme 2*

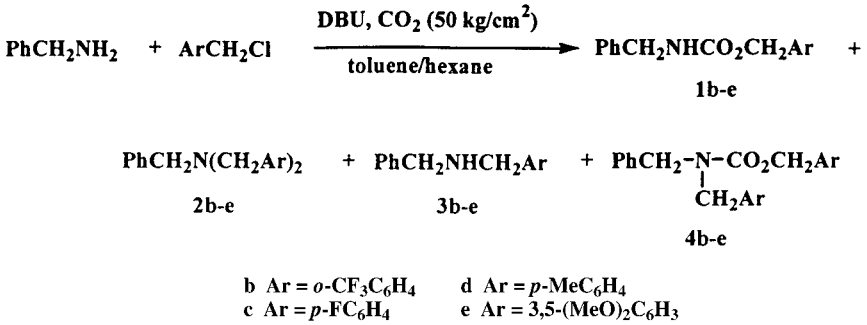



Table 2. *The Reaction of Benzylamine with Benzyl Chlorides under $CO_2$ Atmosphere* (50 kg/cm$^2$) *at 70°*

| *Entry* | $ArCH_2Cl$ | Series | Yield/% [a]) | | | |
|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | **4** |
| *1* | *o*-$CF_3$-$C_6H_4$-$CH_2Cl$ | **b** | 67 | – | 25 | – |
| *2* | *p*-F-$C_6H_4$-$CH_2Cl$ | **c** | 60 | 4 | – | 15 |
| *3* | *p*-Me-$C_6H_4$-$CH_2Cl$ | **d** | 54 | – | 14 | – |
| *4* | *m,m*-$(MeO)_2C_6H_3$-$CH_2Cl$ | **e** | 7 | – | – | |

[a]) Yield of isolated product.

$RNHCO_2^{-+}NH_3R$, *i.e.* the formation of carbamates is generally not affected by substituents at the phenyl ring; however, there is a threshold, since no carbamates are formed if the phenyl ring bears several strong electron-donating groups. One interesting finding is that, in the reaction of benzylamine with *p*-fluorobenzyl chloride under high $CO_2$ pressure, compound **4b**, derived from the further reaction of the $CO_2$-inserted carbamate with *p*-fluorobenzyl chloride, was formed in 15% yield (*Table 2*, *Entry 2*). This phenomenon has never been reported so far.

With other primary amines such as propylamine, butylamine, prop-2-enylamine, cyclohexylamine, or 1-methylbenzylamine, similar tendencies as with benzylamine were observed: low yields of $CO_2$-inserted products **5** were obtained with $K_2CO_3$ or $Cs_2CO_3$ as a base under $CO_2$ atmosphere, and good yields were obtained with DBU as a base under high $CO_2$ pressure in toluene/hexane 1:1 at 70° (*Scheme 3*, *Table 3*). Especially in the cases of propylamine, butylamine, and prop-2-enylamine, *N*-benzylation of the $CO_2$-inserted product occurred to give the corresponding compound **6**. The by-products **7** were also observed.

With secondary amines, *e.g.* diethyl- and dicyclohexylamine, the $CO_2$-inserted products (*e.g.* **8** and **10**, resp.) were obtained only in trace amounts, along with the major tertiary amines RRNR′ (*e.g.* **9** and **11**, resp.), even under the optimized reaction conditions (*Scheme 4*). Especially for diisopropylamine, no reaction occurred because of its steric hindrance. On the other hand, for a cyclic secondary amine such as piperidine, due to its high nucleophilicity, the tertiary amine **12** was formed exclusively under the same reaction conditions (*Scheme 4*).

*Scheme 3*

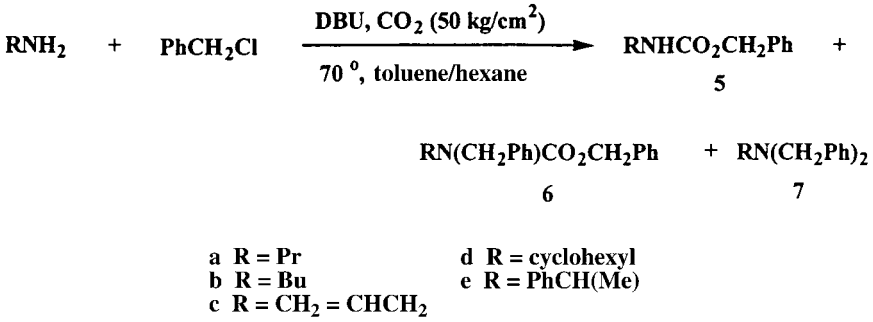



Table 3. *The Reaction of Primary Amines with Benzyl Chlorides under $CO_2$ Atmosphere* (50 kg/cm$^2$) *at 70°*

| *Entry* | $RNH_2$ | Series | Yield/% [a]) | | |
|---|---|---|---|---|---|
| | | | **5** | **6** | **7** |
| *1* | $Me(CH_2)_2NH_2$ | **a** | 86 | 4 | 4 |
| *2* | $Me(CH_2)_3NH_2$ | **b** | 82 | 3 | 8 |
| *3* | $CH_2{=}CHCH_2NH_2$ | **c** | 84 | 6 | trace |
| *4* | cyclo-$C_6H_{11}$ | **d** | 84 | trace | trace |
| *5* | $PhCH(Me)NH_2$ | **e** | 80 | – | 9 |

[a]) Yield of isolated product.

In conclusion, we systematically examined the reaction of amines with benzyl halides under high $CO_2$ pressure and found that, in low-polarity solvent and in the presence of DBU as a base, the $CO_2$-inserted products can be obtained in high yields from primary amines. This reaction procedure, with $CO_2$ as a cheap, benign-nature and abundant reagent, can be used for the protection of primary amines, thus replacing benzyl carbonochloridate (ZCl), which is usually prepared from hazardous phosgene ($COCl_2$).

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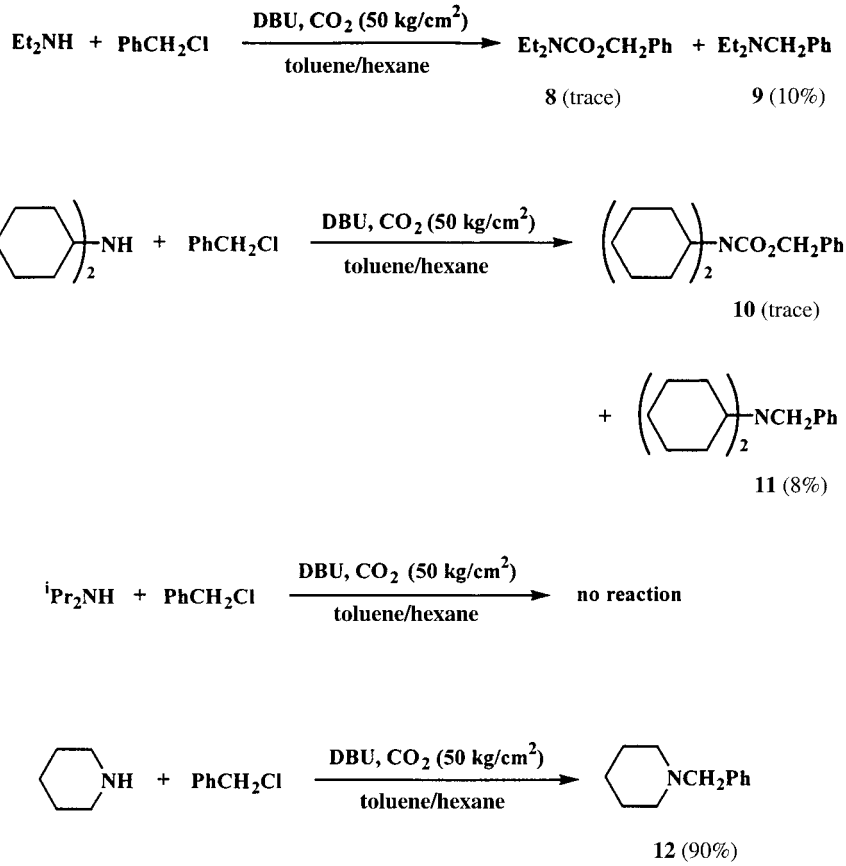
## Experimental Part

*General.* Org. solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. TLC Monitoring: *Huanghai $GF_{254}$* silica gel coated plates. Flash column Chromatography (FC): 200–300 mesh silca gel. M.p.s: *Yanagimoto* micro-melting-point apparatus; uncorrected. IR Spectra: *Perkin-Elmer 983* spectrometer in cm$^{-1}$. $^1$H-NMR Spectra: *Bruker AM-300* spectrometer; $CDCl_3$ solns.; $\delta$ in ppm with $SiMe_4$ as internal standard (= 0 ppm), $J$ in Hz. $^{13}$C-NMR Spectra: data only for $CO_2$-inserted products. MS: *HP-5989* instrument (EI) or *Finnigan MA +* mass spectrometer (HR). Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a *Carlo-Erba 1106* analyzer.

