

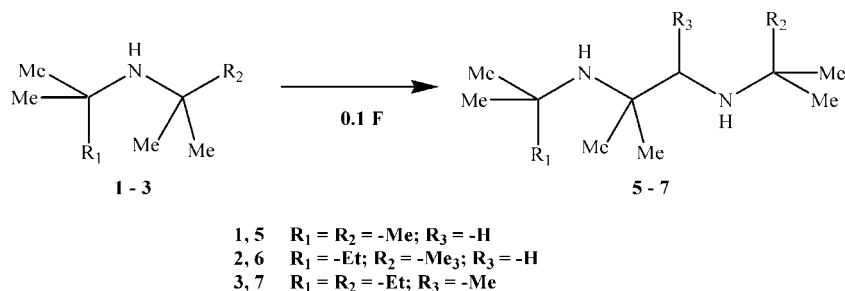
Electrosynthesis of Hindered Alkyl Diamines: Evidence for an Electrocatalytic Anodic Mechanism

Illuminada Gallardo* and Neus Vilà

Departament de Química, Universitat Autònoma de Barcelona, 08193 Barcelona, Spain

Illuminada.Gallardo@uab.cat

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The electrosynthesis of highly hindered secondary alkyl diamines through the formation of C–N bonds has been successfully performed in one-pot under mild conditions using an environmentally friendly method. The electrochemical behavior of four hindered secondary alkyl amines (di-*tert*-butylamine (**1**), *tert*-amyl-*tert*-butylamine (**2**), di-*tert*-amylamine (**3**) and *tert*-amyl-*tert*-octylamine (**4**)) is described. Effects not only of the initial concentration of the corresponding di-*tert*-alkylamine but also of the time on the initial oxidation scan are reported for the first time for the electrochemical behavior of an aliphatic amine. Moreover, valuable mechanistic information has been provided from analysis of the intermediate species and final products generated when electrochemical oxidation was performed. An electrocatalytic mechanism based on the propagation of free radical species leading to highly hindered diamines has been tentatively proposed. The key role played by the radical cation as the intermediate initiator involved in the subsequent propagation cycle has been demonstrated.

Introduction

Aliphatic amines have been widely used in the presence of an oxidant as precursors of aminoxyl radicals¹ that play a key role as initiators in industrial processes based on the polymerization of radical species such as the synthesis of polystyrene.² The major instability of the nitroxide derivatives containing α -hydrogens³ at the high temperatures required for those polymerization processes is well-known. In this sense, the inherent stability displayed by sterically hindered aminoxyl

radicals makes them extremely attractive compounds for such applications. Moreover, sterically hindered alkyl amines are also useful in synthesis as proton scavengers due to an important effect of the steric hindrance on their basicity.⁴ More recently, they have been successfully tested as CO₂ capturers⁵ making them a promising alternative to the continuous strategies developed for reducing carbon dioxide emissions, obviously one of the most serious worldwide environmental problems contributing to global warming nowadays. Particularly, hindered alkyl amines show capacity and absorption rate advantages over conventional linear amines for carbon dioxide removal from gases by absorption in either aqueous amines or aqueous polar organic solvent solution of amines.⁶ Although several methods have been described in the past for the preparation of sterically

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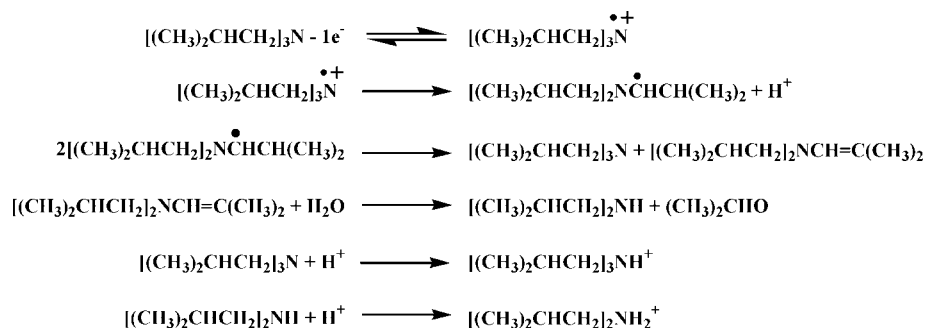
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SCHEME 1



hindered alkyl amines⁷ and diamines,⁸ a major drawback to the use of such versatile compounds is the larger number of steps usually involved in most of their syntheses and more importantly the poor yields obtained. Hence, the development of enhanced synthetic routes toward sterically strained aliphatic amines and diamines has recently gained renewed interest.⁹

Chemical synthesis of *N,N'*-di-*tert*-butyl-2-methylpropylendiamine was first described in the early 1980s by Lai.¹⁰ The synthetic method reported implied the synthesis of the precursor amide derivative from α -haloisobutyramides and *tert*-butylamine with sodium hydroxide in Favorskii-like reactions. The resulting amide derivative was reduced using a chemical reducing agent such as lithium aluminum hydride in refluxing dimethoxyethane.¹¹ In recent years, we have been trying to develop an enhanced general and environmentally favorable route for the synthesis of asymmetric secondary alkyl diamines avoiding the use of chemical reducing agents and in mild conditions. Due to the dimeric nature of the desired compounds, the use of secondary alkyl monoamines with tertiary carbons in the α position to the amino functional group was reasonably considered as a first approach to our purpose since previous examples involving the electrochemical oxidation of aromatic amines have been reported as leading to dimeric derivatives as a result of coupling reactions between radical cations.¹² On the other hand, it has recently been demonstrated that the reactivity of the relatively unstable radical cations of aliphatic amines responding to the general formula $[(R_1R_2\text{CH})\text{NR}_3\text{R}_4]$ is governed by the presence of hydrogen atoms on the α carbon to the amino functional group when they are available.¹³ Hence, the demonstrated anodic mechanism consists first of an electron transfer leading to a radical cation which undergoes a deprotonation through the $\text{C}\alpha\text{-H}$ bond cleavage giving a radical. This radical evolves in the subsequent chemical step through dismutation

into an amine and an enamine, which in the presence of wastewater provides the corresponding less-substituted amine, and aldehyde and protons. This process is outlined in Scheme 1.

Most of the differences between aromatic and aliphatic amino radical cation reactivity must be due to obvious differences in their basic character, in that they are aromatic amines with a much weaker base than alkyl amino groups. In contrast, the electrochemical behavior of substituted aliphatic amines based on the presence of tertiary α -carbons in their structure has received much less attention. From a mechanistic point of view, significant changes should be anticipated for these species because the deprotonation of the corresponding radical cations cannot take place in the same way as described above. In this sense, it is probable that alkyl diamines were obtained by electrochemical oxidation of the corresponding secondary *tert*-alkyl monoamine because the α carbon is blocked in these compounds and an obviously different reactivity must be predicted.

In this paper, we report a new electrochemical method for the preparation of highly hindered secondary alkyl diamines in very good yields. The electrochemical behavior of four di-*tert*-alkylamines (**1–4**) is carefully discussed on the basis of the results obtained by cyclic voltammetry and potential controlled electrolyses used as electrochemical tools.

