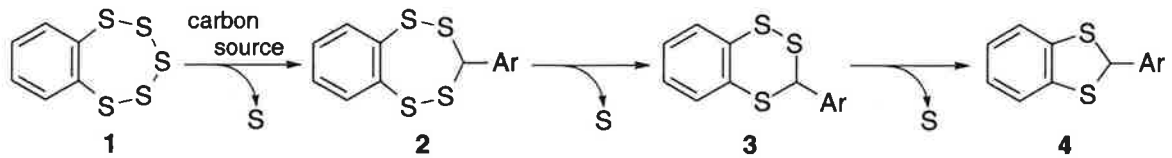
NEW SULFUR-CARBON DISPLACEMENT REACTION AND SYSTEMATIC DESULFURIZATION IN MULTI-SULFUR LINKAGES OF BENZOPENTATHIEPIN

Satoshi Ogawa, Makoto Wagatsuma, and Ryu Sato*

Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka 020, Japan

Abstract - Benzopentathiepin reacts with phosphorus ylides to form a mixture of benzotetrathiepins and benzotrithiins. The carbanion fragment of the phosphorus ylides replaces the one or two sulfur atoms in the multi-sulfur linkages of benzopentathiepin. Systematic desulfurization to form a new cyclic system is accomplished by the use of a combination of phosphorus ylide and triphenylphosphine in the reactions of benzopentathiepin, benzotetrathiepins, and benzotrithiins.

Recently, cyclic benzopolysulfides have generated significant interest, because of their interesting physical properties and recent discovery of the metabolites from marine ascidian, which exhibit potent antitumor activity as well as antifungal activity.[1] We previously reported the synthesis and reactivities of cyclic benzopolysulfides containing multi-sulfur linkages.[2] However, although the scission of the S-S linkage involving desulfurization in such systems is of considerable biological importance, there have been only a few reports on the reactions of cyclic benzopolysulfides with organic phosphorus compounds.[3] During studies on structures, reactivities, and synthetic utility of cyclic benzopolysulfides, we have now found new sulfur-carbon displacement reactions upon treatment of benzopentathiepin with phosphorus ylides and systematic desulfurization with triphenylphosphine. We wish to report here new sulfur-carbon exchange in benzopentathiepin (**1**), desulfurization of the cyclic multi-sulfur linkages fused to benzene ring, and characterization of the resulting new cyclic products, benzotetrathiepins (**2**),[4] benzotrithiins (**3**),[5] and benzodithioles (**4**)[6] (Scheme 1).

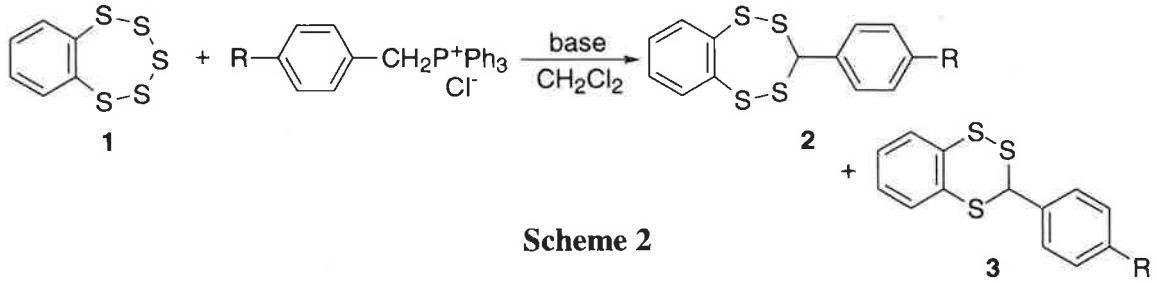


Scheme 1

This paper is dedicated to Prof. Shigeru Oae on the occasion of his 77th birthday.

This study was started aiming to find a new insertion reaction of the carbon fragment into the benzopentathiepin (**1**) with electrophiles or nucleophiles. However, when pentathiepin (**1**) was treated with excess of phenyldiazomethane or diphenyldiazomethane in the presence of catalytic amount of CuCl in refluxing benzene, starting material (**1**) was recovered as a major component along with small amount of undetermined olefinic products. Therefore, we turned our attention to the reactions of pentathiepin (**1**) with carbon nucleophiles such as phosphorus ylides to introduce the carbon fragment into the multi-sulfur linkages.

Phosphonium salts having an acidic proton are well known to generate the corresponding phosphorus ylides in the presence of a base. Benzopentathiepin (**1**) reacted with the phosphorus ylides (**5a-e**) in dichloromethane to form a mixture of 7-membered 3-aryl-1,2,4,5-benzotetrathiepins (**2a-d**) and 6-membered 3-aryl-1,2,4-benzotrithiins (**3a-e**) in moderate yields (Scheme 2). In the former compounds (**2**), one sulfur atom in the multi-sulfur linkages of **1** was replaced by one carbon fragment from the phosphorus ylides, while in the latter ones (**3**), two sulfur atoms of **1** were replaced by one carbon fragment. In order to know the reaction conditions for formation of 3-aryl-1,2,4,5-tetrathiepins (**2**) as major products, we carried out the reactions of pentathiepin (**1**) with phosphorus ylide (**5a**) generated from several bases, NaH, t-BuOK, n-BuLi, and NaOH. These results suggested that NaH was a base of choice in the displacement reaction. We chose the reaction time of 4 h and the temperature of 25 ℃ as the result of several runs under appropriate reaction conditions. These results are summarized in Table 1.



Scheme 2

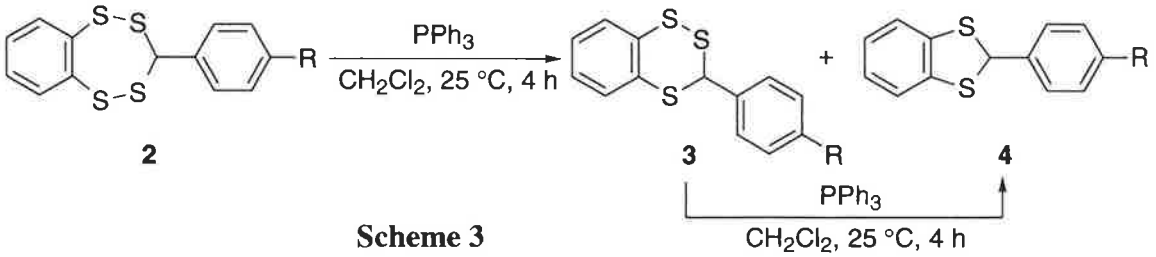
Table 1 Reactions of benzopentathiepin (**1**) with phosphorus ylides (**5a-e**)

R	base (1.0 eq.)	ylide	time (h)	temp. (℃)	total yield (**2** and **3**)[a] (%)		product ratio (**2**/**3**)[b]
CH_3O	NaH	**5a**	4	25	70	(**2a** and **3a**)	35/65
CH_3O	NaH	**5a**	24	25	46	(**2a** and **3a**)	24/76
CH_3O	NaH	**5a**	4	40	67	(**2a** and **3a**)	23/77
CH_3O	NaH	**5a**	4	-15	59	(**2a** and **3a**)	36/64
CH_3O	NaH	**5a**	24	-78	53	(**2a** and **3a**)	24/76
CH_3O	t-BuOK	**5a**	4	25	46	(**2a** and **3a**)	32/68
CH_3O	n-BuLi	**5a**	4	25	21	(**2a** and **3a**)	0/100
CH_3O	NaOH	**5a**	4	25	0	(**2a** and **3a**)	-
CH_3	NaH	**5b**	4	25	70	(**2b** and **3b**)	27/73
H	NaH	**5c**	4	25	67	(**2c** and **3c**)	22/78
Cl	NaH	**5d**	4	25	60	(**2d** and **3d**)	11/89
NO_2	NaH	**5e**	4	25	55	(**2e** and **3e**)	0/100

a) Isolated yield b) Determined by ^{1}H nmr

These new products, (**2**) and (**3**), were easily separated by preparative liquid chromatography after the determination of the ratios of **2/3** by 400 MHz ^{1}H nmr spectroscopy. The structures of **2** and **3** were characterized by physical and spectroscopic means. Especially, the chemical shifts of the methine protons in the ^{1}H nmr spectra of the cyclic component of **2** (5.40-5.44 ppm) and **3** (5.96-6.07 ppm) gave good information about the formation of the cyclic structures, i.e., 7- and 6-membered rings, respectively. Interestingly, the ratio of **2/3** were dramatically affected by the para substituent of the aryl group derived from phosphorus ylides, which will be discussed later.

