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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

OXIDATION OF THE ALKYL-, ARYL-, AND AMINO-SULFONIUM IONS TO THE SULFOXONIUM IONS AND ITS REACTION MECHANISM

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To cite this Article Kobayashi, Michio, Okuma, Kentaro and Takeuchi, Hiroyuki(1979) 'OXIDATION OF THE ALKYL-, ARYL-, AND AMINO-SULFONIUM IONS TO THE SULFOXONIUM IONS AND ITS REACTION MECHANISM', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 163

To link to this Article: DOI: 10.1080/03086647908080355
URL: http://dx.doi.org/10.1080/03086647908080355

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Oxidation of the Alkyl-, Aryl-, and Amino-sulfonium Ions to the Sulfoxonium Ions and Its Reaction Mechanism

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Hitherto, the preparative method of the sulfoxonium ions has been practically limited to the alkylation of the sulfoxides with methyl iodide. The yields of the desired sulfoxonium salts by this method are usually poor except that of trimethylsulfoxonium iodide. Diarylalkyl- or triaryl-sulfoxonium ions can not be prepared by this alkylation.

We wish to report the new general method for the syntheses of these sulfoxonium ions and also of the triaminosulfoxonium ion, a new class of the sulfur compounds, by the oxidation of the appropriate sulfonium salts with the peracids under the basic conditions. The yields usually amount to 50-80%.

Oxidation of (S)(+)-ethylmethylphenylsulfonium perchlorate with perbenzoate in H_2^0 -MeOH gave the (R)(+)-ethylmethylphenylsulfoxonium ion with the retention of the configuration.

The bicyclic sulfonium salt containing the sulfur atom at the bridgehead position could be oxidized by m-chloroperbenzoate to the corresponding sulfoxonium ion.

These findings indicate that the peracid oxidation of the sulfonium salt proceeds by the front-side attack, probably through the sulfurane intermediate.