Results and Discussion

The present paper deals with the particular electrochemical behavior of sterically strained di-*tert*-alkylamines (**1–4**). These compounds display, as a common feature, the absence of hydrogen atoms on the carbon adjacent to the amino functional group, which leads to a different reactivity of their radical cations in comparison with that described for alkyl amines containing $\text{C}\alpha\text{-H}$ bonds in their structure. In this paper, we describe the preparation of asymmetric and highly hindered alkyl diamines (**5–7**) that are electrochemically initiated by generation of catalytic amounts of $1^{\bullet+}$ – $4^{\bullet+}$, in good yields, leading to the development of a simple, environmentally friendly and reagentless method for synthesis of new diamines (**6–7**) in mild conditions (Scheme 2). It should be noted that no dimerization products were detected when *N-tert*-amyl-*N-tert*-octylamine, **4**, was investigated probably due to the higher steric effect of *tert*-octyl groups.

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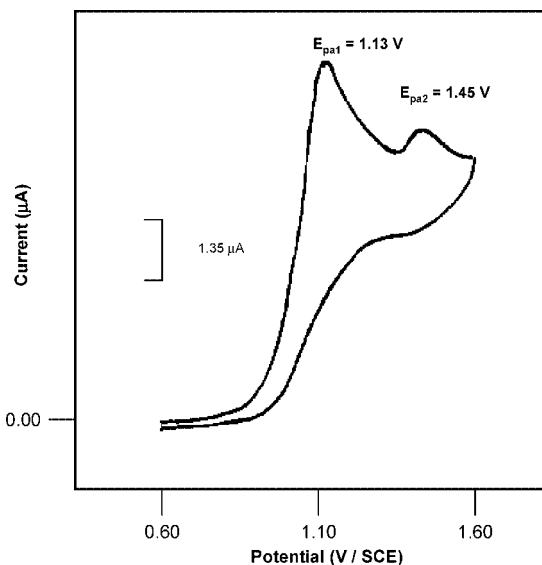
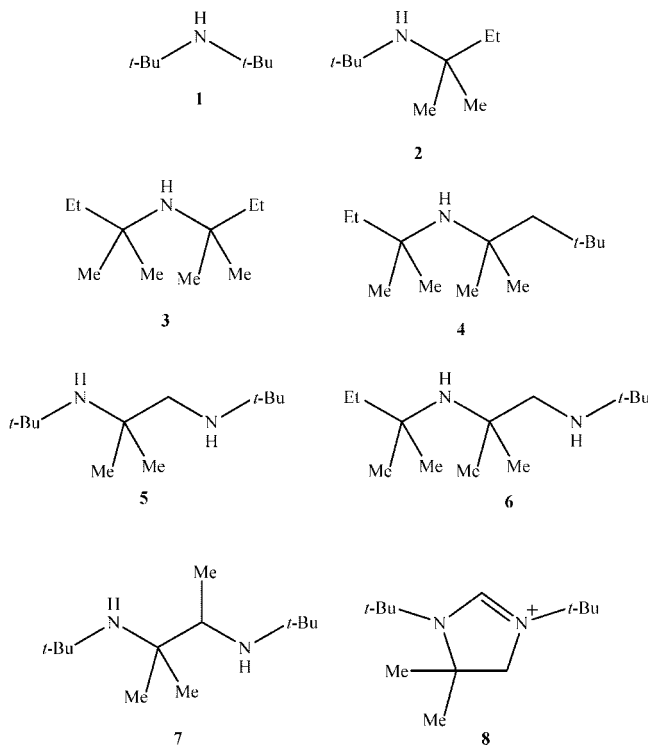


FIGURE 1. Cyclic voltammogram of **1** (6.68 mM) in DMF + *n*-Bu₄NBF₄ 0.1 M on a glassy carbon working electrode (*d* = 0.5 mm). Scan rate: 0.1 V s⁻¹. Reference electrode: SCE. Counter electrode: Platinum disk (*d* = 1 mm).

SCHEME 2



The alkyl monoamines shown in Scheme 2 (**1**–**3**) have similar electrochemical behavior. Two chemically successive irreversible oxidation peaks are observed on the first anodic scan up to 1.60 V/SCE, 1.13 and 1.45 V/SCE for **1**, 1.12 and 1.43 V/SCE for **2**, 1.10 and 1.42 V/SCE for **3**. A characteristic cyclic voltammogram of **1** is shown in Figure 1. The first one-electron wave is ascribed for all the monoamines investigated to the oxidation of the secondary alkyl amino group.

When controlled potential electrolyses were carried out at potentials of ca. 70 mV more positive than the first anodic peak, two different electrochemical behaviors were observed depending on the amount of charge consumed. In this sense, the

TABLE 1. Products and Yields Obtained by Performing Controlled Potential Electrolysis by Passing 0.1 F at the Potential Specified for Each Case in Solutions Containing Alkyl Monoamines, **1**–**4**, (20 mM), in DMF + *n*-Bu₄NBF₄ 0.1 M

amine	<i>E</i> _{app} (V/SCE)	diamine	yield (%)
1	1.20	5	90
2	1.18	6	92
3	1.17	7	90
4	1.18	no dimerization products	–

secondary alkyl diamines **5**–**7** were obtained in good yields when passing 0.1 F, (Table 1, see Experimental Section).

In contrast, when exhaustive controlled potential electrolyses were performed, the anodic current reached a plateau value close to zero when 70% of the theoretical charge was consumed assuming a monoelectronic process. In the particular case of **1**, two products were obtained in such experimental conditions, **5** (67%) and **8** (18%) (Scheme 3).

These preliminary results suggested a complex mechanism to rationalize the electrochemical oxidation of these amines, **1**–**4**. The following discussion will focus on the description of the electrochemical behavior of **1** and the tentatively proposed reaction pathway leading to **5** in order to make the complexity of the overall process occurring upon generation of catalytic amounts of **1**⁺ easier to understand.

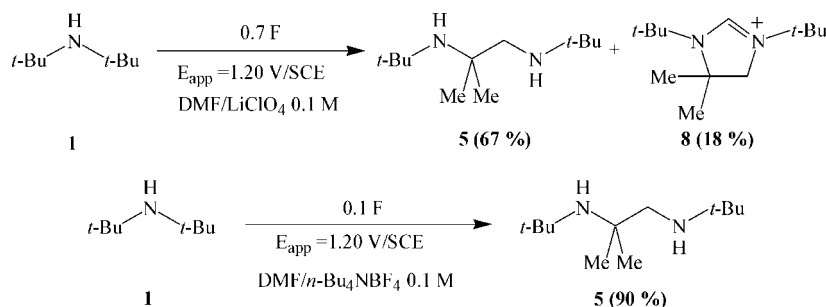
Electrosynthesis of 5. A characteristic cyclic voltammogram of **1** (6.68 mM) in DMF + *n*-Bu₄NBF₄ 0.1 M is shown in Figure 1. Two chemically successive irreversible oxidation peaks located at 1.13 and 1.45 V/SCE are observed on the first anodic scan up to 1.60 V/SCE. The first one-electron wave is ascribed to the oxidation of the secondary alkyl amino group whereas the nature of the species involved in the second oxidation at more positive potentials is uncertain. However, it should be highlighted that effects not only of the initial concentration but also of the time of an initial oxidation scan have been observed for the first time in the electrochemical response of an alkyl amine.

