amino)toluene, analytical sample, mp 83–84° (CH_3CN); nmr (C_6D_6) τ ~2.66 (m, 5, aromatic) and 7.58 (s, 18, NMe_2).

Anal. Calcd for $C_{13}H_{23}N_3$: C, 70.54; H, 10.47; N, 18.98. Found: C, 70.35; H, 10.72; N, 18.72.

Treatment of the triamine with 6 *N* hydrochloric acid afforded dimethylammonium ion and *N,N,N',N'*-tetramethylbenzamidinium ion:[19,20] nmr (H_2O) τ 2.4 (s, 5, aromatic), 6.8 (s, 12, N^+Me_2), and 7.3 (t, 6, $H_2N^+Me_2$). The solution was made basic and was extracted with ether. Evaporation of the ether gave *N,N*-dimethylbenazmide, identical (nmr and vpc) with an authentic sample.

Registry No.—*N,N,N',N',N'',N''*-Hexamethylguanidinium chloride, 30388-20-6, 30388-21-7 (hexafluorophosphate); α,α,α-tris(dimethylamino)toluene, 30388-25-1.

[19] C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, **36**, 2881 (1971).

[20] C. G. Raison, *J. Chem. Soc.*, 3325 (1949).

A Novel Preparation of 3-Oxazoline-2(1*H*)-2-thiones Involving a Benzilic Acid Type Rearrangement

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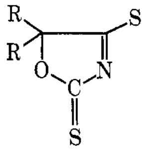
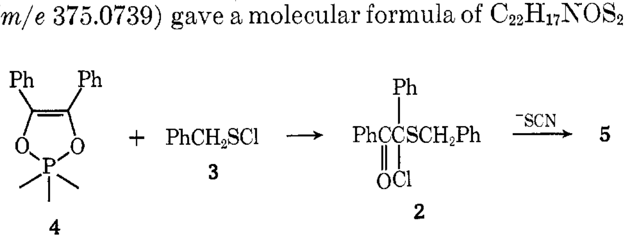
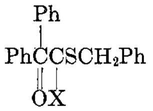
We wish to report that α-benzoyl-α-chlorobenzyl sulfides[2] (2) can be converted in high yield to substituted 3-oxazoline-2(1*H*)-2-thiones (1) by treatment with potassium thiocyanate. When sulfide 2 [prepared by the action of benzyl sulfenyl chloride (3) on the 1,3,2-dioxaphospholene derivative 4][2] was combined with potassium thiocyanate, compound 5 was isolated in 90% yield. Exact mass measurement of 5 (*m/e* 375.0739) gave a molecular formula of $C_{22}H_{17}NOS_2$.



1



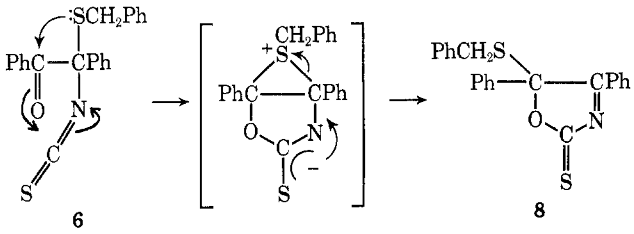
The structure of 5 was deduced as follows. The lack of –CO, –NCS, and –SCN stretching frequencies in the ir spectrum of 5 showed that it was not a simple substitution product (6 or 7).[3] A more deep-seated transformation can be envisaged. From a mechanistic viewpoint two structures for 5 following from 6 are reasonable. Path a, involving an episulfonium intermediate, predicts 8 as the product. Participation by sulfur would not be unexpected and has ample precedent in the literature.[4] Alternatively, phenyl migration, as depicted in path b suggests that thione 5 might be formed.



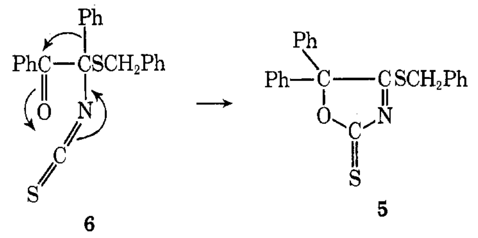
$$\begin{array}{c}Ph\\ |\\ PhCCSCH_2Ph\\ \|\ |\\ OX\end{array}$$

6, X = –NCS
7, X = –SCN

path a

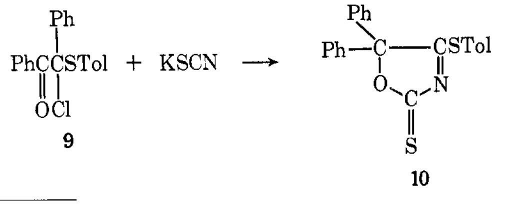


path b



The nmr spectrum of 5 reveals a sharp singlet as the only upfield signal (τ 5.77). This observation is consistent only with structure 5. If 8 were the correct structure, an AB pattern would have been observed for the diastereomeric protons on the benzylic carbon atom.[5] Phenyl migration of this kind has literature precedent in the benzilic acid rearrangement.[6]

Similarly, sulfide 9 was treated with KSCN. An oil, 10, was isolated in 82% yield: tlc homogeneous; *m/e* 375.0726 (calcd for $C_{22}H_{17}NOS_2$, 375.0752); nmr τ 2.10–2.90 (14 H, m), 7.60 (3 H, s). That phenyl migration occurs in this reaction as well was strongly indicated by the similar uv spectra of 5 and 10: 5, λ_{max} 228 nm (ε 3483), 296 (1711); 10, 232 (2970), 295 (1543). While 5 and 10 give expected ir, nmr, mass



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[1] NRCC Scholarship Recipient, 1967–1970.

[2] D. N. Harpp and P. Mathiaparanam, *Tetrahedron Lett.*, 2089 (1970).

[3] Analogous compounds are formed in the reaction of α-chloro ketones and KSCN; see A. Hantzsch and L. Aripides, *Justus Liebigs Ann. Chem.*, **249**, 18 (1888).

[4] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 561–617.

[5] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, pp 93–95. It should be noted that a sharp singlet was observed in a variety of solvents: C_6H_6, $CDCl_3$, CD_3OD, and $(CD_3)_2SO$ at τ 6.00, 5.77, 5.77, and 5.67, respectively. Strong AB coupling is observed in **2** as well as other similar derivatives (see ref 2).

[6] Reference 4, p 636.

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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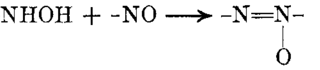
Seven-membered ring systems containing ten π electrons have been of interest because of their potential aromatic character.[4] In earlier papers dealing with the dibenzo[*b*,*f*][1,4,5]thiadiazepine system[5,6] the sulfur moiety was present in the form of the conveniently attained and unreactive sulfone 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]



$$\text{-NHOH} + \text{-NO} \longrightarrow \text{-N}{=}\underset{\substack{| \\ \text{O}}}{\text{N}}\text{-}$$

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,

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[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.