Reaction of Electronically Stabilized Thiones with Benzyne. The Isolation of Thiobenzophenone–Benzyne and Thiopivalophenone–Benzyne Adducts

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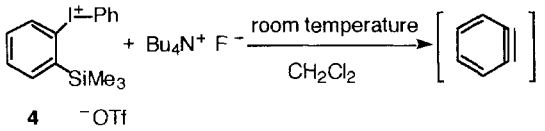
The reaction of thiobenzophenones (**1**) with phenyl[2-(trimethylsilyl)phenyl]iodonium trifluoromethanesulfonate (**4**) in the presence of tetrabutylammonium fluoride afforded the corresponding [4+2] cycloadducts, which are the first examples of thiobenzophenone–benzyne adducts. The reaction of thiopivalophenone (**6**) with benzyne prepared from **4** and tetrabutylammonium fluoride at room temperature gave [2+2] cycloadducts (**7**). When the reaction was carried out in refluxing dichloromethane, a mixture of **7** and [4+2] cycloadducts (**13**) was obtained.

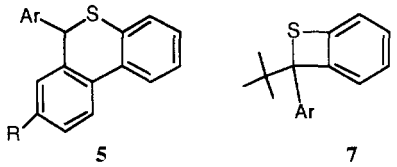
The chemistry of thiones has been extensively studied in recent years because of their unique and interesting properties.[1] Benzyne is a reactive intermediate which reacts with many dienes or olefins to afford the corresponding cycloadducts.[2] However, there are few examples on the reactions of thiones with benzyne. The reported examples on the reaction of compounds related to thiones with benzyne are dithioacetals, products of thiocarbonyl disulfide and benzyne, and dibenzotrithiocin derivatives, products of 1,3-benzodithiole-2-thione and benzyne.[3] However, the reaction of thiobenzophenones (**1**) with benzenediazonium-2-carboxylate (**2**), which is a well-known benzyne precursor, in refluxing 1,2-dichloroethane gave the benzo-1,3-oxathian-4-ones (**3**).[4] Thus, compound **2** did not act as a benzyne precursor. Recently, one of the authors has introduced a new type of benzyne precursor, phenyl[2-(trimethylsilyl)phenyl]iodonium trifluoromethanesulfonate (**4**), which has been found to produce benzyne under very mild conditions (Scheme 1).[5]

As an extension of this study, we have already reported on two preliminary studies. The reaction of benzyne produced from **4** with thiobenzophenones (**1**) afforded the corresponding [4+2] cycloadducts (**5**).[6] The reaction of thiopivalophenones (**6**) with **4** in the presence of tetrabutylammonium fluoride gave the corresponding [2+2] cycloadducts (**7**) in moderate yields (Scheme 2).[7]

The present article is concerned with full accounts of the above two communications, the synthesis of benzothiete by the [2+2] cycloaddition of thiones with benzyne, which forms completely different products from those previously reported, and the difference in the reactivity of three benzyne precursors: **2**, **4**, and 2-trimethylsilylphenyl trifluoromethanesulfonate (**8**).[8]



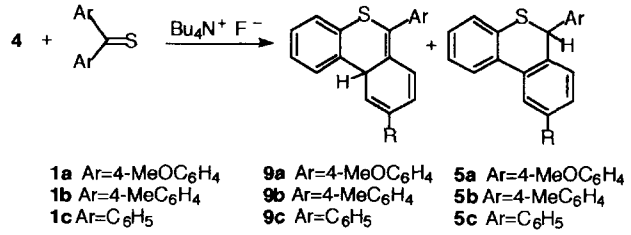
Scheme 1. Formation of benzyne.



Scheme 2. [4+2] and [2+2] Cycloadducts.

Results and Discussion

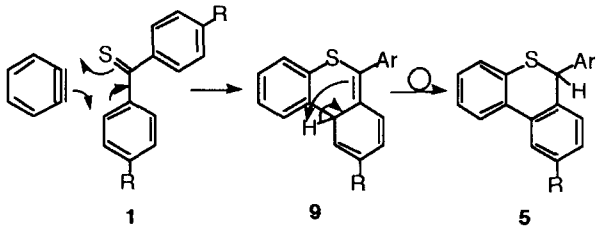
The treatment of **4** with 4,4′-dimethoxythiobenzophenone (**1a**), followed by the addition of tetrabutylammonium fluoride at room temperature, resulted in the formation of cycloadduct (**9a**) and its rearranged product (**5a**) in 15 and 29% yields, respectively (Scheme 3). The structures of the adducts were assigned to 6-phenyl-4*H*-dibenzo[*b*,*d*]thiopyran (**9a**) and 6-phenyl-6*H*-dibenzo[*b*,*d*]thiopyran (**5a**) based on spectroscopic data. Benati et al. reported on the synthesis of **5a** by the reaction of 1,2,3-benzothiadiazole with diphenylcarbene, whose structure was identical with that of **5a**.[9] Other reactions were carried out in a similar manner (Table 1).



