Can simple amines mimic organotin?: Aminoalkyl radicals as halogen-atom transfer (XAT) agents for redox chemistry

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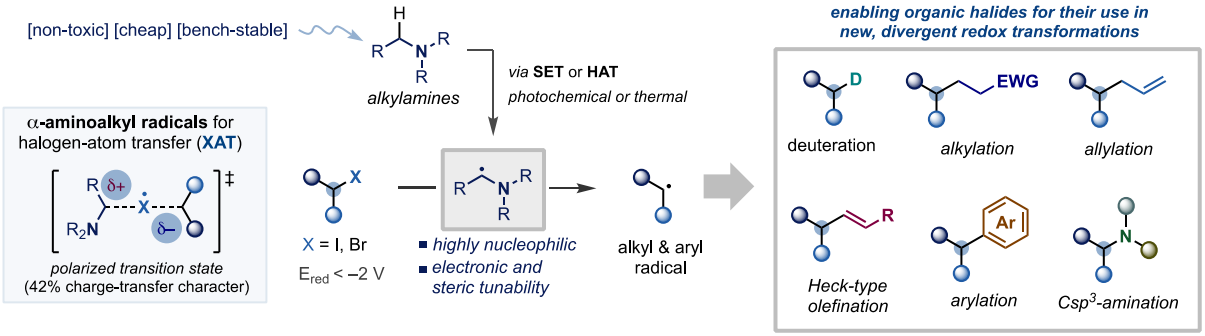
The emergence of (photo)redox catalysis has enabled the development of new methodologies that generate highly reactive radicals under mild conditions [1]. Notwithstanding, the general and reliable generation of carbon radicals from inactivated alkyl and aryl halides remains an unsolved problem in redox chemistry, in view of their often inaccessible SET reduction potentials (E_{red} < –2 V vs SCE) [2]. In fact, nowadays synthetic chemists still rely on the same systems based on halogen-atom transfer (XAT) developed more than 40 years ago to engage organic halides in radical transformations, sometimes underutilized due to the acute toxicity (e.g. tributyltin hydride) or hazards (e.g. explosive initiators) associated to the reagents employed.

We have recently demonstrated how simple amines (*e.g.* triethylamine), some of the cheapest and most common reagents present in any synthetic lab, can be used as surrogates of tributyltin hydride for the homolytic activation of carbon-halogen bonds [3-4]. Aminoalkyl radicals, easily generated under thermal or photochemical conditions from amines, can be engaged in kinetically-favored polarized XAT processes providing effective access to alkyl and aryl radicals. The utility of this strategy has been showcased in a wide range of redox transformations allowing the construction, with high chemoselectivity, of sp^3–sp^3, sp^3–sp^2 and sp^2–sp^2 carbon–carbon and Csp^3–N bonds under mild conditions. Moreover, it has opened a new gateway for the modular use of alkyl and aryl halides in (photo)redox and radical chemistry beyond dehalogenation, further expanding the use of widespread organic halides in redox settings.



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