REACTIONS OF
SULFUR AND SULFUR CONTAINING SPECIES
WITH AMINES

By

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SCOPE AND CONTENTS:

The reactions of S_4N_4 with various amines, particularly benzylamines, have been investigated. Benzylamines give arylimine polysulfides, Schiff's bases and ammonia as products. The stoichiometric equation has been established. The reaction is quite sensitive to structural changes and appears limited to ring substituted benzylamines.

Details of the reactions of primary amines with sulfur, one of the "neglected fields of research", have been investigated. Intermediates have been isolated and characterized and a reaction scheme has been proposed for the sulfur-benzylamine system. In this scheme benzylamine polysulfides and benzylidenimine polysulfides occur as cyclical intermediates. The final products are N-benzylidene benzylamine, ammonia and benzylammonium polysulfides.

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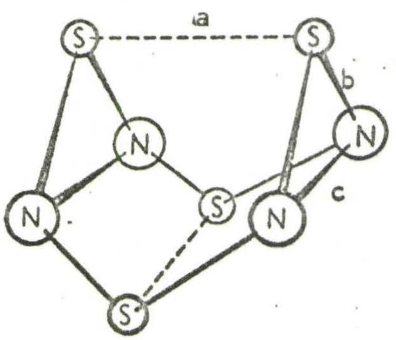
PART I. REACTIONS OF S_4N_4 WITH AMINES

CHAPTER I. INTRODUCTION

1. TETRASULFUR TETRANITRIDE, S_4N_4

Tetrasulfur tetranitride, known since 1835,$^{(1)}$ is generally prepared by the reaction of sulfur monochloride with ammonia, a complex reaction whose mechanism is not clear. Tetrasulfur tetranitride is an orange crystalline solid of m.p. 178°C. It is endothermic with an enthalpy of formation of 110±2 Kcals/mole$^{(2)}$ and detonates on mechanical shock or on heating to near the melting point. The structure of S_4N_4 is shown in Fig. 1. The four sulfur atoms form a bisphenoid while the four nitrogen atoms are coplanar and occupy the corners of a square.

Fig. 1. STRUCTURE OF $S_4N_4$$^{(3)}$



a = 2.58 A.

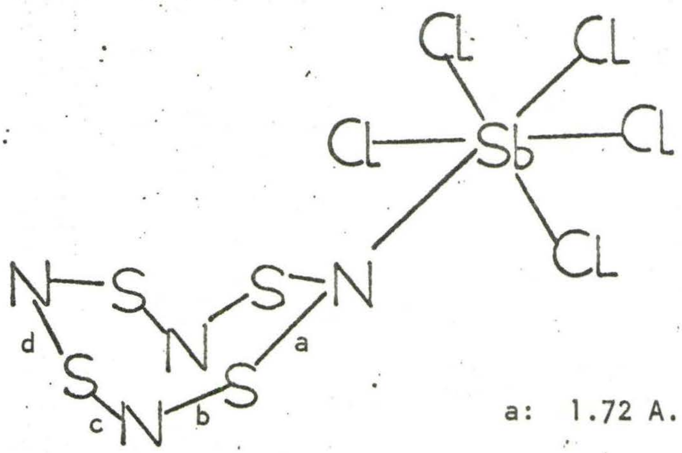
b = 1.62 A.

c ≐ 2.52 A.

The sulfur-sulfur distance (a) of 2.58 A. is longer than the normal sulfur-sulfur single bond length (2.05 A.) but shorter than the sum of the Van der Waals radii of two sulfur atoms (3.70 A.(4)) indicating a significant interaction. The distance between the adjacent nitrogen atoms (c) is 2.52 A. while the sum of two nitrogen Van der Waals radii is 3.0 A.(4) and a single nitrogen-nitrogen bond is 1.40 A.(5) Slight interaction between the nitrogen atoms around the square also appears possible. The sulfur-nitrogen bond length of 1.62 A. for all bonds is shorter than the normal sulfur-nitrogen single bond length (1.76 A. in sulfamic acid, $H_3N^+ - SO_3^-$)(6) or the single bond radii sum of 1.74 A.(5) These facts indicate considerable delocalization of electrons in the S_4N_4 ring system. Several tentative bonding schemes have been proposed.(7,8,9,10)

Because of the difference in electronegativities between sulfur and nitrogen atoms, it is expected that tetrasulfur tetranitride will have a partial negative charge on the nitrogen atoms and a partial positive charge on the sulfur atoms. Consequently, S_4N_4 may act as either a Lewis acid through the sulfur atoms or as a Lewis base through the nitrogen atoms. There are many stable adducts known where S_4N_4 acts as a Lewis base, such as $S_4N_4 \cdot SbC\ell_5$ (Fig. 2)(11) and $S_4N_4 \cdot BF_3$.(12,13) X-ray crystallography of these materials shows that the sulfur-nitrogen ring system has undergone a conformational change. $S_4N_4 \cdot BF_3$ has a very similar structure to that of $S_4N_4 \cdot SbC\ell_5$. The sulfur atoms are nearly planar with two

Fig. 2. $S_4N_4 \cdot SbCl_5$



a: 1.72 A.

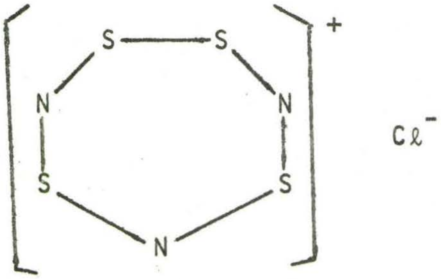
b: 1.55 A.

c: 1.57 A.

d: 1.60 A.

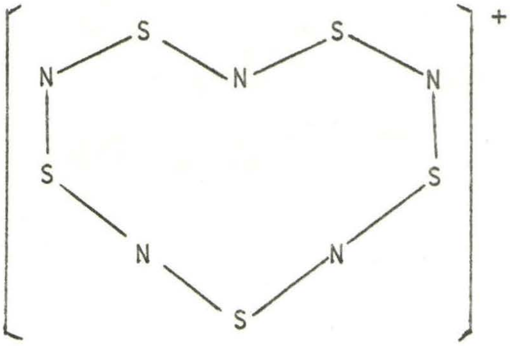
nitrogen atoms above and two below this plane. This conformation change might be rationalized by a weakening of the sulfur-sulfur interaction as a consequence of the drain of electron density from the ring by the Lewis acid. The sulfur-nitrogen bond lengths from the nitrogen atom coordinated to the antimony atom (a) are considerably lengthened to 1.72 A. However, the sulfur-nitrogen bond lengths from the nitrogen atom which is opposite the coordinated one (d) are virtually unaffected.

The S_4N_4 ring undergoes contraction with some Lewis acids. With hydrochloric acid it forms an adduct, $S_4N_4 \cdot 4HCl$,(14) which with a trace of water decomposes to thiotrithiazyl chloride, I. This material is also produced from S_4N_4 with sulfur monochloride(15) and



I

thionyl chloride.(16) The thiotrithiazyl cation has a planar structure with equal sulfur-nitrogen distances. Quite recently, the stable pentathiazyl cation, $S_5N_5^+$, was prepared from S_4N_4 with aluminium chloride in thionyl chloride.(17) This ion has been shown by X-ray diffraction to be a planar heart-shaped ring, II.



II

With Lewis bases, S_4N_4 generally undergoes ring contraction or degradation. These reactions are discussed in the next section.

2. REACTIONS OF S_4N_4 WITH LEWIS BASES

A. AMINES

Schenck(18) described several reactions of S_4N_4 with organic amines in which the reaction products did not retain any of the original S—N linkages of S_4N_4. According to Schenck tertiary amines were inert toward S_4N_4, while primary and secondary aromatic amines, such as aniline, N-methylaniline, diphenylamine and naphthylamine, reacted only at higher temperature to give ammonia, nitrogen, sulfur and hydrogen sulfide.* Primary and secondary aliphatic amines were found to react very readily, however. A typical secondary amine, piperidine, reacted with S_4N_4 at room temperature with the evolution of nitrogen and ammonia. The major non-gaseous product was thiodipiperidine, $C_5H_{10}N—S—NC_5H_{10}$. Schenck measured the quantity of nitrogen gas evolved and established the stoichiometry shown in equation (1). Dimethylamine also gave an analogous compound,

$$3S_4N_4 + 24C_5H_{10}NH = 12(C_5H_{10}N)_2S + 8NH_3 + 2N_2 \tag{1}$$

thiobisdimethylamine, $(CH_3)_2N—S—N(CH_3)_2$.

With ethylamine Schenck was unable to obtain any characterizable products. When S_4N_4 and benzylamine were heated together on a water bath, sulfur and triphenyl-(s)-triazine, III, were obtained. Without heat, Schenck obtained a different product, a yellow crystalline material which melted at 104-105°C. From the elemental analysis (for nitrogen and sulfur), he assigned this compound as the

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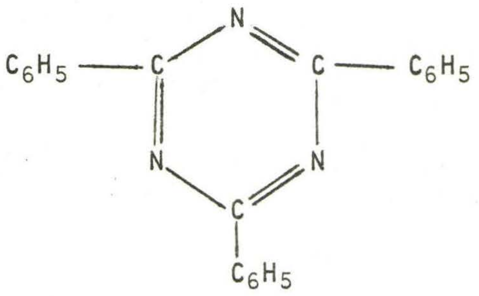
*Products containing organic component were not described.



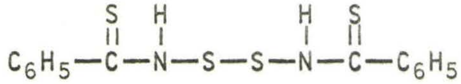
III

thioamide of thiobenzoic acid, IV (2). This structure was challenged

$$3S_4N_4 + 6C_6H_5CH_2NH_2 \longrightarrow 6C_6H_5-\overset{S}{\overset{\|}{C}}-N{=}S + 8NH_3 + 2N_2 \qquad (2)$$

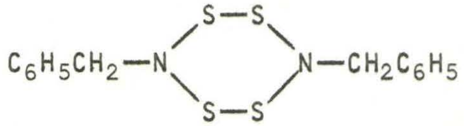
IV

by Levi(19) who prepared the same material (m.p. 100°C) from the reaction of sulfur with benzylamine in the presence of lead (II) oxide. Based on an elemental analysis (C, H, N and S) and a molecular weight of 322, Levi proposed either of structures V or VI. (Levi favored VI, but was unable to exclude V.) VI has been prepared from



$$C_6H_5-\overset{S}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-S-S-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-C_6H_5$$

V



VI

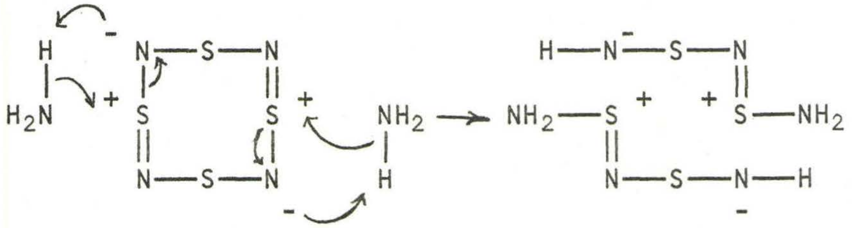
sulfur monochloride and benzylamine,(20) however, and its properties differed from those of the yellow solid.

Schenck (18) also reported that while phenylhydrazine did not react with S_4N_4 at low temperature, it did react vigorously with the evolution of nitrogen and ammonia when heated. For this reaction he proposed equation (3).

$$3S_4N_4 + 12C_6H_5NHNH_2 \longrightarrow 12S + 8NH_3 + 14N_2 + 12C_6H_6 \qquad (3)$$

B. AMMONIA

Ruff and Geisel (21) found that S_4N_4 and liquid ammonia reacted to give an apparent diammoniate of composition $S_4N_4 \cdot 2NH_3$. However, S_2N_2 also reacted with liquid ammonia to give an ammoniate of composition $S_2N_2 \cdot NH_3$ with an identical X-ray powder pattern and electron absorption spectrum. (22) The molecular weight of this material was not reported, but it was suggested that the material was most probably $H{-}\overset{-}{N}{-}S{-}N{=}\overset{+}{S}{-}NH_2$ for the following reasons. Firstly, it decomposed to S_2N_2 and ammonia in high vacuum. Secondly, treatment with triphenylmethyl sodium in ether gave a brown monosodium salt and then a yellow explosive trisodium salt. These were presumed to represent removal of the more acidic imide hydrogen and in the second step the two less acidic amide hydrogens. An analysis of the yellow trisodium salt showed the atomic ratio of N:S:Na to be close to 3:2:3 indicating a formula such as $Na_2N{-}S{-}\overset{-}{N}{-}\overset{+}{S}{=}N{-}Na$. If this view of the structure is correct, the ammonolysis of tetrasulfur tetranitride might be represented as in (4).

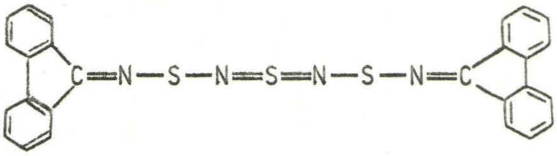


(4)

C. DIAZOMETHANES

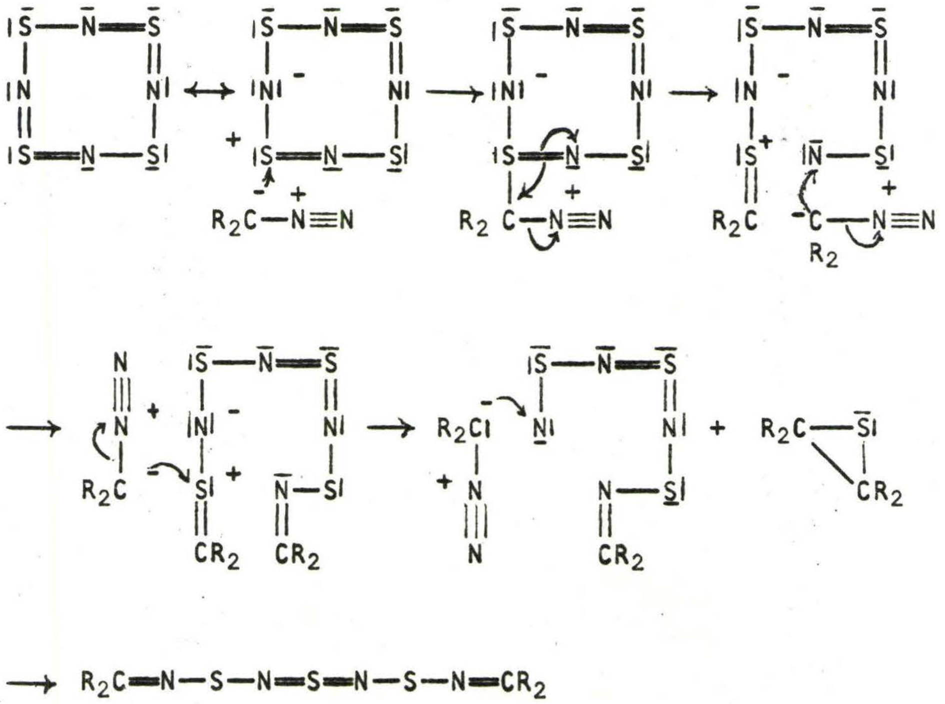
When substituted diazomethanes, such as diphenyldiazomethane or diazofluorene, were reacted with S_4N_4 at room temperature, nitrogen was slowly evolved, and the products isolated were bis-diphenylmethylene-trisulfur-tetranitride, VII, and difluorenylidene-trisulfur-tetranitride, VIII, respectively.

VII



VIII

A molecular weight (for VII only) and an elemental analysis (for both) were in quite good agreement with these compositions although structural data was lacking. Fluck(23) proposed a possible reaction mechanism consisting of a series of nucleophilic attacks by the carbanionic carbon atom, $R_2\overset{-}{C}—\overset{+}{N}\equiv N$, to liberate free nitrogen as shown below. The substituted thirane was also isolated.



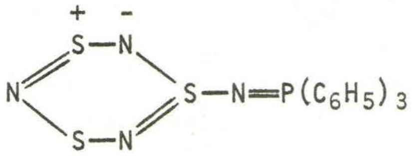
(5)

D. GRIGNARD REAGENTS

Similar types of compounds were reported in the reaction of S_4N_4 with Grignard reagents.(24) Thiodithiazyl diaryls, $X—C_6H_4—S—N{=}S{=}N—S—C_6H_4—X$ (where X = H, p-Cℓ, p-Br and p-CH_3O), were reported to result from the corresponding aryl-magnesium bromide; however, no analytical data or physical or chemical properties for these compounds were given except melting points and solubilities. Therefore, the structures of these compounds can not be considered to be well established. Reaction of ethylmagnesium bromide with S_4N_4 resulted in a different type of compound of composition $C_2H_5S_2N_2$.(25) The structure of this material was proposed to be $C_2H_6S—N{=}S{=}NH$.

E. PHOSPHINES

The weak nucleophile phosphine did not react with S_4N_4,(26) but triphenylphosphine was found to give a red crystalline material of composition $S_3N_4P(C_6H_5)_3$ to which structure IX was assigned.(27,28) Triphenylphosphine sulfide, $(C_6H_5)_3P{=}S$, and trithioformaldehyde $(CH_2S)_3$ were also detected in solution. A molecular weight and an elemental analysis (for C, H, N, S and P) were consistent with the proposed formula but, of course, gave no structural information. Triphenylphosphinemethylene, $(C_6H_5)P{=}CH_2$, was reported to give the same compound IX when reacted with S_4N_4.(27) Tricyclohexylphosphine also gave an analogous compound of composition $S_3N_4P(C_6H_{11})_3$.(28) No mechanism was proposed.



IX

With dichlorophenyl phosphine complete degradation of the S_4N_4 ring system was observed.(29) The overall reaction was found to be as shown in equation (6).

$$
\begin{aligned}
3S_4N_4 + 30C_6H_5PCl_2 \longrightarrow\ & 10C_6H_5P(S)Cl_2 + 2C_6H_5P(Cl)_2NP(S)Cl(C_6H_5) \\
& + 3[C_6H_5P(Cl)_2NP(Cl)_2C_6H_5]Cl + 2[C_6H_5P(Cl)_2NP(Cl)(C_6H_5)NP(Cl)_2C_6H_5]Cl \\
& + [C_6H_5P(Cl)_2NP(Cl)(C_6H_5)NP(Cl)(C_6H_5)NP(Cl)_2(C_6H_5)]Cl \qquad (6)
\end{aligned}
$$

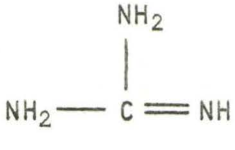
Phosphorous trichloride was also found to attack the S_4N_4 cage in a similar manner giving complete degradation.(30,31) A major product identified was the phosphonitrilic chloride, X.

$$[C\ell_3P{=}N{-}PC\ell_2{=}N{-}PC\ell_3][PC\ell_6]$$

X

F. CYANIDE ION

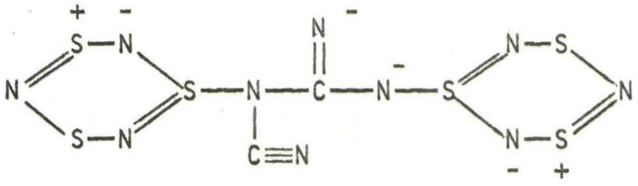
Cyanide ion is known to react readily with elemental sulfur to give thiocyanide$^{(32)}$ and has also been found to react readily with S_4N_4. When S_4N_4 and potassium cyanide were mixed together in dimethylformamide in a mole ratio of 1:2, a red precipitate was obtained whose composition based on an elemental analysis (for K, S, N and C) corresponded to KCN_3S_2.$^{(27)}$ This material was proposed to be a complex containing 2 moles of KSCN per mole of $K_2(C_2N_{10}S_6)$ based on a rather poor molecular weight determination. Since guanidine, XI, was obtained on hydrolysis, the material was inferred to have a carbon atom linked to three nitrogen atoms.



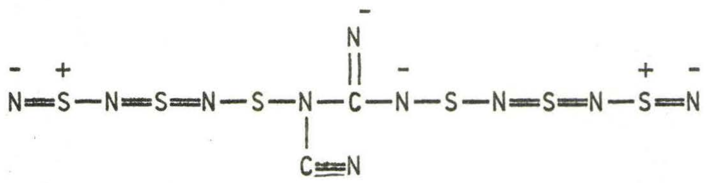
$$NH_2{-}C(NH_2){=}NH$$

XI

The structure of $(C_2N_{10}S_6)^{-2}$ was therefore tentatively proposed to be either XII or XIII.



XII



$$\overset{-}{N}=\overset{+}{S}-N=S=N-S-\underset{\underset{C\equiv N}{|}}{N}-\overset{\overset{\overset{-}{N}}{\|}}{C}-\overset{-}{N}-S-N=S=N-\overset{+}{S}=\overset{-}{N}$$

XIII

G. SUMMARY

Nucleophiles react with S_4N_4 to open the ring system. The products can be roughly classified into four categories.

1. Ring contraction with the retention of the alternating S-N-S-N bond system as reported with triphenyl phosphine.
2. Ring cleavage in which the product retains the alternating S-N-S-N chain system as represented by ammonia, disubstituted diazomethanes and Grignard reagents.
3. Complete degradation of the S_4N_4 system to ammonia, nitrogen and sulfides as exhibited by secondary alkylamines.
4. Complete degradation to products rather unrelated to the starting materials as in the case of benzylamine.

