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A Convenient Electrochemical Method for Conversion of 4-Haloacetophenone to 1-(4-Halophenyl)ethanol

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In the presence of a catalytic amount of Sb(III), 4-fluoro-, 4-chloro-, 4-bromo-, and 4-iodoacetophenone were converted into the corresponding 1-(4-halophenyl)ethanols by an electrochemical method (-3.7 mA/cm^2, 6F/mol, Pb cathode). Each alcohol yielded 91, 94, 98, and 94%, respectively.

1-(4-Halophenyl)ethanols (**2**) are valuable precursors of β-arylaliphatic acids having pronounced physiological activity.[1] The known method for the preparation of **2** has been restricted to a reduction of 4-haloacetophenone (**1**) using reducing agents such as sodium borohydride.[1]

We have previously reported that a reduction of acetophenone could be catalyzed by electrogenerated zerovalent Sb, and gave 1-phenylethanol with a good yield.[2] During our investigation, we wanted to examine whether this electrochemical method could be extended to haloacetophenone which contains two potentially reducible functions.

A typical procedure is as follows: A solution containing 4-iodoacetophenone[3] (0.8 g, 3.3x10^{-3}mol) and a catalytic amount of $SbCl_3$ (30 mg, 1.3x10^{-4}mol) dissolved in a mixed solvent (50 ml) of aqueous 2 M-HCl, EtOH, and n-BuOH (2.5 : 1.0 ; 1.5 V/V) was put into the cathodic compartment of a divided cell using a porous cup as a diaphragm. The solution was electrolyzed using a Pb plate (ca. 21.3 cm^2) as a cathode and a Pt plate (ca. 4.0 cm^2) at a constant current density (-3.7 mA/cm^2) corresponding to the reduction potential of $SbCl_3$ (-0.25 V vs. Ag/AgCl) while stirring at room temperature. After passage of 6F/mol, usual workup of the reaction mixture and recrystallization of the crude product from hexane gave 1-(4-iodophenyl)ethanol (0.7 g, 87%, Run 16).[4]

$SbCl_3$ has a significant effect on both the conversion of **1** and the product distribution (Table 1). The dehalogenation and the formation of the hydrodimer **3** were retarded by the addition of a catalytic ammount of $SbCl_3$ which are affected to the halo-substituent R and the formation of **2** significantly increased.

The mechanism for the selective reduction of **1** has not been clarified, but it is likely that the electrocatalytic hydrogenation by SbH_3,[5,6] which may be generated through a reduction of Sb deposited on the electrode surface by the nascent hydrogen atom, takes place in this system.

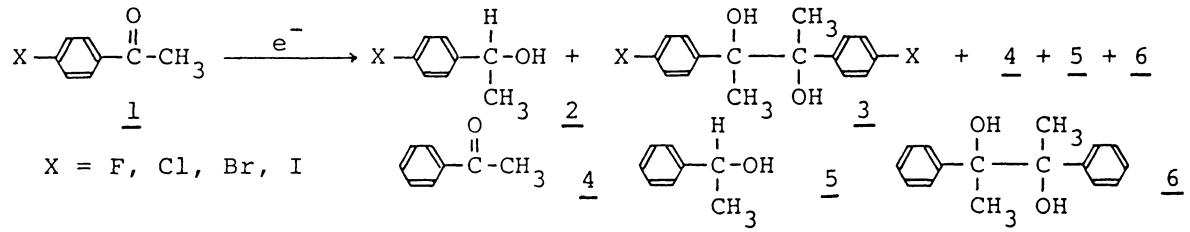

Table 1. Product Distribution of 1-(4-Halophenyl)ethanol

Run	X	Condition [a] $SbCl_3$ / $\times 10^{-5}$mol	Condition [a] Current / F mol^{-1}	1 Conv. / %	Product yields/% 2	3	4	5	6
1	F	0.0	2	97	1	96	0	0	0
2	F	1.7	2	54	54	0	0	0	0
3	F	1.7	6	91	91	0	0	0	0
4	Cl	0.0	2	81	28	45	0	0	9
5	Cl	1.7	2	62	62	0	0	0	0
6	Cl	1.7	6	94	94	0	0	0	0
7	Br	0.0	2	83	17	46	0	0	21
8	Br	1.7	2	73	30	0	0	0	49
9	Br	3.3	2	58	58	0	0	0	0
10	Br	3.3	6	98	98	0	0	0	0
11	I	0.0	2	65	23	0	2	3	37
12	I	1.7	2	46	9	0	1	1	55
13	I	3.3	2	61	28	0	1	1	33
14	I	6.5	2	46	43	0	2	1	0
15	I	13.0	2	49	49	0	0	0	0
16	I	13.0	6	94	94	0	0	0	0

a) Conditions : **1** = 3.3 x 10^{-3}mol ; -3.7 mA/cm^2, Analyzed by GLC.

References
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3) This halide was prepared from iodobenzene by the method of Mastui, *Nippon Kagaku Zasshi*, **45**, 1094(1942).
4) Colorless crystal: mp 40-42 ℃ (lit.[7] mp 40-42 ℃); IR(KBr) 3400, 3200, 2980, 2900, 1585, 1085, 535 cm^{-1}.
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