

Electrochemical Preparation of Strong Bases

Henning Lund

Department of Chemistry, University of Aarhus,
DK-8000 Aarhus C, Denmark

One way of generating a base electrochemically is to reduce a so-called probase, a compound which can form a relatively stable radical anion. The reduction of the first probase, azobenzene, to the radical anion or anion, was used in a Wittig reaction to deprotonate a benzyl-triphenylphosphonium salt in the presence of benzaldehyde with the formation of stilbene (*Z* + *E*) [1].

A strong base may also be prepared by reducing an acid at a platinum electrode in aprotic medium, such as dimethylsulfoxide (DMSO), with evolution of hydrogen, either by reducing protons formed in a predissociation reaction or by direct discharge at the platinum surface with intermediate adsorbed hydrogen. Bases from acids with pK_A -values up to 20 have been prepared by this method [2].

In organic chemistry even stronger bases are sometimes required for synthesis, and in such cases the anion of DMSO ("dmsyl") may be employed. This reagent can be prepared by reacting an alkali metal (K, Na) or an alkali metal hydride (KH, NaH) with DMSO, usually in tetrahydrofuran (THF).

For industrial synthesis the use of these reagents involve some safety problems, and the electrochemical preparation of strong bases may be an attractive alternative. The use of tetraalkylammonium salts as supporting electrolyte is not possible as the strong bases created can be protonated in a Hoffman elimination.

Potassium perchlorate is readily soluble in DMSO and *N,N*-dimethylformamide (DMF) and the salt is not hygroscopic. By reducing a solution of $KClO_4$ in DMSO or DMF with a constant current potassium is formed which deprotonates the solvent to its anion. An advantage of the electrochemical method is that the desired amount of base can be produced by adjusting the constant current and the time of reduction.

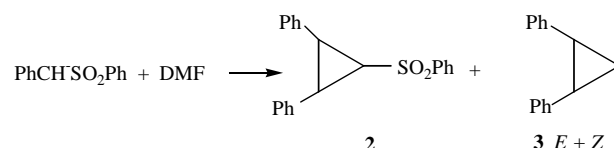
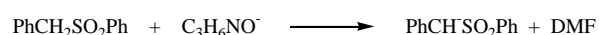
The procedure is very simple: 4 g of $KClO_4$ is dissolved in 100 ml of DMF or DMSO and dried through a column of activated Al_2O_3 . The desired number of coulombs are passed through the solvent in a divided cell and the substrate is added. A few examples are given below.

When DMF is used as solvent the solvent anion deprotonates the substrate and the substrate anion can attack DMF; a carbon atom is thus added to the substrate. Further attack of the DMF-anion may introduce an *N,N*-dimethylcarboxamide group in the intermediate.

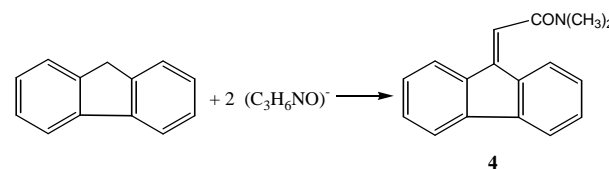
An example is the reaction between the DMF anion, $C_3H_6NO^-$, and acetophenone which results, depending on reaction conditions, in the formation of 1,5-diphenylpenta-1,5-dione (**1**), *N,N*-dimethyl-4-oxo-4-phenylbutyric amide and a compound formed by addition of $CONMe_2$ to **1**. The extra carbon atom in the products comes from DMF. Compound **1** has previously been prepared in 20 % yield from DMF and acetophenone by treating DMF in THF with potassium and adding acetophenone [3].

Another type of reaction is found when benzyl phenyl sulfone is added to a solution of DMF anion in DMF which is heated to about 60° C. The products are 1-phenylsulfonyl-2,3-diphenylcyclopropane (**2**) and (*Z*) and (*E*) 1,2-diphenylcyclopropane (**3**). Substituted phenylcyclopropanes have been prepared by the reaction of benzyl phenyl sulfone with alkenes in the presence of a

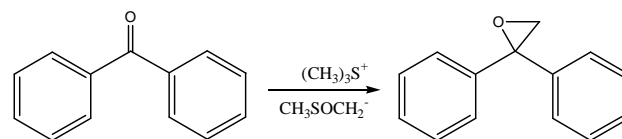
nickel catalyst [4]. In this case the third carbon is the methylene group in the sulfone, whereas in the present reaction it originates from DMF.



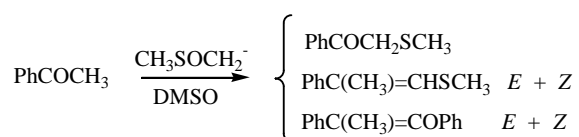
When fluorene is treated with $C_3H_6NO^-$ in DMF the reaction produces *N,N*-dimethylfluorenyleneacetamide (**4**); some fluorenone and traces of phenanthrene are also formed. The reaction involves an attack of the fluorene anion on DMF followed by an attack of $C_3H_6NO^-$ on the intermediate, possibly 9-fluorenylcarbaldehyde.



On reduction of $KClO_4$ in DMSO the DMSO anion is formed. Addition of trimethylsulfonium iodide to this solution produces the trimethylsulfonium ylide; on reaction of the ylide with benzophenone the epoxide is formed. This reaction is well known using chemically produced DMSO anion [5].



Addition of acetophenone to an electrochemically produced $CH_3SOCH_2^-$ results in several products depending on the reaction conditions. Prominent products are the self-condensation product, dyponone, 2-methylmercaptoacetophenone, and 1-methylmercapto-2-phenylpropene. $PhCOCH_2SCH_3$ has previously been formed on heating of $PhCOCH_3$, DMSO and *t*-BuBr [6].



Results obtained using an undivided cell with Mg as sacrificial anode will also be discussed. The substrate anion forms a Grignard reagent with the magnesium salt.

References

1. P. E. Iversen and H. Lund, *Tetrahedron Lett.*, 3523 (1969).
2. S. E. Treimer and D. H. Evans, *J. Electroanal. Chem.*, **449**, 39, (1998); **455**, 19 (1998).
3. S.-i. Kiyooka, T. Yamashita, J.-i. Tashiro, K. Takano and Y. Uchio, *Tetrahedron Lett.*, **27**, 5629 (1986).
4. Y. Gai, M. Julia and J.-N. Verpeaux, *Bull. Soc. Chim. Fr.*, **133**, 805, 817 (1996).
5. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962), **87**, 1353 (1965).
6. E. Armani, A. Dossena, R. Marchelli and G. Casnati, *Tetrahedron* **40**, 2035 (1984).