

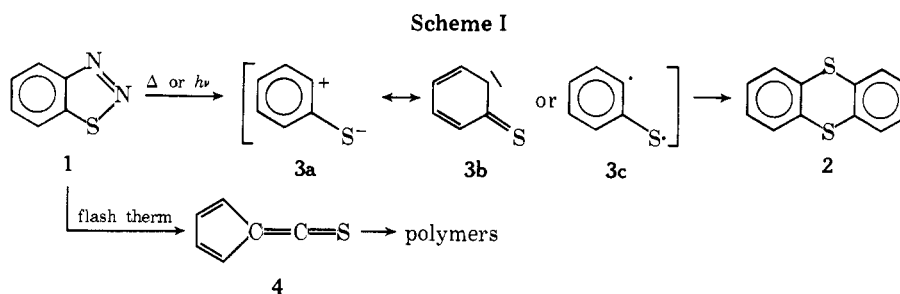
### Thermal Decomposition of 1,2,3-Benzothiadiazole

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Several papers have described the decomposition of thiadiazoles, and several structures have been claimed for the reaction intermediate. It was proposed that the thermal decomposition<sup>1</sup> or photolysis<sup>2</sup> of 1,2,3-benzothiadiazole (1) gives thianthrene (2) by dimerization of the intermediate (3) obtained by cleavage of the heteroaromatic nucleus and nitrogen loss. Two structures were suggested for 3:<sup>2</sup> a 1,3-dipolar form (3a) in resonance with a thioketocarbene (3b) or a 1,3-diradical structure (3c). Recently<sup>3</sup> Seybold and Heibl found that the flash thermolysis of 1,2,3-thiadiazoles may be used as a convenient method for the synthesis of thioketenes, even though thioketene 4 generated from 1 already begins to polymerize at  $-120^\circ\text{C}$ , and could therefore only be detected indirectly. Analogous thioketenes, derived by Wolff rearrangement of the parent thioketocarbenes, were reported by Kirmse and Horner<sup>4</sup> in the photolysis of 1,2,3-thiadiazoles (Scheme I).

3 displays surprisingly sluggish reactivity; it does not add to carbon-carbon double bond or to carbon-nitrogen triple bond, but only to carbon-sulfur double bond. By decomposition of 1 in carbon disulfide, 1,3-benzodithiol-2-thione and spirobis-1,3-benzodithiol were obtained.<sup>5</sup> Our interest in the reactivity<sup>6,7</sup> of 1,2,3-benzothiadiazole (1) has led us to study the thermal decomposition of 1 in various solvents, such as



ethyl acetate, ethyl acetate/phenylacetylene, ethyl acetate/toluene, toluene, and methyl benzoate, in order to gain further information on the structure and reactivity of 3. By decomposition of 1 in ethyl acetate at  $220^\circ\text{C}$ , thianthrene (2), dibenzo[*c,e*]-*o*-dithiin (5), dibenzothiophene (6), and thiophenol (7) were obtained (Scheme II).

Decomposition carried out in toluene or methyl benzoate gave, besides products described above, a mixture of 1-, 2-, 3-,

**Table I. Relative Ratios of 1-, 2-, 3-, and 4-X-Dibenzothiophene (8) and Ratios of Ortho, Meta, and Para Attack of the Intermediate Species 3c (or 3a) on PhX**

X	% of 1-, 2-, 3-, and 4-X-dibenzo- thiophene (8)				% of ortho, meta, and para attack on PhX		
	1-	2-	3-	4-	Ortho	Meta	Para
CH <sub>3</sub>	42 <sup>a</sup>	14 <sup>b</sup>	20 <sup>c</sup>	24 <sup>d</sup>	42	38	20
COOCH <sub>3</sub>	57 <sup>e</sup>	6 <sup>f</sup>	19 <sup>g</sup>	18 <sup>h</sup>	57	24	19