Figure 2 shows the evolution observed in the shape of the initial cyclic voltammograms recorded for **1** as a function of its concentration. Therefore, a unique single irreversible oxidation wave at 1.13 V/SCE is observed on a first anodic scan within the concentration range of **1** below 3.50 mM (Figure 2a). In contrast, a second voltammetric signal clearly emerges at 1.45 V when higher concentrations of **1** are employed (Figure 2b,c).

Moreover, a rigorous voltammetric study performed in diluted solutions containing **1** at concentrations lower than 3.50 mM demonstrated that at least one oxidation scan was a requirement to observe a time effect on the composition of the solutions.

Diluted solutions of **1** were chosen for that purpose because the analysis of the voltammetric data is hugely facilitated by the fact that the oxidation wave at 1.45 V/SCE does not appear in the first anodic scan and clearly emerges during the following repetitive electrochemical measurements. Nevertheless, it should be noted that the same conclusions could be extracted from careful analysis of the experimental data obtained for the entire concentration range studied. A unique single irreversible anodic wave was observed at 1.13 V/SCE on the first oxidation scan recorded in a 3.50 mM solution of **1** (Figure 3a). The solution was kept in an argon atmosphere and an identical oxidation scan was recorded. Two new oxidation peaks were obtained at 1.17 and 1.45 V/SCE. Furthermore, the peak at 1.13 V was no longer detected (Figure 3b). From the voltammetric data obtained, we

SCHEME 3



conclude that an anodic scan is enough to observe an evolution of **1** toward a new product **5** during the cyclic voltammetry time scale.

As a consequence, identical cyclic voltammograms of **1** could not be obtained in an initial scan toward positive potentials when the same experimental conditions were employed, suggesting an evolution of the concentration profile of **1** when very low amounts of charge were consumed (Figure 3). The stability of **1** in solution in the experimental conditions used was also confirmed because two identical solutions containing **1** at concentrations lower than 3.50 mM were prepared. One of these was kept in nitrogen at room temperature overnight. After that period, the cyclic voltammogram recorded displayed the same features as the one obtained for the other fresh solution. Thus, at least one anodic scan is required to observe the changes mentioned for the cyclic voltammetry measurements of **1**.

A series of controlled potential electrolyses, including exhaustive oxidation of **1**, were performed by employing two experimental methodologies that provided important mechanistic information from the kinetic parameters determined.

Consumption of Catalytic Amounts of Charge (0.1 F). Solutions of **1** within the concentration range from 3.50 to 35.0 mM were prepared. After controlled potential electrolysis at 1.20 V/SCE and when catalytic amounts of charge were consumed (0.1 F), the cyclic voltammogram immediately recorded is shown in Figure 3b. The solutions were worked out as detailed in the Experimental Section. No product was detected in the aqueous phase. Analysis of the organic layer shows the presence of only one compound (90%) (Scheme 3), which was characterized by GC-MS, ESI+, ^1H NMR, and elemental analysis and

corresponded to diamine **5** *N,N'*-di-*tert*-butyl-2-methylpropylenediamine (Scheme 1), (see Supporting Information). To confirm these results, chemical synthesis of **5** was performed as described in the Experimental Section. Subsequent analysis by GC-MS, ESI+, ^1H NMR and elemental analysis unequivocally confirmed the identity of **5**.

Exhaustive Controlled Potential Electrolysis of 1. An exhaustive controlled potential electrolysis was performed in a solution containing **1** (20 mM) in DMF at 1.20 V/SCE. The anodic current achieved values close to zero when 70% of the theoretical charge was consumed assuming a monoelectronic process. A cyclic voltammogram recorded at the end of the experiment results in the absence of the first anodic peak whereas the second wave previously detected at 1.45 V/SCE remains unchangeable (Figure 4b). This voltammetric signal is partially reversible at 1.0 Vs $^{-1}$ with $E^0 = 1.40$ V/SCE (Figure 4c).

The electrolyzed solutions were neutralized beforehand, and the organic analytes were subsequently extracted with toluene as previously specified (see Experimental Section). The concentration of unreacted **1** remaining in solution (15%) was estimated from the area peaks obtained in the gas chromatogram. In addition to **1**, the aforementioned compound **5** (67%, Scheme 3) was also detected by GC. Mass spectrometric analysis revealed a molecular mass at 200 *m/z* which was confirmed by ESI+. Most of the solvent and residual amounts of **1** remaining in solution were distilled, leading to the isolation of **5**. In order to obtain additional information concerning the chemical process taking place when exhaustive oxidation of **1** was carried out, the aqueous layer was analyzed by ESI+ in order to detect

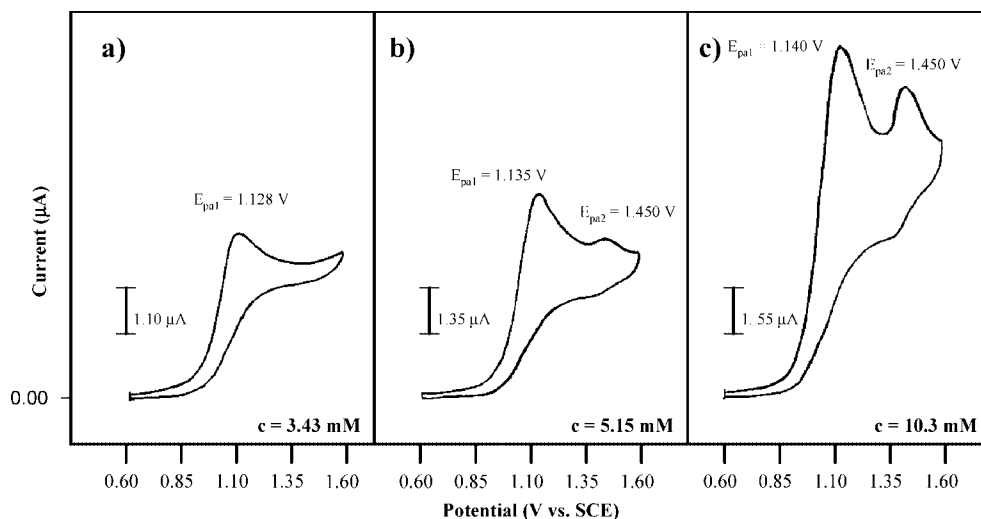


FIGURE 2. Cyclic voltammetry of **1** in DMF + *n*-Bu $_4$ NBF $_4$ 0.1 M on a glassy working carbon electrode ($d = 0.5$ mm), (a) 3.43 mM, (b) 5.15 mM and (c) 10.3 mM. Scan rate: 0.1 Vs $^{-1}$. Reference electrode: SCE. Counter electrode: Platinum disk ($d = 1$ mm).