There are several reports on the desulfurization of cyclic polysulfides with tertiary phosphorus compounds such as phosphines or phosphites.[7] In addition, we have also reported efficient desulfurization of several cyclic benzopolysulfides by phosphites or phosphorus ylides.[3] However, when benzopentathiepin (**1**) was allowed to react with an equimolar amount of tertiary phosphines, ortho-benzenedithiol and recovered pentathiepin (**1**) were obtained by rapid sequential desulfurization of **1**. Thus, we examined the application of the desulfurization with tertiary phosphine to tetrathiepins (**2**) and benzotrithiins (**3**) by the use of triphenylphosphine. When tetrathiepin (**2**) was allowed to react with an equimolar amount of triphenylphosphine, corresponding desulfurization products, trithiins (**3**) and dithioles (**4**), were obtained as a mixture containing the starting material (**2**). Although the product yields were affected by the molar ratio of triphenylphosphine, the product ratio could not be affected by the para substituent of the aryl group in the 3-position of the cyclic structure. Indeed, the yields of dithioles (**4**) were increased with an increase of the molar ratio of triphenylphosphine. These products, (**3**) and (**4**), were easily separated by preparative liquid chromatography after the determination of the ratios of **2/3/4** by 400 MHz ^{1}H nmr spectroscopy. On the other hand, trithiins (**3**) reacted with an equi-



Scheme 3

Table 2 Reactions of benzotetrathiepins (**2**) with triphenylphosphine

R	PPh_3 (eq.)	total yield[a] (**2**,**3**,**4**) (%)	product ratio[b] (**2/3/4**)
CH_3O	1.0	92	48/14/38
CH_3	1.0	91	52/12/36
CH_3	1.5	96	4/34/62
CH_3	2.0	99	0/14/86
H	1.0	97	62/9/29
Cl	1.0	99	59/14/27

a) Isolated yield b) Determined by ^{1}H nmr

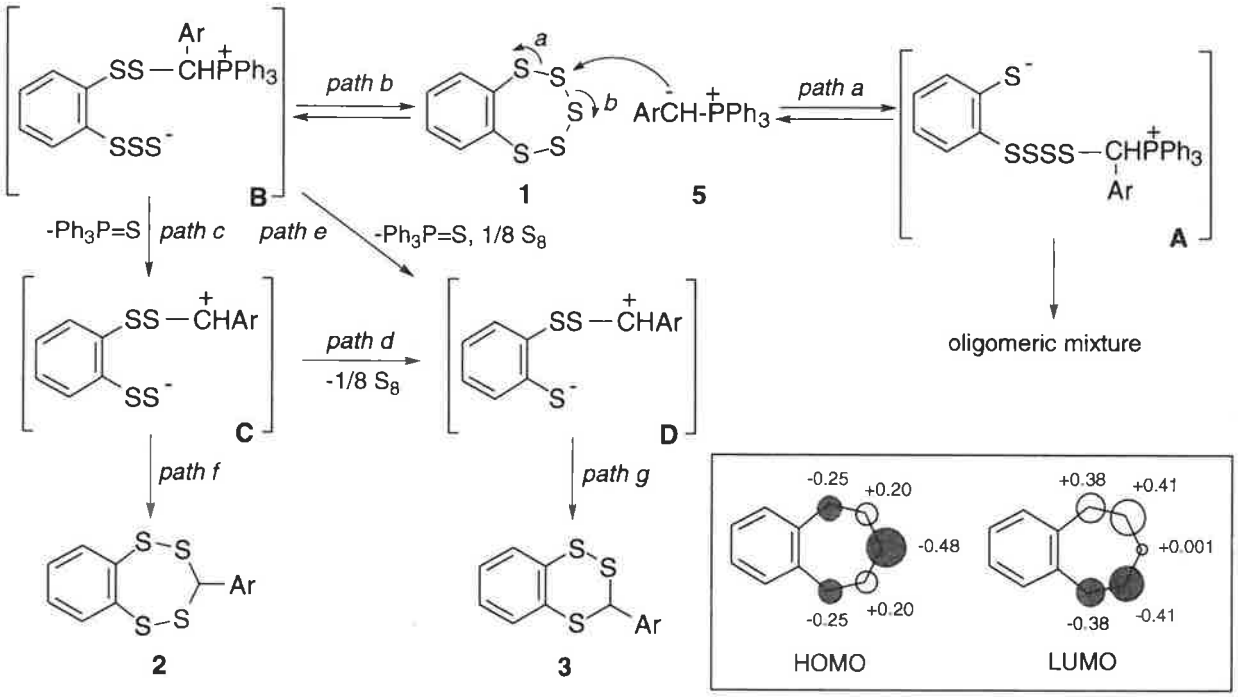
Table 3 Reactions of benzotrithiins (**3**) with triphenylphosphine

R	PPh_3 (eq.)	yield (**4**)[a] (%)
CH_3O	1.0	97 (**4a**)
CH_3	1.0	94 (**4b**)
H	1.0	92 (**4c**)
Cl	1.0	95 (**4d**)
NO_2	1.0	95 (**4e**)

a) Isolated yield

molar amount of triphenylphosphine to give corresponding dithioles (**4**) in excellent yields. These results are shown in Scheme 3 and Tables 2 and 3.

