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Phenyl Migration to Thiophene Ring in Photolysis of 1-Phenylbenzo[b]thiophenium Salts

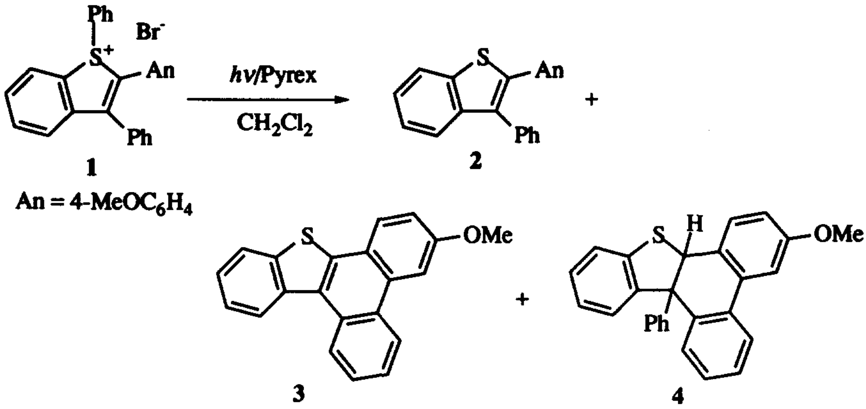
Tsugio Kitamura,* Kunihiko Morizane, Hiroshi Taniguchi, and Yuzo Fujiwara

Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University 36, Hakozaki, Fukuoka 812-81, Japan

Abstract: Photolysis of 1-phenylbenzo[b]thiophenium salts was conducted by use of a Pyrex-filtered high-pressure Hg lamp. The major products in most cases were the phenyl-migrated ones, i.e., 2-phenylbenzo[b]thiophenes and 3-phenylbenzo[b]thiophenes, together with the dephenylated benzo[b]thiophenes. This photochemical behavior is quite different from the thermal ones that provide the ring-opened olefins. The selective phenyl migration to the thiophene ring and the absence of the ionic products are characteristic of benzothiophenium systems. © 1997 Elsevier Science Ltd.

1-Arylbenzo[b]thiophenium salts have unique structural features[1,2] and are expected to exhibit interesting chemical behaviors. Especially, the short, strong Ph-S^+ bond resists the nucleophilic cleavage in the reaction with nucleophiles to cause the ring-opening of the thiophene ring. The reaction of triarylbenzo[b]thiophenium salts with alkoxide anions undergoes a nucleophilic ring-opening reaction to give exclusively 1-alkoxy-1,2-diaryl-2-[2-(arylsulfanyl)phenyl]ethenes.[3] The stereochemistry of the alkoxyethenes is the Z configuration which implies that the ring-opening reaction proceeds with the complete retention of configuration. Further, the thermolysis of triarylbenzo[b]thiophenium halides gives the selective ring-opened haloethenes and the dearylated benzo[b]thiophenes, the ratios of the products being dependent upon the nature of halide anion.[4] On irradiation of 1-phenylbenzo[b]thiophenium salts, however, no ring-opening reactions were observed but the cleavage of the phenyl-sulfur bond followed by the migration of phenyl group took place. Furthermore, 1-phenylbenzo[b]thiophenium salts in photolysis showed characteristic behavior different from triarylsulfonium salts.[5,6] In this paper, we wish to report the novel findings in the photolysis of 1-phenylbenzo[b]thiophenium salts.

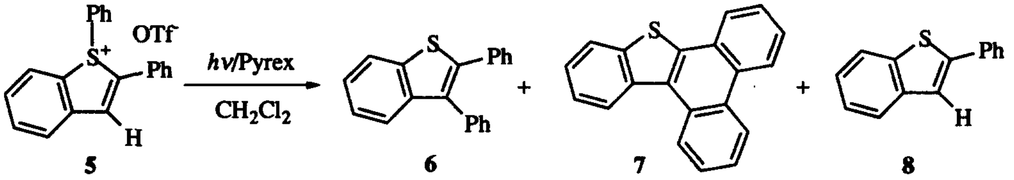
Photolyses of 1-phenylbenzo[b]thiophenium salts were conducted by using a high-pressure Hg lamp (100W) equipped with a Pyrex-filter at 10 °C under N_2 atmosphere. Irradiation of 2-(4-methoxyphenyl)-1,3-diphenylbenzo[b]thiophenium bromide (**1**)[1] (1 mmol) in dichloromethane (100 mL) for 1 h gave a complex mixture of the products. The separation by column chromatography on silica gel yielded 2-(4-methoxyphenyl)-3-phenylbenzo[b]thiophene (**2**) (8 %), 3-methoxyphenanthro[9,10-b]benzo[b]thiophene (**3**)[7] (9 %), and 3-methoxy-8b-phenyl-8b,13a-dihydrophenanthro[9,10-b]benzo[b]thiophene (**4**)[7] (18 %) as the identified products. Products **2** and **3** should be derived from the Ph-S^+ bond fission observed in the thermolysis. However, product **4** has a new, phenyl-migrated skeleton. The migration of phenyl group on the sulfur has not been observed in the thermolysis.



