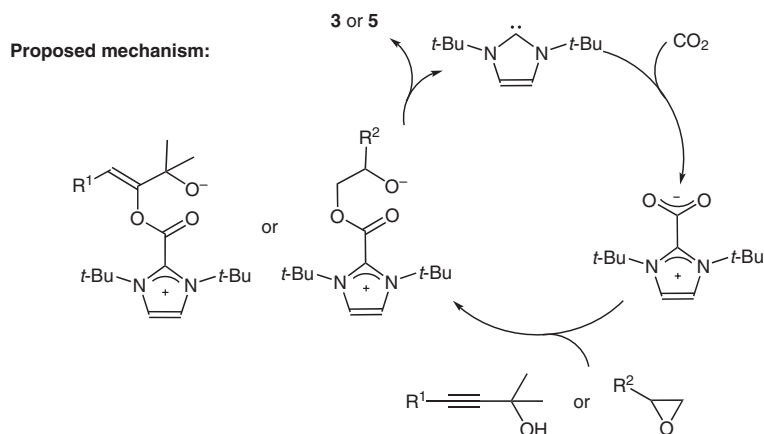
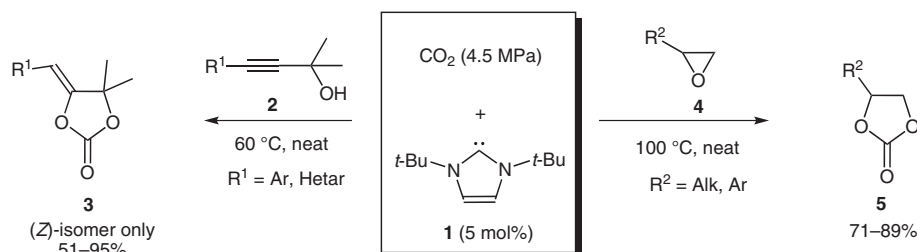


N-Heterocyclic Carbene as Catalyst for CO₂ Fixation



Significance: Ikariya and colleagues report the use of N-heterocyclic carbenes as catalysts for incorporating CO₂ into electrophilic acceptors. Their previous work revealed that phosphane CO₂ adducts formed in supercritical CO₂ generated carbonates **3** from propargylic alcohols **2**. Now, the authors report that the same transformation can be catalyzed by NHC compounds under milder conditions. Optimizing the structure of the NHC, the authors could obtain carbonates **3** in good to excellent yields, and extended the methodology to epoxides **4**. The reaction is proposed to be initiated by the nucleophilic addition of imidazolium-2-carboxylate to the electrophile followed by an intramolecular cyclization of the alkoxide intermediate which regenerates the NHC catalyst.

Comment: Imidazolium carboxylates, prepared by the reaction of CO₂ with NHCs, are well established as carbene transfer agents and used in the synthesis of NHC metal complexes. However, only recently this process has been utilized to chemically transform carbon dioxide. Zhang, Ying and colleagues (*Angew. Chem. Int. Ed.* **2009**, *48*, 3322) reported the reduction of NHC-activated carbon dioxide to methanol. In this work, Ikariya and co-workers demonstrated that CO₂ can also be activated as a nucleophilic fragment. The solvent-free carbonate synthesis is perfectly atom-economical. Excessive pressures and temperatures are a drawback of the method. However, the NHC catalysis reported in this work offers significantly milder reaction conditions compared to previous methods.