

The Chemistry of Transient Diarylgermylenes and Tetraaryldigermenes Generated by the Photolysis of 1,1-Diaryl-3,4-dimethylgermacyclopent-3-enes

Lawrence A. Huck, Cameron R. Harrington, and William J. Leigh

McMaster University

A series of 1,1-diaryl-3,4-dimethyl-germacyclopent-3-enes (**1a-d**) were synthesized and their photochemistry studied by steady-state and nanosecond laser flash photolysis methods. Steady-state photolysis experiments with **1** in the presence of ethanol or isoprene yields the products of trapping of the corresponding diarylgermylene (**2**).

Flash photolysis of **1** leads to the formation of a long-lived transient (λ_{max} ca. 445 nm) that is produced with 2nd order kinetics and decays with pseudo-first order kinetics. Addition of alcohol results in a reduction in the yield of this transient as well as an increase in its decay rate. Based on this behaviour, the transient is assigned to the tetraaryldigermene (**3**), which would form from the dimerization of **2**. Absolute rate constants have been determined for the reaction of **3a,b,c** with ethanol and correlate with Hammett σ constants to yield a positive ρ value.

The diarylgermylenes (**2**) cannot be detected by flash photolysis, but their relative reactivities toward ethanol could be determined qualitatively by monitoring the reduction in the yield of **3** as a function of alcohol concentration. Again, the results suggest a positive Hammett ρ value for the insertion of diarylgermylene into the O-H bond of ethanol. There are three possible mechanisms for ethanol addition to **2** and **3** – concerted and two step-wise (electrophilic or nucleophilic addition). The positive ρ values are inconsistent with the stepwise electrophilic addition mechanism in both cases.

