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ELECTROCHEMICAL REDUCTIONS IN LIQUID AMMONIA: ELECTROLYTIC BIRCH REACTIONS AND CHEMICAL BOND FISSIONS

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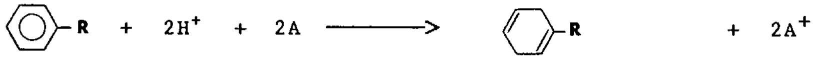
Summary: A procedure of electrochemical reduction in liquid ammonia using a single-compartment cell equiped with a soluble anode is described and illustrated in the case of aromatic compounds and esters.

Birch and Bouveaux-Blanc reductions necessitate a strongly reducing medium which is usually obtained by dissolving an alkaline A in liquid ammonia in the presence of a proton donor(1,2). These two kinds of reactions can be represented by the two equations:

Birch reduction:



(1)

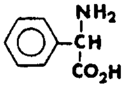
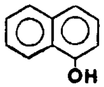
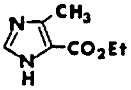
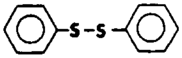
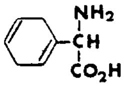
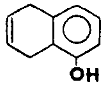
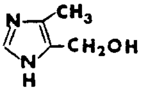
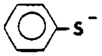
Bouveaux-Blanc reduction:

$$R'CO_2R'' + 4H^+ + 4A \longrightarrow R'CH_2OH + R''OH + 4A^+ \quad (2).$$

As the reaction yield depends on the way the alkaline is introduced in the medium, it seems worthwhile to make the reducing agent using a potential difference between two electrodes in liquid ammonia. The amount of reducing agent can be easily controlled by the intensity between the electrodes and the time of electrolysis. If two unreactive electrodes materials such as Pt or Au are to be used, it is necessary to perform the electrolysis in a two-compartment cell, because in a single-compartment cell, anodic oxidations give protons ($2NH_3 \longrightarrow N_2 + 6H^+ + 6e$), which are further reduced at the cathode, impeding reaction (1) or (2) to proceed. The technical realisation of the two-compartment cell is then the main problem.

We have demonstrated that it is possible to carry out the reaction in a single-compartment cell, using a soluble anode made of Al, Mg or Zn(3). The only possible anodic reaction involves then the metal oxidation followed by its complexation and cannot interfere with the reaction of interest (1) or (2) at the cathode. Such a single-compartment cell is particularly interesting because it does not introduce any supplementary resistance, in opposition to the separator in a two-compartment cell.

In a typical electrolysis, we use a Mg bar as the anode, an Al sheet around the anode bar as the cathode. The electrolyte is an alkaline salt, which is used in a catalytic amount . The electrolyte, the substrate and a proton donor (usually an aliphatic alcohol) are successively introduced in a cell containing about 70 ml ammonia and the electrolysis is performed by fixing a constant intensity between the two electrodes. The voltage between anode and cathode usually stabilizes at 10V. The electrolysis is performed till the appearance of a blue coloration, due to free solvated electrons. This process can be used with any substrate bearing at least one reducible group. It is illustrated in the case of an aromatic cycle reduction following a proton reduction (phenylglycine: A, 1-naphtol: B), an ester reduction following a proton reduction (5-ethoxycarbonyl 4-methyl imidazole: C), a diester reduction (diethyl sebacate: D), a reductive fission (diphenyldisulfide: E). The products are isolated by precipitation (A,B,D) or extraction(C)(4); product E is used in a later experiment . The product yield is calculated from the amount of isolated pure product. The results are summarized in the following table:

	(A)	(B)	(C)	(D)	(E)
Starting material				$(CO_2Et(CH_2)_4)_2$	
(mmol)	25	30	12	8	5
Electrolyte (mmol)	LiOAc,$2H_2O$ 10	NaCl 60 NaI 4	NaCl 75	KBr 30 NaI 4	NaCl 21
Proton donor (ml)	tert-butanol 3	tert-amylol 5	tert-butanol 3	isopropanol 4	
Consumed Mg (mmol)	63	69	37	43	
Intensity (A)	0,6	1	1	1	1
n_e (a)					
theorical	3	3	5	8	2
experimental	5	3,5	7,6	11,4	2,1
Electrical yield (%)(b)	45	90	80	95	95
Product				$(HO(CH_2)_5)_2$	
Product yield(%)	72(c,d)	70	70	95	90
Melting point (°C)		67	241	47	

(a) n_e: number of electrons involved per mole of substrate

(b) the electrical yield is calculated from the amount of consumed Mg, compared to the theoretical number of electrons. It is especially low for phenylglycine, because the aromatic cycle reduction is slow (due to the donor groups NH_2 and CO_2^-);an appreciable amount of electrons produced at the cathode have then time to diffuse to the anode and be oxidized at the anode.

(c) With a C anode, the product yield in the same conditions is zero.

(d) Phenylglycine cannot be separated from dihydrophenylglycine.The total yield is about 90% (dihydrophenylglycine:80%, phenylglycine:20%, obtained by NMR)

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