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ELECTROREDUCTIVE "BARBIER TYPE" ALLYLATION OF IMINES WITH A COMBINATION OF A Pb(0)/Pb(II) REDOX MEDIATOR AND SACRIFICIAL ANODE (Al)

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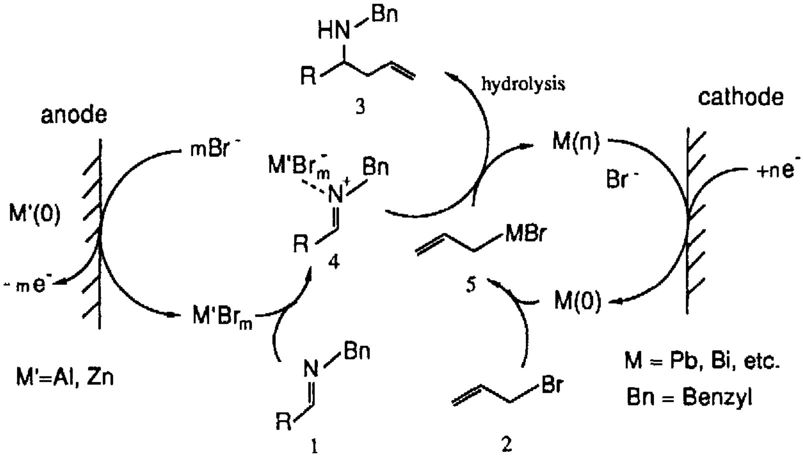
Summary: An electroreductive "*Barbier Type*" allylation of imines with allyl bromide has been performed in a $PbBr_2/Bu_4NBr$/THF-(Al anode)-(Pt cathode) system. A combination of Pb(0)/Pb(II) redox and a sacrificial aluminum anode works as a mediator for both cathodic and anodic electron transfer processes, respectively.

Recently, electroreductive "*Barbier Type*" allylation of carbonyl compounds in a metal-redox mediatory system has attracted much attention from mechanistic and synthetic viewpoints.[1)] Several metal redoxes, e.g., Sn(IV)/Sn(0 or II),[1a)] Pb(II)/Pb(0),[1b)] Ni(II)/Ni(0),[1c)] and Bi(III)/Bi(0),[1d)] have been investigated for this purpose. Meanwhile, none is known about the nitrogen version, the electroreductive "Barbier Type" allylation of imines, presumably due to lack of a proper mediatory system. As a part of our continuing interest in the metal-redox mediated electroreduction, we have studied the electroreductive allylation of imines in various metal- redox mediatory systems. Herein, we describe a new electrolysis system comprising two metal redox couples, Pb(0)/Pb(II) and Al(0)/Al(III), as illustrated in Scheme 1 (M = Pb; M' = Al), in which, "*Barbier Type*" allylation of imines proceeds smoothly.



Scheme 1

The present electroreductive allylation of imines is characterized by its simple operation as follows: a mixture of imine **1a** ($R^1 = R^2$ = Benzyl) and allyl bromide (1:3) in THF containing $PbBr_2$ (0.05 molar equiv) and Bu_4NBr (0.1 *M*) was charged into a beaker-type undivided cell fitted with Pt cathode and Al anode and regulated dc power (10 mA/cm^2) was supplied at ambient temperature until most imine **1a** was consumed (0.8 F/mol). The usual workup of the electrolyte afforded homoallyl amine **3a** in 98% yield (Table 1, entry 1). 2)

The presence of a catalytic amount of $PbBr_2$ is essential in obtaining a satisfactory yield of **3a** since lack of $PbBr_2$ provided inferior yield of **3a** (entry 2). In place of $PbBr_2$, $PbCl_2$, and $BiCl_3$ can be used successfully for the present reaction (entries 3-4), while $ZnCl_2$ and $SnCl_2$ are less effective (entries 5 and 6). On the other hand, a fitting choice of the solvent is also important. Among the solvents so far investigated, only THF and dimethoxyethane (DME) gave satisfactory results (>98%), while other solvents, e.g., dichloromethane, acetonitrile, *N,N*-dimethylformamide, and methanol, resulted in the formation of less than 12% yields of the homoallyl amine **3a**.

Table 1. Electroreductive Allylation of Imine **1a** with MX_n[a)]

Entry	MX_n	Electricity / F/mol	Yield / %[b)]	Recov. **1a** / %
1	$PbBr_2$	0.8	98	—
2	none	2.0	28	—
3	$PbCl_2$	1.4	84	—
4	$BiCl_3$	2.0	88	—
5	$ZnCl_2$	2.0	57	—
6	$SnCl_2$	2.0	46	26

a) A mixture of **1a** (1 mmol), MXn (0.05 mmol), allyl bromide (3 mmol) and Bu_4NBr (0.3 mmol) in THF was electrolyzed at 20 mA/cm^2. b) Isolated yields after column chromatography (SiO_2, EtOAc/hexane: 1/5).

