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Base-Induced Selective Ring Opening of 1-Arylbenzo[b]thiophenium Salts

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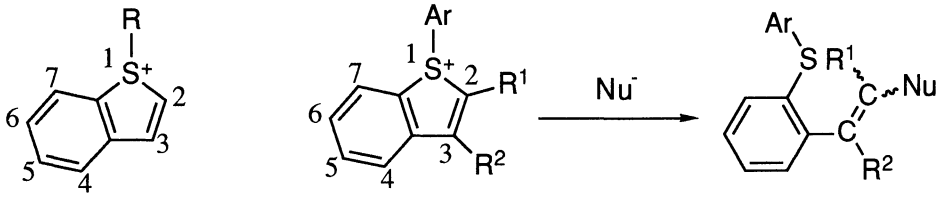
Reactions of 1-arylbenzo[b]thiophenium salts with methoxide anion in methanol caused the fission of the S^+-C(2) bond of the thiophenium ring to produce *o*-(phenylthio)phenyl-substituted methoxyethenes, allenes, or alkynes.

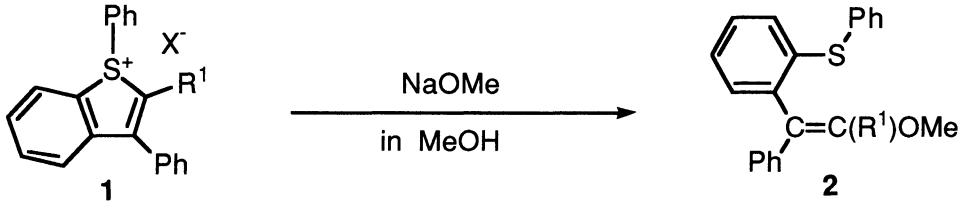
Benzo[b]thiophenium ions have been prepared and characterized but these compounds are restricted to S-alkyl substituted benzo[b]thiophenium ions.[1)] Therefore, the main reaction of the S-alkylbenzo[b]-thiophenium ions is alkylation of nucleophilic substrates.[1)] It is noteworthy that the S-C(2) bond of 1,2,3,5-tetramethylbenzo[b]thiophenium ion is longer than that of the corresponding benzo[b]thiophene[1c)] and that bromine adds to the C(2)-C(3) double bond of 1-methylbenzo[b]thiophenium tetrafluoroborate.[1b)] These results are attributable to the relative lack of aromaticity in the fused thiophenium ring compared with benzo[b]thiophene. If the S^+-R bond of the benzo[b]thiophenium ion is replaced by a strong S^+-Ar bond, the benzo[b]thiophenium ion has an opportunity to cleave the S^+-C(2) bond.



Recently we have found novel preparations of 1-arylbenzo[b]thiophenium salts from bromination of *o*-(arylthio)phenylethenes[2)] and from electrophilic addition of *o*-(arylthio)phenylalkynes.[3)] These 1-aryl-benzo[b]thiophenium salts are stable crystals and are suitable for examining their chemistry. Here we report our findings that the ring opening reaction by the S^+-C(2) bond cleavage occurs with alkoxide anion and the product is markedly dependent upon the substituent.

Reaction of 1-phenylbenzo[b]thiophenium salts was carried out with nucleophiles such as CN^- and SCN^- in acetonitrile at room temperature but no reaction was observed. Interestingly, the reaction with MeO^- in methanol gave the product which was ring-opened.

1,3-Diphenylbenzo[b]thiophenium perchlorate (**1a**) (R^1=H) was treated with NaOMe (2 equiv.) in MeOH at room temperature for 12 h.[4] The reaction produced 1-methoxy-2-phenyl-2-[*o*-(phenylthio)-phenyl]ethene (**2a**) (73% yield) which was derived from ring opening by the cleavage of the carbon-sulfur bond. No products derived from the cleavage of the Ph-S^+ bond were detected. However, 2-aryl-1-phenyl-benzo[b]thiophenium salts (**1b** and **1c**) did not react at room temperature. When **1b** and **1c** were refluxed in MeOH in the presence of NaOMe for 24 h, 1-aryl-1-methoxy-2-phenyl-2-[*o*-(phenylthio)phenyl]ethenes (**2b** and **2c**) were, respectively, obtained quantitatively. It is interesting to compare with the analogous system, alkenylsulfonium salts,[5] in which nucleophiles attack at the β carbon to give Michael type addition products. Accordingly, it is noted that methoxide anion attacks at the C(2) carbon although it is difficult to determine on the basis of the present result whether the substitution proceeds via S_N1, S_N2, or addition-elimination manner.

