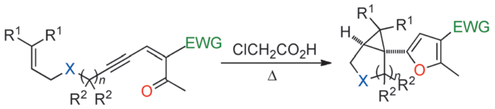
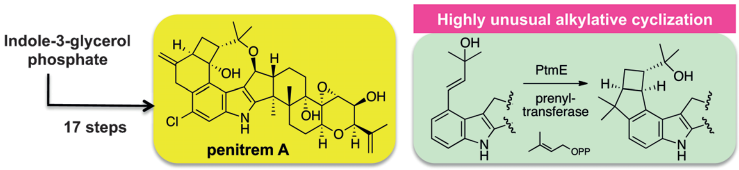
Cascade Reactions



Chloroacetic acid promotes an efficient and diastereoselective intramolecular cascade reaction of electron-deficient ynenones to deliver products featuring a 2,3,5-trisubstituted furan bearing a fused cyclopropyl substituent at the 5-position. Synthetically relevant polycyclic building blocks featuring rings of various sizes and heteroatoms have been synthesized in high yield using this mild acid-catalyzed reaction. EWG = electron-withdrawing group.

Biosynthesis

Front Cover



The gene cluster that is responsible for the biosynthesis of the indole diterpene penitrem A has been identified. Thirteen out of the seventeen involved transformations were elucidated by heterologous reconstitution of the relevant genes and found to feature a prenylation-initiated cationic cyclization (PtmE) and two successive P450-catalyzed oxidative reactions to install the bicyclo[4.2.0]octane skeleton.

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Flashback: 50 Years Ago . . .

The use of mass spectrometry for the analysis of organic compounds was in its infancy but was already being explored by pioneers such as McLafferty and Djerassi. In a Review, Gerhard Spiteller and Margot Spiteller-Friedmann discuss structural elucidation of organic compounds by analysis of the fragmentation products.

Horst Prinzbach et al. reported on the photochemical isomerization of *exo*-tricyclo[3.2.1.0^{2,4}]octene derivatives to form tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane compounds. Various derivatives were investigated, and carboxylic acids were found to isomerize more efficiently than esters. Prinzbach's many achievements were summarized in his Obituary (see *Angew. Chem. Int. Ed.* **2012**, *51*, 11936).

In another Communication, Prinzbach and Arthur Lüttringhaus discussed the proton activity of 1,3-dithiolium cations. NMR spectroscopy was used to measure the half-lives of hydrogen–deuterium exchange at the 2-position. The cations were reacted further to produce tetrathiafulvalene derivatives, the mass spectra of which showed a peak corresponding to the resulting dithiacarbene fragment. Together with Gottfried Schill, Lüttringhaus reported the first templated synthesis of a catenane (for the full story see the Editorial by J. Fraser Stoddart in *Angew. Chem. Int. Ed.* **2014**, *53*, 11102).

H. J. Berthold and H. Knecht published two Communications on the reactions of uranium trichloride and tetrachloride. The first report outlined the reactions of UCl_3 and UCl_4 with liquid ammonia at low temperature to produce ammoniates with the compositions $UCl_3\cdot(6.8\text{–}6.9)NH_3$ and $UCl_4\cdot(7.3\text{–}7.5)NH_3$. In the second Communication, the high-temperature reaction was discussed, and compounds such as UNH_2Cl_2, $U(NH_2)_2Cl$, and UNH_2Cl_3 were found to be formed.

Read more in Issue 5/1965.