spectral,[7] and elemental analyses, they decompose on distillation.

Thus, the reaction to form 3-oxazoline-2(1*H*)-2-thiones appears to be quite general.[8]

Experimental Section

Preparation of 5,5-Diphenyl-4-benzylthio-3-oxazoline-2(1*H*)-2-thione (5).—Potassium thiocyanate (0.50 g, 0.005 mol) was added to a solution of sulfide **2** (1.76 g, 0.005 mol) in anhydrous acetone (10 ml) at room temperature. After a few minutes the KSCN completely dissolved and the solution became cloudy. A while solid appeared on the walls of the flask and the mixture was stirred overnight. The white solid (KCl) was filtered and washed with several portions of dry acetone. These washings were combined and concentrated under reduced pressure. The resulting dark red oil was dissolved in ether and the solution filtered to remove traces of KCl. After concentrating this solution the oil was purified by column chromatography on Florisil using 1:1 hexane–methylene chloride as eluent. The yellow oil (1.69 g, 90%) obtained after concentrating the fractions was homogeneous on tlc: nmr τ 2.10–2.90 (15 H, m), 5.77 (2 H, s).

Anal. Calcd: C, 70.37; H, 4.56; N, 3.73; S, 17.08. Found: C, 70.34; H, 4.70; N, 3.70; S, 17.02.

Preparation of 5,5-Diphenyl-4-*p*-tolylthio-3-oxazoline-2(1*H*)-2-thione (10).—In a similar manner, 1.76 g (0.005 mol) of keto sulfide **9** was converted to 1.54 g (82%) of oxazoline **10**: nmr τ 2.10–2.90 (14 H, m), 7.60 (3 H, s).

Anal. Calcd: C, 70.37; H, 4.56; N, 3.73; S, 17.08. Found: C, 70.24; H, 4.61; N, 3.63; S, 16.94.

Registry No.—**5**, 30651-48-0; **10**, 30589-58-3.

Acknowledgment.—This research was supported by the Defence Research Board of Canada, Grant No. 9530-97.

(7) The mass spectra of both oxazolines **5** and **10** reveal a peak at *m/e* 193. Exact mass measurement indicates a molecular formula of $C_{14}H_{11}N$. This ion may be formulated as $[(C_6H_5)_2C{=}N{=}NH]\cdot^+$ and is easily rationalized as coming directly from oxazoline structures **5** or **10**. In addition, metastable peaks at *m/e* 99.4 were noted further substantiating the 375 → 193 transition.

(8) It has been previously reported [F. Weygand, H. J. Bestmann, and F. Steden, *Chem. Ber.*, **91**, 2537 (1958)] that $RC(=O)CClHSCH_2CH_3$ reacts with KSCN to give 4-oxazoline-2(1*H*)-2-thiones (structurally similar to the title compounds). The mechanism of formation of these 4-oxazolines was rationalized differently from the present work.

Derivatives of Dibenzo[*b*,*f*][1,4,5]thiadiazepine. V.[1] Synthesis of Sulfides and Sulfoxides

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Received December 10, 1970

Seven-membered ring systems containing ten π electrons have been of interest because of their potential aromatic character.[4] In earlier papers dealing with the dibenzo[*b*,*f*][1,4,5]thiadiazepine system[5,6] the sulfur moiety was present in the form of the conveniently attained and unreactive sulfone function. In this paper we wish to report the synthesis of the heterocyclic system in which the 1-thia group is at the sulfide and sulfoxide oxidation levels, while the nitrogen group can be at the hydrazo, azo, and azoxy oxidation states. A synthesis of the sulfides has been described in the literature, albeit in poor yields.[4,7]

Our general approach to the cyclization of appropriately ortho,ortho′-disubstituted phenyl sulfides or sulfoxides consisted of an oxidative or reductive formation of the nitrogen–nitrogen bridge. Various attempts to bring about a reductive cyclization of di(*o*-nitrophenyl) sulfide were unrewarding but instead lead to an effective synthesis of di(*o*-hydroxylaminophenyl) sulfide[6] (**1**), which became the key intermediate for the synthesis of the desired heterocycles. Small changes in the optimum conditions of the reduction resulted in the formation of various dimeric products. Also, various attempts to oxidize di(*o*-aminophenyl) sulfide or to reduce di(*o*-nitrophenyl) sulfoxide were fruitless due to the vulnerability of the sulfide or sulfoxide functions. It is interesting to note that oxidation of the above amino sulfide with sodium perborate[8] resulted in the formation of 5% of di(*o*-aminophenyl) sulfone.

