38.3–39°. Triethyl thionophosphate, the other expected product in this reaction, was obtained in an 89% yield. A considerably longer distillation period, 27 hr., was required in this case, as compared to that required in the reaction of 1-methoxymethylthiirane with triethyl phosphite.[19]

The slow distillation (27 hr.) of a mixture composed of 24.0 g. (0.2 mole) of 1-ethoxy-2-mercaptopropane and 33.2 g. (0.2 mole) of triethyl phosphite gave a 91% yield of ethyl propyl ether, b.p. 62–63°/747 mm. Lit.,[34] b.p. 63–63.4°/760 mm. Triethyl thionophosphate was obtained in 83% yield.

Careful distillation (15 hr.) of a mixture composed of 26.8 g. (0.2 mole) of 1-propoxy-2-mercaptopropane and 33.2 g. (0.2 mole) of triethyl phosphite, gave a 65% yield of dipropyl ether b.p. 89–90°/742 mm., n_D^{20} 1.3801. Lit.,[34] b.p. 90–90.5°/768 mm., n_D^{20} 1.3808. Triethyl thionophosphate was also obtained in a 72% yield. Repetition of this reaction with 30 hr. of heating gave an 87% yield of the ether and an 85% yield of the triethyl thionophosphate.

East Lansing, Mich.

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[34] A. I. Vogel, *J. Am. Chem. Soc.*, 617 (1948).

[Contribution from the Central Research Department, E. I. du Pont de Nemours & Co.]

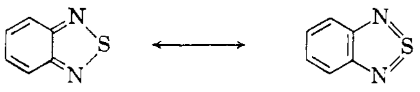
Bis(phenylimino)sulfur

RICHARD CRAMER

Received October 28, 1960

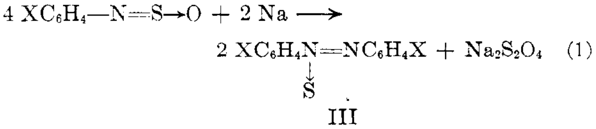
The reaction of aniline with sulfur tetrafluoride or with phenyliminosulfur difluoride yields a metathetical product, $(C_6H_5)_2N_2S$, which is identical with a compound previously obtained through the reaction of thionylaniline with sodium. The new synthetic methods indicate that the structure of the product is $C_6H_5N{=}S{=}NC_6H_5$ and this is supported by additional spectral and chemical evidence.

The first reported compound containing the $>N_2S$ group is piazthiole, obtained in the reaction of thionyl chloride[1] or sulfur dioxide[2] with *o*-phenylenediamine. Piazthiole has generally been formulated as an *o*-quinoid compound (I) but its relative inertness suggests a resonance stabilization to which a benzenoid tetravalent-sulfur structure (II) probably contributes.



I II

In 1956 Goehring and Weiss[3] reported the synthesis of bis(*n*-butylimino)sulfur by the reaction of *n*-butylamine with sulfur tetrachloride. A year later Leandri and Rebora[4] prepared a series of compounds containing the group $>N_2S$ by reaction of a variety of aromatic thionyl imines with metallic sodium (Equation 1). These compounds were



$$4\,XC_6H_4{-}N{=}S{\to}O + 2\,Na \longrightarrow 2\,XC_6H_4\underset{\underset{S}{\downarrow}}{N}{=}NC_6H_4X + Na_2S_2O_4 \quad (1)$$

III

X = H; *o*-, *m*-, or *p*-CH_3; *o*- or *p*-CH_3O; *o*- or *p*-C_2H_5O; *o*-, *m*-, or *p*-Cl; *o*- or *p*-C_6H_5; *p*-Br; *p*-$(CH_3)_2N$

formulated (III) as analogs of azoxybenzene on the following evidence: (1) Desulfurization of either III (X = H) or azoxybenzene with zinc yields azobenzene. (2) Reaction of III with alumina also gives azobenzene apparently by an intramolecular reaction since a mixture of homologs (X = H and X = *p*-C_6H_5,) yields azobenzene and *p,p'*-diphenylazobenzene but no phenylazobenzene. (3) Reaction of either III (X = H) or azoxybenzene with hydrogen bromide produces 2,4-dibromoaniline. Subsequently, Leandri *et al.*[5] interpreted the infrared absorption spectrum of the product from thionylaniline and sodium as supporting structure III.