*Reaction of Amines with Benzyl Chlorides under $CO_2$ Atmosphere: General Procedure 1 (G.P. 1).* $CO_2$ Gas was bubbled into a stirred suspension of benzylamine (300 mg, 2.80 mmol) and DBU (426 mg, 2.80 mmol) in toluene/hexane 1:1 (10 ml) at r.t. for 1 h. Benzyl chloride (354 mg, 2.80 mmol) was added in 1 portion, and $CO_2$ gas was further passed through the mixture. The mixture was stirred at r.t. for 72 h. After evaporation, the residue was purified by CC (silica gel, petroleum ether/AcOEt 1:5) to give **1a** (290 mg, 43%) and **2a** (78 mg, 14%) as white solids.

*Scheme 4*




*Reaction of Amines with Benzyl Chlorides under High $CO_2$ Pressure: General Procedure 2 (G.P. 2).* Benzylamine (300 mg, 2.80 mmol), DBU (426 mg, 2.80 mmol), benzyl chloride (354 mg, 2.80 mmol), anh. toluene/petroleum ether 1:1 (10 ml), and a magnetic stirring bar were placed in the 50-ml glass liner of a stainless-steel autoclave under a $N_2$ purge. After the autoclave was purged several times with $CO_2$, it was pressurized with $CO_2$ (40 atm), sealed, and stirred at r.t. for 24 h. After release of the pressure, the solvent was evaporated and the residue purified by CC (silica gel, petroleum ether/AcOEt 1:4) to give **1a** and **2a**.

*Benzylcarbamic Acid Benzyl Ester* (**1a**) [10c]. According to the *G.P. 2:* white solid (587 mg, 87%). M.p. 60–62°. IR ($CHCl_3$): 1687 (C=O). $^1$H-NMR: 4.39 (*d*, *J* = 5.8, $CH_2$); 5.04 (*s*, NH); 5.14 (*s*, $CH_2$); 7.26–7.37 (*m*, 10 arom. H). $^{13}$C-NMR: 45.19; 66.89; 127.53; 128.14; 128.53; 128.69; 136.51; 138.40; 156.40 (C=O). EI-MS: 287 ($M^{+\cdot}$). Anal. calc. for $C_{15}H_{15}NO_2$ (241.2851): C 74.67, H 6.27, N 5.81; found: C 74.67, H 6.29, N 5.69.

*Tribenzylamine* (**2a**) [11]. According to *G.P. 2:* white solid (39 mg, 7%). M.p. 85–88°. IR ($CHCl_3$): 1601 (C=C). $^1$H-NMR: 3.55 (*s*, 1 $CH_2$); 7.22–7.42 (*m*, 5 arom. H). EI-MS: 287 ($M^{+\cdot}$). HR-MS: 287.1668 ($C_{21}H_{21}N^+$, $M^+$; calc. 287.1674).

*Benzylcarbamic Acid 2-(Trifluoromethyl)benzyl Ester* (**1b**). According to the *G.P. 2:* colorless oil (581 mg, 67%). IR ($CHCl_3$): 1703 (C=O). $^1$H-NMR: 4.39 (*d*, *J* = 5.8, 1 $CH_2$); 5.17 (*s*, NH); 5.19 (*s*, 1 $CH_2$); 7.25–7.63 (*m*, 9 arom. H). $^{13}$C-NMR: 45.19; 65.86; 124.56 (*q*, *J*(C,F) = 3.8); 124.84 (*q*, *J*(C,F) = 3.8); 127.13; 127.58; 127.94 (*q*, *J*(C,F) = 145.2); 128.32 (*q*, *J*(C,F) = 145.2); 128.70; 128.98; 131.13; 137.64; 138.24; 156.11 (C=O). EI-MS: 310 ($MH^{+\cdot}$). HR-MS: 309.0996 ($C_{16}H_{14}F_3NO_2^+$, $M^+$; calc. 309.0977)

