# Photolysis of tertiary amines in the presence of $CO_2$: the paths to formic acid, $\alpha$-aminoacids and 1,2-diamines

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**Abstract.** The photolysis of triethylamine (**1a**) in the presence of carbon dioxide leads to the hydrogenation of $CO_2$, the $\alpha$-C-C coupling of triethylamine (**1a**), and the $CO_2$–insertion into the $\alpha$-C-H $\sigma$-bond of amine **1a**. This reaction is proposed to proceed through the radical ion pair $[R_3N^{\cdot+} \cdot CO_2^{\cdot-}]$ generated by the photoionization of amine **1a** and the electron capture by $CO_2$. The presence of lithium tetrafluoroborate in the reaction medium promotes the efficient and stereoselective $\alpha$-C-C coupling of **1a** by enhancing the production of $\alpha$-dialkylamino radicals and the isomerization of *N,N,N',N'*-tetraethylbutane-2,3-diamine (**4a**).

## Introduction

The C-C and C-H bond-forming reactions of $CO_2$ have become a major research topic in chemistry as a response to the global challenge of reducing anthropogenic $CO_2$ emissions to the atmosphere.[1] The research endeavor aimed to use $CO_2$ as a renewable feedstock for synthetic fuels, and commodity chemicals have produced a variety of transition metal complexes, enzymes and advanced materials as catalysts for the thermal, photochemical, electrochemical and photoelectrochemical reduction of $CO_2$.[2] These systems confront the significant kinetic and thermodynamic barriers posed by a change in molecular geometry from linear to bent, associated with the single electron transfer to the antibonding $\pi^*$ orbital of $CO_2$ $[E^o(CO_2/CO_2^{\cdot-}) = -2.1$ V *vs.* SCE].[3] This reaction, however, can lead to $CO_2$-fixation products, provided that the radical anion intermediate $[CO_2^{\cdot-}]$, a strong reductant itself, finds efficient down-hill reaction pathways, alternative to the back electron transfer to reducible species in the reaction medium. For instance, the efficient hydrogen atom transfer reaction from thiols to the radical anion $[CO_2^{\cdot-}]$,[4] coupled to the ability of $CO_2$ to capture solvated electrons,[5] has allowed us to devise efficient $CO_2$ reduction to formic acid by using iodide as a

photocatalyst.[6] These results showed that the reactivity of the radical anion $[CO_2^{\cdot-}]$ is a crucial factor for developing reductive $CO_2$-fixation processes, and prompted us to further explore electron transfer reactions that involve $CO_2$.

Triethylamine (**1a**) has been used as a sacrificial electron donor[7] in the oligo(*p*-phenylenes) photocatalyzed reduction of $CO_2$ to formic acid and carbon monoxide,[8] and this reaction has been explored theoretically[9] in order to design a task-specific recyclable amine for selective $CO_2$ reduction to formic acid.[10] Recently, this reaction has been applied to the $\alpha$-carboxylation of tertiary amines.[11] These reports have shown that tertiary amine **1** and its radical cation [**1**$^{\cdot+}$] are the actual species which perform the activation of $CO_2$ in these reactions. However, the reaction paths followed by different reaction intermediates, the competitive processes involved, and the final products derived from **1** under different reaction conditions, which should provide critical information about the reactivity of the radical anion $[CO_2^{\cdot-}]$, have not been accurately described to date. In order to bridge this gap, and to thus acquire additional information on the reductive pathways of $CO_2$, we decided to explore the photoionization of tertiary amines **1** under UV irradiation[12] in the presence of $CO_2$ to avoid interferences in the electron and hydrogen transfer steps associated with the use of photocatalysts.

We herein report that the UV-photolysis of tertiary amines **1** in the presence of $CO_2$ leads to formic acid (**2**) and $\alpha$-amino acids **3** as $CO_2$-capture products, and also to 1,2-diamines **4**. The product distributions found under the different reaction conditions reveal the involvement of the radical ion pair [**1**$^{\cdot+}\cdot CO_2^{\cdot-}$], iminium ions and $\alpha$-aminoalkyl radicals as reaction intermediates. The information disclosed herein about the chemistry of the radical anion $[CO_2^{\cdot-}]$ and the reaction paths under these reaction conditions will be useful for designing $CO_2$-capture processes.


**Results**

Triethylamine (**1a**) was selected as the model substrate for the first series of experiments.[13] Amine **1a**, used either neat or in anhydrous acetonitrile solution (0.3 M), was placed inside a quartz test tube, which was capped with a rubber septum, and was treated with $CO_2$ (20 psi) at 0 °C for 20 min with stirring. The concentration of $CO_2$ in acetonitrile was estimated to be 0.241 M from the solubility reported for $CO_2$ in propionitrile[14] at 1 bar and 25 °C (initial molar ratio **1a**: $CO_2$ of 1.24:1). The reaction mixture was irradiated for 3 h at room temperature with a compact twin-tube germicidal lamp (254 nm, 36 W) to give transparent solutions with a thin solid layer on the tube wall for the reactions in acetonitrile, and white solid suspensions for the neat reactions and in the presence of $LiBF_4$. The acidic reaction products were quantified by removing the volatiles under vacuum, dissolving the residue in either a basic or neutral solution of phenol as an external standard in $D_2O$, and analyzing the sample by NMR. The analysis and quantification of the basic products were performed in a second identical experiment, in which the reaction mixture was treated with 37% hydrochloric acid prior to removing the volatiles under a vacuum. The residue was then dissolved in a phenol solution, used as the external standard, in $D_2O$, and was analyzed by NMR. The work-up procedures prevented acetaldehyde being detected in the reaction mixtures. The

