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Novel phenyl migration of 1-phenylbenzo[*b*]thiophenium triflates in the thermolysis

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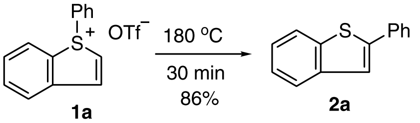
Abstract—Thermolysis of 1-phenylbenzo[*b*]thiophenium triflates at 180°C causes phenyl migration to give 2-phenylbenzo[*b*]thiophenes in high yields. Interestingly, the thermolysis of 1-phenylbenzo[*b*]thiophenium triflates having a substituent at the 2 position affords the corresponding 3-phenylbenzo[*b*]thiophenes. On the basis of the thermolysis of 2-(4-methylphenyl)-1-phenylbenzo[*b*]thiophenium triflate, a consecutive [1,5] sigmatropic rearrangement is proposed for the phenyl migration. © 2002 Elsevier Science Ltd. All rights reserved.

Although syntheses of a great variety of cyclic sulfonium salts have been reviewed extensively,[1] no 1-arylbenzo[*b*]thiophenium salts have been reported. Synthesis of benzo[*b*]thiophenium salts has been so far conducted by alkylation of benzothiophenes,[2] but 1-alkylbenzo[*b*]thiophenium salts do not have enough stability for their reactivity to be examined. It is expected that 1-arylbenzo[*b*]thiophenium salts are more stable than the corresponding 1-alkylbenzo[*b*]thiophenium salts because of the strong aryl–sulfur bond. However, introduction of aryl groups on the sulfur is difficult.[3] We have reported that 1-arylbenzo[*b*]thiophenium salts can be prepared by electrophile-induced intramolecular cyclization of arylethenes and -ethynes bearing arylthio groups at the *ortho* position.[4] Furthermore, we have found a convenient direct method for the synthesis of 1-phenylbenzo[*b*]thiophenium salts by using diphenyliodonium triflate and benzo[*b*]thiophenes.[5] 1-Phenylbenzo[*b*]thiophenium salts, in contrast to the corresponding benzo[*b*]thiophenes,[6] undergo ring-opening reactions induced by nucleophiles or bases to provide substituted alkenes or alkynes.[7] The cycloaddition of 1-phenylbenzo[*b*]thiophenium triflates with dienes also takes place.[8]

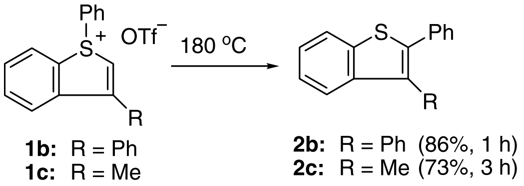
The photolysis of 1-phenylbenzo[*b*]thiophenium salts leads to some competing reactions such as the migration of the phenyl group to the 2 and 3 positions and dephenylation.[9] However, in this study, we have found that the thermolysis of 1-phenylbenzo[*b*]thiophenium triflates leads to the regioselective migration of the phenyl group without the ring opening of the thiophene ring and the elimination of the phenyl group, also suggesting that this method is of practical use for the synthesis of phenyl-substituted benzo[*b*]thiophenes.

Thermolysis of 1-phenylbenzo[*b*]thiophenium triflate (**1a**) was conducted by simply heating the crystalline benzothiophenium salt at 180°C in an oil bath for 30 min. 2-Phenylbenzo[*b*]thiophene (**2a**) was obtained in 86% yield as the sole product (Eq. (1)). The thermolysis at a lower temperature resulted in a lower yield of **2a**. Furthermore, the thermolysis of 3-substituted 1-phenylbenzo[*b*]thiophenium triflates (**1b** and **1c**) gave the corresponding 2-phenylbenzo[*b*]thiophenes (**2b** and **2c**) in 86 and 73% yields, respectively (Eq. (2)). 1-(4-Methylphenyl)benzo[*b*]thiophenium triflate (**3**) also afforded 2-(4-methylphenyl)benzo[*b*]thiophene (**4**) in 89% yield (Eq. (3)).



(1)

The above results indicate that the aryl group at the sulfur migrates regioselectively to the 2 position of benzo[*b*]thiophene ring. However, if the 2 position of the benzothiophenium triflate is occupied by a substituent, does the phenyl migration take place in the thermolysis?



(2)

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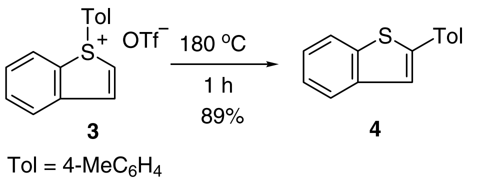
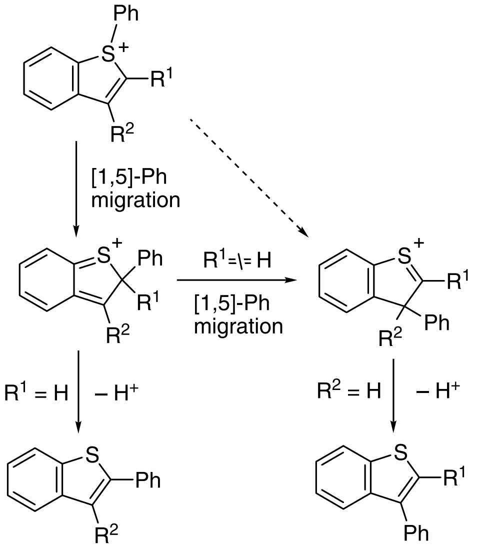
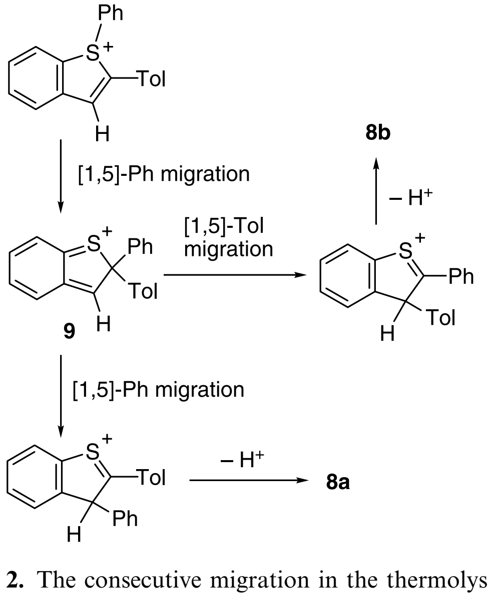


