Visible-Light-Mediated Remote Aliphatic C-H Functionalizations through a 1,5-Hydrogen Transfer Cascade


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Aliphatic C-H functionalization has become the focus of intense research given the ubiquitous presence of C(sp^3)–H bonds in organic molecules and, thus, their synthetic potential. The highly unreactive nature of C(sp^3)–H bonds towards metals typically translates into harsh reaction conditions and a lack of selectivity. Shu and Nevado describe a redox-neutral, light-mediated functionalization of unactivated C(sp^3)–H bonds via iminyl radicals. A 1,5-H transfer followed by the functionalization of a C(sp^2)–H bond takes place in aqueous media producing a variety of fused ketones. A reversible 1,5-H transfer was identified as the rate determining step. Furthermore, careful choice of the reaction conditions also enables the formation of C(sp^3)–N bonds.

2,4,6-Tri(hydroxy)-1,3,5-triphosphinine, P$_3$C$_3$(OH)$_3$: The Phosphorus Analogue of Cyanuric Acid


Cyanuric acid (C$_3$H$_3$N$_3$O$_3$), discovered by Wöhler nearly two centuries ago, serves as a useful basic chemical nowadays. It is widely used as cross-linker in bulk polymers but also finds application in more sophisticated materials, such as in supramolecular assemblies and molecular sheets. The unknown phosphorus analogue of cyanuric acid, P$_3$C$_3$(OH)$_3$, may become an equally useful building block for phosphorus-based polymers or other specialized materials. Suter, Benkő, Grützmacher and coworkers describe the synthesis of 2,4,6-tri(hydroxy)-1,3,5-triphosphinine and its P$_3$C$_3$(OR)$_3$-derivatives. Although rather labile, these compounds can be η$_6$-coordinated to transition metals via the aromatic P$_3$C$_3$ unit, which results in stable molecules and opens possibilities to use complexes of P$_3$C$_3$(OR)$_3$ as building blocks or cross-linkers for polymeric materials.

Azaindoles as Zinc-Binding Small-Molecule Inhibitors of the JAMM Protease CSN5


Cullin-RING ligases (CRLs) represent the largest family of E3 ubiquitin ligases. CSN5 is the zinc metalloprotease subunit of the COP9 signalosome, an important regulator of CRLs. Elevated expression of CSN5 has been found in several types of cancers. Altmann and coworkers describe the discovery of azaindoles as a new class of CSN5 inhibitors, which interact with the active-site zinc ion through an unprecedented binding mode. Nanomolar inhibitors led to degradation of the substrate recognition subunit Skp2 and reduced the viability of HCT116 cells. The study provides a proof-of-concept for the potential of CSN5 inhibitors as anticancer agents.

Template-Free Hierarchical Self-Assembly of a Pyrene Derivative into Supramolecular Nanorods


The design of self-assembled, functional nanomaterials with precise control over the positioning of the constitutive building blocks in three dimensions is a major challenge in supramolecular chemistry. Hierarchical self-assembly is defined as the assembly of molecular building blocks into supramolecular structures of increasing order and complexity. Herein, Dalgarino, Shahghaldian and coworkers describe a new pyrene derivative that yields stable and well-defined nanorods by hierarchical self-assembly in the absence of template. X-ray diffraction studies allowed elucidation of the three dimensional packing of this pyrene derivative within the self-assembled nanorods.

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