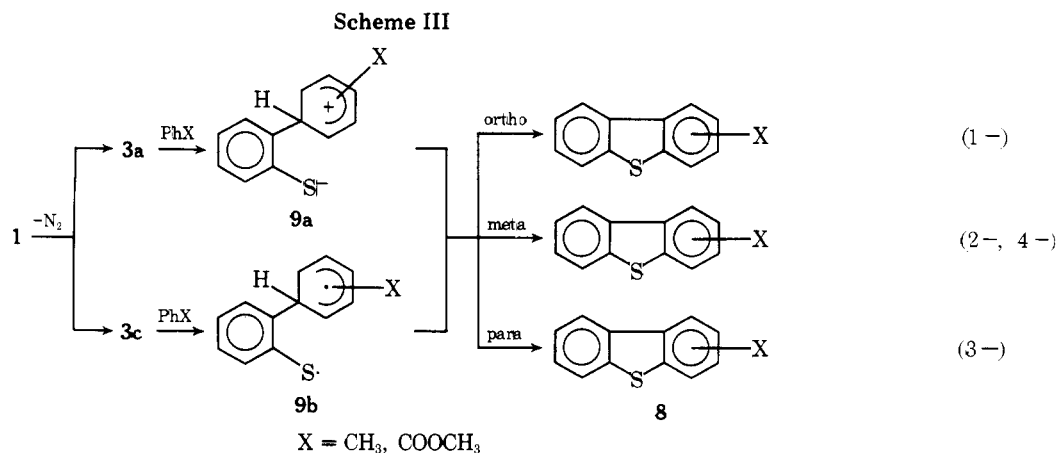
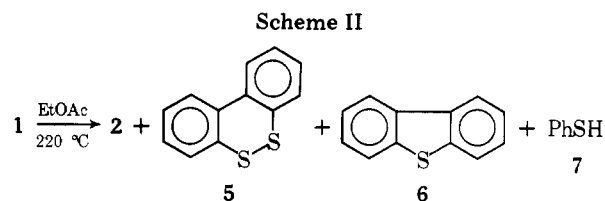
Registry numbers: <sup>a</sup> 31317-07-4; <sup>b</sup> 20928-02-3; <sup>c</sup> 16587-52-3; <sup>d</sup> 7372-88-5; <sup>e</sup> 40488-61-7; <sup>f</sup> 22099-28-1; <sup>g</sup> 60718-96-9; <sup>h</sup> 60718-97-0.

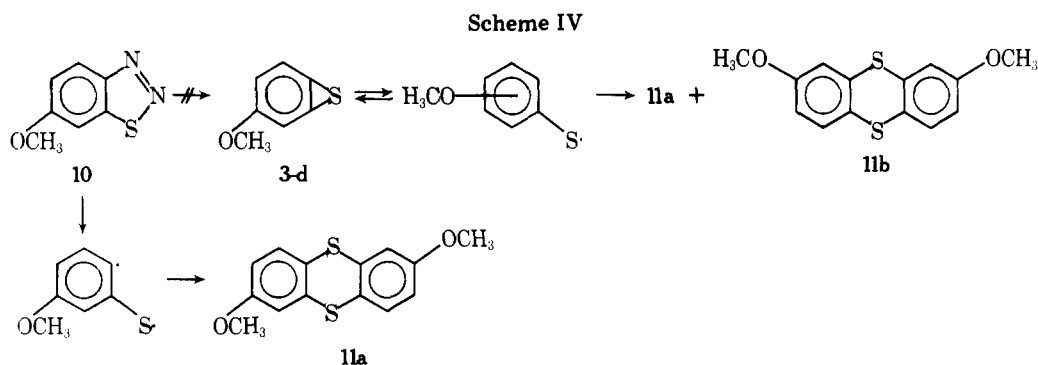
and 4-methyl- and 1-, 2-, 3-, and 4-methoxycarbonyldibenzothiophene (8). The relative isomer ratios are listed in Table I.

8 could arise from attack on the monosubstituted benzene ring either by the carbonium ion of 3a and following trapping of ionic  $\sigma$  complex 9a or by the carbon radical of 3c and trapping of radical  $\sigma$  complex 9b (Scheme III).