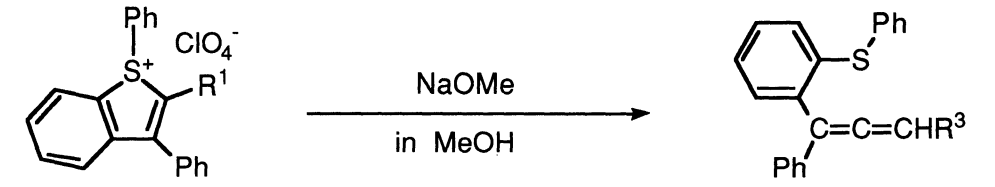


1 **2**

1a:R^1 = H, X = ClO_4
1b:R^1 = Ph, X = Br
1c: R^1 = *p*-$MeOC_6H_4$, X = Br

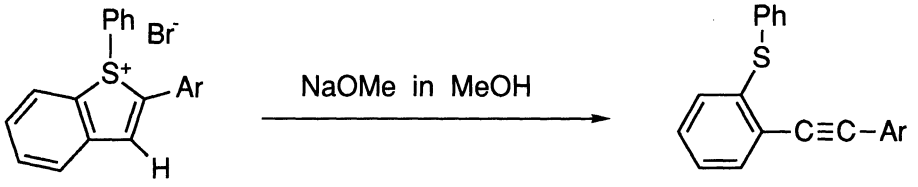
2a: R^1 = H (73%)
2b: R^1 = Ph (100%)
2c: R^1 = *p*-$MeOC_6H_4$ (100%)

On the other hand, methoxyethenes **2** were not formed in the cases of 2-alkyl- and 3-unsubstituted benzo[b]thiophenium salts (**1d**, **1e**, **1f**, and **1g**). When 2-methyl-1,3-diphenylbenzo[b]thiophenium perchlorate (**1d**) was treated with NaOMe in MeOH at room temperature for 12 h, 1-phenyl-1-[*o*-(phenylthio)phenyl]propa-1,2-diene (**3a**) was formed in a 89% yield. No signs of methoxyethene **2** could be detected in the crude reaction mixture by NMR spectroscopy (250 MHz). The formation of allene derivative **3a** means that the presence of a relatively acidic proton causes elimination rather than substitution. Similar elimination reaction was observed in the case of *n*-propyl-substituted benzo[b]thiophenium perchlorate (**1e**) which produced ethyl-substituted allene **3b**. The same situation causing elimination holds also for the cases of 3-unsubstituted benzo[b]thiophenium salts. Reaction of 2-aryl-1-phenylbenzo[b]thiophenium bromides (**1f** and **1g**) with NaOMe in MeOH at room temperature yielded 1-aryl-2-[*o*-(phenylthio)phenyl]ethynes (**4a** and **4b**) quantitatively.



1d: R^1 = Me
1e: R^1 = *n*-Pr

3a: R^3 = H (89%)
3b: R^3 = Et (100%)

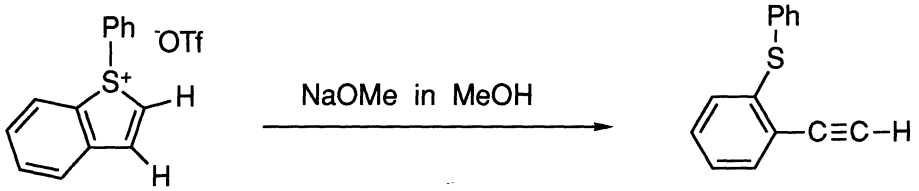


1f: Ar = Ph
1g: Ar = *p*-$MeOC_6H_4$

4a: Ar = Ph (100%)
4b: Ar = *p*-$MeOC_6H_4$ (100%)

These base-induced eliminations are attributed to the inductive effect of the positive sulfur atom[6] since the corresponding benzo[b]thiophenes do not undergo such ring-opening reactions under similar conditions.

Furthermore, the most fundamental system, i.e., a 1-phenylbenzo[b]thiophenium ion, was examined to evaluate the substantial property toward alkoxide ion: substitution or elimination. When 1-phenylbenzo[b]-thiophenium triflate (**1h**) was treated with NaOMe (2 equiv.) in MeOH at room temperature, *o*-(phenylthio)-phenylethyne (**5**) was obtained quantitatively. It is, therefore, suggested that the hydrogen on the position C(3) is most easily abstracted and the resulting anion causes the cleavage of S^+-C(2) bond to give alkynes.



1h

5 (100%)

In summary, we found that the specific bond break of the S^+-C(2) bond in 1-arylbenzo[b]thiophenium ions takes place by reaction with alkoxide anion. The bond-breaking reaction follows substitution by alkoxide anion or elimination to an allene or alkyne and is strongly dependent on the presence of hydrogen atom at the α position of the substituent R^1 or at the position C(3) in the 1-arylbenzo[b]thiophenium ions. The parent 1-phenylbenzo[b]thiophenium ion **1h** undergoes elimination to alkyne **5**.

