Computer-Assisted Design of Ionic Liquids for Efficient Synthesis of 3(2*H*)-Furanones: A Domino Reaction Triggered by CO_2

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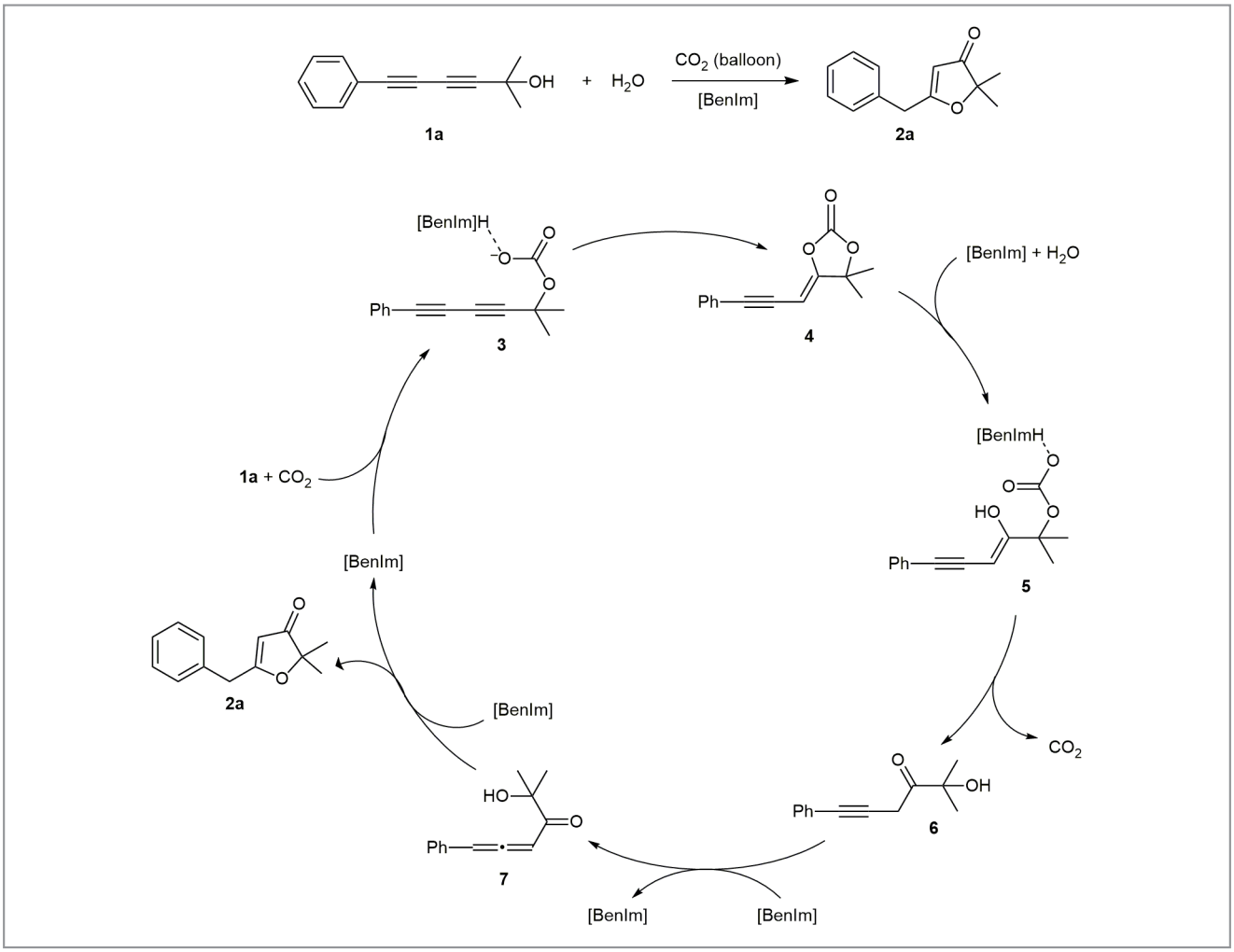
CO_2 capture and utilization (CCU) has attracted much attention during this decade in the context of green economy. Ionic liquids (ILs) exhibit particularly attractive properties for CCU, due to their tunable structures that can be harnessed for absorption and activation of CO_2. Recently, the group of Professor Congmin Wang at Zhejiang University (P. R. of China) discovered that the basicity of ILs is the key to influencing the gas absorption capacity, such as in the case of CO_2 and SO_2.[1] In addition, a moderate basicity of IL is also crucial to ensuring its high catalytic activity in the synthesis of alkylidene carbonates from propargylic alcohols and atmospheric-pressure CO_2.[2] Previously, the choice of base catalysts was often based on experience and experiment trial and error. Professor Wang explained: "We wanted to develop an innovative strategy to easily predict the best range of basicity by DFT calculations. If that worked, it would save more time on catalyst screening."



