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Photosonochemical catalytic ring opening of α -epoxyketones

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Abstract

The combination of ultrasound and photochemical methods has been used for the catalytic ring opening of α -epoxyketones by I-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (NBTPT) as photocatalyst in methanol. Sonication of these compounds in the presence of NBTPT did not result in the opening of epoxide ring, but the use of ultrasound increased the rate of photoreaction.

Background

The advantages of ultrasound-assisted chemical reactions include higher yields, shorter reaction times and milder reaction conditions when compared with classical methods. [1-5] The effect of ultrasound has mostly been shown by increasing the yields of reactions and in some cases changing the ratio of products formed. The most important effects of ultrasound arise from acoustic cavitation: formation, growth, and implosive collapse of bubbles in the liquid by passing ultrasonic waves through this medium. [3,6] The implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. This leads to development of temperatures up to 5000 K and high pressures of 1800 atm and cooling rates in excess of 1010 K/s within the cavities during their collapse. [3,6] In all of these reactions it was found that ultrasound accelerates the reactions. [7-17]

It is well known that the substituted pyridinium cations are good electron acceptors. [18] Garcia and coworkers have used N-alkyl-2,4,6-triphenylpyridinium tetrafluor-oborate as photosensitizer in the photochemical cyclization of 5-methyl-4-hexenoic acid to the corresponding γ -

lactone. [19] In our recent study, we have used 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (NBTPT) as photocatalyst in a highly diastereoselective ring opening of α -epoxyketones in acetone solution with the formation of 1.3-dioxolanes. [20]

Ring opening of epoxides and α -epoxyketones in the presence of various nucleophiles has received considerable attention in recent years, partially owing to current interest in single electron transfer (SET) process and also because of potential application in organic synthesis. Such reactions have been recognized as important processes not only in thermal but also in photochemical transformations. Single electron transfer (SET) induced ring opening reactions of epoxides and α -epoxyketones have demonstrated C-C and C-O bond cleavages through photo-induced electron transfer by various electron donors such as triethylamine (TEA), [21] tribenzylamine (TBA) [20] and 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI) [22-24] or thermally induced single electron transfer by electron donating compounds such as samarium diiodide, [25] tributyltin hydride [26] and bis(cyclopentadienyl)titanium(III) chloride. [27] Ring opening reactions of epoxides and α -epoxyketones have