Attempts in this laboratory to learn if aniline and sulfur tetrachloride would yield Leandri's "azothiobenzene" (III) resulted inconclusively in extensive chlorination of aniline. When sulfur tetrafluoride and, subsequently, phenyliminosulfur difluoride became conveniently accessible through syntheses developed by Tullock[6] and Smith[7] and their co-workers, these compounds were used in reactions analogous to the Goehring and Weiss synthesis of bis(*n*-butylimino)sulfur (equations 2 and 3).

$$2\,C_6H_5NH_2 + SF_4 + 4(CH_3)_3N \longrightarrow C_6H_5N{=}S{=}NC_6H_5 + 4(CH_3)_3N{\cdot}HF \quad (2)$$

$$C_6H_5N{=}SF_2 + C_6H_5NH_2 + 2(CH_3)_3N \longrightarrow C_6H_5N{=}S{=}NC_6H_5 + 2(CH_3)_3N{\cdot}HF \quad (3)$$

The products of these reactions had infrared absorption spectra identical with the product from reaction of thionylaniline and sodium; the spectra are

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[1] A. Michaelis and A. Buntrock, *Ann.*, **274**, 253 (1893).

[2] O. Hinsberg, *Ber.*, **22**, 2899 (1889).

[3] M. Goehring and G. Weiss, *Angew. Chem.*, **68**, 678 (1956).

[4] G. Leandri and P. Rebora, *Gazz. chem. ital.*, **87**, 503 (1957).

[5] A. Foffani, G. Leandri, I. Zanow, and C. Carpanelli, *Tetrahedron Letters*, No. 11, p. 21 (1959).

[6] C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

[7] W. C. Smith, C. W. Tullock, R. D. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.* **82**, 551 (1960).

compared in Table I. It is proposed that the products are properly formulated as bis(phenylimino)sulfur. Although the product of reaction 1 might reasonably be expected to be a sulfur analog of azoxybenzene, it is believed that reactions 2 and 3 are much more likely to lead to bis(phenylimino)sulfur.

TABLE I

ABSORPTION SPECTRA OF $(C_6H_5)_2N_2S$

A. Infrared (cm.$^{-1}$)

From $C_6H_5N{=}SF_2$: 634s, 731m, 758s, 803m, 828w, 900m, 913m, 957m, 972w, 997m, 1025m, 1070s, 1152m, 1170m, 1218s, 1265s, 1298s, 1448s, 1480s, 1589s, 1680w, 1730w, 1795w, 1880w, 1950w, 2080w, 3080v.s.

From $C_6H_5N{=}S{\rightarrow}O^a$: 1070, 1448

B. Ultraviolet (mμ)

From $C_6H_5N{=}SF_2$: 220 (shoulder, log ϵ = 3.98); 245 (shoulder, log ϵ, 3.89); 350 (shoulder, log ϵ, 3.89); and 410 (peak, log ϵ, 3.98) (ethanol solution)

From $C_6H_5N{=}S{\rightarrow}O^b$: 410 (peak, log ϵ, 3.99) (*n*-hexane solution)

[a] Results given in ref. 5. [b] G. Leandri and P. Rebora, *Experientia*, **13**, 70 (1957).

Analogous products are obtained in the reaction of ammonia or amines with sulfur monochloride,[8a] sulfur dichloride,[8b] thionyl chloride,[8c] thionyl fluoride,[8d] or sulfuryl fluoride.[8e]

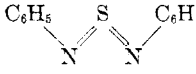
It is noteworthy that nitrogen compounds in which sulfur replaces oxygen—*e.g.*, sulfur analogs of amine oxides, nitroso compounds, or, even, nonpolymeric nitrogen oxides—are nonexistent. It may seriously be doubted that sulfur is sufficiently electronegative to form a dative bond with nitrogen as does oxygen in azoxybenzene.

It remains to consider the chemical and spectral evidence supporting Leandri's proposed structure. It is true that desulfurization (with zinc or alumina) would require less structural reorganization of "azothiobenzene" than of bis(phenylimino)sulfur. However, it is quite possible that desulfurization involves an intramolecular rearrangement of which there are many examples including the rearrangement of sulfonium ions to sulfides.[9] Cleavage by hydrogen halides to yield aniline hydrohalides, the third reaction mentioned as supporting an "azothiobenzene" structure also occurs with thionyl imines,[10] $RN{=}S{=}O$. As the bisiminosulfur compounds are formally derived from thionyl imines by replacement of the oxygen of the latter compounds by an imino group, a chemical similarity of thionyl imines and bisiminosulfurs is not unexpected. Accordingly, hydrogen halide cleavage is compatible with both formulations.

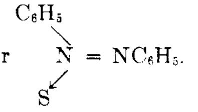
The hydrolytic behavior of R_2N_2S resembles that of thionylimines and, consequently, supports their formulation as $RN{=}S{=}NR$. Lower alkyl thionyl imines and Goehring's bis(*n*-butylimino)sulfur are both very water sensitive. Aromatic thionyl imines and bis(phenylimino)sulfur are hydrolyzed more slowly. Azoxybenzene is not sensitive to water and its sulfur analog might be expected to resist hydrolysis.

