Ring Expansion of NHC-derived Chromonylbenzimidazoliums Yielding 3-Methylene-3,4-dihydroquinoxalin-2(1*H*)-ones

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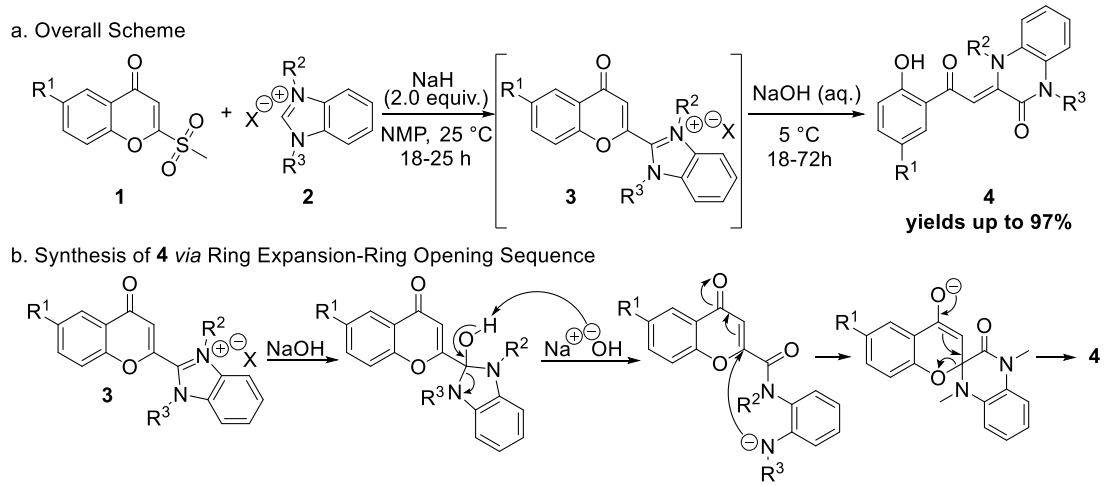
3-Methylene-3,4-dihydroquionxalin-2(1*H*)-ones are a class of compounds which have shown biological activities including anticancer and antidiabetic activities.[1] We have discovered a new route towards this class of compounds through a ring expansion-ring opening sequence. Deprotonation of benzimidazole-based *N*-heterocyclic carbenes (NHCs) **2** by NaH allows for the reaction with 2-(methylsulfonyl)chromones **1** which likely generates chromonylbenzimidazolium salts **3** in situ. Treatment of **3** with a 5 M aqueous solution of NaOH at 5 °C generates the desired 3-methylene-3,4-dihydroquionxalin-2(1*H*)-ones **4**. NHCs bearing linear alkyl substituents (e.g. *n*-hexyl) on the nitrogen atoms performed best with the corresponding products being obtained in up to 97% yield. Increasing the steric bulk of the *N*-substituents on **2** dramatically decreased the yields of the quinoxalinones. When a *N,N'*-dibenzyl protected benzimidazole-based NHC was reacted with 2-(methylsulfonyl)-4*H*-chromen-4-one, the resulting *N,N'*-dibenzyl protected quinoxalinone was obtained in 54% yield. Other NHCs derived from triazolium, imidazolium, and thiazolium salts provided either poor yields or no product, highlighting the importance of the NHCs having an aromatic backbone. Adding a chlorine atom at position 6 (R^1) of chromone **1** highlighted the importance of electronic effects on this reaction with the corresponding quinoxalinone being obtained in 42% yield. Further investigations of the electronic effects of different substituents on both the chromone and benzimidazole core, as well as investigations using different leaving groups on the chromone, are currently underway.



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