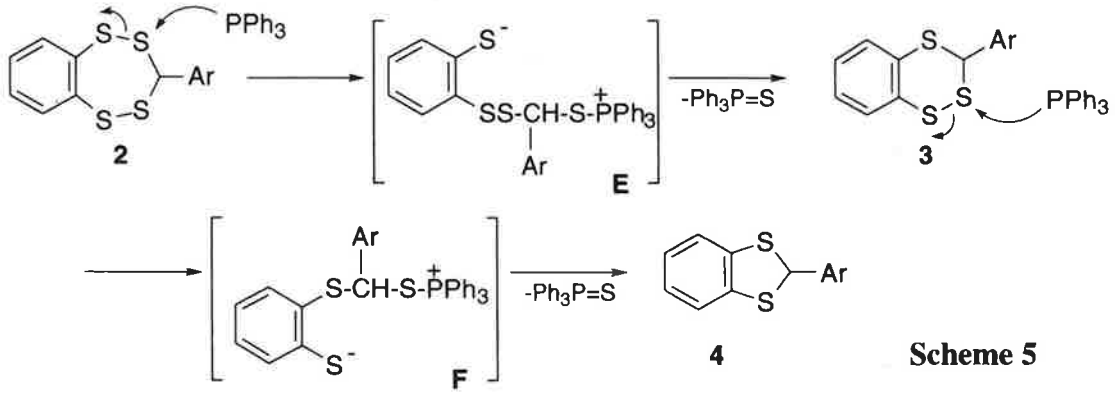
Based on these results, the plausible pathways of the sulfur-carbon displacement reaction of benzopentathiepin (**1**) with phosphorus ylides are illustrated in Scheme 4. In an attempt to understand the initial reaction site in pentathiepin (**1**), semiempirical PM3 calculations were carried out.[8,9] The computed HOMO and LUMO of pentathiepin (**1**) are depicted in Figure 1. The density gradient of the virtual LUMO of the polysulfide ring suggests a significant favoring of the nucleophilic attack on the sulfur atom at the 2-position of the five sulfur atoms. Therefore, the carbanion of phosphorus ylide initially attacks the sulfur atom at the 2-position to form a zwitterionic intermediate (**A**) (*path a*) and (**B**) (*path b*). The intermediate (**A**) would presumably form an oligomeric mixture via an unstable cyclic benzopolysulfide with three (trithiole) or four sulfur atoms (tetrathiin), which could not be specified.[10] The intermediate (**B**) is readily transferred to **C** along with triphenylphosphine sulfide (*path c*). When the intermediate (**C**) has an electron-withdrawing aryl substituents, rapid desulfurization presumably takes place to form a thermodynamically more stable intermediate (**D**). Alternatively, a relatively stable intermediate **C** having an electron-donating aryl substituents takes the course of both *path d* and *path f*. On the other hand, the direct formation of the intermediate (**D**) from **B** (*path e*) cannot be ruled out. Finally, the intermediates (**C**) and (**D**) react intramolecularly, giving tetrathiepin (**2**) (*path f*) and trithiin (**3**) (*path g*), respectively. The three pathways (*path c, d, e*) would compete because tetrathiepin (**2**) could not produce trithiin (**3**) upon treatment with phosphorus ylides.



Scheme 4

Figure 1

The plausible reaction pathways for the desulfurization of benzotetrathiepin (**2**) with triphenylphosphine are shown in Scheme 5. Triphenylphosphine initially attacks the sulfur atom at the 2-position of tetrathiepin (**2**) to form a zwitterionic intermediate (**E**). The intermediate (**E**) reacts intramolecularly by the attack of thiolate anion to carbon atom, giving benzotrithiin (**3**) together with triphenylphosphine sulfide. The resulting trithiin (**3**) is also desulfurized by the similar pathways to give benzodithiole (**4**) via an intermediate (**F**) which is formed by the initial attack of triphenylphosphine at the 2-position in the trithiin framework.



