M. Photolytic Cleavage of R-X Bonds

Photolysis of benzhydryl derivatives generally leads to mixtures of radicals $Ar_2CH^{\cdot}$ and carbocations Ar_2CH^{+}. The efficiency and mechanism of the photo-cleavage were studied by nanosecond laser flash photolysis and femtosecond spectroscopy. The radical/carbocation ratio depends on the photoelectrofuge (Ar_2CH), the photonucleofuge (X), the counterion (in case of onium precursors), and the solvent (# 331). As electron transfer interconverts radicals and carbocations during the first nanoseconds (#344), the radical/carbocation ratio observed by nanosecond spectroscopy does not reflect the real ratio of homolytic vs. heterolytic bond cleavage. Recipes, how to obtain an optimal ratio of carbocations on the nanosecond time-scale have been summarized (review # 351).