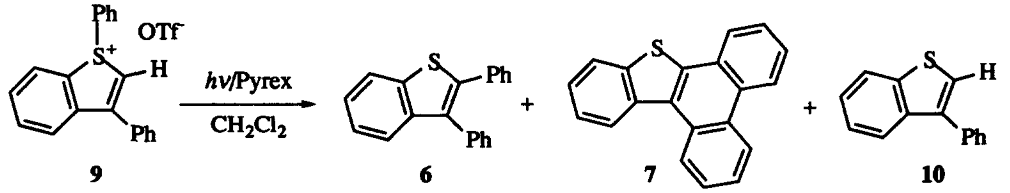
1 **2** **3** **4**

An = 4-$MeOC_6H_4$

Then, photolyses of the more simplified diphenylbenzo[b]thiophenium triflates (**5** and **9**)[2] were conducted to examine the possibility of such phenyl migration. Similarly, a solution of **5** (1 mmol) in dichloromethane (100 mL) was irradiated for 1 h in the presence of pyridine (1.5 mmol) as a buffer. After removal of the solvent, the product mixture was submitted to column chromatography on alumina to remove the resinous materials. The fraction eluted with dichloromethane was analyzed by GC. The GC analysis showed the formation of 2,3-diphenylbenzo[b]thiophene (**6**) (49 %), phenanthro[9,10-b]benzo[b]thiophene (**7**) (14%), and 2-phenylbenzo[b]thiophene (**8**) (19 %). The formation of **6** and **7** indicates that the migration of phenyl group occurs even in the diphenyl system **5**. Interestingly, the similar photolysis of 1,3-diphenylbenzo[b]thiophenium triflate (**9**) gave **6** (33%), **7** (5%), and 3-phenylbenzo[b]thiophene (**10**) (23%). These results suggest that the phenyl group on the sulfur can migrate either to the 2 or 3 position of the benzothiophene ring. Furthermore, the absence of pyridine as the buffer did not affect the yields of the products. When 1-phenylbenzo[b]thiophenium triflates were irradiated in methanol, the product distributions were almost the same as the results in the photolysis with dichloromethane and gave no methanol-incorporated products.



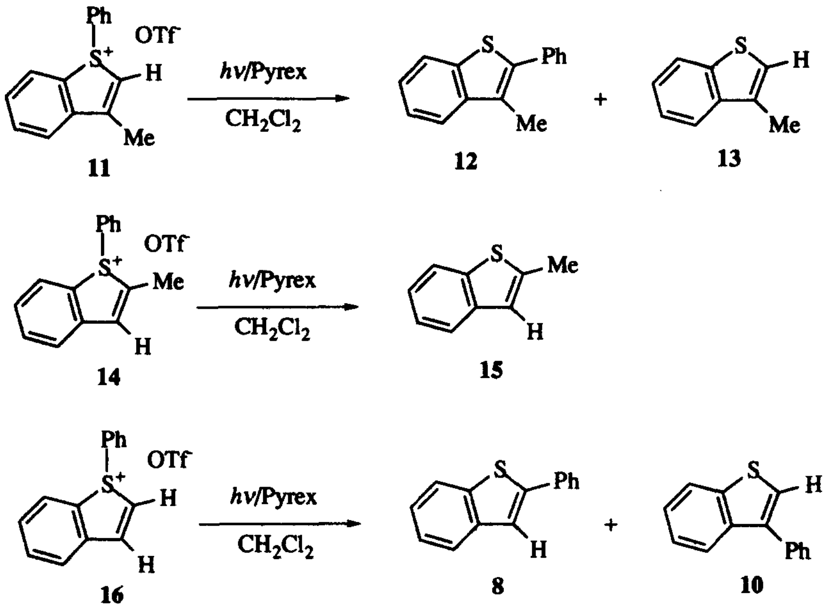
5 **6** **7** **8**



9 **6** **7** **10**

The methyl-substituted one, 3-methyl-1-phenylbenzo[b]thiophenium triflate (**11**)[2] also exhibits the same behavior in the photolysis, giving 3-methyl-2-phenylbenzo[b]thiophene (**12**) and 3-methylbenzo[b]thiophene (**13**) in 36 and 2% yields, respectively. However, the photolysis of 2-methyl-3-