(3)

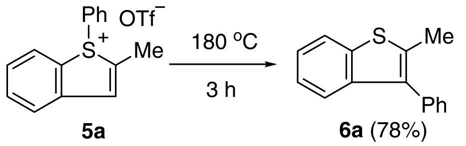
Then, the thermolysis of 2-substituted 1-phenylbenzo[*b*]thiophenium triflates (**5**) was conducted. The reaction required a prolonged time to almost complete the reaction. Heating 2-methyl-1-phenylbenzo[*b*]thiophenium triflate **5a** at 180°C for 3 h gave 2-methyl-3-phenylbenzo[*b*]thiophene (**6a**) in 78% yield (Eq. (4)). The similar thermolysis of 1,2-diphenylbenzo[*b*]thiophenium triflate **5b** for 1 h yielded 2,3-diphenylbenzo[*b*]thiophene (**6b**) (74%) (Eq. (5)). These results indicate that the phenyl group migrated selectively to the 3 position when the 2 position was occupied.



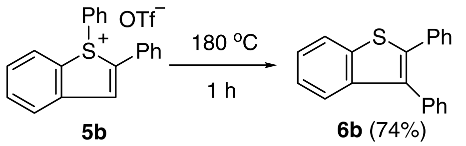
Scheme 1. Possible mechanism for phenyl migration.



Scheme 2. The consecutive migration in the thermolysis of **7**.



(4)

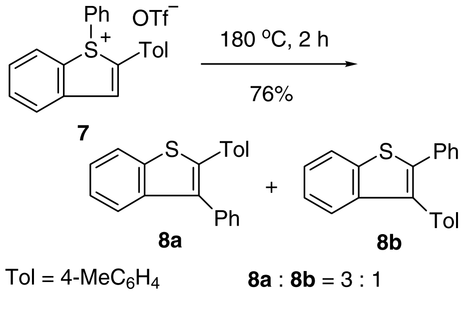


(5)

On the basis of X-ray crystal structural analysis of 1-phenylbenzo[*b*]thiophenium triflate **1a**,[5] it is indicated that the stereochemistry around the sulfur is tetrahedral and the hybridization is *sp*^{3}. This structural result suggests that the benzothiophenium system bears a resemblance to the structure of the indene system. It is known that phenyl-substituted indenes in the thermolysis undergo [1,5] sigmatropic rearrangement of the phenyl group.[10] Accordingly, the phenyl migration in the thermolysis of 1-phenylbenzo[*b*]thiophenium triflates can be explained by a [1,5] sigmatropic rearrangement. In the thermolysis of **5**, the formation of the benzothiophene **6** is rationalized by consecutive [1,5] sigmatropic rearrangements of the phenyl group. A possible mechanism of the phenyl migration is shown in Scheme 1.

There is another possibility, i.e. that the phenyl group on the sulfur migrates directly to the 3 position. To verify the consecutive migration of phenyl group shown in Scheme 1, we examined the thermolysis of 2-(4-methylphenyl)-1-phenylbenzo[*b*]thiophenium triflate (**7**). If the phenyl migration takes place via consecutive migration, the two different substituents, phenyl and 4-methylphenyl groups exist at the 2 position of the intermediate **9** which is formed by the first migration of the phenyl group. Since the two substituents have nearly an equal extent of migratory aptitude,[11] it is expected that the second migration gives a mixture of phenyl- and 4-methylphenyl-migrated products.

Actually, heating **7** at 180°C for 2 h gave a mixture of 2-(4-methylphenyl)-3-phenylbenzo[*b*]thiophene (**8a**) and 3-(4-methylphenyl)-2-phenylbenzo[*b*]thiophene (**8b**) in 76% yield (a 3:1 ratio of **8a** and **8b**) (Eq. (6)). This result implies that the phenyl migration competes with the 4-methylphenyl migration after the first migration of the phenyl group to the 2 position. Therefore, the formation of a mixture of **8a** and **8b** is in accord with the consecutive mechanism shown in Scheme 2.



(6)

In summary, we have found that the thermolysis of 1-phenylbenzo[*b*]thiophenium triflates undergoes regioselective phenyl migration to give 2-phenylbenzo[*b*]thiophenes. In the case of 2-substituted 1-phenylbenzo[*b*]thiophenium triflates, the arylation of the 3 position occurs via consecutive rearrangement.

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