MECHANOCHEMICAL BIRCH REDUCTION WITH CALCIUM METAL

Bachelor's thesis

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Abstract

Traditional Birch reduction uses alkali metals such as lithium, sodium, or potassium in liquid ammonia at temperatures below -33^{0}C to produce unconjugated 1,4-cyclohexadienes from arenes. This method is time-consuming, hazardous and requires tedious experimental procedure and set-up. Benkeser reduction that uses low molecular weight amines instead of liquid ammonia often gives over-reduced products. Despite the drawbacks, these traditional reductions remain in use as dominant approaches. Therefore, the aim of the present work was to develop the first calcium-mediated mechanochemical Birch reduction that represents a more sustainable and safer alternative to the traditional Birch approaches.

Firstly, optimisation studies were conducted on model substrates. Screening of metals showed the potential of calcium metal, and the optimal amount was concluded to be two equivalents. Ethylenediamine was found to be the optimal ligand and THF was kept as a LAG additive. Optimal milling conditions were shown to be 60 minutes of milling at the frequency of 30 Hz. For the reduction of arenes with electron-donating groups, an additional protic source was found to be necessary, and solid ammonium chloride was chosen as the best source. In addition, comparative studies with solution state reaction proved the activation of calcium metal with mechanical milling.

As a result of optimisation studies two protocols were developed and a scope of substrates was carried out. Most of the substrates chosen for this work gave good yields of pure product, but some limitations were found as well.

The results of this work show that mechanochemistry can be used to perform solution state reactions more simply and safely while giving efficient results. These findings suggest that further research with different metal-mediated reactions using mechanochemistry could deliver good and even unexpected results.