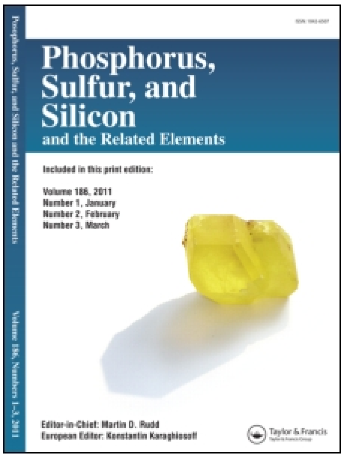


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

5-Arylthianthreniumyl Perchlorates as Synthetic Intermediates

Kyongtae Kim[a]; Han Jo Rim[a]; Hyun Ock Kim[a]; Sang Wook Kim[a]; Young Hee Rim[a]; Song Seok Shin[a]; Man Nyoung Kim[a]
[a] Department of Chemistry, Seoul National University, Seoul, Korea

To cite this Article Kim, Kyongtae , Rim, Han Jo , Kim, Hyun Ock , Kim, Sang Wook , Rim, Young Hee , Shin, Song Seok and Kim, Man Nyoung(1994) '5-Arylthianthreniumyl Perchlorates as Synthetic Intermediates', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 427 — 428

To link to this Article: DOI: 10.1080/10426509408034263

URL: http://dx.doi.org/10.1080/10426509408034263

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 427–428
Reprints available directly from the publisher
Photocopying permitted by license only

Published under license by Gordon and Breach Science Publishers SA
Printed in the United States of America