However, as show in Table I, the ortho, meta, para isomer ratios of  $\sigma$  complex 9 better agree with a radical mechanism rather than an ionic one, thus indicating that the intermediacy of the dipolar species 3a is not very likely.

We can also exclude the intervention of a benzothiirene as reaction intermediate, as claimed by Cadogan and co-workers<sup>8</sup> to explain the formation of 2 by thermolysis of *o*-bromobenzenethiolate. Analogous thiirenes, in equilibrium with the parent thioketocarbenes, were also proposed by Rees<sup>9</sup> in the



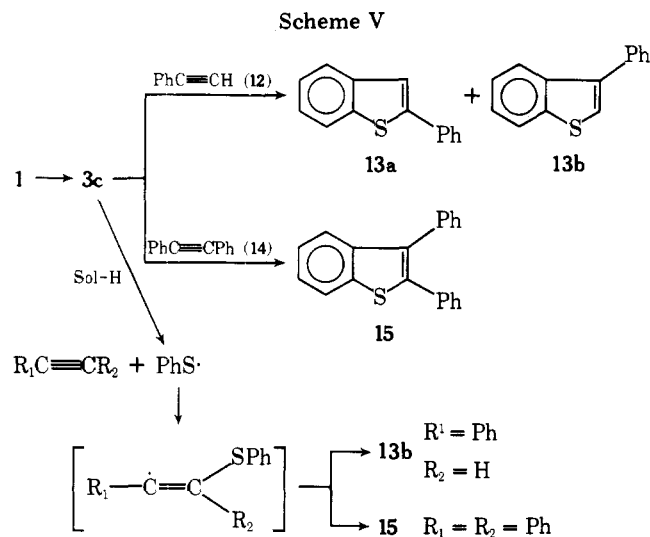


**Table II. Relative Yields (%) of the Products Obtained by Decomposition of 1**

Solvent	2	5	6	8	13	15
Ethyl acetate	42	46	12			
Monosubstituted benzene	33	37	10	20		
Tolane	27	30	8			17
Phenylacetylene	31	34	9		26	

reaction of 4,5-disubstituted 1,2,3-thiadiazoles with nona-carbonyldiiron. In fact, decomposition of 6-methoxy-1,2,3-benzothiadiazole (10) gives only 2,7-dimethoxythianthrene (11a) instead of a mixture of 11a and 2,8-dimethoxythianthrene (11b), which would be expected from reaction of the 3-methoxybenzothiirene (3d) (Scheme IV).

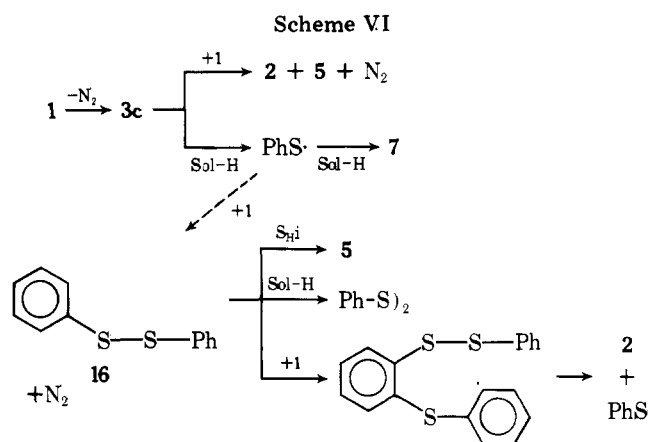
When the decomposition of 1 was carried out in the presence of phenylacetylene (12), 2- and 3-phenylbenzo[*b*]thiophene (13a and 13b) were obtained together with 2 and 5; moreover, decomposition of 1 in toluene (14) gave 2,3-diphenylbenzo[*b*]thiophene (15) and a mixture of *cis*- and *trans*-1-phenylthiostilbene, which formed from addition of 7 on the triple bond.<sup>10</sup> 13 and 15 can be explained as cycloaddition products of 3 with 12 and 14, though addition of phenylthio radicals, followed by intramolecular cyclization of the intermediate carbon radical, cannot be completely ruled out in the formation of 13b and 15 (Scheme V).