In many cases (ammonia, secondary amines, Grignard reagents) the nucleophiles attack at sulfur; however, in other cases (triphenyl phosphine and disubstituted diazomethane) both sulfur and nitrogen are proposed to undergo attack by the nucleophiles. In some cases (Grignard reagents and cyanide ion) the compositions of the products are not very reliable, while in others (benzylamine, disubstituted diazomethane and triphenylphosphine) the structures of the products are not known with certainty. In both amines and phosphines slight differences in nucleophilicity lead to drastic changes in the products.

3. AIMS OF THE PRESENT WORK

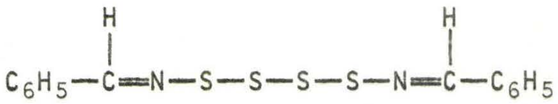
The wide variety of apparent nucleophilic substitution reactions and the generally poor characterization of the products clearly warrants further work before any generalization about substitution on S_4N_4 can be drawn. Of the various nucleophiles described, the reaction of benzylamine seems most peculiar although the structure of the product is not clear. The work described in this section is aimed at establishing the correct structure of the benzylamine-S_4N_4 reaction products, as well as the stoichiometric equation for this reaction. The latter point is particularly important since attempts to formulate mechanistic interpretations of nucleophilic substitution on S_4N_4 have been frustrated by the lack of even an overall chemical equation to describe the reactions.

Since changes in nucleophiles apparently cause such drastic changes in products, the effect of ring substituted benzylamines will be investigated in the hope of learning the effect of slight changes in the nucleophilicity of the attacking base. Other amines such as α-methylbenzylamine, butylamine, allylamine and phenylhydrazine, will also be investigated.

CHAPTER II. RESULTS AND DISCUSSION

1. CHARACTERIZATION OF ARYLIMINE POLYSULFIDES

When the reaction of tetrasulfur tetranitride with benzylamine was repeated as described by Schenck(18) (about 1 mole of S_4N_4 to 7 moles of benzylamine at room temperature), an exothermic reaction occurred. This was accompanied by several color changes (orange to green to brilliant yellow), and ammonia was evolved. Yellow needles of m.p. 100.5 ∿ 102°C were obtained by washing the reaction mixture with ice cold methanol. These appeared to be identical to the material described by Schenck and constituted the major crystalline product. The elemental analysis (for C, H, N and S) corresponded quite closely to the composition $[C_7H_6NS_2]_x$, and the molecular weight (osmometric in benzene) showed x to be 2. This was in agreement with Levi's(19) observations on his sample formed in the reaction of sulfur with benzylamine in the presence of lead (II) oxide. The properties of this yellow solid were, however, inconsistent with both of Levi's proposed structures (V and VI) and also with that of Schenck (IV). It should have been formulated as benzylidenimine tetrasulfide, XIV, based on the following evidence.



$$C_6H_5-\overset{\overset{H}{|}}{C}=N-S-S-S-S-N=\overset{\overset{H}{|}}{C}-C_6H_5$$

XIV

The elemental analysis was consistent with any of the four structures. The molecular weight of 322 clearly eliminated structure

IV, but was consistent with the three other structures. The NMR spectrum showed a sharp singlet at -7.87 ppm and a multiplet at -7.05 to -7.48 ppm (Fig. 3). Integration indicated one proton for the singlet and five protons for the multiplet (phenyl group). This eliminated structure VI. It was not possible to rule out V on this basis although it would have been rather surprising to have found such a sharp singlet for a thioamide proton (usually about 0.5 ppm wide or more). However, the IR spectrum showed no N-H stretching absorption (above 3100 cm^{-1}) eliminating structure V. There was, however, a weak band at 1630 cm^{-1} assignable to a $C{=}N-$.

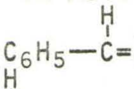
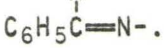
Furthermore, two analogous compounds were isolated from the same reaction mixture whose NMR spectra (Figs. 4 and 5) were quite similar to that of the yellow solid XIV. They each showed one sharp singlet downfield of a phenylmultiplet, and integration of these gave 1:5 in both cases. Elemental analyses and molecular weights confirmed the NMR spectral indication that these two compounds had the same organic component as XIV. In these compounds three and two sulfur atoms replaced the four in XIV. Table 1 lists NMR chemical shifts of benzylidene protons,  $C_6H_5-\overset{H}{C}=$, for various compounds with a benzylidenimine group,  $C_6H_5\overset{H}{C}{=}N-$. Chemical shifts for benzylidene protons in the known compounds (first 5 entries) lie between -7.73 ppm and -8.61 ppm. The chemical shifts of the low field singlets for the three compounds isolated from the reaction of tetrasulfur tetranitride with benzylamine (entries 6-8) lie in this region. Thus, chemical shifts also confirmed the benzylidenimine structures.

Fig. 3. NMR SPECTRUM OF BENZYLIDENIMINE TETRASULFIDE

(IN CCl_4)

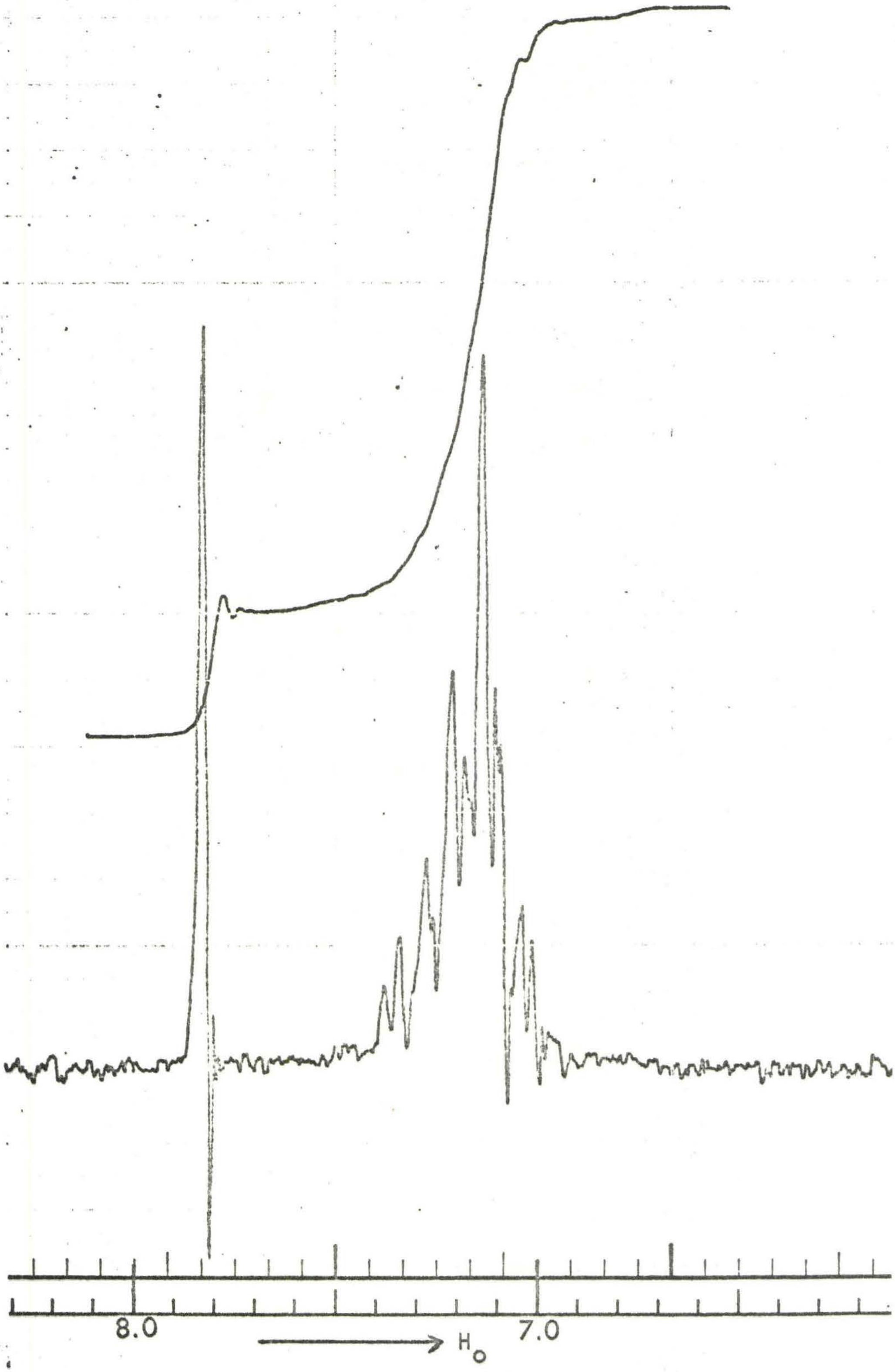


Fig. 4. NMR SPECTRUM OF BENZYLIDENIMINE TRISULFIDE

(IN $CC\ell_4$)

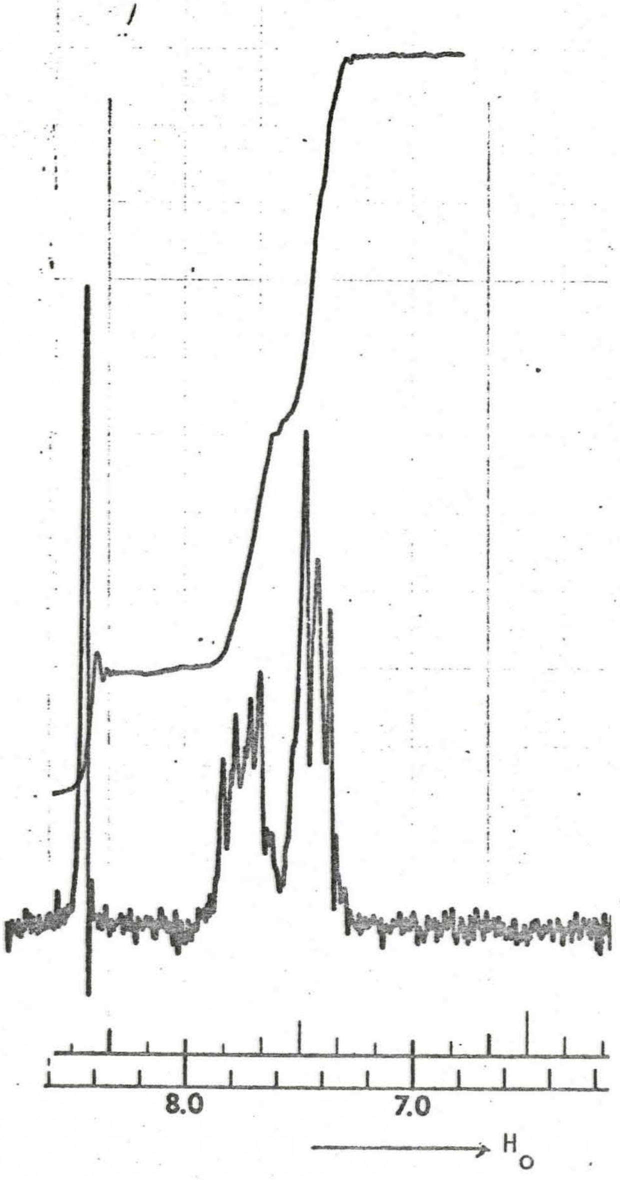
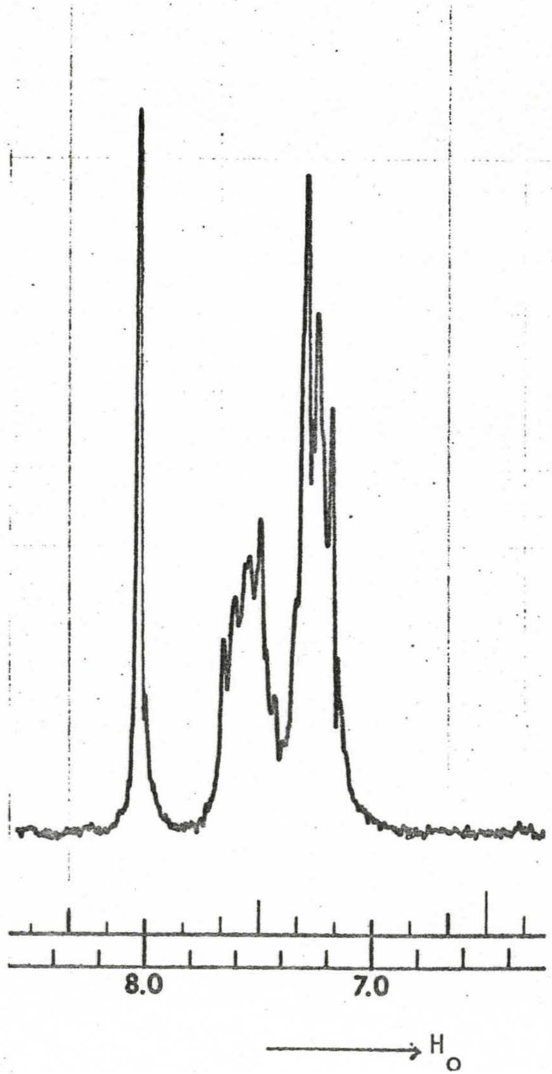
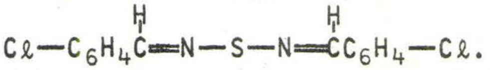


Fig. 5. NMR SPECTRUM OF BENZYLIDENIMINE DISULFIDE

(IN $CC\ell_4$)

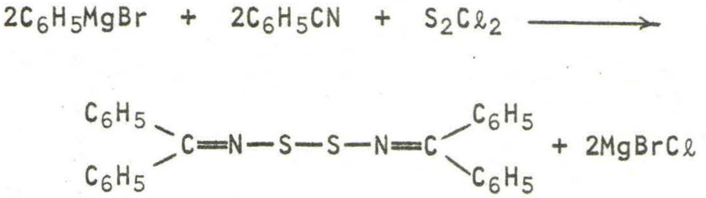


The last compound in Table 1, an analogous monosulfide prepared from S_4N_4 and p-chlorobenzylamine, is of particular interest. The NMR spectrum was very similar to that of compound IV, with a sharp singlet downfield of the phenyl multiplet (areas 1:4; Fig. 15). The elemental analysis showed only one sulfur atom per two nitrogen atoms, and with a molecular weight of 322, the NMR spectrum required this compound to have a symmetrical structure. There is only one possible symmetrical structure with one sulfur which satisfies the other requirements: p-chlorobenzylidenimine monosulfide,



$C\ell{-}C_6H_4\overset{H}{C}{=}N{-}S{-}N{=}\overset{H}{C}C_6H_4{-}C\ell$. The similarity in NMR spectra then requires similar structures for the other materials.

Pyrolysis of benzylidenimine tetrasulfide gave elemental sulfur, benzonitrile and triphenyl-s-triazine, III. This result also supports structure XIV. A similar arylimine disulfide (disubstituted on both benzylidene-carbons) had been previously prepared by a completely different route $^{(35)}$ starting from phenyl magnesium bromide, benzonitrile and sulfurmonochloride as shown in equation (7). The evidence for structure was mainly chemical and included the method of synthesis

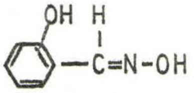


(7)

XV

and the observed reactions. Thus, XV was found to react with concentrated hydrochloric acid to give benzophenone imine hydrochloride,

Table 1. NMR CHEMICAL SHIFTS FOR VARIOUS BENZYLIDENIMINE COMPOUNDS

Entry No.	Compounds	C_6H_5- (ppm)	$-\overset{H}{\overset{\vert}{C}}=N-$ (ppm)	Solvents
1	$C_6H_5CH=N-N=CHC_6H_5$	-7.34 and -7.75	-8.52	$CC\ell_4$(33a)
2	$C_6H_5CH=N-\overset{H}{\overset{\vert}{N}}-C_6H_5$	-6.50 to -7.70	-7.73	acetone(33b)
3	$CH_3OC_6H_4CH=N-N=CHC_6H_4CH_3O$	-6.95 and -7.78	-8.61	$CDC\ell_3$(33c)
4			-8.18	$CDC\ell_3$(34a)
5	$C_6H_5CH=N-CH_2C_6H_5$	-7.16 to -7.80	-8.22	$CC\ell_4$
6	$C_6H_5CH=N-S_4-N=CHC_6H_5$	-7.12 to -7.55	-8.02	$CDC\ell_3$
		-7.05 to -7.48	-7.87	$CC\ell_4$
7	$C_6H_5CH=N-S_3-N=CHC_6H_5$	-7.32 to -7.88	-8.42	$CC\ell_4$
8	$C_6H_5CH=N-S_2-N=CHC_6H_5$	-7.24 to -7.84	-8.14	$CC\ell_4$
9	$CH_3OC_6H_4CH=N-S_4-N=CHC_6H_4CH_3O$*	-6.67 to -7.52	-7.95	$CDC\ell_3$
10	$C\ell C_6H_4CH=N-CH_2C_6H_4C\ell$	-7.32 to -7.92	-8.44	$CDC\ell_3$
11	$C\ell C_6H_4CH=N-S_4-N=CHC_6H_4C\ell$	-7.23	-7.98	$CDC\ell_3$
12	$C\ell C_6H_4CH=N-S-N=CHC_6H_4C\ell$	-7.44 to -7.87	-8.65	$CDC\ell_3$

---

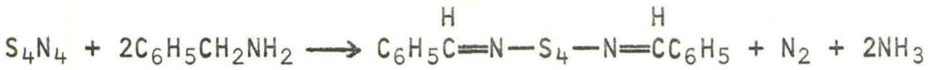
*CH_3O- at -3.85 ppm.

$(C_6H_5)_2C{=}NH{\cdot}HC\ell$, and sulfur monochloride, while with dilute sulfuric acid it was hydrolyzed to benzophenone, ammonia and sulfur. Pyrolysis followed by treatment with acid also gave benzophenone imine hydrochloride.

2. TETRASULFUR TETRANITRIDE WITH BENZYLAMINE

A. STOICHIOMETRY

As described above, S_4N_4 reacts very readily with benzylamine to give a mixture of sulfur and benzylidenimine polysulfides in which the tetrasulfide predominates. Schenck's$^{(19)}$ proposed reaction, corrected to the benzylidenimine tetrasulfide structure, is given in equation (8). Ammonia was measured in the reaction to verify this



$$S_4N_4 + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5\overset{H}{C}{=}N{-}S_4{-}N{=}\overset{H}{C}C_6H_5 + N_2 + 2NH_3 \qquad (8)$$

equation. When a five-fold excess of acid ($5\ HC\ell/S_4N_4$) was used to trap the ammonia, the acid trap was found to be basic at the end of the reaction. Clearly more than 5 moles of NH_3/mole of S_4N_4 was evolved rather than the two required by equation (8). Formation of benzylidenimine tetrasulfide from benzylamine represents oxidation, and taking nitrogen to retain its -3 oxidation state in ammonia, sulfur must be reduced. The change in sulfur is from +3 in S_4N_4 to $+\frac{1}{2}$ in benzylidenimine tetrasulfide--a change of $2\frac{1}{2}$/sulfur or $10e^-/S_4N_4$. Each conversion of two benzylamines to a benzylidenimine tetrasulfide, however, only represents a $4e^-$ change. An additional oxidized product representing a $6e^-$ change is required. Schenck's equation used the conversion of 2 nitrogens (-3 oxidation state) of S_4N_4 to a N_2 (0 oxidation state) for this purpose. It is clear from the large quantity of ammonia evolved, however, that all of the nitrogen of S_4N_4 must go to ammonia. Since 80 ∿ 85% of sulfur has been accounted for already, the oxidized product must arise from benzylamine.

Column chromatography on silica gel separated this product in the form of N-benzylidene benzylamine, $C_6H_5CH{=}N{-}CH_2C_6H_5$, along with benzaldehyde, the latter arising from hydrolysis of the former on the column. N-benzylidene benzylamine is formally derivable from benzylamine by a $2e^-$ oxidation and subsequent elimination of ammonia. Thus, 3 moles of N-benzylidene benzylamine would be required to account for the missing $6e^-$ change. One might then formulate the overall reaction as:

$$\begin{aligned} S_4N_4 + 8C_6H_5CH_2NH_2 &\longrightarrow C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 \\ &+ 3C_6H_5CH{=}N{-}CH_2C_6H_5 + 7NH_3 \end{aligned} \tag{9}$$

where the 3 N-benzylidene benzylamines are needed to complete reduction of the sulfur from the +3 to the +½ formal oxidation state. Four moles of ammonia arise from the four nitrogens of S_4N_4 and the remaining three result from the formation of the 3 moles of N-benzylidene benzylamine. To test this proposed equation a reaction was run using an 8 to 1 molar ratio of benzylamine to S_4N_4 where quantitative isolation of all products was attempted.

Tetrasulfur tetranitride, 5 mmoles, and 40 mmoles of benzylamine were found to evolve 34 mmoles of ammonia. The reaction mixture was separated by washing with cold methanol. The methanol insoluble solids contained mainly benzylidenimine tetrasulfide with a small amount of sulfur and benzylidenimine di- and trisulfides. The methanol soluble part contained mainly N-benzylidene benzylamine with a small amount of benzylidenimine tetrasulfide. After evaporation of the solvent the latter ratio was estimated from an NMR spectrum. From this ratio and the total weight (after removal of the methanol) the quantity of N-benzylidene benzylamine formed was found to be 14 mmoles. From the total weight of solids the number of mmoles[*] of benzylidenimine polysulfides was found to be 5.2. The stoichiometry of equation (9) was, therefore, quite closely approximated (calcd. coefficients 1:8:1:3:7; found 1:8:1.0:2.8:6.8).

This equation does not show benzaldehyde as a product, and indeed it was not observed unless the reaction mixture was chromatographed on silica gel. Apparently, benzaldehyde is a hydrolysis product of the Schiff's base (10).

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[*] The molecular weight of the mixture of sulfur and arylimine polysulfides was assumed to be that of benzylidenimine tetrasulfide since

$$\begin{aligned} C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 &= xC_6H_5CH{=}N{-}S_3{-}N{=}CHC_6H_5 \\ &\quad + yC_6H_5CH{=}N{-}S_2{-}N{=}CHC_6H_5 + (4-3x-2y)S \end{aligned}$$

This approximation should be fairly good regardless of the sizes of x and y; however, since the sum of x and y is less than 0.1, the approximation is quite accurate.

$$C_6H_5CH{=}N{-}CHC_6H_5 + H_2O \longrightarrow C_6H_5CHO + C_6H_5CH_2NH_2 \qquad (10)$$

When an excess of benzylamine (∿22moles of benzylamine/mole of S_4N_4) was used as solvent, no benzylidenimine polysulfide was obtained. The yield of N-benzyidene benzylamine increased considerably and an orange solid, subsequently identified as benzylammonium polysulfide, $(C_6H_5CH_2NH_3)_2S_x$, was obtained in addition to a small amount of benzylammonium thiosulfate, $(C_6H_5CH_2NH_3)_2S_2O_3$. This must be due to reaction of benzylidenimine polysulfide with the excess benzylamine. This reaction and the characterization of the products will be discussed later.

When the ratio of S_4N_4 to benzylamine was 1:8, the yield was almost quantitative based on equation (9). When benzylamine was used in less than a 1:8 molar ratio, reaction (9) was still observed, but the yield of products decreased. When this reaction was followed by NMR spectroscopy, the final products were found to be present along with the starting materials even in the early stages of the reaction (5 minutes). The concentration of final products increased, and the concentration of reactants decreased as time passed; the reaction was completed in about 15 hours. Since no peaks not assignable to reactants or products were observed at any time, there were no intermediates formed in high enough concentration to be detected by NMR.

B. SOLVENTS

Since the reaction as run (neat amine + S_4N_4) was heterogeneous and would not be useful for solid amines, the effect of various solvents on the reaction was briefly investigated. A nonpolar solvent, benzene, resulted in a very slow reaction (if any). A large quantity of starting material was recovered with no indication of more than a trace of benzylidenimine polysulfides.

Acetone resulted in rapid loss of S_4N_4 and amine; however, this appears to be a Willgerodt-Kindler reaction.* Dimethylformamide, pyridine and triethylamine gave benzylidenimine polysulfides, but the yields were lower than in the absence of solvent. Yields of benzylidenimine polysulfides under similar conditions are recorded in Table 2 based both on total sulfur present in the polysulfides and on the total molar quantity of benzylidenimine polysulfides formed (i.e., equation 9).

Table 2. EFFECT OF SOLVENTS

	Amount of Solvent† (ml)	Yield (%)	
		Based on Total Sulfur	Based on Equation (9)
NO SOLVENT		80	100
DMF	4	45	52
PYRIDINE	4	48	60
TRIETHYLAMINE	4	63	91

†Per 2 ml benzylamine + ∿500 mg S_4N_4.

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*Although S_4N_4 has not previously been examined as a sulfur source under Willgerodt-Kindler conditions, its reactivity in this sense is probably not too surprising. See introduction section of Part II for a discussion of the Willgerodt-Kindler reactions.

3. EFFECT OF PARA SUBSTITUTION

The benzylamines reacted (in addition to unsubstituted benzylamine) were p-methoxy, p-chloro and p-nitrobenzylamines. The order of the Hammett σ values is:(36)

$$p\text{-}CH_3O\ (\sigma_p = -0.27) > p\text{-}H\ (\sigma_p = 0.00) >$$
$$p\text{-}C\ell\ (\sigma_p = +0.23) > p\text{-}NO_2\ (\sigma_p = +0.78)$$

p-Methoxy- and p-chlorobenzylamines, like unsubstituted benzylamine, gave p-substituted benzylidenimine tetrasulfide as the major product. With p-nitrobenzylamine the major product was elemental sulfur; benzylidenimine polysulfides were not present. The yields of p-substituted benzylidenimine polysulfides are shown in Table 3.

Table 3. EFFECT OF PARA SUBSTITUTION

SUBSTITUENTS	YIELD OF BENZYLIDENIMINE POLYSULFIDES* (%)	YIELD OF SULFUR**
$p\text{-}CH_3O$	82.0	0
H	100	∿1
$p\text{-}C\ell$	79.2	14.8
$p\text{-}NO_2$	-	47.6

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[*] Based on equation (9).

[**] Based on total sulfur.

The yield of elemental sulfur increased as the Hammett σ values increase. Unsubstituted benzylamine showed the highest yield of benzylidenimine polysulfides; a change of the σ constant in either way resulted in a slight decrease. However, there is no obvious substituent effect since the yields are reasonably high with both p-methoxy and p-chlorobenzylamine. Since the substituent effect was small for these two, it is surprising that p-nitrobenzylamine did not produce any benzylidenimine polysulfide. p-Nitrobenzylamine must have undergone some other reaction--perhaps reduction of the nitro group.

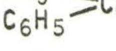
4. TETRASULFUR TETRANITRIDE WITH OTHER AMINES

When phenylhydrazine was reacted with S_4N_4 (8:1 mole ratio), diphenyl disulfide, $C_6H_5S_2C_6H_5$, diphenyl monosulfide, $C_6H_5SC_6H_5$, elemental sulfur and ammonia were produced. In this reaction only about 2.2 moles of ammonia/mole of S_4N_4 were evolved. Thus, nitrogen gas must have been formed here directly from S_4N_4. Had a reaction analogous to that with benzylamine occurred to give $C_6H_5{-}N{=}N{-}S_x{-}N{=}N{-}C_6H_5$ followed by breakdown of this to $C_6H_5S_xC_6H_5 + 2N_2$, it should still have resulted in evolution of 7 moles of ammonia. Therefore, the reaction is quite different from that of benzylamine and appears best formulated as in (11). The

$$S_4N_4 + 2C_6H_5NHNH_2 \longrightarrow C_6H_5S_xC_6H_5 + (4 - x)S + 2NH_3 + 3N_2 \qquad (11)$$

where $x = 1$ and 2

yield of diphenylpolysulfides based on equation (11) is 74%.

α-Methylbenzylamine,  $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!CHNH_2$, gave a complex mixture of products; however, none was analogous to the benzylidenimine polysulfides isolated with benzylamine. Although complete characterization of the products was not attempted, no product could be found in which the CH_3-protons occurred as a singlet in the NMR spectrum (as required for a C═N bond). Since para substituted benzylamines showed electronic effects to be fairly unimportant in determining the yield of arylimine polysulfides, the failure to obtain arylimine polysulfides from α-methylbenzylamine can probably not be explained on electronic grounds. It is rather difficult to explain this result as a steric effect of the methyl group since this would not be expected to be particularly large. Nevertheless, either steric factors or direct participation of the second C-H of the benzyl-CH_2-group at some stage of the reaction appear to be the only alternatives.

n-Butylamine reacted fairly rapidly with tetrasulfur tetranitride (13:1 molar ratio) to give n-butylammonium thiosulfate, $(n\text{-}C_4H_9NH_3)_2S_2O_3$ (almost 70% of total sulfur). Since n-butylamine was used in fairly substantial excess, this is, at least, somewhat analogous to the benzylamine reaction where benzylammonium polysulfide, $(C_6H_5CH_2NH_3)_2S_x$ (oxidizable to benzylammonium thiosulfate, $(C_6H_5CH_2NH_3)_2S_2O_3$), is the product with a substantial excess of amine.* n-Butylammonium thiosulfate is assumed to be an oxidized product of n-butylammonium polysulfides, $(n\text{-}C_4H_9NH_3)_2S_x$. It may be possible that with more careful control of reaction conditions some other intermediate products may be isolable.

When allylamine reacted with S_4N_4, a polymeric substance whose composition was not determined resulted.

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*See page 32.

It appears at this point that the reaction of S_4N_4 to give arylimine polysulfides is fairly specific, being limited to ring substituted benzylamines.

5. REACTIONS OF BENZYLIDENIMINE POLYSULFIDE

A. PYROLYSIS

Previously, the chemistry of arylimine polysulfides was limited almost entirely to acidic hydrolysis. A brief survey of the chemistry of benzylidenimine tetrasulfide was consequently undertaken.

The mass spectrum of benzylidenimine tetrasulfide failed to show the parent peak. Instead, unexpected species such as S_x^+ (x = 8, 7, 6, 5, 4, 3, 2, 1) as well as $C_6H_5C{\equiv}N^+$ were observed. The sulfur species with $x > 4$ clearly arise from thermal decomposition rather than fragmentation, and the whole mass spectrum is, therefore, probably that of pyrolysis products.

When benzylidenimine tetrasulfide was heated to 105°C (just above the melting point) in vacuo, it gave hydrogen sulfide, elemental sulfur, benzonitrile and triphenyl-s-triazine, III, as the main products along with some ammonia. Thus, the main decomposition is described by equation (12). The yield of sulfur based on equation (12) was 82%, and

$$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 \longrightarrow H_2S + (C_6H_5C{\equiv}N)_x + \frac{3}{8}S_8 \qquad (12)$$

67% of the total nitrogen was found in the triphenyl-s-triazine and benzonitrile. Equation (12) can not explain the presence of ammonia; therefore, some other reaction must occur in competition with (12). Benzonitrile is known to trimerize quite readily in the presence of base or methanol around 110 ∿ 120° at very high pressures (6000 ∿ 7000 atmospheres),(37) but as this reaction was carried out in vacuo, it is rather unlikely that benzonitrile is first formed and then trimerized. Triphenyl-s-triazine must have formed through some other path.

B. PHOTOLYSIS

Photolysis of benzylidenimine tetrasulfide resulted in decomposition to lower polysulfides and elemental sulfur as shown in equation (13).

$$\mathrm{RCH{=}N{-}S_4{-}N{=}CHR} \xrightarrow{h\nu} \mathrm{RCH{=}N{-}S_3{-}N{=}CHR} \\ + \mathrm{RCH{=}N{-}S_2{-}N{=}CHR} + \mathrm{RCH{=}N{-}S{-}N{=}CHR} + \mathrm{S} \qquad (13)$$

where $R = C_6H_5$.

Benzylidenimine monosulfide has not yet been fully characterized, but the existence of this material is fairly certain. NMR spectra of the mixture of benzylidenimine polysulfide often contained 4 singlet peaks down field from the phenyl multiplets: -8.02, -8.14, -8.42 and -8.61 ppm. The former three peaks have been assigned for tetra-, di- and trisulfides, respectively. The last peak must have a similar structure to the other three since there is no other peak besides the phenyl multiplets (i.e., $-CH_2-$ or $\overset{H}{-N-}$) and it does not correspond to any other likely products (i.e.,-12.28 ppm for benzoic acid(33d) or -10.00 ppm for benzaldehyde(34b)). Table 4 shows the R_f values for various benzylidenimine polysulfides which indicates that the longer the sulfur-sulfur chain the less polar is the substance. The species responsible for the -8.61 ppm peak in the NMR spectrum had an R_f value

Table 4. R_f VALUES FOR BENZYLIDENIMINE POLYSULFIDES

$$y-C_6H_4CH{=}N-S_x-N{=}CHC_6H_4-y$$

	y		
x	H*	p-Cℓ*	p-CH_3O**
4	0.46	0.49	0.73
3	0.40	-	0.68***
2	0.36	-	-
1	-	0.28	-

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*Silica gel - carbon disulfide.

**Silica gel - methylene chloride.

***This material is not fully characterized; however, see page 31.

of 0.24 (silica gel-carbon disulfide with 0.80 for sulfur) which indicates this species is more polar than benzylidenimine disulfide. Furthermore, almost all compounds containing sulfur develop a dark brownish color on TLC plates when sprayed with silver nitrate solution. As this is the case for this species, it is believed to be benzylidenimine monosulfide.

C. DISPROPORTIONATION

Benzylidenimine trisulfide left on the bench top for several weeks in carbon tetrachloride disproportionated into benzylidenimine tetrasulfide and benzylidenimine disulfide. When this reaction was followed by NMR spectra, the ratio of benzylidenimine tetrasulfide to benzylidenimine disulfide was found to be 1:1 at all times. A TLC of this reaction mixture did not show any free elemental sulfur.

$$2RCH{=}N{-}S_3{-}N{=}CHR \longrightarrow RCH{=}N{-}S_4{-}N{=}CHR + RCH{=}N{-}S_2{-}N{=}CHR \qquad (14)$$

$$R = C_6H_5\text{-}$$

After a few weeks (when about a quarter of the trisulfide had decomposed), the reaction appeared to stop. This is not an equilibrium mixture since an equimolar mixture of tetrasulfide and disulfide in carbon tetrachloride solution on the bench top did not produce any trisulfide during a period of several months. No explanation is offered.

Benzylidenimine trisulfide was also observed to decompose fairly rapidly on silica gel. Although TLC showed pure trisulfide as a single spot, repeated preparative scale TLC separations of a di-, tri- and tetrasulfide mixture resulted in pure tetra and disulfides but did not give a pure trisulfide fraction. When trisulfide was left on a TLC plate in the air (in the dark), it decomposed after several hours to a new unidentified material. Fractional crystallization from methanol was the method of choice in obtaining pure benzylidenimine trisulfide. A similar observation was made for a material which was probably p-methoxy benzylidenimine trisulfide. This appeared to disproportionate into p-methoxy benzylidenimine tetrasulfide and p-methoxy benzylidenimine disulfide in hot methanol.

D. WITH BENZYLAMINE

When benzylidenimine tetrasulfide was added to excess benzylamine, an immediate exothermic reaction occurred. Addition of anhydrous ether to the resulting reddish brown solution gave an orange solid, XVI. Tetrasulfur tetranitride, sulfur and heptasulfurimide (S_7NH) were all found to give similar reddish brown solutions with excess benzylamine from which orange solids precipitated on addition of anhydrous ether. These orange solids were not stable in air and decomposed continuously with evolution of hydrogen sulfide. They were very similar, but the orange solid from S_7NH (XVII) looked to be somewhat more unstable decomposing even in the dry box in an inert atmosphere.

These orange solids resembled benzylammonium hexasulfide prepared by Levi(38) from sulfur, benzylamine and hydrogen sulfide. Their NMR spectra supported this structure [3 absorptions of relative areas 5:2:3 at -7.0 ppm, -3.96 ppm and ∿-6.2 ppm which corresponded to C_6H_5-, $-CH_2$-, and $-NH_3^+$, respectively]. When a sample of the orange solid XVIII, obtained from sulfur, was left in the air for several days, it decomposed slowly with evolution of hydrogen sulfide to give sulfur and benzylammonium thiosulfate. The thiosulfate presumably arose by air oxidation of either the polysulfide or of one of its intermediate hydrolysis products.

A sample of XVII was dissolved in methanol. It decomposed quite quickly to give hydrogen sulfide, benzylamine and sulfur. The molar ratio of the latter two was 1:3.2. This result (based on equation (15)) led to an average sulfur chain length of between 7 to 8.

$$(C_6H_5NH_3)_2S_x \longrightarrow 2C_6H_5CH_2NH_2 + H_2S + (x-1)S \qquad (15)$$

Levi's presumption of a <u>hexa</u>sulfide was based solely on a fairly good (averaged) composition determined by quantitative decomposition to H_2S, sulfur and benzylamine. However, nitrogen analysis of the orange solids XVI and XVIII indicated an average sulfur chain length of 6 to 7, while for XVII (from S_7NH), it was between 8 and 9.

Three orange solids, XVI, XVII and XVIII, were pyrolyzed to give sulfur, thiobenzamide, 3,5-diphenyl-1,2,4-thiadiazole, diphenyl polysulfide, and N-benzylthiobenzamide. These materials were isolated by chromatography and the molar ratio of each are shown in Table 5. The same products resulted from the three orange solids but differed slightly in relative amounts. Either the solids differed in sulfur chain length or they were mixtures of a specific benzylammonium polysulfide (perhaps hexasulfide) with elemental sulfur where the ratios of these two components varied in the three samples.

When XVIII was dissolved in benzylamine, it immediately gave a reddish-brown solution. Therefore, it is very likely that benzylammonium polysulfide is responsible for the reddish-brown color of the solution when tetrasulfur tetranitride, sulfur, benzylidenimine tetrasulfide or heptasulfurimide reacted with benzylamine. The solution of XVIII in benzylamine when heated gave N-benzylthiobenzamide.*

6. SPECTRA OF BENZYLIDENIMINE POLYSULFIDES

A. NMR SPECTRA

The chemical shift of the methylene group in alkyl polysulfides,

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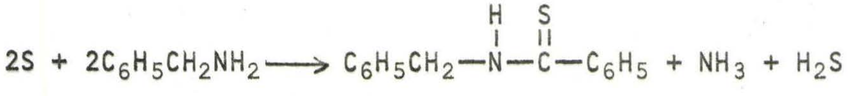
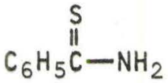
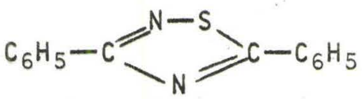
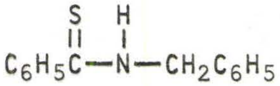
*This material can also be obtained by refluxing sulfur in benzylamine(39) as shown in equation (16).



$$2S + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2-\overset{\overset{\textstyle H}{|}}{N}-\overset{\overset{\textstyle S}{\|}}{C}-C_6H_5 + NH_3 + H_2S \qquad (16)$$

Table 5. PYROLYSIS PRODUCTS FROM BENZYLAMMONIUM POLYSULFIDES

$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$ + excess $C_6H_5CH_2NH_2$	XVI
S_7NH + excess $C_6H_5CH_2NH_2$	XVII
S_8 + excess $C_6H_5CH_2NH_2$	XVIII

Products	Yields*		
	XVI	XVII	XVIII
S	4.37	1.86	1.17
$C_6H_5CH_2S_xCH_2C_6H_5$ $(x = 2 \sim 6)$	0.930	2.98	0.71
 $C_6H_5C(=S){-}NH_2$	1.00	1.00	1.00
	0.532	1.83	1.48
$C_6H_5CH_2CH_2C_6H_5$	-	-	0.81
 $C_6H_5C(=S){-}NH{-}CH_2C_6H_5$	0.31	-	-

---

*Yields are expressed by molar ratio of products.

$RCH_2S_xCH_2R$, has been reported to be quite sensitive to sulfur chain length.(40,41) For dimethyl polysulfides and dibenzyl polysulfides the absorption moved downfield as the number of sulfur atoms in the chain increased while for methyl chloro polysulfides, CH_3S_xCl, the absorption moved upfield as the number of sulfurs increased. The difference in chemical shifts between two members of a series became smaller as the sulfur chain length increased in both cases.

In the case of the unsubstituted benzylidenimine polysulfides, the chemical shifts of the benzylidene protons are quite different. Although it might have been expected from the above that as the sulfur chain increased the chemical shifts would move consistently downfield or upfield, this was not the case. The tetrasulfide came at highest field, the disulfide was in the middle and the trisulfide was at lowest field. In any case estimating the number of sulfurs from the relative chemical shifts alone is obviously dangerous. The R_f value is a much better criterion for this purpose. As shown in Table 4, the R_f values increase as the number of sulfurs increase in all cases.

B. UV-VISIBLE SPECTRA

Electronic absorption spectra were obtained for benzylidenimine tetra-, tri- and disulfides. These are shown in Fig. 6. Benzylidenimine tetrasulfide showed three maxima: λ_{max} at 243 mμ ($\varepsilon = 1.52 \times 10^4$), 303 mμ ($\varepsilon = 2.26 \times 10^4$) and 333 mμ ($\varepsilon = 1.52 \times 10^4$). Benzylidenimine trisulfide showed two maxima: λ_{max} at 242 mμ ($\varepsilon = 1.30 \times 10^4$) and 309 mμ ($\varepsilon = 2.40 \times 10^4$). Benzylidenimine disulfide showed two maxima: 294 mμ ($\varepsilon = 2.84 \times 10^4$) and 304 mμ ($\varepsilon = 2.86 \times 10^4$).

A study of the UV spectra of a series of dibenzylpolysulfides of varying chain length has been previously reported.(42) A broad maximum near 300 mμ was observed which became more intense and was displaced toward longer wave length as the number of sulfur atoms increased. Dibenzylmonosulfide showed a λ_{max} at 260 cm^{-1} ($\varepsilon = 0.16 \times 10^4$) while for dibenzylhexasulfide, the λ_{max} occurred at 320 cm^{-1} ($\varepsilon = 0.50 \times 10^4$). A similar observation was made for the bis(triphenylmethyl) polysulfides,

$(C_6H_5)_3C—S_x—C(C_6H_5)_3$,(43) where the monosulfide had a λ_{max} at 280 cm^{-1} ($\varepsilon = 0.4 \times 10^4$) and the octasulfide had a λ_{max} at 330 mμ ($\varepsilon = 0.5 \times 10^4$). These simple trends were not observed in the benzylidenimine polysulfides. There are at least two absorptions in the 240 ∿ 340 mμ region for benzylidenimine disulfide and trisulfide, and there are three absorptions for the tetrasulfide. The bands for the di- and trisulfides are both rather broad, and it is possible, perhaps even likely, that two or more absorptions overlap in this region. Comparing the spectra of benzylidenimine polysulfides with those of the Schiff's base, N-benzylidene methylamine (λ_{max} at 246 mμ, $\varepsilon = 1.72 \times 10^4$)(44) and with elemental sulfur (λ_{max} = 275, 265, 230 mμ, $\varepsilon = 0.09 \times 10^4$, 0.09×10^4 and 0.14×10^4, respectively)(45) also showed no obvious similarity.