The most convenient cyclization of **1** was found to occur when the hydroxylamino sulfide is oxidized with 15% less than the theoretical amount of peracetic acid (PAA) to give a 73% yield of the cyclic azoxy sulfide **2a**. Aqueous ferric chloride also gave an acceptable (45%) yield of **2a**, while other oxidizing agents, such as *p*-benzoquinone, lead oxide, air, and others, were found to be ineffective. Most likely the oxidation of one hydroxylamino group in **1** to the nitroso function sets the stage for the intramolecular ring closure according to the known reaction[9–11]

$$-NHOH + -NO \longrightarrow -N{=}\overset{\displaystyle O}{\overset{|}{N}}-$$

The reduction of the azoxy sulfide **2a** could not be arrested at the azo stage but proceeded readily to the hydrazo sulfide **3a**, which was found to be readily dehydrogenated by means of air or ferric chloride to the desired azo sulfide **4a**.

The cyclization of the hydroxylamino sulfide **1a** with the calculated amount of PAA or perbenzoic acid (PBA) gave a 70% yield of the azoxy sulfoxide **2b**. As expected, the azoxy sulfide **2a** was readily oxidized to the azoxy sulfoxide **2b**, and both heterocycles could be converted to the corresponding azoxy sulfone.[6,12]

The preparation of the hydrazo sulfoxide **3b** and azo sulfoxide **4b** was achieved by means of the analogous sequence of reactions described for the sulfide series,

(1) For paper IV, see H. H. Szmant and R. Infante, *J. Org. Chem.*, **26**, 4173 (1961).

(2) Department of Chemistry, University of Detroit, Detroit, Mich. 48221.

(3) Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada.

(4) N. L. Allinger and G. A. Youngdale, *J. Amer. Chem. Soc.*, **84**, 1020 (1962).

(5) H. H. Szmant and R. L. Lapinski, *ibid.*, **78**, 458 (1956).

(6) H. H. Szmant and Y. L. Chow, *ibid.*, **79**, 4382, 5583 (1957).

(7) M. F. Grundon and B. T. Johnston, *J. Chem. Soc. B*, 255, 260 (1966).

(8) S. T. Mehta and M. T. Vakilwala, *J. Amer. Chem. Soc.*, **74**, 563 (1952).

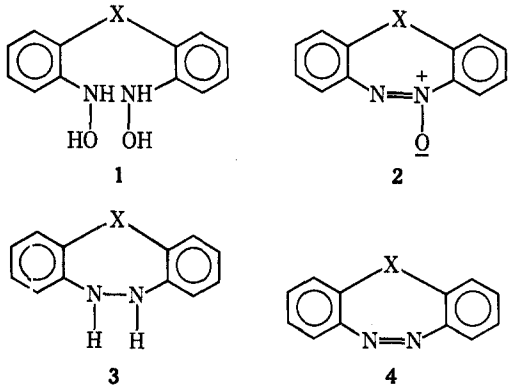
(9) M. F. Grundon and B. J. Johnston, *J. Chem. Soc. B*, 260 (1966).

(10) C. J. W. Gutch and W. A. Waters, *ibid.*, 751 (1965).

(11) E. J. Geels, R. Konaka, and C. A. Russell, *Chem. Commun.*, 13 (1965).

(12) N. L. Allinger and G. A. Youngdale, *J. Org. Chem.*, **24**, 2059 (1959). This paper also corrects the incorrect conclusions concerning the existence of isomers suggested in ref 6.

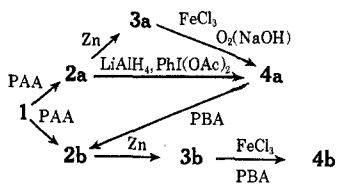
and these and additional successful transformations in this family of compounds are summarized below.