*Benzyl[2-(trifluoromethyl)benzyl]amine* (**3b**). According to *G.P. 2:* colorless oil (138 mg, 25%). IR ($CHCl_3$): 1601 (C=C). $^1$H-NMR: 3.84 (*s*, $CH_2$); 3.89 (*s*, $CH_2$); 7.26–7.67 (*m*, 4 arom. H). EI-MS: 265 ($M^{+\bullet}$). HR-MS: 265.1071 ($C_{15}H_{14}F_3N^+$, $M^+$; calc. 265.1078)

*Benzylcarbamic Acid 4-Fluorobenzyl Ester* (**1c**). According to the *G.P. 2:* white solid (437 mg, 60%). M.p. 45–48°. IR ($CHCl_3$): 1714 (C=O). $^1$H-NMR: 4.39 (*d*, $J$ = 6.0, 1 $CH_2$); 5.0 (*s*, NH); 5.10 (*s*, 1 $CH_2$); 7.25–7.50 (*m*, 9 arom. H). $^{13}$C-NMR: 45.17; 66.12; 127.02; 127.54; 128.14; 128.43; 129.66 (*d*, $J$(C,F) = 6.0); 130.09 (*d*, $J$(C,F) = 6.0); 138.33; 156.29 (C=O); 162.55 (*d*, $J$(C,F) = 225.9). EI-MS: 260 ($M$H$^+$). HR-MS: 259.1014 ($C_{15}H_{14}FNO_2^+$, $M^+$; calc. 259.1009).

*Benzyl[bis(4-fluorobenzyl)]amine* (**2c**). According to *G.P. 2:* colorless oil (41 mg, 4%). IR ($CHCl_3$): 1600 (C=C). $^1$H-NMR: 3.49 (*s*, 1 $CH_2$); 3.52 (*s*, 1 $CH_2$); 6.96–7.02 (*m*, 4 arom. H); 7.29–7.35 (*m*, 8 arom. H). EI-MS: 323 ($M^{+\bullet}$). HR-MS: 323.1476 ($C_{21}H_{19}F_2N^+$, $M^+$; calc. 323.1486).

*Benzyl(4-fluorobenzyl)carbamic Acid 4-Fluorobenzyl Ester* (**4c**). According to *G.P. 2:* colorless oil (136 mg, 15%). IR ($CHCl_3$): 1696 (C=O). $^1$H-NMR: 4.41 (br. *s*, 2 $CH_2$); 5.19 (*s*, 1 $CH_2$); 7.0–7.50 (*m*, 13 arom. H). $^{13}$C-NMR: 49.21; 66.12; 66.86; 127.53; 127.54; 128.11; 128.66; 129.84; 129.95; 130.06; 132.40 (*d*, $J$(C,F) = 6.2); 133.07 (*d*, $J$(C,F) = 6.2); 137.15; 156.54 (C=O); 162.35 (*d*, $J$(C,F) = 245.6). EI-MS: 368 ($M$H$^{+\bullet}$). HR-MS: 259.1396 ($C_{22}H_{19}F_2NO_2^+$), $M^+$; calc. 367.1384).

*Benzyl Carbamic Acid 4-Methylbenzyl Ester* (**1d**). According to *G.P. 2:* white solid (386 mg, 54%). M.p. 72–74°. IR ($CHCl_3$): 1682 (C=O). $^1$H-NMR: 2.35 (*s*, Me); 4.38 (*d*, $J$ = 6.0, 1 $CH_2$); 5.10 (*s*, NH); 5.10 (*s*, 1 $CH_2$); 7.25–7.63 (*m*, 9 arom. H). $^{13}$C-NMR: 21.19; 45.17; 66.86; 127.51; 128.31; 128.68; 129.22; 133.48; 138.00; 138.44; 156.47 (C=O). EI-MS: 255 ($M^{+\bullet}$). HR-MS: 255.1257 ($C_{16}H_{17}NO_2^+$, $M^+$; calc. 255.1259).

*Benzyl(4-methylbenzyl)amine* (**3d**). According to *G.P. 2:* colorless oil (82 mg, 14%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 2.36 (*s*, Me); 3.78 (*s*, 1 $CH_2$); 3.81 (*s*, 1 $CH_2$); 5.10 (*s*, 1 $CH_2$); 7.14–7.40 (*m*, 9 arom. H). EI-MS: 210 ([$M$ – H$^+$). HR-MS: 211.1348 ($C_{15}H_{17}N^+$, $M^+$; calc. 211.1361).