Scheme 5

We conclude from this study that the desulfurization mechanisms of the cyclic benzopolysulfides by the use of phosphorus compounds are complex and unclear now, because the zwitterionic intermediates (**A**) to (**F**) are too unstable to be isolated or detected directly by spectroscopic techniques. However, we have obtained three types of new cyclic benzopolysulfides, benzotetrathiepins (**2**) (7-membered C3S4), benzotetrathiins (6-membered C3S3) (**3**), and benzotrithioles (5-membered C3S2) (**4**), from benzopentathiepin (7-membered C2S5) (**1**) by taking advantage of a new synthetic strategy by the use of two types of phosphorus compounds, phosphorus ylide and triphenylphosphine.

EXPERIMENTAL

All melting points are uncorrected. Nmr spectra were obtained with a Bruker AC-400 spectrometer. Ir spectra were recorded on a JASCO FT IR-7300 spectrophotometer. Mass spectra were taken with a Hitachi M-2000 mass spectrometer. Elemental analyses were performed on a Yanagimoto MT-3 analyzer. Preparative liquid chromatography was performed on a JAI Model LC-908. Silica gel used for column chromatography was Wakogel C-200. All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., Kanto Chemical Co., Inc., or Aldrich Chemical Co. The reaction solvents were further purified by general methods.

Reactions of Benzopentathiepin (1) with Phosphorus Ylides (5)

A typical procedure is as follows. To a stirred solution of benzopentathiepin (**1**) (24 mg, 0.1 mmol) in CH_2Cl_2 (3 ml) was added a mixture of 4-methoxybenzyltriphenylphosphonium chloride (42 mg, 0.1 mmol) and sodium hydride (10 mg, 0.25 mmol). The reaction mixture was stirred at 25 ℃ for 4 h

under N_2 atmosphere and then treated with water (5 ml). The resulting organic layer was extracted with CH_2Cl_2 (3 x 5 ml) and dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was purified by column chromatography (silica gel; eluent, CCl_4) and preparative liquid chromatography to give 3-(4-methoxyphenyl)-1,2,4,5-benzotetrathiepin (**2a**) and 3-(4-methoxyphenyl)-1,2,4-benzotrithiin (**3a**) in 25 and 45% yields, respectively.

3-(4-Methoxyphenyl)-1,2,4,5-benzotetrathiepin (2a)

Colorless crystals; mp 153-154 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 3.79 (3H, s, CH_3), 5.40 (1H, s, CH), 6.86 (2H, dd, J=8.7, 2.1 Hz, PhH), 7.19 (2H, dd, J=8.7, 2.1 Hz, PhH), 7.40 (2H, dd, J=5.6, 3.4 Hz, ArH), 7.89 (2H, dd, J=5.6, 3.4 Hz, ArH); $^{13}C\{^1H\}$ nmr (100MHz, $CDCl_3$) δ 55.3, 64.4, 114.6, 129.2, 129.5, 130.7, 135.0, 144.7, 160.3; ir (KBr) 1604, 1508, 1254, 1174, 1029, 843; ms (m/z) 324 (M^+); Anal. Calcd for $C_{14}H_{12}OS_4$: C, 51.81; H, 3.73. Found: C, 51.92; H, 3.91.

3-(4-Methylphenyl)-1,2,4,5-benzotetrathiepin (2b)

Colorless crystals; mp 173-174 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 2.33 (3H, s, CH_3), 5.41 (1H, s, CH), 7.15 (4H, br s, PhH), 7.40 (2H, dd, J=5.6, 3.4 Hz, ArH), 7.89 (2H, dd, J=5.6, 3.4 Hz, ArH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 21.3, 65.1, 127.7, 129.9, 130.6, 134.4, 135.0, 139.4, 144.7; ir (KBr) 1508, 1441, 1427, 1182, 829; ms (m/z) 308 (M^+); Anal. Calcd for $C_{14}H_{12}S_4$: C, 54.50; H, 3.92. Found: C, 54.89; H, 4.24.

3-Phenyl-1,2,4,5-benzotetrathiepin (2c)

Colorless needles; mp 141-142 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 5.44 (1H, s, CH), 7.24-7.27 (2H, m, PhH), 7.32-7.35 (3H, m, PhH), 7.39 (2H, dd, J=5.6, 3.5 Hz, ArH), 7.89 (2H, dd, J=5.6, 3.5 Hz, ArH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 65.6, 127.8, 129.2, 129.3, 130.6, 135.0, 137.4, 144.7; ir (KBr) 1490, 1453, 1441, 1426, 1161, 788; ms (m/z) 294 (M^+); Anal. Calcd for $C_{13}H_{10}S_4$: C, 53.02; H, 3.42. Found: C, 52.66; H, 3.54.

