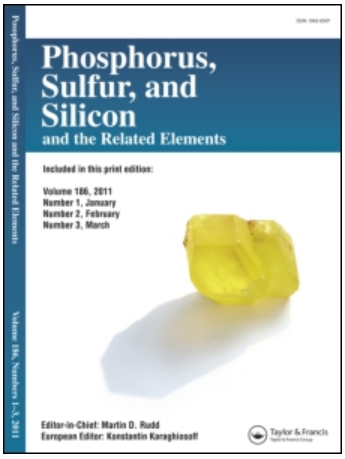

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kim, Yong Hae and Choi, Hyun Chul(1997) 'Novel β-Masked Formylation of α,β-Unsaturated Ketones and Lactones by Tetra-n-Butylammonium Sulfate Radical', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 327 — 328
To link to this Article: DOI: 10.1080/10426509708545532
URL: http://dx.doi.org/10.1080/10426509708545532

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 327–328
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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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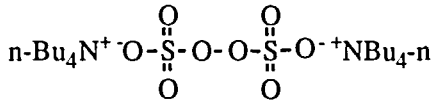
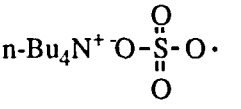
Tetra-n-butylammonium peroxydisulfate was prepared and found to be a good source of tetra-n-butylammonium sulfate radical by its oxygen - oxygen bond cleavage. The sulfate radical can be utilized for the efficient organic syntheses in organic solvents. Electron deficient olefins such as α,β-unsaturated 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 (~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**, $(TBA)_2S_2O_8$) 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
$(TBA)_2S_2O_8$



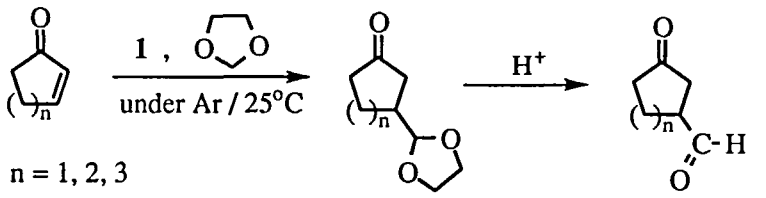
2

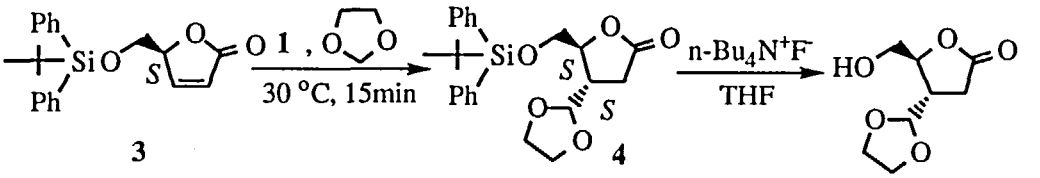
Tetra-n-butylammonium sufate radical

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-

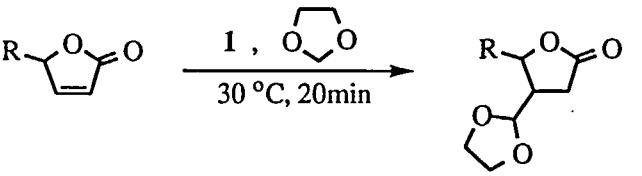
butyldiphenylsilyloxymethyl)-2(5*H*)-furanose (**3**) was synthesized from L-glutamic acid[4] and reacted with 1,3-dioxolane in the presence of **1** to afford β-masked formylated products (**4**) in the extremely high diasterofacial selectivity (ca 100 %).[5]





96%, ~100% de

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



R = H : 90%

R = CH_3 : 92%

R = C_4H_9 : 94%

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