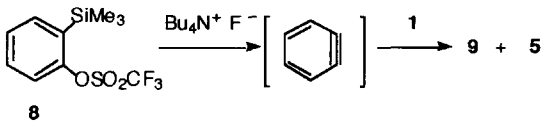
1a Ar=4-MeOC$_6$H$_4$ **9a** Ar=4-MeOC$_6$H$_4$ **5a** Ar=4-MeOC$_6$H$_4$
1b Ar=4-MeC$_6$H$_4$ **9b** Ar=4-MeC$_6$H$_4$ **5b** Ar=4-MeC$_6$H$_4$
1c Ar=C$_6$H$_5$ **9c** Ar=C$_6$H$_5$ **5c** Ar=C$_6$H$_5$

Scheme 3. Reaction of **1** with benzyne from **4**.

In all cases, precursor **4** was consumed within 10 min, while a small amount of thiones still remained unreacted. Thus, when **1a** was reacted with 6 mol amt. of **4** at room temperature, the yields of **9a** and **5a** were improved to 25 and 45% yields, respectively. When this reaction was carried out in refluxing toluene, the obtained products were only the rearranged ones (Entries 4 and 7). When the present reaction was carried out at 0 °C, the ratios of unrearranged **9** to **5** were higher (Entries 1 and 5). Interestingly, the reaction of thiobenzophenone **1c** with benzyne afforded adducts of the same type, **9c** and **5c**, but **9c** was found to be unstable at room temperature. When the reaction mixture was subjected to column chromatography by elution with hexane-dichloromethane, the fraction containing **9c** and **5c** turned blue. The proton NMR spectrum of this mixture shows the adduct **5c** and thiobenzophenone **1c**, which suggested that a retro-Diels–Alder reaction occurred under these conditions. When isolated **9b** was heated in refluxing toluene for 6 h, **5b** was obtained in 70% yield. Thus, the reaction might proceed as follows: when benzyne is formed, thiobenzophenone **1** is immediately attacked by benzyne to afford the corresponding Diels–Alder adduct **9**. This adduct is aromatized by 1,3-prototropy to give **5** (Scheme 4). We then tried the reaction of **1** with *o*-trimethylsilyphenyl triflate (**8**), which is also known as a benzyne precursor,[8] followed by the addition of tetrabutylammonium fluoride to compare its reactivity with that of **4**. A treatment of **1** with **8**, followed by the addition of tetrabutylammonium fluoride at room temperature, resulted in the formation of **5** and **9** (Scheme 5). The results are given in Table 2. Generally, the yields of products **5** and **9** were lower than those of the reaction of **1** with **4**. While the solubility of **8** toward dichloromethane was better than



Scheme 4. Reaction mechanism.



8

Scheme 5. Reaction of **1** with **8**.

Table 1. Reaction of Thiobenzophenones with **4**[a)]

Entry	Ar	Conditions			Products (Yield/%)[b)]	
		Solvent	Temp/°C	Time/min	**9**	**5**
1	4-MeOC$_6$H$_4$	CH_2Cl_2	0	10	**9a** 10	**5a** 32
2	4-MeOC$_6$H$_4$	CH_2Cl_2	R.T.	5	**9a** 15	**5a** 29
3	4-MeOC$_6$H$_4$	CH_2Cl_2	Reflux	3	**9a** 5	**5a** 44
4	4-MeOC$_6$H$_4$	Toluene	Reflux	1	**9a** 0	**5a** 38
5	4-Tol	CH_2Cl_2	0	5	**9b** 17	**5b** 28
6	4-Tol	CH_2Cl_2	R.T.	2	**9b** 15	**5b** 45
7	4-Tol	Toluene	Reflux	1	**9b** 0	**5b** 37

a) All reaction was carried out by using 2 mol amt. of **1**. b) Benzophenones were obtained as side products (10—18% yields).

Table 2. Reaction of **1** with **8**

Entry	**1**	Conditions				Products (Yield/%)[a)]	
		Solvent	**8** (mol amt.)	Temp/°C	Time/min	**9**	**5**
1	**1a**	CH_2Cl_2	1.5	0	60	**9a** 2	**5a** 12
2	**1a**	CH_2Cl_2	2	R.T.	30	**9a** 5	**5a** 20
3	**1a**	CH_2Cl_2	2	−30	30	**9a** 4	**5a** 12
4	**1a**	Acetonitrile	4	R.T.	30	**9a** 10	**5a** 46
5	**1a**	Acetonitrile	4	Reflux	10	**9a** 12	**5a** 48
6	**1b**	CH_2Cl_2	2	0	50	**9b** 6	**5b** 13
7	**1b**	CH_2Cl_2	4	R.T.	20	**9b** 12	**5b** 35
8	**1b**	Acetonitrile	4	Reflux	10	**9b** 5	**5b** 29
9	**1c**	CH_2Cl_2	4	Reflux	20	**9c** 0	**5c** 22

a) Benzophenones were obtained as side products (10—18% yields).

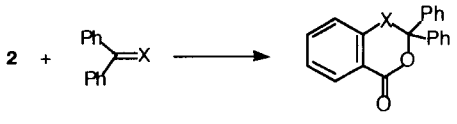
that of **4**, the present reaction could be performed at −30 °C, which resulted in the formation of **5** and **9** in 4 and 12% yields, respectively (Entry 4).

