

A Computational Study of Chlorocarbene Addition to Cyclooctyne

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We are interested in the extent to which nonstatistical dynamics controls halocarbene additions to strained π -systems. To this end, we are calculating the potential energy surfaces for the reactions of cyclooctyne (**1**) with dichloro- and phenylchlorocarbenes (**2**). As with other chlorocarbene additions to strained substrates (e.g. cyclopropenes), the addition to **1** is very exothermic: $\Delta H_{1+2 \rightarrow 3} = -77$ kcal/mol, $\Delta H_{1+2 \rightarrow 5} = -107$ kcal/mol, $\Delta H_{1+2 \rightarrow 7} = -117$ kcal/mol. The conversion of **3** \rightarrow **4** requires less than 2 kcal/mol of activation energy, as does **4-Ph** \rightarrow **6-Ph**. We are currently investigating the possibility that a single transition state for the initial addition of **1** + **2** leads directly to **3** and to **4**.