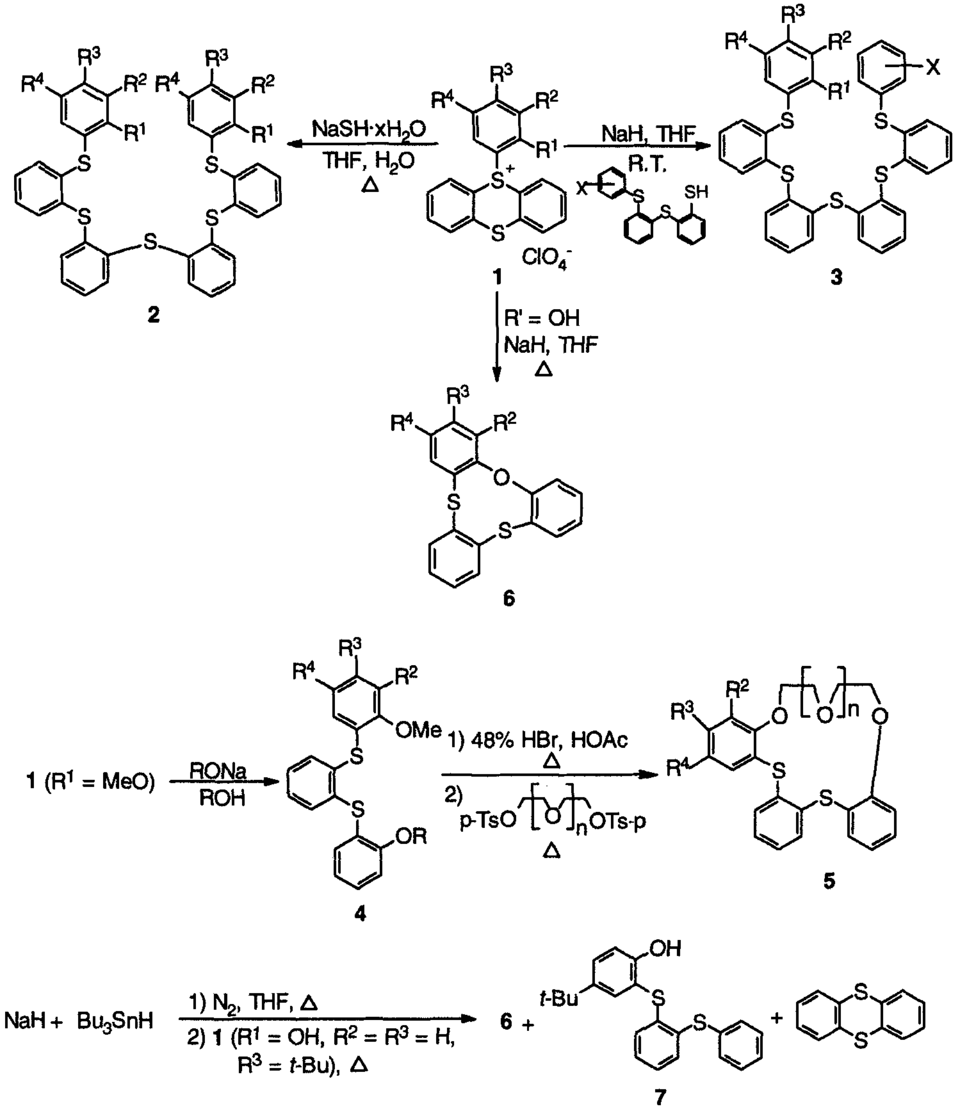
5-ARYLTHIANTHRENIUMYL PERCHLORATES AS SYNTHETIC INTERMEDIATES

KYONGTAE KIM, HAN JO RIM, HYUN OCK KIM, SANG WOOK KIM, YOUNG HEE RIM, SONG SEOK SHIN, AND MAN NYOUNG KIM
Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Although polyarylthioethers have generally been synthesized by the nucleophilic displacement of aryl halides with thiolate in an amide solvent at reflux,[1] the polyarylthioethers consisting of ortho arylthiophenyl moieties can not be prepared by the method foregoing because of the involvement of severe steric hindrance.

In continuation of our studies on the exploration of the synthetic utility of 5-arylthianthreniumyl perchlorates (**1**),[2] we have found that treatment of **1** with sodium hydrosulfide ($NaSH{\cdot}xH_2O$) in aqueous benzene (1:10, v/v), aqueous THF (1:10, v/v), or CH_3CN at reflux gave symmetrical polyarylthioethers **2** in excellent yields.[3] Treatment of 2-mercapto-2'-(arylthio)diphenyl sulfides with NaH in THF, followed by the addition of **1** at room temperature afforded unsymmetrical polyarylthioethers (**3**) in 37-93 % yields.[3] Similar treatment of 5-(2-methoxyaryl)thianthreniumyl perchlorate (**1**, R^1 = MeO) with various alkoxides in the corresponding alcohols at reflux gave dialkoxy compounds (**4**), which can be utilized as a synthon for the synthesis of dithiaoxa cyclic compounds (**5**) after dealkylation of the alkoxy functionalities of **4**. The reaction of 5-(2-hydroxyaryl)thianthreniumyl perchlorate (**1**, R^1 = OH) with NaH (3 equiv) in THF at reflux gave 9-membered dithiaoxa compounds (**6**) (84-96 %) along with a small amount of thianthrene.

In order to ascertain the possible involvement of a radical mechanism[4,5] for the conversion of **1** (R^1 = OH) to **6**, **1** (R^1 = OH, R^2 = R^3 = H, R^4 = *t*-Bu) was added to a mixture of a different ratio of NaH to Bu_3SnH in THF under nitrogen atmosphere. From the reactions were obtained **6** (R^2 = R^3 = H, R^4 = *t*-Bu), 2-(4-*t*-butyl-2-hydroxyphenylthio)diphenyl sulfide (**7**), and thianthrene. The formation of **7** might be rationalized on the basis of a radical mechanism.



REFERENCES

1. J. R. Campbell, J. Org. Chem., 29, 1830 (1964).
2. K. Kim and H. J. Rim, Tetrahedron Lett., 5363 (1991).
3. S. S. Shin, M. N. Kim, H. O. Kim and K. Kim, Tetrahedron Lett., 34, 8649 (1993).
4. B. Boduszek, H. J. Shine and T. K. Venkatachalam, J. Org. Chem., 54, 1616 (1989).
5. E. J. Madaj, Jr., D. M. Snyder and W. E. Truce, J. Amer. Chem. Soc., 108, 3466 (1986).