Oxidation and reduction are two important transformations in organic chemistry. Although several oxidation and reduction reactions are studied in practical organic chemistry, Birch reduction as an experiment, is generally avoided. It is rather taught in theory sessions only. There are certain practical difficulties and hazards associated with these experiments. Benkeser reduction, however, is a safer variant of Birch reduction which can be performed by students under the supervision of a teacher. Foregoing text is a comparative account between Birch and Benkeser reductions. Additionally, it also provides an experimental procedure to prepare electride salt solutions which can be employed for a variety of reductions.

Introduction

Electrons are fundamental particles with unit negative charge and strong reducing properties. Electride salts are those in which electrons serve as anions. Such type of salts can be generated by dissolving active metals like sodium or lithium in liquidammonia or lower amines. Electride salts generated by dissolving lithium metal in liquid ammonia is represented as \([\text{Li(NH}_3\text{n)}\text{]}^+e^-\). Lithium metal in liquid ammonia (or lower amines like ethylamine) generates dark blue colored solutions. These solutions contain large number of solvated electrons. Lithium cation on solvation gets trapped into a sphere of ammonia molecule and the lone pair on nitrogen (negative dipole) solvates the positive charge on the cation. This solvation sphere produces a barrier between the Li\(^+\) ions and the electrons, and their reverse combination is delayed.

Keywords
Electride salts, Birch reduction, Benkeser reduction, solvated electrons.

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Thus, at mean time, there are more number of free electrons available in the solution. These electrons show exceptionally high lifespan and hence can be used for chemical reactions. These solutions are, therefore, potential sources of solvated electrons. *Figure 1* comprise two diagrammatic depictions exhibiting the solvation phenomenon (the representation is irrespective of the dimensions of molecules, atoms and ions). Solutions enriched with solvated electrons have strong reducing properties towards many compounds. In the past, these solutions have been used for several organic reductions. Birch and Benkeser reduction are the two important reductions of such a kind.

**Birch Reduction (Na in Liquid Ammonia)**

Arthur John Birch in 1944 discovered that the sodium in liquid ammonia converts benzene to dihydrobenzene. This method latter became popular as Birch reduction. Ammonia gas can be liquefied (boiling point $= -33.3^\circ$C, freezing point $-77^\circ$C) by reducing its temperature. The liquid ammonia so obtained has strong ionizing properties. Metals like sodium and lithium dissolve in liquid ammonia and have been used for reduction. *Figure 2* shows two early examples of Birch reduction.

Birch reduction appears quite simple on paper, but there are cer-

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**Figure 1.** Solvation of lithium cation.
Ammonia gas needs drying prior to liquefaction. Desiccants like CaO or molecular sieves are generally used for drying purpose. Desiccant like CaCl₂ are not suitable as they react exothermically with ammonia gas. Liquefaction of ammonia needs negative temperature, and the required temperature is achieved using liquid nitrogen, dry ice or other cooling equipment like an immersion cooler. The temperature has to be controlled throughout the course of reaction. There are potential dangers of explosion in case the temperature of the system rises above the boiling point (−33°C) of liquid ammonia. Additionally, there are risks arising through handling of reactive metals like sodium and a hazardous gas like ammonia.

**Benkeser Reduction (Li in Lower Amines)**

Robert A. Benkeser in 1954 proposed an alternative and simplified version of Birch reduction. It was noticed that not only liquid ammonia, but lower amines also can be used to generate solvated electrons. Lithium was considered as a safer alternative for sodium, and naphthalene was reduced to octalin with this method. Under these conditions, the reaction provides a 80:20 mixture of 9-10 and 1, 9 octalins (*Figure 3*). This is a minor disadvantage of Benkesar reduction.

Lithium has limited solubility in lower amines and the solubility reduces significantly with increase in molecular weight of the...
Amines. Benkeser successfully used lower amines like ethylamine and propylamine. There are certain reports where ethylene diamine is also used as solvent as lithium metal readily dissolves (2.9−1 mols.L−1, 2.012 g.L−1) in EDA. Ethylenediamine alone cannot be used as solvent at lower temperatures as it freezes into solid (melting point 8°C) and an additional amine as solvent is necessary for reactions at lower temperatures. Lower amines like n-propylamine or isopropylamine are thus used as solvents which offer sufficient fluidity to the reaction whilst solvating metal ions and electrons. These amines also can be easily removed on completion of reaction as they have lower boiling points. This combination gives a dark blue coloration even at room temperature and contains strong concentrations of solvated electrons. The reduction can be carried out in EDA alone, but removal of EDA (boiling point 116°C) needs higher temperature. Aqueous workups are preferred in such cases. Benkeser’s modifications has simplified the experiment and has also minimized the experimental hazards associated with Birch reduction. Additionally the experimental assembly became quite simple. The reduction offers high practical convenience and these reductions can be carried out in a round bottom flask guarded with a nitrogen balloon.

Generation of Electride Salts Solutions (Li/EDA/n-propylamine)

Figure 3. Benkeser reduction.

The blue coloration of the electride salt solutions is actually the emission spectrum of the electrons.

*Note: The experiment should be performed in the presence of experienced teacher only. Refer to the reaction assembly and depiction given below. Use laboratory gloves and goggles while performing the experiment. Cool n-propylamine and ethylenediamine bottles before opening. Read MSDS of related chemicals.
before experiments.

The electride salt solutions can be easily generated in the laboratories from lithium, ethylenediamine and n-propylamine. Prepare an oven dried two neck 25 ml round bottom flask with a Teflon coated stirring bar (central neck carrying a rubber septum and side neck guarded with nitrogen balloon) for reaction. Cut 50 mg of lithium metal into small pieces under paraffin oil. Wash these pieces with petroleum ether and quickly dry them by pressing between folds of blotting paper and immediately transfer into the flask. Secure the flask neck with a septum. Add to this flask 0.5 ml of ethylene diamine with a syringe and start a slow stirring. Streaks of blue coloration appear in the flask. Cool the flask using ice bath and slowly (drop by drop) dilute the content by injecting 10 ml of n-propylamine so that the blue colour in the flask does not diminish. The deep blue coloration is due to solvated electrons. These solvated electrons can be used for the reduction

![Figure 4. General setup required to prepare electride salt.](image)
of many organic molecules. The reactive electride salt solution shall be decomposed by slow addition of tert-butanol under cold conditions to dispose it safely.

**Conclusion**

Electride salts solution are strong reducing mediums in organic chemistry. These solutions can reduce aromatic compounds, and there are variety of applications of these salt solutions.

**Suggested Reading**

