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SAMARIUM-CATALYZED ELECTROCHEMICAL REDUCTION OF ORGANIC HALIDES

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<u>Abstract:</u> Electroreduction of a series of organic halides including chloro- and fluoroderivatives bearing various functional groups is effected in good yields in the presence of a catalytical amount of SmCl₃. Reactions are carried out in DMF in a single-compartment cell fitted with a consumable magnesium anode.

The reduction of carbon-halogen bonds to their parent hydrocarbons is a well established reaction in organic synthesis¹. Sml₂ is used as powerful reducing agent in a variety of reactions, developed by Kagan and other groups²⁻⁴. Among them, Inanaga et al. described the use of Sml₂ to promote the reduction of organic halides in the presence of HMPA⁵. The conversion of certain P-CI compounds into the corresponding P-H derivatives by the action of Sml₂ has been recently reported⁶. However, in all these reactions, more than one mol of Sml₂ per mol of substrate must be used.

Electrochemical reduction constitutes a useful method for the dehalogenation of aromatic halides^{7,8}. Cathodic reduction of simple bromo- or iodo derivatives RX can be accomplished. Side-reactions are however elimination (R(-H)) and dimerization (R-R). In contrast, the

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electroreduction of aromatic chlorides and fluorides has not been thoroughly studied because of their lower reactivity.

We focused our interest in the use of electrogenerated samarium species for organic synthesis, and we recently described the Sm-catalyzed reductive coupling of carbonyl compounds to pinacols⁹.

The present study is on the preparative electroreductive dehalogenation of halides in the presence of samarium species and on the compatibility of several functional groups. The combination of both samarium chemistry and electrochemistry enables us to use of a catalytic amount of SmCl₃ as the catalyst precursor. The active catalytic species (Sm²⁺) will be generated and recycled by continuous electrochemical reduction.

Results are collected in Table 1. The reduction of a series of alkyl, vinyl and aryl bromides (entries 1-6) is carried out almost quantitatively. Electron-donor or acceptor substituents on the aromatic ring are compatible with the reaction conditions. In the case of vinyl bromide of entry 6, a carefull electrolysis stopped at 2 F/mol is necessary to avoid styrene dimerization. Several aryl chlorides (entries 7-10,14) were dehalogenated in good yields. It is remarkable that reductible groups such as -CN or -COOR remain untouched until the C-CI is completely cleaved. A prolonged electrolysis in the case of entries 8 and 9 leaded to products of further reduction of the nitrile or ester functions. Completely dechlorinated product was obtained on reaction of 1,3,5-trichlorobenzene (entry 10).

In terms of fluorine derivatives, the C-F bond is one of the least reactive toward reduction and oxidative addition to metal centers¹⁰. However, we obtained a partial C-F cleavage in the case of methyl-2,6-difluorobenzoate (entry 11) to its monofluoro derivative. By-products result from the reduction of the ester function. In the absence of SmCl₃, only products derived from reduction of the ester function are observed. The C-F bond of methyl-2-fluorobenzoate was not cleaved under our conditions. The benzilic fluoride bond in trifluoromethyl benzene (entry 12) yielded a mixture of mono- and bis-defluorinated products together with some coupling compounds.

Table 1 : Samarium-catalyzed electroreduction of organic halides

	e, SmCl3 (10 %)	
R-X		R-H
	DMF, n-Bu4N+BF4^	

Entry	RX	Product	Yield
1	1-Br-n-C ₁₀ H ₂₁	n-C ₁₀ H ₂₂	70 %
2	C ₆ H ₅ Br	C ₆ H ₆	100 %
3	o-Br-C ₆ H ₄ -OMe	C ₆ H ₅ -OMe	100 %
4	p-Br-C ₆ H ₄ -CO ₂ Me	C ₆ H ₅ -CO ₂ Me	100 %
5	p-Br-C ₆ H ₄ -F	C ₆ H ₅ F	100 %
6	C ₆ H ₅ CH=CH-Br	C ₆ H ₅ CH=CH ₂	90 %
7	o-Cl-C6H4-OMe	C ₆ H ₅ -OMe	95 %
8	0-Cl-C6H4-CN	C ₆ H ₅ -CN	90 %
9	o-Cl-C6H4.CO2Me	C ₆ H ₅ -CO ₂ Me	98 %
10	1,3,5-Cl ₃ -C ₆ H ₃	C ₆ H ₆	95 %
11	2,6-F ₂ -C ₆ H ₃ -CO ₂ Me	2-F-C ₆ H ₄ -CO ₂ Me	58 %ª
12	C6H5-CF3	$C_{6}H_{5}CHF2 + C_{6}H_{5}CH_{2}F + C_{6}H_{5}CF_{2}CF_{2}C_{6}H_{5} (69:12:19)$	80 %a
13	Br		70 %
14		п и	80 %

a) Yield of RH relative to the converted RX : entry 11, conversion 66 % ; entry 12 : 63 %.

Reactions proceed in DMF containing tetrabutylammonium salts as supporting electrolyte in the absence of any added proton source. During the electrolysis of chloroderivatives of entries 10 or 14, aliquots were quenched with D_2O ; however, no deuterium was incorporated into the products. This indicates that the reduction may be considered complete before the aqueous work-up. The reaction proceeds through hydrogen abstraction from the solvent or from the supporting electrolyte¹¹.

The electroreductive dehalogenation of bromobenzenes as well as that of some chlorinated aromatic ethers in DMF has been shown to proceed through anionic intermediates¹². Thus, electrolysis of 1-allyloxy-2-chlorobenzene (entry 14), used as a probe for radical intermediates, has been described to give dehalogenation with only traces of cyclized compound¹². Under our conditions, in the absence of SmCl₃, the dechlorinated (non-cyclized) product was obtained in 35 % yield. Instead, in the presence of a catalytic amount of SmCl₃, the cyclization becomes nearly quantitative, with only traces (1-2 %) of non cyclized R-H. The presence of the samarium species seems to favour a radical mechanism¹³. There is, however, no clear evidence concerning the radical/anion nature of the intermediates: the presence of samarium did not favour radical intermediates in the electrolysis of 6-bromohex-1-ene, in which cyclized products were formed in low yield.

In conclusion, the association of electrochemistry and SmCl₃ enables a smooth and efficient reduction of organic halides, including chlorides and fluorides bearing various functional groups, in a samarium -catalyzed reaction.

Experimental:

In a typical procedure, the organic halide (5 mmol) is introduced in a one-compartment electrochemical cell fitted with a central magnesium anode and a nickel foam cathode (20 cm²)¹⁴. A distilled DMF (35ml) / n-tetrabutylammonium tetrafluoroborate (0.3 mmol) solution containing 10% molar anh. $SmCl_3$ (0.5 mmol, Alfa) was stirred and electrolyzed at constant intensity of 100 mA and at room temperature until disappearance of the starting material (followed by GC). The reactions were completed after 2-3 F per mol of halide (except for entry 11, stopped after 1.3 F/mol and entry 12 stopped after 2.15 F/mol because of passivation). No proton source was added to the reaction mixture. The DMF solution is then acidified with aq. HCl (0.1 M) and extracted with pentane. The organic layer is washed with water, dried over MgSO₄ and evaporated. Products are either purified and isolated by column chromarography on silica-gel with pentane-ether mixtures as eluent, or their yields calculated by GC with decane as internal standard.

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