It has long been known that benzenediazonium 2-carboxylate (**2**) reacts with dienes to give the corresponding cycloadducts.[1] However, **1c** reacted with **2** to afford 3,1-benzooxathian-4-one, **3**, which is not a benzyne adduct.[4] We also found that the reaction of selenobenzophenone (**10**) with **2** or diphenyliodonium-2-carboxylate afforded the corresponding 3,1-benzooxaselenan-4-one (**11**) (Scheme 6).[10] These results suggested that **2** and diphenyliodonium-2-carboxylate did not act as benzyne precursors under these conditions.

Recently, many benzyne precursors have been developed.[2] However, the properties of thiobenzophenones **1** are difficult to reconcile with those of the precursors of benzyne and also with the reaction conditions where benzyne is generated; acidic or basic conditions and the presence of oxidizing reagents or strong nucleophiles should be avoided.[3] In the case of **2** and diphenyliodonium-2-carboxylate, a much higher temperature was required. Similarly, the generation of benzyne by using a strong base, such as butyllithium, is not acceptable for a reaction with thiobenzophenone **1**, since butyllithium attacks thiobenzophenone **1** to give tetraphenylethylene.[11] Because of this limitation, no report describing the reaction of benzyne with thiones in the actual sense has appeared. The present reaction requires only a fluoride anion at low temperature, and can be carried out under very mild conditions. Our work is the first true example of the reaction of thiones with benzyne.

The reaction of thiobenzophenone **1** with dienes usually affords the Diels–Alder adducts, whereas the reaction with olefins results in the formation of bicyclic products.[12] Schatz and Sauer have reported that thiobenzophenone shows high dienophilic reactivity based on a kinetic investigation.[13] Huisgen et al. also reported that thiobenzophenone shows unusually high dipolarophilic activity.[14] However, some dienes, such as norbornadiene, act as olefins, but not as dienes.[12] We are interested in the reactivity whether the reaction proceeds through a [2+2] or [4+2] manner. The present result shows that [4+2] cycloaddition overcomes [2+2] cycloaddition. Thus, it has been clarified that benzyne acts as a dienophile in the present reaction.

Our next interest is the isolation of [2+2] cycloadducts in the reaction of electronically stabilized thiones with benzyne. 2*H*-1-Benzothietes (**7**), which would be the products of [2+2] cycloadducts of thiones with benzyne, are interesting compounds because of their unique reactivity toward dienophiles.[15] These compounds were generally synthesized by the photolysis or flash vacuum pyrolysis of the corresponding precursors. However, there had been no report on the simple [2+2] cycloaddition reaction of thiones with benzyne. These results prompted us to investigate the reactivity of **4** with thiopivalophenones (**6**) as to whether **7** would be produced or not.



1c X=S
10 X=Se

3 X=S
11 X=Se

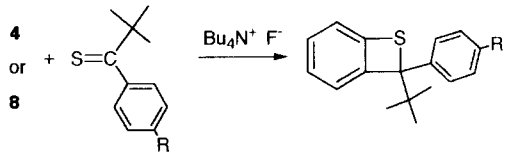
Scheme 6. Reaction of **2** with **1c** or **10**.

The reaction of **4** with *p*-methoxylthiopivalophenone (**6a**) in the presence of tetrabutylammonium fluoride afforded 2-*t*-butyl-2-*p*-methoxyphenyl-2*H*-benzo[*b*]thiete (**7a**), 1,2-cycloadduct, in 58% yield (Scheme 7). When this reaction was carried out by using **8** as a benzyne precursor, **7a** was obtained in 24% yield. In every case, no other cycloadducts, such as [4+2] cycloadducts, were identified. The results are given in Table 3.

The structure of **7** was determined based on their ^{1}H and ^{13}C NMR spectra. The best yields were obtained by using of **4** as a benzyne precursor in a dichloromethane solution at room temperature (Entries 3,7, and 8).

Previously, the parent 2*H*-1-benzothiete was obtained by the photochemical ring contraction of 3-diazobenzo[*b*]thiophen-2(3*H*)-one,[15] by flash vacuum pyrolysis (1000 °C, 0.05 Torr, 1 Torr = 133.322 Pa) of 1-benzothiophene 1,1-oxide,[16] by gas-phase dehydration (700 °C) of *o*-mercaptobenzyl alcohol,[16] or by flash vacuum pyrolysis of thiophenols.[17] Recently, Meier has found that 2-oxo-4*H*-3,1-benzoxathiin decomposes at 140 °C to give 2*H*-1-benzothiete (**7d**).[16] Spiro-linked 4*H*-1,3-benzodithiins have been obtained from the reaction of 2*H*-1-benzothiete with thiocarbonyl compounds.[18] Thus, the present is the first practical synthesis of 2*H*-1-benzothietes via a [2+2] cycloaddition reaction.

How do we account for the difference in the reactivity? A bulky *t*-butyl group prevents a plane to be made between phenyl and carbonyl in **6**. A PM3 calculation suggests that the dihedral angle between thiocarbonyl and the phenyl group of the most stable structure in **6b** is 60°. Actually, the max-



6a R=MeO
6b R=Me
6c R=H
6d R=PhO

7a R=MeO
7b R=Me
7c R=H
7d R=PhO

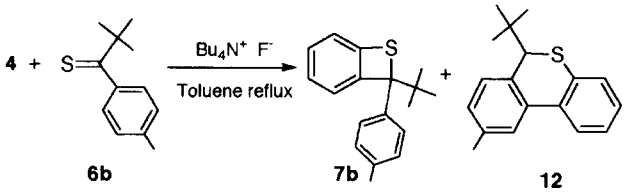
Scheme 7. Reaction of **6** with benzyne.

