Organic Seminar
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Anion Relay Chemistry: Broadening the Horizon
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Nature efficiently synthesizes complex molecules in an iterative mode, often with stereo- and regiochemical control.[1] Chemists have employed biomimetic syntheses to achieve the types of chemical control strategies observed in Nature. However, most biomimetic syntheses require multistep processes including isolation and purification of intermediates at each step. In addition, the time and material costs have motivated the search for more facile chemical transformations. Multi-component reactions alleviate these shortcomings by converting simple starting materials in one-pot into functionalized molecules with high structural complexity, and thus eliminate multiple isolation and purification steps. Anion Relay Chemistry (ARC), an efficient multi-component-union protocol, can potentially increase efficiency at each reaction step.[1,2]

ARC involves successful migration of a negative charge either through the bonding network (e.g. Michael-type addition) or through space, using a relay agent. The [1, 2]-Brook rearrangement (Fig. 1, inset) is a classic example of the latter.[3,4] Depending on the initial and final loci of the negative charge after rearrangement, through-space ARC is subdivided into two categories, namely, Type I and Type II.[2,5-7] For Type I ARC, the negative charge subsequently returns to the original atom (Fig. 2); whereas for Type II, the negative charge is transferred to a distal site (Fig. 3). Thus, ARC can be used to successfully control the relay of a negative charge through a series of bifunctional molecules (acting both as nucleophile and electrophile) in an iterative manner that is similar to “living polymerization.”[6]

Fig. 1

Fig. 2

Fig. 3

References: