LEWIS BASE-CATALYZED REARRANGEMENTS OF ELECTRON-POOR CYCLOPROPANES

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Cyclopropanes have been used as versatile building blocks in organic synthesis owing to its intrinsic ring strain. Transition-metal catalysis and Lewis acid catalysis have been the most common approaches for the ring opening of the cyclopropanes; however, organocatalytic activation of cyclopropanes has been seldom reported. We herein report several organocatalytic Lewis base-catalyzed rearrangements of electron-poor cyclopropanes. In this regard, a highly efficient organocatalytic DABCO-catalyzed Cloke–Wilson rearrangement of cyclopropylketones to 2,3-dihydrofurans have been developed [1]. We also found that hydroxylamine could not only catalyze the Cloke–Wilson rearrangement of cyclopropylketones, but also promote a subsequent Boulton–Katritzky reaction to afford isoxazole products in one pot [2]. Meanwhile, electron-deficient vinylcyclopropanes (VCPs) can serve as a C_5 synthon under phosphine catalysis, leading to an efficient rearrangement of vinylcyclopropylketones to cycloheptenones [3]. In addition, substrate-dependent rearrangements of electrondeficient alkylidenecyclopropanes (ACPs) has been developed for the synthesis of triand tetrasubstituted furans, and trisubstituted dienones in good yields.

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^[2] W. Wei, Y. Tang, Y. Zhou, G. Deng, Z. Liu, J. Wu, Y. Li, J. Zhang, S. Xu, Org. Lett. 2018, 20, 6559–6563.

^[3] J. Wu, Y. Tang, W. Wei, Y. Wu, Y. Li, J. Zhang, Y. Zheng, S. Xu, Angew. Chem., Int. Ed. 2018, 57, 6284–6288.