C. IR SPECTRA

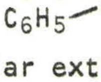
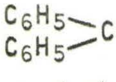
There were many bands in the IR spectra of the benzylidenimine polysulfides prepared; however, all showed weak absorption between 1640 cm^{-1} and 1670 cm^{-1} as well as fairly strong absorption around 850-863 cm^{-1}. These regions summarized in Table 6 represent the C=N stretching frequency (normally found between 1640-1670 cm^{-1})(46) and the N-S stretching frequency (found between 700 ∿ 900 for a N-S bond order between one and two)(47). The intensity of the C=N band is known to be quite variable.(46) Oximes show very weak C=N stretching absorptions. Acetophenone oxime,  $(C_6H_5)(C_6H_5)C{=}N—OH$, for example, shows a C=N stretching absorption whose molar extinction coefficient is almost one-twentieth of that of the Schiff's base,  $(C_6H_5)(C_6H_5)C{=}N—R$.(48) For all of the benzylidenimine polysulfides prepared, the C=N stretching absorption was also observed to be very weak.

Fig. 6. ELECTRONIC ABSORPTION SPECTRA OF BENZYLIDENIMINE POLYSULFIDES (IN METHANOL)

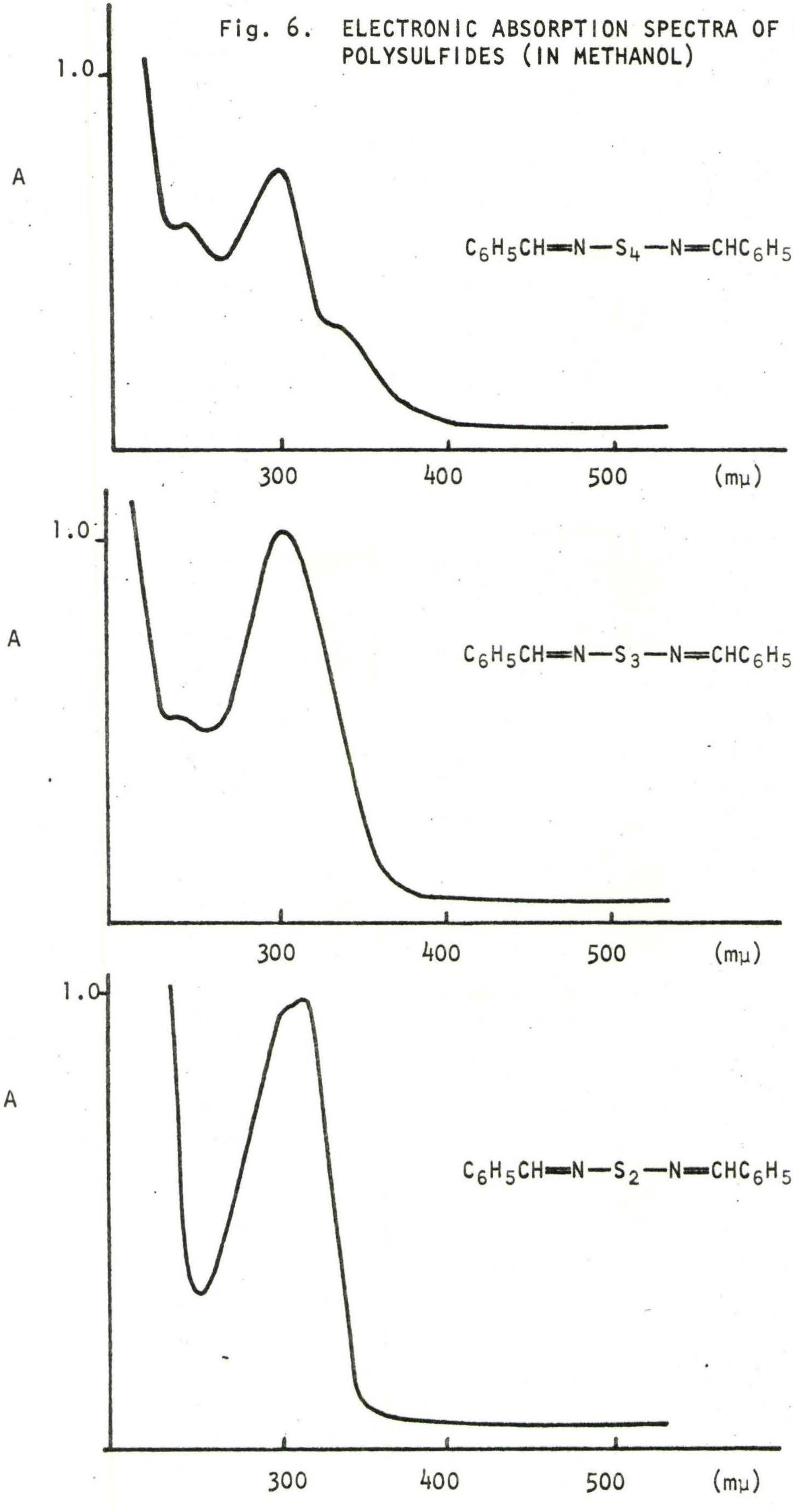


Table 6. C═N AND S—N STRETCHING FREQUENCIES FOR BENZYLIDENIMINE POLYSULFIDES

$$y\text{—}C_6H_4CH\text{═}N\text{—}S_x\text{—}N\text{═}CHC_6H_4\text{—}y$$

y	x	C═N (cm^{-1})	S—N (cm^{-1})
H	4	1630	853
H	3	1658	850
H	2	1655	853
Cℓ	4	1640	853
Cℓ	1	1640	852
CH_3O	4	1670	863

The S—N stretching frequency has been found to be related to the N—S bond length by the empirical equation (17).(47) The S—N bond lengths estimated from equation (17) are essentially constant

$$\gamma_{SN} = 0.0483(\mu_{SN}) + 1.099 \tag{17}$$

where: γ_{SN} = bond length in A.

μ_{SN} = wave length in μ.

at 1.66 A. for all of the imines prepared. This is somewhat shorter than the "normal" S—N single bond length of 1.76 A. (sulfamic acid, $H_3N^+\text{—}SO_3^-$) or the single bond radii sum of 1.74 A. but is longer than the S—N bond in tetrasulfur tetranitride (1.61 A.). These facts suggest that the S—N bond in the benzylidenimine polysulfides has at least some double bond character. The bond order is estimated as 1.5

from the empirical graph given by Chapman and Waddington.(10)* If these empirical relationships hold for the polysulfides, the suggested increase in bond order over a normal N—S single bond might be interpreted as evidence for d_π-p_π double bonding between the Schiff's base and the adjacent sulfur.

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*For comparison S_4N_4 has a bond order of 1.65.

CHAPTER III SUMMARY AND CONCLUSIONS

Tetrasulfur tetranitride reacts very readily with benzylamines to give ammonia, N-benzylidene benzylamine and benzylidenimine polysulfides according to equation (9). There was no obvious electronic effect on this reaction as judged from the yields of ring substituted benzylidenimine polysulfides. Dilution by solvents generally decreased the yield; however, triethylamine is synthetically useful since the yield is still in excess of 90%.

$$\begin{aligned} S_4N_4 + 8C_6H_5CH_2NH_2 &\longrightarrow C_6H_5CH{=}N{-}S_x{-}N{=}CHC_6H_5 \\ &+ 3C_6H_5CH{=}N{-}CH_2C_6H_5 + 7NH_3 \end{aligned} \tag{9}$$

where $x = 4, 3, 2$ and 1.

These reactions offer a synthetic route to arylimine polysulfides with monosubstituted α-carbons.* The previously described route(35) is only useful for arylimine polysulfides with disubstituted α-carbons. The S_4N_4-benzylamine reaction seems to be quite sensitive to small structural changes. α-Methylbenzylamine did not give an analogous compound, while phenylhydrazine was found to undergo a completely different reaction.

$$S_4N_4 + 2C_6H_5NHNH_2 \longrightarrow C_6H_5S_xC_6H_5 + (4-x)S + 2NH_3 + 3N_2 \tag{11}$$

where $x = 1$ and 2.

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*See, however, page 127 for a better path to these compounds.

The benzylidenimine polysulfides are fairly stable crystalline materials, but the trisulfides were found to be less stable than the di- or tetrasulfides. They all decompose readily under strongly acidic or basic conditions. Photolysis leads to decomposition into lower arylimine polysulfides. They are not stable above their melting point, decomposing mainly to hydrogen sulfide, benzonitrile, triphenyl-s-triazine and elemental sulfur.

There is an indication of multiple bonding between the polysulfide chain and the benzylidenimine fragment shown by the S—N stretching frequencies.

The overall nucleophilic substitution reaction of S_4N_4 with excess benzylamines leads to N-benzylidene benzylamine, ammonia and benzylammonium polysulfide as per equation (18)[*]

$$S_4N_4 + \left(\frac{12x + 16}{x}\right) C_6H_5CH_2NH_2 \longrightarrow \left(\frac{6x + 4}{x}\right) C_6H_5CH{=\!=}N{-}CH_2C_6H_5$$

$$+ \left(\frac{10x + 4}{x}\right) NH_3 + \frac{4}{x} (C_6H_5CH_2NH_3)_2S_x \qquad (18)$$

where x = 6-7 and is the number of sulfur atoms in the benzylammonium polysulfide chain. This is conveniently broken into two separate steps. First, the formation of benzylidenimine polysulfide from S_4N_4,

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[*] This stoichiometry is obtained by combining equation (9) with the known stoichiometric reaction of benzylidenimine tetrasulfide with benzylamine, as established in Part II of this thesis. This equation is derived on page 159.

and second, subsequent reaction of the benzylidenimine polysulfide with benzylamine to give the final products. The former reaction can be made nearly quantitative by careful control of the molar ratio of reactants. Although there are several obvious color changes during the reaction of S_4N_4 with benzylamine to give benzylidenimine polysulfides, no intermediates of sufficient stability to be detected by NMR spectroscopy were present, and indeed, benzylidenimine tetrasulfide and N-benzylidene benzylamine were observable almost immediately upon mixing the reactants. The mechanism is not clear at this time, but all of the nitrogen of S_4N_4 goes to ammonia and the attack of the nucleophile is specifically on sulfur.

CHAPTER IV EXPERIMENTAL

1. INSTRUMENTAL

A. NUCLEAR MAGNETIC RESONANCE SPECTRA

Proton NMR spectra were obtained on a Varian Associates Instrument, Model A.60 or T.60. Solvents used were reagent grade carbon tetrachloride, deuterochloroform and dimethyl-d_6 sulfoxide. Blank spectra were run on all solvents. Tetramethyl silane was used as an internal reference, and chemical shifts are reported as parts per million upfield from this reference.

B. INFRARED AND ULTRAVIOLET-VISIBLE SPECTRA

Infrared spectra were obtained on a Beckman IR-5 spectrophotometer. Samples were prepared as nujol mulls or as thin films between sodium chloride plates. Solution spectra were run in reagent grade carbon tetrachloride solution using 0.5 mm sodium bromide cells.

Ultraviolet-visible spectra were obtained on a Cary Model 14 UV spectrophotometer using standard 10 mm silica absorption cells and spectroanalyzed methanol as solvent.

C. MOLECULAR WEIGHTS

Molecular weight determinations were obtained on a Mechrolab Model 301A Vapor Pressure Osmometer with benzene as solvent. The calibration curve was established using dibenzyl disulfide. The calibration curve was checked regularly.

D. ELEMENTAL ANALYSIS

For analyses of nitrogen only, a Coleman Nitrogen Analyzer Model

29 was used. For complete analyses of carbon, hydrogen, sulfur, nitrogen and halogens, samples were sent to Schwarzkopf Microanalytical Laboratory (56-19, 37th Avenue, Woodside, N.Y. 11377). For benzylamine disulfide (unstable in room temperature), the sample was stored at dry ice temperature prior to analysis by Microanalysis Laboratories Ltd. (329 St. George St., Toronto 5, Ont.).

E. MELTING POINTS

Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected.

F. PH METER

Acid-base titrations were done on a Corning PH Meter Model 7 equipped with a glass electrode, a reference calomel electrode and an automatic temperature compensator. Calibration was done using a buffer solution of PH 7.00.

G. DRY BOX

The handling of moisture or air sensitive materials was carried out in a dry box, Vacuum/Atmosphere Corporation Dry Lab. Model HE-43, equipped with Dry Train Model HE 93B.

2. SOLVENTS AND CHEMICALS

Reagent grade solvents and chemicals were used except for column chromatography where hexane, benzene, ether and methanol were U.S.P. grade. Sulfur was "precipitated" grade. The solvents and chemicals were used without further purification unless specified.

3. CHROMATOGRAPHY

A. THIN LAYER CHROMATOGRAPHY

Silica gel GF_{254} (E. Merck, Germany) was applied in the usual manner(49) to give a 0.25 mm layer. Plates were dried in air at least 12 hours prior to use.

Eluents were normally either carbon disulfide or methylene chloride, and elution was allowed to proceed through a distance of 15 cm. In order to detect the spots, the plates were examined under an ultraviolet lamp and/or were developed by spraying with an aqueous solution of silver nitrate. As the degree of activation varied slightly, a standard reference mixture was also spotted on each plate.

B. COLUMN CHROMATOGRAPHY

Column chromatography was used to separate many reaction mixtures. The absorbent used was silica gel (Grace 100 ∿ 200 mesh). The ratio of absorbent to sample was in the range of 20:1 to 75:1. Eluents were hexane, benzene, ether, methanol and various mixture of these. The rate of change of solvent polarity was dependent upon the relative R_f values of components in the sample.

Fractions of 100 ml were collected and solvents stripped on a rotary evaporator. Tared flasks were used so that the weight of each fraction could be determined directly.

4. PREPARATION OF TETRASULFUR TETRANITRIDE

Tetrasulfur tetranitride was prepared from sulfur monochloride and ammonia in the usual manner(50) except that the crude product was extracted with benzene using a Soxhlet extractor. A dark red orange solution was obtained from which orange needles precipitated. After several recrystallizations from benzene, this solid showed only one spot on TLC and melted sharply at 178°C <u>d</u>.

5. REACTIONS OF TETRASULFUR TETRANITRIDE WITH AMINES

A. BENZYLAMINE

(i) WITHOUT SOLVENT

(a) PRELIMINARY

Tetrasulfur tetranitride (1.99 g, 10.8 mmoles) was placed in a 100 ml three-necked flask with a magnetic stirring bar. A rubber serum stopper was placed at one of the necks, and another was connected to a cylinder of dry nitrogen. The third neck was connected to a gas washing bottle with 250 ml of aqueous hydrochloric acid solution (containing 50.0 mg. equivalents of hydrochloric acid). Benzylamine was degassed under vacuum in order to remove any free ammonia which might have been present due to hydrolysis. 8.0 ml of benzylamine (73 mmoles) was introduced through the rubber serum stopper by syringe. The reaction mixture was stirred for 14 hours at room temperature with a continuous nitrogen flow. The S_4N_4 dissolved in the benzylamine to give an orange color which gradually changed to green, dark moss green, and after 30 minutes became brownish yellow and more viscous. These color changes were accompanied by evolution of heat and ammonia. After 5 hours the reaction mixture did not seem to be changing but gas evolution continued. As gas evolution decreased, the reaction mixture became more viscous, and eventually, after about 14 hours, the reaction mixture solidified to a yellow chunk. The aqueous hydrochloric acid solution was found to be basic--i.e., more than 50 mmoles of ammonia were generated. The reaction mixture was chromatographed on 250 g of silica gel. Products were eluted in the order given in Table 7.

Benzylidenimine tetrasulfide was purified by recrystallization from methanol to give yellow needles of m.p. 100.5 ∿ 102°C. Anal. Calcd. for $C_{14}H_{12}N_2S_4$: C, 49.97; H, 3.59; N, 8.32; S, 38.11; Mol. Wt., 336. Found: C, 49.54; H, 3.67; N, 8.70; S, 37.70; Mol. Wt., 332. NMR and IR spectra of this material are shown in Fig. 3 and Fig. 7, respectively.

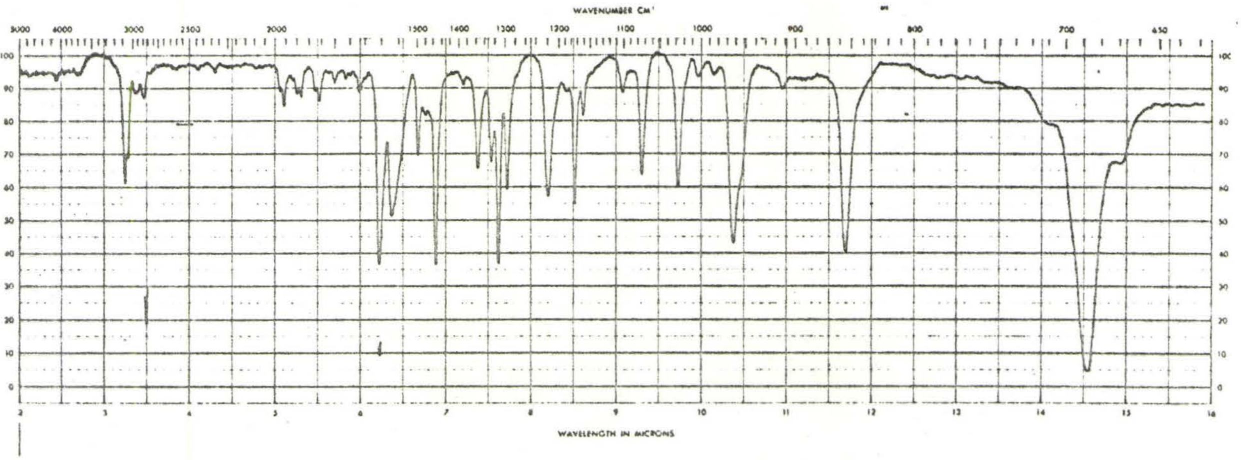

Fig. 7. IR SPECTRUM OF BENZYLIDENIMINE TETRASULFIDE (IN CCl_4)

Benzylidenimine trisulfide was purified by recrystallization from methanol to give colorless white needles of m.p. 125-126°C. Anal. Calcd. for $C_{14}H_{12}N_2S_3$: C, 55.23; H, 3.97; N, 9.20; S, 31.59; Mol. Wt. 304. Found: C, 55.07; H, 4.12; N, 8.98; S, 32.04; Mol.

Table 7. PRODUCTS OF S_4N_4 WITH BENZYLAMINE

Products	R_f*	Eluent	Amount** (mg)	No. of mmoles	Yield*** (%)
Sulfur	0.80	Hexane	18	0.56****	1.3
Benzylidenimine tetrasulfide	0.46	13% benzene in hexane	2460	7.32	67.7
Benzylidenimine trisulfide	0.40	13% benzene in hexane	220	0.73	5.0
Benzylidenimine disulfide	0.36	15% benzene in hexane	410	1.50	7.0
N-Benzylidene benzylamine	0.06	20% ether in benzene	1850	9.49	-
Benzaldehyde	0.05	40% ether in benzene	1950	18.4	-
Benzylamine	0.00	50% methanol in ether	-	-	-

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*Silica gel - carbon disulfide.

**When mixtures were obtained, the amount of each component was calculated on the basis of integrated NMR spectra.

***Yield is based on total sulfur.

****mg atoms.

Wt. 306. NMR and IR spectra of this material are shown in Fig. 4 and Fig. 8, respectively.

Benzylidenimine disulfide was purified by recrystallization from methanol to give nearly colorless white needles of m.p. 100 ∿ 100.5°C. Anal. Calcd. for $C_{14}H_{12}N_2S_2$: C, 61.74; H, 4.44; N, 10.28; S, 23.54; Mol. Wt., 272. Found: C, 61.16; H, 4.20; N, 10.41; S, 23.74; Mol. Wt., 271. NMR and IR spectra of this material are shown in Fig. 5 and Fig. 9, respectively.

N-Benzylidene benzylamine was obtained as an oil with a boiling point of ∿105°C at 0.1 mmHg. The NMR and IR spectra were identical to those of an authentic sample prepared from benzylamine and benzaldehyde.(51)

Benzaldehyde was identified by its characteristic odor and also by comparison of its NMR and IR spectra with those of an authentic sample.

(b) MOLAR RATIO OF 1:8

The reaction was repeated using 922 mg (5.01 mmoles) of S_4N_4 and 4.4 ml (40.3 mmoles) of benzylamine. The gas washing bottle contained 50.0 mg equivalents of hydrochloric acid. After 20 hours of stirring with a continuous nitrogen flow, the hydrochloric acid solution was diluted to 500 ml. A 25.0 ml aliquot of this solution required 8.20 ml of 0.100 N sodium hydroxide solution for neutralization. Therefore, 16.4 mmoles of acid remained, and 33.6 mmoles of ammonia were evolved.