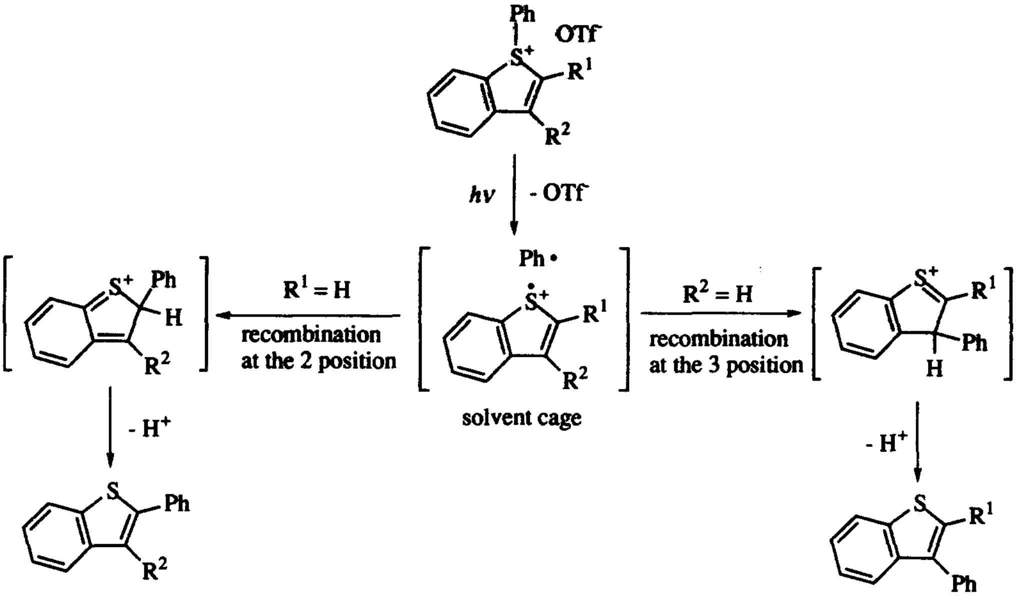
phenylbenzo[b]thiophene (**14**)[2] did not give the phenyl-migrated product but yielded 2-methylbenzo[b]thiophene (**15**) in 66% yield.[8] The GC analysis of the volatile component showed the formation of benzene. As expected, the photolysis of the parent 1-phenylbenzo[b]thiophenium triflate (**16**)[2] afforded 2- and 3-phenylbenzo[b]thiophenes (**8** and **10**) in 8 and 12% yields, respectively, although the formation of the resinous materials decreased in the yields of benzothiophenes.



The phenyl migration of 1-phenylbenzo[b]thiophenium salts has been observed in the photolysis and is characteristic of the photochemical behavior because it does not occur in the thermolysis. The phenyl group in the benzothiophene skeleton does not migrate to the benzene ring at all but only to the 2- or 3-position of the thiophene ring without the significant selectivity. No methanol-incorporated products such as anisole have not be detected in the photolysis in methanol.

The characteristic behavior of 1-phenylbenzo[b]thiophenium salts observed above is different from that of triarylsulfonium salts[5,6] that undergo the ionic cleavage as the major path in the direct photolysis. Accordingly, the phenyl migration in the photolysis of 1-phenylbenzo[b]thiophenium salts may proceeds with a homolytic cleavage of the phenyl-S bond followed by the recombination of the species in the solvent cage as shown in Scheme 1. The loss of the positional selectivity[9] at the thiophene ring and the absence of the trapped products by methanol support this process. The dephenylated benzo[b]thiophenes and benzene may be formed via hydrogen abstraction from the solvent.[5,6]

In summary, we have found that the photolysis of 1-phenylbenzo[b]thiophenium triflates undergoes phenyl migration into the 2 or 3 position of the benzothiophene ring. This behavior is quite different from that in the thermolysis of the 1-phenylbenzo[b]thiophenium salts.



Scheme 1. Possible Mechanism for Phenyl Migration

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7. Spectral data of new products are as follows. **3**: mp: 152-153 °C (EtOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.01 (s, 3 H, OMe), 7.23-7.73 (m, 5 H, ArH), 7.96-8.05 (m, 3 H, ArH), 8.66 (d, J = 7.3 Hz, 1 H, ArH), 8.74 (d, J = 8.2 Hz, 1 H, ArH), 8.96 (d, J = 8.2 Hz, 1 H, ArH); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.49, 105.03, 116.89, 122.38, 123.09, 123.91, 124.30, 124.64, 124.87, 125.20, 126.10, 126.61, 127.33, 127.77, 129.10, 130.20, 130.89, 137.70, 138.32, 138.79, 158.93. Calcd for $C_{21}H_{14}OS$: C, 80.23; H, 4.49. Found: C, 79.98; H, 4.58. **4**: mp: 228-229 °C (benzene-EtOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.83 (s, 3 H, OMe), 5.48 (s, 1 H, CH), 6.69-7.42 (m, 16 H, ArH), 7.94 (d, J = 7.8 Hz, 1 H, ArH); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.45, 62.71, 62.85, 109.90, 113.36, 122.43, 122.74, 123.48, 124.49, 127.07, 127.68, 127.93, 128.09, 128.53, 128.66, 129.00, 130.04, 130.98, 134.34, 134.82, 134.95, 142.88, 143.39, 146.79, 160.34. Calcd for $C_{27}H_{20}OS$: C, 82.62; H, 5.14. Found: C, 82.57; H, 5.18.
8. It is not clear that **14** does not undergo the phenyl migration. Compared with the corresponding phenyl-substituted salt **5**, the recombination in the reaction of **14** may generate an unstable intermediate for lack of stabilization by phenyl substituent.
9. The selective migration to the *ortho* position of the phenyl group has been observed in the direct photolysis of triphenylsulfonium triflate.[6]

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