

## Function of Ynolates

Mitsuru Shindo

(Institute for Materials Chemistry and Engineering, Kyushu University)

Ynolates are not only the precursors of alkynyl ethers, but also of metalated ketenes acting as ketene precursors, their chemistry showing interesting facets that are impossible to attain with the enolates. The fact that ynolates can act as precursors in the synthesis of other reactive species will prompt us to focus their attention on this potentially useful and exciting field. An ynolate reacts with an electrophile to give a ketene, which reacts with a nucleophile to afford an enolate. It can react with an electrophile to furnish a ketone, which is attacked by a nucleophile to give an alkoxide. Thus, a smart design would enable the one-pot successive reaction sequence. Based on this concept, we have developed ynolate-initiated one-pot cascade reactions providing multisubstituted carbocycles and heterocycles. Since ynolates are compact strong nucleophiles, even sterically congested substrates can react with them. We have also developed the torquoselective olefination of carbonyl compounds. Ynolates add to a carbonyl group to give the  $\beta$ -lactone enolate, which is immediately ring-opened at ambient temperature to furnish olefins in good yields. The *E/Z* selectivity is controlled by the torquoselectivity in the electrocyclic ring-opening reaction. We found highly stereoselective olefination of acylsilanes,  $\alpha$ -heterosubstituted ketones, and esters affording the corresponding tetrasubstituted olefins. Synthetic application of the multisubstituted olefins which have not been accessed so far is also mentioned. Ynolates will be standard reactive species in synthetic organic chemistry in near future.