

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpss20>

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

Yong Hae Kim & Hyun Chul Choi

^a Department of Chemistry , Korea Advanced Inst. of Science and Technology , Yusong-gu, Taejon 305-701, Korea

^b Department of Chemistry , Korea Advanced Inst. of Science and Technology , Yusong-gu, Taejon 305-701, Korea

Published online: 17 Mar 2008.

To cite this article: Yong Hae Kim & Hyun Chul Choi (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, DOI: [10.1080/10426509708545532](https://doi.org/10.1080/10426509708545532)

To link to this article: <http://dx.doi.org/10.1080/10426509708545532>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

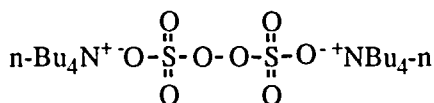
Novel β -Masked Formylation of α,β -Unsaturated Ketones and Lactones by Tetra-*n*-Butylammonium Sulfate Radical

YONG HAE KIM* and HYUN CHUL CHOI

*Department of Chemistry, Korea Advanced Inst. of Science and
 Technology, Yusong-gu, Taejon 305-701, Korea*

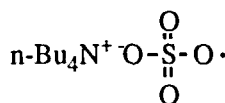
Tetra-*n*-butylammonium peroxydisulfate was prepared and found to be a good source of tetra-*n*-butylammonium sulfate radical by its oxygen-oxygen bond cleavage. The sulfate radical can be utilized for the efficient organic syntheses in organic solvents. Electron deficient olefins such as α,β -unsaturated 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
 $(\text{TBA})_2\text{S}_2\text{O}_8$



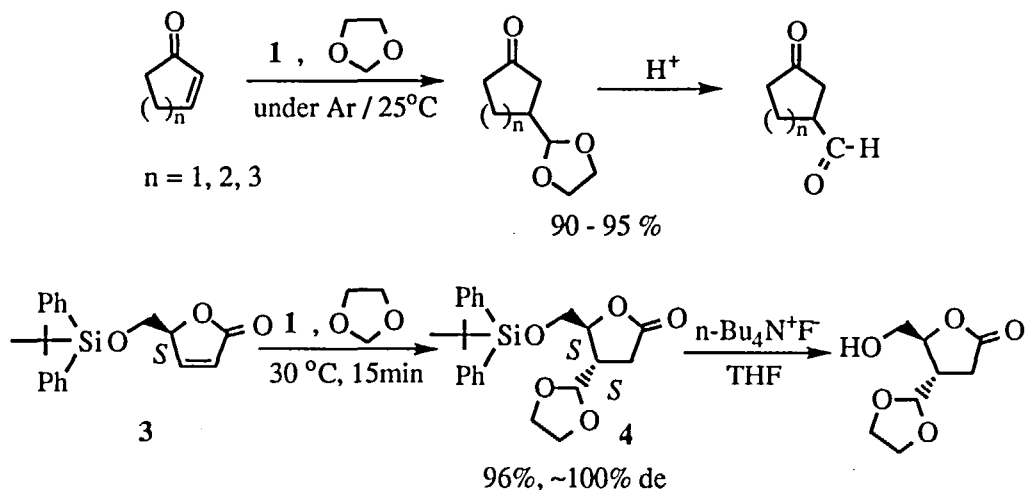
2

Tetra-*n*-butylammonium
 sulfate radical

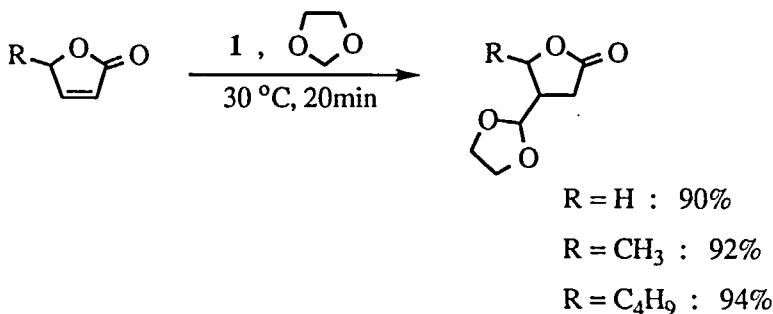
In contrast to the known metal peroxydisulfate such as sodium and potassium peroxydisulfate which are soluble in aqueous media, **1** is very soluble in most of organic solvents. Thus **1** gains of great advantage over metal peroxydisulfate or ammonium peroxydisulfate in forming relatively stable sulfate 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.



REFERENCES

1. Y. H. Kim, in *Organic Peroxides*, edited by W. Ands (John Wiley & Sons, 1992), Chapt. 8 " Sulfur and Phophorus Peroxide"
2. J. C. Jung, H. C. Choi, and Y. H. Kim, *Tetrahedron Lett.* 34, 6063 (1993).
3. Y. H. Kim and J. C. Jung, unpublished data.
4. S. Hanessian and S. P. Sahoo, *Tetrahedron Lett.* 26, 5627, 5631 (1985)
5. Y. H. Kim and H. C. Choi, unpublished data