

DICHLOROCARBENE FROM CHLOROFORM PYROLYSIS

P. S. Skell and M. S. Cholod
The Pennsylvania State University, University Park, Pa. 16802

Although cyclopropane formation from photolysis of suitable diazo compounds in the presence of an olefin is generally regarded to proceed through a free divalent carbon intermediate, there is much question as to the nature of the intermediate when alpha-elimination reactions are carried out in the presence of olefins to form cyclopropanes. Some species as ICH_2ZnI and LiCHCl_2 have been postulated as directly transferring the CXY moiety to olefin forming cyclopropanes without the intermediacy of a free carbene, but rather a carbene complex or carbenoid. On the other hand, indications are that the action of base on CHF_2X (X = Cl, Br) yield a free carbenic species, CF_2 .

In the instance of dichlorocarbene produced through alpha-elimination, there is much controversy as to whether the intermediate carbene is a free or a complexed species. The aim of this work was to resolve this conflict by comparing the reactivity of an unambiguously free dichlorocarbene with that of the species from alpha-elimination.

Unambiguously free dichlorocarbene was produced via chloroform pyrolysis: chloroform was passed through a pyrolysis zone ($\sim 1400^\circ$) which led into a high vacuum system, allowing molecular flow to a cooled solution of substrate. The substances leaving the pyrolysis chamber experienced a 10^{-5} second free flight before encountering the stirred liquid solution of olefin and hydrocarbon solvent. The dichlorocyclopropanes formed under these conditions are the products derived from the reaction of free dichlorocarbene with the olefin substrate. This variety of dichlorocarbene was found to add stereospecifically to the 2-butenes as does the dichlorocarbene from base and chloroform.

Reactions were run in which olefin pairs were allowed to compete for the free dichlorocarbene. Results of these competitions were compared with those for dichlorocarbene systematically generated by a number of alpha-elimination reactions in a variety of solvents, and over an extensive temperature range.

The reactivity of trichloromethylithium, a dichlorocarbene precursor stable at low temperatures ($\sim -80^\circ$) was also studied. The mode of reaction of this compound with olefins is of great interest, since it can conceivably react by both a carbene and an organometallic route.

Arrhenius plots were made for the relative reactivities of pairs of olefins. A common line was obtained independent of the mode of generation of the dichlorocarbene, with alpha-elimination or pyrolysis of chloroform.

Since all methods of generating dichlorocarbene gave an intermediate showing the same selectivity it follows that all generate the same intermediate, free dichlorocarbene.