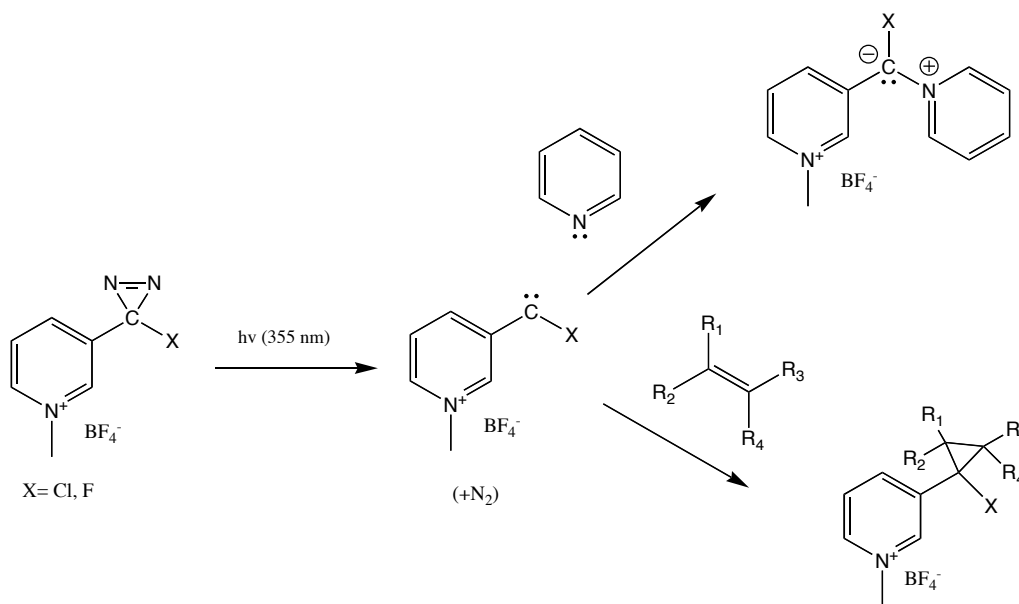


Halo(Pyridinium)Carbenes: Electrophilic Reactive Intermediates

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The reactivity of chloro(3-pyridinium)- and fluoro(3-pyridinium)carbenes was examined by laser flash photolysis. The carbenes were generated from the corresponding diazirine precursors. Although the halo(pyridinium)carbenes were highly reactive and decayed within the timeframe of the ns laser pulse, their generation was verified by the observation of carbene ylides formed with acetone, acetonitrile, and pyridine, which are readily visible in the UV-vis range. The short lifetime of the transient carbenes precluded direct observation, however the relative order of reactivity of these species with a set of electron-rich and electron-poor alkenes was determined using the pyridine-ylide method. The results show that for all alkenes investigated the halo(pyridinium)carbenes are strongly electrophilic species, reacting faster with the more electron-rich alkenes. This contrasts the previously reported ambiphilic nature of the closely related halo(pyridyl)-carbenes.¹ The small spread of reactivities observed in the halo(pyridinium)carbene-alkene reactions (up to 100 times lower than those of their halo(pyridyl)-counterparts) reveals their very reactive nature. Computational studies demonstrated that the alkene(HOMO)-carbene(LUMO) interaction is predominant for the carbene-alkene reactions, providing support for the strongly electrophilic nature of these reactive intermediates.



1. Moya-Barrios, R., Schepp, N.P., and Cozens, F.L. *J. Org. Chem.* 2009, **74**, 1148-1155.