*Benzylbis(3,5-dimethoxybenzyl)amine* (**2e**). According to *G.P. 2:* colorless oil (81 mg, 7%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 3.58 (*s*, 2 $CH_2$); 3.64 (*s*, 1 $CH_2$); 3.84 (*s*, 4 MeO); 6.40 (*s*, 2 arom. H); 6.68 (*s*, 4 arom. H); 7.14–7.50 (*m*, 5 arom. H). EI-MS: 408 ($M$H$^+$). HR-MS: 407.2101 ($C_{25}H_{29}NO_4^+$, $M^+$; calc. 407.2097).

*Propylcarbamic Acid Benzyl Ester* (**5a**). According to *G.P. 2:* colorless solid (456 mg, 86%). M.p. 42–44°. IR ($CHCl_3$): 1700 (C=O). $^1$H-NMR: 0.92 (*t*, $J$ = 7.5, Me); 1.51 (*quint*, $J$ = 7.5, 1 $CH_2$); 3.16 (*q*, $J$ = 7.5, 1 $CH_2$); 4.77 (*s*, NH); 5.09 (*s*, 1 $CH_2$); 7.26–7.36 (*m*, 5 arom. H). $^{13}$C-NMR: 11.17; 23.16; 42.76; 128.05; 128.08; 128.47; 136.62; 156.41 (C=O). EI-MS: 193 ($M^{+\bullet}$). Anal. calc. for $C_{11}H_{15}NO_2$: C 68.37, H 7.82, N 7.25; found: C 68.45, H 7.89, N 7.39.

*Benzyl(propyl)carbamic Acid Benzyl Ester* (**6a**). According to *G.P. 2:* colorless oil (28 mg, 4%). IR ($CHCl_3$): 1696 (C=O). $^1$H-NMR: 0.83 (*t*, $J$ = 7.5, Me); 1.37–1.68 (*m*, 1 $CH_2$); 3.15–3.28 (*m*, 1 $CH_2$); 4.50 (*s*, 1 $CH_2$); 5.17 (*s*, 1 $CH_2$); 7.13–7.45 (*m*, 10 arom. H). $^{13}$C-NMR: 11.20; 21.33; 47.91; 50.17; 67.10; 127.22; 127.76; 127.86; 128.42; 128.49; 128.52; 136.45; 137.98; 156.41 (C=O). EI-MS: 254 ([$M$ – 29]$^{+\bullet}$). HR-MS: 283.1587 ($C_{18}H_{21}NO_2^+$, $M^+$; calc. 283.1572).

*Dibenzylpropylamine* (**7a**). According to *G.P. 2:* colorless oil (25 mg, 4%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 0.92 (*t*, $J$ = 7.5, Me); 1.51 (*quint*, $J$ = 7.5, 1 $CH_2$); 3.16 (*q*, $J$ = 7.5, 1 $CH_2$); 3.54 (*s*, 2 $CH_2$); 7.0–7.46 (*m*, 10 arom. H). EI-MS: 239 ($M^{+\bullet}$). HR-MS: 239.1667 ($C_{17}H_{21}N^+$, $M^+$; calc. 239.1674).

*Butylcarbamic Acid Benzyl Ester* (**5b**) [12]. According to *G.P. 2:* colorless oil (476 mg, 82%). IR ($CHCl_3$): 1701 (C=O). $^1$H-NMR: 0.91 (*t*, $J$ = 7.3, Me); 1.27–1.37 (*m*, 1 $CH_2$); 1.38–1.52 (*m*, 1 $CH_2$); 3.15–3.22 (*m*, 1 $CH_2$); 4.77 (*s*, NH); 5.09 (*s*, 1 $CH_2$); 7.26–7.36 (*m*, 5 arom. H). $^{13}$C-NMR: 13.68; 19.85; 32.02; 40.80; 66.54; 128.03; 128.48; 136.70; 156.41 (C=O). EI-MS: 208 ($M$H$^{+\bullet}$). HR-MS: 207.1273 ($C_{12}H_{17}NO_2^+$, $M^+$; calc. 207.1259).

