Cyclooctyne (1) was successfully synthesized and purified, and was reacted with dibromo- and dichlorocarbene (:CX₂, X= Br, 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 :CX₂, but the structure does not correspond to 3. Rearrangement of 3 is likely occurring. Also, we were able to conclude that :CX₂ addition to cyclooctyne does not produce cyclooctenocyclopropenone (6) by comparison of an authentic sample of the cyclopropenone with our :CX₂ + 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 :CX₂ with cycloheptyne (10), focusing on the synthesis of its precursor, cycloheptenocyclopropenone, 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.