1 2

3 4

a, X = S
b, X = SO



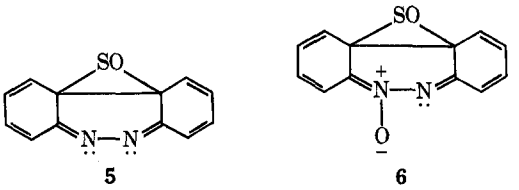
Characteristic of the compounds in the sulfoxide series was their propensity to undergo the dethionylation reaction,[13] *i.e.*, an extrusion of the sulfoxide moiety.[14] However, while all three sulfoxides (**2b**, **3b**, and **4b**) decomposed at their respective melting points, the ease of dethionylation under milder conditions was found to depend on the nature of the nitrogen function. Thus, the hydrazo and azoxy sulfoxides **2b** and **3b**, respectively, could be easily crystallized from warm solvents without extensive decomposition, while the azo sulfoxide **4b** was very labile and decomposed easily to benzocinnoline either in solution or in the crystalline state. A more recent study of this dethionylation reports[15] a first-order rate constant of 1.42×10^{-4} sec^{-1} for the decomposition of **4b** in toluene solution at 65°, and an activation eneergy of about 26 kcal/mol. The facile dethionylation of **4b** explains the formation of benzocinnoline as a byproduct of the oxidation of the hydrazo sulfoxide **3b** by means of peracids. The observation that potassium permanganate in acetone converted **3b** to the azoxy sulfone in good yield suggests that this oxidizing agent reacts more rapidly with the sulfoxide function than the other reagents. Also, the use of 1 molar equiv of PBA with the azo sulfide **4a** gave a mixture of unreacted starting material together with some azo and azoxy sulfoxides, **4b** and **2b**, respectively, and benzocinnoline, while a 2.5 molar excess of PBA gave a 75% yield of the azoxy sulfoxide **2b** together with some benzocinnoline and its *N*-oxide. These results suggest that the sulfide function is more susceptible to oxidation by PBA than the azo group, and that, unless the latter is also rapidly oxidized, the intermediate azo sulfoxide **4b** tends to undergo the dethionylation reaction.

(13) H. H. Szmant in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Oxford, 1961, p 163.

(14) B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, Oxford, 1967, pp 84–86.

(15) Y. L. Chow, J. N. S. Tam, J. E. Blier, and H. H. Szmant, *Chem. Commun.*, 1604 (1970).

As stated above, unlike the azo sulfoxide **4b**, the other sulfoxides in this series were less susceptible to dethionylation. Thus, the hydrazo sulfoxide **3b** could be refluxed in methanol for 2 days without change. On the other hand, in acetic acid solution, it apparently decomposed readily because of rapid air oxidation. The result that the dethionylation of the azoxy sulfoxide **2b** (under vigorous conditions) gave not only the expected benzocinnoline *N*-oxide but also a significant yield of benzocinnoline itself is noteworthy and is of interest in connection with the mechanism of the dethionylation reaction.[13,14] The difference in the dethionylation of **2b** and **4b** seems to be related to the relative ease with which the corresponding valence-tautomeric episulfoxides **5** and **6** are formed.[15]



5 6

Experimental Section[16]

Oxidative Ring Closure of 1. A.—The hydroxylamino sulfide, mp 119°, was prepared in 75% yield by the reduction of the correspondong nitro compound as described previously.[6] A suspension of crude **1** (8.6 g) in glacial acetic acid (250 ml) was cooled with an ice bath. PAA (0.9 *M*, 60 ml) was added dropwise over a 15-hr period while the solution was stirred. The solution gradually turned dark green and deposited needlelike crystals. The mother liquor was poured into water to give a precipitate from which an additional amount of needles was obtained. Two crystallizations from 2-propanol afforded the azoxy sulfide **2b** (5.5 g, 73%), mp 165–167°. Further recrystallization from methanol gave analytically pure **2b**: mp 167–168° (lit.[5] mp 166–167°); uv max 316 mμ (ε 4600), 245 (15,100), 210 (20,000).

B.—The same oxidation procedure as described above was applied to 9 g of crude **1** except that 3 molar equiv of PAA was used. At the end of the 24-hr period 4.5 g of pale yellow precipitate, mp 202° dec, was collected. The mother liquor was poured into water (500 ml) to give a precipitate which gave an additional amount of the pale yellow crystals (1.8 g) on recrystallization from acetic acid. An additional recrystallization from acetic acid gave analytically pure azoxy sulfoxide **2b**: mp 208° dec; uv max 300–340 mμ (ε 4100), 245 (11,500), 220 (27,600).

Anal. Calcd for $C_{12}H_8O_2N_2S$: C, 59.00; H, 3.30; N, 11.47; S, 13.11. Found: C, 59.01; H, 3.11; N, 11.00; S, 13.25.

The azoxy sulfoxide **2b** was also obtained in excellent yields when azoxy sulfide **2a** was oxidized with 1 molar equiv of either PAA in acetic acid or PBA in chloroform at ice temperature.

