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Significance: Zhao and co-workers report the synthesis of the ryanodane diterpenoid (+)-garajonone as well as its non-natural epimer 3-epi-garajonone. Key to the synthesis is a 1,2-addition and carbonylative Heck reaction to construct the carbocycle of the natural product. From a common intermediate, both (+)-garajonone and 3-epi-garajonone were accessed.

hydration

Comment: Allylic alcohol C was obtained through 1,2-addition of metalated arene B to enone A. Subsequent Babler-Dauben reaction gave rise to vinyl bromide **D**, which underwent a Pd-catalyzed carbonylative Heck reaction furnishing ester **F**. Upon debenzylation, ester hydrolysis, and phenol oxidation, dienone I was obtained. Weitz-Scheffer epoxidation of I was used to mask the bridging olefin and enable regioselective hydrogenation with concomitant epoxide opening. The obtained alcohol was inverted through elimination and Mukaiyama hydration furnishing tertiary alcohol K.

(±)-Garajonone

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Synthesis of Natural Products

Key words

(+)-garajonone ryanodane diterpenoid

1,2-addition

Babler-Dauben reaction

carbonylative Heck reaction

Weitz-Scheffer epoxidation