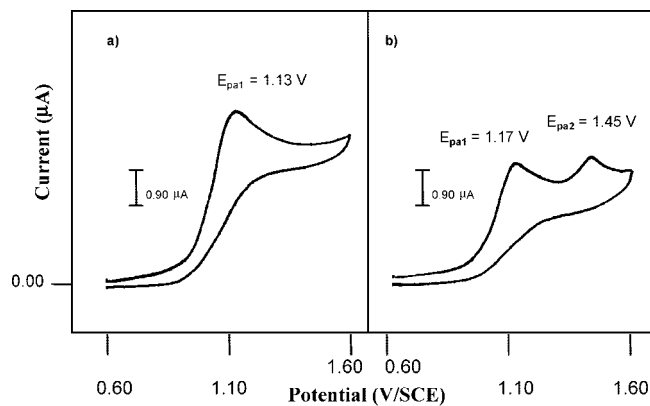


FIGURE 3. Cyclic voltammetry of **1** (3.50 mM) in DMF + *n*-Bu₄NBF₄ 0.1 M. (a) First oxidation scan ($t = 0$), (b) second oxidation scan ($t = 20$ min). Scan rate: 0.1 Vs⁻¹. Reference electrode: SCE. Counter electrode: Platinum disk ($d = 1$ mm).

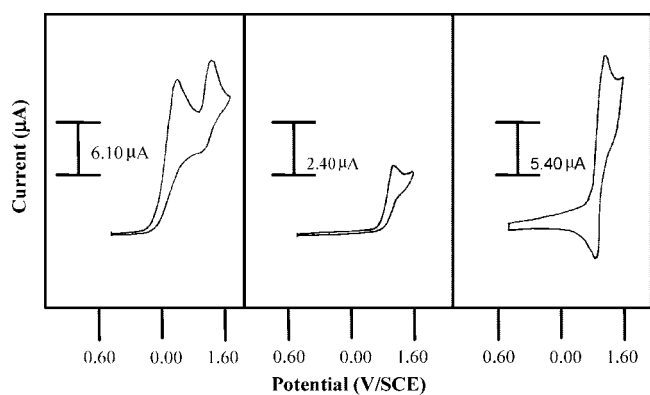


FIGURE 4. Cyclic voltammograms of a solution containing **1** (20.0 mM) in DMF + LiClO₄ 0.1 M. (a) Before exhaustive oxidation at 1.20 V/SCE, scan rate 0.1 Vs⁻¹, (b) after consumption of 0.7 F, scan rate 0.1 Vs⁻¹, and (c) after consumption of 0.7 F, scan rate 1.0 Vs⁻¹.

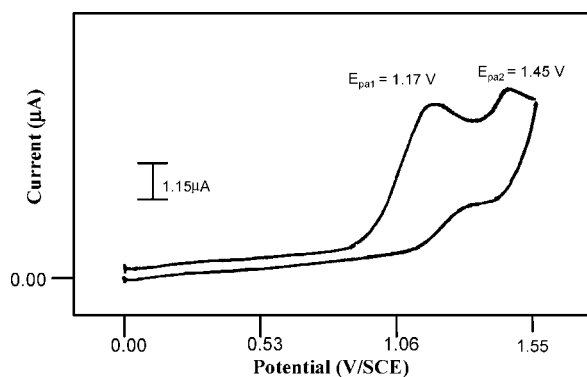


FIGURE 5. Cyclic voltammetry of a solution containing **5** (4.53 mM) in DMF + *n*-Bu₄NBF₄ 0.1 M on a glassy carbon working electrode ($d = 0.5$ mm). Scan rate: 0.1 Vs⁻¹. Reference electrode: SCE. Counter electrode: Platinum disk ($d = 1$ mm).

possible cationic species. This analysis led us to detect a new compound with $m/z = 211$. After further additional chemical analysis this new species was assigned to the formation of 1,3-di-*tert*-butyl-4,5-dihydro-1H-imidazol-3-ium, **8** (18%), (Schemes 2 and 3).

The electrochemical characterization of **5** was required to determine the different elemental steps that might explain the experimental evidence indicated during electrochemical oxidation of **1**. A typical cyclic voltammogram of *N,N'*-di-*tert*-butyl-

2-methyl-1,2-propyldiamine, **5**, (4.53 mM) in DMF + *n*-Bu₄NBF₄ 0.1 M is shown in Figure 5. Two chemically irreversible anodic peaks are observed on a first oxidation scan at 1.17 and 1.45 V/SCE respectively. That cyclic voltammogram is analogous to that obtained in Figure 3b. The first voltammetric signal is monoenergetic whereas a significantly lower anodic current is involved in the second peak. The partial reversibility was also obtained for **5** by increasing the scan rate up to 60 Vs⁻¹ giving $E_s^0 = 1.22$ V/SCE. This diamine has two secondary amino functional groups. One of these has C–H bonds in the α position to the nitrogen and taking into account the oxidation mechanism reported previously for aliphatic amines containing α -hydrogens (Scheme 1),^{13g} an electron transfer leading to a radical cation which undergoes a deprotonation through the C α -H bond cleavage giving a carbon centered radical, a first approach to the operative mechanism according to these preliminary results is shown in Scheme 4.

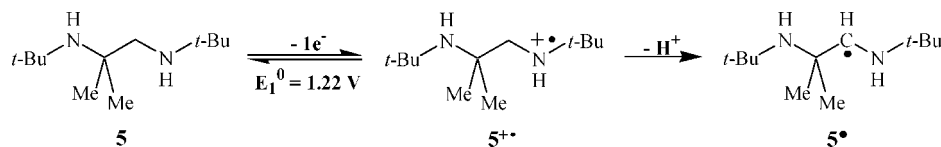
Because aliphatic amines and diamines are well-known strong bases, careful addition of known amounts of H⁺ to a solution of **5** should lead to changes in its composition due to the formation of either **5H**⁺ or **5H**₂²⁺. The cyclic voltammetry analysis in acidic media was carried out by careful addition of controlled amounts of perchloric acid to a solution containing **5** (8.31 mM) in DMF + *n*-Bu₄NBF₄ 0.1 M (Figure 6). Quaternary ammonium salts are nonelectroactive species within the potential window scanned. According to these premises, obvious changes in the form of the cyclic voltammograms as a function of the concentration of H⁺ in solution should be expected. Addition of 0.5 equiv of acid would correspond to an equimolar solution of **5/5H**⁺, resulting in a decrease in the first anodic peak at 1.17 V ascribed to the oxidation of **5** (Figure 6b). Further addition up to an equivalent of perchloric acid would lead to a solution containing **5H**⁺. The cyclic voltammogram recorded in such experimental conditions exhibits a monoenergetic wave at 1.45 V/SCE attributed to the oxidation of the neutral amino group remaining in **5H**⁺ (Figure 6c). A residual anodic current is still observed at 1.17 V suggesting the simultaneous coexistence of several acid–base equilibria. No voltammetric signal is observed on addition of a second equivalent of perchloric acid (not shown), which would be in good agreement with the presence of **5H**₂²⁺.

The proton generated by the chemical reaction following electron transfer when **5** is electrochemically oxidized would be able to form **5H**⁺. The neutral alkyl amino group of **5H**⁺ is oxidized at 1.45 V/SCE (Figure 4b), which is more positive than what would be expected for a secondary alkyl amine (Scheme 5).

