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Preparation and Crystal Structure of a Parent 1-Arylbenzo[b]thiophenium Triflate and Its Derivatives

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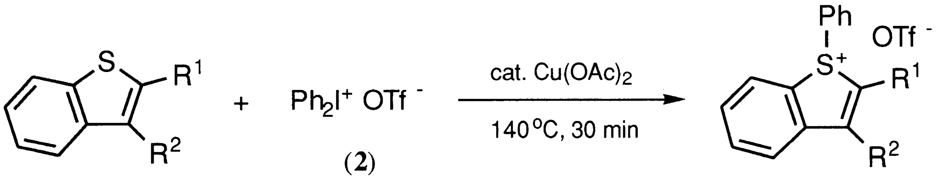
A parent 1-phenylbenzo[b]thiophenium triflate is prepared by reaction of benzo[b]thiophene and diphenyliodonium triflate and the single crystal X-ray analysis shows a pyramidal structure about sulfur and a short phenyl-sulfur bond. The less-substituted 1-phenylbenzo[b]thiophenium triflates are prepared successfully by this method.

Recently much interest has been paid to chemistry of sulfonium salts in connection with the chemistry of hypervalent organosulfur compounds 1) and the application to important photoinitiators for acid catalyzed processes.2) Benzo[b]thiophenium salts are interesting heterocyclic sulfonium systems3) but the investigation has been confined to the S-alkyl substituted systems. The S-alkylation of benzo[b]thiophenes is achieved by using alkyl halides in the presence of silver salts or a powerful alkylating agent4) and the S-alkylbenzo[b]thiophenium salts show the pyramidal structure around sulfur and the dealkylating property. However, the corresponding S-arylated benzo[b]thiophenium salts have not been investigated.

We have found that electrophile-induced cyclization of [2-(arylthio)phenyl]-substituted alkenes5) or alkynes6) is a useful method for the preparation of 1-arylbenzo[b]thiophenium salts. However, some problems remain in this procedure: (a) The intramolecular cyclization is strongly dependent upon the substituent. Unsubstituted or less-substituted [2-(arylthio)phenyl]ethenes or ethynes give poor yields of the cyclized benzo[b]thiophenium salts. (b) Preparation of the starting *ortho*-substituted substrates is not simple and needs several steps. Despite the difficulty in the preparation of the parent system, the preparation is required to learn the fundamental property of the benzo[b]thiophenium ion.

S-Arylation of benzo[b]thiophene using a benzenediazonium salt7) is not suitable for the present purpose. Diaryliodonium salts have been used effectively in arylation of nucleophilic substrates.8) Especially, Crivello and Lam have prepared triarylsulfonium salts by arylation of diaryl sulfides.9) This simple method prompted us to apply to arylation of benzo[b]thiophenes. Here we report a direct S-arylation of benzo[b]thiophenes to solve the problems for the intramolecular cyclization and describe a crystal structure of the simplest, parent 1-phenylbenzo[b]thiophenium triflate.

A direct arylation of benzo[b]thiophenes was examined using diphenyliodonium triflate and a copper(II) catalyst. Heating a mixture of benzo[b]thiophene (**1a**) and diphenyliodonium triflate (**2**) in the presence of a catalytic amount of copper(II) acetate was carried out at 140 °C for 30 min under N_2 atmosphere. After washing off the resulting iodobenzene with ether, white crystals of 1-phenylbenzo[b]thiophenium triflate (**3a**) were obtained in 87% isolated yield.



(1) (2) (3)

a: $R^1 = R^2 = H$
b: $R^1 = H$, $R^2 = Me$
c: $R^1 = Me$, $R^2 = H$
d: $R^1 = R^2 = Me$

a: $R^1 = R^2 = H$; (87%)
b: $R^1 = H$, $R^2 = Me$; (81%)
c: $R^1 = Me$, $R^2 = H$; (94%)
d: $R^1 = R^2 = Me$; (94%)

The arylation using diphenyliodonium triflate (**2**) works well in the cases of the methyl-substituted benzo[b]thiophenes (**1b-d**). Especially, it is noteworthy that the phenylation of unsubstituted benzo[b]thiophene (**1a**) give a high yield of 1-phenylbenzo[b]thiophenium triflate (**3a**), which cannot be prepared by other methods using intramolecular cyclization.[5,6] 1-Phenylbenzo[b]thiophenium triflates (**3**) were stable even in nucleophilic solvents (i.e., alcohols, DMSO, and pyridine). The structures of **3** were fully characterized by ^1H and ^{13}C NMR, IR spectra, and the combustion analysis.

