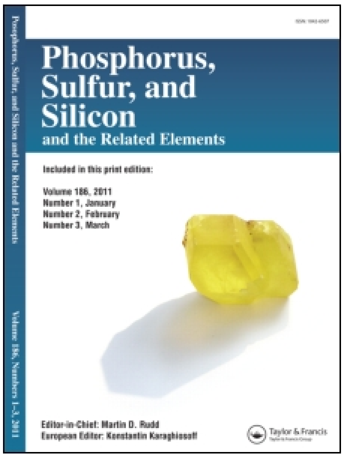

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Activation and Facile Dealkylation of Monooxides of 1,8-Bis(alkylthio)naphthalene and 2,2'-Bis(alkylthio)biphenyl with Triflic Anhydride via Dithiadications

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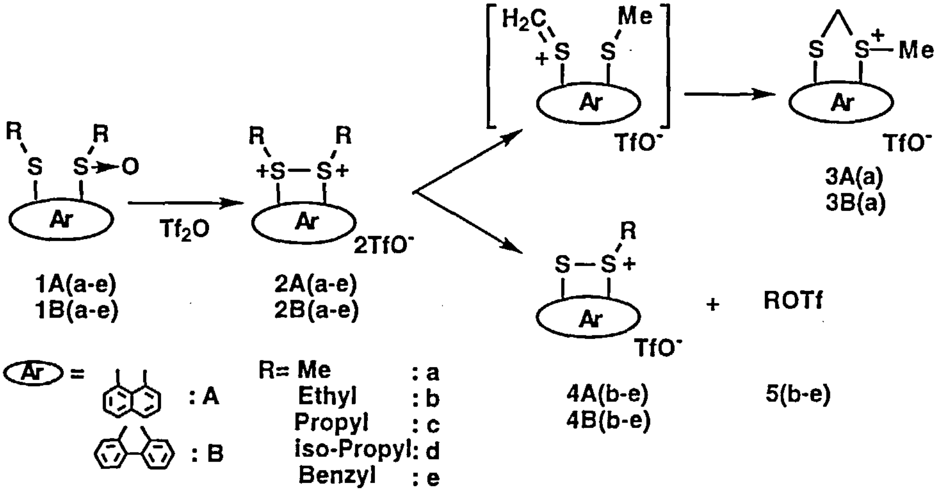
Abstract Dithiadications bearing 1,8-bis(alkylthio)naphthalene **2A(a-e)** and 2,2'-bis(alkylthio)biphenyl **2B(a-e)** structure undergo either the facile deprotonation from the methyl group or dealkylation from the methylene groups by the triflate anion. Dications **2A(a)** and **2B(a)** having methyl groups were deprotonated readily to afford cyclic sulfonium salts **3A(a)** and **3B(a)**. However, dithiadications **2A(b-e)** and **2B(b-e)** having ethyl, propyl, isopropyl and benzyl groups were readily dealkylated even at -45°C to give thiasulfonium salts **4A(b-e)** and **4B(b-e)** and alkyl triflates **5(a-e)** in good yields. The intermediary formation of dithiadications **2A(a-e)** and **2B(a-e)** were confirmed by direct observation using NMR spectroscopy, D-labelled experiments and trapping experiments.

KEY WORDS DEPROTONATION AND DEALKYLATION OF DITHIADICATIONS

Dications of chalcogens are of considerable current interest in heteroatom chemistry. Monooxides of cyclic bissulfides, i.e., 1,5-dithiacyclooctane and dinaphtho[1,8-*bc*]-1,5-dithiocin undergo deoxygenation on treatment with conc. H_2SO_4 or triflic anhydride (Tf_2O) to afford readily the corresponding *stable* dithiadications *via* through-space interaction between the sulfur atoms. Other dithiadications which have an acyclic structure have also been reported but not been studied well due to its instability.

Our attempt to provide dithiadications which have flexible structures were successfully achieved by the reaction of monosulfoxides **1A(a-e)** and **1B(a-e)** of acyclic 1,8-bis(alkylthio)naphthalene and 2,2'-bis(alkylthio)biphenyl with Tf_2O, but unexpectedly, facile deprotonation or dealkylation of these dithiadications was found to proceed quite rapidly (Scheme 1).[1]



SCHEME 1

Dithiadications **2A(a)** and **2B(a)** having methyl groups were deprotonated to afford cyclic sulfonium salts **3A(a)** and **3B(a)** , though the formation of dithiadications could not be observed by NMR spectroscopy. However, dithiadications **2A(b-e)** and **2B(b-e)** having ethyl, propyl, isopropyl and benzyl groups were found to be readily dealkylated even at -45°C to afford thiasulfonium salts **4A(b-e)** and **4B(b-e)** and alkyl triflates **5(b-e)** in good yields. The intermediary formation of dithiadications **2A(a-e)** and **2B(a-e)** was confirmed by the direct observation using NMR spectroscopy, D-labelled experiments and trapping experiments.

This transformation is also interested in view of the activation of the C-S bond of the sulfonium compounds, since except in the case of S-adenosyl methionine (SAM) which mediates methyl transfer to DNA or bioactive compounds *in vivo*, dealkylation of the alkyl group on the sulfonium sulfur atom does not occur readily.

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1. Hidetaka Shima, Ryoji Kobayashi, Tatsuya Nabeshima and Naomichi Furukawa, *Tetrahedron Lett.* **37**, 667 (1996).