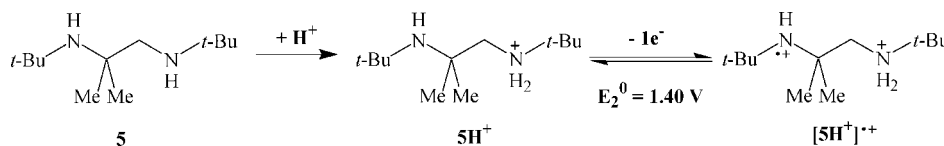
From this experimental evidence, we conclude that the second wave observed for **1** (Figure 1) is due to the presence in solution of **5H**⁺. Furthermore, such a result would explain why a unique anodic peak at 1.45 V/SCE was observed when exhaustive controlled potential electrolyses of **1** were performed (Figure 4b,c). **1** and **5** are simultaneously oxidized. Thus, the corresponding **5**^{•+} would evolve through a deprotonation yielding **5H**⁺, which is responsible for the oxidation wave at 1.45 V/SCE. In addition, the presence of **5H**₂²⁺ cannot be ruled out because it is a nonelectroactive species.

However, the mechanism through which **1** evolves into **5** was still unclear at this point. For this reason, electrochemical studies within the scan rates ranging from 0.1 to 100 Vs⁻¹ were performed to determine thermodynamic (E^0) and kinetic (k_s^{ap} , k , and α) parameters associated to that oxidation process

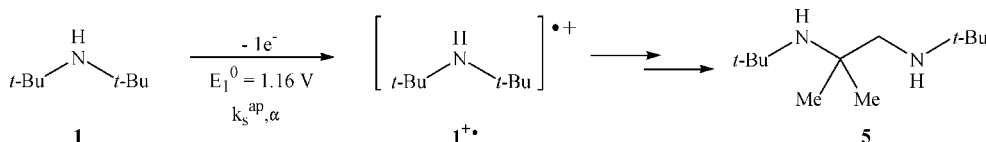
SCHEME 4



SCHEME 5



SCHEME 6



and to establish the reaction pathway. For that purpose, accurate experimental measurements were carried out by cyclic voltammetry. Freshly diluted solutions of **1** (3.50–10.0 mM) were prepared and initial cyclic voltammograms were recorded. The electrochemical study at low concentrations of **1**, when only one oxidation peak is observed, enabled us to determine thermodynamic ($E_{1^{•+}/1}^0 = 1.16$ V/SCE) and kinetic electrochemical parameters ($k_s^{\text{ap}} = 3.2 \times 10^{-3}$ cm s $^{-1}$, $\alpha=0.5$) associated to the oxidation process. Despite the dimeric nature of **5**, the chemical process following the electron transfer is not a second order chemical reaction because the potential peak values are not concentration dependent (Scheme 6).¹⁴

Further kinetic studies based on the generation of catalytic amounts of $1^{•+}$ were designed in order to estimate crucial kinetic parameters such as the chemical order reaction with respect to **1**. Solutions of **1** within the concentration range from 15 to 35 mM were prepared. This experimental approach was based on the consumption of equal amounts of charge in all the cases which led to a constant initial concentration of the radical cation, $[1^{•+}]_0$, for each solution. Evolution of the concentration profiles for **1** and **5** was followed by GC-MS analyses of aliquots taken at different reaction times. Attempts to estimate the kinetic order

reaction with respect to **1** from the concentration profiles obtained were performed by means of the initial rates method.

$$\ln v_0 = \ln k' + b \ln [1]_0 \quad (1)$$

The concentration profiles obtained for **1** were well-fitted to a second order polynomial within the time interval from 0 to 8 min. This mathematical approach eventually results in a fractional kinetic order with respect to **1**, $b = 1.3$, which strongly supports the idea that a mechanism based on the propagation of radical intermediates is operative. A catalytic cycle could be tentatively proposed as the operative mechanism from a rigorous analysis of the kinetic data obtained. Such a reaction pathway would only be initiated when low amounts of $1^{•+}$ were electrochemically generated on the electrode surface.

Mechanistic Proposal for the Evolution of 1. According to the experimental data available a fair mechanistic approach would consist of a first monoelectronic transfer leading to $1^{•+}$ which would later initiate a complex process based on the propagation of radical intermediates in solution eventually leading to **5** in very good yields. As mentioned earlier, a second order chemical reaction following the electron transfer has been discarded since the electrochemical parameters associated to the oxidation process are concentration nondependent. As the widely

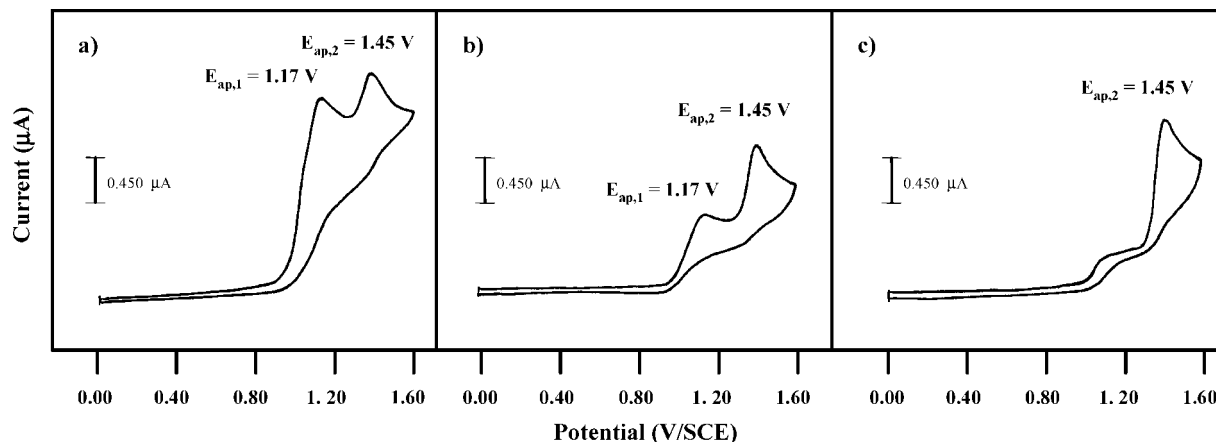
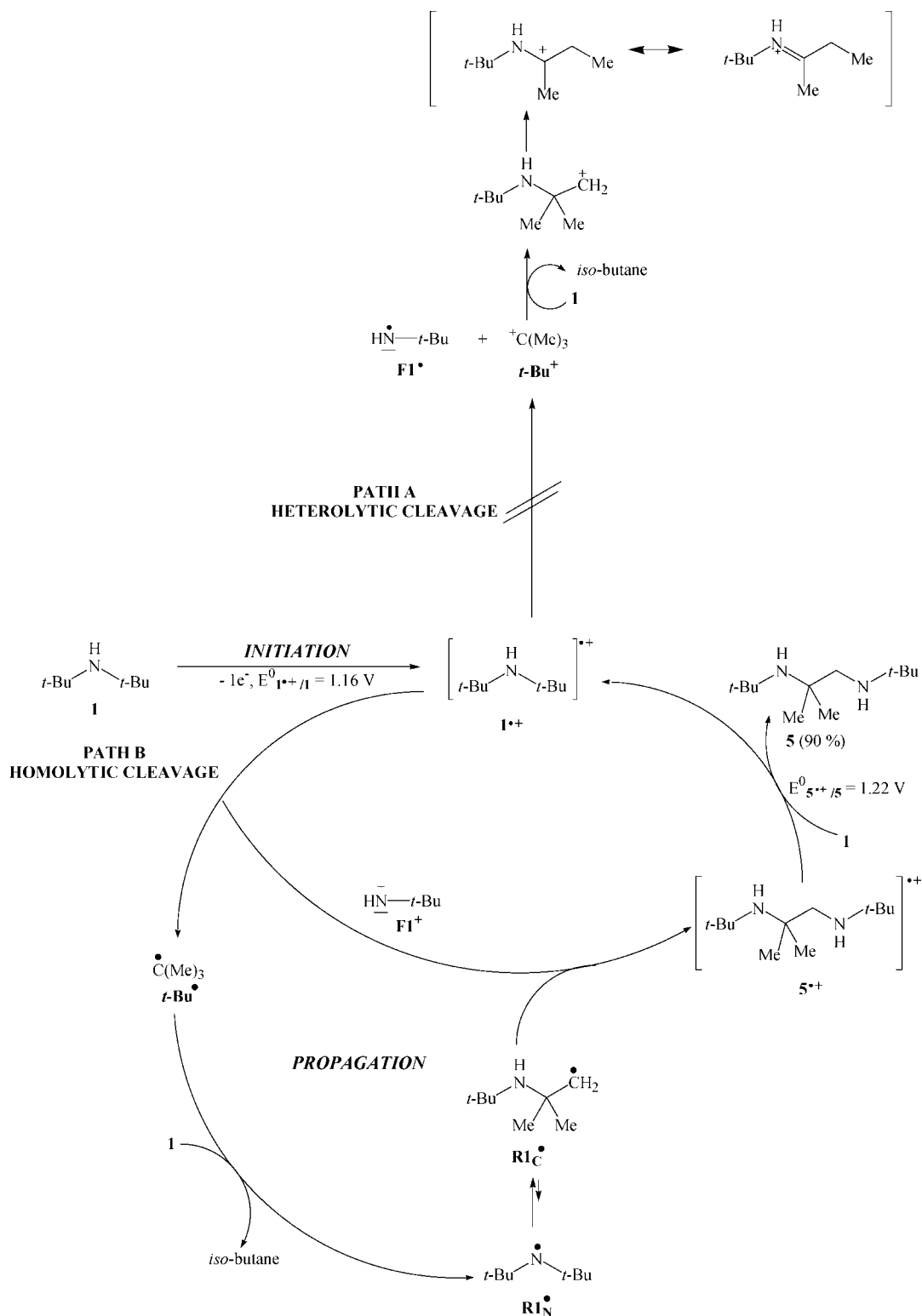


