

The Novel One Step Syntheses of Benzobis- and Benzotris[1,2,5]thiadiazole (1)

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The reaction of tetrasulfur tetranitride with alkoxybenzenes such as anisole (**1a**), *o*- (**1b**), *m*- (**1c**), *p*-dimethoxybenzenes (**1d**), and benzyl ether (**1e**) was investigated. Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]-tris[1,2,5]thiadiazole (**2**) and benzo[1,2-*c*:3,4-*c'*]bis[1,2,5]thiadiazoles (**3a** and **3b**) were isolated.

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Though tetrasulfur tetranitride, N₄S₄, was first synthesized by Gregory (2) in 1835, its structure was not clear until an X-ray study was carried out by Clark (3). We have been trying to develop a new synthetic reagent and our brief survey of the literature revealed that little is known about the reaction of tetrasulfur tetranitride with organic compounds; tetrasulfur tetranitride was found to react with aryl ethanes (4), 9,10-dihydrophenanthrene (5), tetrahydronaphthalene (5) and acetylenes (6,7) to give corresponding 1,2,5-thiadiazole derivatives.

In the reaction of tetrasulfur tetranitride with acetylenes, toluene (8) used as a solvent was found to react with tetrasulfur tetranitride at reflux temperature to give triphenyl-*s*-triazine in poor yield with long reaction time. During our investigation for a more suitable solvent, we encountered a novel reaction of tetrasulfur tetranitride with alkoxybenzenes, which is reported herein.

The reaction of tetrasulfur tetranitride with excess alkoxybenzenes (1) such as anisole (**1a**), *ortho*- (**1b**), *meta*- (**1c**), and *para*-dimethoxybenzene (**1d**) and benzyl phenyl ether (**1e**) was carried out at 120° for 24 hours and the results are summarized in Table I.

It was found in the reaction of tetrasulfur tetranitride with **1a** and **1e** that the two novel products such as benzo-

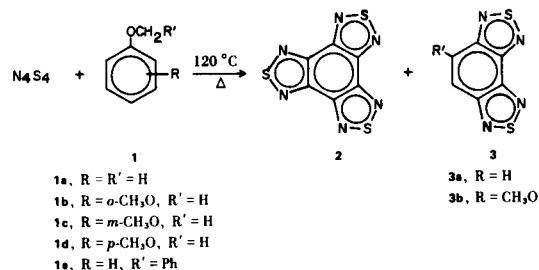
Table I

The Reaction of Tetrasulfur Tetranitride with Excess Alkoxybenzenes (1) at 120° for 24 Hours

Run	1	Mole % Yield of Products		
		2	3a	3b
1 (a)	a	1.9	0.7	---
2 (a)	b	0.7	0	0.4
3 (a)	c	0	0	0.4
4 (a)	d	0	0	0
5 (a)	e	3.6	1.6	---
6 (b)	e	4.2	2.3	---
7 (b) (c)	e	3.9	2.1	---
8 (b) (d)	e	4.1	3.7	---
9 (b) (d)	e	4.5	4.3	---

(a) One g. of tetrasulfur tetranitride was heated in 4 g. of **1**.
(b) Two g. of tetrasulfur tetranitride were heated in 4 g. of **1**.
(c) Air was introduced during heating. (d) The reaction was carried out under the slow (run 8) and moderate (run 9) stream of nitrogen.

[1,2-*c*:3,4-*c'*:5,6-*c''*]-tris- (**2**) (**9**) and benzo[1,2-*c*:3,4-*c'*]-bis[1,2,5]thiadiazole (**3a**) (**9,10**) were obtained, respectively. The structures of **2** and **3a** were deduced from elemental analysis and spectral data, and further confirmed by the comparison of the ir spectra with those of authentic specimens (**9,11**).



While the reported preparation (**9**) of **2** and **3a** involved many steps, the reaction of tetrasulfur tetranitride with **1e** provides a one-step synthesis of **2** and **3a**, in spite of low yields.

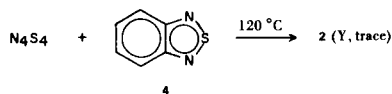
In the reaction of tetrasulfur tetranitride with **1b**, **2** and **3a** were obtained but not **3b**. In contrast to **1b**, **1c** afforded only **3b**, and **1d** gave a large amount of resinous materials. As is shown in Table I, the yields of both **2** and **3a** are made almost twice when **1e** was used in place of **1a**. If the initiation of the reaction between tetrasulfur tetranitride and **1** originated with a free radical as is postulated in the reaction of tetrasulfur tetranitride with 9,10-dihydrophenanthrene and tetrahydronaphthalene (5), this increase of the yields could be understood on the basis of the high reactivity of the benzylic protons.

In this context, we studied the effects of oxygen and nitrogen on the reaction of tetrasulfur tetranitride with **1**.

The air-introduction during the reaction was found unexpectedly not to effect on the yields of both **2** and **3a**. While the yield of **2** was not remarkably effected by nitrogen stream, that of **3a** was almost doubled. The reason of these effects is not clarified.

In order to get some information about the intermediacy of 2,1,3-benzothiadiazole (**4**) in the reaction of tetrasulfur tetranitride with **1**, **1a** was heated at 120° in excess of **4** for 24 hours to afford only a detectable amount of **2** but not any amount of **3a**. The reaction of tetrasulfur tetranitride with **1a** in the presence of **3a** was

also carried out for checking the possibility of the formation of **2** from **3a**, however, no remarkable increase of the yield of **2** was observed.



The above results might suggest that **4** should not be the intermediate for the formation of **3a**, and **3a** should not be for the formation of **2**. Therefore, the 1,2,5-thiadiazole rings might be fused in one step but not stepwise to benzene ring to give **2** and **3**. In contrast to **1**, benzene, toluene, and xylene did not give the corresponding benzo-1,2,5-thiadiazole derivatives, so that, the alkoxy group might play an important role in the formation of **2** and **3**.

EXPERIMENTAL

All melting points are not corrected. The ^1H nmr spectra were recorded on a Hitachi R-20 nmr spectrometer in deuteriochloroform with tetramethylsilane (δ 0.00) as an internal standard. The ir spectra were taken on a Nippon Bunko IR-S spectrophotometer as potassium bromide pellets. The uv spectra were recorded on a Hitachi 124 spectrometer in ethanol. The measurement of high resolution mass spectra was carried out by Nissei Sangyo Co. Ltd. Elemental analyses were performed by Mr. M. Sudo of the Kyushu University.

Materials.

Tetrasulfur tetranitride (**12**) and benzo[2,1,3]thiadiazole (**13**) (**4**) were prepared according to the reported methods. The alkoxybenzenes were commercial grade and used without purification.

General Procedures.

A mixture of 1 g. (Run 1-5) or 2 g. (Run 6-7) of tetrasulfur tetranitride in 4 g. of **1** was stirred by magnetic stirrer at 120° for 24 hours, and then the reaction mixture was allowed to come down to 70° . To it was added 4 ml. of benzene and benzene solution was cooled to room temperature and column chromatographed on activated alumina (Sumitomo KC-30) using benzene as an eluent. After sulfur and unreacted **1** were eluted, compound **2** and **3** were eluted with chloroform.

Benzo[1,2-c:3,4-c':5,6-c'']tris[1,2,5]thiadiazole (**3**).

This compound had m.p. $> 300^\circ$ (in sealed tube, started to sublime in the open tube around 250°), lit. (10), m.p. 345° (in a sealed tube); colorless needles (chloroform); Exact mass: Calcd. for $\text{C}_6\text{N}_6\text{S}_3$: 251.9246. Found: 251.9334.

Anal. Calcd. for $\text{C}_6\text{N}_6\text{S}_3$: C, 28.56; H, 0.00; N, 33.31. Found: C, 28.72; H, 0.00; N, 33.30.

Benzo[1,2-c:3,4-c']bis[1,2,5]thiadiazole (**3a**).

This compound had m.p. $182-184^\circ$, lit. (10), m.p. $179-180.5^\circ$; lit. (11), m.p. 173.5° ; colorless prisms (petroleum ether, b.p. $60-80^\circ$); uv (ethanol): λ max (log ϵ): 287 nm (4.57); ^1H nmr

(deuteriochloroform): δ ppm 7.93 (s, lit. (10), 7.97).

Anal. Calcd. for $\text{C}_6\text{H}_2\text{N}_4\text{S}_2$: C, 37.10; H, 1.03; N, 28.84. Found: C, 37.47; H, 1.11; N, 28.76.

4-Methoxybenzo[1,2-c:3,4-c']bis[1,2,5]thiadiazole (**3b**).

This compound had m.p. $200-202^\circ$; pale yellow needles (*n*-hexane); ^1H nmr (deuteriochloroform): δ ppm 4.11 (3, s, OCH_3), 7.12 (1, s); uv (ethanol): λ max (log ϵ): 297 nm (4.57).

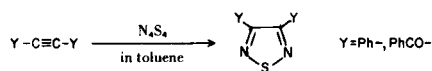
Anal. Calcd. for $\text{C}_7\text{H}_4\text{ON}_4\text{S}_2$: C, 37.52; H, 1.80; N, 25.00. Found: C, 37.86; H, 1.81. N, 24.84.

Acknowledgment.

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(8) When 1 g. of tetrasulfur tetranitride was refluxed in 10 ml. of toluene for 3 days, 30 mg. of triphenyl-s-triazine was isolated, and 0.52 g. of tetrasulfur tetranitride contaminated with sulfur was recovered. (This result means that although toluene is not an ideal solvent for the reaction of tetrasulfur tetranitride with organic compounds, it is practical.)

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(11) The ir spectrum of our **2** is completely identical with that of Professor Carmack's benzotris-[1,2,5]thiadiazole. However, a band at 7.12μ reported by Carmack, *et al.* (9), did not show up on our measurement of both of our **2** and his **2**.

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