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 decomposition¹ or photolysis² 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 3:² a 1,3-dipolar form (3a) in resonance with a thicketocarbene (3b) or a 1,3-diradical structure (3c). Recently³ 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 thicketene 4 generated from 1 already begins to polymerize at -120 °C, and could therefore only be detected indirectly. Analogous thicketenes, derived by Wolff rearrangement of the parent thicketocarbenes, were reported by Kirmse and Horner⁴ 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.⁵ Our interest in the reactivity^{6,7} of 1,2,3-benzothiadiazole (1) has led us to study the thermal decomposition of 1 in various solvents, such as

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

	1-, 2- t	% , 3-, and hiophen	% of ortho, meta, and para attack on PhX				
X	1-	2-	3-	4-	Ortho	Meta	Para
CH ₃ COOCH ₃	42ª 57ª	14^b 6^f	20° 19 ^g	$rac{24^d}{18^h}$	42 57	$\frac{38}{24}$	20 19

Registry numbers: ^a 31317-07-4; ^b 20928-02-3; ^c 16587-52-3; ^d 7372-88-5; ^e 40488-61-7; ^f 22099-28-1; ^g 60718-96-9; ^h 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 σ complex **9a** or by the carbon radical of **3c** and trapping of radical σ complex **9b** (Scheme III).

However, as show in Table I, the ortho, meta, para isomer ratios of σ complex 9 better agree with a radical mehanism 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-workers⁸ to explain the formation of **2** by thermolysis of *o*-bromobenzenethiolate. Analogous thiirenes, in equilibrium with the parent thioketocarbenes, were also proposed by Rees⁹ in the





ethyl acetate, ethyl acetate/phenylacetylene, ethyl acetate/ tolane, 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 °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 II. Relative Yields (%) of the Products Obtained by Decomposition of 1

Solvent	2	5	6	8	13	15
Ethyl acetate Monosubstituted	42	46	12			
benzene	$\frac{33}{27}$	37 30	10 8	20		17
Phenylacetylene	31	34	9		26	τ,

reaction of 4,5-disubstituted 1,2,3-thiadiazoles with nonacarbonyldiiron. In fact, decomposition of 6-methoxy-1,2,3benzothiadiazole (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 tolane (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.¹⁰ 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 $aryl^6$ and $thiyl^7$ 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, ¹¹ 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 16,⁷ 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),¹ dibenzo[c,e]-o-dithiin (5),¹² diphenyl disulfide,¹³ 1-, 2-, 3-, and 4-methyldibenzothiophene,^{14,15} 1-, 2-, 3-, and 4-methoxycarbonyldibenzothiophene,^{15,16} 6-methoxybenzothiadiazole (10),¹⁷ 2- and 3-phenylbenzothiophene,^{18,19} 2,3-diphenylbenzothiophene,²⁰ and *cis*- and *trans*phenylthiostilbene²¹ 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 sulfide²² (11.5 g, 0.05 mol) with Leuckart reaction modified by Campaigne,²³ was dissolved in sodium methylate, 1 M (50 ml), and added to a solution of 2-nitro-4-methoxychlorobenzene²⁴ (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 $C_{20}H_{17}NO4S_2$: 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-methoxychlorobenzene²⁵ as described above, mp 104–105 °C. Anal. Calcd for $C_{20}H_{17}NO_4S_2$: 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_2 over 10% palladium on charcoal of the parent nitro derivative, mp 101–102 °C. Anal. Calcd for $C_{20}H_{19}NO_2S_2$:

Notes

C, 65.0; H, 5.18; S, 17.35; N, 3.79. Found: C, 65.0; H, 5.16; S, 17.34; N, 3.84.

2-Amino-5,5'-dimethoxy-2'-phenylthiodiphenyl sulfide was obtained from the parent nitro derivative by reduction as described above, mp 105-107 °C. Anal. Calcd for C₂₀H₁₉NO₂S₂: C, 65.0; H, 5.18; S, 17.35; N, 3.79. Found: C, 65.0; H, 5.31; S, 17.23; N, 3.90.

2,7-Dimethoxythianthrene (11a) was synthesized as described in the literature.²⁶ n-Pentyl nitrite (0.015 mol) was added to a solution of 2-amino-4,5'-dimethoxy-2'-phenylthiodiphenyl sulfide (0.01 mol) in ethyl acetate (50 ml). The mixture was kept at 50 °C for 5 h and then the solvent was evaporated. The residue was chromatographed on a silica gel column, and the thianthrene (11a) obtained in 45% yield: mp 134-135 °C (lit. 131,²⁷ 133 °C²⁸); IR v (CS₂) 1290 (s), 1260 (s), 1230 (s), 1220 (s), 1180 (m), 1105 (m), 1050 (s), 1040 (s), 1020 (m), 870 (m), $860 (m), 840 (s), 810 (s), 800 cm^{-1} (s).$

2,8-Dimethoxythianthrene (11b) was obtained from 2-amino-5,5'-dimethoxy-2'-phenylthiodiphenyl sulfide in 45% yield as described above: mp 104-105 °C; IR v (CS₂) 1295 (s), 1290 (s), 1280 (m), 1260 (s, doublet), 1230 (s, doublet), 1225 (s), 1220 (s), 1180 (m), 1105 (m), 1050 (s), 1045 (s), 1040 (s), 1030 (m), 870 (m), 860 (m), 840 (s), 810 (s), 800 cm⁻¹ (s).

