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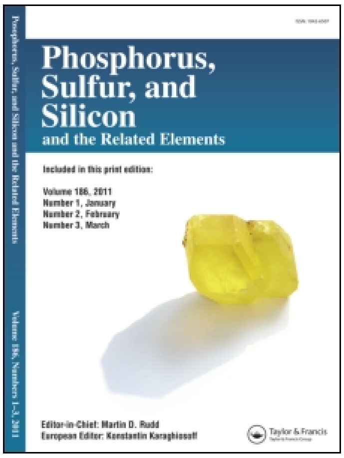

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Synthesis and Characterization of Thiophenetriptycene-8-sulfenic Acid

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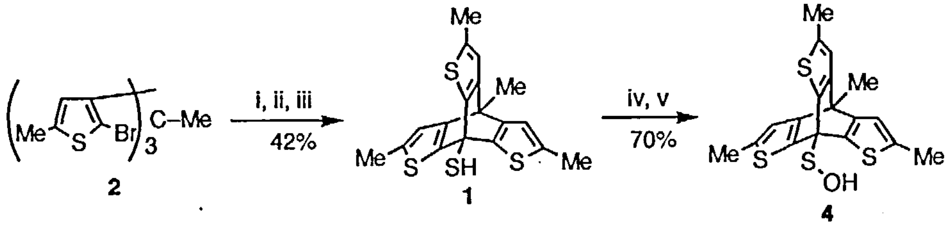
Abstract: Reaction of the trilithium salt, prepared by treatment of 1,1,1-tris(2-bromo-5-methyl-3-thienyl)ethane, with *O,O'*-diethyl thiocarbonate gave thiophenetriptycene-8-thiol in 42% yield. The thiol was not oxidized with *m*-chloroperoxybenzoic acid (MCPBA). However, treatment of the thiol with NaH in THF followed by oxidation with MCPBA gave thiophenetriptycene-8-sulfenic acid in 70% yield. The structure of the sulfenic acid was determined by spectroscopic means and X-ray single-crystal analysis.

KEY WORDS: Thiol, Oxidation, Sulfenic Acid, Thiophenetriptycene

Although most of sulfenic acids are extremely reactive intermediates,[1] some sulfenic acids stabilized by intramolecular interactions and steric protection or electronic effects of substituents have been isolated.[1,2] The isolable sulfenic acids were, in most cases, synthesized by solvolysis of sulfenate esters or β-elimination of sulfoxides. We report here the first example of the preparation of an isolable sulfenic acid, where the sulfur atom is bonded to the sp^3 carbon atom, by peroxyacid oxidation of the corresponding sodium thiolate with utilizing the 8-thiophenetriptycyl group[3] as a steric protection group for the sulfenic acid resistant to further oxidation.

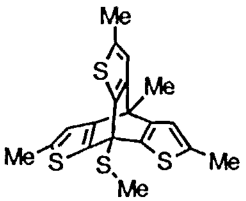
Thiophenetriptycene-8-thiol **1** was prepared by reaction of the trilithium salt, prepared by treatment of tribromide **2** with *t*-butyllithium in THF at -78 °C, with *O,O'*-diethyl thiocarbonate[4] in 42% yield.



i: *t*-BuLi, THF, –78 °C; ii: $S{=}C(OEt)_2$, –78 °C to refl.; iii: H_3O^+; iv: NaH, THF, r.t.; v: MCPBA, 0 °C.

We first examined direct oxidation of the thiol **1** with MCPBA. Surprisingly, thiol **1** was unreactive to MCPBA in CH_2Cl_2, while sulfide **3** was readily oxidized with MCPBA in dichloromethane at 0 °C to yield the corresponding sulfoxide. This contrast would be ascribed to the intrinsically lower nucleophilicity of the thiol sulfur in **1** than that of the sulfide sulfur in **3**. So, thiol **1** was converted to the sodium salt to increase nucleophilicity. Thus, treatment of thiol **1** with a 1.5 molar amount of NaH in THF at room temperature followed by oxidation with a 1.3 molar amount of MCPBA gave the desired sulfenic acid **4** in 70% yield. Under the conditions, neither the corresponding disulfide nor thiosulfinate was formed.

Sulfenic acid **4** is a pale yellow, crystalline compound and stable for a long time in the dark. The structure of **4** was determined by its spectroscopic data[5] and X-ray single-crystal structure analysis.[6] The sulfenic acid **3** is light-sensitive and decomposes to sulfine **4** on exposure to light. The isomerization also occurs by heating or by treatment with an acid. The reaction of **3** with methyl propiolate gave sulfoxide **5** in 72% yield.



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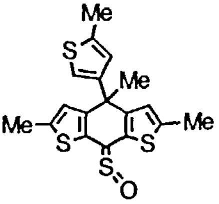

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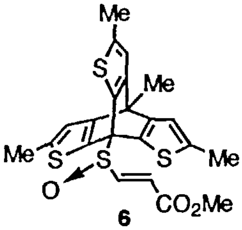

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5. Sulfenic acid **4**: ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.33 (s, 9H), 3.71 (s, 1H, SOH), 6.65 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.8 (CH_3), 15.3 (CH_3), 50.2 (2×C), 119.6 (CH), 135.0 (C), 148.5 (C), 158.2 (C);IR (KBr) 3456 (O-H) cm^{-1}.
6. Crystal data for **4**: trigonal, $P\bar{3}$, $a = 20.340(3)$ Å, $b = 20.340(3)$ Å, $c = 10.028(2)$ Å, $V = 3593$ Å^3, $Z = 8$, $R = 0.0709$, $R_w = 0.0861$. Selected bond lengths and angles: C-S: 1.833(9) Å; S-O: 1.622(9) Å; ∠C-S-O: 102.3(5)°.