Turning to the spectral evidence relating to the structure of $(C_6H_5)_2N_2S$, Foffani *et al.*[5] report only two strong absorption bands viz. 1070 and 1448 cm.$^{-1}$; other absorptions (of undisclosed frequency) are ascribed to ring vibrations. The 1070 cm.$^{-1}$ absorption was identified with the symmetrical stretching vibration of N→O in azoxybenzenes (1325 ±10 cm.$^{-1}$) on the assumption that the corresponding N→S frequency can be calculated by a simple mass effect. The ratio between carbonyl and thiocarbonyl frequencies ranges from 1.6 to 1.14[11] so the frequency expected for N→S would be 830 to 1160 cm.$^{-1}$ The 1448 cm.$^{-1}$ absorption was identified with the asymmetric stretching vibration of N→O in azoxybenzenes (1465 ± 15 cm.$^{-1}$) with no correction for a mass effect, although the authors point out that this absorption falls near to a ring vibration.

The infrared absorption of $(C_6H_5)_2N_2S$ ascribed to vibrations of the $>N_2S$ group appears to resemble the absorption of sulfur dioxide more closely than it does azoxybenzene and thus to correspond more closely to frequencies expected for



than for



The 1448 cm.$^{-1}$ absorption is assumed to be a ring vibration. In addition to the absorption at 1070 cm.$^{-1}$, we have found in all samples of bis(phenylimino)sulfur an absorption at 1265 cm.$^{-1}$ which is believed to correspond to an S—N vibration. (Since Foffani, *et al.* did not report the frequencies of all absorptions they, too, may have observed this band.) Corresponding to absorptions of 1070 cm.$^{-1}$ and 1265 cm.$^{-1}$ for bis(phenylimino)sulfur, sulfur dioxide absorbs at 1151 cm.$^{-1}$ and 1361 cm.$^{-1}$.[12] It will be noted that the differences between corresponding absorptions of these two compounds are of the same order of magnitude.

A comparison of the electronic spectra of azoxybenzene[13] (max. 261 mμ; log ϵ, 3.87) and bis(phenylimino)sulfur (max. 410 mμ; log ϵ, 3.95) suggests

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[8] (a) H. B. Van Valkenburgh and J. C. Bailar, *J. Am. Chem. Soc.*, **47**, 2134 (1925); (b) O. Ruff and E. Geisel, *Ber.*, **37**, 1573 (1904); (c) A. Michaelis, *Ann.*, **274**, 200 (1893); (d) M. Goehring and G. Voigt, *Ber.*, **89**, 1050 (1956); (e) W. Traube and E. Reubke, *Ber.*, **56**, 1661 (1923).

[9] C. R. Hauser, S. W. Kantor, and W. R. Brasen, *J. Am. Chem. Soc.*, **75**, 2660 (1953).

[10] A. Michaelis and G. Junghans, *Ann.*, **274**, 233 (1893).

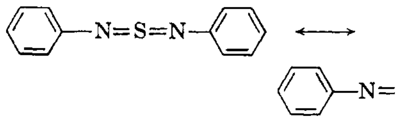
[11] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley and Sons, Inc., New York, 1957, p. 356.

[12] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1945, p. 285.

[13] H. Dahn and H. v. Castelmur, *Helv. Chim. Acta*, **36**, 638 (1953).

they do not have a similar structural relationship to azobenzene[13] (max. 442 mμ; log ε, 2.73).

The color of bis(phenylimino)sulfur may be attributed to resonance forms such as IV.



IV

EXPERIMENTAL

Synthesis of bis(phenylimino)sulfur from phenyliminosulfur difluoride and aniline. A 500-ml. flask fitted with a solid carbon dioxide-cooled condenser, a jacketed dropping funnel, and a magnetic stirrer was charged with 16.1 g. (0.1 mole) phenyliminosulfur difluoride[7] and 100 ml. (liquid) trimethylamine. A solution of 9.3 g. (0.1 mole) aniline in 10 ml. trimethylamine was added during a period of 0.75 hr. from the jacketed dropping funnel. After the mixture had stood at the reflux temperature of trimethylamine for 20 hr., the liquid product was decanted from insoluble trimethylamine hydrofluoride and concentrated at 25° to give 18 g. of red liquid. This material distilled in a molecular still at a pressure of 0.3 mm. when the temperature of the heating block of the still was 97°. As ebullition occurred, this temperature is believed to be the approximate boiling temperature at 0.3 mm. The yield was 15 g. or 70% of theory. The product is a bromine-colored liquid with a density $d_4^{25} = 1.190$.

Anal. Calcd. for $C_{12}H_{10}N_2S$: S, 14.96; N, 13.08; mol. wt. 214. Found: S, 15.03; N, 13.43; mol. wt. 218.

