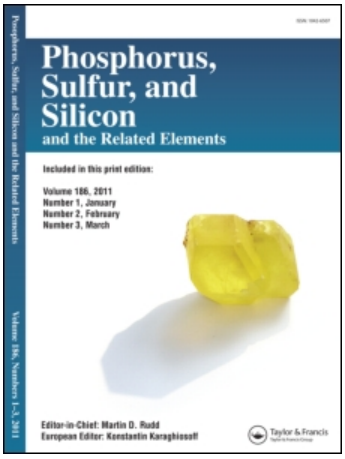


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Tsugio Kitamura; Kunihiko Morizane; Masa-Aki Miyaji; Shin-Ichi Soda; Hiroshi Taniguchi; Yuzo Fujiwara

To cite this Article Kitamura, Tsugio , Morizane, Kunihiko , Miyaji, Masa-Aki , Soda, Shin-Ichi , Taniguchi, Hiroshi and Fujiwara, Yuzo(1997) 'Synthesis and Reactions of 1-Phenylbenzo[b]thiophenium Salts', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 465 — 466
To link to this Article: DOI: 10.1080/10426509708545600
URL: http://dx.doi.org/10.1080/10426509708545600

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 465–466
Reprints available directly from the publisher
Photocopying permitted by license only

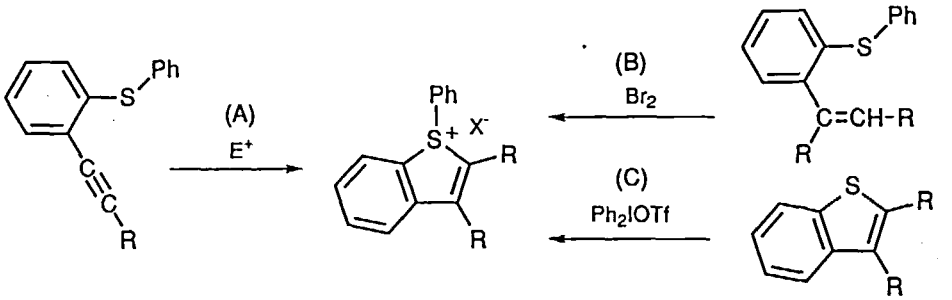
Synthesis and Reactions of 1-Phenylbenzo[b]thiophenium Salts

TSUGIO KITAMURA,* KUNIHIKO MORIZANE, MASA-AKI MIYAJI, SHIN-ICHI SODA, HIROSHI TANIGUCHI, and YUZO FUJIWARA
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812-81, Japan

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,[1] 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.[1] 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.

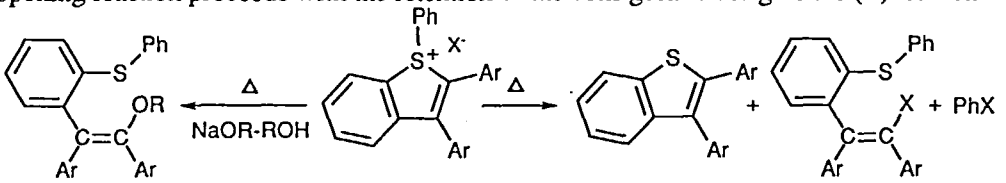
1-Phenylbenzo[b]thiophenium salts have been found to be successively prepared by the following three methods:[2] (A) intramolecular cyclization of [*o*-(phenylsulfanyl)-phenyl]alkynes with electrophiles such as proton, Br_2, and PhSCl; (B) bromine-induced cyclization of [*o*-(phenylsulfanyl)phenyl]ethenes; (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.



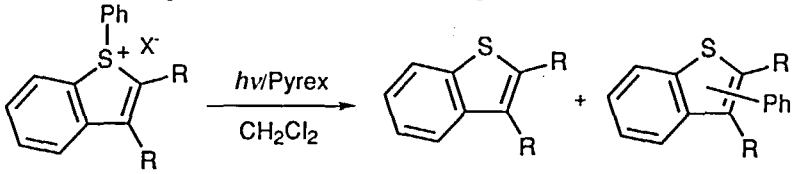
The prepared 1-phenylbenzo[b]thiophenium salts are quite stable even in the presence of nucleophilic solvents. The thermal decomposition of 1,2,3-triarylbenzo[b]-thiophenium halides in refluxing toluene gives 1,2-diaryl-1-halo-2-[2-(phenylsulfanyl)-

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.

REFERENCES

1. C. C. Dittmer and B. H. Patwardhan, in *The Chemistry of the Sulphonium Group*, edited by C. J. M. Stirling and S. Patai (John Wiley & Sons, New York, 1981), Chap. 13, pp. 387-521.
2. T. Kitamura, S. Soda, H. Kawasato, and H. Taniguchi, *Tetrahedron*, **49**, 5055 (1993); T. Kitamura, M. Yamane, R. Furuki, H. Taniguchi, and M. Shiro, *Chem. Lett.*, **1993**, 1703; T. Kitamura, T. Takachi, M. Miyaji, H. Kawasato, and H. Taniguchi, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 1907.