



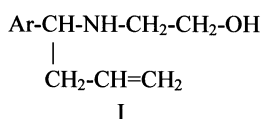
Electrochemical reductive allylation of *N*-benzylideneethanolamine

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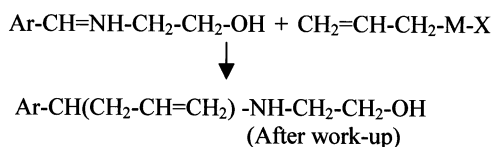
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Abstract—Electrochemical reductive allylation of *N*-benzylideneethanolamine by allyl bromide mediated by a Pb(II)/Pb(0) redox couple is reported. © 2002 Elsevier Science Ltd. All rights reserved.

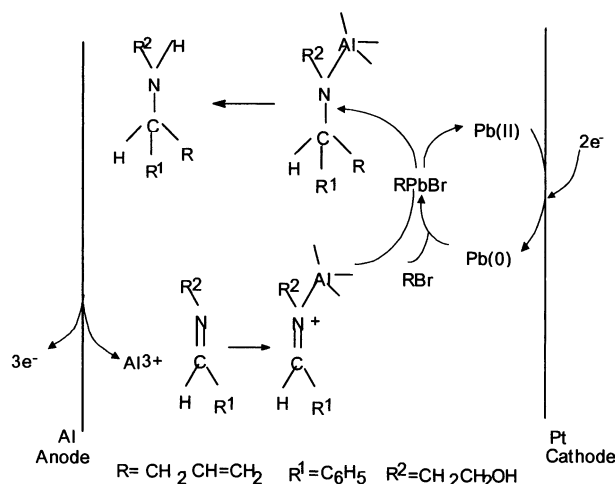
'Barbier type' allylation of imines using allylmetal reagents is a convenient route for the synthesis of homoallylamines. Metals such as boron,¹ tin,² magnesium,³ zinc,⁴ lead,⁵ and titanium⁶ have been reported to be effective as the partner in the organometallic reagents. Torii's group has reported the use of Pb(0)^{5b} and Ti(0)⁶ catalytically using Al as the chemical reducing agent for PbBr₂ and TiCl₄, and Pb(0) generated electrochemically from PbBr₂ for the allylation of various aldimines and ketimines. Catalysis by AlX₃ generated in situ chemically in the first two cases and electrochemically from the sacrificial aluminum anode in the third case, was found to be essential for the success of the reaction. In the present study our objective was to prepare *N*-alkylethanolamines as part of a study on the electrochemical oxidation of aminoalcohols and model compounds of type I were required.



Reductive allylation of the Schiff's base of aromatic aldehydes with ethanolamine suggested itself as a possible synthetic route.



The presence of the hydroxyl group in the starting material posed a problem in the use of usual organometallic reagents. However, the organotin reagents have been used successfully for reactions with carbonyl compounds (but not imines) bearing hydroxyl and other active hydrogen groups and, in fact, the electrochemical reaction has been done in methanol–water–acetic acid solutions.⁷ With this background information to hand, the electrochemical allylation of benzylideneethanolamine as a model compound was attempted. Lead and tin were selected as promising mediators. Some other metal ions were also tried. The reaction scheme may be represented as outlined in Scheme 1.



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Scheme 1. Electrochemical reductive amination of imines.

The reactions were carried out in a beaker-type undivided cell of 250 ml capacity. A platinum wire (15 cm long) coiled around a glass rod or a platinum gauze was used as the cathode. The anode was a perforated aluminum sheet (5×7 cm) rolled into a cylindrical shape. The cathode was positioned inside the cylindrical anode and properly fixed to prevent contact between the two. Dry THF was used as the solvent. (Analar THF was dried over precalcined 3 Å molecular sieves). Tetrabutylammonium bromide (6.6 mmol/100 ml of solvent) was used as the electrolyte. The Schiff's base formed from benzaldehyde and ethanolamine was purified by distillation under vacuum. Allyl bromide was prepared from allyl alcohol by a reported procedure.⁸ In a typical experiment, a solution of 2.98 g (20 mmol) of the Schiff's base, 7.26 g (60 mmol) of allyl bromide, 0.367 g (1 mmol) of PbBr₂ and 2.13 g (6.6 mmol) of tetrabutylammonium bromide in 100 ml of THF were placed in the cell.

The electrolysis was carried out under constant current conditions (0.1 A for 10 h) with magnetic stirring. Variations were done by (i) replacing the platinum cathode by lead, (ii) replacing the allyl bromide by allyl chloride and (iii) increasing the applied potential and (iv) replacing the lead bromide by Bi(NO₃)₃, CdSO₄, SnCl₂·2H₂O or Zn(Ac)₂·2H₂O. After the electrolysis the solvent was removed by distillation and a small portion of the residue was dissolved in dichloromethane, washed with water to remove the electrolytes and directly analyzed by gas chromatography. (Chemito GC 8610 HR. SE 30 column; temperature programmed from 100 to 250°C, flame ionization detector). The bulk of the product mixture was treated with dilute HCl, washed with dichloromethane to remove neutral components. The HCl extract was neutralized with alkali and extracted with dichloromethane to recover the basic components. This mixture was once again analyzed by GC and then subjected to column chromatography by successively eluting with hexane, hexane/ethyl acetate with an increasing proportion of ethyl acetate and finally with ethyl acetate/methanol mixtures. All the fractions were analyzed by GC and those fractions which gave single peaks in the GC were appropriately combined to give four fractions which were homogeneous. These were analyzed by proton NMR and mass spectroscopy.^{9a,b,c} Some of the reaction products (total mixture) were subjected to GC-MS analysis. Some components which could not be separated by column chromatography were identified by GC retention time comparison with suspected authentic samples. The results are presented in Table 1.

