CHEMISTRY COLLOQUIUM

Title: A Radical Solution to an Old Problem. Some New Perspectives for Organic Synthesis

Guest Speaker:

WED. SEPT. 7, 2016, 12:00 PM
HUTCHISON HALL, ROOM 140
LANDER AUDITORIUM
UNIVERSITY OF ROCHESTER
DEPARTMENT OF CHEMISTRY

Professor Samir Zard
Laboratoire de Synthèse Organique,
Ecole Polytechnique - FRANCE

Abstract: 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. In the course of our study of the scope and limitations of this chemistry, we have uncovered a few surprising transformations. Recent results and some mechanistic aspects will be presented and discussed briefly.

Host: Professor Robert Boeckman, email: Robert.Boeckman@rochester.edu