3-(4-Chlorophenyl)-1,2,4,5-benzotetrathiepin (2d)

Colorless needles; mp 139-140 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 5.40 (1H, s, CH), 7.21 (2H, dd, J=8.5, 1.9 Hz, PhH), 7.33 (2H, dd, J=8.5, 1.9 Hz, PhH), 7.42 (2H, dd, J=5.7, 3.4 Hz, ArH), 7.90 (2H, dd, J=5.7, 3.4 Hz, ArH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 64.7, 129.2, 129.5, 130.7, 135.0, 135.3, 135.9, 144.6; ir (KBr) 1487, 1440, 1404, 1085, 1013, 842; ms (m/z) 296 (M^+-Cl); Anal. Calcd for $C_{13}H_9ClS_4$: C, 47.47; H, 2.76. Found: C, 47.23; H, 2.86.

3-(4-Methoxyphenyl)-1,2,4-benzotrithiin (3a)

Colorless needles; mp 137-138 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 3.82 (3H, s, CH_3), 5.96 (1H, s, CH), 6.89 (2H, dd, J=8.7, 2.0 Hz, PhH), 7.14 (1H, td, J=7.6, 1.4 Hz, ArH), 7.22 (1H, td, J=7.6, 1.4 Hz, ArH), 7.41 (1H, dd , J=7.6, 1.4 Hz, ArH), 7.48 (2H, dd, J=8.7, 2.0 Hz, PhH), 7.52 (1H, dd, J=7.6, 1.4 Hz, ArH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 55.3, 60.7, 114.3, 125.4, 127.9, 129.2, 129.4, 130.2, 130.7, 134.1, 139.2, 160.3; ir (KBr) 1603, 1508, 1451, 1256, 1167, 1030, 844; ms (m/z) 292 (M^+); Anal. Calcd for $C_{14}H_{12}OS_3$: C, 57.50; H, 4.14. Found: C, 57.52; H, 4.23.

3-(4-Methylphenyl)-1,2,4-benzotrithiin (3b)

Colorless needles; mp 73.5-74 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 2.63 (3H, s, CH_3), 5.96 (1H, s, CH), 7.14 (1H, td, J=7.6, 1.4 Hz, ArH), 7.18 (2H, dd, J=8.6, 1.7 Hz, PhH), 7.22 (1H, td, J=7.6, 1.4 Hz, ArH), 7.41 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.43 (2H, dd, J=8.6, 1.7 Hz, PhH), 7.52 (1H, dd, J=7.6, 1.4 Hz, ArH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 21.3, 60.9, 125.4, 127.9, 128.0, 129.6, 130.2, 130.7, 134.3, 134.4, 139.1, 139.3; ir (KBr) 1605, 1506, 1451, 1421, 1105, 837; ms (m/z) 276 (M^+); Anal. Calcd for $C_{14}H_{12}S_3$: C, 60.82; H, 4.38. Found: C, 60.45; H, 4.54.

3-Phenyl-1,2,4-benzotrithiin (3c)

Colorless needles; mp 61-62 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 5.99 (1H, s, CH), 7.16 (1H, td, J=7.6, 1.4 Hz, ArH), 7.24 (1H, td, J=7.6, 1.4 Hz, ArH), 7.35-7.40 (3H, m, PhH), 7.43 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.54 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.54-7.57 (2H, m, PhH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 60.4, 125.8, 128.3, 129.1, 129.4, 130.6, 130.9, 135.0, 135.4, 136.4, 138.7; ir (KBr) 1452, 1423, 1252, 1174, 1026, 751; ms (m/z) 262 (M^+); Anal. Calcd for $C_{13}H_{10}S_3$: C, 59.50, H, 3.84. Found: C, 59.27; H, 3.76.

3-(4-Chlorophenyl)-1,2,4-benzotrithiin (3d)

Colorless needles; mp 78-78.5 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 5.97 (1H, s, CH), 7.18 (1H, td, J=7.6, 1.4 Hz, ArH), 7.26 (1H, td, J=7.6, 1.4 Hz, ArH), 7.34 (2H, dd, J=8.5, 2.0 Hz, PhH), 7.44 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.49 (2H, dd, J=8.5, 2.0 Hz, PhH), 7.55 (1H, dd, J=7.6, 1.4 Hz, ArH), $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 61.1, 125.5, 128.0, 128.1, 128.9, 129.3, 130.4, 130.8, 134.7, 137.5, 139.0; ir (KBr) 1487, 1453, 1438, 1405, 1085,1012,843; ms (m/z) 296 (M^+); Anal. Calcd for $C_{13}H_9ClS_3$: C, 52.60; H, 3.06. Found: C, 52.54; H, 3.10.