Table 3. Reaction of Benzyne with **6**

Entry	Precursor	**6**	Solvent	**7** (Yield/%)	Recovered **6** (%)
1	**4** (2 mol amt.)	**6a**	CH_3CN	**7a** 48	30
2	**4** (4 mol amt.)	**6a**	CH_3CN	**7a** 58	32
3	**4** (2 mol amt.)	**6a**	CH_2Cl_2	**7a** 49	30
4	**8** (2 mol amt.)	**6a**	CH_3CN	**7a** 19	9
5	**8** (4 mol amt.)	**6a**	CH_3CN	**7a** 24	22
6	**8** (2 mol amt.)	**6a**	CH_2Cl_2	**7a** 12	20
7	**4** (2 mol amt.)	**6b**	CH_2Cl_2	**7b** 51	11
8	**4** (2 mol amt.)	**6c**	CH_2Cl_2	**7c** 44	35
9	**4** (2 mol amt.)	**6d**	CH_2Cl_2	**7d** 48	30

imum wavelength (n, π^*) of **6b** is 560 nm, which is 34 nm shorter than that of thiobenzophenone (594 nm).[19,20] Thus, **6** is too hard to act as a diene toward dienophiles. When this reaction was carried out at elevated temperature, the situation should be different. Interestingly, [4+2] cycloadducts were obtained by using **4** in refluxing toluene as a benzyne precursor. The treatment of *p*-methylthiopivalophenone **6b** with **4** in the presence of tetrabutylammonium fluoride resulted in the formation of a mixture of **7b** and [4+2] cycloadducts (**12**) (Scheme 8). The structure of [4+2] adduct **12** was confirmed by its spectroscopic analysis along with an X-ray crystallographic analysis (Fig. 1).[21]

We have been interested in the reactivity of **6** toward **2**, since Dittmer et al. and Tokunaga et al. reported that **2** does not act as benzyne toward thiobenzophenone,[4] whereas, Nakayama et al. have reported that the reaction of trithiocarbonates with **2** gave [3+2] dipolar addition products.[3] In the latter case, **2** acted as a benzyne precursor. The treatment of **6b** with **2** in refluxing dichloromethane resulted in the formation of 2-*t*-butyl-2-*p*-tolyl-3,1-benzooxathiane-4-one (**13**) in 82% yield along with a small amount of **7b** (8%) (Scheme 9). This result suggested that both intermediates, 2-carboxylatephenyl cation (**14**) and benzyne, existed in the



Scheme 8. Reaction of **6b** with benzyne at elevated temperature.

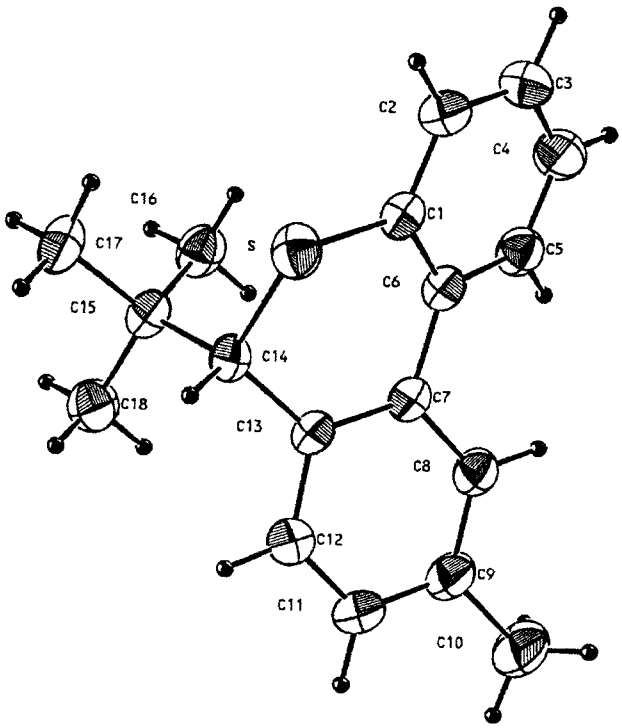
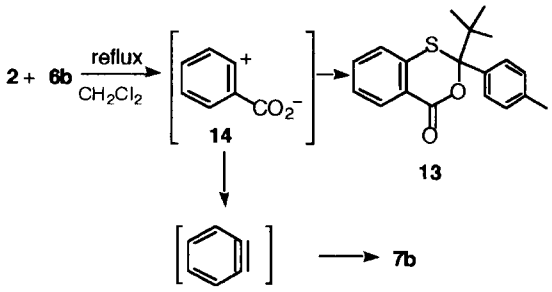
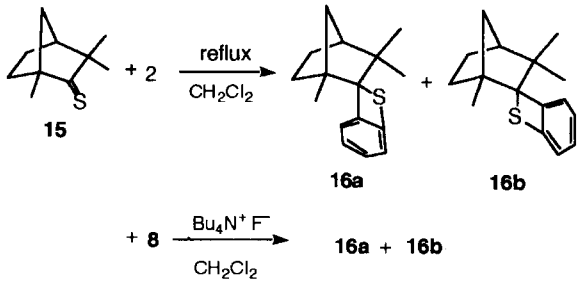


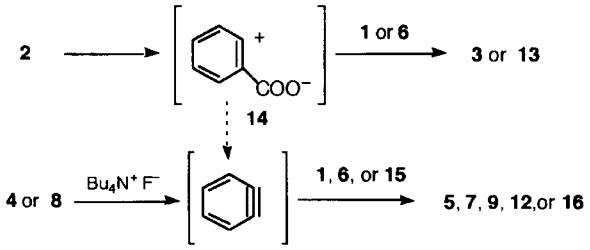
Fig. 1. X-Ray crystallographic structure of **12**.