FIGURE 6. Cyclic voltammetry of **5** (8.31 mM) in DMF + $n\text{-Bu}_4\text{NBF}_4$ 0.1 M on a glassy carbon working electrode ($d = 0.5$ mm). (a) In the absence of H^+ , (b) after addition of 0.5 equiv of H^+ , and (c) After addition of 1.0 equiv of H^+ . Scan rate: 0.1 Vs $^{-1}$. Reference electrode: SCE. Counter electrode: Platinum disk ($d = 1$ mm).

SCHEME 7



accepted C_α -H bond cleavage is not possible in the case of the di-*tert*-alkylamines here described, **1-4**, the first order chemical reaction following the electron transfer is limited to either the N-H or the C_α -N bond cleavage. The N-H dissociation has been discarded due to three main reasons:

First, because of the well-known basic character of the aliphatic amines, it should be expected that the H^+ generated by such a chemical reaction were able to react with the starting

material, **1**, leading to **1H⁺** which is a nonelectroactive species within the potential range investigated and eventually would lead to a significant decrease in the yield of **5**.

Second, the expected hydrazines formed via coupling reaction between the nitrogen centered radicals^{13c} have been ever detected as products of the electrochemical oxidation process.

Finally, further oxidation of those nitrogen centered radicals would not occur according to the monoelectronic processes always observed by cyclic voltammetry.

Consequently, to our understanding, the C_{α} -N bond cleavage would be the only way to rationalize the evolution of the radical cations of those di-*tert*-alkylamines, $1^{+\bullet}$ - $4^{+\bullet}$, through a first order chemical reaction

At this point, assuming that the decomposition of the radical cations, $1^{+\bullet}$ - $4^{+\bullet}$, occurs through the C_{α} -N bond dissociation, two possibilities should still be taken into account:

A *heterolytic* C_{α} -N bond cleavage (Path A, Scheme 7) that would lead to a nitrogen centered radical ($F1^{\bullet}$) and a *tert*-butyl cation ($t\text{-Bu}^+$).

A *homolytic* C_{α} -N bond cleavage (Path B, Scheme 7) that would lead to a cationic fragment ($F1^+$) and a *tert*-butyl radical ($t\text{-Bu}^{\bullet}$).

Because different intermediate species would be generated throughout each path as outlined in Scheme 7, heterolytic cleavage (path A) would be readily distinguished from a homolytic bond dissociation (path B).

Both species, the *tert*-butyl cation ($t\text{-Bu}^+$) and the *tert*-butyl radical ($t\text{-Bu}^{\bullet}$), would be able to react with the starting material **1** leading to isobutane detected in the gas phase by GC-MS.¹⁵ The *tert*-butyl cation would react with **1** leading to a primary carbocation (much less stable than the tertiary one), which would evolve through a Wagner-Meerwein rearrangement¹⁶ leading to a primary iminium cation but would ever lead to **5** (path A, Scheme 7). On the other hand, *tert*-butyl radical intermediate, most likely would abstract a hydrogen atom from the starting material, **1**, which would eventually lead to the carbon-centered radical specie ($R1_C^{\bullet}$), (path B, Scheme 7). According to other authors, the abstraction of the hydrogen atom from the amino group should be favored¹⁷ because this reaction, like other hydrogen atom transfers between heteroatoms,¹⁸ has very low activation energy. The subsequent nitrogen centered radical, $R1_N^{\bullet}$ obtained would easily evolve through a sigmatropic shift reaction leading to the carbon centered radical intermediate $R1_C^{\bullet}$ (path B, Scheme 7).

In summary, the mechanistic proposal outlined in Scheme 7, consists of a homolytic C_{α} -N bond cleavage leading to $t\text{-Bu}^{\bullet}$ and $F1^+$. The *tert*-butyl radical would abstract a hydrogen atom from the starting material, **1**, leading to isobutane and a carbon centered radical, $R1_C^{\bullet}$. Because **5** is obtained in very good yields (90%) when catalytic amounts of $1^{+\bullet}$ are electrochemically generated by consumption of few amounts of charge (0.1 F), $5^{+\bullet}$ probably comes from the reaction between $F1^+$ and $R1_C^{\bullet}$. According to the standard potentials determined by cyclic voltammetry for both species, $5^{+\bullet}$ would be able to oxidize **1** through a homogeneous electron transfer process occurring in solution which would eventually lead to **5**. Therefore, $1^{+\bullet}$ will be regenerated and a new cycle should start with no further electrochemical assisted oxidation.

(14) Andrieux, C.-P.; Savéant, J. M. *Electrochemical Reactions in Investigations of Rates and Mechanism of Reaction Techniques of Chemistry*; Bernasconi, C. F. Ed.; Wiley: New York, 1986; Vol. VI/4E, p 305.

(15) Isotopic distribution of the compound detected in the gas phase is in good agreement with the mass spectrum reported in the literature for isobutane when electronic impact is used as the ionization source.

(16) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 3rd ed.; John Wiley & Sons: New York, 1985.

(17) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328.

(18) (a) Krellick, R. W.; Weissmann, S. I. *J. Am. Chem. Soc.* **1962**, *84*, 306. (b) Krellick, R. W.; Weissmann, S. I. *J. Am. Chem. Soc.* **1966**, *88*, 2645. (c) DaRooge, M. A.; Mahoney, L. R. *J. Org. Chem.* **1967**, *32*, 1.

Similar conclusions were extracted when analogous electrochemical studies were extended to further secondary *tert*-alkyl amines (**2**-**3**). Hindered secondary alkyl diamines (**6**-**7**) were obtained in very good yields (Table 1) when the process was electrochemically initiated as described for **1**. Thus, a mechanistic approach as proposed for **1** should be operative in all the cases investigated. Only one exception to that electrochemical behavior was encountered for *tert*-amyl-*tert*-octylamine (**4**) most likely due to higher steric hindrance due to the presence of *tert*-octyl groups.

Concluding Remarks. The electrochemical synthesis of highly hindered secondary alkyl diamines through the formation of C-N bonds has been successfully performed in one-pot in mild conditions using an environment friendly method. A promising route for synthesizing highly hindered alkyl amines is carefully described and appears to be an alternative to the much less efficient and much longer chemical procedure previously reported. This study demonstrates the crucial role played by the electrochemically generated radical cation, ($1^{+\bullet}$ - $3^{+\bullet}$) starting a process based on the propagation of radical intermediates that eventually evolve into highly hindered aliphatic diamines, **5**-**7**. It should be highlighted that only low amounts of charge (0.1 F) are required in the electrochemically initiated process to afford the secondary alkyl diamines described (**5**-**7**). From a mechanistic point of view, it should also be mentioned that this is the first case reported for an alkyl amine evidencing a C_{α} -N bond cleavage at the radical cation level because the C_{α} -H has been widely demonstrated when it is available.

Experimental Section

General Considerations. DMF ("SDS pour syntheses peptidiques) and *n*-Bu₄NBF₄ (Fluka puriss) were used without further purification.

Starting Materials. *N*-*tert*-amyl-*N*-*tert*-butylamine (**2**), *N,N*-di-*tert*-amylamine (**3**), and *N*-*tert*-amyl-*N*-*tert*-octylamine (**4**) were obtained from Aldrich. All the commercially available reactants were of the highest purity and used without further purification.

Synthesis of *N,N*-di-*tert*-butylamine (1**).** *N,N*-di-*tert*-butylamine (**1**) was prepared as previously reported in the literature.¹⁹ After purification by means of distillation under vacuum, **1** was isolated as a colorless liquid (0.46 g, 51%): bp 118 - 120 °C (lit.¹⁹ 120 °C). ¹H NMR (CDCl₃, 250 MHz, δ ppm) 1.25 (s, 18H), 2.75 (s, 1H); MS (70 eV) *m/z* (%) 129 (11.2) [M^+], 114 (25.6), 72 (83.9), 57 (100); MS (PCI, NH₃) *m/z* (%) 130 (100) [$M + 1$], 72 (18.3), 57 (25.8).

Synthesis of *N*-*tert*-butyl-2-*tert*-butylamino-2-methylpropionamide. The *N*-*tert*-butyl-2-*tert*-butylamino-2-methylpropionamide was synthesized as previously reported by Lai.¹⁰ The pale-yellow solid obtained was chromatographed on a silica gel column using methylene chloride/ethyl acetate (50:50) as eluent. Yield: 65%. ¹H NMR (CDCl₃, 250 MHz, δ ppm): 1.17 (s, 9H), 1.35 (s, 15H); MS (70 eV) *m/z* (%) 214 (0.1) [M^+], 199 (0.5), 143 (0.6), 114 (72.0), 98 (5.5), 87 (1.5), 58 (100), 41 (20.6); MS (PCI, NH₃) *m/z* (%) 215 (100) [$M + 1$], 159 (4.2), 114 (2.3); Anal. Calcd for C₁₂H₂₆N₂O: C, 67.2; H, 12.2; N, 13.1; O, 7.5. Found: C, 67.1; H, 12.4; N, 13.2; O, 7.3.

Synthesis of *N,N'*-di-*tert*-butyl-2-methylpropylenediamine (5**).** **Chemical Synthesis.** Several unsuccessful attempts were made to afford **5** by adopting the known chemical methods reported for the conversion of amides into the corresponding amine derivatives.^{10,11} To this purpose, either lithium aluminum

(19) Back, T. G.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, *8*, 924.

hydride (LiAlH_4) or the so-called Superhydride, lithium triethylborohydride (LiEt_3BH), were used in anhydrous tetrahydrofuran as reducing agents. The reactions were followed by gas chromatography. No reaction was observed when using LiAlH_4 and undesired products were obtained when Super-Hydride was used as the reducing agent probably due to further decomposition of **5** in the experimental conditions. Finally, the use of a solvent with a high boiling point was the key to obtaining **5** by a chemical synthesis detailed below. An oven-dried three-necked, round-bottomed flask equipped with a reflux condenser and a magnetic stir bar was charged with lithium aluminum hydride (0.29 g, 7.63 mmol) and anhydrous bis(2-methoxyethyl) ether (4 mL) was added at room temperature in a nitrogen atmosphere. The solution was carefully heated at reflux temperature (160 °C) and *N-tert-butyl-2-tert-butylamino-2-methylpropionamide* (0.35 g, 1.56 mmol) in anhydrous bis(2-methoxyethyl) ether (0.5 mL) was slowly added to the colorless solution. The mixture was left to reflux in a nitrogen atmosphere for 48 h. After that period, the crude was cooled to 5–10 °C with an ice bath and the excess LiAlH_4 was decomposed by careful dropwise addition of 0.25 mL of water, followed by 0.25 mL of 15% NaOH, and finally by 0.75 mL of water. The mixture was left to warm to room temperature and stirred for an additional hour. The resulting aqueous mixture was extracted three times with 20 mL of toluene. The organic layers were dried with sodium sulfate and then concentrated in vacuo. The residue was distilled at low pressure, and **5** was afforded as a colorless liquid (0.15 g, 48%). $^1\text{H NMR}$ (CDCl_3 , 250 MHz, δ ppm): 1.07 (s, 9H), 1.15 (s, 6H), 1.19 (s, 9H), 2.36 (s, 2H); MS (70 eV) m/z (%) 200 (0.5) [M^+], 185 (6.0), 172 (0.8), 157 (2.0), 143 (4.1), 128 (7.7), 115 (1.7), 99 (49.5), 86 (100), 72 (37.4), 5 (69.5), 41 (45.1); ESI+ m/z (%) 201.1 (7) [$\text{M} + 1$], 145.1 (4), 128.1 (100), 72.4 (33); Anal. calcd for $\text{C}_{12}\text{H}_{28}\text{N}_2$: C, 71.9; H, 14.0; N, 14.1. Found: C, 71.7; H, 14.1; N, 14.2.