Scheme 1 Hydration of diyne alcohol

Professor Wang continued: "The CO_2-triggered domino reaction to achieve the synthesis of 3(2*H*)-furanones was selected as the model reaction (Scheme 1). There are two reasons for our choice of this reaction: 1) 3(2*H*)-furanones are important structures in many natural products; therefore, an environmentally benign method of synthesizing them was expected to be of profound significance; 2) this reaction can occur without a metal catalyst, and that would make our research easier."

The basicity of the catalyst is clearly important in many base-catalyzed reactions, while the K_a value is one of the criteria representing basicity. Thus, the group compared the pK_a values of raw material and several traditional anions. "To our surprise, diyne alcohol showed stronger basicity than imidazole," said Professor Wang. He continued: "Then, inspired by our previous findings that CO_2 could facilitate hydrogen abstraction, we recalculated the pK_a value of **1a** while CO_2 was also taken into consideration. As shown in Figure 1, the pK_a value of that complex decreased to between that of BenIm and Triz. To our delight, the prediction was consistent with experiments, where $[N_{4444}][Triz]$ and $[N_{4444}][BenIm]$ had better catalytic activities than other ILs."

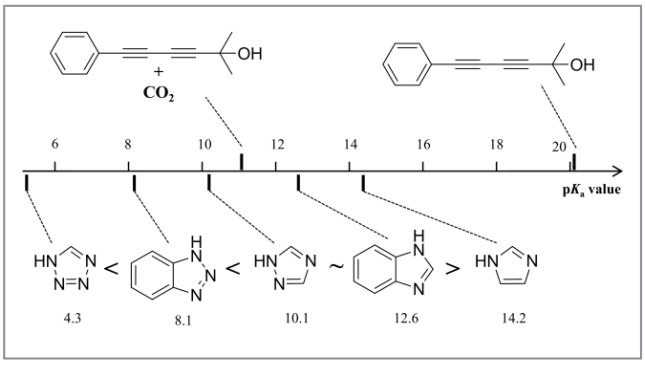


Figure 1 The pK_a relationship of the complex of **1a** and CO_2, **1a** and anions

However, the group was puzzled to find that the cations in the ILs also affected the reaction. Initially, the reaction mechanism was investigated by DFT calculations (Figure 2). Professor Wang explained: "By using NMR spectroscopic investigations (Figure 3) and DFT calculations, we found the basicity of ILs was different when they had different cations. Clearly, that is the reason that led to different catalytic activities."

Professor Wang remarked that this reaction can be expanded to other diyne alcohols, and the catalyst is reusable: "When 10 mmol of **1a** was used, a high yield of **2a** was obtained after six hours," he added.

"Importantly, I believe this manuscript presents a strategy to predict the catalytic activities of catalysts before experiments. Notably, we also discovered the influence of cations by the combination of NMR spectra and quantum-chemical calculations," said Professor Wang.

He concluded: "We hope this method can be also used in other base-catalyzed reactions and CCU processes."