3-(4-Nitrophenyl)-1,2,4-benzotrithiin (3e)

Pale yellow needles; mp 100.5-101 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 6.07 (1H, s, CH), 7.24 (1H, td, J=7.6, 1.4 Hz, ArH), 7.31 (1H, td, J=7.6, 1.4 Hz, ArH), 7.50 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.60 (1H, dd, J=7.6, 1.4 Hz, ArH), 7.73 (2H, dd, J=8.8, 2.1 Hz, PhH), 8.22 (2H, dd, J=8.8, 2.1 Hz, PhH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 59.9, 124.0, 126.4, 128.7, 129.0, 131.1, 137.0, 138.0, 145.6, 148.1; ir (KBr) 1603, 1455, 1346, 1108, 861; ms (m/z) 307 (M^+); Anal. Calcd for $C_{13}H_9NO_2S_3$: C, 50.79; H, 2.95. Found: C, 50.72; H, 2.93.

Desulfurization of 3-Aryl-1,2,4,5-benzotetrathiepin (2) with Triphenylphosphine

A typical procedure is as follows. To a solution of 3-(4-methoxyphenyl)-1,2,4,5-benzotetrathiepin (**2a**) (12 mg, 0.037 mmol) in CH_2Cl_2 (5 ml) at -10 ℃ was added triphenylphosphine (10 mg, 0.037 mmol). The reaction mixture was stirred at 25 ℃ for 4 h under N_2 atmosphere and then treated with water (5 ml). The resulting organic layer was extracted with CH_2Cl_2 (3 x 5 ml) and the extract was dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was purified by column chromatography (silica gel; eluent, CCl_4). The product ratios were determined by 400 MHz ^1H nmr.

Desulfurization of 3-Aryl-1,2,4,-benzotrithiin (3) with Triphenylphosphine

A typical procedure is as follows. To a stirred solution of 3-(4-methoxyphenyl)-1,2,4-benzotrithiin (**3a**) (15 mg, 0.05 mmol) in CH_2Cl_2 (5 ml) was added triphenylphosphine (16 mg, 0.06 mmol). The reaction mixture was stirred at 25 ℃ for 4 h under N_2 atmosphere and then treated with water (5 ml). The resulting organic layer was extracted with CH_2Cl_2 (3 x 5 ml) and dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was purified by column chromatography (silica gel; eluent, CCl_4) and preparative liquid chromatography to give 2-(4-methoxyphenyl)-1,3-benzodithiole (**4a**) in 97% yield.

2-(4-Methoxyphenyl)-1,3-benzodithiole (4a)

Colorless needles; mp 71-71.5 ℃ (lit.,[6] 71-72 ℃).

2-(4-Methylphenyl)-1,3-benzodithiole (4b)

Colorless needles; mp 76-76.5 ℃ (lit.,[6] 77-78 ℃).

2-Phenyl-1,3-benzodithiole (4c)

Colorless needles; mp 70.5-71 ℃ (lit.,[6] 72-73 ℃).

2-(4-Chlorophenyl)-1,3-benzodithiole (4d)

Colorless needles; mp 72.5-73 ℃ (lit.,[6] 74-75 ℃).

2-(4-Nitrophenyl)-1,3-benzodithiole (4e)

Yellow needles; mp 86-86.5 ℃ ($CHCl_3$/n-hexane); ^1H nmr (400 MHz, $CDCl_3$) δ 6.06 (1H, s, CH), 7.10 (2H, dd, J=5.8, 3.3 Hz, ArH), 7.23 (2H, dd, J=5.8, 3.3 Hz, ArH), 7.66 (2H, dd, J=8.8, 1.8 Hz, PhH), 8.16 (2H, dd, J=8.8, 1.8 Hz, PhH); $^{13}C\{^1H\}$ nmr (100 MHz, $CDCl_3$) δ 54.6, 122.2, 124.1, 126.3, 127.7, 136.4, 147.8, 147.9; ir (KBr) 1596, 1523, 1444, 1345, 1106, 857; MS (m/z) 275 (M^+); Anal. Calcd for $C_{13}H_9NO_2S_2$: C, 56.70; H, 3.30. Found: C, 56.85; H, 3.21.

