an analogous fashion. Full analytical and spectroscopic data (ir, NMR) for these compounds are listed in Tables II and III (see paragraph at end of paper regarding supplementary material).

3-Carbomethoxymethylene-3,4-dihydro-7-nitro-2-oxo-2*H*-1,4-benzothiazine (29). A solution of DMAD (1.5 g, 0.0105 mol) in AnalaR methanol (5 ml) was added in one portion to a stirred suspension of 6-nitrobenzothiazole (1.8 g, 0.01 mol) in a mixture of AnalaR methanol (55 ml) and water (10 ml). The mixture was heated under reflux for 5 h, during which time the 6-nitrobenzothiazole gradually dissolved and a bright yellow solid precipitated. The reaction mixture was cooled and the solid collected by filtration, washed with ether, and dried. This gave 1.7 g (60%) of **29** as bright yellow needles: mp 305–310 °C dec; ir (Nujol) ν_{N-H} 3225 cm^{-1}, $\nu_{C=O}$ 1690 (lactone), and 1670 cm^{-1} (unsaturated ester). The NMR spectrum could not be recorded as the solid is completely insoluble in all common solvents.

Anal. Calcd for $C_{11}H_{18}N_2O_5S$: C, 47.14; H, 2.86; N, 10.00; S, 11.43. Found: C, 47.23; H, 2.81; N, 10.12; S, 11.48.

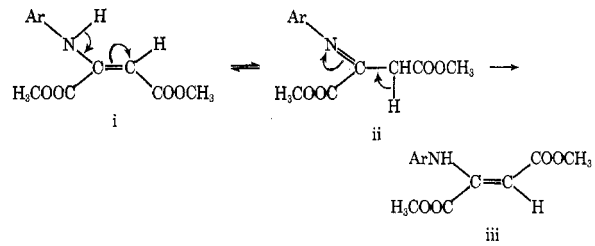
Acknowledgments. Two of us (T.S.B.S. and G.C.A.B.) acknowledge the receipt of Science Research Council Scholarships.

Supplementary Material Available. Full analytical and spectroscopic (ir, NMR) data for compounds **3, 9, 11, 13, 15, 17, 19, 21, 23,** and **25** are listed in Tables II and III (2 pages). Ordering information is given on any current masthead page.

Registry No.—**1,** 95-16-9; **3,** 55052-31-8; **8,** 58249-57-3; **9,** 58249-58-4; **10,** 36894-61-8; **11,** 58249-59-5; **12,** 2942-07-6; **13,** 58268-61-4; **14,** 768-11-6; **15,** 58249-60-8; **16,** 58249-61-9; **17,** 58249-62-0; **18,** 58249-63-1; **19,** 58249-64-2; **20,** 19989-66-3; **21,** 58249-65-3; **22,** 53218-26-1; **23,** 58249-66-4; **24,** 30132-83-3; **25,** 58249-67-5; **26,** 58249-68-6; **27,** 58249-69-7; **28,** 2942-06-5; **29,** 58249-70-0; **36,** 58249-71-1; **39,** 58249-72-2; **44,** 6265-92-5; DMAD, 503-17-3; 5-aminobenzothiazole, 1123-93-9; 6,6′-dinitro-3,3′,4,4′-tetramethoxydiphenyl disulfide, 58249-73-3; 4-amino-6-methoxybenzothiazole, 58249-74-4; 4,6-dichloro-7-aminobenzothiazole, 58249-75-5; 2,2′-bis(4-methoxybenzoylamino)diphenyl disulfide, 58249-76-6; 6-aminobenzothiazole, 533-30-2.

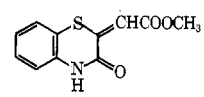
References and Notes

(1) Preliminary communication: A. McKillop and T. S. B. Sayer, *Tetrahedron Lett.*, 3081 (1975).
(2) H. Ogura, K. Kikuchi, H. Takayanagi, K. Furuhata, Y. Iitaka, and R. M. Acheson, *J. Chem. Soc., Perkin Trans. 1*, 2316 (1975).
(3) A. F. Bedford, P. B. Edmonson, and C. T. Mortimer, *J. Chem. Soc.*, 2927 (1962).
(4) E. G. Lovering and K. J. Laidler, *Can. J. Chem.*, **38,** 2367 (1960).
(5) Other mechanisms for cis–trans isomerism are possible, e.g., i ⇌ ii → iii.



i ii iii

(6) It is interesting to note that 2-aminothiophenol reacts with DMAD in ether to give iv, and not the thiolactone corresponding to **32:** P. Rajagopalan and C. N. Talaty, *Tetrahedron*, **23,** 1911 (1967).



iv

(7) R. M. Acheson, M. W. Foxton, and G. R. Miller, *J. Chem. Soc.*, 3200 (1965).
(8) I. Spieler and B. Prijs, *Helv. Chim. Acta*, **33,** 1429 (1950).
(9) W. A. Boggust and W. Cocker, *J. Chem. Soc.*, 355 (1949).
(10) M. G. Ast and M. T. Bogert, *Recl. Trav. Chim. Pays-Bas*, **54,** 917 (1935).
(11) H. H. Fox and M. T. Bogert, *J. Am. Chem. Soc.*, **61,** 2013 (1939).
(12) A. T. Blomquist and L. I. Diuguid, *J. Org. Chem.*, **12,** 718 (1947).
(13) W. Scottand and G. W. Watt, *J. Org. Chem.*, **2,** 148 (1938).
(14) P. E. Todesco and P. Vivarelli, *Boll. Sci. Fac. Chim. Ind. Bologna*, **22,** 16 (1964); *Chem. Abstr.*, **61,** 8291*e* (1964).
(15) C. Gruenert and K. Wiechert, *Z. Chem.*, **10,** 188 (1970).
(16) J. D. Kendall and H. G. Suggate, *J. Chem. Soc.*, 1503 (1949).
(17) M. T. Bogert and F. D. Snell, *J. Am. Chem. Soc.*, **46,** 1308 (1924).
(18) L. M. Clark, *J. Chem. Soc.*, 2313 (1938).
(19) R. F. Hunter, *J. Chem. Soc.*, 125 (1930).
(20) J. Ehrlich and M. T. Bogert, *J. Org. Chem.*, **12,** 522 (1947).

Reaction of 1,2,3-Benzothiadiazole with Arylthio Radicals†

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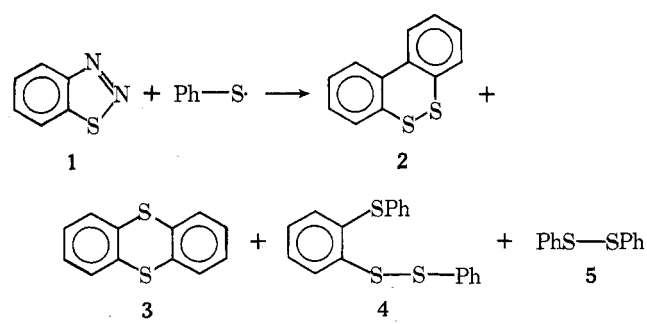
The reaction of 1,2,3-benzothiadiazole (1) with phenylthio radicals afforded dibenzo[*c,e*]-*o*-dithiin, thianthrene, and 2-(phenylthio)diphenyl disulfide. A mechanism is proposed which assumes initial attack of phenylthio radical at the sulfur atom of 1 to give radical 6, a key intermediate in this reaction.

Homolytic aromatic thioarylations have been achieved in a very limited number of cases and only if certain conditions are satisfied. High homolytic reactivity of the substrate and a strongly oxidizing medium allow direct substitution to occur on furan[1] and thiophene[2] rings. Indirect substitution has been observed at high temperatures with halobenzenes,[3] while intramolecular indirect substitutions occur easily when arylthio radical displaces an arylthio, phenoxy, and mercapto group to give a stable product such as dibenzothiophene or thianthrene.[4]

We now have found what is, to the best of our knowledge, the first example of an aromatic SH2 reaction effected by thiyl radicals at heterocyclic sulfur atom. In Scheme I are reported the products obtained from reaction between 1,2,3-benzothiadiazole (1) and phenylthio radicals

Scheme I



1 2 3 4 5

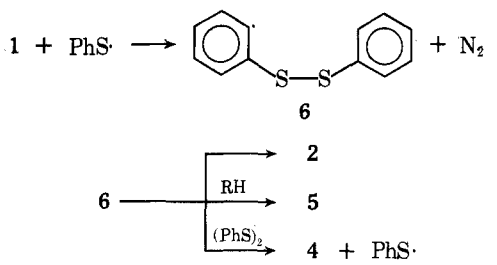
generated both by hydrogen abstraction from thiophenol with 2-cyanopropyl radicals[5] and by thermal decomposition of diphenyl disulfide (at 165 °C).[6] Under the latter

† Dedicated to Professor Martino Colonna on his 70th birthday.

more vigorous conditions part of the asymmetric disulfide (4) disproportionates giving rise to the 2,2′-bis(phenylthio)diphenyl disulfide. Traces of dibenzothiophene, probably derived from radical attack on 2, are also present in the high-temperature reaction.[4] Thermal unassisted decomposition of 1[7] has been proved, by independent experiments, to be unimportant at this temperature.

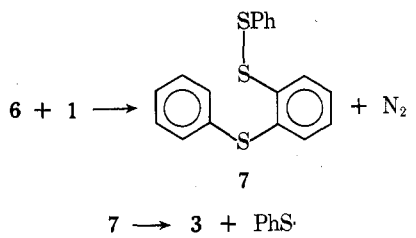
We believe that the attack of thioaryl radicals at the sulfur atom of benzothiadiazole (1), leading to the radical intermediate 6 by fission of the heteroaromatic ring and nitrogen loss, represents the first step of the reaction. Radical 6 may be considered as the key intermediate since all reaction products can be easily rationalized in terms of the following reactions (Scheme II). Thus 6 can lead to dibenzo[c,e]-o-dithiin (2) by intramolecular cyclization, to diphenyl disulfide (5) by hydrogen abstraction from the solvent, and to 2-(phenylthio)diphenyl disulfide (4) by an SH2 reaction on the sulfur atom of the disulfide present in the reaction mixture (Scheme II).

Scheme II



The ortho-substituted phenyl radical (6) can in addition react with 1 to afford the aryl radical 7,[8] which then leads to thianthrene (3) by homolytic intramolecular substitution on the sulfur atom of the S–S bond linked to the adjacent benzene ring (Scheme III).

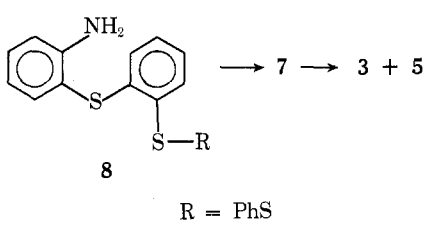
Scheme III



The foregoing mechanism assumes the intermediacy of the two substituted aryl radicals 6 and 7; moreover, the radical 7 should be formed from 6. Several independent experiments have been carried out in order to gain indirect support for this interpretation. By aprotic diazotization of 8 with n-pentyl nitrite thianthrene (3) and diphenyl disulfide (5) were obtained. The radical pathway of this reaction, which leads to intermediate 7, was demonstrated on analogous compounds where R = Ph, CH_3.[9]

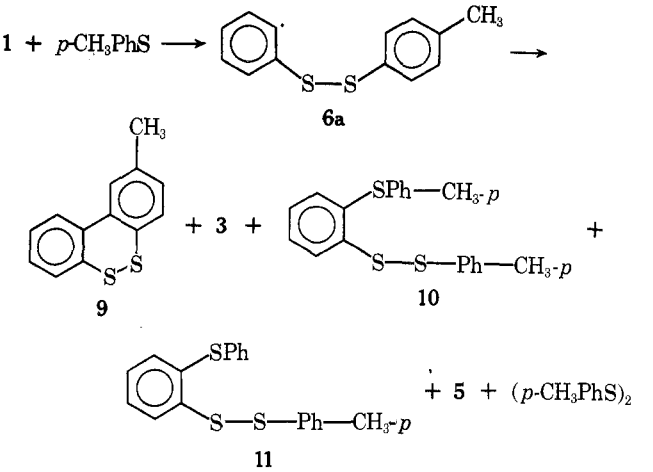
It is interesting to note that, as indicated in Scheme IV, the intramolecular SH2 reaction at the sulfur atom leading to 3 with phenylthio radical as leaving group appears to be much faster than the intramolecular homolytic substitution on the adjacent benzene ring and the hydrogen abstraction reaction. The intermediacy of 6 was demonstrated as follows. When the 1,2,3-benzothiadiazole (1) was allowed to react with p-tolylthio radicals, generated from the parent thiophenol and AIBN, 2-methyldibenzo[c,e]-o-dithiin (9), thianthrene (3), and a mixture of asymmetric disulfides (10, 11) were obtained (Scheme V).

Scheme IV



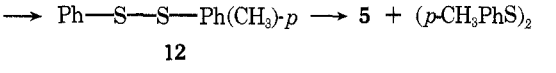
R = PhS

Scheme V



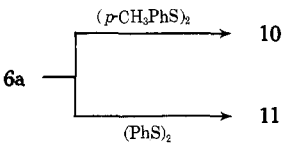
The formation of 9, in this case, shows clearly that 6a, analogous to 6, is the key intermediate of the reaction, from which 9 arises by intramolecular cyclization.

Unsubstituted diphenyl disulfide was also separated; this product can derive from the asymmetric disulfide 12 generated by the hydrogen abstraction reaction of 6a. It is



actually well known that asymmetrical disulfides easily "disproportionate" in organic solvent giving mixtures of the symmetrical ones.[10]

Reaction of 6a with the disulfides present in the reaction mixture could account for the formation of 10 and 11.



Experimental Section

The reaction products were identified, when possible, by mixture melting points with prepared authentic specimens, and by comparison of their ir (Perkin-Elmer 257) and NMR (JEOL 60 MHz) spectra, or by low-resolution mass spectral analysis (JEOL JMS D100).

2-(phenylthio)diphenyl disulfide (4) was obtained from 2-mercaptodiphenyl sulfide[11] and benzenesulfenyl chloride[12] in ethanol-free chloroform. To the solution was added a small quantity of copper bronze, and the mixture was stirred for 3 h. Column chromatography of the reaction mixture on silica gel gave the disulfide as an oil, yield 60%. Anal. Calcd for $C_{18}H_{14}S_3$: C, 66.21; H, 4.32; S, 29.46. Found: C, 66.07; H, 4.34; S, 29.62. Mass spectrum m/e (rel intensity) 326 (55) M^+, 294 (8), 292 (13), 252 (7), 250 (6), 217 (87), 185 (39), 184 (100), 110 (34), 109 (31).

2-(o-Aminophenylthio)diphenyl Disulfide (8). The crude 2-amino-2′-mercaptodiphenyl sulfide obtained from 2-nitro-2′-aminodiphenyl sulfide[13] under the conditions of the modified Leuckart reaction as described by Campaigne[14] was allowed to react with benzenesulfenyl chloride[12] as described above. Column chromatography of the reaction mixture on silica gel gave the title product as

a colorless oil which is easily decomposed by light, yield 50%. Anal. Calcd for $C_{18}H_{15}NS_3$: C, 63.3; H, 4.43; N, 4.10; S, 28.17. Found: C, 63.38; H, 4.53; N, 4.02; S, 27.89. Mass spectrum: *m/e* (rel intensity) 341 (56) M^+, 309 (34), 276 (15), 232 (91), 199 (100).

Anal. Calcd for $C_{18}H_{15}NS_3$·HCl (mp 150 °C): C, 57.19; H, 4.27; N, 3.71; S, 25.45; Cl, 9.38. Found: C, 57.19; H, 4.22; N, 3.82; S, 25.25; Cl, 9.45.

