Synthesis and crystal structure of an arenesulfenyl iodide with unprecedented stability

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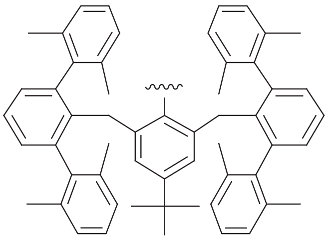
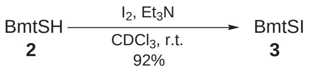
An arenesulfenyl iodide with unprecedented stability was synthesized by oxidation of a thiol bearing a novel bowl-type substituent with iodine, whose monomeric structure was determined by X-ray crystallographic analysis.

Sulfenyl iodides (RSI) have been suggested to play decisive roles as reaction intermediates in iodination reactions in the human thyroid gland[1] as well as in iodine oxidation of thiols.[2] Although more information concerning simple well defined sulfenyl iodides is desirable, the study of their chemistry has been hampered by their instability resulting from the ready disproportionation reaction (2RSI $\longrightarrow$ RSSR + I_2), the ΔH value of which is -4.30 kcal mol^{-1}.[3] In the solid state they are much less stable partly because of the large sublimation energy of solid I_2 (14.9 kcal mol^{-1}). Several aromatic acylsulfenyl iodides have been isolated and shown to be stable at room temperature for several hours, but they decompose below 50 °C.[4] The only structural analysis of a sulfenyl iodide was carried out for Ph_3CSI at -118 °C,[5] which is stable in the solid state at -78 °C and in solution in the dark.[6] Thus, no sulfenyl iodide stable at room temperature has so far been structurally characterized.[7] On the other hand, the reported value of the S–I bond dissociation energy is not so small (49.4 ± 2 kcal mol^{-1} for HS–I),[8] suggesting that this species will be stable if the disproportionation process is suppressed. Recently, we reported that a stable arenesulfenic acid can be obtained by direct oxidation of a thiol by taking advantage of a novel bowl-type substituent **1** (denoted as Bmt hereafter).§[9,10] Here we describe the synthesis of an arenesulfenyl iodide with unprecedented stability by iodine oxidation of the corresponding arenethiol, along with its crystal structure.



1 ≡ Bmt

The sulfenyl iodides isolated so far have been synthesized mostly by halide exchange reaction of the corresponding sulfenyl chloride[6] or oxidation of the corresponding heavy metal thiolates.[4,11] There has been no example of the synthesis of a stable sulfenyl iodide by iodine oxidation of a thiol although this reaction has been considered to involve a sulfenyl iodide as an intermediate and seems to be the most straightforward synthetic pathway to it. Oxidation of thiol **2**[12] bearing the Bmt group with an equimolar amount of I_2 in the presence of triethylamine in $CDCl_3$ resulted in the quantitative formation of sulfenyl iodide **3**, which was isolated by silica gel chromatography as dark brown crystals in 92% yield (Scheme 1).¶ The stability of **3** 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. It is stable at room temperature in air for more than several months. In the UV–VIS spectrum, **3** showed an absorption maximum at 328 nm in chloroform.



Scheme 1

The structure of **3** was finally established by X-ray crystallographic analysis.‖ An ORTEP drawing of **3** is shown in Fig. 1 with selected bond lengths and angles. The figure clearly shows that the two rigid *m*-terphenyl units surround the S–I functionality like the brim of a bowl, thus preventing the disproportionation process effectively. It was reported that in the crystal structure of Ph_3CSI at -118 °C the molecules are linked *via* short S···I contacts of 3.210(4) Å so that a zig-zag chain is formed.[5] By contrast, the shortest intermolecular S···I distance in **3** is 6.654(2) Å, clearly indicating its monomeric nature. The S–I bond length [2.386(2) Å] is distinctly shorter than that of Ph_3CSI [2.406(4) Å] probably because of the absence of the intermolecular interaction. The S–I moiety is almost perpendicular to the benzene plane [I(1)–S(1)–C(1)–C(2) angle, 87.7(6)°].

In spite of its high thermal stability, sulfenyl iodide **3** undergoes ready reactions with some reagents. Treatment of **3** with butane-1-thiol (8 equiv.) in the presence of triethylamine reduced it to the parent thiol **2** with the formation of a small

