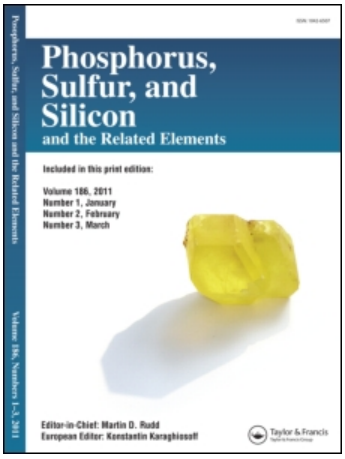

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Formation and Characterization of Tetrabutylammonium Sulfate Radical: Application to Organic Synthesis

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FORMATION AND CHARACTERIZATION OF TETRABUTYLAMMONIUM SULFATE RADICAL: APPLICATION TO ORGANIC SYNTHESIS

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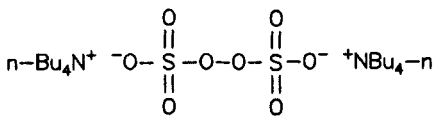
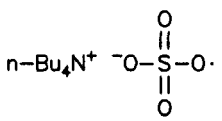
Abstract n-Tetrabutylammonium Peroxydisulfate has been successfully synthesized and turned out to be a sulfate radical source which can be utilized for the efficient organic syntheses: chemoselective oxidations of alcohols to ketones, 2-tetrahydrofuranylation of alcohols, ß-masked formylation of α,ß-unsaturated ketones, high diastereofacial formylation of α,ß-unsaturated ketones in five membered ring systems, and α-masked formylated ketones of nitroolefins.

Tetrabutylammonium peroxydisulfate was prepared by the reaction of tetrabutylammonium hydrogen sulfate with potassium peroxydisulfate in the phase transfer reaction system in water and methylene chloride.[1,2]



1

Tetrabutylammonium Peroxydisulfate
$((TBA)_2S_2O_8)$

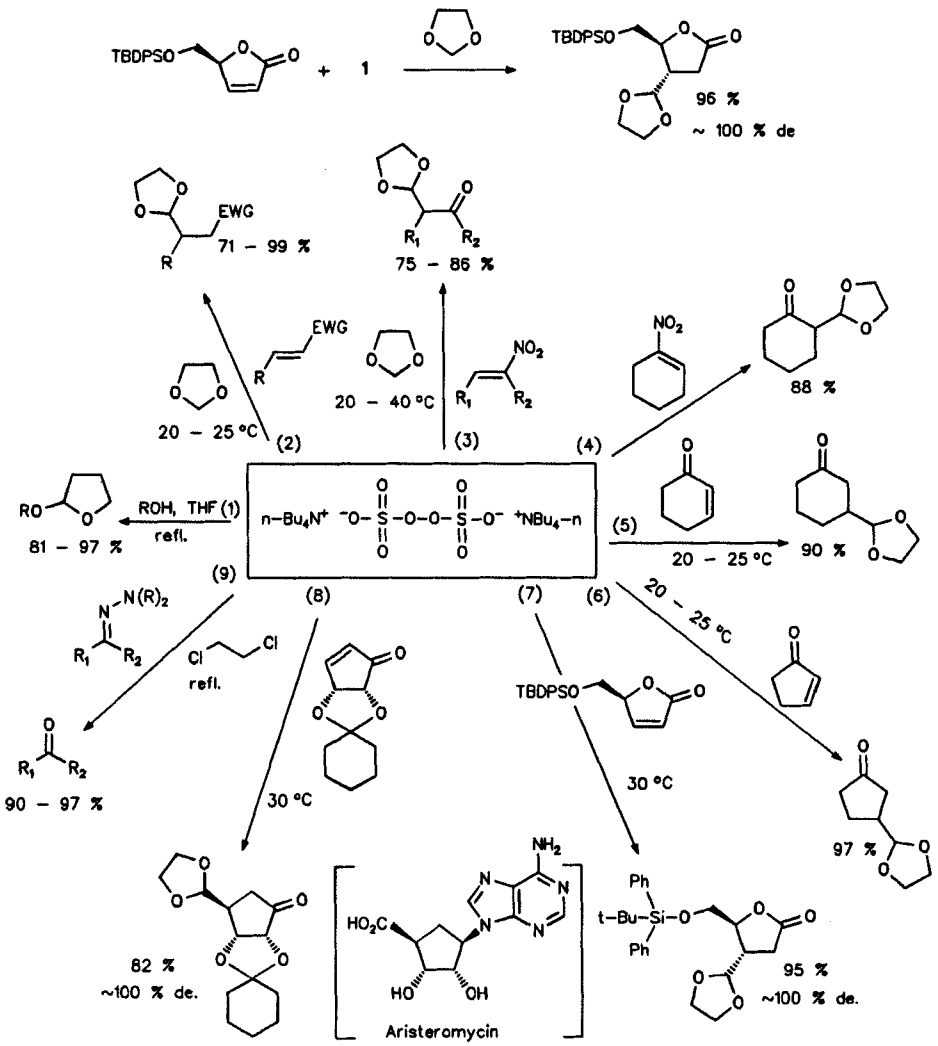


2

Tetrabutylammonium Sulfate radical

In contrast to the known peroxydisulfates such as sodium peroxydisulfate which are only soluble in aqueous media, $(TBA)_2S_2O_8$ (**1**) is very soluble in most of organic solvents such as benzene, CH_2Cl_2, $CHCl_3$, acetonitrile, THF and acetone. Thus various efficient reactions with **1** have been developed in aprotic organic solvents. The peroxydisulfate (**1**) gains of great advantage over metal peroxydisulfates in forming clean-cut

sulfate radical (**2**) under the anhydrous conditions where formation of hydroxyl radical can be avoided.



Various allylic or benzylic primary or secondary alcohols were oxidized to the corresponding aldehydes or ketones in excellent yields respectively in the presence of **1** in organic solvents under argon atmosphere.

Direct tetrahydrofuranylation and tetrahydropyranylation of alcohols: Under the similar conditions described above in THF or THP (tetrahydropyrane), alcohols containing multifunctional

groups were tetrahydrofuranylated[2] ot tetrahydropyranylated.[3] Thus, the one step etherfications can be useful methods for protecting alcohols. These procedures are remarkably simple and can be carried out through radical coupling under nearly neutral conditions. ß-Masked formylation of α,ß-unsaturated ketones: The electron-deficient olefins reacted with 1,3-dioxolane in the presence of **1** to give ß-masked formylated product by 1,4-addition in excellent yields.[3] The reaction apears to be initiated via formation of 1,3-dioxolane radical by electron transfer from one of the two oxygens of dioxolane to sulfate radical. The oxolane radical may add to the double bond of the electron-deficient olefin. While various nitroolefins reacted with **1** in 1,3-dioxolane to give the corresponding α-masked formylated ketones.

The stereoselective functionalization at the C-3 of the α,ß-unsaturated lactones has been examined. (S)-5-(t-butyldiphenylsiloxylmethyl)-2 (5H)-furanose was treated with **1** in 1,3-dioxolane to give one diastereoisomer (ca. 100 % de) of ß-masked formylated lactone.[3]
Many other α,ß-unsaturated lactones are ß-masked formylated.

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