References

1) a) D. C. Dittmer and B. H. Patwardhan, "The Chemistry of the Sulphonium Group," ed by C. J. M.

Stirling and S. Patai, John Wiley & Sons, New York (1981), Chap. 13; b) R. M. Acheson and D. R. Harrison, *J. Chem. Soc., C*, **1970**, 1764; c) R. M. Acheson, R. J. Prince, G. Procter, and J. D. Wallis, *J. Chem. Soc., Perkin Trans. 2*, **1981**, 266.

2) T. Kitamura, H. Kawasato, S. Kobayashi, and H. Taniguchi, *Chem. Lett.*, **1986**, 399.

3) T. Kitamura, T. Takachi, H. Kawasato, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, **30**, 7445 (1989).

4) General procedure: A solution of 1-phenylbenzo[b]thiophenium salt **1** (1 mmol) in MeOH (20 cm^3) containing NaOMe (2-3 mmol) was stirred at room temperature or refluxed. After evaporation of the solvent and extraction of the residue with ether, the product was separated and purified by column chromatography on silica gel or alumina. 1-Methoxy-2-phenyl-2-[*o*-(phenylthio)phenyl]ethene (**2a**) (one isomer): ^{1}H NMR ($CDCl_3$) δ 3.62 (s, OMe), 6.61 (s, =CH), 7.11-7.31 (m, ArH); MS (m/z) 318 (M^+, 100), 287 (M^+-OMe, 83), 197 (61), 165 (59). 1-Methoxy-1,2-diphenyl-2-[*o*-(phenylthio)phenyl]ethene (**2b**) (one isomer): Mp 90-96 °C; ^{1}H NMR ($CDCl_3$) δ 3.40 (s, OMe), 6.97 (s, Ph), 7.10-7.40 (m, ArH); MS (m/z) 394 (M^+, 100), 363 (M^+-OMe, 50), 269 (69). 1-Methoxy-1-(*p*-methoxyphenyl)-2-phenyl-2-[*o*-(phenylthio)phenyl]-ethene (**2c**) (one isomer): Mp 139-141 °C; ^{1}H NMR ($CDCl_3$) δ 3.41 (s, OMe), 3.77 (s, OMe), 6.75-7.40 (m, ArH); MS (m/z) 424 (M^+, 100), 393 (M^+-OMe, 28), 299 (49). 1-Phenyl-1-[*o*-(phenylthio)phenyl]-propa-1,2-diene (**3a**): ^{1}H NMR ($CDCl_3$) δ 5.09 (s, $=CH_2$), 7.12-7.29 (m, ArH); MS (m/z) 300 (M^+, 41), 223 (M^+-Ph, 100), 221 (44); IR (neat) 1940 cm^{-1} (C=C=C). 1-Phenyl-1-[*o*-(phenylthio)phenyl]penta-1,2-diene (**3b**): ^{1}H NMR ($CDCl_3$) δ 1.07 (t, J = 7 Hz, Me), 2.12 (quint, J = 7 Hz, CH_2), 5.61 (t, J = 7 Hz, =CH), 7.08-7.32 (m, ArH); MS (m/z) 328 (M^+, 42), 251 (M^+-Ph, 100); IR (neat) 1946 cm^{-1} (C=C=C). 1-Phenyl-2-[*o*-(phenylthio)-phenyl]ethyne (**4a**): ^{1}H NMR ($CDCl_3$) δ 6.98-7.64 (m, ArH); MS (m/z) 286 (M^+, 100); IR (neat) 2216 cm^{-1} (C≡C). 1-(*p*-Methoxyphenyl)-2-[*o*-(phenylthio)phenyl]ethyne (**4b**):[3] Mp 82-85 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, OMe), 6.77-7.51 (m, ArH); MS (m/z) 316 (M^+, 100), 301 (M^+-Me, 29); IR (Nujol) 2212 cm^{-1} (C≡C). *o*-(Phenylthio)phenylethyne (**5**): Mp 47-50 °C; ^{1}H NMR ($CDCl_3$) δ 3.42 (s, ≡CH), 6.94-7.52 (m, ArH); MS (m/z) 210 (M^+, 100); IR (neat) 3288 (≡C-H), 2100 cm^{-1} (C≡C).

5) W. v. E. Doering and K. C. Schreiber, *J. Am. Chem. Soc.*, **77**, 514 (1955).

6) For a recent review, C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, **91**, 165 (1991).

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