Treatment of the reaction mixture with ice cold absolute methanol gave a pale yellow solution and left some solids undissolved. The

Fig. 8. IR SPECTRUM OF BENZYLIDENIMINE TRISULFIDE (IN CCl_4)

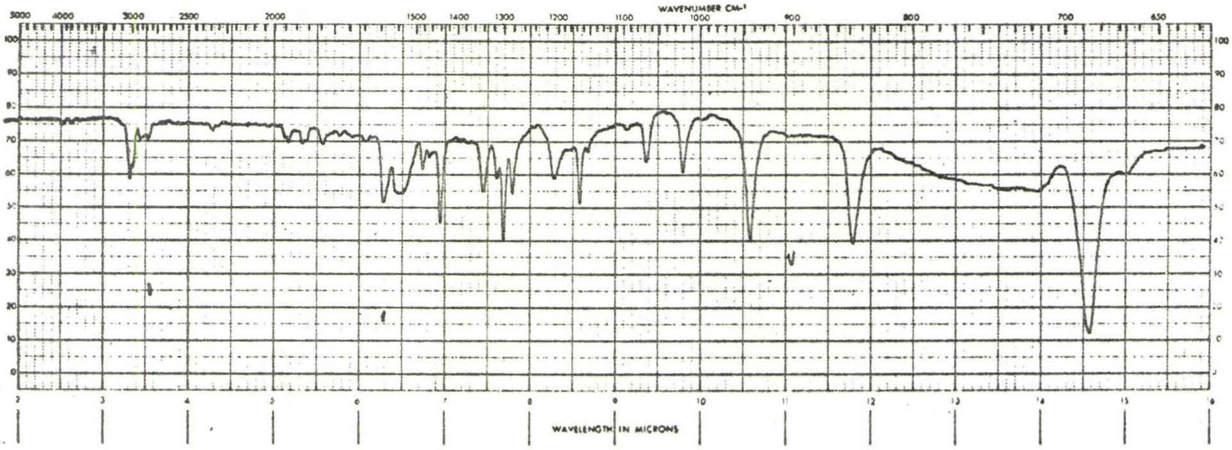
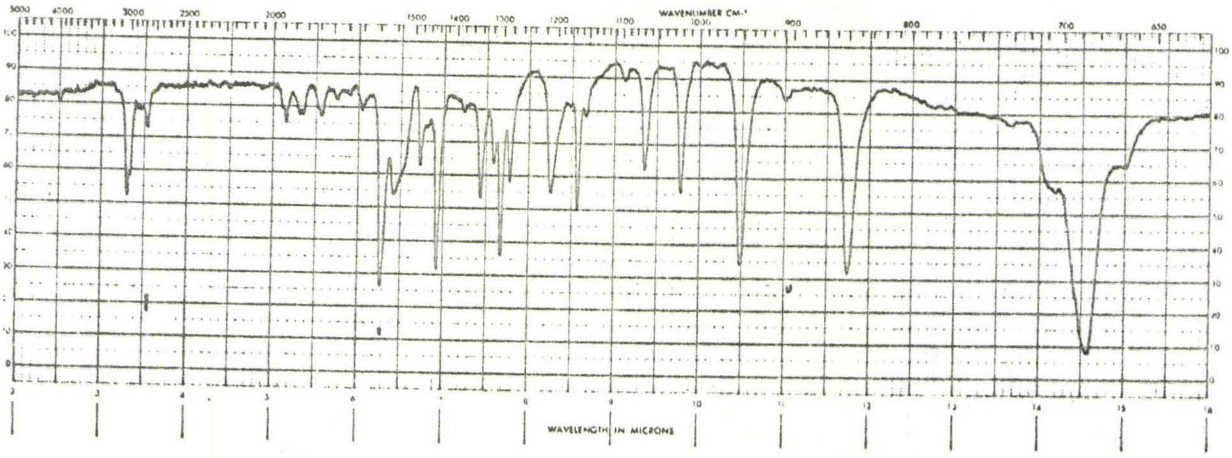


Fig. 9. IR SPECTRUM OF BENZYLIDENIMINE DISULFIDE (IN CCl_4)



solids were filtered and after drying weighed 1.21 g. Their TLC showed mainly benzylidenimine tetrasulfide along with small amounts of sulfur and benzylidenimine tri- and disulfides. The methanol was removed from the filtrate in vacuo to give 3.26 g of oil. TLC indicated this oil to be mainly N-benzylidene benzylamine with a small amount of benzylidenimine tetrasulfide. From the NMR spectrum the molar ratio of these two was estimated to be 5.3 to 1.0. Yields of products are summarized in Table 8.

Table 8. REACTION OF S_4N_4 WITH BENZYLAMINE IN MOLAR RATIO OF 1:8

	Compounds	Amount (mg)	No. of mmoles	Ratio
Starting Materials	S_4N_4	922	5.01	1.00
	Benzylamine	4320	40.3	8.05
Products	Ammonia	-	33.6	6.70
	Solid*	1730	5.15	1.03
	N-benzylidene benzylamine	2740	14.0	2.80

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*This solid is mainly benzylidenimine tetrasulfide with small amounts of sulfur and benzylidenimine tri- and disulfides. To calculate the number of mmoles, this solid was assumed to be benzylidenimine tetrasulfide since

$$RCH{=}N{-}S_4{-}N{=}CHR = xRCH{=}N{-}S_3{-}N{=}CHR + yRCH{=}N{-}S_2{-}N{=}CHR + (4-3x-2y)S \quad \text{if } R = C_6H_5.$$

(c) NMR STUDY OF REACTION PATH

The reaction was repeated using 1.340 g (7.28 mmoles) of S_4N_4 and 6.30 ml of benzylamine (57.7 mmoles). Periodically, a sample was withdrawn, dissolved in $CDC\ell_3$ and its NMR taken. The first sample taken five minutes after the reaction started showed peaks for benzylidenimine tetrasulfide and N-benzylidene benzylamine in addition to big peaks for starting benzylamine. As time passed, the peaks of the former two materials increased while those for the latter decreased in relative intensity. After about 2 hours nearly half of the benzylamine had been converted to products. Even after 8 hours small amounts of benzylamine remained; however, after 14 hours no benzylamine peak was observed. During the course of this investigation NMR spectra failed to show any other peaks.

(ii) EFFECT OF SOLVENTS

(a) BENZENE

Tetrasulfur tetranitride (516 mg, 2.80 mmoles) was dissolved in 10 ml of benzene, and 2 ml (18.3 mmoles) of benzylamine was introduced. The reaction was stirred for 20 hours under nitrogen, and a TLC was taken. It showed large quantities of S_4N_4 and almost no benzylidenimine tetrasulfide.

(b) ACETONE

Tetrasulfur tetranitride (511 mg, 2.78 mmoles) was dissolved in 10 ml of acetone, and 2 ml (18.3 mmoles) of benzylamine was added. The solution became dark reddish brown fairly quickly. The reaction mixture was stirred for 10 hours under nitrogen whereupon a TLC indicated no trace of either benzylidenimine tetrasulfide or tetrasulfur tetranitride. The solvent was stripped off to give an uncharacterized viscous tar with a vile odor.

(c) DIMETHYLFORMAMIDE

Tetrasulfur tetranitride (508 mg, 2.76 mmoles) was dissolved in 4 ml of DMF. Although the solid did not go into solution completely, 2 ml of benzylamine (18.3 mmoles) was introduced. The color of the solution immediately became green and slowly changed to yellowish brown. The reaction mixture was stirred for about 24 hours under nitrogen. The solvent was removed under vacuo. The products were dissolved in a small amount of methanol and partly separated by crystallization. The composition of the mixtures of benzylidenimine polysulfides was estimated by NMR integration. Products obtained were sulfur (99 mg, 3.09 mg atoms, 28% of total sulfur), benzylidenimine tetrasulfide (303 mg, 0.902 mmoles, 32.8% of total sulfur), benzylidenimine trisulfide (47 mg, 0.154 mmoles, 4.2% of total sulfur), benzylidenimine disulfide (122 mg, 0.449 mmoles, 8.1% of total sulfur) and N-benzylidene benzylamine.

(d) PYRIDINE

Tetrasulfur tetranitride (530 mg, 2.88 mmoles) was dissolved in 4 ml of pyridine, and 2 ml of benzylamine (18.3 mmoles) was added. The reaction mixture was stirred for about 24 hours under nitrogen. The solvent was stripped off in vacuo, and the reaction mixture was dissolved in a small amount of hot methanol. Benzylidenimine tetrasulfide (467 mg, 1.38 mmoles, 48.2% of total sulfur) crystallized out and was collected by filtration. The other polysulfides were found only in trace amounts.

(e) TRIETHYLAMINE

Tetrasulfur tetranitride (524 mg, 2.84 mmoles) was dissolved in 4 ml of triethylamine, and 2 ml of benzylamine (18.3 mmoles) was added. After 24 hours of stirring under nitrogen, the solvent was removed in vacuo to give sulfur (63 mg, 2.0 mg atom, 17.5% of total sulfur), benzylidenimine tetrasulfide (506 mg, 1.51 mmoles, 53.1% of total sulfur), benzylidenimine disulfide (156 mg, 0.574 mmoles, 10.1% of total sulfur), benzylidenimine tetrasulfide (trace) and N-benzylidene benzylamine.

(f) 1:8 RATIO IN TRIETHYLAMINE

Tetrasulfur tetranitride (506 mg, 2.75 mmoles) and 2.4 ml of benzylamine (22 mmoles) were allowed to react in 4 ml of triethylamine. After 10 hours of stirring under nitrogen, the solvent was removed in vacuo to give sulfur (33 mg, 1.03 mmoles, 9.40% of total sulfur), benzylidenimine tetrasulfide (662 mg, 1.97 mmoles, 71.6% of total sulfur), benzylidenimine trisulfide (66.6 mg, 0.219 mmoles, 5.98% of total sulfur), benzylidenimine disulfide (119 mg, 0.437 mmoles, 7.85% of total sulfur) and N-benzylidene benzylamine (1450 mg, 7.45 mmoles).

(g) EXCESS OF BENZYLAMINE

Tetrasulfur tetranitride (500 mg, 2.72 mmoles) was covered with 6.4 ml of benzylamine (∿59 mmoles) and stirred under a dry nitrogen atmosphere. The S_4N_4 dissolved in the benzylamine to give an orange color; however, the solution quite quickly changed to green, then orange, then bloody red and after 24 hours was reddish brown and quite viscous. Upon addition of anhydrous ether, hydrogen sulfide was slowly evolved, and a reddish solution as well as an orange precipitate was obtained. The orange solid was filtered off (about 650 mg), and the red ether solution was evaporated to give 5.75 g of material which, when chromatographed on silica gel, yielded the products shown in Table 9. The orange solid melted at 90-97°C _d_ in an evacuated sealed capillary and decomposed continuously in air with the evolution of hydrogen sulfide. After several days in air it was a mixture of sulfur and a new white solid. This white solid was slightly soluble in methanol, quite soluble in water and insoluble in non-polar organic solvents. It was recrystallized from methanol to give m.p. 173-174°C _d_. A series of qualitative tests to determine the anion present in this salt were carried out on aqueous solutions. With lead acetate, a white solid precipitated. With silver nitrate solution, a yellowish solid precipitated which soon turned brown. With barium chloride, a white solid precipitated which was soluble in dilute hydrochloric acid but not in acetic acid. Potassium permanganate solutions were very readily discolored. Anal. Calc. for $C_{14}H_{20}N_2S_2O_3$: N, 8.80. Found: N, 8.53. The IR spectrum showed a strong N—H stretch at 3280 cm^{-1} as shown in Fig. 10. The NMR spectrum in D_2O showed 3 peaks: -7.20 ppm* (5.0 H for C_6H_5-), -4.74 ppm* (peak for HDO and NH_3^+ exchanging) and -3.74 ppm*

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*The chemical shifts show only relative locations for the 3 peaks since no reference was used.

Table 9. S_4N_4 WITH EXCESS BENZYLAMINE

Products	R_f*	Eluent	Amount (mg)	No. of mmoles
Sulfur**	0.80	Hexane	132	4.13***
Solids XIX****	0.57 0.35 0.23 0.19	60% benzene in hexane	96	-
N-Benzylidene benzylamine	0.06	20% ether in benzene	1775	9.11
Benzaldehyde	0.05	40% ether in benzene	1950	18.4
Benzylammonium** thiosulfate	∿0.00	90% methanol in ether	212	0.647
Benzylamine	∿0.00	Methanol	Large quantity	

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*Silica gel - carbon disulfide.

**This material might be formed by decomposition of the orange solid, part of which dissolved in ether.

***mg atoms.

****Solid XIX has 4 components whose R_f values fit those of S_7NH and the three isomeric $S_6(NH)_2$. Crystallization from ether gave 50 mg of colorless solid which melted at 112-113°C and had an R_f value of 0.57. This material was S_7NH; however, additional attempts failed to reproduce these materials. The starting S_4N_4 did not contain these materials.

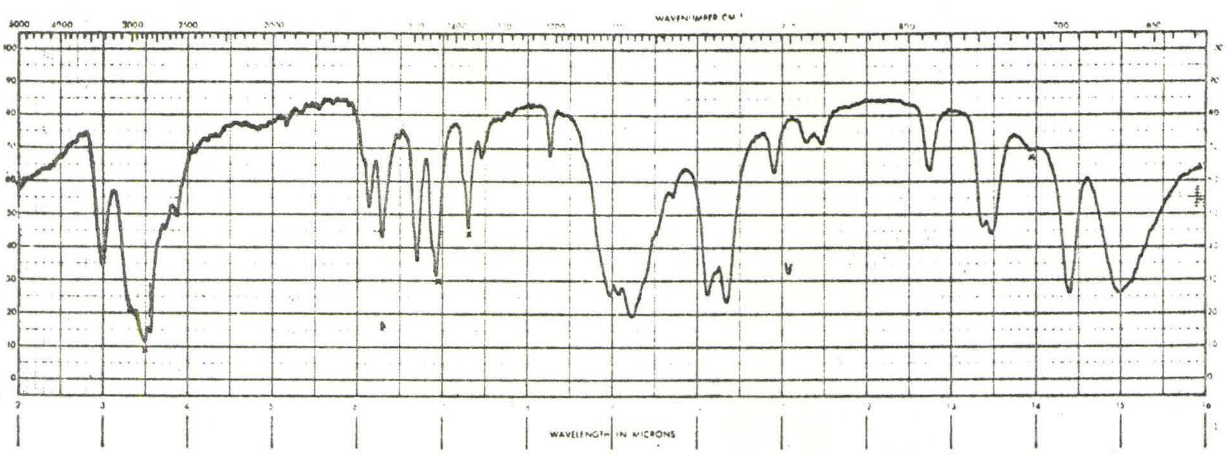

Fig. 10. IR SPECTRUM OF BENZYLAMMONIUM THIOSULFATE (NUJOL MULL)

(2.0 H for -CH_2-). These data indicate this material to be benzylammonium thiosulfate, $(C_6H_5CH_2NH_3)_2S_2O_3$.

B. p-CHLOROBENZYLAMINE

(i) PRELIMINARY

Tetrasulfur tetranitride (533 mg, 2.90 mmoles) was covered with 2 ml of p-chlorobenzylamine (~15.5 mmoles) and stirred under dry nitrogen for 24 hours. The S_4N_4 slowly dissolved to give a reddish brown solution. A basic gas evolved while the solution slowly turned to a thick yellow paste. The reaction mixture was separated by chromatography on 150 g of silica gel. The products obtained are shown in Table 10.

p-Chlorobenzylidenimine tetrasulfide was recrystallized from

Table 10. S_4N_4 WITH p-CHLOROBENZYLAMINE

Products	R_f[*]	Eluent	Amount (mg)	No. of mmoles	Yield[**] (%)
Sulfur	0.80	Hexane	73	2.28[***]	19.6
p-Cℓ Benzylidenimine tetrasulfide	0.49	20% benzene in hexane	566	1.39	47.8
p-Cℓ Benzylidenimine monochloride	0.28	50% benzene in hexane	242	0.82	7.3
p,p'-dichloro-N-benzylidene benzylamine	0.09	Benzene	320	1.21	-
dark brown viscous material	∿0.0	Methanol	700	-	-

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[*] Silica gel - carbon disulfide.

[**] Based on total sulfur.

[***] mg atoms.

methanol to give yellow needles of m.p. 114.5-116°C. Anal. Calcd. for $C_{14}H_{10}N_2S_4C\ell_2$: C, 41.48; H, 2.49; N, 6.91; $C\ell$, 17.49; S, 31.64; Mol. Wt., 405. Found: C, 41.56; H, 2.65; N, 6.91; $C\ell$, 17.31; S, 31.80; Mol. Wt., 395. IR and NMR spectra are shown in Fig. 11 and Fig. 14.

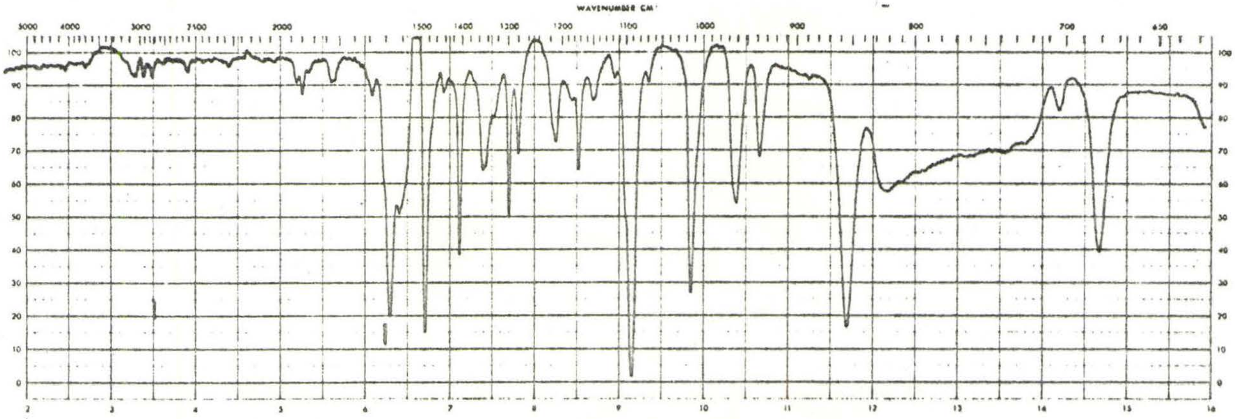


Fig. 11. IR SPECTRUM OF p-CHLOROBENZYLIDENIMINE TETRASULFIDE (IN $CC\ell_4$)

p-Chlorobenzylidenimine monosulfide was also purified by recrystallization from methanol and gave yellow needles of m.p. 146.2-146.8°C. Anal. Calcd. for $C_{14}H_{10}N_2SC\ell_2$: C, 54.38; H, 3.26; N, 9.06; $C\ell$, 22.93; S, 10.77; Mol. Wt., 309. Found: C, 54.15; H, 3.25; N, 9.56; $C\ell$, 22.86; S, 10.88; Mol. Wt., 322. IR and NMR spectra are shown in Fig. 12 and Fig. 15.