The relative yields of the products obtained from decomposition of 1 in the different solvents are listed in Table II.

The rather low yields of 8, 13, and 15 could be attributed to the high reactivity of 1, which has been shown to have high reactivity with aryl<sup>6</sup> and thiyl<sup>7</sup> radicals toward diradicalic 3c, rather than the low reactivity of 3c toward monosubstituted benzenes or triple bonds. On these bases, 2 and 5 could arise

from induced decomposition on 1 by the carbon and sulfur radical end of 3c, respectively; 6 very probably arises from 5 by interaction with a radical species,<sup>11</sup> while 7 is the hydrogen abstraction reaction product of 3c via thiyl radical. An alternative route to 2 and 5 could be the thioarylation of 1 by thiyl radicals through the radical intermediate 16,<sup>7</sup> but we can exclude a large contribution of this reaction because if hydrogen abstraction reaction by carbon radical were faster than induced decomposition on 1, only small amounts of 2 should be formed (Scheme VI).



### Experimental Section

Gas chromatographic analysis was carried on with a Varian Model 1440/1 instrument (5% FFAP and 5% APL on Varaport 80-100 columns). The reaction products were identified by mixture melting points with prepared authentic specimens or by comparison of their IR (Perkin-Elmer 257) and NMR (JEOL 60 MHz) spectra.

Thianthrene (2), dibenzothiophene (6), and thiophenol are commercial products. 1,2,3-Benzothiadiazole (1),<sup>1</sup> dibenzo[*c,e*]-o-dithiin (5),<sup>12</sup> diphenyl disulfide,<sup>13</sup> 1-, 2-, 3-, and 4-methylidibenzothiophene,<sup>14,15</sup> 1-, 2-, 3-, and 4-methoxycarbonyldibenzothiophene,<sup>15,16</sup> 6-methoxybenzothiadiazole (10),<sup>17</sup> 2- and 3-phenylbenzothiophene,<sup>18,19</sup> 2,3-diphenylbenzothiophene,<sup>20</sup> and *cis*- and *trans*-phenylthiostilbene<sup>21</sup> were prepared as described in the literature.

**2-Nitro-4,5'-dimethoxy-2'-phenylthiodiphenyl Sulfide.** The crude 2-mercapto-4-methoxydiphenyl sulfide, obtained from 2-amino-4-methoxydiphenyl sulfide<sup>22</sup> (11.5 g, 0.05 mol) with Leuckart reaction modified by Campaigne,<sup>23</sup> was dissolved in sodium methylate, 1 M (50 ml), and added to a solution of 2-nitro-4-methoxychlorobenzene<sup>24</sup> (9.5 g, 0.05 mol). The mixture was refluxed for 3 h, then poured into cold water. The yellow solid was filtered, washed with 2% NaOH, and crystallized with EtOH, mp 103-105 °C. Anal. Calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>4</sub>S<sub>2</sub>: C, 60.1; H, 4.29; S, 16.05; N, 3.51. Found: C, 60.19; H, 4.28; S, 16.09; N, 3.60.

**2-Nitro-5,5'-dimethoxy-2'-phenylthiodiphenyl sulfide** was prepared from 2-mercapto-4-methoxydiphenyl sulfide and 2-nitro-5-methoxychlorobenzene<sup>25</sup> as described above, mp 104-105 °C. Anal. Calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>4</sub>S<sub>2</sub>: C, 60.1; H, 4.29; S, 16.05; N, 3.51. Found: C, 59.62; H, 4.47; S, 16.18; N, 3.55.

**2-Amino-4,5'-dimethoxy-2'-phenylthiodiphenyl sulfide** was obtained by reduction with H<sub>2</sub> over 10% palladium on charcoal of the parent nitro derivative, mp 101-102 °C. Anal. Calcd for C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub>S<sub>2</sub>:

