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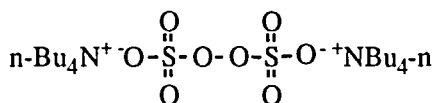
Novel β -Masked Formylation of α,β -Unsaturated Ketones and Lactones by Tetra-*n*-Butylammonium Sulfate Radical

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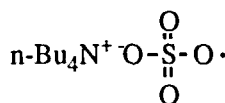
Tetra-*n*-butylammonium peroxydisulfate was prepared and found to be a good source of tetra-*n*-butylammonium sulfate radical by its oxygen - oxygen bond cleavage. The sulfate radical can be utilized for the efficient organic syntheses in organic solvents. Electron deficient olefins such as α,β -unsaturated ketones or lactones were smoothly β -masked formylated by treatment of the olefins with 1,3-dioxolane in the presence of tetra-*n*-butylammonium peroxydisulfate. Extremely high diastereofacial selectivity ($\sim 100\%$ de) was obtained in β -masked formylation of α,β -unsaturated lactone, (*S*)-5-(*t*-butyldiphenyl silyloxymethyl)-2(5*H*)-furanose.

Tetra-*n*-butylammonium peroxydisulfate (**1**, $(\text{TBA})_2\text{S}_2\text{O}_8$) was synthesized by treatment of tetra-*n*-butylammonium hydrogen sulfate with potassium peroxydisulfate in the phase transfer reaction system in water and methylene chloride.^{1,2}



1

Tetra-*n*-butylammonium peroxydisulfate
 $(\text{TBA})_2\text{S}_2\text{O}_8$



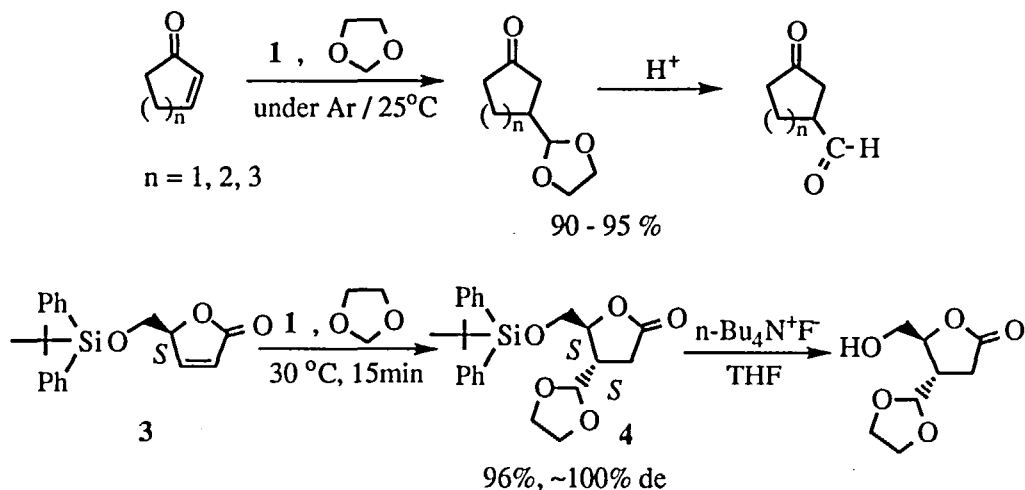
2

Tetra-*n*-butylammonium
 sulfate radical

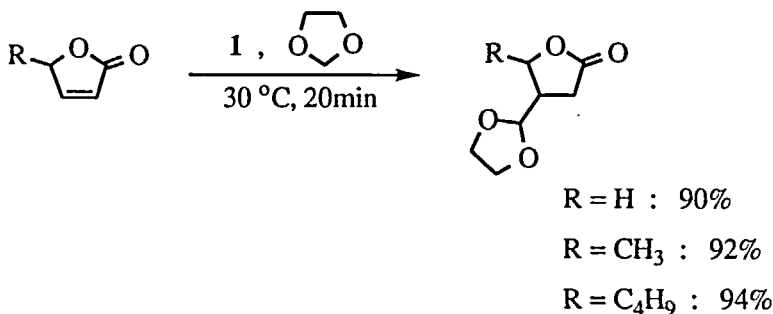
In contrast to the known metal peroxydisulfate such as sodium and potassium peroxydisulfate which are soluble in aqueous media, **1** is very soluble in most of organic solvents. Thus **1** gains of great advantage over metal peroxydisulfate or ammonium peroxydisulfate in forming relatively stable sulfate radical (**2**) under the anhydrous conditions. The α,β -unsaturated ketone reacted with 1,3-dioxolane in the presence of **1** in acetonitrile to give β -masked formylated products in excellent yields. The products can be readily converted to the corresponding aldehydes.³

Chiral butyrolactons have shown considerable potential as synthetic intermediates in asymmetric synthesis of carbohydrates. Chiral butenolides (*S*)-5-(*t*-

butyldiphenylsilyloxymethyl)-2(5*H*)-furanose (3) was synthesized from L-glutamic acid⁴ and reacted with 1,3-dioxolane in the presence of 1 to afford β -masked formylated products (4) in the extremely high diastereofacial selectivity (ca 100 %).⁵



The stereoselectivity was determined by both chiral column chromatography and NOE experiment in ¹NMR. Simple α,β -unsaturated lactones were smoothly β -masked formylated under mild conditions to give high chemical yields.



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