Scheme 9. Reaction of **2** with **6b** in refluxing CH_2Cl_2.



Scheme 10. Reaction of **15** with benzyne.



Scheme 11. The Difference in the reactivity between **2** and **4** or **8**.

present reaction. *t*-Butyl group of **6b** might somewhat prevent an attack of **14** with **6b**, suggesting the formation of a small amount of benzyne, which finally reacted with **6b**.

Actually, the reaction of thiofenchone (**15**), a more hindered and isolable thioketone, with **2** in refluxing dichloromethane led to a mixture of 1 : 1 adducts (**16a**, **16b**) in 52% yield. The structures of **16a** and **16b** were confirmed by their spectroscopic analysis. Thus, **2** acted as a benzyne precursor in the present reaction. When **8** was used as a benzyne precursor, a mixture of compounds **16a** and **16b** was obtained in 72% yield at room temperature (Scheme 10).

In summary, the present results have shown that **4** and **8** are good benzyne precursors under mild conditions, in contrast with **2** (Scheme 11). The present reaction provides a practical method for the synthesis of 2*H*-1-benzothiete derivatives. The reaction proceeds under mild conditions (room temperature, neutral and aprotic solvent). Sterically congested thiones, such as **6** and **15**, reacted with benzyne to afford a [2+2] cycloadducts.

Experimental

General: All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F_{254}) and flash column chromatography was performed with silica (Merck,

70—230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 100 MHz) were recorded in $CDCl_3$ solvent, and chemical shifts are expressed in ppm relative to internal TMS.

Materials: Thiones (**1a—c**, **6a—c**, and **15**) were prepared by reactions of the corresponding ketones with tetraphosphorus decasulfide.[4,19]

Reaction of 4,4′-Dimethoxythiobenzophenones 1a with Phenyl[2-(trimethylsilyl)phenyl]iodonium Trifluoromethanesulfonate 4. To a solution of **1a** (0.158 g, 1 mmol) and **4** (1.026 g, 2 mmol) in dichloromethane (25 mL) was added dropwise a solution of tetrabutylammonium fluoride (2.1 mL, 1.0 M in THF, 1 M = 1 mol dm^{-3}) at room temperature. The deep-blue solution turned pale yellow within 10 min. After being stirred for 1 h, the solution was washed with water to remove tetrabutylammonium triflate and the organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated to afford a brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (1 : 1) to afford a mixture of products. Careful separation by silica-gel chromatography by elution with hexane afforded **9a** (0.050 g, 0.15 mmol) and **5a** (0.097 g, 0.29 mmol).

9a: Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.72 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 5.21 (s, 1 H, CH), 6.72 (d, 2 H, J = 9 Hz, Ar), 6.80 (dd, 1 H, J = 3 and 8 Hz, Ar), 6.92 (d, 2 H, J = 9 Hz, Ar), 6.97 (d, 1 H, J = 3 Hz, Ar), 7.21 (dd, 2 H, J = 2 and 6 Hz, Ar), 7.28 (d, 1 H, J = 8 Hz, Ar), 7.37 (d, 1 H, J = 7 Hz, Ar), 7.41 (d, 1 H, J = 7 Hz, Ar). HRMS: Found: m/z 394.0955. Calcd for $C_{21}H_{18}O_2S$: (M^+), 334.1027.

5a: Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.74 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 5.13 (s, 1 H, CH), 6.75 (d, 2 H, J = 9 Hz, Ar), 6.84 (dd, 1 H, J = 2 and 8 Hz, Ar), 6.99 (d, 1 H, J = 8 Hz, Ar), 7.13 (d, 2 H, J = 9 Hz, Ar), 7.19 (dd, 1 H, J = 3 and 8 Hz, Ar), 7.23 (dd, 1 H, J = 2 and 3 Hz, Ar), 7.32 (br, 2 H, Ar), 7.78 (d, 1 H, J = 8 Hz, Ar). HRMS: Found: m/z 274.0855. Calcd for $C_{19}H_{14}S$: (M^+), 274.0816.

Compounds **9b** (0.045 g, 0.15 mmol) and **5b** (0.136 g, 0.45 mmol) were obtained in a similar manner by using **1b** (0.226 g, 1.0 mmol) and **4** (1.026 g, 2.0 mmol).

9b: Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.24 (s, 3 H, Me), 2.32 (s, 3 H, Me), 5.24 (s, 1 H, CH), 6.90 and 6.99 (d, 4 H, J = 8 Hz, MeC_6H_4), 7.05 (d, 1 H, J = 9 Hz, Ar), 7.28—7.28 (m, 4 H, Ar), 7.37 (dd, 1 H, J = 2 and 8 Hz, Ar), 7.41 (dd, 1 H, J = 2 and 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 20.96 (Me), 20.97 (Me), 52.28 (CH), 126.47, 126.70, 127.17, 127.47, 127.57, 128.92, 129.31, 129.49, 132.84, 133.20, 134.58, 136.01, 136.59, 137.79, 138.23 (Ar). HRMS: Found: m/z 302.1139. Calcd for $C_{21}H_{18}S$: (M^+), 302.1129.