A suitable single crystal of **3a** was obtained by a slow evaporation from a mixed solvent of CH_2Cl_2 and CCl_4 and analyzed by a single crystal X-ray diffraction.[10] The crystal structure and relevant structural data are given in Fig. 1 and Table 1, respectively. A racemic pair of 1-phenylbenzo[b]thiophenium triflate **3a** exists in the unit cell. The structure consists of the sulfonium cations and triflate anions. The short interionic S...O distances are 3.014(5) and 3.017(5) Å, which are shorter than van der Waals S...O separation (3.15 Å).[11] The bonds around the sulfur are pyramidally arranged and the angles around the sulfur are 91.4(2), 104.5(2), and 105.4(2)°, suggesting that the sulfur is in a state of sp^3 hybridization. The characteristic structural change is in the short phenyl-sulfur bond compared with 1,2,3,5-tetramethylbenzo[b]thiophenium tetrafluoroborate (**4**).[4g] The bond length of the phenyl-sulfur bond is 1.786(4) Å and the carbon-sulfur bond lengths in the ring are 1.769(5) and 1.764(4) Å. The bond length of the phenyl-sulfur bond (1.786 Å) is shorter than the corresponding methyl-sulfur bond (1.806 Å) of **4**.[4g] Furthermore, the bond lengths in the thiophene ring of the parent benzo[b]thiophenium triflate (**3a**) are short in 0.021-0.038 Å compared with the case of 1,2,3-triphenylbenzo[b]thiophenium perchlorate.[5b] This is attributed to the elongation by the substituent, phenyl group.

In summary, we have found direct S-arylation of benzo[b]thiophenes providing 1-arylbenzo[b]thiophenium salts. This preparation is excellent in the synthesis of a parent, unsubstituted 1-phenylbenzo[b]thiophenium ion. The parent 1-phenylbenzo[b]thiophenium triflate prepared by this method is analyzed by a single crystal X-ray diffraction. The studies on the scope and limitations of this method and the detail mechanism on the arylation are now in progress.

Table 1. Selected Interatomic Distances and Bond Angles

a) Bonded distances (Å)	
S(1) - C(1)	1.769(5)
S(1) - C(7)	1.764(4)
S(1) - C(9)	1.786(4)
C(1) - C(2)	1.308(8)
C(2) - C(8)	1.447(7)
C(7) - C(8)	1.401(6)
(b) Non-bonded distances (Å)	
S(1) ... O'(1)	3.014(5)
S(1) ... O(3)	3.017(5)
(c) Bond angles (deg)	
C(1) - S(1) - C(7)	91.4(2)
C(1) - S(1) - C(9)	104.5(2)
C(7) - S(1) - C(9)	105.4(2)

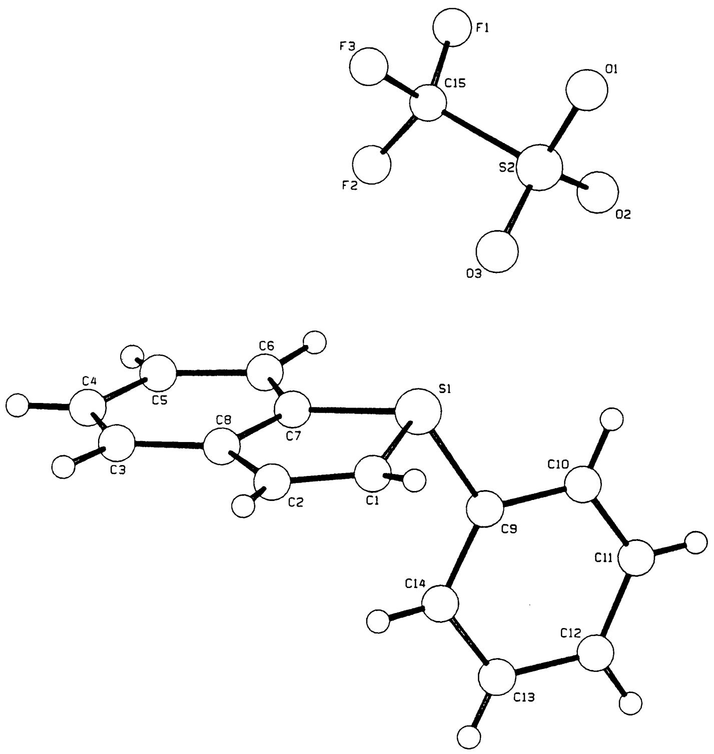


Fig. 1. PLUTP representation of **3a** (50.0% probability ellipsoids).

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10) Crystal data of **3a**: $C_{15}H_{11}F_3O_3S_2$, FW = 360.37, crystal dimensions 0.300 x 0.300 x 0.050 mm, triclinic, space group P1 (#2), a = 9.928(2), b = 10.285(3), c = 9.754(2) Å, α = 93.10(2), β = 119.10(1), γ = 110.34(2)^o, V = 785.2(4) Å^3, Z = 2, D_c = 1.524 g/cm^3. All measurements were made on a Rigaku AFC 5R diffractometer with graphite monochromated CuKα radiation λ = 1.54178 Å, μ = 34.90 cm^{-1}. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1747 observed reflections ($I > 3.00\sigma(I)$) and 239 variable parameters and converged with unweighed and weighted agreement factors of R = 0.058 and R_w = 0.076.

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