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Stereoselective Total Synthesis of Eburnane-Type Alkaloids Enabled by Conformation-Directed Cyclization and Rearrangement

Synthesis of Eburnane-Type Alkaloids

**Significance:** Zhu and co-workers present their recent efforts to access eburnane-type alkaloids using a highly divergent approach. The presented route features an \( \alpha \)-iminol rearrangement to access the trans-fused core in intermediate D. The conformational bias allowed to close the remaining six-membered ring of the eburnane core in a diastereoselective fashion. The divergent design of the route uses key intermediates D and E to access four different eburnane alkaloids with good yields.

**Comment:** \( \alpha \)-iminol rearrangement of C led to key intermediate D. Oxidative cleavage of the diol and reduction yielded hexacyclic aminal F as a single diastereomer. Lewis acid induced 1,2-alkyl shift of F furnished (+)-terengganensine B. Reduction to alcohol G and Brønsted acid mediated rearrangement allowed synthesis of (+)-larutensine. Oxidation of diol D to the corresponding diketone and subsequent oxidative bond cleavage gave pentacyclic amide I. (+)-Melokhanine E was obtained in five additional steps and was then converted into (+)-eburnamonine by means of an aza-pinacol rearrangement.