In our study the yields of the homoallylamine are invariably less than those reported in the literature for the benzylamine–benzaldehyde Schiff's bases. The yield of the expected product is very much dependent on the various experimental parameters. PbBr₂ as mediator, THF as solvent, aluminum as sacrificial anode, Pt as cathode and tetrabutylammonium bromide as electrolyte were found to be the best in these studies. Based

Table 1. Allylation of *N*-benzylideneethanolamine^a

S. No.	Yield (%) ^b
1	80
2 ^c	25
3 ^d	20
4 ^e	10–12

^a Al anode, Pt cathode (unless otherwise stated). 20 mmol of Schiff's base (C₆H₅-CH=N-CH₂-CH₂-OH) in 100 ml THF, 3–10 mmol of tetrabutylammonium bromide, 1 mmol of PbBr₂ (unless otherwise stated); 60 mmol of allyl bromide (unless otherwise stated), constant current (1 A) 10 h.

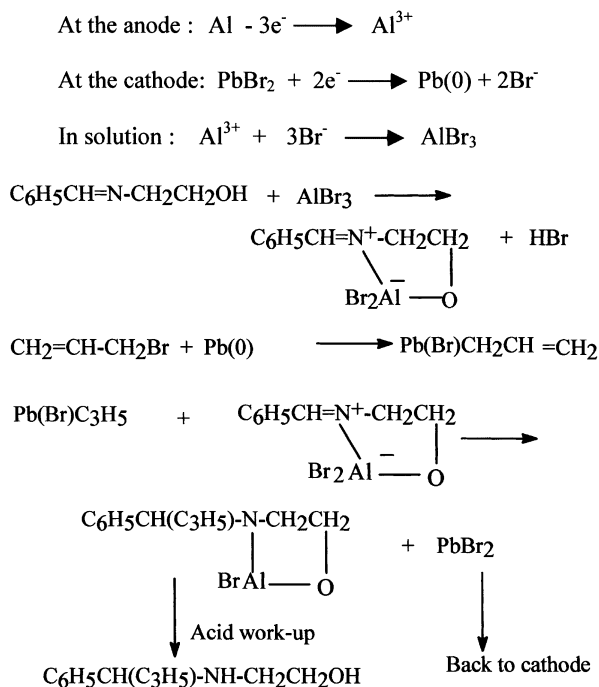
^b Yield (based on Schiff's base) of homoallylamine. Other products isolated and identified: benzaldehyde, tributylamine, *N,N*-diallyl-ethanolamine. Also unidentified higher boiling components were present.

^c Lead cathode instead of platinum.

^d Allyl chloride instead of allyl bromide.

^e Bi(III), Cd(II), Sn(II) and Zn(II) salts as mediators instead of PbBr₂.

on literature information, the following scheme is presented for the reaction.



The observed by-products are (i) tributylamine, (ii) *N,N*-diallylethanolamine, (iii) benzaldehyde and higher boiling amine components. Tributylamine arises from the electrolyte, tetrabutylammonium bromide by Hoffmann elimination induced by electrogenerated bases. These by-products can be decreased by working at lower electrode potentials. Benzaldehyde and diallylethanolamine arise by hydrolysis of the starting material (Schiff's base) brought about by traces of water being present in the solvent (THF). The Schiff's base itself is not readily hydrolyzed by water at room temperature. However, the presence of acid (Lewis acid–AlBr₃) catalyses the hydrolysis. This was verified by an independent experiment where a 0.01 M solution of Schiff's base in THF containing traces of water was kept for 5 h with and without the addition of 0.01 M

HBr acid. An internal standard (naphthalene) for GC analysis was also added. In the former experiment (without acid) the Schiff's base was 95%. In the latter (acid added) the Schiff's base had undergone hydrolysis to the extent of 40%. The ethanolamine acid formed by hydrolysis is allylated by allylbromide forming diallyl-ethanolamine (triallylethanolammonium bromide may also be formed but is lost during work-up, being water soluble. Unallylated ethanolamine itself is also lost during work-up due to the same reason). The higher boiling basic components present in the reaction mixture may include products of reductive dimerization of the imine mediated by the Pb(0)/Pb(II) redox couple catalyzed by Lewis acid. Such reductive dimerization of imines brought about by a Pb/Al-bimetal redox system is known.¹⁰

The observation that the reaction is successful, albeit with lower yields, even with substrates bearing a hydroxyl group was promising and further studies are in progress to optimize the reaction conditions and to access other substrates.

Acknowledgements

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9. (a) Product I: 1-phenyl-*N*-(hydroxyethyl)-but-3-enylamine. Mass spectrum: *m/z* 191 ($M^{+•}$ 3%), 160 (50%), 150 (4%), 131 (5%), 120 (2%) 105 (5%), 91 (100%), 77 (4%) 65(12%) NMR spectrum: As expected; (b) Product II: tributylamine mass spectrum: *m/z* 185 ($M^{+•}$ 5%), 142 (100%), 100 (95%), 58 (30%) NMR spectrum: As expected; (c) Product III: *N,N*-diallylethanolamine mass spectrum: *m/z* 141 ($M^{+•}$, 5%), 110 (100%), 86 (26%), 60 (30%) NMR spectrum: As expected.
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