Abstract

In the present work, suitably functionalized arylsydnones were used to synthesize a variety of 4-acyl-sydnones and diacyl sydnones, both as potential precursors to novel sydnoquinolines. The approach to the diacyl species is based on the discovery that activated sydnones brominate in both the 4 position of the sydnone ring and on the phenyl ring. Thus, it seemed likely that Friedel-Crafts reactions on an activated sydnone would give diacylated species for McMurray coupling to sydnoquinolines.

Friedel-Crafts acylations on the 4 position of the sydnone ring have been achieved in high yields using 4 equivalents of various alkyl anhydrides, 25 mol % of bismuth triflate and lithium perchlorate in anhydrous acetonitrile at 95 °C. Various para-substituted phenyl sydnones with different electron withdrawing and electron donating substituents were used to explore the effect of the attachment on the reaction time and yields of the acylation with acetic anhydride. Additionally, four other alkyl anhydrides were employed to test their utility with phenyl sydnone. The reaction times were consistent with the electron withdrawing or donating nature of the para substituents. Thus, electron-donating groups appeared to speed up the process, whereas the reactions were slower in the presence of electron-withdrawing moieties. The reaction times involving phenylsydnone and other alkyl anhydrides were consistent with the steric hindrance of the anhydride; bulkier species leading to longer reaction times.

With optimized conditions available for the monoacylation process, it was of interest to explore diacylation using the activated sydnone, 3-(3, 5-dimethoxyphenyl) sydnone. Many attempts were made to prepare the diacyl sydnone, but no methods thus far have given only the desired diacyl product. For example, when the activated sydnone was reacted under the standard conditions with acetic anhydride, two different products were isolated. They were identified by $^1$H and $^{13}$C NMR as the desired 4-acetyl-3-(2-acetyl-3, 5-dimethoxyphenyl) sydnone and the mono-acyl contaminant 4-acetyl-3-(3, 5-dimethoxyphenyl) sydnone. Variations of the amount of catalysts and the anhydride have been employed in an attempt to achieve complete conversion. Further studies are focusing on optimizing this process.