5b: Colorless crystals; mp 89—91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.26 (s, 3 H, Me), 2.42 (s, 3 H, Me), 5.12 (s, 1 H, CH), 6.95 (d, 1 H, J = 8 Hz, Ar), 7.02 (d, 2 H, J = 8 Hz, Ar), 7.10 (d, 3 H, J = 8 Hz, Ar), 7.14—7.28 (m, 2 H, Ar), 7.32 (dd, 1 H, J = 2 and 7 Hz, Ar), 7.6 (br s, 1 H, Ar), 7.81 (d, 1 H, J = 2 and 7 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 21.05 (Me), 21.36 (Me), 47.35 (CH), 125.40, 126.35, 126.97, 127.17, 127.81, 128.05, 128.69, 128.86, 129.09, 132.53, 133.70, 134.29, 134.56, 136.99, 137.32, 137.41 (Ar). Anal. Found: C, 82.96; H, 6.30%. Calcd for $C_{21}H_{18}S$: C, 83.41; H, 6.00%. HRMS: Found: m/z 302.1159. Calcd for $C_{21}H_{18}S$: (M^+), 302.1129.

Compound **5c** (0.025 g, 0.091 mmol, 9.1%) was obtained in a similar manner by using **1c** (0.198 g, 1.0 mmol) and **4** (1.026 g, 2.0 mmol).

5c: ^{1}H NMR ($CDCl_3$) δ = 5.17 (s, 1 H, CH), 7.07 (d, 1 H, J = 8 Hz, Ar), 7.12—7.40 (m, Ar), 7.80 (d, 1 H, J = 8 Hz, Ar), 7.82 (d, 1 H, J = 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 47.77 (CH), 125.46, 126.30, 126.51, 127.32, 127.36, 127.94, 127.98, 128.01, 128.16, 128.39, 128.70, 129.35, 129.57, 132.21, 134.46, 136.21, 140.10 (Ar). HRMS: Found: m/z 274.0855. Calcd for $C_{19}H_{14}S$: (M^+), 274.0816.

Reaction of 6 with 4 Followed by the Addition of Tetrabutylammonium Fluoride. To a solution of 4-methoxythiopivalophenone (**6a**, 0.104 g, 0.5 mmol) and **4** (1.026 g, 2.0 mmol) in dichloromethane (15 mL) was added dropwise a solution of tetrabutylammonium fluoride (2.1 mL, 1.0 M THF) at room temperature. The purple solution turned pale yellow within 1 h. After being stirred for 1 h, the solution was washed with water, dried over anhydrous magnesium sulfate, filtrated, and evaporated to give a brown oil of the adduct, which was purified by silica-gel chromatography by elution with hexane to afford 2-*t*-butyl-2-*p*-methoxyphenyl-1-benzothiete (**7a**). Starting **6a** was recovered in 32% (0.033 g, 0.16 mmol).

7a: (0.082 g, 0.29 mmol). Colorless oil. ^{1}H NMR ($CDCl_3$) δ = 1.08 (s, 9 H, *t*-Butyl), 3.78 (S, 3 H, OMe), 6.80 (d, 1 H, J = 8 Hz, Ph), 7.00 (d, 2 H, J = 8 Hz, Ar), 7.12 (t, 1 H, J = 7 Hz, Ph), 7.19 (t, 1 H, J = 8 Hz, Ph), 7.21 (d, 1 H, J = 8 Hz, Ph), 7.43 (d, 2 H, J = 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 26.88 (CH_3), 38.06 (C), 55.32 (OMe), 80.88 (C–S), 111.86, 121.55, 122.86, 123.48, 128.58, 130.44, 132.13, 139.85, 145.01, 158.01 (Ar). HRMS: Found: m/z 284.1233. Calcd for $C_{18}H_{20}S$: (M^+), 284.1235.

A colorless oil of 2-*t*-butyl-2-*p*-tolyl-1-benzothiete (**7b**) was obtained in a similar manner by using **6b** (0.096 g, 0.50 mmol) and **4** (0.513 g, 1.0 mmol). Under these conditions, **6b** (0.011 g, 0.055 mmol) was recovered in 11%.

7b: (0.068 g, 0.26 mmol). ^{1}H NMR ($CDCl_3$) δ = 1.08 (s, 9 H, *t*-Butyl), 2.32 (s, 3 H, Tol–Me), 6.97 (d, 1 H, J = 8 Hz, Ph), 7.03 (d, 2 H, J = 8 Hz, Tol), 7.09 (t, 1 H, J = 8 Hz, Ph), 7.14—7.27 (m, 2 H, Ph), 7.40 (d, 2 H, J = 8 Hz, Tol). ^{13}C NMR ($CDCl_3$) δ = 20.96 (Tol–Me), 26.79 (CH_3), 38.06 (C), 81.13 (C–S), 121.55, 123.07, 123.60, 127.24, 128.72, 129.38, 136.29, 137.08, 140.05, 145.22 (Ar). HRMS: Found: m/z 268.1287. Calcd for $C_{18}H_{20}S$: (M^+), 268.1286.