**Table 1**. Photolysis of triethylamine (**1a**) and $CO_2$ under different conditions.[a]



$$1a \xrightarrow[\text{254 nm}]{\underset{h\nu}{CO_2}} HCOOH + 3a + 4a + Et_2NH \quad (1)$$
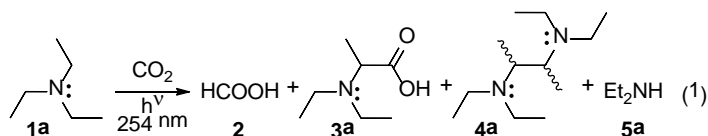
| Run | Reaction conditions[b] | Conv.[c] (%) | Product distribution (%)[d] | | | | |
|---|---|---|---|---|---|---|---|
| | | | **2** | **3a** | **4a** | **5a** | **3a/** |
| | | | | | D,L:meso | | **2a** |
| 1[e] | neat, $CO_2$ | 15 | 8 | 15 | 7 <br> 1:1.1 | 40 | 1.9 |
| 2[e] | ACN, $CO_2$ | 36 | 22 | 15 | 40 <br> 1:1.3 | 14 | 0.7 |
| 3[e] | ACN, $CO_2$ <br> (6 h) | 44 | 14 | 12 | 46 <br> 1.2:1 | 16 | 0.9 |
| 4 | ACN, $CO_2$, LiBF$_4$ (1.5 h) | 28 | 11 | 20 | 69 <br> 2.6:1 | -- | 2.0 |
| 5 | ACN, $CO_2$, LiBF$_4$ | 72 | 8 | 14 | 79 <br> 4:1 | -- | 1.9 |
| 6 | ACN, $CO_2$, LiBF$_4$ (6 h) | 77 | 10 | 15 | 75 <br> 5.8:1 | -- | 1.6 |
| 7[e] | CH, $CO_2$ | 6 | 3 | 4 | 2 | 30 | 1.3 |
| 8[e] | ACN, Ar | 14 | -- | -- | 22 <br> 1:1.4 | 20 | -- |
| 9[e] | ACN, Ar, LiBF$_4$ | 25 | -- | -- | 6 <br> 1.3:1 | 77 | -- |

[a] The reactions performed at room temperature with a 35 W low-pressure mercury lamp. CH: cyclohexane, ACN: acetonitrile. The figures are the average of at least three independent experiments and fall within a standard deviation of 15 %. [b] The reactions performed for 3 h, except where noticed. [c] Amine **1**, captured as the ammonium salt of acids **2** and **3**, was considered unconverted. [d] Molar distribution. Mass balances >80 %. [e] Additional products[16] were found in yields within the 0.2-18 % range, depending on the reaction conditions.

reaction products were identified by comparing with the authentic samples prepared by alternative procedures, and were quantified from their integrals in the ^{1}H NMR spectrum. The results obtained under the different conditions are shown in Equation 1 and Table 1.

The control experiments performed with [13]$CO_2$ showed no evidence for oxalic acid, formaldehyde or methanol as products. The solutions of formic acid (**2**) in acetonitrile proved stable under irradiation in the presence of excess triethylamine (**1a**) (**1a**:**2** 2:1), while the reaction run in the presence of LiBF$_4$ led to an 8% loss of formic acid (**2**). The reactions performed with water as a cosolvent led to the quantitative recovery of the unreacted starting materials, which was attributed to the formation of unreactive triethylammonium hydrogencarbonate.[15] The UV spectra of the amine **1a** solutions in anhydrous acetonitrile ($3\cdot10^{-3}$ M), recorded before and after $CO_2$-intake at 20 psi for 20 min at room temperature, showed no significant differences (Figure 1).

**Figure 1**. UV spectra of a 4.3 x $10^{-3}$ M solution of triethylamine (**1a**) in acetonitrile before and after saturation with $CO_2$ at 20 psi and room temperature. The concentration of $CO_2$ was estimated to be 0.241 M from the solubility reported[14] for $CO_2$ in propionitrile at 1 bar and 25 $^{o}$C.
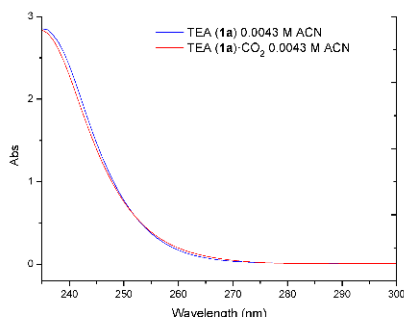


The irradiation of triethylamine (**1a**), both neat and in acetonitrile solution, and saturated with $CO_2$, led to substrate conversions of 15% and 36%, respectively, to give diethylamine (**5a**) (40%), *N,N*-diethylalanine (**3a**) (15%) and formic acid (**2**) (8%) for the neat reaction (Run 1, Table 1), and with diethylamine (**5a**) (14%), amino acid **3a** (15%), formic acid (**2**) (22%) and *N,N,N',N'*-tetraethylbutane-2,3-diamine (**4a**) (40 %) as a *ca.* 1:1 *D,L*:*meso* mixture for the reaction in acetonitrile (Run 2, Table 1). Prolonging the irradiation time to 6 h did not significantly improve the conversion of **1a**, but diminished formic acid formation (**2**) (Run 3, Table 1). Note that the formation of unreactive ammonium salts from amino acid **3a**, formic acid (**2**) and *N,N*-diethylcarbamic acid from $CO_2$ and diethylamine (**5a**)[15] precluded the quantitative conversion of substrate **1a**.

The irradiation of an acetonitrile solution of triethylamine (**1a**) and $CO_2$ in the presence of $LiBF_4$ (0.1 M) under our standard conditions (Run 5, Table 1) led to a 72% substrate conversion, which gave *N,N,N',N'*-tetraethylbutane-2,3-diamine (**4a**) as the major product (79 %), with small amounts of amino acid **3a** (14 %) and formic acid (**2**) (8 %). The ionic additive suppressed diethylamine (**5a**) formation and promoted more selective reactions (Runs 4-6, Table 1). It was noteworthy that diamine **4a** formed as a 4:1 *D,L*:*meso* mixture under these conditions, unlike the unselective reactions observed in the absence of $LiBF_4$ (Run 2, Table 1), and that the *D,L:meso* isomer ratio increased from 2.6 to 5.8 as the irradiation time was prolonged from 1.5 h to 6 h (Runs 4-6, Table 1). The irradiation of a 1:1.3 *D,L:meso* mixture of diamine **4a**, $CO_2$ and $LiBF_4$ in acetonitrile under our standard conditions, performed as a control experiment, led to a 1.2:1 *D,L:meso* isomer ratio. However in this case, no significant $CO_2$-capture products were formed. The small amounts of formic acid (**2**) observed in the presence of $LiBF_4$ (Runs 4-6, Table 1) can be attributed to its depletion through competing photolytic pathways, as suggested by the control experiments.

The reactions in cyclohexane as the solvent (Run 7, Table 1) proceeded, however, with a very low substrate conversion (6 %) to give diethylamine (**5a**) as the main product (30 %), with small amounts of formic acid **2** (3 %), amino acid **3a** (4 %), and diamine **4a** (2 %), and a complex mixture of basic products.

The photolysis of triethylamine (**1a**) in an inert atmosphere was performed as the control experiments (Runs 8 and 9, Table 1) and was analyzed as described above. The reaction in acetonitrile gave diethylamine (**5a**) (20%), diamine **4a** as a *ca.* 1:1 *D,L*:*meso* mixture (22%), and smaller amounts of additional basic products,[16] which agrees with the reported results.[13] Substrate conversion was 14% in this case. The presence of LiBF$_4$ in the reaction medium slightly increased the substrate conversion (25%) and changed the product distribution to preferentially give diethylamine (**5a**) (Run 8, Table 1). These reactions were expected to compete under our reaction conditions.

The reactions of a series of asymmetric tertiary amines **1** with CO$_2$ were performed in the acetonitrile solution under our standard conditions. The reaction mixtures were analyzed by NMR, and the acidic reaction products were identified by comparing with authentic samples prepared by alternative procedures. Substrate conversions were established from the NMR spectra after the acidic work-up. The complexity of the reaction mixtures in these cases prevented the basic products that derived from amines **1c-f** being identified and quantified. The results are shown in Table 2.

**Table 2**. Photochemical carboxylation of tertiary amines **1** with CO$_2$ in acetonitrile.[a]

| Run | 1 | $E^o_{ox}$ (V)[b] | Conv. (%) | Product (yield %)[c] | | 3/2 |
|---|---|---|---|---|---|---|
| | | | | 3 | 2 | |
| 1 | **1a** | 0.73[17] | 36 | **3a** (15) | 20 | 0.7 |
| 2 | **1b** | 0.73[17] | 41 | **3b** (22) | 12 | 1.8 |
| 3 | **1c** | 0.83[18] | 60 | **3c** (9) | 5 | 1.8 |
| 4 | **1d** | 0.68[17] | 63 | **3d** (68)  **3d'** (3) | 5 | 14.0 |
| 5 | **1e** | 0.80[17] | 65 | **3e** (8)  **3e'** (10) | 8 | 2.2 |
| 6 | **1f** | 0.65[19] | 79 | **3e'** (13) | 6 | 2.0 |
| 7 | **1g** | 0.56[20] | -- | -- | -- | -- |
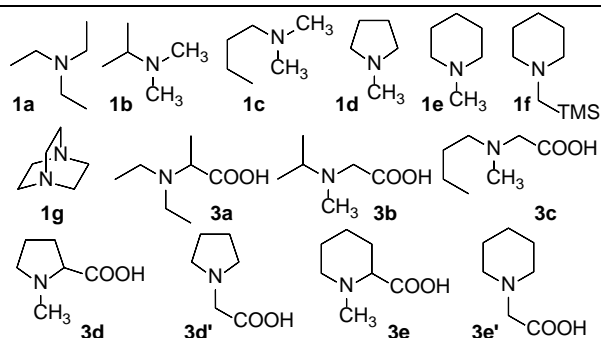


[a] Reactions performed at room temperature for 3 h with a 36 W low-pressure mercury lamp. Products were identified by a comparison with authentic samples. See Supplementary Information for details. [b] Oxidation potentials *vs.* SCE.[17-20] [c] Product yields referred to converted amine **1**.

The irradiation of amines **1** and $CO_2$ produced amino acids **3** and formic acid (**2**) as $CO_2$-activation products (Table 2). The carboxylation reaction showed a strong preference for the methyl positions in all cases, except for *N*-methylpyrrolidine (**1d**), which preferentially reacted at the ring position (Run 4, Table 2). The carboxylation of *N*-(trimethylsilyl)methylpiperidine (**1f**) took place at the sililated carbon atom exclusively (Run 6, Table 2). Selectivity amino acid (**3**):formic acid (**2**) was found to be *ca* 2:1, except for triethylamine (**1a**) (**3a:2** 1:1.5) and *N*-methylpyrrolidine (**1d**) (**3d:2** 14:1). 1,4-Diazabicyclo[2,2,2]octane (DABCO) (**1g**) was unreactive under our reaction conditions.

**Discussion**

The results reported in Table 1 show that the photolysis of triethylamine (**1a**) in a $CO_2$ environment in the absence of photocatalysts leads to formic acid (**2**) and amino acid **3a** as $CO_2$-capture products, and to diamine **4a** as the C-C coupling product. The different product distribution observed in relation to the reactions run in an inert atmosphere, and the improvement of reaction productivity observed by increasing the polarity of the solvent and the ionic strength of the solution (Table 1), strongly suggest the involvement of electron transfer processes[21,22] and the radical ion pair [$\mathbf{1}^{\cdot+}\cdot CO_2^{\cdot-}$] as the primary reaction intermediate. The generation of the radical ion pair [$\mathbf{1a}^{\cdot+}\cdot CO_2^{\cdot-}$] may proceed through the photoionization of triethylamine (**1a**),[12] [$E^o(\mathbf{1a}^{\cdot+}/\mathbf{1a}) = 0.73$ V *vs*. SCE],[17] and the capture of the ejected electron by $CO_2$,[6] [$E^o(CO_2/CO_2^{\cdot-}) = -2.1$ V *vs*. SCE].[3] The absence of a significant charge transfer band in the UV spectrum of triethylamine (**1a**) and $CO_2$, both neat and in acetonitrile solution (Figure 1), and the equilibrium constant of 0.046 reported[23] for the formation of the electron donor-acceptor complex [$\mathbf{1a}\cdot CO_2$] in pentane at $25^o$C and 100 psi (6.89 bar), suggest that the electron donor-acceptor complex [$\mathbf{1a}\cdot CO_2$] plays a minor role in this process.

Reaction products can be rationalized in terms of the reactivity of the radical ions [$\mathbf{1a}^{\cdot+}$] and [$CO_2^{\cdot-}$], which has been described in the photocatalytic reduction of $CO_2$[8,9] and other substrates[7] with triethylamine (**1a**) used as sacrificial electron donors (Scheme 1). Thus the hydrogen atom transfer from the amine radical cation [$Et_3N^{\cdot+}$] to the radical anion [$CO_2^{\cdot-}$] gives an iminium and formate ion pair (**III**) in equilibrium with 1-(diethylamino)ethyl formate **V**, which leads to formic acid, diethylamine (**5a**) and acetaldehyde in the aqueous work-up (Scheme 1).

Conversely, the formal $CO_2$-insertion into the C-H $\sigma$-bond adjacent to the nitrogen atom to give amino acid **3a** can be rationalized through the proton transfer from the amine radical cation [$\mathbf{1a}^{\cdot+}$] to the radical anion [$CO_2^{\cdot-}$], followed by the coupling of the resulting $\alpha$-diethylaminoethyl and formyl radicals (**II**) in the solvent cage (Scheme 1).[24] This reaction path of the radical ion pair [$\mathbf{1a}^{\cdot+}\cdot CO_2^{\cdot-}$] is not described in the theoretical study available in the literature,[9] which shows that the reaction coordinate initiated by the proton transfer from the amine radical cation to the oxygen atom of the $CO_2$ radical anion bifurcates to downhill paths leading to the hydrogen transfer to the carbon atom and to a back electron transfer to amine **1a** and $CO_2$.

**Scheme 1**. Primary reaction paths in the photolysis of triethylamine (**1a**) and $CO_2$.[8,9]
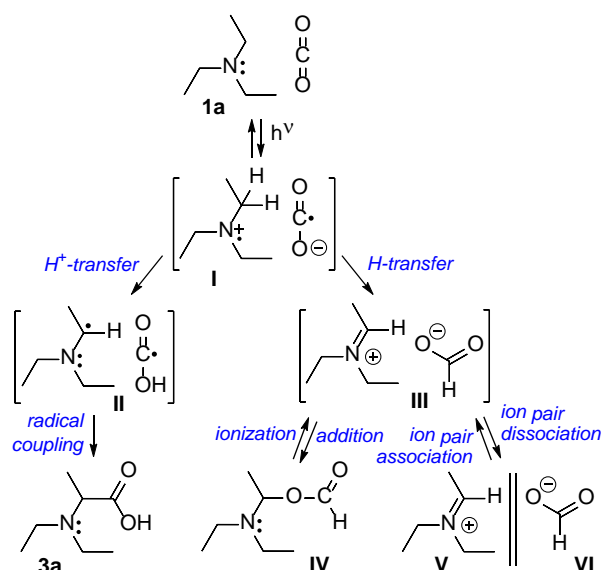


The increase in the solvent's polarity from cyclohexane, to triethylamine (**1a**) and to acetonitrile improves both formic acid (**2**) and diamine **4a** production (Runs 1, 2 and 7, Table 1). Indeed polar solvents are expected to enhance formic acid formation (**2**) since the dipole moment of the reacting system increases in the hydrogen atom transfer step, which leads to a ion pair, while it decreases in the proton transfer step, which leads to a radical pair (Scheme 1).[25] The fact that amino acid **3a** formation does not significantly diminish under conditions that favor the separation of the radical ion pair, *e.g.,* polar solvents and ionic additives (Runs 2 and 5, Table 1),[25] implies that proton and hydrogen atom transfer reactions are faster than the dissociation of the contact radical ion pair $[\mathbf{1a}^{\cdot+}\cdot CO_2^{\cdot-}]$[21,22] and, therefore, the free solvated radical anion $[CO_2^{\cdot-}]$ is not a significant intermediate under our conditions unless it arises from formic acid (**2**) or formate **VI** through alternative processes.[26]

The enhanced diamine **4a** formation observed when going from cyclohexane, to triethylamine (**1a**) and to acetonitrile as solvents (Runs 1, 2 and 7, Table 1), and in the presence of $LiBF_4$ (Runs 2 and 5, Table 1), suggests that the solvent's polarity and the ionic strength of the solution improve the production of $\alpha$-diethylaminoethyl radicals (**VII**). These intermediates probably arise from iminium cations $\mathbf{V}$[27] formed through the ionization of 1-(diethylamino)ethyl formate (**IV**) (Scheme 1), which compete with $CO_2$ for the electrons photo-ejected from amine **1a** (Scheme 2). The proton transfer reaction from amine radical cation $[\mathbf{1a}^{\cdot+}]$[7] to the $\alpha$-diethylaminoethyl radical (**VII**) from the reductive process in the solvent cage (Scheme 2), or to free amine **1a** in solution, further improves the formation of radicals **VII** for the C-C coupling reaction. Polar solvents and ionic additives promote i) electron and hydrogen transfer processes,[22,25] ii) the ionization of the (diethylamino)ethyl formate (**IV**), and iii) the separation of the iminium-formate ion pair **III** (Scheme 1),[25] thus enhancing the release of iminium cations **V** and formate anions (**VI**) to the solution, and therefore diamine **4a** formation at

**Scheme 2**. Reaction paths leading to 2,3-bis(diethylamino)butane (**4a**).



**4a** (*meso* + *D,L*)
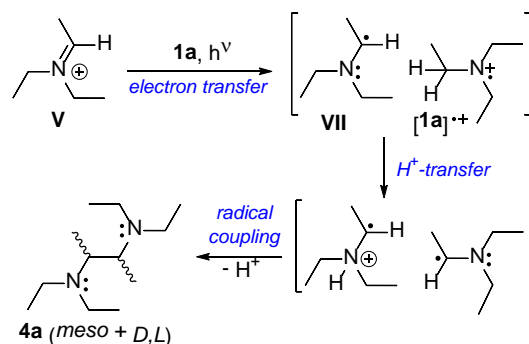
the expense of diethylamine (**5a**) (Run 5, Table 1). The results show that formic acid formation (**2**) diminishes under these conditions (Run 5, Table 1),[26] which is probably due to side reactions of formic acid (**2**) and formate **VI** with the radical and radical ion intermediates.

The coupling of the pair of $\alpha$-diethylaminoethyl radicals (**VII**) is expected to give diamine **4a** as a *ca.* 1:1 *D,L:meso* mixture, and this is indeed the case for the reactions performed in acetonitrile (Runs 2 and 3, Table 1). The reactions run in the presence of LiBF$_4$ (Runs 4-6, Table 1), however, showed the progressive isomerization of diamine **4a** to give its *D,L*-isomer as the reaction time increased. The isomerization of 1,2-diamines under electron transfer conditions is known to proceed[28] through the exergonic $\beta$-C-C $\sigma$-bond cleavage (Scheme 3) to give an iminium ion and an $\alpha$-aminoalkyl radical, followed by a back electron transfer to the iminium cation, and also by the coupling of the resulting radical pair.[28] With diamine **4a** [$E^o$(**1a**$^{.+}$/**1a**) = 0.57 V *vs.* SCE],[17] the isomerization equilibrium displaces toward the *D,L* stereoisomer as the relative spatial orientation of methyl groups C$_1$ and C$_4$ determines[29] that, first, the *antiperiplanar* conformation required for the $\beta$-cleavage[28] is more stable for the *meso* intermediate [*meso*-**4a**$^{.+}$] than for its *D,L* stereoisomer [*D,L*-**4a**$^{.+}$]; and, second, the *sinperiplanar* conformation, established by the *N,N*-two-centre-three-electrons[30] interaction, is more stable for [*D,L*-**4a**$^{.+}$] than for [*meso*-**4a**$^{.+}$] (Scheme 3). The presence of LiBF$_4$ in the reaction medium improves the electron transfer processes[22] and thus facilitates the isomerization process. The radical cation [**1a**$^{.+}$], the iminium cation **V** and CO$_2$ may be suitable oxidants to generate the radical cation [**4a**$^{.+}$] under our reaction conditions. This unproductive side process, along with the capture of the starting amine **1** as unreactive ammonium salts by carboxylic acids **2** and **3,** and the carbamic acid formed from secondary amines **5** and CO$_2$,[15] and the competition of iminium ion intermediates **V** with CO$_2$ as electron sinks, contribute to reduce the efficiency of the CO$_2$-reduction processes under these conditions.