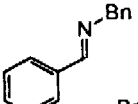
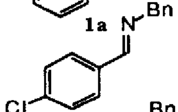
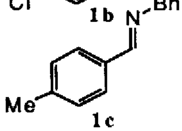
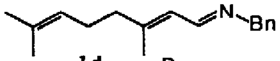
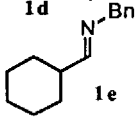
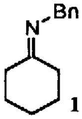
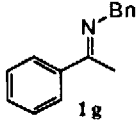
In order to suppress undesired anodic reactions, the metals to be used as an anode should have an anodic dissolution potential less positive than the oxidation potentials of the organic materials present or to be formed *in situ*.3) Furthermore, the metal ions released to the electrolysis media should be associated with imines **1** as a Lewis acid to form iminium ion **4** (Scheme 1). In the present case, aluminum may satisfy all such requirements (Table 2, entry 1). A similar result was obtained with zinc anode (entry 3), whereas nickel, tin, lead, and platinum anodes are not feasible for this electrolysis system (entries 4-7). It is worthy to note that the electrolysis was completed by passing only 0.7-0.8 F/mol of electricity (entries 1 and 3), though the formation of the allyllead reagents **5** (M = Pb) should, in principle, consume 2 F/mol of electricity. Such contradictory results can be reasonably understood by assuming that the chemical reduction of lead(II) to lead(0) with aluminum competes with the electrochemical reduction. In the former, aluminum works as an electron source, but the chemical reduction alone does not occur without supplying the electric current (entry 2). Therefore, it is very likely that aluminum surface might be activated by passage of the electricity.

Table 2. Electroreductive Allylation of Imine **1a** with Various Anode Materials

Entry	Anode	Electricity F/mol	Yield[b] %	Entry	Anode	Electricity F/mol	Yield[b] %
1	Al	0.8	98	5	Sn	2.0	— (89)
2	Al	—	— (63)	6	Pb	2.0	— (88)
3	Zn	0.5	93	7	Pt	2.0	—
4	Ni	0.3	— (84)				

a) Carried out with metal anode (1.5 x 2 cm^2). b) Isolated yields; numbers in parenthesis indicating recovered **1a**.

Table 3. Electroreductive Allylation of Imines[a]

Entry	Imines 1	2 mmol	Electricity[b] F/mol	Yield[c] %
1	 **1a**	1.1	1.0	86
2	 **1b**	1.5	1.2	85
3	 **1c**	1.5	1.2	94
4	 **1d**	1.5	0.8	86
5	 **1e**	1.5	0.7	98
6	 **1f**	3	1.2	70
7	 **1g**	3	2.0	38

a) Carried out with imine **1** (1 mmol), PbBr$_2$ (0.05 mmol), and Bu$_4$NBr (0.05 *M*) in THF (6 ml) at 20 mA/cm^2 using Al anode and Pt cathode. b) Based on imine **1**. c) Isolated yields after column chromatography (SiO$_2$, EtOAc/hexane: 1/5).

The combination system of the Pb(0)/Pb(II) redox couple and dissolving aluminum anode can be successfully applied to the allylation of various imines (Table 3). Allylation of aromatic and aliphatic aldimines **1a-e** proceeded smoothly to afford the corresponding homoallylamines **3a-e** in 85-98% yields (entries 1-5). 1,2- Addition took place exclusively with α,β–unsaturated aldimine **3d** (entry 4). On the other hand, ketimines **1f** and **1g** derived from cyclohexanone and acetophenone are less reactive, affording the corresponding homoallylamines **3f** (70%) and **3g** (38%), respectively (entries 6 and 7).

Although the reaction mechanism is still unclear, both anodic and cathodic reactions seem to complete the "*Barbier Type*" allylation of imines **1**; one for the formation of Lewis acid ($AlBr_3$) and the other for the generation of zero valent lead (Scheme 1). The generated lead(0) may react with allyl bromide **2** to form an allyllead complex **5**[4] and, at the same time, the association of the aluminum salt with imines **1** produces the iminium ions **4**. Subsequently, the reaction of the allyllead complex **5** with the iminium ions **4** furnishes the homoallylamines **3** together with lead(II) salt, the latter of which would be again submitted to the cathodic reduction, regenerating zero valent lead.

Further applications of the Pb(0)/Pb(II) redox mediated electroreduction are in progress.

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4) The allyllead complex 5 has been prepared by the reaction of allyl bromide with metal lead or *in situ* generated zero valent lead: H. Tanaka, S. Yamashita, T. Hamatani, Y. Ikemoto, and S. Torii, *Chem. Lett.*, 1986, 1611; H. Tanaka, S. Yamashita, T. Hamatani, Y. Ikemoto, and S. Torii, *Syn. Commun.*, 17, 789 (1987); H. Tanaka, S. Yamashita, Y. Ikemoto, and S. Torii, *Tetrahedron Lett.*, 29, 1721 (1988), and references cited therein.

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