Preparation of Hydrazo Sulfide 3a.—To a solution of azoxy sulfide **2a** (300 mg) in glacial acetic acid (12 ml) was added zinc dust (1.5 g) in several portions over a 2-min period while the reaction mixture was agitated at 35–40°. The solution was quickly filtered through a Büchner funnel. The filtrate was poured into ice water (oxygen free by boiling) to give a white precipitate (260 mg), mp 91–95°. Recrystallization from Skellysolve C afforded white needles of **3a**, mp 100–101.5° (lit.[4] mp 102–103°). While **3a** is stable in the solid state it is sensitive to air oxidation in solution. A similar reduction of **2a** at 90° caused ring opening and gave 70% di(*o*-aminophenyl) sulfide.

Preparation of Azo Sulfide 4a. A.—A ferric chloride (500 mg) solution in water (10 ml) was added at room temperature to a solution of the hydrazo sulfide **3a** (175 mg) in methanol (37 ml). The reaction mixture immediately assumed a dark orange color. It was warmed briefly on a hot plate and then poured into ice

(16) Elemental analyses were performed by Dr. Strauss and Dr. Weiler, Oxford, England. Uv spectra were determined in methanolic solutions by means of a Beckman DU instrument.

water to give orange crystals (85 mg). Two recrystallizations from Skellysolve C gave orange crystals of the azo sulfide **4a**: mp 143.5–145° (lit.[4] mp 140–141°); uv max 424 mμ (ε 782), 418 (765), 310 (4355), 240 (14,800).

A quantitative yield of azo sulfide was obtained when air was bubbled through a methanolic solution of **3a** containing a trace of sodium hydroxide.

B.—A solution of the azoxy sulfide **2a** (250 mg) in dry ether was stirred with lithium aluminum hydride (210 mg) for 1 hr while the reaction mixture was cooled in an ice bath. The light green solution was decomposed in the usual manner and gave a crude product containing yellow and white crystals. The crude product was oxidized with phenyliodoso acetate in acetic acid to give an orange solid (228 mg), mp 131–136°. This was recrystallized from Skellysolve C to give pure **4a**.

Prepartion of the Hydrazo Sulfoxide 3b.—Zinc dust (2.5 g) was added in several portions over a 2–3-min period to a solution of the azoxy sulfoxide **2b** (800 mg) in acetic acid (50 ml) while the reaction mixture ws agitated at 50–55°. The reaction mixture was stirred for an additional 10 min and was filtered. The crude product was precipitated from ice water and was recrystallized three times from methanol to afford white needles of the hydrazo sulfoxide (650 mg), mp 188–189° dec.

Anal. Calcd for $C_{12}H_{10}ON_2S$: C, 62.60; H, 4.38; N, 12.16; S, 13.91. Found: C, 62.50; H, 4.00; N, 12.00; S, 13.64.

Although **3b** is stable in the solid state or in a methanolic solution, an acetic acid solution of **3b** is rapidly oxidized by air to give brown tar. In acetone solution **3b** (30 mg) and excess potassium permanganate solution gave the expected azoxy sulfone[6,12] (**2**, X = SO_2).

Preparation on Azo Sulfoxide 4b. A.—An aqueous solution (10 ml) of ferric chloride (1.5 g) was added at room temperature to a solution of hydrazo sulfoxide **3b** (253 mg) in methanol (40 ml). Additional methanol was added dropwise to remove the resulting cloudiness. The solution was set aside at room temperature for 2 hr, and then diluted with ice water (150 ml) and cooled overnight in a refrigerator to give orange needles (230 mg), mp 135° dec. A metal spatula was blackened when dipped in a hot methanolic or Skellysolve B solution of this compound. Recrystallization from Skellysolve B gave orange needles of the azo sulfoxide **4b**: mp 138° dec; uv max 306 mμ (ε 2000), 232 (18,700).

Anal. Calcd for $C_{12}H_8ON_2S$: C, 63.14; H, 3.53; N, 12.28; S, 14.05. Found: C, 62.69; H, 3.68; N, 11.34; S, 14.31.

The filtrates from the recrystallization of **4b** gave light yellow crystals of benzocinnoline, mp and mmp 153–156°. Authentic benzocinnoline, mp 156°, was prepared according to Badger, *et al.*[17]

B.—A mixture of hydrazo sulfoxide **3b** (100 mg), PBA (0.219 *M*, 3 ml), and chloroform (10 ml) was shaken for 2 min before being quenched with 5% sodium hydroxide solution (5 ml). The chloroform solution was worked up in a usual way to afford **4b** (85 mg), mp 137° dec.