Compound **7c** was obtained in a similar manner by using **6c** (0.178 g, 1.0 mmol) and **4** (1.026 g, 2.0 mmol). Under these conditions, **6c** (0.062 g, 0.035 mmol) was recovered in 35%.

2-*t*-Butyl-2-phenyl-1-benzothiete (7c): (0.130 g, 0.51 mmol). Colorless crystals; mp 114—115 °C. ^{1}H NMR ($CDCl_3$) δ = 1.10 (s, 9 H, *t*-Butyl), 7.01 (d, 1 H, J = 8 Hz, Ph), 7.12 (t, 1 H, J = 7 Hz, Ph), 7.20—7.30 (m, 5 H, Ph), 7.52 (d, 1 H, J = 7 Hz, Ph). ^{13}C NMR ($CDCl_3$) δ = 26.71 (CH_3), 38.04 (C), 81.11 (C–S), 121.53, 123.13, 123.66, 126.62, 128.80, 129.48, 140.05, 145.10 (Ph). HRMS: Found: m/z 254.1127. Calcd for $C_{17}H_{18}S$: (M^+), 254.1129. Anal. Found: C, 80.03; H, 7.22%. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.15%.

Compound **7d** was obtained in a similar manner by using **6d** (0.27 g, 1.0 mmol) and **4** (1.026 g, 2.0 mmol). Under these conditions, **6d** was recovered in 30% (0.081 g, 0.30 mmol).

2-*t*-Butyl-2-*p*-phenoxyphenyl-1-benzothiete (7d): (0.167 g, 0.48 mmol). Pale-yellow oil. ^{1}H NMR ($CDCl_3$) δ = 1.10 (s, 9 H, *t*-Butyl), 6.91 (d, 2 H, J = 9 Hz, Ph), 6.99—7.14 (m, 5 H, Ar), 7.21 (br d, 2 H, J = 8 Hz, Ar), 7.32 (t, 2 H, J = 9 Hz, Ar), 7.47 (d, 2 H, J = 9 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 26.87 (CH_3), 38.26 (C), 80.68 (C–S), 116.57, 118.90, 121.56, 122.89, 123.21, 123.60, 128.72, 129.56, 130.67, 134.69, 139.76, 144.83, 155.72, 156.73 (Ar). HRMS: Found: m/z 347.1470. Calcd for $C_{23}H_{22}SO$: (M^++1), 347.1470.

Reaction of 6a with 8 Followed by the Addition of Tetrabutyl-

ammonium Fluoride. To a solution of **6a** (0.208 g, 1.0 mmol) and **8** (1.064 g, 4.0 mmol) in acetonitrile (15 mL) was added dropwise a solution of tetrabutylammonium fluoride (4.2 mL, 1.0 M THF) at room temperature. After being stirred for 3 h, the solution was washed with water, and three times extracted with dichloromethane (10 mL). The combined extracts were dried over anhysrous magnesium sulfate, filtrated, and evaporated to give a brown oil of the adduct, which was purified by silica-gel chromatography by elution with hexane to afford **7a** (0.068 g, 0.24 mmol). The starting **6a** was recovered in 22% (0.046 g, 0.22 mmol).

Reaction of 6b with 4 in The Presence of Tetrabutylammonium Fluoride in Refluxing Toluene. To a refluxing solution of **6b** (0.192 g, 1.0 mmol) and **4** (0.1026 g, 2.0 mmol) in toluene (30 mL) was added dropwise a solution of tetrabutylammonium fluoride (2.5 mL, 1.0 M in THF, 2.5 mmol) for 15 min. The solution turned orange-brown. After refluxing for 2 h, the reaction mixture was cooled to r.t. and concentrated to give brown oily crystals, which were chromatographed on silica-gel by elution with hexane to give **7b** (0.043 g, 0.16 mmol) and 6-*t*-butyl-9-methyl-6*H*-dibenzo[*b*,*d*]-thiopyran **12** (0.115 g, 0.43 mmol).

12: Colorless crystals; mp 88—89 °C. ^{1}H NMR ($CDCl_3$) δ = 0.83 (s, 9 H, *t*-Butyl), 2.42 (s, 3 H, Tol–Me), 3.58 (s, 1H, CH), 7.11 (m, 2 H, Ar), 7.19 (m, 2 H, Ar), 7.38 (m, 1 H, Ar), 7.56 (s, 1 H, Ar), 7.75 (m, 1 H, Ar). ^{13}C NMR ($CDCl_3$) δ = 21.25 (Tol–Me), 27.43 (CH_3), 38.45 (C), 53.83 (C–S), 124.36, 125.34, 126.40, 127.27, 127.38, 130.08, 130.30, 133.32, 133.96, 134.55, 136.78 (Ar). Anal. Found: C, 80.05; H, 7.56%. Calcd for $C_{18}H_{20}S$: C, 80.60; H, 7.46%. HRMS: Found: *m/z* 268.1297. Calcd for $C_{18}H_{20}S$: (M^+), 268.1286.

