PHOTOCHEMISTRY OF BENZYLALLENE: PHOTOCHEMICAL PATHWAYS TO NAPHTHALENE

JOSHUA A. SEBREE, NATHAN KIDWELL, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; ALEX NOLAN, ROBERT MCMAHON, *Department of Chemistry, University of Wisconsin, Madison WI 53706*; TALITHA SELBY, *Department of Chemistry, University of Wisconsin Washington County, West Bend, WI 53095*; MAREK ZGIERSKI, *National Research Council Canada, Ottawa, ON*.

Recently, many groups have suggested that the flexible side chain of alkylated benzene rings may play an important role in the formation of fused ring compounds. Here we present the conformer-specific, vibrationally-resolved electronic spectroscopy of benzylallene along with a detailed analysis of the products formed via its ultraviolet photoexcitation. Benzylallene is the minor product of the recombination of benzyl and propargyl radicals. The mass-selective resonant two-photon ionization spectrum of benzylallene was record showing an origin at 37483 cm^{-1}. UV-UV holeburning showed that only one conformer was present in the expansion and rotational band contour analysis showed the allene unit to be pointing away from the phenyl ring. The photochemistry of benzylallene was carried out by counterpropagating the expansion with a photoexcitation laser. The laser was timed to interact with the gas pulse in a reaction channel to initiate reactions. The reactions were quenched upon exiting the channel. Products were then interrogated using mass-selective resonant two-photon ionization techniques. The UV-Vis spectra of products were compared to literature for identification. Product distributions at various excitation wavelengths were recorded. Using 193 nm light, eight products were observed including two radicals, benzyl and benzylallenyl, and several mass 128 isomers including naphthalene. Photoexcition at the S_0-S_1origin of benzylallene yielded only four products including naphthalene. One important note is that at the lower energy excitation, over three times as much naphthalene was observed. A combination of isotopic substitution and calculations has been used in the determination of a mechanism for naphthalene formation.