General Procedure for the Electrosynthesis of Hindered Alkyl Diamines, 5–7. Two methodologies were used to afford the hindered diamines (**5–7**) by electrochemical oxidation of the corresponding amine depending on the amount of electricity supplied. The experimental procedure followed in both cases is detailed below for the particular electrosynthesis of **5**.

Exhaustive Anodic Oxidation of 1. Under an argon atmosphere, a controlled potential electrolysis was carried out in a solution of **1** (0.20 mmol) in DMF containing LiClO_4 (0.1 M) as a supporting electrolyte at 1.20 V/SCE. The anodic current reached a plateau value close to zero when 70% of the theoretical charge, assuming a mono-electronic process, was consumed. At the end of the anodic oxidation process, the electrolyzed samples were poured into 10 mL of a sodium hydroxide aqueous solution (0.05 M). The resulting aqueous mixture was extracted three times with 10 mL of toluene. The organic layers were dried with sodium sulfate and then concentrated in vacuo. The residue was distilled at low pressure and **5** was afforded as a colorless liquid (0.025 g, 67%). Characterization of **5** by $^1\text{H NMR}$, electron ionization mass spectroscopy (EIMS), positive-ion mode electrospray ionization (ESI+), and elemental analysis was consistent with the previous data obtained when using the chemical synthesis.

Synthesis of 5 Electrochemically Initiated. In an argon atmosphere, a controlled potential electrolysis was carried out in a solution of **1** (0.35 mmol) in DMF containing LiClO_4 (0.1 M) as a supporting electrolyte at 1.20 V/SCE. The anodic oxidation was stopped when 0.1 F (0.34 C) were consumed. The partially electrolyzed solution was stirred and kept in an argon atmosphere for an additional hour. After that period, the electrolyzed samples were poured into 10 mL of a sodium hydroxide aqueous solution (0.05 M). The resulting aqueous mixture was extracted three times with 10 mL of toluene. The organic layers were dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was distilled at low pressure and **5** was afforded as a colorless

liquid (0.032 g, 90%). Characterization of **5** by $^1\text{H NMR}$, electron ionization mass spectroscopy (EIMS), positive-ion mode electrospray ionization (ESI+), and elemental analysis was consistent with the previous data obtained when using the chemical synthesis.

Unless otherwise indicated, the electrolyses used to be performed in solutions containing *n*- NBu_4BF_4 0.1 M as supporting electrolyte. In our particular case and taking into account that **8** is an imidazolium ion, the lithium salts could be more easily separated from **8** than the quaternary ammonium salts. However, identical electrochemical experiments performed using both supporting electrolytes confirm that the choice of the supporting electrolyte does not have any effect neither in the mechanism occurring when few amounts of the radical cation are electrochemically generated nor in the yield of **5** when only catalytic amounts of charge were employed in the electrochemical oxidation of **1**.

Chemical Oxidation of 1. In addition to the electrochemical experiments described above, chemical oxidation of **1** was also carried out under nitrogen atmosphere by using NOBF_4 as an oxidizing agent. Those experiments evidenced that 0.05 equivalents of NOBF_4 lead to **5** in good yields (85–90%) in a time reaction that varies from 25 to 40 min depending on the $[\text{I}]_0$. In summary, those experiments displayed the same trend observed when electrochemical oxidation was performed suggesting that the same mechanism previously predicted is operative since only few amounts of the chemical oxidant are required to afford **5**.

Electrosynthesis of *N-tert-butyl-*N'*-tert-amyl-2-methylpropylenediamine (6).* **6** was synthesized from *tert*-amyl-*tert*-butylamine (**2**) by electrochemical procedures analogous to those used for the synthesis of the *N,N'*-di-*tert*-butyl-2-methylpropylenediamine (**5**) by applying 1.19 V/SCE. Yield: 92%. $^1\text{H NMR}$: (CDCl_3 , 250 MHz, δ ppm): 0.78 (t, 3 H), 0.93 (s, 6 H), 1.03 (m, 2H), 1.15 (s, 6H), 1.38 (s, 9H), 2.42 (s, 2 H); MS (70 eV) m/z (%) 214 (0.1) [M^+], 199 (12.3), 185 (21.9), 143 (8.8), 129 (95.7), 113 (3.0), 98 (1.1), 84 (4.3), 72 (100), 57 (45.2), 43 (11.2); MS (PCI) m/z 215 (93.4) [$\text{M} + 1$], 159 (56.2), 145 (100); Anal. calcd for $\text{C}_{13}\text{H}_{30}\text{N}_2$: C, 72.8; H, 14.1; N, 13.1. Found: C, 72.7; H, 14.3; N, 13.0.

Electrosynthesis of *N,N'*-di-*tert*-amyl-2-methyl-2,3-butylenediamine (7). **7** was synthesized from di-*tert*-amylamine (**3**) by the electrochemical procedures analogous to those used for the synthesis of the *N,N'*-di-*tert*-butyl-2-methylpropylenediamine (**5**) by applying 1.17 V/SCE. Yield: 90%. $^1\text{H NMR}$: (CDCl_3 , 250 MHz, δ ppm): 0.72 (t, 6 H), 0.83 (d, 3 H), 0.91 (s, 6 H), 1.20 (s, 12H), 1.40 (m, 4H), 2.62 (qd, 1 H); MS (70 eV) m/z (%) 242 (0.1) [M^+], 199 (0.1), 185 (21.9), 143 (8.8), 129 (95.7), 113 (3.0), 98 (1.1), 84 (4.3), 72 (100), 57 (45.2), 43 (11.2); MS (PCI) m/z 243 (95.6) [$\text{M} + 1$], 173 (65.3), 157 (100); Anal. calcd for $\text{C}_{15}\text{H}_{34}\text{N}_2$: C, 74.3; H, 14.1; N, 11.6. Found: C, 74.7; H, 14.0; N, 11.3.

Instrumentation and Procedure. Cyclic Voltammetry. Glassy carbon working electrodes were obtained from Tokai (diameter = 0.5 mm). A platinum disk electrode was used as a counter electrode (diameter = 1 mm). Electrochemical measurements were performed with a homemade solid-state amplifier potentiostat with positive feedback IR drop compensation and a Tacussel GDTP 4 generator. The cyclic voltammograms were displayed on a Tektronix (2212) instrument. All potential measurements were measured and quoted vs an SCE separated from the solution by a double frit system containing either *n*- Bu_4BF_4 0.1 M. Prior to the electrochemical measurements, the glassy carbon surface was cleaned by polishing with 1 μm diamond paste. After polishing, the electrode was rinsed with ethanol.

Controlled Potential Electrolysis. Electrochemically initiated syntheses of diamines were performed using PAR 273A potentiostat in a dark ("brown glassware") conical three-electrode cell equipped with a methanol jacket. The temperature was fixed to 10 °C, in all cases by means of a thermostat. A graphite rod was used as the working electrode, while a platinum bar and a saturated calomel electrode (SCE) were separated from the

solution by a double frit system containing either *n*-Bu₄BF₄ or LiClO₄ 0.1 M depending on the electrosynthetic methodology employed.¹²

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Supporting Information Available: General procedures and spectral characterization data for selected compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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