Reaction of 1,2,3-Benzothiadiazole (1) with Thiophenol and AIBN. A solution of 1,2,3-benzothiadiazole (1,[7] 1.36 g, 1×10^{-2} mol), thiophenol (1.10 g, 1×10^{-2} mol), and AIBN (1.6 g) in ethyl acetate was refluxed for 1 h. Column chromatography of the reaction mixture on silica gel with light petroleum (bp 40–70 °C) as eluent gave diphenyl disulfide (**5**,[15] 1.37 g 6.3×10^{-3} mol), thianthrene (**3**, 0.19 g, 0.9×10^{-3} mol), dibenzo[*c,e*]-*o*-dithiin (**2**,[16] 0.06 g, 0.3×10^{-3} mol), and 2-(phenylthio)diphenyl disulfide (**4**, 0.33 g, 1×10^{-3} mol).

Reaction of 1,2,3-Benzothiadiazole (1) with Diphenyl Disulfide. A solution of 1,2,3-benzothiadiazole (**1**,[7] 2.04 g, 1.5×10^{-2} mol) and diphenyl disulfide[15] (1.64 g, 0.75×10^{-2} mol) in methyl benzoate (28 ml) was warmed at 165 °C for 20 h. The solvent was distilled under vacuum (17 mmHg) and the residue was chromatographed on silica gel with light petroleum as eluent. The following products were separated: diphenyl disulfide (**5**,[15] 0.9 g, 4.13×10^{-3} mol), dibenzothiophene (0.05 g, 0.27×10^{-3} mol), thianthrene (**3**, 0.35 g, 1.62×10^{-3} mol), dibenzo[*c,e*]-*o*-dithiin (**2**,[16] 0.45 g, 2.08×10^{-3} mol), 2-(phenylthio)diphenyl disulfide (**4**, 0.45 g, 1.38×10^{-3} mol), and 2,2'-bis(phenylthio)diphenyl disulfide (0.20 g, 0.46×10^{-3} mol), identified by mixture melting point with an authentic specimen obtained from 2-mercaptodiphenyl sulfide[11] by oxidation with bromine in chloroform, mp 124–125 °C. Mass spectrum: *m/e* (rel intensity) 434 (38) M^+, 217 (100), 184 (49). GLC analysis of a solution of **1** (0.136 g, 1×10^{-3} mol) in methyl benzoate, heated at 165 °C for 20 h, showed unchanged **1** (94%). Thianthrene (**3**) and dibenzo[*c,e*]-*o*-dithiin (**2**) were not present.

Reaction of 1,2,3-Benzothiadiazole (1) with *p*-Methylthiophenol and AIBN. A solution of 1,2,3-benzothiadiazole (1.77 g, 1.3×10^{-2} mol), *p*-methylthiophenol (1.62 g, 1.3×10^{-2} mol), and AIBN (2.40 g) in ethyl acetate (23 ml) was refluxed for 1 h. The solvent was evaporated and the residue was chromatographed on silica gel with light petroleum as eluent. The following products were eluted in the order cited: a mixture of diphenyl and *p,p'*-ditolyl disulfide[17] (0.63 g), thianthrene (**3**, 0.31 g, 1.43×10^{-3} mol), and 2-methyldibenzo[*c,e*]-*o*-dithiin (**9**, 0.08 g, 0.34×10^{-3} mol), mp 95 °C. Anal. Calcd for $C_{13}H_{10}S_2$: C, 67.75; H, 4.4; S, 27.85. Found: C, 67.7; H, 4.65; S, 27.45. **9**, by desulfuration with Raney nickel in boiling ethanol, gave 3-methylbiphenyl.

A mixture of 2-(*p*-tolylthio)phenyl-*p*-tolyl disulfide (**10**) and 2-(phenylthio)phenyl-*p*-tolyl disulfide (**11**, 0.4 g) was also separated. The ratio of **10** to **11**, determined by NMR spectra, was 65:35.

Aprotic Diazotization of 2-(*o*-Aminophenylthio)diphenyl Disulfide (8). A. To a solution of **8** in boiling ethyl acetate an equimolecular amount of *n*-pentyl nitrite was added carefully. After nitrogen evolution was finished (~5 min) the solvent was evaporated and the residue chromatographed on silica gel. Thianthrene (**3**) and diphenyl disulfide (**5**) was separated in 90% yields.

B. The diazotization of **8** in methyl benzoate at 165 °C yields **3**, **5**, and thianthrene *S*-oxide,[18] mp 143–144 °C.

