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First [4 + 2] Cycloaddition of 1-Phenyl-1-benzothiophenium Salts with Dienes

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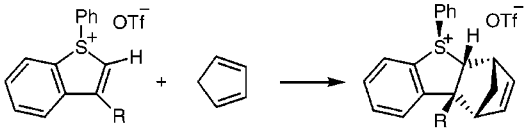
ABSTRACT



1: R = H, Me, Ph

2: R = H, Me, Ph

The reaction of 1-phenyl-1-benzothiophenium triflates 1 (R = H, Me, and Ph) with cyclopentadiene successfully proceeded to give the corresponding cycloadducts, respectively, in good yields. The single-crystal X-ray analysis of 1 (R = H) showed the *endo* isomer. Similarly, 1,3-diphenylisobenzofuran reacted with 1 (R = H) to give the corresponding cycloadduct. These novel [4 + 2] cycloadditions of 1-phenyl-1-benzothiophenium triflates as the first example clearly indicate the olefinic nature of the thiophene ring arising from the lack of aromaticity.

Hypervalent or polycoordinated main-group compounds have attracted much current interest because of their unique structure and chemical properties. Synthesis and reactions of thiophenes and benzothiophenes have been extensively investigated,[1] but those of 1-thiophenium and 1-benzothiophenium salts have received much less attention.[2] We have previously found that 1-phenyl-1-benzothiophenium salts can be prepared by intramolecular cyclization of *o*-(phenylsulfanyl)phenyl-substituted ethenes[3] and alkynes[4] and by direct S-phenylation of benzothiophenes.[5] The most important and notable property is a high stability of the 1-phenyl-1-benzothiophenium salts, which enables a wide variety of investigations and may disclose unknown chemistry of the 1-benzothiophenium ion.

We have found that the 1-phenyl-1-benzothiophenium salts undergo nucleophilic substitution to lead to ring-opened alkenes or dephenylation products.[6] The crystal structure of 1-phenyl-1-benzothiophenium triflate[5] reveals that the stereochemistry around the sulfur atom is tetrahedral and the short C═C double bond length (1.308 Å) of the thiophene ring is within the observed range of the C═C double bond

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(1) For recent reviews, see: (a) Nakayama, J. In *Comprehensive Heterocyclic Chemistry II*; Bird, C. W., Ed.; Elsevier: Oxford, U.K., 1996; 607−677. (b) Rajappa, S.; Natekar, M. V. In *Comprehensive Heterocyclic Chemistry II*; Bird, C. W., Ed.; Elsevier: Oxford, U.K., 1996; Vol. 2, pp 491−605.

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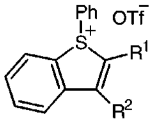
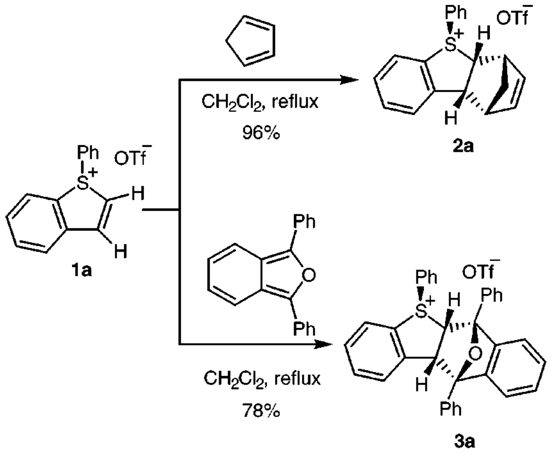
length (1.30−1.37 Å)[7] in arylethene systems. From the crystal structure, it is suggested that the aromaticity of the thiophene ring is destroyed and the C=C bond of the thiophene ring shows an olefinic nature.[8] As a consequence, it is expected that the 1-phenyl-1-benzothiophenium salts can be regarded as diphenyl(vinyl)sulfonium salts and behave as dienophiles in the Diels−Alder reaction. To examine this olefinic nature, we have conducted a Diels−Alder reaction of 1-phenyl-1-benzothiophenium salts with dienes. Here we report the first example of the cycloaddition of 1-phenyl-1-benzothiophenium triflates, clearly indicating the olefinic nature that has been expected from the crystal structure.

1-Phenyl-1-benzothiophenium triflates (**1**) were readily prepared by reaction of the corresponding 1-benzothiophenes with diphenyliodonium triflate.[5] To our delight, the reaction of 1-phenyl-1-benzothiophenium triflate (**1a**) with cyclopentadiene in CH_2Cl_2 successfully proceeded to give the cycloadduct (**2a**)[9] in 96% yield, as shown in Scheme 1.



1a: $R^1 = R^2 = H$
1b: $R^1 = H, R^2 = Me$
1c: $R^1 = H, R^2 = Ph$
1d: $R^1 = R^2 = Me$
1e: $R^1 = R^2 = Ph$

Scheme 1



Since the NMR spectra and elemental analyses are consistent with the structure of cycloadduct **2a**, it is suggested that only one isomer of the possible *endo* and *exo* adducts is present. From the single-crystal X-ray analysis of **2a**,[10] the phenyl ring on the sulfur exists above the thiophene ring and the cyclopentadiene-derived component is below the ring as depicted in Figure 1. The shape of the component derived from the cyclopentadiene clearly shows the *endo* adduct. It is, therefore, clear that 1-phenyl-1-benzothiophenium triflate **1a** acts as the dienophile and the Diels−Alder reaction proceed selectively in an *endo* manner.

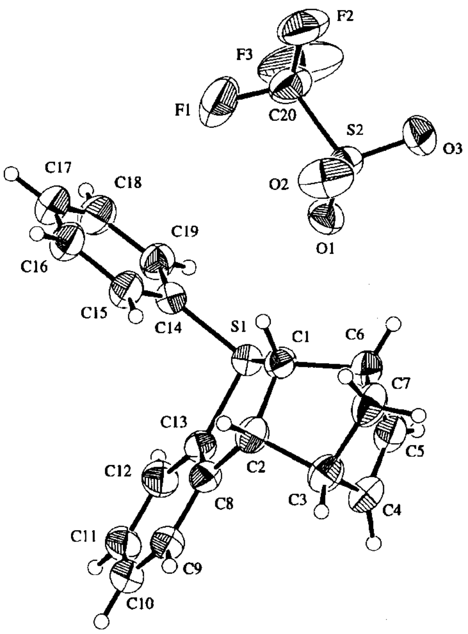


Figure 1. Crystal structure of cycloadduct **2a**.

Although other dienes such as 2,3-dimethyl-1,3-cyclohexadiene and 1,3-diphenylisobenzofuran were examined in

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[7] Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701−1709.

[8] Some recent reports on the theoretical study of 1-methylthiophenium ion suggest that thiophenium ion acts as a diene to undergo [4 + 2] cycloaddition, see: (a) ref 2g. (b) Zhang, S.-Z.; Sato, S.; Horn, E.; Furukawa, N. *Heterocycles* **1998,** *48*, 227−234. (c) Jursic, B. S.; Zdravkovski, Z.; Whittenburg, S. L. *J. Chem. Soc., Perkin Trans. 2* **1996**, 455−459.

