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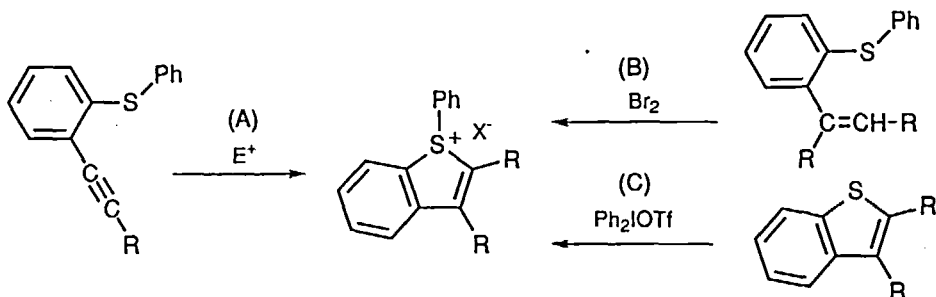
## Synthesis and Reactions of 1-Phenylbenzo[b]thiophenium Salts

TSUGIO KITAMURA,\* KUNIIHIKO MORIZANE, MASA-AKI MIYAJI,  
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1-Phenylbenzo[b]thiophenium salts are prepared and reacted under thermal and photochemical conditions. The chemical behaviors are discussed.

Although chemistry of cyclic sulfonium salts has been extensively studied,<sup>1</sup> benzo[b]thiophenium salts are little noted. The benzo[b]thiophenium salts investigated so far are alkylated ones and labile even in nucleophilic solvents to undergo dealkylation.<sup>1</sup> Thus, several 1-phenylbenzo[b]thiophenium salts have been prepared and examined the chemical behavior. In this paper we report the synthetic methods of 1-phenylbenzo[b]thiophenium salts and the photochemical and thermal reactions.

1-Phenylbenzo[b]thiophenium salts have been found to be successively prepared by the following three methods:<sup>2</sup> (A) intramolecular cyclization of [*o*-(phenylsulfanyl)-phenyl]alkynes with electrophiles such as proton, Br<sub>2</sub>, and PhSCl; (B) bromine-induced cyclization of [*o*-(phenylsulfanyl)phenyl]ethenes; (C) direct phenylation of benzo[b]thiophenes with diphenyliodonium triflate. Methods A and B are suitable for preparation of substituted 1-phenylbenzo[b]thiophenium salts. Method C is applied to unsubstituted and less substituted ones.

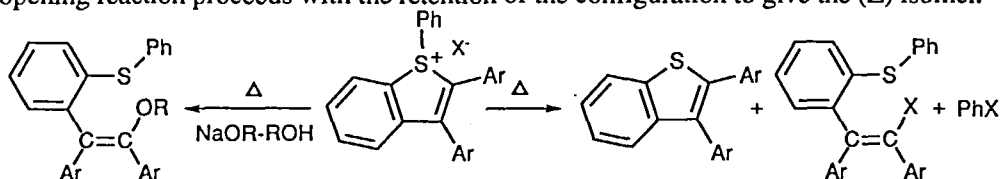


The prepared 1-phenylbenzo[b]thiophenium salts are quite stable even in the presence of nucleophilic solvents. The thermal decomposition of 1,2,3-triarylbenzo[b]thiophenium halides in refluxing toluene gives 1,2-diaryl-1-halo-2-[2-(phenylsulfanyl)-

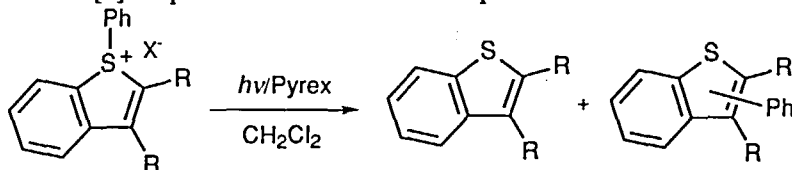
phenyl]ethenes, 2,3-diarylbenzo[b]thiophenes, and halobenzenes. The formation of benzo[b]thiophenes and halobenzenes is attributed to the cleavage of the Ph-S bond with halide ion. The 1-haloethenes are derived from nucleophilic ring opening of the thiophene ring with halide ion and the stereochemistry is (Z) configuration.

Interestingly, the product distribution is dependent upon the halide ion: Cl, Br, and I. The reaction with chloride ion leads to a competition of the Ph-S bond cleavage and the ring opening, whereas iodide ion undergoes the Ph-S bond cleavage only.

On the other hand, the reaction with alkoxide ions results in the exclusive formation of 1-alkoxy-1,2-diaryl-2-[2-(phenylsulfanyl)phenyl]ethenes. The ring-opening reaction proceeds with the retention of the configuration to give the (Z) isomer.



Photochemical reaction of benzo[b]thiophenium salts is complicated. Irradiation of 1-phenylbenzo[b]thiophenium salts with a Pyrex-filtered high-pressure Hg lamp gives benzo[b]thiophenes and 2- and 3-phenylbenzo[b]thiophenes. The phenyl-substituted benzo[b]thiophenes are characteristic of photochemical reaction.



The photochemical reactions of 1-phenylbenzo[b]thiophenium salts are quite different from the thermal reactions. The photochemical fission of the Ph-S bond generating the radical ion pair followed by the recombination is reasonable for the formation of the phenyl-substituted benzo[b]thiophenes.

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