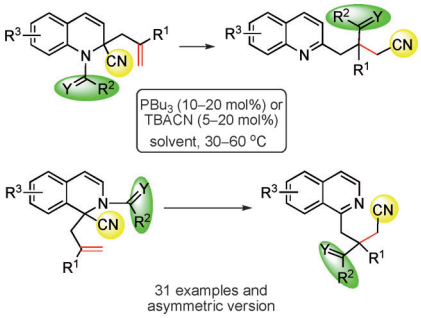
Synthetic Methods

J.-M. Chen, G.-F. Zou,
W.-W. Liao* _____ 9296 – 9300

Metal-Free Intramolecular Carbocyanation of Activated Alkenes: Functionalized Nitriles Bearing β-Quaternary Carbon Centers

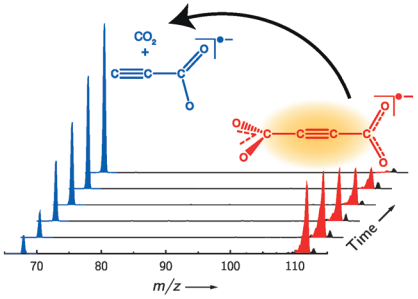


The CN shuffle: The described intramolecular alkenyl- and acylcyanation reaction of activated alkenes proceed by cleavage of a C–N bond. This protocol provides access to functionalized acyclic nitriles with quaternary carbon centers under neutral and mild reaction conditions, demonstrates broad scope, and good functional-group compatibility and versatility. Y = O or CHR^4; R^1,R^4 = electron-withdrawing group; TBACN = tetrabutylammonium cyanide.

Radicals

B. L. J. Poad,* B. B. Kirk,
P. I. Hettiarachchi, A. J. Trevitt,
S. J. Blanksby, T. Clark* _____ 9301 – 9304

Direct Detection of a Persistent Carbonyloxyl Radical in the Gas Phase



Long lived: Carbonyloxyl radicals ($RCO_2^{\bullet}$) are reactive intermediates that play key roles in initiating polymerization reactions. This reactivity also makes their direct observation difficult. For the first time a persistent organic $RCO_2^{\bullet}$ radical is detected in the gas phase, its extraordinary longevity is attributed to the high barrier towards fragmentation owing to the endothermicity of the decarboxylation products.

DOI: 10.1002/anie.201306077

50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Angewandte Chemie has always published a broad range of Reviews: The first Review (by E. Jucker) was on the chemistry of psychotherapeutic agents, including neuroleptics, antidepressants, and tranquilizers. In other Reviews, F. Drawart and O. Bachmann discussed how radiocarbon-labeled compounds could be separated and detected in the gas phase, O. Glemser outlined the preparation, properties, and structure of cyclic and acyclic sulfur–nitrogen halides, and E. Wiberg et al. discussed the chemistry of metal silyls $M(SiR_3)_n$, where M is Zn, Hg, Al, or Sn, and R is hydrogen or an organic group.

These days Communications are often around four pages long. Fifty years ago, this was enough for the entire Communications section! Three of the Communications were on organotin chemistry: H. Schumann et al. reported on the preparation of organotin phosphides from either organotin halides or lithium triorganyltin species. W. P. Neumann et al. published two Communications, the first on H–D exchange in trialkyltin, germanium, and silicon hydrides, and the second on addition reactions of organotin hydrides onto olefins in the presence of aluminum trialkyl species, which act as a catalyst.

Read more in Issue 9/1963.