*Benzyl(butyl)carbamic Acid Benzyl Ester* (**6b**). According to *G.P. 2:* colorless oil (25 mg, 3%). IR ($CHCl_3$): 1695 (C=O). $^1$H-NMR: 0.83–0.91 (*m*, 2 Me); 1.27–1.38 (*m*, 2 $CH_2$); 1.39–1.58 (*m*, 2 $CH_2$); 3.15–3.28 (*m*, 2 $CH_2$); 4.50 (*s*, 1 $CH_2$); 5.17 (*s*, 1 $CH_2$); 7.13–7.45 (*m*, 10 arom. H). $^{13}$C-NMR: 13.80; 19.98; 30.10; 30.26; 45.98; 46.96; 50.17; 67.14; 127.25; 127.81; 127.89; 128.44; 128.52; 138.02; 156.41 (C=O). EI-MS: 207 ([$M$ – 90]$^+$]. HR-MS: 297.1719 ($C_{19}H_{23}NO_2^+$, $M^+$; calc. 297.1729).

*Butyldibenzylamine* (**7b**) [13]. According to *G.P. 2:* colorless oil (36 mg, 8%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 0.91 (*t*, $J$ = 7.3, Me); 1.27–1.37 (*m*, 1 $CH_2$); 1.38–1.52 (*m*, 1 $CH_2$); 3.15–3.22 (*m*, 1 $CH_2$); 5.09 (*s*, 2 $CH_2$); 7.26–7.36 (*m*, 10 arom. H). EI-MS: 163 ([$M$ – 90]$^+$]. HR-MS: 163.1347 ($C_{11}H_{17}N^+$; $M^+$; calc. 163.1361).

*Prop-2-enylcarbamic Acid Benzyl Ester* (**5c**). According to *G.P. 2:* colorless oil (452 mg, 84%). IR ($CHCl_3$): 1701 (C=O). $^1$H-NMR: 3.80 (*s*, 1 $CH_2$); 5.10 (*s*, 1 $CH_2$); 5.06–5.20 (*m*, 1 $CH_2$); 5.73–5.93 (*m*, 1 H); 7.26–7.36 (*m*, 5 arom. H). $^{13}$C-NMR: 43.28; 66.52; 115.74; 127.92; 128.26; 128.32; 134.37; 136.39; 156.21 (C=O). EI-MS: 192 ($M$H$^+$). HR-MS: 191.0954 ($C_{11}H_{14}NO_2^+$, $M^+$; calc. 191.0946).

*Benzyl(prop-2-enyl)carbamic Acid Benzyl Ester* (**6c**). According to *G.P. 2:* colorless oil (47 mg, 6%). IR ($CHCl_3$): 1700 (C=O). $^1$H-NMR: 3.80 (*s*, 1 $CH_2$); 4.53 (*s*, 1 $CH_2$); 5.10 (*s*, 1 $CH_2$); 5.06–5.20 (*m*, 1 $CH_2$); 5.73–5.93 (*m*, 1 H); 7.26–7.36 (*m*, 10 arom. H). $^{13}$C-NMR: 49.03; 67.05; 67.25; 117.45; 127.29; 127.74; 127.96; 128.05; 128.45; 128.48; 133.15; 137.53; 156.41 (C=O). EI-MS: 282 ($MH^+$). HR-MS: 281.1429 ($C_{18}H_{19}NO_2^+$, $M^+$; calc. 281.1416).

*Cyclohexylcarbamic Acid Benzyl Ester* (**5d**) [12]. According to *G.P. 2:* colorless solid (522 mg, 84%). M.p. 80–83°. IR ($CHCl_3$): 1701 (C=O). $^1$H-NMR: 1.0–1.25 (*m*, 3 H); 1.27–1.52 (*m*, 1 $CH_2$); 1.52–1.80 (*m*, 3 H, $CH_2$); 1.81–2.0 (*m*, 2 H, $CH_2$); 3.40–3.60 (*m*, CH); 4.65 (*s*, NH); 5.09 (*s*, 2 H, $CH_2$); 7.26–7.36 (*m*, 5 arom. H). $^{13}$C-NMR: 24.78; 25.50; 33.41; 49.91; 66.48; 128.05; 128.13; 128.52; 136.74; 156.41 (C=O). EI-MS: 234 ($MH^+$). Anal. calc. for $C_{15}H_{15}NO_2$ (233.3062): C 72.07, H 8.21, N 6.00; found: C 72.09, H 8.02, N 5.76.

*(α-Methylbenzyl)carbamic Acid Benzyl Ester* (**5e**). According to *G.P. 2:* colorless oil (571 mg, 80%). IR ($CHCl_3$): 1714 (C=O). $^1$H-NMR: 1.48 (*d*, *J* = 6.9, Me); 4.85–4.88 (*m*, CH); 5.02 (*s*, NH); 5.05 (*d*, *J* = 12.3, 1 H); 5.12 (*d*, *J* = 12.3, 1 H); 7.20–7.46 (*m*, 10 arom. H). $^{13}$C-NMR: 22.51; 50.81; 66.76; 125.94; 127.36; 128.11; 128.52; 128.67; 136.51; 155.57 (C=O). EI-MS: 256 ($MH^+$). HR-MS: 255.1243 ($C_{16}H_{17}NO_2^+$, $M^+$; calc. 255.1259).

*(α-Methylbenzyl)dibenzylamine* (**7e**). According to *G.P. 2:* colorless oil (76 mg, 9%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 1.42 (*d*, *J* = 6.9, Me); 3.68 (*d*, *J* = 13.8, CH); 3.78 (*d*, *J* = 13.8, CH); 3.92 (*q*, *J* = 6.7, CH); 7.20–7.50 (*m*, 10 arom. H). EI-MS: 302 ($MH^+$). HR-MS: 301.1832 ($C_{22}H_{23}N^+$; $M^+$; calc. 301.1830).

*Diethylcarbamic Acid Benzyl Ester* (**8**). According to *G.P. 2:* colorless oil (6 mg, 1%). IR ($CHCl_3$): 1700 (C=O). $^1$H-NMR: 1.07 (*t*, *J* = 7.2, 2 Me); 2.52 (*q*, *J* = 7.2, 2 $CH_2$); 5.12 (*s*, 1 $CH_2$); 7.13–7.50 (*m*, 5 arom. H). EI-MS: 207 ($M^+$). HR-MS: 207.1250 ($C_{12}H_{17}NO_2^+$, $M^+$; calc. 207.1259).

*Benzyldiethylamine* (**9**) [14]. According to *G.P. 2:* colorless oil (59 mg, 10%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 1.02 (*t*, *J* = 7.4, 2 Me); 2.51 (*q*, *J* = 7.3, 2 $CH_2$); 3.57 (*s*, 1 $CH_2$); 7.14–7.40 (*m*, 5 arom. H). EI-MS: 210 ($[M-H]^+$). HR-MS: 163.1358 ($C_{11}H_{17}N^+$; $M^+$; calc. 163.1361).

*Dicyclohexylcarbamic Acid Benzyl Ester* (**10**). According to *G.P. 2:* colorless oil (9 mg, 1%). IR ($CHCl_3$): 1719 (C=C). $^1$H-NMR: 1.17–1.40 (*m*, 5 $CH_2$); 1.40–1.78 (*m*, 5 $CH_2$); 4.20–4.22 (*m*, 2 $CH_2$); 5.37 (*s*, 1 $CH_2$); 7.26–7.58 (*m*, 5 arom. H). EI-MS: 316 ($MH^+$). HR-MS: 315.2197 ($C_{20}H_{29}O_2N^+$, $M^+$; calc. 315.2198).

*Benzyldicyclohexylamine* (**11**). According to *G.P. 2:* colorless oil (61 mg, 8%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 0.82–1.50 (*m*, 6 $CH_2$); 1.51–2.01 (*m*, 4 $CH_2$); 2.47–2.65 (*m*, 2 CH); 3.75 (*s*, 1 $CH_2$); 7.14–7.40 (*m*, 5 arom. H). EI-MS: 272 ($MH^+$). HR-MS: 271.2292 ($C_{19}H_{29}N^+$; $M^+$; calc. 271.2300).

N-*Benzylpiperidine* (**12**) [15]. According to *G.P. 2:* colorless oil (441 mg, 90%). IR ($CHCl_3$): 1602 (C=C). $^1$H-NMR: 1.23–1.51 (*m*, 1 $CH_2$); 1.52–1.73 (*m*, 2 $CH_2$); 2.30–2.48 (*m*, 2 $CH_2$); 7.20–7.40 (*m*, 5 arom. H). EI-MS: 175 ($M^+$). HR-MS: 175.1364 ($C_{12}H_{17}N^+$, $M^+$; calc. 175.1361).

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