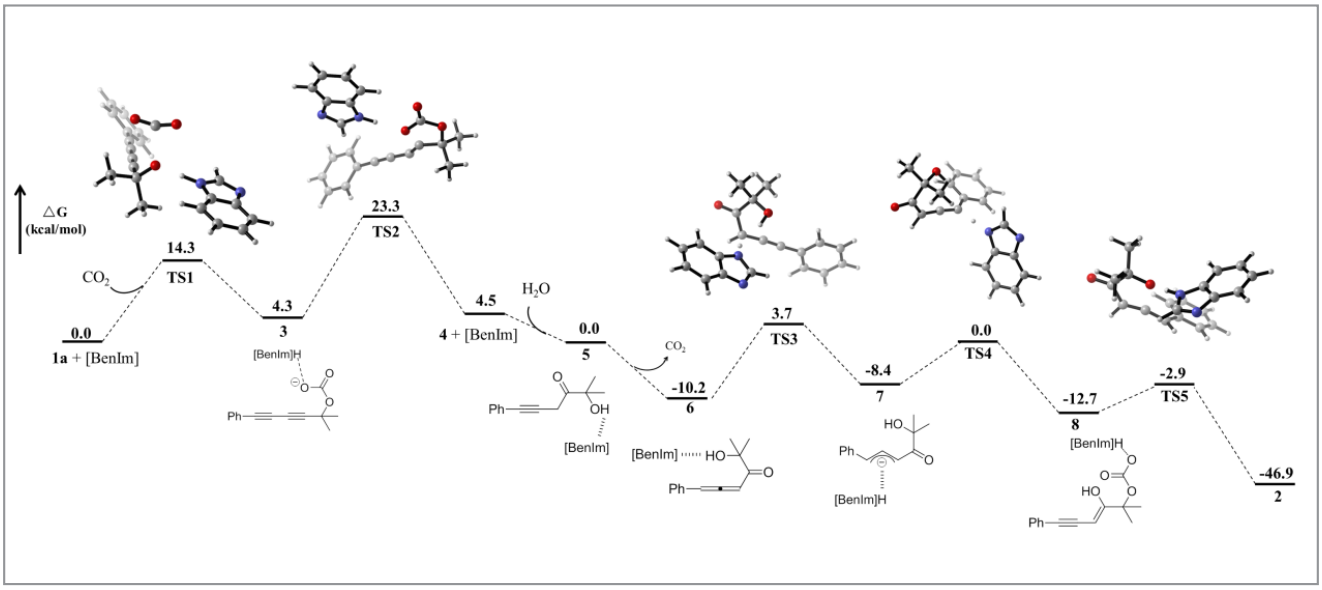


Figure 2 Computational studies of the reaction mechanism (reprinted with permission from *J. Am. Chem. Soc.* **2016**, *138*, 14198)

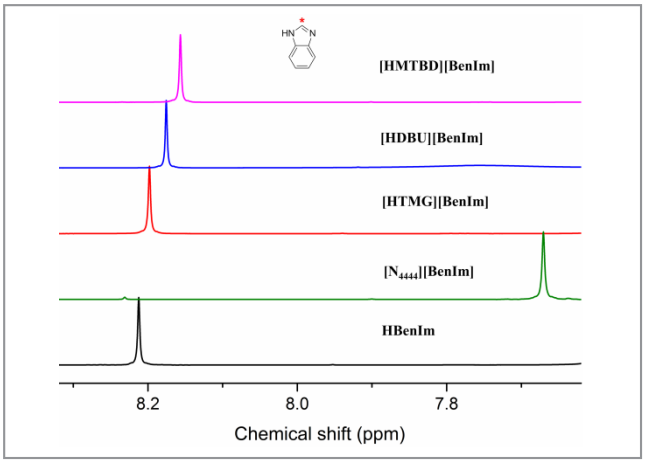


Figure 3 ^{1}H NMR spectra of HBenIm, [N_{4444}][BenIm], [HTMG][BenIm], [HDBU][BenIm] [HMTBD][BenIm]

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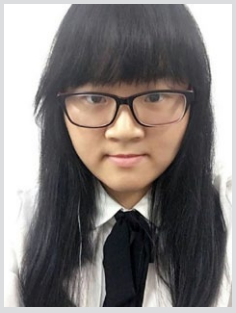

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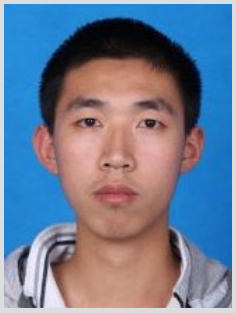

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