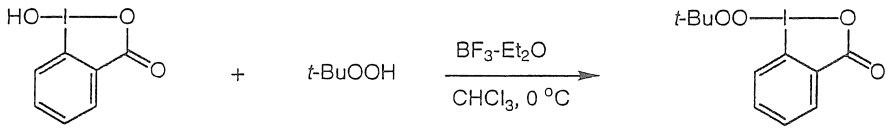
Utilization of Fossil Seawater Component in Organic Synthesis

Masahito Ochiai and Takuya Sueda
Faculty of Pharmaceutical Sciences, University of Tokushima

Summary

Japan is dependent on the importation of the majority of raw materials from overseas, but can be proud for the production of iodine, where it is a leading manufacturer in the world. Industrial iodine is produced from fossil seawater obtained from underground. More than 80% of the produced iodine is exported to various countries of the world. However, we have to rely on the United States and Europe for importation of the majority of the products into which iodine is incorporated, for instance, an x-ray contrast medium or a photosensitive agent for photographic film. Our iodine resource is not fully utilized. Our attention has been directed to hypervalent organo-λ^3-iodanes with low toxicity and we are making a study of its use in synthetic organic chemistry.

The organo-λ^3-iodanes which contain an alkylperoxy group as a ligand has not been synthesized probably because of its high tendency to decompose. We have recently found that the Lewis acid-catalyzed ligand exchange of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one **1** with *tert*-butyl hydroperoxide affords the crystalline peroxy-λ^3-iodane **2**. The peroxy-λ^3-iodane **2** is very stable in the solid state and can be stored at room temperature for over one year with no decomposition.



1 **2**

Iodane **2** is an interesting compound since it contains *tert*-butylperoxy group and a trivalent iodine in the same molecule, both of which are powerful oxidants. Our study was directed to a development of new oxidation reactions using the iodane **2** and the following results were obtained.

1) The peroxy-λ^3-iodane **2** oxidizes benzyl and allyl ethers to the esters at room temperature in the presence of alkali metal carbonates. Since this reaction is compatible with many protecting groups, this new method provides a convenient and effective alternative to the usual reductive deprotection.

2) Benzyl and propargyl alcohols are oxidized to the carbonyl compounds with the iodane **2**. The reaction involves generation of α-hydroxy radicals, which can be trapped with electron deficient vinyl sulfones. α-Oxy radicals are also generated from cyclic ethers and acetals by the reaction with the iodane **2**.