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REFERENCES AND NOTES

1. F. D. Toste and I. W. J. Still, *J. Am. Chem. Soc.*, 1995, **117**, 7261; B. S. Davidson, P. W. Ford, and M. Wahlman, *Tetrahedron Lett.*, 1994, **35**, 7185; P. F. Searle and T. F. Molinski, *J. Org. Chem.*, 1994, **59**, 6600; R. S. Compagnone and D. J. Faulkner, *Tetrahedron*, 1994, **50**, 12785; M. Litaudon, F. Trigalo, M -T. Martin, F. Frappier, and M. Guyot, *Tetrahedron*, 1994, **50**, 5323; P. F. Ford, M. R. Narbut, J. Belli, and B. S. Davidson, *J. Org. Chem.*, 1994, **59**, 5955; P. F. Ford and B. S. Davidson, *J. Org. Chem.*, 1993, **58**, 4522; V. Behar and S. J. Danishefsky, *J. Am. Chem. Soc.*, 1993, **115**, 7017; M. Litaudon and M. Guyot, *Tetrahedron Lett.*, 1991, **32**, 911; B. S. Davidson, T. F. Molinski, L. R. Barrows, and C. M. Ireland, *J. Am. Chem. Soc.*, 1991, **113**, 4709.
2. S. Ogawa, S. Saito, T. Kikuchi, Y. Kawai, S. Niizuma, and R. Sato, *Chem. Lett.*, 1995, 321; S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida, and R. Sato, *Tetrahedron Lett.*, 1994, **35**, 5469; S. Ogawa, N. Yomoji, S. Chida, and R. Sato, *Chem. Lett.*, 1994, 507.
3. R. Sato, T. Murata, S. Chida, and S. Ogawa, *Chem. Lett.*, 1993, 1325; R. Sato and S. Satoh, *Synthesis*, 1991, 785.
4. R. Sato, S. Satoh, and M. Saito, *Chem. Lett.*, 1990, 139; F. Fehér and B. Engelen, *Z. Naturforsch*, 1979, **34b**, 426; F. Fehér and B. Engelen, *Z. Anorg. Allg. Chem.*, 1979, **452**, 37; F. Fehér, F. Malcharek, and K. Glinka, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 331
5. R. Sato, Y. Kanazawa, Y. Akutsu, and M. Saito, *Heterocycles*, 1989, **29**, 2097.
6. For examples, see: I. Dagani and R. Fochi, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1133; I. Dagani and R. Fochi, *Synthesis*, 1976, 759.

7. For recent examples, see: T. Matsumoto, N. Tokitoh, and R. Okazaki, *Organomatallics*, 1995, **14**, 1008; H. Suzuki, N. Tokitoh, S. Nagase, and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11578; N. Tokitoh, T. Matsumoto, K. Manmaru, and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 8855; N. Tokitoh, Y. Matsuhashi, M. Goto, and R. Okazaki, *Chem. Lett.*, 1992, 1595; N. Tokitoh, Y. Matsuhashi, and R. Okazaki, *Tetrahedron Lett.*, 1992, **33**, 5551; N. Tokitoh, T. Matsumoto, H. Ichida, and R. Okazaki, *Tetrahedron Lett.*, 1991, **32**, 6877.

8. PM3 Calculations for pentathiepin (**1**) were carried out on a HITAC M680/160E computer by MOPAC Version 6.02 [(QCPE No. P015), J. J. Stewart, *QCPE Bull.*, 1989, **9**, 10; Revised as Ver. 6.01 by T. Hirano, University of Tokyo, for HITAC and UNIX machines, *JCPE Newsletter*, 1989, **10**, 1; Revised as Ver. 6.02 by present authors]. The structure of **1** was optimized by Allinger's MM2(77) molecular mechanics force field.[9]

9. N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127. Additional parameters were given in the following papers. N. L. Allinger, M. J. Hickey, and J. Kao, *J. Am. Chem. Soc.*, 1976, **98**, 2741; J. Kao, C. Eyermann, E. Southwick, and D. Leister, *J. Am. Chem. Soc.*, 1985, **107**, 5323; H. -D. Beckhaus, *Chem. Ber.*, 1983, **116**, 86.

10. Although 5,8-disubstituted benzotetrathiins and 4,7-disubstituted benzotrithioles[2] have been isolated, simple benzene fused tetrathiin and trithiole are unstable in the solid-state. Unpublished results in our laboratory.

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