Thermal Decomposition of 1,2,3-Benzothiadiazole (1). A. In Ethyl Acetate. A solution of 1 (2.70 g, 0.02 mol) in ethyl acetate (50 ml) was kept in a "bomb" at 220 °C for 18 h. The crude was washed with 5% aqueous NaOH. From alkaline solution, after acidification and extraction with Et_2O , thiophenol was separated (0.1 g, 5%). The organic layer was chromatographed on a silica gel column; dibenzothiophene (6, 0.11 g, 6%), thianthrene 2, 0.43 g, 20%), and diben $z_0[c,e]$ -o-dithiin (5, 0.48 g, 22%) with small amounts of diphenyl disulfide (0.04 g, 2%) were separated. Independent experiments were carried out to prove the thermal stability of the products in reaction conditions. Thianthrene (2), dibenzothiophene (6), and thiophenol (7) were recovered unchanged, while dibenzodithiin (5) gave dibenzothiophene (3%).

B. In Toluene. A solution of 1 (3.3 g, 0.024 mol) in toluene (33 ml) was kept in a "bomb" at 220 °C for 18 h. By column chromatography on silica gel of the crude was separated, with 2, 5, and 6, a mixture of 1-, 2-, 3-, and 4-methyldibenzothiophene (~12%). The relative yields, determined by ratio of peak areas of methyl groups in the NMR spectrum, are 42, 14, 20, and 24%, respectively. The assignment of peaks was determined by comparison with NMR spectra of authentic specimens.

C. In Methyl Benzoate. A solution of 1 (2.6 g, 0.019 mol) in methyl benzoate (30 ml) was treated as described above. The relative yield of 1-, 2-, 3-, and 4-methoxycarbonyldibenzothiophene (\sim 12%) separated by chromatography on a silica gel column, determined by GLC analysis, are 57, 6, 19, and 18%, respectively.

D. In Diphenylacetylene. A solution of 1 (1.36 g, 0.01 mol) and tolane (13, 1.78 g, 0.01 mol) in ethyl acetate (15 ml) was thermolyzed at 220 °C for 18 h. By column chromatography on a silica gel column dibenzothiophene (6, 3%), thianthrene (2, 11%), dibenzo[c,e]-o-dithiin (5, 12%), 2,3-diphenylbenzothiophene (15, 7%), and a cis-trans mixture of 1-phenylthiostilbene (7%) were separated. The indicated yields were detected by GLC analysis of the reaction mixture.

E. In Phenylacetylene. A solution of 1 (1.36 g, 0.01 mol) and phenylacetylene (1.00 g, 0.01 mol) in ethyl acetate (15 ml) was thermolyzed as above. By column chromatography 6 (5% yield), 2 (17%), 5 (18%), 2-phenylbenzothiophene (13a, 10%), and 3-phenylbenzothiophene (13b, 4%) were separated.

Thermal Decomposition of 6-Methoxy-1,2,3-benzothiadiazole (10). 10 was heated at 205 °C for 18 h in a "bomb". The crude was chromatographed on a silica gel column and the thianthrene was isolated: mp 134-135 °C; IR spectra of this fraction and 11a were identical; mixture melting point with 11a was undepressed.

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Registry No.-1, 273-77-8; 2, 92-85-3; 5, 230-26-2; 6, 132-65-0; 10, 1753-90-8; 11a, 54815-69-9; 11b, 60718-98-1; 13a, 1207-95-0; 13b, 14315-12-9; 15, 22751-52-6; 2-nitro-4,5'-dimethoxy-2'-phenylthiodiphenyl sulfide, 60718-99-2; 2-mercapto-4-methoxydiphenyl sulfide, 60718-00-8; 2-nitro-4-methoxychlorobenzene, 10298-80-3; 2-nitro-5,5'-dimethoxy-2'-phenylthiodiphenyl sulfide, 60719-01-9; 2-nitro-5-methoxychlorobenzene, 28987-59-9; 2-amino-4,5'-dimethoxy-2'phenylthiodiphenyl sulfide, 60719-02-0; 2-amino-5,5'-dimethoxy-2'-phenylthiodiphenyl sulfide, 60719-03-1; diphenyl disulfide, 882-33-7; cis-1-phenylthiostilbene, 41796-39-8; trans-phenylthiostilbene, 24466-59-9; phenylacetylene, 501-65-5.

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An Improved Synthesis of 1-Picryl-2,2-diphenylhydrazyl Radical. Purification and Storage of 1,1-Diphenylhydrazine as the Tosylate Salt¹

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The conventional synthesis of 1-picryl-2,2-diphenylhydrazyl (DPPH) free radical requires as an intermediate 1,1diphenylhydrazine (3), which is picrylated and then oxidized to the radical with lead dioxide.² The classical (and until recently the only) synthesis of 3 proceeds from diphenylamine by sequence a:3

$$\frac{\text{Ph}_{2}\text{NH}}{1} \xrightarrow{\text{HONO}} \frac{\text{Ph}_{2}\text{N}-\text{NO}}{\text{or NOCl}} \xrightarrow{\text{Zn, AcOH}} \frac{\text{Ph}_{2}\text{N}-\text{NH}_{2}}{\text{or LiAlH}_{4}} \xrightarrow{\text{Ph}_{2}\text{N}-\text{NH}_{2}} (a)$$

Simultaneous reductive cleavage of the N-N bond during conversion of 2 to 3 has been well documented, 4 as have the labor and erratic results in the separation of the "pure" hydrazine. Heroic efforts devoted to purification of 3 give a crystalline solid variously reported⁵ to melt through the range 31-44 °C, but the usual product is an oil identified only by its boiling point in a vacuum distillation. Furthermore, in our experience both the hydrazine and its hydrochloride deteriorate upon storage after purification, so it is impossible to maintain a stock of the compound which can be relied upon for further synthetic work.

Anselme and Koga⁶ have published an alternate route to 3 from 1 by Curtius rearrangement of 1,1-diphenylcarbamyl azide (5) dissolved in a tertiary alcohol, followed by hydrolysis of the tert-alkyl 3,3-diphenylcarbazate formed: