Synthesis of (±)-Paeoniflorigenin

**Significance:** In 1993, Corey and Wu reported the synthesis of (±)-paeoniflorigenin, a natural product from the roots of *Paenia lactiflora*, which are widely used in traditional Chinese medicine. The approach relies on oxidative annulation of dihydro-5-m-cresol ether A and SmI<sub>2</sub>-induced, Reformatsky-type cyclization from an α-chloro nitrile.

**Comment:** The synthesis commenced with annulation of A and B to give γ-lactone C. Chlorination followed by Prilezhaev epoxidation yields E. Cyclization is achieved by treating lactol F with an excess of TMS-triflate. Exposure of H to SmI<sub>2</sub> leads to formation of the carbon skeleton of paeoniflorigenin. Protection of the secondary alcohol followed by reduction of the nitrile gives K. Benzoylation and global deprotection completed the total synthesis of (±)-paeoniflorigenin in 13 steps from A.