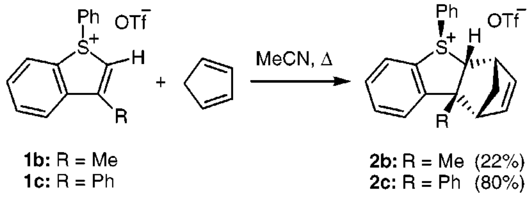
[9] **2a**: mp 147.1−147.2 °C; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.87$ (s, 2H; CH_2), 3.53 (s, 1H.; CH), 3.96 (s, 1H; CH), 5.03−5.12 (m, 2H; 2CH), 5.75−5.78 (m, 1H; CH), 6.42−6.45 (m, 1H; CH), 7.45−7.67 (m, 9H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 46.6$, 47.9, 50.2, 56.6, 72.8, 127.0, 127.1, 129.0, 130.5, 130.9, 131.1, 131.2, 133.79, 133.84, 134.4, 138.7, 147.8. **2b**: mp 133−134 °C; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.92$ (s, 3H; CH_3), 1.96 (d, $J = 10.2$ Hz, 1H; CH), 2.04 (d, $J = 10.2$ Hz, 1H; CH), 3.17 (s, 1H; CH), 4.13 (s, 1H; CH), 4.48 (d, $J = 3.9$ Hz, 1H; ArH), 5.73−5.75 (m, 1H; CH), 6.39−6.42 (m, 1H; CH), 7.51−7.76 (m, 9H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 28.3$, 47.5, 48.7, 54.2, 63.7, 78.4, 125.9, 127.5, 128.5, 128.9, 130.7, 130.9, 131.2, 132.7, 134.2, 134.3, 140.4, 152.6. **2c**: mp 84−87 °C; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.81$ (d, $J = 9.6$ Hz, 1H; CH), 1.98 (d, $J = 9.6$ Hz, 1H; CH), 4.04 (s, 1H; CH), 4.33 (s, 1H; CH), 5.01 (d, $J = 4.2$ Hz, 1H; ArH), 5.82−5.84 (m, 1H; CH), 6.67−6.70 (m, 1H; CH), 7.20−7.32 (m, 5H; ArH), 7.41 (d, $J = 7.8$ Hz, 1H; ArH), 7.58−7.72 (m, 8H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 47.8$, 49.2, 52.8, 72.6, 79.6, 125.2, 127.0, 127.6, 128.0, 128.2, 128.4, 129.5, 130.1, 130.9, 131.1, 134.2, 134.4, 135.7, 139.5, 141.4, 152.8. **3a**: mp 165−166 °C; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 5.18$ (d, $J = 8.3$ Hz, 1H; CH), 6.18 (d, $J = 8.3$ Hz, 1H; CH), 6.60 (d, $J = 7.2$ Hz, 1H; ArH), 7.01 (t, $J = 7.2$ Hz, 1H; ArH), 7.28−7.99 (m, 21H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 59.8$, 74.1, 90.0, 93.6, 122.0, 122.6, 125.9, 126.7, 127.9, 128.7, 128.9, 129.10, 129.12, 129.3, 129.466, 129.474, 129.7, 130.3, 130.7, 131.6, 131.8, 133.2, 134.1, 134.2, 134.9, 141.0, 143.8, 144.9.

[10] **Crystal structure analysis of 2a**: $C_{20}H_{17}O_3F_3S_2$ ($M = 462.47$); crystal dimensions $0.30 \times 0.30 \times 0.15$ mm, monoclinic, space group $P2_1/a$ (No. 14), $a = 10.468(2)$, $b = 12.889(2)$, and $c = 14.915(1)$ Å, $\beta = 104.693(9)°$, $V = 1946.5(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.455$ g cm^{-3}, $\mu = 2.909$ mm^{-1}, $T = 296(1)$ K; Rigaku AFC 7R diffractometer; Cu Kα radiation ($\lambda = 1.54178$ Å), scan method $\omega - 2\theta$; 3842 data measured; 3632 independent reflections, $R(\mathrm{int}) = 0.014$. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2720 observed reflections ($I > 3.00\sigma(I)$) and 254 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.062$ and $R_w = 0.096$.

the Diels−Alder reaction, only 1,3-diphenylisobenzofuran reacted with 1-phenyl-1-benzothiophenium triflate **1a** to give cycloadduct **3a**[9] in 78% yield (Scheme 1).

Similarly, we examined the Diels−Alder reaction of substituted 1-phenyl-1-benzothiophenium triflates (**1b**−**e**). Although the reaction of 3-methyl-1-phenyl-1-benzothiophenium triflate (**1b**) with cyclopentadiene in MeCN did not give cycloadduct **2b**, the same reaction in a sealed tube at 50 °C for 96 h afforded cycloadduct **2b**[9] in 22% yield (Scheme 2). On the other hand, the Diels−Alder reaction of 1,3-diphenyl-1-benzothiophenium triflate (**1c**) with cyclopentadiene proceeded more effectively than that of **1b** to give the corresponding cycloadduct (**2c**)[9] in 25% yield. This reaction was much improved by conducting it in a sealed tube at 60 °C to yield **2c** in 80% yield (Scheme 2).

Scheme 2



However, no cycloadducts were obtained in the reaction of 2,3-dimethyl-1-phenyl-1-benzothiophenium and 1,2,3-triphenyl-1-benzothiophenium triflates (**1d** and **1e**). Accordingly, it is suggested that the Diels−Alder reaction of 1-phenyl-1-benzothiophenium salts is strongly influenced by steric hindrance at the 2 and 3 position.

In summary, we have found a new [4 + 2] cycloaddition of 1-phenyl-1-benzothiophenium triflates **1** with cyclopentadiene and 1,3-diphenylisobenzofuran and experimentally confirmed the olefinic nature of the thiophene ring arising from the lack of the aromaticity.

Supporting Information Available: X-ray structural information on cycloadduct **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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