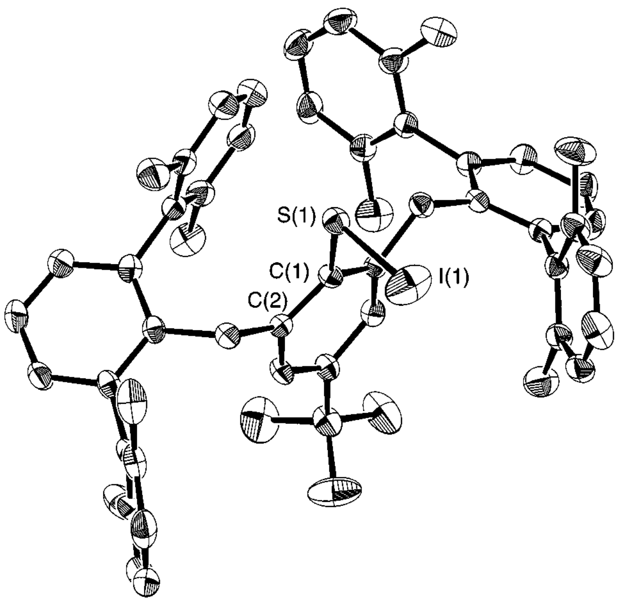
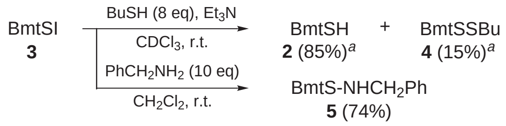
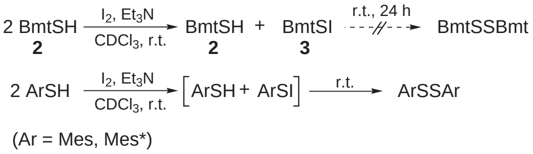


Fig. 1 Crystal structure of **3** (ORTEP drawing; thermal ellipsoids at 30% probability level). Selected bond lengths (Å), bond angles (°), and torsion angle (°): S(1)–I(1), 2.386(2); S(1)–C(1), 1.783(7); I(1)–S(1)–C(1), 101.3(2); I(1)–S(1)–C(1)–C(2), 87.7(6).



Scheme 2 [a] Estimated by ^{1}H NMR

amount of disulfide **4** (Scheme 2). The reaction of **3** with benzylamine (10 equiv.) readily afforded sulfenamide **5**. On the other hand, **3** was found to be unreactive toward thiol **2** bearing the same substituent. Oxidation of **2** with 0.5 equiv. of I_2 in the presence of triethylamine afforded a 1 : 1 mixture of **2** and **3**, no disulfide formation being detected even after 24 h at room temperature (Scheme 3). These results imply that two species which are otherwise incompatible can be present in the same system with retention of their reactivities toward other reagents when they bear a bowl-type substituent. Under the same conditions, 2,4,6-trimethylbenzenethiol (MesSH) was immediately oxidized to MesSSMes and even 2,4,6-tri-*tert*-butylbenzenethiol (Mes*SH) afforded Mes*SSMes* although the reaction was much slower. Apparently, the bowl-shaped structure of the Bmt group is more effective for prevention of dimerization than a Mes* group, where the functionality is more closely shielded.



Scheme 3 Mes* = $C_6H_2Bu^t_3$-2,4,6

This work was partly supported by Grants-in-Aid for Scientific Research (No. 07854035 and 94187) from the Ministry of Education, Science, Sports and Culture, Japan. We also thank Tosoh Akzo Co., Ltd. for the generous gift of alkyllithiums. M. H. is grateful to the Japan Society for the Promotion of Science for the Postdoctoral Fellowship for Foreign Researchers.

Notes and References

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§ Bmt denotes 4-*tert*-butyl-2,6-bis[(2,2'',6,6''-tetramethyl-*m*-terphenyl-2'-yl)methyl]phenyl.

¶ **3:** mp 252–257 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (s, 9H), 1.95 (brs, 24H), 3.70 (brs, 4H), 6.46 (s, 2H), 6.84 (brs, 8H), 6.94 (t, ^3J = 7.3 Hz, 4H), 7.03 (d, ^3J = 7.5 Hz, 4H), 7.33 (t, ^3J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0 (q), 30.8 (q), 34.7 (s), 34.8 (t), 125.0 (d), 126.8 (d), 127.0 (d), 127.5(d), 129.3 (d), 129.4 (s), 136.2 (s), 137.2 (s), 140.8 (s), 142.1 (s), 146.2 (s), 151.1 (s); UV–VIS ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 328 nm (4000 dm^3 mol^{-1} cm^{-1}).

‖ *Crystal data* for $3 \cdot 0.5C_7H_8$: $C_{59.5}H_{61}SI$, M = 935.10, monoclinic, space group $P2_1/n$, a = 15.668(8), b = 17.47(1), c = 18.71(1) Å, β = 105.91(4)°, U = 4926(4) Å^3, Z = 4, D_c = 1.261 g cm^{-3}, μ = 7.30 cm^{-1}. The intensity data were collected at 293 K on a Rigaku AFC7R diffractometer with Mo-Kα radiation (λ = 0.71069 Å), and the structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3789 observed reflections [$I > 3.00\sigma(I)$] and 539 variable parameters with $R(R_w)$ = 0.058(0.045). CCDC 182/944.

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Received in Cambridge, UK, 1st May 1998; revised manuscript received 10th July 1998; 8/05449E