Oxidation of Azo Sulfide 4a with PBA.—A solution containing azo sulfide **4a** (400 mg), a calculated amount of 0.335 *M* PBA, and chloroform (20 ml) was set aside for 2 days at room temperature. The products were worked up in the usual manner. One molar equivalent of PBA gave **2b**, **4b**, **4a**, and benzocinnoline; 2 molar equiv of PBA gave **2b** (59%), benzocinnoline (15%), and benzocinnoline *N*-oxide (10%); 2.5 molar equiv of PBA gave **2b** (75%) and benzocinnoline *N*-oxide (6%).

Benzocinnoline *N*-oxide was compared with an authentic sample prepared according to the method of King and King,[18] mp and mmp 135–137°.

Dethionylation of 2b.—A solution of 650 mg of **2b** in 7 ml of concentrated sulfuric acid was heated at 100° for 40 min and then poured on ice. The dark, insoluble product (350 mg) was given a charcoal treatment in benzene, and 100 mg (19%) of white, crystalline benzocinnoline *N*-oxide, mp 135–137°, was isolated. The acidic filtrate was neutralized with 6 *N* sodium hydroxide and a pale yellow precipitate, 210 mg (44%), was collected and identified as benzocinnoline.

Registry No.—**2b**, 30338-26-2; **3b**, 30388-27-3; **4b**, 30117-56-7.

(17) G. M. Badger, J. McSeidler, and B. Thomson, *J. Chem. Soc.*, 3207 (1951).

(18) F. E. King and T. J. King, *ibid.*, **825** (1945).

Derivatives of Dibenzo[*b*,*f*][1,4,5]thiadiazepine. VI.[1] Nitro and Amino Compounds

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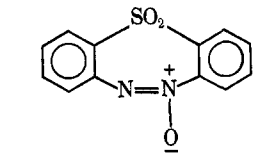
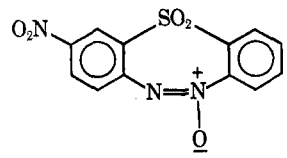
Received December 10, 1970

In previous papers of this series the ring-substituted derivatives of dibenzo[*b*,*f*][1,4,5]thiadiazepine were prepared by the ring closure of appropriately substituted diphenyl sulfides or sulfones. This paper presents the results of the nitration of the azoxy sulfone **1** and the chemistry of the resulting mono- and dinitro compounds.

Although the successful nitration of various acyclic azobenzenes is described in the literature,[4,5] the application of this reaction to the azo sulfone **5** (R = H)



1



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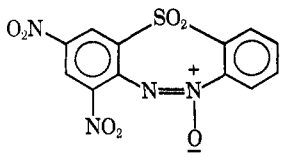

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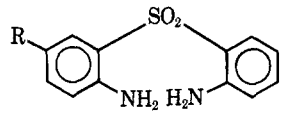

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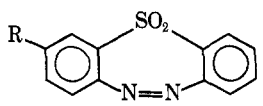
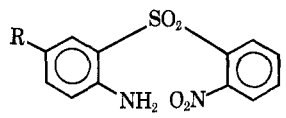
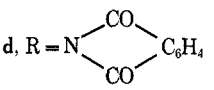


5



6

a, R = NH_2
b, R = $NHCOCH_3$
c, R = $NHSO_2C_6H_5$



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gave extensive tar formation even under the mildest conditions that were attempted. On the other hand, the nitration of the azoxy sulfone **1** gave the mono- and dinitro products, which are deduced to be the 9-nitrodibenzo[*b*,*f*][1,4,5]thiadiazepine 5,11,11-trioxide (**2**) and the corresponding 7,9-dinitro derivative (**3**), respectively. The choice of rings in the electrophilic substitution follows from the known behavior of azoxybenzenes,[6-8] and the assignment of the position is

(1) For paper V, see H. H. Szmant and Y. L. Chow, *J. Org. Chem.*, **36**, 2887 (1971).

(2) Department of Chemistry, University of Detroit, Detroit, Mich. 48221.

(3) Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada.

(4) J. Werner and E. Stiasny, *Ber.*, **32**, 3256 (1899).

(5) J. Burns, H. McCombie, and M. Scarborough, *J. Chem. Soc.*, 2928 (1928).

(6) L. C. Behr, *J. Amer. Chem. Soc.*, **76**, 3672 (1954).

(7) T. Ukai and Y. Ito, *J. Pharm. Soc. Jap.*, **3**, 821 (1953).

(8) K. H. Schündehütte in "Methoden der Organischen Chemie," Vol. 10, 4th ed, part 3, G. Thieme Verlag, Stuttgart, 1965, p 745.