

Reversible reservoirs for radicals: new perspectives for organic synthesis and for polymer chemistry

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Radical reactions offer many of the properties desired by synthetic organic chemists, in terms of variety, mildness of conditions, and a selectivity that is often complementary to that of ionic chemistry, making many protection steps superfluous. There is however one major difficulty, which derives from the propensity of radicals to interact with themselves (dimerisation, disproportionation) with extremely fast rates that are close to diffusion. In order to overcome this complication, it is essential to keep the steady-state concentration of radical species very low. This can be accomplished for example by contriving a chain reaction where the propagating steps are themselves quite fast, as for example in the typical, and now extremely popular, stannane based processes. While various *unimolecular* cyclisation and fragmentation steps can be efficiently incorporated into the radical sequence, kinetically slower *bimolecular* transformations, and in particular *intermolecular* additions to un-activated alkenes, have proven more difficult to implement. In the case of stannanes, the relatively slow addition to the alkene has to compete with premature hydrogen atom abstraction from the organotin hydride, a step that is usually thousands of times faster.

Over the years, we have shown that xanthates and related thiocarbonylthio derivatives allow the generation of radicals under conditions where the radicals possess a considerably increased effective lifetime, even in a concentrated medium. Intermolecular additions to un-activated alkenes, as well as a variety of reputedly difficult radical transformations can now be easily accomplished. No metals, heavy or otherwise, are required, and the starting materials and reagents are cheap and readily available. Complex, densely functionalized structures can be constructed in a convergent, modular fashion. This chemistry has also proved to be applicable to the synthesis of block polymers and for exploiting bio-sourced raw material. Recent results and some mechanistic aspects will be presented and discussed briefly.