The regioselectivity observed in the carboxylation of unsymmetrical amines **1b-f** with CO$_2$ in acetonitrile solution to give $\alpha$-amino acids **3** (Table 2) well agrees with the relative ability of the radical cation [**1**$^{.+}$] to meet the stereoelectronic requirement for C-H $\sigma$-bond activation; i.e., the alignment of the $\alpha$-C-H $\sigma$-bond *antiperiplanar* to the singly

**Scheme 3**. Isomerization of 2,3-bis(diethylamino)butane (**4a**) under electron transfer conditions.
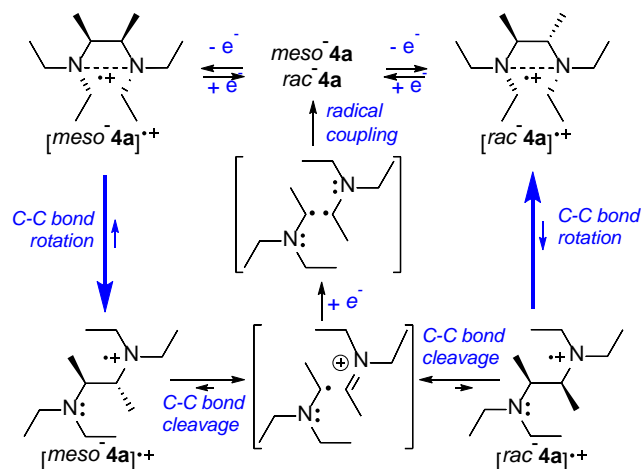


occupied non bonding orbital of the nitrogen atom.[7] Thus the activation of the $\alpha$-C-H bonds in the *n*-butyl- and *iso*-propyl groups of the species [**1b**·⁺] and [**1c**·⁺] respectively requires one methyl/propyl and two methyl/methyl *gauche* interactions, but only hydrogen/alkyl *gauche* interactions in the case of the methyl groups. Accordingly, carboxylation occurs exclusively in the methyl groups of amines **1b** and **1c** (Entries 2-3, Table 2) which are, moreover, statistically favored. The regioselectivity observed in the carboxylation of *N*-methylpyrrolidine (**1d**) can be attributed to a favorable geometry to activate the ring positions, and also to the relief of the eclipsing interactions in the ring system associated with the formation of the radical intermediate,[31] which are responsible for the low bond dissociation energy reported[31c] for the $\alpha$-C-H bond of five-membered heterocycles compared to their linear and six-membered ring counterparts.[31c] *N*-methylpyperidine (**1e**), which lack this efficient activation, undergoes carboxylation evenly at the ring positions and in the methyl group. DABCO (**1g**) is generally unreactive under electron transfer conditions because its rigid bicyclic geometry prevents the activation of $\alpha$-C-H bonds.[7] Finally, the reluctance of diamine **4a** to give $CO_2$-capture products under our standard reaction conditions may result from the *N,N*-interaction[29,30] established in the amine radical cation [**4a**·⁺], which prevents it from adopting the conformation required to activate the $\alpha$-C-H $\sigma$-bond.[7] The carboxylation of *N*-trimethylsilylmethylpiperidine (**1f**) (Run 6, Table 2) appears to prefer the trimethylsilyl group to the proton in order to migrate to the oxygen atom of the radical anion [$CO_2$·⁻].[32]

The results shown in Table 2 reveal a different impact of the substrate structure on the proton and hydrogen atom transfer paths of the radical ion pair [**1**·⁺·$CO_2$·⁻]. Thus the proton transfer is more efficient for amines **1b,c,e**, with **3:2** ratios *ca.* 2:1, which might be attributed to a statistical preference of the proton transfer to one of the two oxygen atoms of the radical anion [$CO_2$·⁻] over the hydrogen transfer to the carbon atom. However, *N*-methylpyrrolidine (**1d**) (**3:2** 14:1) and triethylamine (**1a**) (**3:2** 1:1.4) deviate from this trend in opposite directions (Table 2). These results suggest that the stereoelectronic requirements for the activation of the $\alpha$-C-H bond of [**1**·⁺] are stronger

for the proton transfer step than for the hydrogen atom transfer step since the reactive conformation of the radical cation [**1a$^{\cdot+}$**] has entropic and conformational barriers which are absent in the cyclic radical cation [**1e$^{\cdot+}$**]. Further rationalization of these observations would require a more accurate description of the coordinates and transition states of the reactions than that presently available.[9]

The results show that the substrate structure and the reaction conditions determine the reaction paths in the photolysis of amines **1** in the presence of $CO_2$. Some features are relevant for designing photochemical $CO_2$-capture reactions with tertiary amines **1** as reductants: i) the photoinduced electron transfer from amine **1** to $CO_2$ competes with the reaction paths available for the photoexcited amine **1**, and becomes less efficient as the structural complexity of amine **1** increases; ii) the structural factors which favor the reactive conformation of radical cation [**1$^{\cdot+}$**] improves the proton transfer process and the α-carboxylation reaction over the hydrogen atom transfer and the formation of formic acid (**2**); iii) *N*-methylpyrrolidine (**1d**) proved to be particularly well suited for carboxylation at the ring α-positions, while triethylamine (**1a**) preferentially undergoes hydrogen transfer to give formic acid (**2**); iv) the involvement of free amine **1** as a base in these reactions contributes to diminish the substrate conversion; v) polar solvents and ionic additives favor the electron transfer processes, yet trigger polar pathways which release α-dialkylaminoalkyl radicals into the solution and lead to 1,2-diamines **4** as the major products.

## Conclusions

In summary, the reactions of tertiary amines **1** with $CO_2$ under UV irradiation lead to the $CO_2$-insertion into the α-C-H σ-bond of amine **1**, the hydrogenation of $CO_2$, and the α-C-C coupling of amine **1**. These reactions are proposed to initiate with the photoionization of amine **1** and the capture of the photodetached electrons by $CO_2$ to give the radical ion pair [$R_3N^{\cdot+} \cdot CO_2^{\cdot-}$]. The reaction products reveal the dual character of the radical anion [$CO_2^{\cdot-}$], which abstracts either a hydrogen atom or a proton from the radical cation [$R_3N^{\cdot+}$] to give the secondary reactive intermediates that lead to formic acid (**2**), amino acids **3** and diamines **4**. The reaction is extremely sensitive to the reaction conditions and the substrate structure. The reaction paths that lead to $CO_2$-fixation products under these conditions are hampered by the side processes associated with the reaction products, such as the formation of ammonium carboxylates and carbamates, and the competition of iminium ions with $CO_2$ as electron acceptors.

## Experimental Section

**General.** Solvents were purified by standard procedures,[33] degassed by freeze-pump-thaw, and stored under argon. Commercial amines **1** were distilled from sodium hydroxide and stored under argon. High resolution mass spectrometry (HRMS) was performed with a TRIPLETOF$^F$ 5600 (ABSciex) by using Electrospray in positive mode (ESI+).

**Synthesis of *N*-((trimethylsilyl)methyl)piperidine (1f).**[34] Piperidine (6.2 mL, 62.8 mmol) and (chloromethyl)trimethylsilane (4 mL, 28.6 mmol) g) were placed into a 25 mL stainless steel reactor equipped with a magnetic stirring bar. The reactor was firmly closed and was allowed to stand for 15 days at 60 $^{\circ}$C with stirring. The reaction mixture was transferred to a separatory funnel with pentane and water. The organic layer was dried with anhydrous $MgSO_4$ and the solvent was evaporated under a vacuum to give 4.6 g (94 % yield) of a colorless liquid. The liquid residue was treated with benzoyl chloride (1.1 equiv) at room temperature with stirring for 10 min. The mixture was treated with water (0.5 mL) and $NaHCO_3$ (0.2 g) for 30 min with stirring. The residue was distilled from solid NaOH under a vacuum (30 $^{\circ}$C, $10^{-2}$ mbar) to give a colorless liquid (4.0 g, 82 % yield).

**N-(Trimethylsilyl)methylpiperidine (1f) [17877-17-7].**[35] 82%, 4.0 g, colorless liquid; $^1$H NMR (300 MHz, $D_2O$): δ (ppm) 0.05 (s, 9 H), 1.36 (dt, J = 11.3, 5.8 Hz, 2 H), 1.55 (dt, J = 11.0, 5.6 Hz, 4 H), 1.88 (s, 2 H), 2.31 (br t, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) -0.90, 24.0, 26.4, 51.9, 58.6. MS (EI+, 70ev) *m/z*: 41 (5), 55 (4), 73 (7), 98 (100), 142 (2), 156 (10), 171 (8). HRMS (ESI+) *m/z*: (M+H$^+$) Calcd for $C_9H_{22}NSi$: 172.1522, found: 172.1509.

**Preparation of *N,N*-dialkyl-α-aminoacids (3a-e). General procedure.**[36] A 0.8 M solution of α-bromoacetic acid in diethylether (5.8 mmol) was added drop-wise to 3 mL of *N*-methyl-*N*-(1-methylethyl)amine (28.8 mmol) at 0 $^{\circ}$C with magnetic stirring. The mixture was allowed to stand for 10 h at room temperature with stirring. Volatiles were removed under a vacuum and the residue was treated with 8 mL of a 1.5 M aqueous solution of NaOH (11.6 mmol) at room temperature with stirring. The mixture was evaporated under a vacuum at 40 $^{\circ}$C until constant weight was reached. The solid residue was dissolved in $D_2O$ and the solution was analyzed by $^1$H and $^{13}$C NMR. The solid was dissolved in 10 mL of ultrapure water and the solution was treated with a standardized 0.5 M hydrochloric acid at room temperature and with stirring until a sharp change in pH was observed (pH 4.3, 13 mL). The resulting solution was evaporated under a vacuum and the solid was washed with 3x10 mL of absolute ethanol with stirring and was centrifuged. The ethanolic solution was evaporated under a vacuum and the solid residue was redissolved in water and evaporated under a vacuum until the NMR spectra in $D_2O$ showed that ethanol was absent. The hygroscopic solid (0.7 g, 93 % yield) was stored in a desiccator. The products were also characterized in basic medium.

**Preparation of *N,N*-dialkyl-α-aminoacids (3d'-e'). General procedure.**[37] To a solution of proline (0.5 g, 4.3 mmol) in 60 mL of methanol placed in a 25-mL stainless steel tubular reactor, 0.52 mL of a 37 % aqueous formaldehyde (1.6 equiv) and 0.125 g palladium on carbon 10 % w.w. (0.03 equiv) were added at room temperature with stirring. The reactor was tightly closed, pressurized with hydrogen (10 bar) and allowed to stand at room temperature for 12 h with stirring. The reaction mixture was filtered and the solid was washed with methanol. The solution was evaporated under a vacuum and the solid residue was dried under a vacuum at 50 $^{\circ}$C for 8 h. The product (0.5 g, 89 % yield) was stored in a desiccator. The products were also characterized in basic medium.

**2-(Diethylamino)propanoic acid (3a) [98204-12-7].**[38] 85%, 1.1 g, white solid; ^{1}H NMR (300 MHz, D$_2$O): δ (ppm) 1.32 (q, $J$=7.2 Hz, 6H), 1.48 (d, $J$= 7.2 Hz, 3H,), 3.09-3.40 (m, 4H), 3.87 (q, $J$= 7.2 Hz, 1H). ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 8.9, 9.8, 12.0, 45.5, 45.6, 62.0, 174.8. MS (EI+, 70ev) $m/z$: 42 (11), 44 (23), 56 (17), 70 (8), 72 (33), 100 (100), 130 (5), 145(M$^{.+}$, 4). HRMS (ESI+) $m/z$ : (M+H$^+$) Calcd for C$_7$H$_{16}$NO$_2$: 146.1176, found: 146.1168.

**2-(*N-iso*propyl-*N*-methylamino)acetic acid (3b) [1105044-89-0].**[39] 93%, 0.7 g, white solid; ^{1}H NMR (300 MHz, D$_2$O): δ (ppm) 1.33 (dd, $J$= 6.0 Hz, 6H), 2.83 (s, 3H), 3.53 (d, $J$= 15.0Hz, 1H), 3.62 (m, $J$ = 6 Hz, 1H), 3.81 (d, $J$ = 15 Hz, 1H) ; ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 16.0, 16.5, 37.9, 55.2, 58.4, 171.1; EM (EI+, 70ev) $m/z$: 42(12), 44(100), 56(10), 70 (15), 116 (24), 131 (M$^{.+}$, 5). HRMS (ESI+) $m/z$ (M+H$^+$): Calcd for C$_6$H$_{14}$NO$_2$ : 132.1025, found: 132.1004.

**2-(*N*-Butyl-*N*-methylamino)acetic acid (3c) [23590-11-6].**[40] 82%, 1.0 g, white solid; ^{1}H NMR (300 MHz, D$_2$O): δ (ppm) 0.98 (t, $J$ = 7.5 Hz, 3H), 1.43 (m, $J$ = 7.5 Hz, 2H), 1.77 (m, $J$ = 9.0 Hz, 2 H), 2.95 (s, 3H), 3.09-3.36 (m, 2H), 3.78 (dd, $J$ = 18.0 Hz, 7.5 Hz, 2H). ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 13.2, 19.5, 26.1, 41.7, 57.2, 58.6, 170.8. MS (EI+, 70ev) $m/z$: 29 (14), 41 (33), 42 (54), 44 (92), 58 (85), 74 (85), 100 (84), 102 (100), 145 (M$^{.+}$, 18). HRMS (ESI+) $m/z$ (M+H$^+$): Calcd for C$_7$H$_{16}$NO$_2$: 146.1181, found: 146.1173.

**_N_-methyl-2-pyrrolidincarboxylic acid (3d) [68078-09-1].**[36] 85%, 0.5 g, white solid; ^{1}H NMR (300 MHz, D$_2$O): δ (ppm) 1.91-2.25 (m, 3H), 2.42-2.60 (m, 1H), 2.94 (s, 3H), 3.08-3.23 (m, 1H), 3.68-3.81 (m, 1H), 3.85-3.95 (m, 1H). ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 23.2, 29.2, 41.1, 56.7, 71.0, 174.1. MS (EI+, 70ev) $m/z$: 42 (30), 57 (5.5), 70 (6), 82 (13), 84 (100) 129 (M$^{.+}$, 1). HRMS (ESI+) $m/z$ (M+H$^+$): Calcd for C$_6$H$_{12}$NO$_2$: 130.0868, found: 130.0859.

**2-(Pyrrolidine-1-yl)acetic acid (3d') [37386-15-5].**[36] 73%, 1.0 g, white solid; ^{1}H RMN (300 MHz, D$_2$O): δ (ppm) 2.10 (m, 4H), 3.25-3.65 (br m, 4H), 3.82 (s, 2H). ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 23.2, 55.2, 57.9, 171.5. MS (EI+, 70ev) $m/z$: 42 (20), 55 (10), 70 (1.5), 84 (100), 129 (M$^{.+}$, 4). HRMS (ESI+) $m/z$ (M+H$^+$): Calcd for C$_6$H$_{12}$NO$_2$: 130.0868, found: 130.0858.

**_N_-methyl-2-piperidinecarboxylic acid (3e) [7730-87-2].**[37] 86%, 0.5 g, white solid; ^{1}H NMR (300 MHz, D$_2$O): δ (ppm) 1.52-1.90 (m, 5H), 2.15-2.27 (br d, 1H), 2.86 (s, 3H), 3.03 (dt, $J$ = 13.5, 3.0 Hz, 1H), 3.42-3.55 (m, 2H). ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 21.3, 22.9, 28.4, 42.7, 54.7, 69.4, 174.6. MS (EI+, 70ev) $m/z$: 42(13), 55(3.5), 70 (26), 82 (2.5), 84 (2.0), 98 (100), 143(M$^{.+}$, 1). HRMS (ESI+) $m/z$ (M+H$^+$): Calcd for C$_7$H$_{14}$NO$_2$: 144.1024, found: 144.1019.

**2-(Piperidin-1-yl)acetic acid (3e') [3235-67-4].**[41] 93%, 0.27 g, white solid; ^{1}H RMN (300 MHz, D$_2$O): δ (ppm) 1.50 (m, 1H), 1.50 (m, 5H), 2.99 (dt, $J$ = 12 Hz, 3 Hz, 2H), 3.56 (br d, 2H), 3.67 (s, 2H). ^{13}C RMN (75 MHz, D$_2$O): δ (ppm) 21.4, 23.1, 54.3, 59.0, 170.5. MS (EI+, 70ev) $m/z$: 42 (11), 55 (7), 70 (6), 98 (100), 143 (M$^{.+}$, 2). HRMS (ESI+) $m/z$ (M+H$^+$): Calcd for C$_7$H$_{14}$NO$_2$: 144.1024, found: 144.1004.

**2-(Diethylamino)propanoic acid hydrochloride [3a(H⁺)].**[38] ^{1}H NMR (500 MHz, $D_2O$, HCl): δ (ppm) 1.06 (t, J=9.0 Hz, 6H), 1.29 (d, J= 6.0 Hz, 3H), 2.84-3.20 (m, 4H), 4.06 (q, J= 9.0 Hz, 1H). ^{13}C RMN (126 MHz, $D_2O$, HCl): δ (ppm) 9.1, 9.7, 10.6, 46.7, 47.7, 59.2, 171.6.

**Sodium 2-(diethylamino)propanoate (3aCOONa) [98204-12-7].**[38] ^{1}H NMR (500 MHz, $D_2O$): δ (ppm) 1.12 (t, J = 12 Hz, 6 H), 1.30 (d, J = 15 Hz, 3 H), 2.71-2.95 (m,4 H), 3.50 (q, J = 12 Hz, 1 H); ^{13}C NMR (126 MHz, $D_2O$): δ (ppm) 10.9, 14.6, 44.7, 61.6, 179.9.

**Sodium 2-(N-isopropyl-N-methylamino)acetate (3bCOONa) [1105044-89-0].**[39] ^{1}H NMR (500 MHz, $D_2O$): δ (ppm) 1.02 (d, J = 5 Hz, 6 H), 2.23 (s, 3 H), 2.88 (m, J = 5 Hz, 1 H),3.08 (s, 2 H); ^{13}C NMR (126 MHz, $D_2O$): δ (ppm) = 17.6, 37.4, 52.8, 57.2, 179.5.

