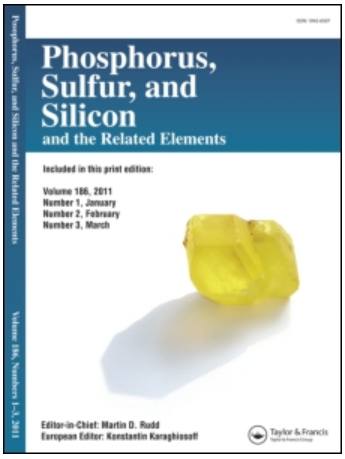

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Synthesis and Properties of the Parent Thiophene 1,1-Dioxide

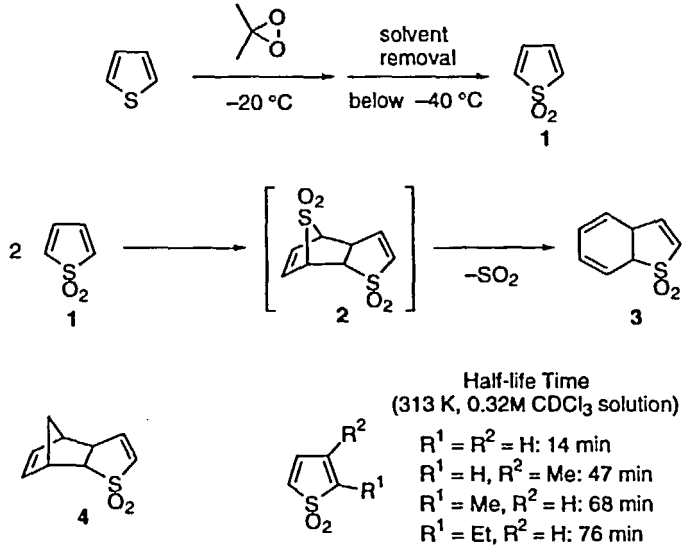
HIDEHIRO NAGASAWA, YOSHIAKI SUGIHARA, AKIHIKO ISHII and JUZO NAKAYAMA

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338–8570, Japan

Thiophene 1,1-dioxides are synthetically and theoretically important compounds which act as 2π- or 4π-components in a range of cycloadditions. Our recent exhaustive literature survey has revealed that more than 300 papers had appeared on the chemistry of thiophene 1,1-dioxides. Among them, at least 33 papers have described the chemistry of the parent thiophene 1,1-dioxide (**1**) theoretically or experimentally. However, despite such enormous efforts, **1** has eluded isolation most likely as a result of a rapid cyclodimerization process. Thus, most of the evidence for its existence comes from chemical trapping experiments. We report here the synthesis, isolation, and full characterization of **1**[1] and its monosubstituted derivatives.

Previously **1** was mainly generated by elimination methods. The method of our choice is the oxidation of thiophene with dimethyldioxirane (DMD). Thus, a dilute solution of thiophene in Me_2CO was treated with DMD (3 equiv) at –20 °C for 36 h. The solvent and the unreacted thiophene were removed thoroughly below –40 °C under reduced pressure, which left **1** in pure form as colorless crystals. The presumed intermediary thiophene 1-oxide is oxidized with DMD faster than thiophene and the yield of **1** is quantitative based on the thiophene consumed. Removal of the solvent below –40 °C is crucial to isolate **1** in pure form to prevent decomposition when concentrated. The dioxide melted at about 6 °C with decomposition and then solidified slowly on standing because of the formation of dimeric and trimeric products.

The structure of **1** was fully characterized by spectroscopies (^{1}H- and ^{13}C-NMR, IR, Raman, UV, and MS). Standing a dilute solution resulted in the dimerization of **1** in a Diels-Alder mode to give **2** (Ea = 64.4 kJ•mol^{-1} and ΔS = –59.8 JK^{-1}mol^{-1}), which rapidly extruded SO_2 to give **3** as the final product. Many attempted reactions of **1** with dienes and dienophiles failed because of the efficient dimerization of **1**, except that cyclopentadiene gave the adduct **4** in good yield. Monosubstituted derivatives, such as 2-methyl-, 3-methyl-, 2-ethyl-, 2-bromo-, and 3-bromothiophene thiophene 1,1-dioxides, are also prepared in similar ways. The half-life times of these compounds are given below.



References

[1] Preliminary results: J. Nakayama, H. Nagasawa, Y. Sugihara, and A. Ishii, *J. Am. Chem. Soc.*, **119**, 9077 (1997).