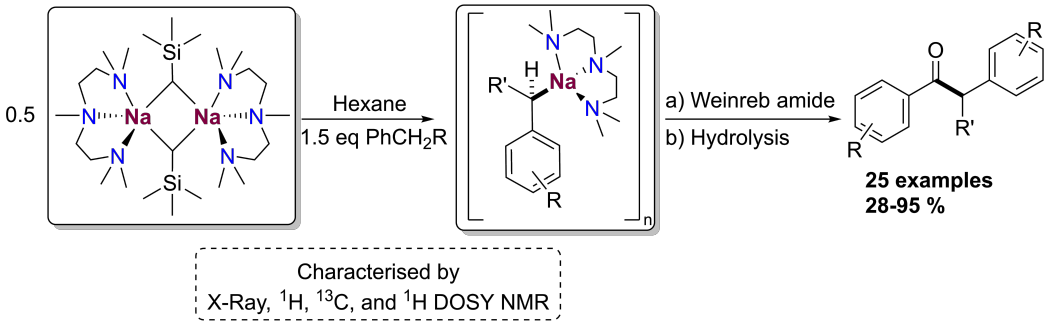
Highly Reactive Hydrocarbon Soluble Alkylsodium Reagents for Benzylic Aroylation of Toluenes using Weinreb Amides

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Alkyl sodium reagents have been proposed as an alternative to organolithiums, one of the workhorses of synthetic chemistry.[1] Several factors, however, have hindered their wider synthetic application in organic synthesis. They are plagued by poor solubility in hydrocarbon solvents and low stability in donating ethereal solvents. These impediments have made them inconvenient for widespread use by synthetic chemists, leading to a lower accessibility when compared with their lighter lithium congeners. Despite these limitations, recent reports in the field of organosodium chemistry have focused on the development of new reactivity and have demonstrated the potential of these powerful reagents in synthesis, surpassing the reactivity obtained with other organometallic reagents.[2][3] However, the nature of the sodiated intermediates in both the solid state and in solution remains poorly understood, missing an opportunity to improve upon these systems.

In this communication, we report on the exploitation of the Lewis basicity of PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine) to access and characterise a hydrocarbon soluble alkyl sodium reagent. This astoundingly soluble reagent was subsequently used towards the development of a facile and selective route for benzylic metalation of the corresponding nonactivated toluene derivatives. We demonstrate the reactivity of the formed benzyl sodiums through application in benzylic aroylation with a Weinreb amide to access synthetically useful 2-aryl acetophenones, and in their reactivity towards C=X double bonds (X = C, N or O). Reaction intermediates were characterised using a combination of X-ray crystallography and ^{1}H DOSY (Diffusion Ordered SpectroscopY) NMR, providing the first reported synthetic and structural insights on the constitution of the intermediates in these reactions, advancing our understanding of how these systems operate in solution.[4]



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