**Sodium 2-(N-butyl-N-methylamino)acetate (3cCOONa) [23590-11-6].**[40] ^{1}H NMR (500 MHz, $D_2O$): δ (ppm) 0.90 (t, J = 7.4 Hz, 3 H), 1.30 (m, 2 H), 1.46 (m, 2 H), 2.27 (s, 3 H), 2.47-2.44 (m, 2 H),3.05 (s, 2 H); ^{13}C NMR (126 MHz, $D_2O$): δ (ppm) 13.3, 20.2, 28.4, 41.4, 56.2, 60.6, 178.8.

**Sodium N-methyl-2-pyrrolidincarboxylate (3dCOONa) [849145-28-4].**[36] ^{1}H NMR (300 MHz, $D_2O$): δ (ppm) 1.69-1.84 (m, 3H), 2.03-2.18 (m, 1H), 2.27 (s+m, 4H), 2.79 (m, 1H), 2.95 (m, 1H). ^{13}C RMN (75 MHz, $D_2O$): δ (ppm) 22.5, 29.7, 40.1, 55.7, 70.8, 182.0.

**Sodium 2-(pyrrolidin-1-yl)acetate (3d'COONa) [201931-57-9].**[42] ^{1}H NMR (500 MHz, $D_2O$): δ (ppm) 1.79 (m, 4 H), 2.63 (m, 4 H), 3.17 (s, 2 H); ^{13}C NMR (126 MHz, $D_2O$): δ (ppm) 23.4, 53.6, 59.6, 178.9.

**Sodium N-methyl-2-piperidinecarboxylate (3eCOONa) [7730-87-2].**[36] ^{1}H NMR (500 MHz, $D_2O$): δ (ppm) 1.18-1.8 (m, 7H), 2.04 (td, J = 3 Hz, 12 Hz, 1H), 2.13 (s. 3H), 2.49 (dd, J = 3 Hz, 9 Hz, 1H), 2.82 (dt, J = 12 Hz, 3 Hz, 1H); ^{13}C NMR (126 MHz, $D_2O$): δ (ppm) 23.6, 25.3, 53.9, 63.0, 178.7.

**Sodium 2-(piperidin-1-yl)acetate (3e'COONa) [91724-68-4].**[42] ^{1}H NMR (500 MHz, $D_2O$): δ (ppm) 1.43 (m, 2H), 1.56 (m, 4 H),2.47 (br m, 4 H), 2.97 (s, 2 H). ^{13}C NMR (126 MHz, $D_2O$): δ (ppm) 23.2, 24.9, 53.6, 62.6, 178.3.

**Photochemical reactions of amines 1 and $CO_2$. General procedures.** Triethylamine (**1a**), either used neat or in anhydrous acetonitrile solution (0.3 M), was placed (3.7 mL) inside a quartz test tube that was capped with a rubber septum, and was treated with $CO_2$ (20 psi) for 20 min at 0 °C with stirring. After removing the stirring bar, the test tube was sealed with a rubber septum, and was then fixed to the motor unit of a rotary evaporator (150 rpm). Reaction mixtures were irradiated for 3 h at room temperature with a compact twin-tube germicidal lamp (254 nm, 36 W) placed in parallel 2 cm above the test tube. Reaction mixtures were transparent solutions with a thin solid layer on the tube wall for the reactions in acetonitrile solution, and white solid suspensions for the reactions used neat. After removing volatiles under a vacuum, the residue was dissolved with 3 mL of a 0.078 M solution of phenol, used as the external standard, in $D_2O$ to which one drop of 37 % hydrochloric acid was added to improve solubility. The solution was analyzed by NMR to quantify the acidic reaction products. The analysis and quantification of the basic products were performed in a second identical

experiment, which was treated with 37 % hydrochloric acid prior to removing volatiles under a vacuum. The residue was dissolved with 3 mL of a 0.078 M solution of phenol, used as the external standard in $D_2O$, and the solution was analyzed by NMR. The sodium salts of the acidic products were characterized in a third experiment by evaporating the reaction mixture under a vacuum by dissolving the residue in 3 mL of a 0.75 M solution of sodium hydroxide, and using 0.05 M of phenol as an external standard in $D_2O$, and the basic solution was extracted with 3 mL of benzene. The aqueous layer and the organic layer were respectively analyzed by NMR and gas chromatography-mass spectrometry.

**Preparation of *N,N,N',N'*-tetraethylbutane-2,3-diamine (4a).** A 0.3 M acetonitrile solution of triethylamine (**1a**) (3 mL) was placed inside a quartz test tube that was capped with a rubber septum, and was treated with $CO_2$ (20 psi) for 20 min at 0 °C with stirring. After removing the stirring bar, the test tube was sealed with a rubber septum, and was then fixed to the motor unit of a rotary evaporator, set at 150 rpm. The solution was irradiated for 3 h at room temperature with a compact twin-tube germicidal lamp (254 nm, 36 W) placed in parallel 2 cm above the test tube. The same reaction was performed 6 times. The combined reaction mixtures were treated with 37 % hydrochloric acid prior to removing volatiles under a vacuum. The residue was treated with 10 mL of a 2.5 M solution of sodium hydroxide and the basic solution was extracted with 3x10 mL of *n*-pentane. The organic layer was dried with anhydrous $MgSO_4$ and evaporated under a vacuum to yield a colorless liquid (0.79 g, 73%), which was analyzed by NMR in acidic $D_2O$ and by gas chromatography-mass spectrometry.

*N,N,N',N'*-tetraethylbutane-2,3-diamine (4a) [4a: 3653-11-0; 4a·HCl: 1071696-23-5].[43] 73%, 0.79 g, colorless liquid; ^{1}H NMR (300 MHz, $D_2O$, HCl): $\delta$ (ppm) *D,L* 0.86 (t, 12 H), 0.94 (d, 6H), 2.82 (br m, 4 H), 2.93 (br m, 2 H), 3.50 (br q, 2H); *meso* 0.87 (t, 12 H), 1.00 (d, 6 H), 2.75 (br m, 4 H), 3.10 (br m, 2 H), 3.40 (br q, 2 H). ^{13}C RMN (75 MHz, $D_2O$, HCl): $\delta$ (ppm) *D,L* 9.9, 46.1, 47.4, 58.3; *meso* 9.6, 46.4, 48.6, 57.8. MS (EI+, 70ev) *m/z*: 29 (7.6), 42 (9.8), 44 (18.6), 56 (12), 70 (9.1), 72 (15), 84 (2.7), 86 (1.8), 99 (4.5), 100 (100), 112 (1.2), 128 (4.5), 141 (0.1), 155 (2.3), 169 (2.9), 200 (M$^{.+}$, 1).

**Supporting Information.** The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXX. ^{1}H and ^{13}C NMR spectra (PDF).

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