

Department of Chemistry

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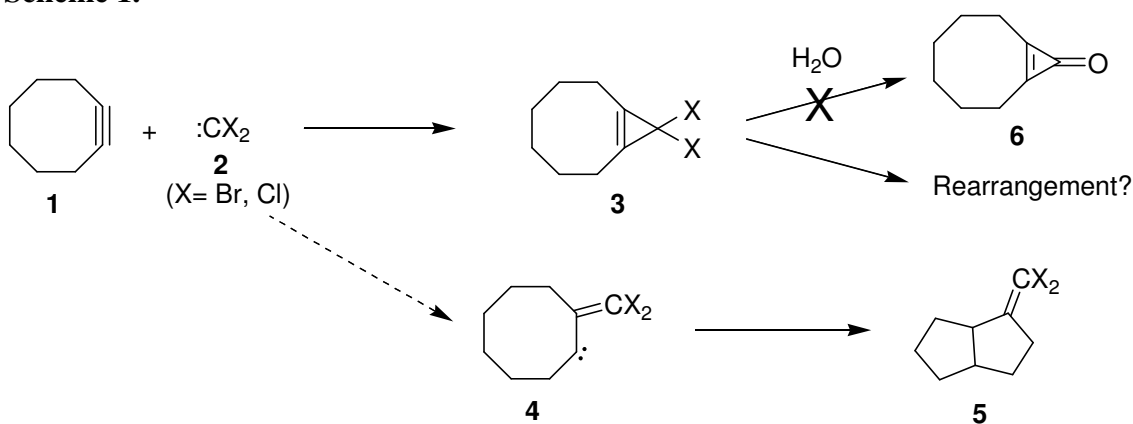
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Reactivity of Dihalocarbenes with Cycloalkyne

Cyclooctyne (**1**) was successfully synthesized and purified, and was reacted with dibromo- and dichlorocarbene ($:CX_2$, $X = \text{Br}, \text{Cl}$) in an effort to isolate and analyze the addition products and to elucidate a mechanism for the addition (Scheme 1). Thus far, we have been able to conclude that the products have incorporated $:CX_2$, but the structure does not correspond to **3**. Rearrangement of **3** is likely occurring. Also, we were able to conclude that $:CX_2$ addition to cyclooctyne does not produce cyclooctenocyclopropanone (**6**) by comparison of an authentic sample of the cyclopropanone with our $:CX_2$ + cyclooctyne product mixtures. Previous work in our laboratory showed that product **5-Cl₂** was also not generated by **1** + **2**.

We have also begun investigations of the possible reactivity of $:CX_2$ with cycloheptyne (**10**), focusing on the synthesis of its precursor, cycloheptenocyclopropanone, **9** (Scheme 2). *cis*- and *trans*-2,8-Dibromocyclooctanones have been made and purified. The *trans* isomer has been converted to **9**. Subsequent photolyses of **9** to generate cycloheptyne have been inconclusive, complicated by the fact that **9** appears to decompose over time even at low temperature.

Scheme 1.



Scheme 2.

