

Supporting Information

Preparation of the supporting electrolyte. The cell, filled with anhydrous NH_3 (50-70 mL) and equipped with a polyethylene magnetic bar (inert to the solvated electrons) was kept at $-40\text{ }^\circ\text{C}$ (bath temperature). The cell was swept with Argon and an atmosphere of this gas was kept over the solution during the reaction. NH_4BF_4 was added up to a 0.16-0.2 M concentration while argon was bubbling into the solvent. When used as an additive, *t*-BuOH (2 or 2.5 mL) was introduced at this point. The stopper of the cell was replaced by another one equipped with the two electrodes. The precise weight of the magnesium anode before the experiment was known. The solution was electrolysed cathodically at a constant current of 0.2 to 0.5 A up to the total reduction of NH_4^+ ions and any traces of water. The solution displayed the characteristic blue colour of solvated electrons and the electrolysis was then continued for 40 coulombs to ensure the complete reduction of NH_4^+ . During this first phase, NH_4^+ has been reduced to NH_3 and H_2 at the cathode and Mg^{++} has been produced at the anode. Therefore the cell contains a solution of $\text{Mg}(\text{BF}_4)_2$ in NH_3 (Scheme 1 in main text). In the second phase, $\text{Mg}(\text{BF}_4)_2$ is the supporting electrolyte for the preparation of solvated electrons in the presence of Mg^{++} formed at the anode.

Mass spectra. Mass spectra obtained for compounds **2**,¹ **4** and **6**² were similar to that described in database or literature. In one experiment (Table 1, entry 4 in main text), we found 32% of two reduction products **3** and **5** ($M = 134$). These structures were proposed by comparison with the mass spectra described in literature³ or database.¹

The reaction of **7** with the solvated electrons led to compounds **8-11** (Scheme 4 in main text). **8** and **9** were identified by GC-MS analysis by comparison with authentic samples. Mass spectra obtained for compounds **8**¹ and **9**⁴ were similar to that described in databases or

literature. Structures **10** and **11** are proposed by comparison with described compounds **5**³ and **6**.²

5, *m/z* (relative intensity): 134 (M^+ , 53); 119 (46); 117 (19); 115 (14); 105 (17); 92 (55); 91 (100); 79 (14); 65 (10); 51 (6).

6, *m/z* (relative intensity): 262 (M^+ , 21); 132 (9); 130 (5); 119 (8); 118 (11); 117 (100); 115 (24); 91 (10).

10, *m/z* (relative intensity): 136 (M^+ , 90); 121 (100); 119 (19); 107 (14); 103 (36); 94 (18); 93 (32); 91 (67); 79 (27); 77 (51); 66 (29).

11, *m/z* (relative intensity): 266 (M^+ , 33); 134 (16); 132 (31); 121 (19); 120 (11); 119 (100); 91 (79).

References

- (1) From SDBSWeb : <http://www.aist.go.jp/RIODB/SDBS/> (National Institute of Advanced Industrial Science and Technology).
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- (4) Kuroono, N.; Honda, E.; Komatsu, F.; Orito, K.; Tokuda, M. *Tetrahedron* **2004**, *60*, 1791-1801.
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TABLE 5: Kinetic parameters obtained from the Andrieux-Savéant formalism⁵ applied to relative yields of the products issuing from the reduction of **1** and **7** by solvated electrons.^a

Substrate	1	1	1	7	7
Exp. Cond. ^b	K / e	Mg / e	Mg / e	Mg / e	Mg / e
[e ⁻] M	0.02	0.028	0.16	0.026	0.135
2 or 8 ^c	2.5	2	30	<0.5	4
4 or 9+10 ^c	70	78	57	79	80
2x6 or 2x11 ^c	27.5	20	13	21	16
R _{cyc} ^d	0.72	0.80	0.81	0.79	0.83
σ ^e	40	40	1.2	>500	20
ρ ^f	1.6	3.1	8	2.8	5
k _E ^g	9 10 ⁹	5 10 ⁹	2 10 ⁹	5 10 ⁹	3 10 ⁹
δ ^h	2 10 ⁻³	3 10 ⁻³	0.2 10 ⁻³	2 10 ⁻³	0.1 10 ⁻³

^a Data obtained in NH₃ from Table 1, 3 and 4 in the main manuscript. ^b Reduction in a solution of solvated electrons of concentration [e⁻] in the presence of K⁺ or Mg²⁺ cations. ^c Relative yield of the uncyclized, cyclized or cyclized dimeric products obtained by reduction of the substrate **1** or **7**. ^d Relative yield of the cyclized product (**4** or **9+10**), R_{cyc} = 4/[(**4** + (**2x6**)] or R_{cyc} = (**9+10**)/[(**9** + **10** + **2x11**)]. ^e Kinetic parameter corresponding to the competition between radical cyclization and radical reduction obtained from the yield of uncyclized product with the theoretical variation predicted in Figure 2 of Ref. 5. ^f Kinetic parameter corresponding to the competition between cyclized radical dimerization or reduction obtained from the relative yield of cyclized product, R_{cyc}, with the theoretical variation predicted in Figure 1 for the given pre-determined σ value. ^g Rate constant of the reduction of the substrate **1** or **7** by the solvated electron, in M⁻¹s⁻¹, obtained from ρ and equation 2 in the main manuscript. The other rates in eq.2 are considered at the diffusion limit k_{diff} = 3 x 10¹⁰ M⁻¹ s⁻¹ in liquid NH₃ at -40°C. ^h Diffusion layer thickness, in cm, obtained from k_E and σ and equation 1 in the main manuscript.

Figure 1. Predicted variation of the relative amount of cyclized radical with the kinetic parameters ρ and σ . The figure corresponds to correction of Figure 3 in Ref. 5. The numbers on the figure correspond to values of σ that range in the direction of the arrows in the decreasing order. Here $R_{\text{cyc}} = \% \text{Cyc} = [\text{Cyc}]/([\text{Cyc}] + 2[\text{Dim}])$.