The infrared spectrum of the liquid was recorded on a Perkin-Elmer model 21 double beam instrument with sodium chloride optics. The electronic spectrum of ethanol solutions of bis(phenylimino)sulfur was measured on a Cary Model 14 double beam spectrophotometer.

From aniline and sulfur tetrafluoride. A solution of 42 g. (0.5 mole) aniline in 125 ml. trimethylamine was stirred at reflux temperature and 27 g. (0.25 mole) gaseous sulfur tetrafluoride[6] was introduced during 1 hr. A moderately exothermic reaction occurred and after 3 hr. the trimethylamine solution was decanted and concentrated at 25°. The residue was distilled through a 6 in. Vigreux column. After 6.4 g. aniline had distilled, 16.0 g. (37% yield) bis(phenylimino)sulfur was collected. It boiled at 114° at 0.8 mm. and had an infrared absorption spectrum identical with the product from phenyliminosulfur difluoride and aniline.

From thionylaniline. A suspension of sodium metal (3.2 g., 0.14 g.-atom) in 3.2 g. toluene was added to a solution of 10 g. (0.1 mole) thionylaniline in 75 ml. toluene and the stirred mixture was heated. At the reflux temperature there was a vigorous reaction which subsided quickly. The mixture was heated 1.5 hr. more, filtered and distilled through a 6 in. Vigreux column. Bis(phenylimino)sulfur distilled at 100°/2 mm. The yield was 2.1 g., 20%. The infrared absorption spectrum was identical with that of the product from phenyliminosulfur difluoride and aniline.

Chemistry of bis(phenylimino)sulfur. Hydrolysis. Samples (0.1 ml.) of bis(phenylimino)sulfur were added to test tubes containing: (1) 0.5 ml. water, (2) 0.5 ml. aqueous 10% sodium hydroxide, (3) 0.5 ml. aqueous 10% hydrogen chloride, (4) 0.4 ml. dioxane + 0.2 ml. water, (5) 0.4 ml. dioxane + 0.2 ml. aqueous 10% sodium hydroxide, and (6) 0.4 ml. dioxane + 0.2 ml. aqueous 10% hydrogen chloride. All of the mixtures initially contained two phases but after 20 hr. almost all the bis(phenylimino)sulfur in solutions 4 and 6 had dissolved and aniline sulfate crystallized from the solution. After 5 days all the mixtures except 1 and 2 had reacted.

Aniline sulfate was identified by comparison of its infrared absorption with an authentic sample.

Bromination. A solution of 1.6 g. (7.5 mmoles) of bis(phenylimino)sulfur in 10 ml. carbon tetrachloride was treated with 5 g. (30 mmoles) of bromine in 20 ml. carbon tetrachloride. A solid, presumably 2,4,6-tribromoaniline hydrobromide, precipitated immediately and after 15 min. was filtered and washed with carbon tetrachloride.

Anal. Calcd. for $C_6N_5NBr_4$: Br, 77.82, S, 0. Found: Br, 75.59, S <0.1. A broad infrared absorption in the range 3.5 to 4.0 μ with peaks at 3.60 μ and 3.92 μ indicates an amine salt.

Acknowledgment. Interpretations of the infrared spectra were made by R. C. Lord of the Massachusetts Institute of Technology and by Naomi E. Schlichter of this laboratory.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Some Aminolysis and Deammonation Reactions of Dialkylsulfamyl Chlorides and Sulfamide with Polyamines

ANTONIO VANDI, THERALD MOELLER, AND LUDWIG F. AUDRIETH

Received January 27, 1961

Reactions of *N*,*N*-disubstituted sulfamyl chlorides and of sulfamide with aliphatic primary and secondary diamines have been employed to prepare sulfamide derivatives of the types $R_2NSO_2NH(CH_2)_nNHSO_2NR_2$ and $H_2NSO_2NH(CH_2)_nNHSO_2NH_2$. Further deammonation to yield a linear polymer of the composition $(\text{—}NH(CH_2)_6NHSO_2\text{—})_n$ has been noted when sulfamide and 1,6-hexanediamine are allowed to react under appropriate conditions. The white, crystalline compounds obtained have been characterized in terms of analyses and melting points. Cross-linking in the polymeric material is precluded by the presence of a strong NH stretching absorption at 3280 cm.$^{-1}$ In the aromatic series, the only characterizable product has been obtained from the reaction of *p*-phenylenediamine with *N*,*N*-dimethylsulfamyl chloride.

A number of striking analogies between sulfamide and urea can be distinguished. It might be anticipated, on this basis, that treatment of sulfamide with sufficiently basic amines should lead to deammonation and the formation of various substituted sulfamides. Indeed, several compounds of the general types $RNHSO_2NH_2$, $RNHSO_2NHR$, $R_2NSO_2NH_2$, R_2NSO_2NHR, and $R_2NSO_2NR_2$, where the R-