Reaction of 6c with 2 in Refluxing Dichloromethane. To a solution of **6c** (0.178 g, 1.0 mmol) in dichloromethane was added 2-carboxybenzenediazonium chloride (0.738 g, 4.0 mmol) was added in one portion. The suspension was refluxed for 1 h and the reaction mixture was evaporated to give a reddish-brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (1 : 1) to afford colorless crystals of 2-*t*-butyl-2-phenyl-3,1-benzooxathiane-4-one (**13c**) (0.235 g, 0.79 mmol). Compound **7c** (0.015 g, 0.060 mmol) was obtained in 6% yield.

13c: Colorless crystals; mp 122—123 °C. ^{1}H NMR ($CDCl_3$) δ = 1.16 (s, 9 H, *t*-Butyl), 7.05 (t, 1 H, *J* = 8 Hz, Ph), 7.17 (t, 1 H, *J* = 6 Hz, Ph), 7.20 (d, 1 H, *J* = 8 Hz, Ph), 7.28 (t, 1 H, *J* = 8 Hz, Ph), 7.58 (br s, 2 H, Ph), 7.90 (dd, 1 H, *J* = 2 and 8 Hz, Ph). ^{13}C NMR ($CDCl_3$) δ = 26.31 (CH_3), 40.06 (C), 101.44 (C–S), 124.53, 125.88, 127.06, 127.66, 128.06, 128.80, 131.45, 133.21, 136.57, 138.67 (Ph), 164.25 (CO). HRMS: Found: *m/z* 299.1109. Calcd for $C_{18}H_{18}O_2S$: (M^++1), 299.1106.

The reaction of **6b** with **2** was carried out in a similar manner by using **6b** (0.192 g, 1.0 mmol) and **2** (0.738 g, 4.0 mmol). 2-*t*-Butyl-2-*p*-tolyl-3,1-benzooxathiane-4-one (**13b**) was obtained in 82% yield (0.256 g, 0.82 mmol). Compound **7b** was obtained in 8% yield (0.021 g, 0.08 mmol).

13b: Colorless crystals; mp 144—145 °C. ^{1}H NMR ($CDCl_3$) δ = 1.15 (s, 9 H, *t*-Butyl), 2.22 (s, 3 H, Tol–Me), 6.97 (d, 2 H, *J* = 8 Hz, Tol), 7.06 (t, 1 H, *J* = 7 Hz, Ar), 7.20 (d, 1 H, *J* = 7 Hz, Ar), 7.29 (t, 1 H, *J* = 8 Hz, Ar), 7.44 (br d, 2 H, *J* = 8 Hz, Tol), 7.91 (dd, 1 H, *J* = 2 and 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 20.94 (Tol–Me), 26.20 (CH_3), 40.53 (C), 101.58 (C–S), 124.70, 125.95, 127.80, 127.96, 128.86, 131.67, 133.33, 135.83, 136.96, 138.03 (Ar), 164.60 (CO). HRMS: Found: *m/z* 313.1260. Calcd for $C_{19}H_{20}O_2S$: (M^++1), 313.1262. Anal. Found: C, 73.28; H, 6.22%. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45%.

Reaction of Thiofenchone 15 with 2 in Refluxing Dichloromethane. To a solution of **15** (0.050 g, 0.3 mmol) in dichloromethane was added 2-carboxybenzenediazonium chloride (0.332 g, 1.8 mmol) in one portion. The suspension was refluxed for 1 h and the reaction mixture was evaporated to give a reddish-brown oil, which was chromatographed over silica gel by elution with hexane to afford a colorless oil of the adduct (7 : 1 mixture of **16a** and **16b**).

16a: ^{1}H NMR ($CDCl_3$) δ = 1.09 (s, 3 H, Me), 1.22 (s, 3 H, Me), 1.29 (s, 3 H, Me), 1.35—1.95 (m, 7 H, CH and CH_2), 6.85 (d, 1 H, *J* = 8 Hz, Ar), 6.93 (d, 1 H, *J* = 8 Hz, Ar), 6.97 (t, 1 H, *J* = 8 Hz, Ar), 7.15 (t, 1 H, *J* = 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 18.90 (Me), 25.50 (Me), 25,99 (CH_2), 31.24 (CH_2), 31.22 (CH_2), 33.95 (Me), 43.02 (CH_2), 48.20 (C), 50.01 (CH), 54.20 (C), 120.45, 122.65, 124.00, 128.19, 128.90, 130.88 (Ar). HRMS: Found: *m/z* 244.1303. Calcd for $C_{16}H_{20}S$: (M^+), 244.1286.

Compound **16a** contained a small amount of **16b** and could not be isolated.

Table 4. Crystal and Intensity Collection Data for **12**

	12
Formula	$C_{18}H_{20}S$
Formula weight	268.12
Size of crys./mm	0.50 × 0.30 × 0.40
Space group	$P2_1/n$ (14)
a/Å	10.501(2)
b/Å	19.550(5)
c/Å	7.210(1)
β/°	98.80
V/Å^{-3}	1462.74(0)
Z	4
T/K	296
No. of reflns measured	2902
No. of reflns unique	2659
R	0.063
R_w	0.097

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21 The X-ray crystallographic analysis of **12** was carried out by using Enraf–Nonius CAD4 diffractometer. Selected data were shown in Table 4. The complete $F_o - F_c$ data are deposited as Document No. 73005 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 136441.