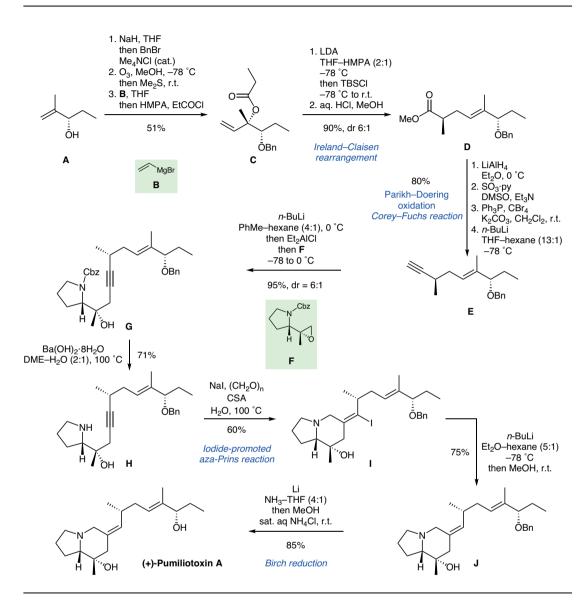
N.-H. LIN, L. E. OVERMAN*, M. H. RABINOWITZ, L. A. ROBINSON, M. J. SHARP, J. ZABLOCKI (UNIVERSITY OF CALIFORNIA, IRVINE, USA)

Efficient Total Syntheses of Pumiliotoxins A and B. Applications of Iodide-Promoted Iminium Ion-Alkyne Cyclizations in Alkaloid Construction

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Total Synthesis of (+)-Pumiliotoxin A



Significance: Overman and co-workers report the total synthesis of (+)-pumiliotoxin A. The alkaloid was isolated in 1967 from the skin of the Panamanian poison frog *Dendrobates pumilio*. The skin secretions of these frogs have been employed by the Noanamá and the Emberá Native American tribes to poison blow darts.

Comment: Alkyne **E** is coupled with prolinederived building block **F** through an aluminummediated epoxide opening. The octahydroindolizine motif is constructed through an iodide-promoted aza-Prins reaction. The synthesis was completed after a deiodination and Birch reduction sequence, thus giving access to (+)-pumiliotoxin A.

Category

Synthesis of Natural Products

Key words

(+)-pumiliotoxin A dendrobatid alkaloid

Ireland-Claisen rearrangement

Parikh-Doering oxidation

Corey-Fuchs reaction

iodide-promoted aza-Prins reaction



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