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Catalyst-free dehalogenation of 5-bromopyrimidine derivatives using DMF/trialkylamine as the hydrogen source

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A wide range of synthetically valuable transformations in organic chemistry involve reduction process through which functionalization can be easily performed in the course of the reaction. While several reduction methodologies utilizing transition metals as catalysts, non-catalytic methods are of more interest as they offer safe and inexpensive synthetic protocols. Most of the reports on dehalogenation of pyrimidines include reduction in the presence of transition metal catalysts such as palladium, zinc dust, etc. While for halouracil dehalogenation goes through irradiation in aqueous alcoholic solvents, thermolysis in acetamide, sonication in the presence of indium metal, and reduction under physiological conditions. To the best of our knowledge, metal catalyst-free dehalogenation of halogenated uracil/ pyrimidines has not been reported in the literature. This report presents a novel metal catalyst-free dehalogenation procedure in a mixture of DMF and trialkylamines introducing the combination of DMF- R_3N as a potential reductive system. The system can tolerate amine and sulfide functionalities. Our results may provide a new route to the reduction of more other organic compounds in the future.

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Ultrafast time-resolved spectroscopic studies of the electronic properties and reactivities of phenyloxenium ions reactive intermediates

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Phenyloxenium ions are reactive intermediates of formula $R-O^+$. These species are the isoelectronic oxygen analog of the more familiar nitrene class of intermediates but bear a formal positive charge on hypovalent oxygen. The phenylnitrenium ion and benzyl cation have been deeply studied for theoretical computations and characterized by the time-resolved spectroscopies. Although oxenium ions are often important reactive intermediates in synthetic chemistry and enzymology, the lack of general methods to photogenerate these species has hindered their study by directly detecting and studying their chemical reactivities, lifetimes, spectroscopic signatures and electronic configurations. In addition, the free oxenium ion is a very short-lived species in the solution and the traditional methods cannot take a snapshot of it. Therefore, ultrafast time-resolved spectroscopies are required to capture these short-lived intermediates. Recently, we used selected protonated hydroxylamine salts as novel photoprecursors to generate the singlet ground state parent phenyloxenium ion, the open shell singlet and triplet biphenyl oxenium ion and triplet ground state phenyloxenium ion as a product from the photoheterolysis of the aryl hydroxylamine tetrafluoroborate salt. A combination of femtosecond and nanosecond transient absorption spectroscopy, nanosecond time-resolved resonance Raman spectroscopy (ns-TR³), cryogenic matrix EPR spectroscopy, computational analysis and photoproduct studies allowed us to trace essentially the complete arc of the photophysics and photochemistry of this photoprecursor and permitted a first look at these oxenium ions.

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