19 Dissolving Metal Reductions

19.1 Introduction

The products formed in dissolving metal reductions are often determined by the presence or absence of a proton source, as well as by other experimental conditions such as the particular metal and solvents used [1–3]. These differences may result from protonation of the initial anion radicals to yield radical intermediates, as well as from the ability of the proton source to limit the basicity of the media. Based on the analogy between a trimethylsilyl group and a proton, it is not surprising that TMS-Cl is able to influence the course of dissolving metal reductions.

This chapter will be organized by functional groups. Often several different combinations of reagents and solvents have been applied to reduce a single functional group. These may lead to diverse results. Solvent, metal, temperature, as well as the ratio of substrate to TMS-Cl influence the course of these reductions. Despite this number of variables, a coherent picture of these reductions may be possible.

French workers have made major contributions to our knowledge of dissolving metal reductions of unsaturated functional groups in the presence of TMS-Cl. They have utilized TMS-Cl with either lithium in THF (A) or magnesium in HMPT (B) as reduction systems.

19.2 Ketones and Aldehydes

Ketones and aldehydes undergo dissolving metal reduction in the presence of a proton source to yield alcohols, while in the absence of a proton source pinacol dimers are the usual products [4]. Reduction of ketones which have α-hydrogens with magnesium in HMPT or TMU and TMS-Cl leads to a mixture of products: bis-1,2-(trimethylsilyloxy)alkanes, and equal amounts of alkoxytrimethylsilanes and trimethylsilyl enol ethers. Formation of these products can be accounted for as follows. Initial electron transfer to the ketone forms a ketyl (anion radical) which reacts with TMS-Cl to yield a α-trimethylsilyloxyalkyl radical. Dimerization of such radicals yields bis-1,2-(trimethylsilyloxy)alkanes, while radical disproportionation results in equal amounts of alkoxytrimethylsilanes and trimethylsilyl enol ethers [5].
With cyclohexanone only the disproportionation products, cyclohexanoxo-trimethylsilane and trimethylsilyloxy-cyclohexene are found [5].

On the other hand, benzophenone and t-butyl phenyl ketone react with B to yield diphenyl trimethylsilyl trimethylsilyloxy-methane and t-butyl phenyl trimethylsilyl trimethylsilyloxy-methane, respectively. These products result from a second electron transfer to the initial diphenyltrimethylsilyloxy-methyl or t-butyltrimethylsilyloxy-benzyl radicals to yield the corresponding carbanions which react with a second equivalent of TMS-Cl. Carbanion formation is probably favored by the phenyl groups. Dimerization of these radicals to form pinacol products may also be disfavored due to steric hinderance [6, 7].

Addition of THF to the HMPT or TMU solvent favors formation of pinacol products with benzophenone. Electron transfer to the silyloxy radicals may be slower in THF due to its decreased cation solvating ability [8].

With the reduction system (B), the ratio of benzaldehyde to TMS-Cl influences the distribution of products. A 1:1 ratio favors 1,2-diphenyl-1,2-bis(trimethylsilyloxy)ethane whereas a 2:1 ratio of TMS-Cl to benzaldehyde favors formation of α-trimethylsilyl-α-trimethylsilyloxytoluene [9].