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Mechanism of Addition of Dihalocarbenes to Cycloheptyne and 3,3-Difluorocyclooctyne

This work investigates the threshold strain energy needed in a substrate containing a π bond to induce dynamic control of the reaction of that strained substrate with dichlorcarbene. The strained substrates explored here are cycloheptyne and 3,3-difluorocyclooctyne with E_{strain} = 25 and 17 kcal/mol, respectively.

Cycloheptyne has been previously generated photochemically and thermally from cycloheptenocyclopropenone by Breslow and by Krebs. In our hands, we have synthesized cycloheptenocyclopropenone in two steps from cyclooctanone. We have attempted to form the known cycloheptyne trimer from cycloheptenocyclopropenone, neat and in solution, photochemically at room temperature and at 77 K, and thermally at 250 °C. The photolyses seemed to show some formation of the trimer, though the putative product was neither stable nor isolable and therefore could not be characterized. The thermolysis failed to form any of the trimer after a considerably longer reaction time than had been necessary in previous experiments.

Cycloheptenocyclopropenone was also photolyzed with a phenanthryl dichlorocarbene precursor at room temperature in an effort to form its addition product with cycloheptyne. Though the reaction mixture contained some products, no carbene addition products were observed.

Progress was also made on the synthesis of 3,3-difluorocyclooctyne. Cyclooctanone was transformed via sequential silyl enol either formation–fluorination steps to the vinyl triflate of 2,2-difluorocyclooctanone. The final step of the six-step synthesis, treatment of the vinyl triflate of 2,2-difluorocyclooctanone with lithium diisopropylamine to generate 3,3-difluorocyclooctyne, did not prove to be successful. Further work will be required to complete the synthesis of 3,3-difluorocyclooctyne.

Once 3,3-difluorocyclooctyne is synthesized and the formation of cycloheptyne is confirmed, each will be reacted with dichlorocarbene and the addition products of 3,3-difluorocyclooctyne + CCl_2 and of cycloheptyne + CCl_2 will be characterized. The identities of these products will help determine the mechanism of carbene addition and also the influence of reaction dynamics, if at all, on the reactions.