Acknowledgment. We thank Consiglio Nazionale delle Ricerche (Rome) for financial support.

Registry No.—**1**, 273-77-8; **4**, 58074-42-3; **8**, 58074-43-4; **8** HCl, 58074-44-5; **9**, 58074-45-6; 2-mercaptodiphenyl sulfide, 53691-60-4; benzenesulfonyl chloride, 931-59-9; 2-amino-2'-mercaptodiphenyl sulfide, 58074-46-7; thiophenol, 108-98-5; diphenyl disulfide, 882-33-7; 2,2'-bis(phenylthio)diphenyl disulfide, 58074-47-8; *p*-methylthiophenol, 1073-72-9.

References and Notes

(1) L. Benati, C. M. Camaggi, and G. Zanardi, *J. Org. Chem.*, **40**, 966 (1975).
(2) Ya. A. Gol'dfard, G. P. Pokhil, and L. J. Beben'kii, *Dokl. Chem.*, **167**, 385 (1966).
(3) L. Benati, C. M. Camaggi, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 2817 (1972).
(4) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *Gazz. Chim. Ital.*, **105**, 841 (1975).
(5) R. M. Kellog in "Methods in Free Radical Chemistry", Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, N.Y., 1970, p 4.
(6) M. Minch, Thesis, Oregon State University, Corvallis, Oregon, 1965.
(7) P. Jacobson and H. Jansen, *Justus Liebigs Ann. Chem.*, **277**, 218 (1893).
(8) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1276 (1974).
(9) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1272 (1974).
(10) K. U. Ingold and B. P. Roberts in "Free Radical Substitution Reactions", Wiley, New York, N.Y., 1971 p 209.
(11) N. Marziano, *Boll. Sedute Accad. Gioenia Sci. Nat. Catania*, **6**, 80 (1961); *Chem. Abstr.*, **58** 4454*h* (1963).
(12) H. Lecker and F. Holschneider, *Ber.*, **57**, 755 (1924).
(13) H. H. Hodgson and J. H. Wilson, *J. Chem. Soc.*, **127**, 440 (1925).
(14) E. Campaigne and S. W. Osborn, *J. Org. Chem.*, **22**, 561 (1957).
(15) H. Lecker, *Ber.*, **58**, 409 (1925).
(16) W. L. F. Amarego and E. E. Turner, *J. Chem. Soc.*, 1665 (1956).
(17) K. H. Slotta and W. Franke, *Ber.*, **63**, 678 (1930).
(18) K. Fries and W. Vogt, *Justus Liebigs Ann. Chem.*, **381**, 312 (1911).

Chemistry of the Sulfur–Nitrogen Bond. XI. Synthesis and Thermal Decomposition of *N,N'*-Thiodiamines

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The synthesis and thermal decomposition of *N,N'*-thiodiamines (**1**) and *N,N'*-thioareneaminopiperidines (**5**) were investigated. Series **1** was prepared by addition of piperidine-1-sulfenyl chloride to the aryl amine at −20 °C. An intermediate in the formation of **1** is **5** which is obtained in good yield when the addition of the sulfenyl chloride to the aryl amine is carried out at −78 °C. Azobenzene (**6**), aryl amine, and sulfur are the principal products in the thermal decomposition of **1**. A mechanism involving the initial formation of thionitrosobenzene (ArN=S) was proposed. The thermal decomposition of **5** yields aryl amine and lower amounts of azobenzene. Homolytic cleavage of the S–N bond in **5** followed by recombination of the intermediate radicals yields **1** which is believed to account for the formation of **6**. Oxidation of **1** under anhydrous conditions yields *N*-sulfinylaniline.

N,N'-Thiodianilines (**1**) are a class of important sulfur–nitrogen compounds that have received relatively little attention. Their importance stems from the fact that they are at present the only known source of thionitrosobenzene (**2**).[2,3] The existence of **2** was demonstrated in the thermal decomposition of **1** by trapping with 2,3-dimethyl-1,3-butadiene to yield the 1,2-thiazine **3**.[2] An unstable *N*-thionitrosoamine (R_2N–N=S) has been reported.[4] Attempts to pre-