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Kei Goto; Michel Holler; Gaku Yamamoto; Renji Okazaki

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Syntheses and Structures of Stable Sulfenyl Iodides Bearing Novel Bowl-Type and Dendrimer-Type Substituents

KEI GOTO^a, MICHEL HOLLER^b, GAKU YAMAMOTO^a and
RENJI OKAZAKI^b

^a*Department of Chemistry, School of Science, Kitasato University, 1-15-1
Kitasato, Sagami-hara 228-8555, Japan and* ^b*Department of Chemistry,
Graduate School of Science, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-0033, Japan*

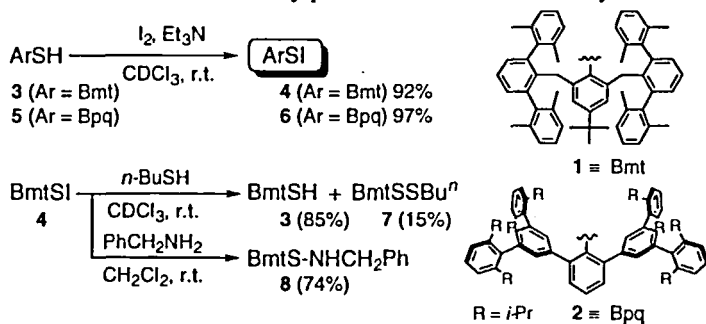
Arenesulfenyl iodides with unprecedented stability were synthesized by iodine oxidation of the corresponding arenethiols bearing bowl-type and dendrimer-type substituents. X-ray crystallographic analysis established their monomeric structures.

Keywords: sulfenyl iodides; steric protection; X-ray analysis; oxidation

Sulfenyl iodides (RSI) have been postulated as important intermediates of iodination reaction in the human thyroid gland as well as in iodine-oxidation of thiols. However, information about them is very scant because of their instability resulting from their very easy disproportionation reaction ($2\text{RSI} \rightarrow \text{RSSR} + \text{I}_2$) and no sulfenyl iodide stable at room temperature has so far been structurally characterized.^[1] In order to clarify their role in the organic and biological reactions, it is considered to be prerequisite to study its chemistry by using a stable well-defined compound. Recently, we reported the synthesis of a stable

arenesulfenic acid by direct oxidation of a thiol by taking advantage of a novel bowl-type substituent.^[2] Here we report the syntheses of arenesulfonyl iodides with unprecedented stability by iodine oxidation of the corresponding areneithiols along with their crystal structures.

Oxidation of thiol **3** bearing a bowl-type substituent **1** with an equimolar amount of I_2 in the presence of triethylamine resulted in the quantitative formation of sulfonyl iodide **4**, which was isolated by silica gel chromatography as dark brown crystals. The stability of **4** was remarkable both in the crystalline state and in solution; it showed a melting point at 257 °C and no decomposition was observed even after heating at 80 °C for 12 h in toluene-*d*₈. The structure of **4** was established by X-ray crystallographic analysis. It was found that the S-I functionality is surrounded by the two rigid *m*-terphenyl units and sufficiently separated from those of neighboring molecules. In spite of high thermal stability, **4** undergoes ready reactions with some reagents such as 1-butanethiol and benzylamine. A stable sulfonyl iodide was also synthesized by taking advantage of a novel dendrimer-type substituent **2**, which is more easily accessible. Iodine oxidation of thiol **5** afforded sulfonyl iodide **6**, whose structural analysis revealed that the molecular cleft of **2** effectively protects the S-I functionality.



References

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