Fig. 12. IR SPECTRUM OF p-CHLOROBENZYLIDENIMINE MONOSULFIDE

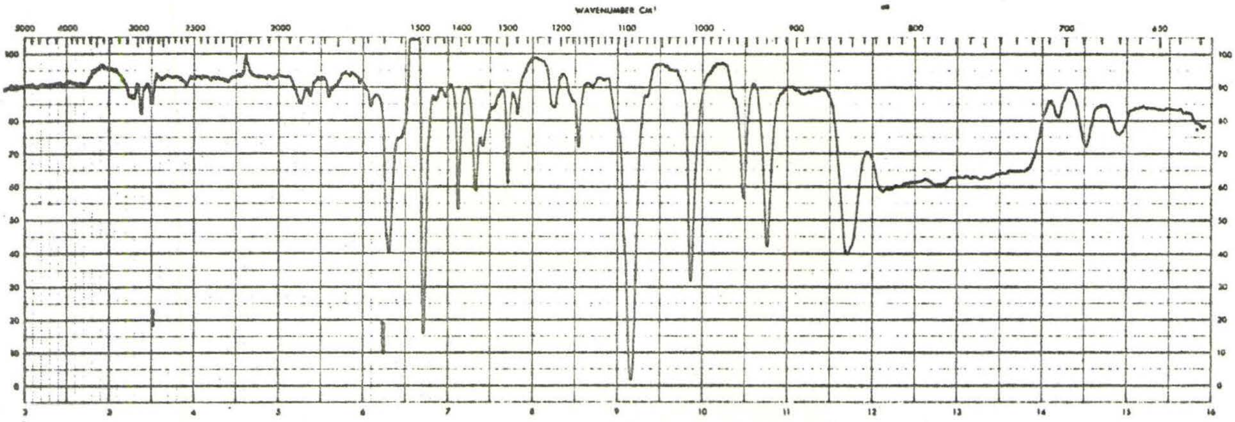


Fig. 13. IR SPECTRUM OF p,p'-DICHLORO-N-BENZYLIDENE BENZYLAMINE

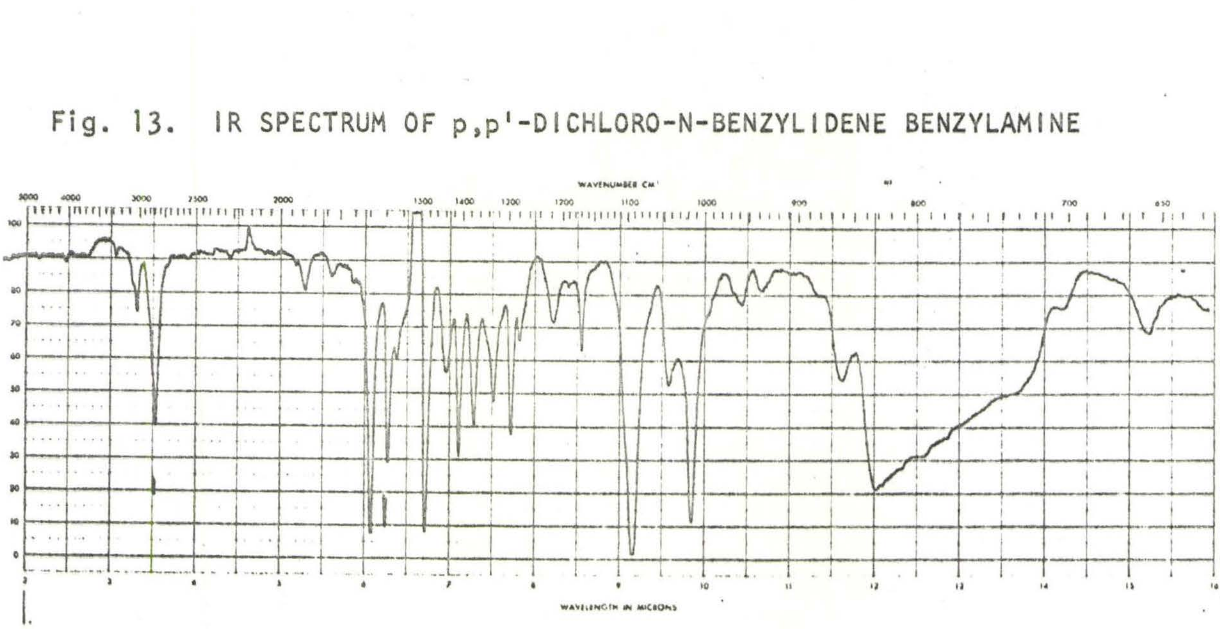


Fig. 14. NMR SPECTRUM OF p-CHLOROBENZYLIDENIMINE TETRASULFIDE

(IN CCl_4)

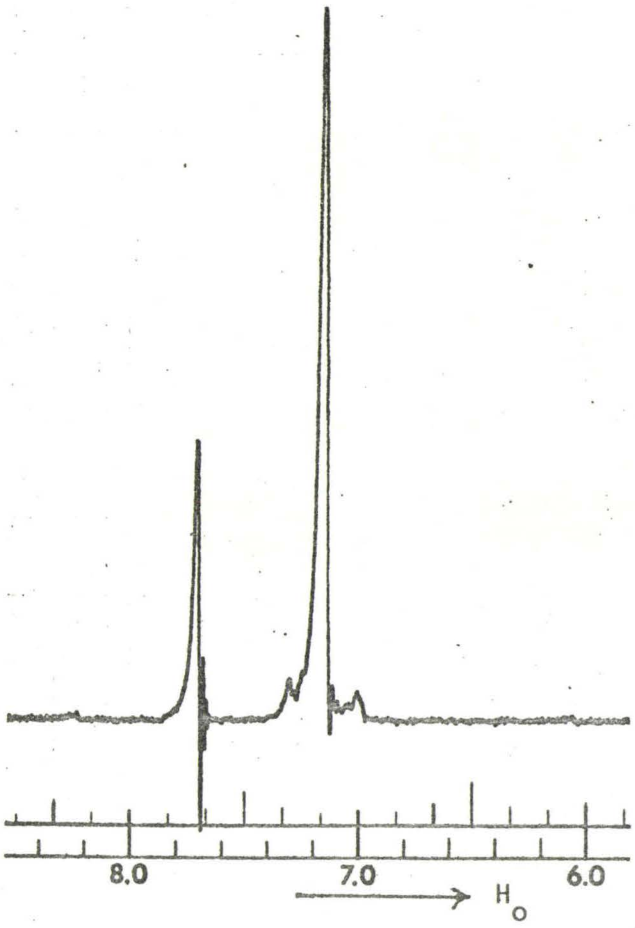


Fig. 15. NMR SPECTRUM OF p-CHLOROBENZYLIDENIMINE MONOSULFIDE

(IN CCl_4)

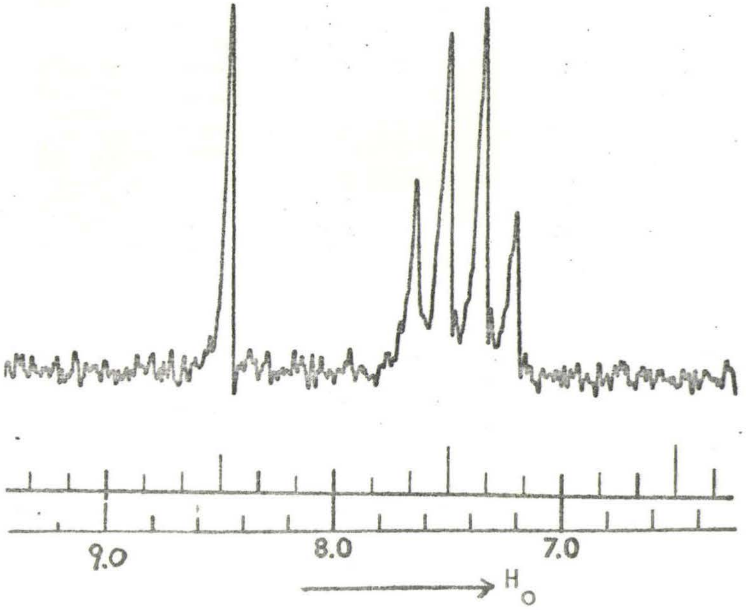
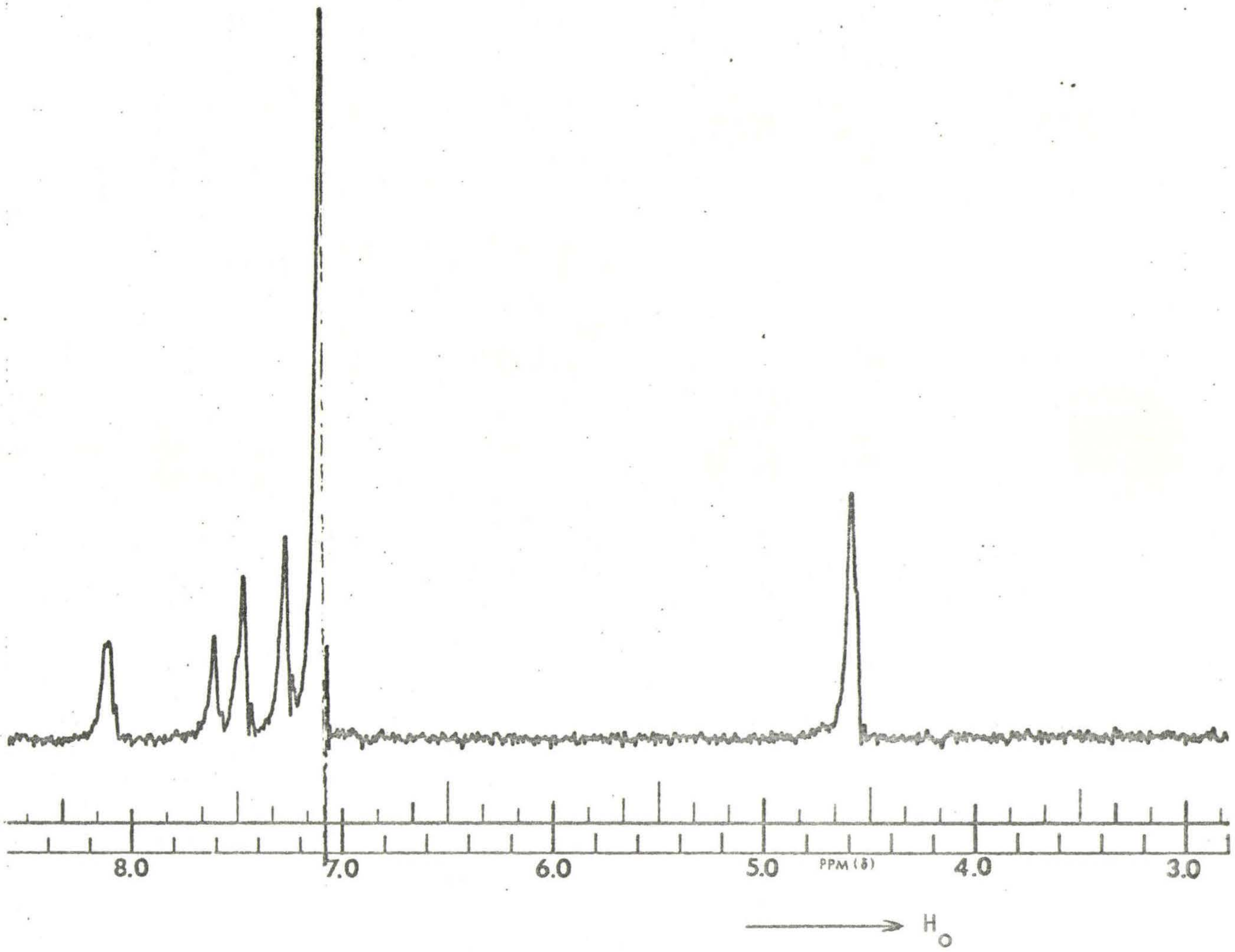


Fig. 16. NMR SPECTRUM OF p,p'-DICHLORO-N-BENZYLIDENE BENZYLAMINE

(IN $CC\ell_4$)



p,p'-Dichloro-N-benzylidene benzylamine was recrystallized from methanol to give thin white plates of m.p. 62-65°C. Anal. Calcd. for $C_{14}H_{11}NC\ell_2$: C, 63.66; H, 4.20; N, 5.30; Cℓ, 26.84; Mol. Wt., 264. Found: C, 63.57; H, 4.18; N, 5.31; Cℓ, 26.58; Mol. Wt., 281. IR and NMR spectra are shown in Fig. 13 and Fig. 16.

(ii) MOLAR RATIO OF 1:8

Tetrasulfur tetranitride (344 mg, 1.87 mmoles) was reacted with p-chlorobenzylamine (2.11 g, 14.9 mmoles). The products obtained were chromatographed to give sulfur (33 mg, 1.03 mmoles, 13.8% of total sulfur), p-chlorobenzylidenimine tetrasulfide (598 mg, 1.48 mmoles, 79.2% of total sulfur) and p,p'-dichloro-N-benzylidene benzylamine (1170 mg, 4.43 mmoles). p-Chlorobenzylidenimine monosulfide was found in only trace amounts in one fraction along with two other uncharacterized materials and the tetrasulfide.*

C. p-METHOXYBENZYLAMINE

(i) PRELIMINARY

Tetrasulfur tetranitride (542 mg, 2.94 mmoles) was covered with 2 ml of p-methoxybenzylamine (∿16 mmoles) and stirred under nitrogen. S_4N_4 dissolved to give a brownish solution. In 10 minutes the

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*A TLC of this mixture showed four spots: 0.49, 0.38, 0.30 and 0.25 (silica gel-carbon disulfide with 0.80 for sulfur). The first is tetrasulfide, and the last is monosulfide. All of these spots developed a dark brown color on spraying with aqueous silver nitrate solution. The two middle spots are probably p-chlorobenzylidenimine tri- and disulfide.

solution became green in color and slowly changed to yellowish brown. These color changes were accompanied by the evolution of a basic gas. The reaction mixture was left overnight whereupon it solidified. Ice cold methanol was added and p-methoxybenzylidenimine tetrasulfide precipitated as a yellow solid (710 mg). Recrystallization from absolute ethanol gave yellow plates of m.p. 112-113°C. Anal. Calcd. for $C_{16}H_{16}N_2S_4O_2$: C, 48.46; H, 4.07; N, 7.06; S, 32.34; Mol. Wt., 397. Found: C, 48.59; H, 4.24; N, 7.10; S, 32.66; Mol. Wt., 391. IR and NMR spectra are shown in Fig. 17 and Fig. 18.

Evaporation of the methanol solution gave a yellow oil. This was dissolved in chloroform, and 93 mg of a white solid precipitated (m.p. 230°C d). This solid was insoluble in most organic solvents, slightly soluble in water and very soluble in dilute hydrochloric acid. An aqueous solution of this material gave a white precipitate with lead acetate solution and discolored potassium permanganate solution. Thus, it was assumed to be p-methoxybenzylammonium thiosulfate.

The remaining yellow viscous oil was purified by column chromatography. Elution with 5% ether in benzene gave 140 mg of a yellow crystalline material identified by melting point and NMR spectra as p-methoxybenzylidenimine tetrasulfide. Elution with 100% ether gave 620 mg of anisaldehyde identified by comparison of its NMR and IR spectra with those of an authentic sample.(33e, 52a) Elution with 80% methanol in ether gave a dark oil which was identified as p-methoxybenzylamine by comparison of its NMR spectrum with that of an authentic sample. Yields are summarized in Table 11.

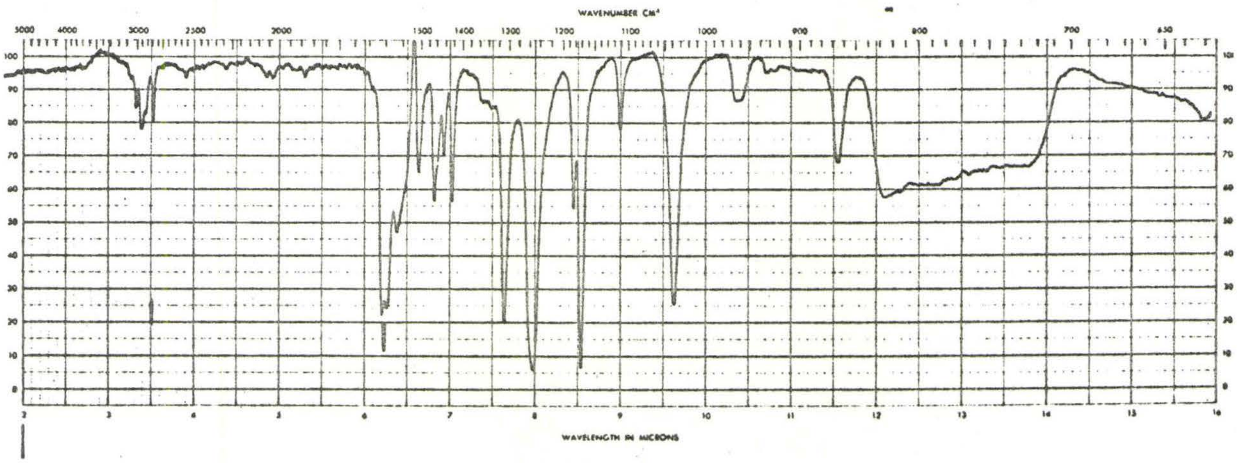

Fig. 17. IR SPECTRUM OF p-METHOXYBENZYLIDENIMINE TETRASULFIDE (IN CCl_4)

(ii) MOLAR RATIO OF 1:8

The reaction was repeated with a larger amount of starting material and a mole ratio of 1 S_4N_4 to 8 p-methoxybenzylamine. Tetrasulfur tetranitride, 2.00 g (10.8 mmoles), was reacted with 10.9 ml of p-methoxybenzylamine (~86.6 mmoles) under nitrogen. After 12 hours of stirring, the reaction mixture was washed with ice cold methanol. The insoluble solid consisted of 3.13 g of p-methoxybenzylidenimine tetrasulfide. TLC of the methanol

Fig. 18. NMR SPECTRUM OF p-METHOXYBENZYLIDENIMINE TETRASULFIDE

(IN CCl_4)

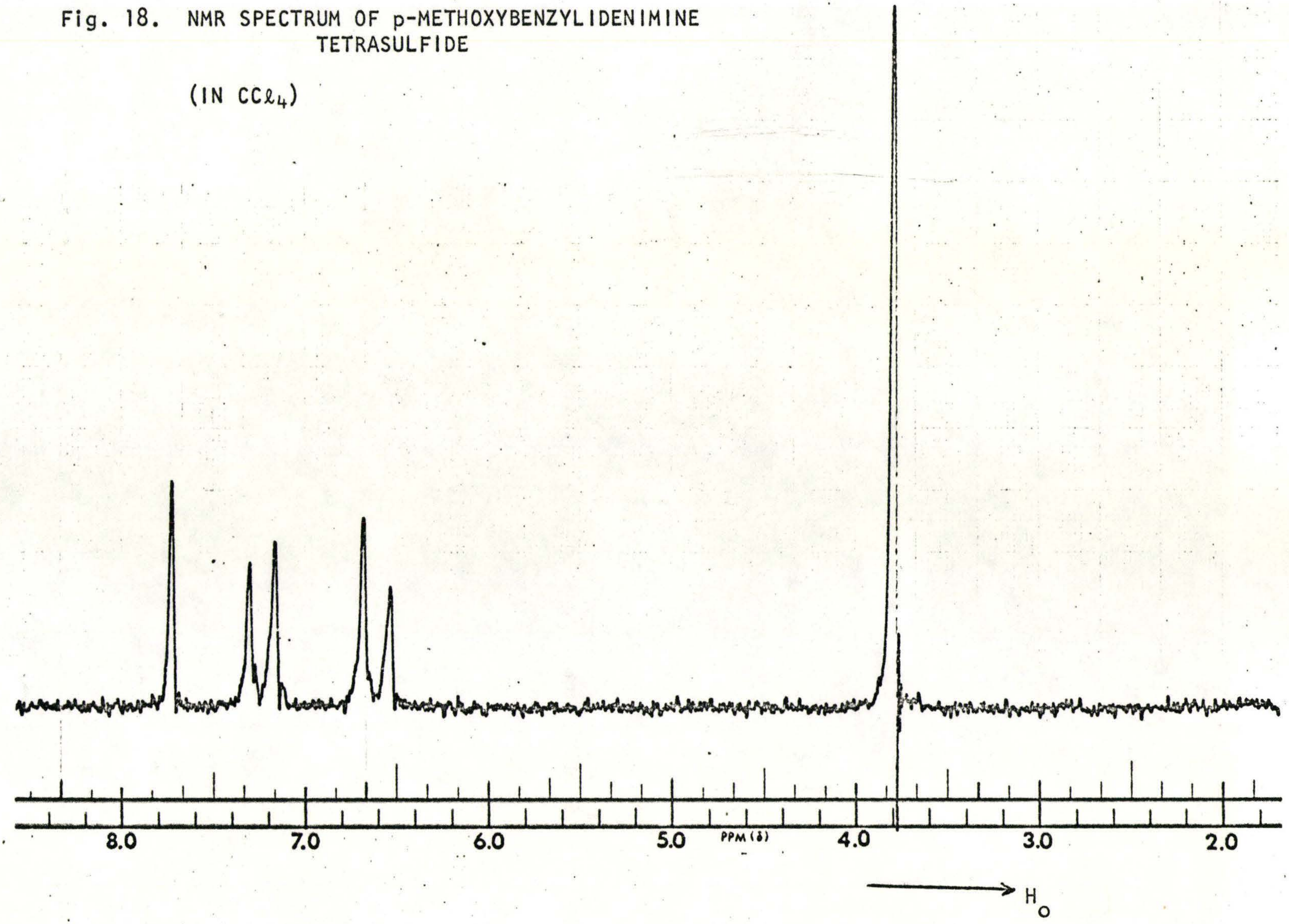

Table 11. S_4N_4 WITH p-METHOXYBENZYLAMINE

Products	R_f*	Eluent	Amount** (mg)	No. of mmoles	Yield*** (%)
p-Methoxybenzylidenimine tetrasulfide	0.73	5% ether in benzene	850	2.14	72.8
Anisaldehyde	0.40	ether	620	5.17	-
Dark Oil	∿0	80% methanol in ether	-	-	-
p-Methoxybenzylammonium thiosulfate	∿0	-	93	0.24	16.3

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*Silica gel - methylene chloride.

**The total weight obtained from both crystallization and chromatography.

***Based on total sulfur.

solution showed several spots; R_f values of these were 0.72, 0.68, 0.61, 0.56, 0.40 and a streak near the origin (silica gel-methylene chloride, with 0.73 for p-methoxybenzylidenimine tetrasulfide and 0.40 for anisaldehyde). The major component (R_f 0.40) was apparently anisaldehyde. The methanol solution was kept in the freezer, and 372 mg of a yellow solid precipitated. This material gave two spots on TLC (R_f: 0.73 and 0.68, silica gel-methylene chloride, with p-methoxybenzylidenimine tetrasulfide 0.73). An NMR spectrum of this material is shown in Fig. 19. Comparison of Fig. 19 with Fig. 18 shows this solid to consist of two similar materials, one of which is p-methoxybenzylidenimine tetrasulfide. The other material is presumably also a p-methoxybenzylidenimine polysulfide (R_f: 0.68

and NMR chemical shift for $\mathrm{H{-}\overset{|}{C}{=}}$: -8.14 ppm). The molar ratio of these two materials was roughly 1:1. Attempted fractional crystallization from hot methanol led to decomposition of one of the two components. As shown in Fig. 20, the phenyl region and the p-methoxy region became more complex, and a new peak appeared at -8.40 ppm (cf. Fig. 19). The peak at -8.14 ppm decreased in size in comparison to the peak at -7.95 ppm ($\mathrm{H{-}\overset{|}{C}{=}N}$ for tetrasulfide). This new peak is also assumed to be due to a p-methoxypolysulfide.*

The original solvent from which these solids (372 mg) were obtained was removed in _vacuo_ to give 8.45 g of oil. A TLC of this oil indicated mainly two species: R_f at 0.40 and a streak near the origin (silica gel-methylene chloride, with 0.73 for p-methoxybenzylidenimine tetrasulfide and 0.40 for anisaldehyde). An NMR spectrum of this material in CS_2, however, did not show an aldehyde proton (-9 ∿ -11 ppm). 500 mg of material was chromatographed on silica gel to give mainly anisaldehyde and p-methoxybenzylamine. 1.0 g was distilled under reduced pressure. A yellow oil was obtained at 175 ∿ 180°C (0.1 mm Hg) which eventually crystallized at room temperature to a solid of m.p. 36.5-37.5°C (Lit.(53) m.p. for p,p'-

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*These two new p-methoxybenzylidenimine polysulfides are believed to be the tri- and disulfides. Unsubstituted benzylidenimine trisulfide disproportionates into tetra- and disulfide (cf. equation 14 on page 31). The same phenomenon is believed to be occurring here. -8.14 ppm is apparently the trisulfide and -8.40 ppm is the disulfide.

Peaks with arrows correspond to those of p-methoxybenzylidenimine tetrasulfide.

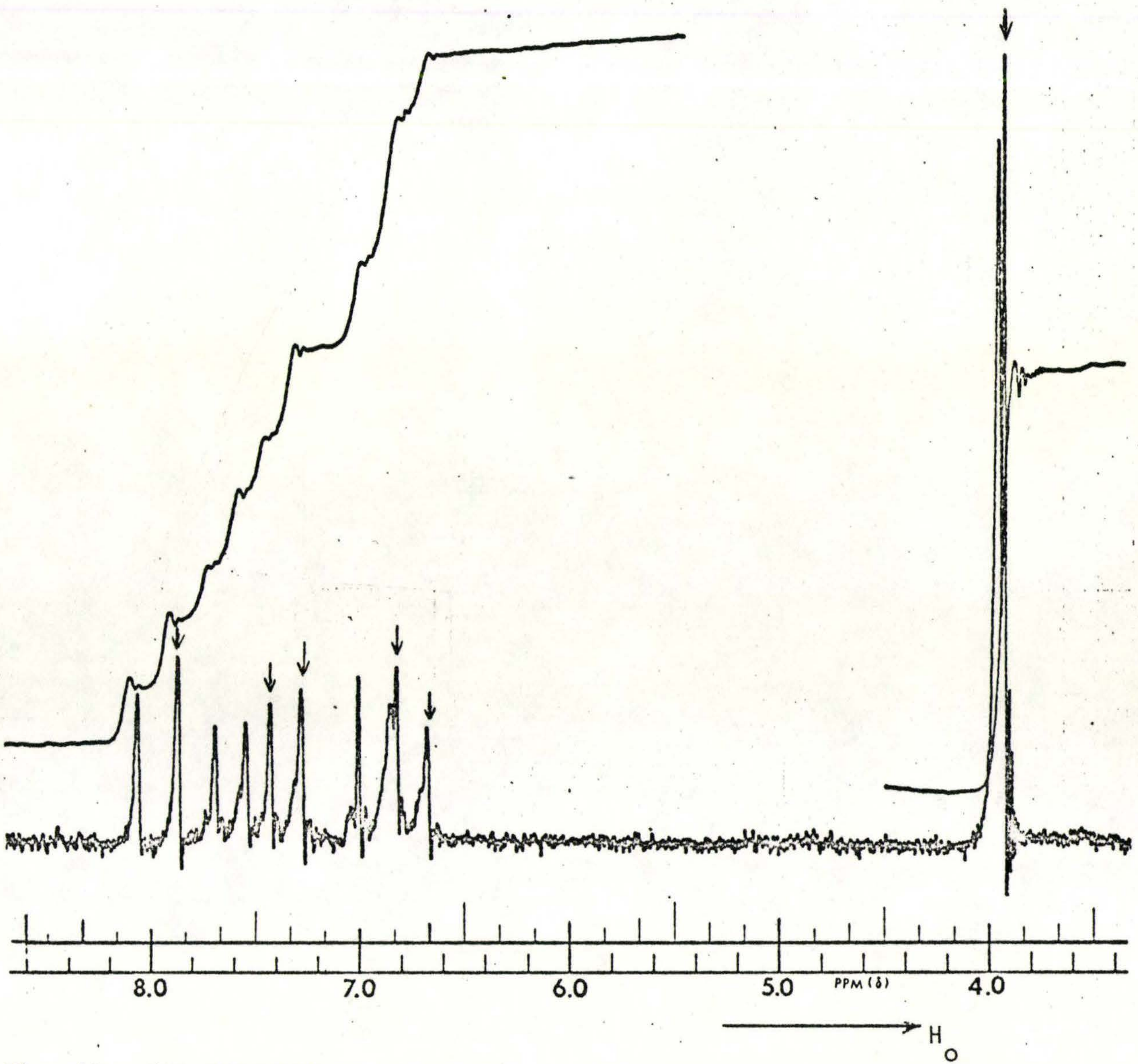

Fig. 19. NMR SPECTRUM OF MIXTURE OF p-METHOXYBENZYLIDENIMINE POLYSULFIDES (IN CS_2)

Peaks with arrow correspond to those of p-methoxybenzylidenimine tetrasulfide.

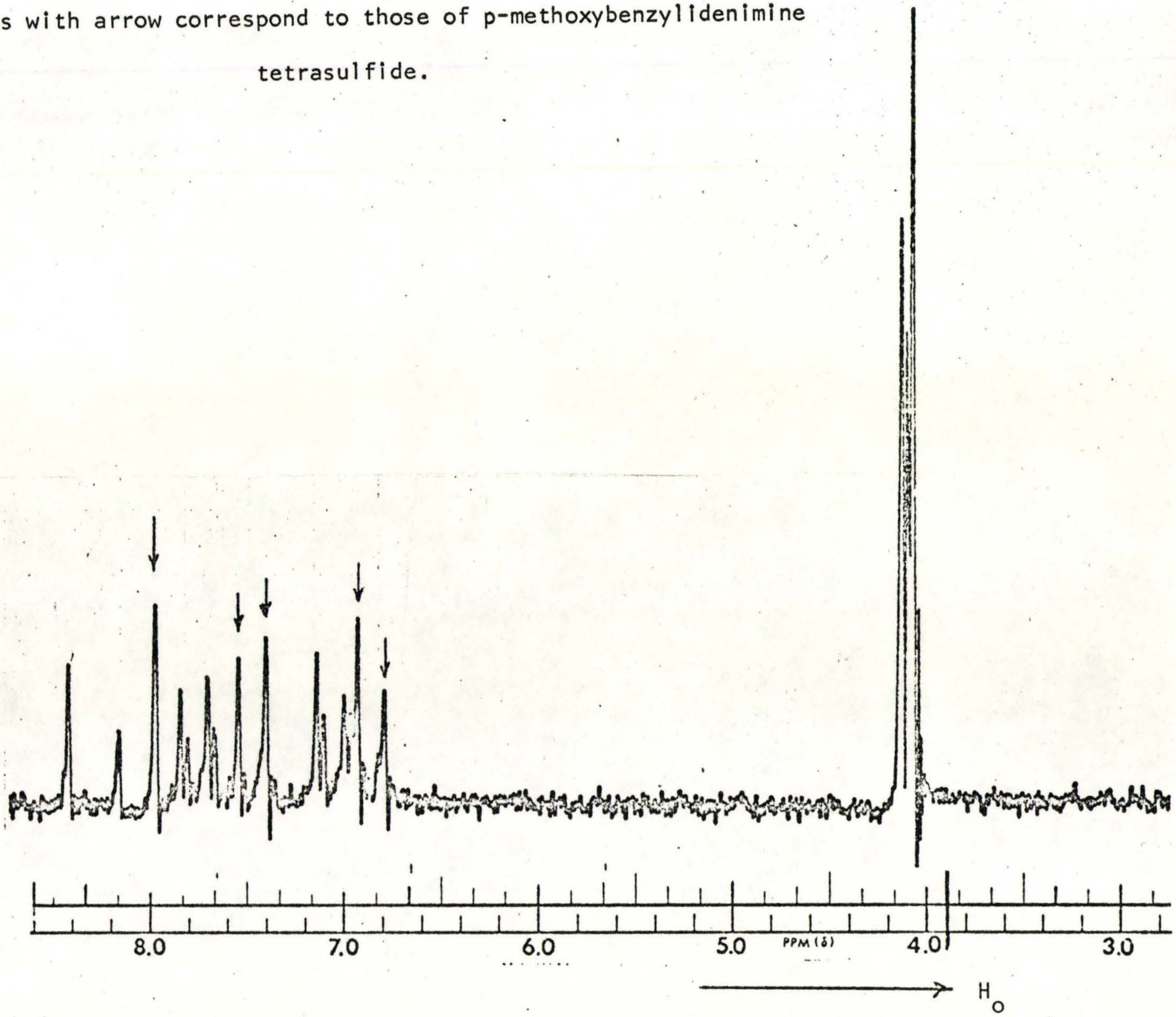

Fig. 20. NMR SPECTRUM OF MIXTURE OF p-METHOXYBENZYLIDENIMINE POLYSULFIDES AFTER RECRYSTALLIZATION (IN CS_2)

dimethoxy-N-benzylidene benzylamine is 37-38°C). The NMR spectrum of this material was taken [-3.62 ppm (singlet, 3.0 H, CH_3O-), -4.58 ppm (broad singlet, 1.9 H, -CH_2-), -6.58 to -7.80 ppm (multiplet, 4.1 H, -C_6H_4-) and -8.10 ppm (broad singlet, 1.0 H, $H-\overset{|}{C}=N$)] and was quite consistent with that expected for p,p'-dimethoxy-N-benzylidene benzylamine. Yields are summarized in Table 12.

Table 12. S_4N_4 WITH p-METHOXYBENZYLAMINE (1:8 RATIO)

Products	Amount (mg)	No. of mmoles	Yield* (%)
p-Methoxybenzylidenimine tetrasulfide	3320	8.37	77.5
p-Methoxybenzylidenimine trisulfide	178	0.488	4.4
p,p'- dimethoxy-N-benzylidene benzylamine	8450	31.5	-

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*Based on total sulfur.

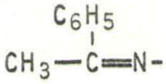
D. p-NITROBENZYLAMINE

p-Nitrobenzylamine was prepared from potassium phthalimide (obtained from phathalimide and potassium ethoxide(54)) and p-nitrobenzylbromide.(55,56) The NMR spectrum of p-nitrobenzylamine showed 3 absorptions: -1.72 ppm (broad singlet, 2.2H, -NH_2), -4.05 ppm (singlet, 2.0 H, -CH_2-) and -7.36 to -8.34 ppm (multiplet, 4.1 H, -C_6H_4-). The melting point of the hydrogen chloride salt was 249-250°C (Lit. 250°C(57) and 256°C d(58)).

p-Nitrobenzylamine (2.0 g, 18 mmoles) was added to a flask containing S_4N_4 (500 mg, 2.72 mmoles). The reaction mixture became very viscous. 2 ml of dimethylformamide (enough to allow the mixture to be stirred) was added, and the reaction continued for 12 hours. The product, a very viscous dark brown gum, was dissolved in hot methanol. From this solution 166 mg of elemental sulfur (5.19 mg atoms, 47.6% of total sulfur) precipitated.

The mother liquor contained a viscous tar whose NMR spectrum showed no peaks down field of the phenyl multiplet. Characterization of this material was not undertaken.

E. d,ℓ-α-METHYLBENZYLAMINE

Tetrasulfur tetranitride (656 mg, 3.56 mmoles) was covered with 2 ml of α-methylbenzylamine (16 mmoles) under a nitrogen atmosphere. The reaction mixture immediately became brownish red, and a basic gas was evolved. After stirring for 24 hours, the reaction mixture became very viscous. It was dissolved in methanol and cooled to 0°C whereupon 159 mg of sulfur (4.97 mg atoms, 34.9% of total sulfur) precipitated. Further cooling to -20°C did not precipitate any additional solid. A TLC of this solution showed a streak from the origin to an R_f value of 0.34 (silica gel-carbon disulfide with 0.80 for sulfur). This material was separated by chromatography after the methanol had been removed *in vacuo*. Separation was very poor and each fraction obtained was a mixture of viscous dark brown materials. The NMR spectrum of each fraction was taken, but no material was present with a singlet methyl peak as required for a  $CH_3-\overset{C_6H_5}{\overset{|}{C}}=N-$ group. Characterization of these materials failed mainly because satisfactory separation could be achieved by neither distillation, recrystallization, column chromatography nor preparative scale TLC.

F. PHENYLHYDRAZINE

(i) WITHOUT SOLVENT

Tetrasulfur tetranitride, 514 mg (2.80 mmoles), was placed in a 100 ml flask and cooled to 0°C. A slow stream of nitrogen was introduced, and the outlet gas was led into a gas washing bottle containing 7.00 mg equivalents of hydrochloric acid in 70 ml of water. 2.15 g of phenylhydrazine (19.9 mmoles) was added and immediately solidified. The ice bath was removed and the reaction mixture was allowed to warm up with stirring until the phenylhydrazine melted. Around 20°C the tetrasulfur tetranitride slowly dissolved in the phenylhydrazine. The temperature was carefully controlled during the exothermic reaction so as not to exceed 25°C. The brownish orange solution of S_4N_4 changed slowly to brilliant yellowish orange and eventually to yellow. A precipitate was also observed. After 6 hours of stirring, no more gas evolved. The reaction mixture was kept stirring for an additional 6 hours at room temperature.

The acid trap solution was diluted to 100 ml and a 50 ml aliquot was titrated with 0.075 N potassium hydroxide solution. 4.45 ml of base were required to neutralize the excess acid. Therefore, 0.688 mg equivalents of acid remained, and 6.33 mg equivalents of ammonia had evolved. The reaction mixture was separated by column chromatography. Hexane eluted 221 mg of elemental sulfur (6.90 mg atom, 62.4% of total sulfur). Elution by 15% benzene in hexane gave 196 mg of a white solid which was recrystallized from methanol to give diphenyldisulfide of m.p. 59-60°C (lit(52) 60-61°C), R_f value 0.57 (silica gel-carbon disulfide, with 0.80 for sulfur), molecular weight by mass spectrum 218 (calcd. for $C_{12}H_{10}S_2$: 218), nitrogen analysis <0.2%. NMR and IR spectra were identical to those of authentic diphenyldisulfide.(33f,52b)

Elution with 20% benzene in hexane gave 122 mg of colorless oil identified as diphenylmonosulfide (R_f value 0.49, molecular weight by mass spectrum 186 (calcd. for $C_{12}H_{10}S$: 186), nitrogen analysis <0.2%). The NMR and IR spectra were identical to those of authentic diphenylmonosulfide.(33g,52c)

More polar solvents eluted considerable amounts of viscous red materials. TLC showed many spots (6 or 7 in $CH_2C\ell_2$). R_f values of many of these spots corresponded to R_f values of air oxidation products of phenylhydrazine (obtained by leaving phenylhydrazine in the air for a week). Characterization of these components were not attempted.

(ii) TRIETHYLAMINE AS A SOLVENT

Tetrasulfur tetranitride and phenylhydrazine were reacted in 5 ml of triethylamine and worked up as described above. The reaction temperature was kept at 0°C for 30 hours. The amounts of starting materials and products are listed in Table 13.

G. n-BUTYLAMINE

Tetrasulfur tetranitride (302 mg, 1.64 mmoles) was dissolved in

Table 13. S_4N_4 WITH PHENYLHYDRAZINE IN TRIETHYLAMINE

Starting Materials	Amount (mg)	No. of mmoles	Yield[**] (%)
S_4N_4	504	2.74	-
$C_6H_5NHNH_2$	2 (ml.)	∿20.4	-
Products			
Sulfur	95	2.96[*]	27.0
$C_6H_5S_2C_6H_5$	326	1.49	27.2
$C_6H_5SC_6H_5$	99	0.531	4.85

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[*] mg atoms.

[**] Yield is based on the percentage of total sulfur present in the starting S_4N_4.

n-butylamine (2 ml, ∿22 mmoles) in a 50 ml flask equipped with a water cooled condenser and a calcium chloride drying tube. The solution, which became red in color, was stirred for 2 days. Excess butylamine was removed in vacuo to give a red oil containing some crystalline material. The red oil dissolved in anhydrous ether and left 646 mg of colorless crystals which were collected by filtration. This white solid was insoluble in most organic solvents but was soluble in hot alcohol and in water. It was recrystallized from ethanol to give colorless plates of m.p. 193°C d. A sodium fusion of this material followed by the sodium nitroprusside test(60) indicated the presence of sulfur. An aqueous solution of the white solid gave a white precipitate with lead acetate solution, a white precipitate with barium chloride solution and a yellowish precipitate which turned black in a short period with silver nitrate solution. The aqueous solution also discolored potassium permanganate solution. These tests indicated that the anion was either thiosulfate, $S_2O_3^=$, or sulfite, $SO_3^=$. Nitrogen analysis showed 10.5% N (calcd. for $C_8H_{24}N_2S_2O_3$: N, 10.8 and for $C_8H_{24}N_2SO_3$: N, 12.3). The IR spectrum, Fig. 21, indicated an alkylammonium cation.

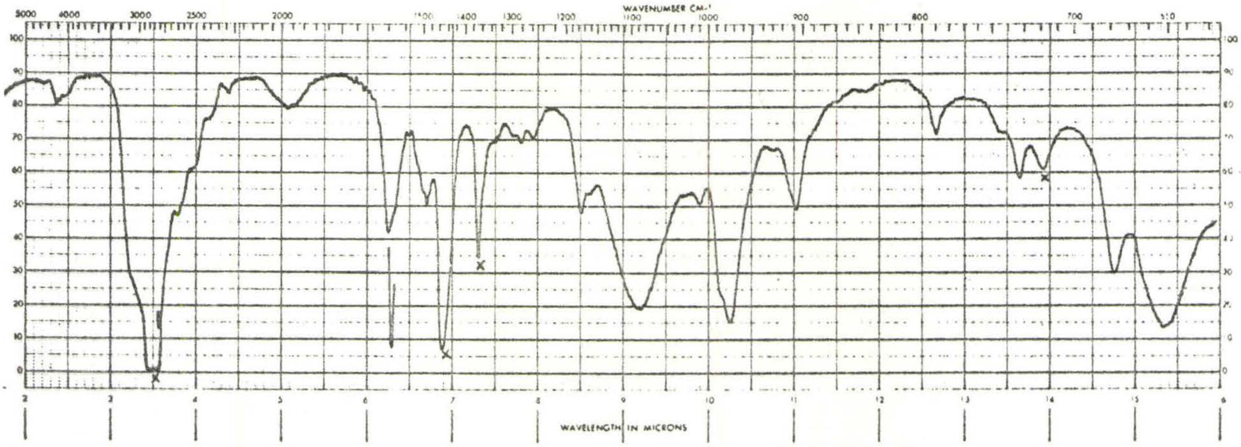


Fig. 21. IR SPECTRUM OF BUTYLAMMONIUM THIOSULFATE (NUJOL MULL)

H. ALLYLAMINE

Allylamine (2 ml, ~27 mmoles) was added to S_4N_4 (501 mg, 2.72 mmoles). Ammonia evolved quickly, and the color changed from orange red to dark brown. In 6 hours the reaction mixture became very viscous. The excess allylamine was removed in vacuo leaving a dark brown viscous sticky material. This material did not dissolve in ether, benzene, hexane or alcohol. It was assumed that polymerization had occurred, and no further characterization was attempted.

6. REACTION OF BENZYLIDENIMINE POLYSULFIDES

A. PYROLYSIS OF BENZYLIDENIMINE TETRASULFIDE

Benzylidenimine tetrasulfide (711 mg, 2.12 mmoles) was placed in a 100 ml flask which was evacuated to 7×10^{-4} mm Hg and sealed. The flask was heated to 105°C in an oil bath. This temperature was just above the melting point of benzylidenimine tetrasulfide. As the solid fused, some gas evolution was observed. An oil boiled off at this temperature and condensed on the side wall of the flask above the oil bath level. After 7 hours the reaction mixture was cooled. When the flask was opened, a basic gas was detected by PH paper, and hydrogen sulfide was detected by wet lead acetate paper. The non-volatile products were separated by column chromatography. Pure hexane eluted 222 mg of elemental sulfur (6.94 mg atom). Elution with 13% benzene in hexane gave 45 mg of unreacted benzylidenimine tetrasulfide (0.13 mmoles). Elution with 20% benzene in hexane gave 234 mg of a colorless solid. Recrystallization from a hexane-benzene mixture gave colorless needles (R_f value, 0.14, silica gel-carbon disulfide, with 0.80 for sulfur) of m.p. 234.5-235.5°C (Lit. for triphenyl-(s)-triazine is 235-235.4°C(19) and 231-232°C(37)). The IR spectrum of this material was identical to that of authentic triphenyl-(s)-triazine(61). A 1:1 mixture of benzene and hexane eluted 59 mg of benzonitrile (0.572 mmoles) identified by comparison of its IR and NMR spectra with those of an authentic sample.

B. PHOTOLYSIS OF BENZYLIDENIMINE TETRASULFIDE

A small amount (110 mg) of pure (TLC, NMR) benzylidenimine tetrasulfide was dissolved in 100 ml of anhydrous ether and placed in a Pyrex tube. The solution was stirred under nitrogen and subjected to a UV light source (λ > 280 mμ) for 12 hours. TLC of the resulting solution showed 6 spots whose R_f values were: 0.80, 0.46, 0.40, 0.36, 0.24 and 0.06 (silica gel-carbon disulfide, with 0.80 for sulfur and with 0.46 for benzylidenimine tetrasulfide). The ether was removed in *vacuo*, and the remaining solid was dissolved in carbon tetrachloride. An NMR spectrum of this solution showed 4 peaks down field of the phenyl multiplet: -7.95 ppm, -8.18 ppm, -8.44 ppm and -8.61 ppm. The ratios of these were 3.0:0.8:1.2:1.0, respectively. Separation was not undertaken.

C. DISPROPORTIONATION OF BENZYLIDENIMINE TRISULFIDE

Benzylidenimine trisulfide (15 mg) was dissolved in 0.5 ml of carbon tetrachloride. The NMR spectrum of this solution showed peaks for only benzylidenimine trisulfide (-7.32 to -7.88 ppm for phenyl group and -8.42 ppm for -CH═N-), and a TLC of this solution showed only one spot. The capped NMR tube was kept at room temperature. After two days the NMR spectrum showed two small extra peaks at -7.90 and -8.12 ppm. These two peaks grew in intensity relative to the intensity of the -CH═N- peak of benzylidenimine trisulfide for about 10 days. At this time the ratio of these three peaks,

-7.90 ppm:-8.12 ppm:-8.42 ppm, was 1:1:6. This ratio did not change after 4 months. A TLC of this solution did not show any sulfur.

Approximately 30 mg of a 1:1 mixture of benzylidenimine tetrasulfide and benzylidenimine disulfide was prepared in carbon tetrachloride. The NMR spectrum of this solution showed only peaks assignable to these two materials. This solution was kept in a capped NMR tube at room temperature for a month. Another NMR spectrum was then taken; no change could be observed.

D. BENZYLIDENIMINE TETRASULFIDE WITH BENZYLAMINE

(i) IN AIR

Benzylidenimine tetrasulfide (350 mg, 1.04 mmoles) dissolved in benzylamine (2 ml, ∿18 mmoles) very readily to give a yellowish solution which turned reddish brown in a few minutes at room temperature. No precautions were taken to exclude moisture or oxygen. After a day a precipitate appeared which was filtered and washed with anhydrous ether. About 200 mg of white solid of m.p. 173∿174°C d was obtained. This solid was quite soluble in water and fairly soluble in hot methanol but insoluble in cold methanol and ordinary organic solvents. Aqueous solutions of this material discolored potassium permanganate solution and gave a white precipitate with lead acetate solution. An IR spectrum was found to be identical with that of benzylammonium thiosulfate (cf. Fig. 10).

Ether was removed from the filtrate, and an NMR of the residual oil in $CDC\ell_3$ showed the presence of N-benzylidene benzylamine and benzylamine.

(ii) UNDER A DRY NITROGEN ATMOSPHERE

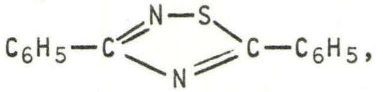
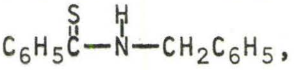
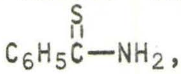
Benzylidenimine tetrasulfide (510 mg, 1.52 mmoles) was dissolved in benzylamine (2710 mg, 25 mmoles) under a dry nitrogen atmosphere and was stirred for 24 hours. The reaction mixture was placed in a dry box. Anhydrous ether was introduced into the reaction mixture and stirred well. An orange solid, XVI, precipitated which was filtered and washed with ether. This orange solid XVI decomposed in air with the evolution of H_2S. The m.p. in an evacuated sealed tube was 93-96°C d. Nitrogen analysis gave 6.67%. Calcd. for $C_{14}H_{10}N_2S_6$: N, 6.85 and for $C_{14}H_{10}N_2S_7$: N, 6.37.

The filtrate was concentrated to give an oily material. This material was separated by column chromatography to give 55 mg of sulfur (1.72 mmoles), 425 mg of N-benzylidene benzylamine (2.18 mmoles), 310 mg of benzaldehyde (2.93 mmoles) and a substantial quantity of benzylamine.

(iii) PYROLYSIS OF BENZYLAMMONIUM POLYSULFIDE, XVI

Benzylammonium polysulfide, XVI, obtained as above, was placed in a glass tube in the dry box and evacuated. (The weight was not recorded.) The tube was sealed and put into an oven whose temperature was kept between 170-180°C. After 12 hours the tube was cooled and opened. A very strong odor of hydrogen sulfide was noted. This was confirmed by wet lead acetate paper.

The non-volatile products were separated by column chromatography. Hexane eluted 73 mg of elemental sulfur (2.28 mmoles). Elution by 20 $\sim$ 40% benzene in hexane gave 119 mg of dibenzylpolysulfides,

$C_6H_5CH_2S_xCH_2C_6H_5$ (x = 2, 3, 4, 5 and 6[(40)]). Elution with benzene gave 66 mg of a white solid. Recrystallization from ethanol gave 3,5-diphenyl-1,2,3-thiadiazole, , of m.p. 89-90°C (Lit.[(62)] 89-90°C). This was identified by comparison of melting point (mixed melting point undepressed), IR and NMR spectra with those of the authentic material prepared from thiobenzamide and iodine.[(63)] Ether eluted 37 mg of N-benzylthiobenzamide,  $C_6H_5C(=S)-N(H)-CH_2C_6H_5$, of m.p. 85°C (Lit.[(39)] 84-85°C) which was identified by comparison of melting point (mixed melting point undepressed), IR and NMR spectra with those of the authentic material prepared from sulfur and benzylamine.[(39)] Elution with 30% methanol in ether gave 72 mg of a yellow solid. This was recrystallized from benzene to give thiobenzamide,  $C_6H_5C(=S)-NH_2$, of m.p. 113-114°C (Lit.[(64)] 115-116°C). This material was identified by comparison of melting point (mixed melting point undepressed), IR and NMR spectra with those of the authentic material prepared from benzonitrile and hydrogen sulfide.[(64,65)]

7. REACTION OF SULFUR WITH BENZYLAMINE

A. PREPARATION OF BENZYLAMMONIUM POLYSULFIDE, XVIII

Benzylamine (5 ml, 45.8 mmoles) was added to 1.08 g of sulfur (33.8 mmoles), and the mixture was stirred for 24 hours under a nitrogen atmosphere. A fairly rapid exothermic reaction occurred. The color of the solution became reddish brown, and a basic gas was evolved. The reaction mixture was placed in the dry box. Anhydrous ether was added to the flask and stirred well. A red oil slowly dissolved in the ether, and an orange solid, benzylammonium polysulfide XVIII, remained undissolved.

The ether soluble part was shaken with dilute hydrochloric acid and extracted with ether. The ether layer contained 190 mg of sulfur (5.94 mg atom) and 206 mg of N-benzylthiobenzamide.

XVIII was filtered and washed with anhydrous ether. 1.94 g of XVIII was obtained which melted at 93-94°C d. (in an evacuated sealed tube). Nitrogen analysis gave 6.54%. Calcd. for $C_{14}H_{10}N_2S_6$: N, 6.85 and for $C_{14}H_{10}N_2S_7$: N, 6.37. An NMR spectrum of this compound in dry dimethyl-d^6 sulfoxide showed 3 peaks: -3.96 ppm (singlet, 1.7 H, $-CH_2-$), -6.32 ppm (broad singlet, 3.4 H, $-NH_3^+$) and -7.00 ppm (broad singlet, 5.0 H, C_6H_5-).

"Authentic"(38) benzylammonium hexasulfide,* $(C_6H_5CH_2NH_3)_2S_6$, was prepared from benzylamine, sulfur and H_2S, m.p. 96°C d. (in an evacuated sealed tube). It was an orange solid which decomposed slowly in air with evolution of hydrogen sulfide and eventually gave elemental sulfur and benzylammonium thiosulfate. The NMR spectrum of this "authentic" benzylammonium hexasulfide was taken in dry dimethyl-d^6 sulfoxide. It showed 3 peaks: -3.96 ppm (singlet, 1.9 H, $-CH_2-$), -6.18 ppm (broad singlet, 3.1 H, $-NH_3^+$) and -7.00 ppm (broad singlet, 5.0 H, C_6H_5-). This is essentially the same as that of the orange solid XVIII except for a very slight shift in the NH_3^+ peak.

Benzylammonium polysulfide, XVIII, left in air also evolved hydrogen sulfide and changed to a wettish looking dark red solid quite

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*See page 91.

quickly. At this stage a benzylamine like odor was noticed. In 24 hours it became a yellowish solid and was partly soluble in cold methanol. The yellow solid which remained undissolved was found to be elemental sulfur. The methanol solution contained mainly benzylammonium thiosulfate. The approximate ratio of g atoms of sulfur to moles of thiosulfate was 4:1.

Another sample of benzylammonium polysulfide, XVIII, was removed from the dry box and immediately added to methanol. Hydrogen sulfide gas evolution was observed, and the orange color disappeared very quickly. A yellow solid was deposited which was filtered to give 344 mg of sulfur (10.7 mg atom). The methanol solution contained 357 mg of benzylamine (3.3 mmoles).

When XVIII was subjected to a Soxhlet extraction with anhydrous ether in the dry box for 24 hours, XVIII was found to be completely decomposed into sulfur and benzylamine. Although not observed, hydrogen sulfide was also probably a product. The quantities of these products were not measured.

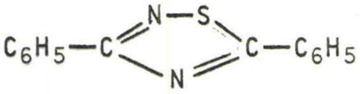
B. PYROLYSIS OF BENZYLAMMONIUM POLYSULFIDE, XVIII

A sample of benzylammonium polysulfide, XVIII, was placed in a tube in the dry box (weight was not measured). The tube was evacuated, sealed and heated for 12 hours at 170-180°C. The products obtained on chromatography are listed in Table 14.

C. BENZYLAMMONIUM POLYSULFIDE, XVIII, WITH BENZYLAMINE

Benzylammonium polysulfide, XVIII (568 mg), obtained from sulfur and benzylamine, was dissolved in 8 ml of benzylamine. The orange

Table 14. PYROLYSIS OF BENZYLAMMONIUM POLYSULFIDE, XVIII

Products	R_f[*]	Eluent	Amount (mg)	No. of mmoles
Sulfur	0.80	Hexane	188	5.87[**]
$C_6H_5-CH_2-CH_2-C_6H_5$[***]	0.63	15% benzene in hexane	74	0.406
$C_6H_5CH_2S_xCH_2C_6H_5$ (x = 3,4,5 and 6)	0.59-0.35	30% benzene in hexane	88	0.358[****]
	0.20	80% benzene in hexane	177	0.745
 $C_6H_5-C(=S)-NH_2$	0.05	20% ether in benzene	69	0.503

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[*] Silica gel - carbon disulfide.

[**] mg atoms.

[***] Colorless solid, m.p. 49-51°C (Lit.(66) 52°C), NMR and IR spectra of this material were identical to those in the literature.(33h,52d)

[****] Total of the four components, estimated from NMR.(40)

color of the polysulfide immediately changed to a dark reddish brown. It was refluxed for three hours during which time the color slowly changed to pale yellow and vigorous hydrogen sulfide evolution was observed. The reaction mixture was dissolved in hot hexane. Upon cooling 600 mg of N-benzylthiobenzamide (2.82 mmoles) of m.p. 86°C was obtained.

8. REACTION OF HEPTASULFURIMIDE WITH BENZYLAMINE

A. PREPARATION OF BENZYLAMMONIUM POLYSULFIDE, XVII

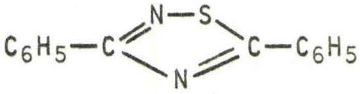
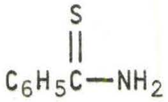
Benzylamine (4.2 ml, 38.6 mmoles) was added to 1.00 g of heptasulfurimide, S_7NH (4.60 mmoles), under a dry nitrogen atmosphere. The solution immediately became blue. After one minute it was dull green, and in 4-5 minutes at room temperature it became reddish. The exothermic reaction was quite fast. After stirring for 10 hours, the dark red solution was placed in the dry box, and an aliquot was removed (from the dry box) and heated with a free flame until it boiled. The red color became pale yellow, and evolution of hydrogen sulfide was observed. After cooling it solidified and was recrystallized from hexane to give N-benzylthiobenzamide of m.p. 84°C (mixed melting point with authentic sample was undepressed).

The other part of the dark red solution was stirred with anhydrous ether in the dry box. About 400 mg of orange solid XVII precipitated. This was filtered and washed with anhydrous ether to give a material of m.p. 95-97°C _d_ (in an evacuated sealed tube). Anal. Calcd. for $C_{14}H_{10}N_2S_8$: N, 6.06 and for $C_{14}H_{10}N_2S_9$: N, 5.67. Found: N, 5.82. This material is not stable even in the dry box; it slowly became dark brownish and looked "wet". In air benzylammonium polysulfide XVII decomposed with the evolution of hydrogen sulfide to give sulfur and benzylammonium thiosulfate. The ether soluble part was shaken with aqueous hydrochloric acid. The ether layer contained sulfur and N-benzylthiobenzamide (m.p. 84°C).

B. PYROLYSIS OF BENZYLAMMONIUM POLYSULFIDE, XVII

Some of the benzylammonium polysulfide, XVII, was placed in a tube in the dry box and evacuated (weight was not measured). The tube was sealed and heated to 170 ∿ 180°C for 12 hours. The products obtained were separated by column chromatography and are listed in Table 15.

Table 15. PYROLYSIS OF BENZYLAMMONIUM POLYSULFIDE, XVII

Products	R_f*	Eluent	Amount (mg)	No. of mmoles
Sulfur	0.80	Hexane	174	5.45**
$C_6H_5CH_2S_xCH_2C_6H_5$ ($x = 2,4,5$)	0.60∿0.30	20% benzene in hexane	214	0.865***
	0.20	Benzene	127	0.534
 $C_6H_5C(=S)-NH_2$	0.05	Ether	40	0.292

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*Silica gel - CS_2.

**mg atoms.

***Total of the three components estimated from NMR.(40)

PART II. REACTIONS OF SULFUR WITH A PRIMARY AMINE

CHAPTER V. INTRODUCTION

1. SULFUR IN LIQUID AMMONIA

Sulfur in liquid ammonia forms highly colored conducting solutions. The colors of these solutions change with concentration.(67) Dilute solutions are bluish green while concentrated solutions are dirty greenish red in color; the latter turn more greenish on heating.(68) Sulfur is very soluble in liquid ammonia (38.85 weight % at -84.6°C), and the solubility is almost constant in the temperature range -84.6°C to -20.5°C.(69)

Moissan(70) proposed that solvated sulfur species, $S\cdot(NH_3)_x$, were responsible for the colors although he observed that solutions of sulfur in liquid ammonia reacted with Ca(II) or Hg(II) to give the corresponding metal sulfides. Ruff and Geisel(71) proposed the equilibrium (19) based on chemical behavior. By adding silver iodide to the bluish solution of

$$10S + 4NH_3 \rightleftharpoons 6H_2S + S_4N_4 \qquad (19)$$

sulfur in ammonia, S_4N_4 was obtained in almost 90% yield and AgS in 100% yield based on this equilibrium.(71) Elemental sulfur was also recovered when hydrogen sulfide was added to an S_4N_4-NH_3 solution.

Bergstrom(72) found that sulfur solutions in liquid ammonia reacted very readily with cyanide ion giving thiocyanates, that neither H_2S nor S_4N_4 in liquid ammonia reacted with cyanide ion, and that ammonium polysulfide (prepared by the action of sulfur upon an ammonium monosulfide solution) slowly reacted with cyanide ion. He consequently suggested that ammonium polysulfides were present in sulfur-ammonia solutions.

Ruff and Hecht(69) established a phase diagram for sulfur in ammonia which showed an eutectic point at -79.7°C (16.3 weight % sulfur), a flat maximum at -78.3°C (∿24 weight % of S) and a solubility limit of 38.8 weight % of S at -84.6°C. The maximum in the freezing point curve corresponded to $S(NH_3)_6$ (23.8% of S). They suggested that the nearly constant solubility of sulfur with varying temperature (in the range of -20.5 ∿ -84.6°C) indicated the existence of a compound $S(NH_3)_3$ (38.5% of S) and therefore concluded that (19) was of minor importance since sulfur was, for the most part, present in the form of the above solvates.

Electrical conductivity measurements on sulfur and S_4N_4 showed them both to be fairly strong electrolytes in liquid ammonia. For sulfur, however, a large fraction was present in a nonconducting form, possibly as a polyatomic anionic species; the average number of sulfur of this polyatomic anion was suggested(73) to be at least two to three.

The electronic absorption spectra of liquid ammonia solutions of sulfur (at -35°C) exhibited maxima at 580 ($\varepsilon = 7.6^*$), 430 ($\varepsilon = 27^*$) and 297 mμ ($\varepsilon = 130^*$).(74) These absorptions were quite different from the absorption observed for sulfur in inert solvents where bands occurred at 275 ($\varepsilon = \sim 900$), 265 ($\varepsilon \sim 900$) and 230 mμ ($\varepsilon \sim 1400$)(45). The spectrum of sulfur in benzene has been assigned to the S_8 molecule. Thus, it is apparent that the species in ammonia is not the S_8 molecule.

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*Based on analytical concentration (in g atoms) of sulfur.

The bands observed for sulfur in liquid ammonia changed in intensity with changing temperature and concentration but not in a uniform manner. The band at 580 mμ decreased in intensity while the other two bands increased with a decrease in temperature.(74) The bands at 430 and 580 mμ obeyed Beer's law up to 10^{-3} M (the other band was not studied), butat higher concentrations strong positive deviations were observed for both of these bands. The extinction coefficient for the 580 mμ band increased more rapidly than that for the 430 mμ band at high concentrations.(73) These observations showed that at least two different species were in equilibrium in the sulfur-ammonia system. Zipp and Evers(73) suggested the absorbence at 430 and 580 mμ could be augmented further by the formation of polysulfide species which absorbed at 400 and 600 mμ at higher concentration.

Equation (19) shows S_4N_4 and hydrogen sulfide in equilibrium. Therefore, the spectra of hydrogen sulfide,(76) S_4N_4(74,77) and mixtures of these two(74,77) in liquid ammonia have been investigated. Hydrogen sulfide showed an absorption band at 270 mμ ($\varepsilon = 9.14 \times 10^3$). A freshly prepared S_4N_4 solution in liquid ammonia exhibited a band at 254 mμ ($\varepsilon = 9.27 \times 10^3$) which decreased with time, giving rise to a new band at 360 mμ ($\varepsilon = 6.0 \times 10^3$). This change was complete in 10 minutes and the band at 254 mμ had disappeared. The new band at 360 mμ was tentatively assigned to the species $S_2N_2 \cdot NH_3$(71,78) or its ionization product (20). Neither the band at 270 mμ nor the band at 254 and/or 360 mμ were observed for sulfur-ammonia solutions.

$$S_4N_4 + 2NH_3 \longrightarrow 2S_2N_2{\cdot}NH_3 \qquad (20)$$

Solutions containing a mixture of S_4N_4 and hydrogen sulfide exhibited band maxima only at 360 and 270 mμ, respectively. These bands were characteristic of S_4N_4 and hydrogen sulfide solutions in liquid ammonia. If equilibrium (19) existed and the point of equilibrium lay far to the left, it might be expected that the mixture of hydrogen sulfide and S_4N_4 would generate the species characteristic of elemental sulfur. On the other hand, if the equilibrium lay far to the right, sulfur solutions in ammonia would be expected to show the same spectrum as that of a mixture of S_4N_4 and hydrogen sulfide. Spectroscopic observations thus indicated that the species S_8, H_2S, S_4N_4 and $S_2N_2{\cdot}NH_3$ were not present in appreciable concentration. Hence, equilibrium (19) does not exist to an appreciable extent.

In summary, the electrical conductivity data indicated that although ions were present, a large fraction of the sulfur was in a nonconducting form. The spectroscopic data indicated that at least two species other than S_8, H_2S and S_4N_4 were in equilibrium. Equilibrium (19) was found to be unimportant for sulfur in liquid ammonia and thus far no alternative has been proposed.

2. REACTIONS OF SULFUR WITH AMINES

Sulfur dissolves very readily in amines to give very intense colors ranging from red to green. The heat of solution is normally high. In 1930 Levi(38) found that the orange solution obtained by addition of sulfur to benzylamine precipitated benzylammonium hexasulfide when hydrogen sulfide was added. This reaction was later shown to occur with any amine, primary, secondary or tertiary (21).(79)

$$2RR_1R_2N + (x-1)S + H_2S \longrightarrow (RR_1R_2N)_2H_2S_x \tag{21}$$

The number of sulfur atoms, x, in the polysulfide ions depended on the amine used and was typically between 6 and 9.(79)

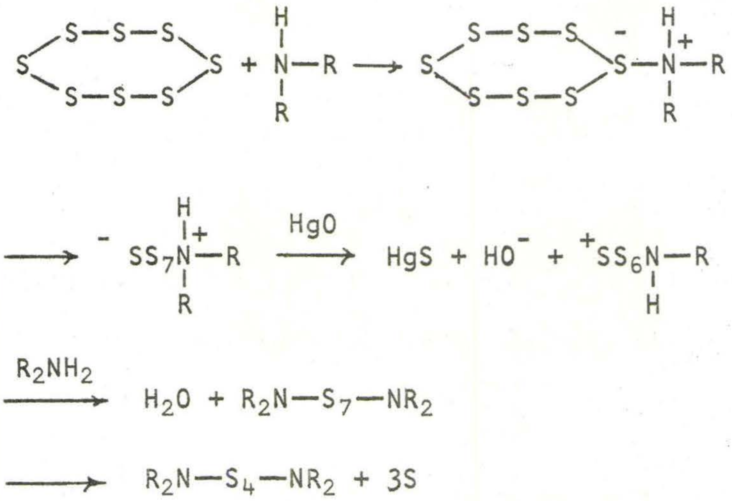
Subsequently, it was shown that primary amines(80) and secondary amines(38) gave alkylammonium polysulfides without adding any hydrogen sulfide, but that tertiary amines(81,82) did not react with sulfur unless small amounts of impurities were present such as H_2S or SO_2. These polysulfides were presumed responsible for the initial colors observed when sulfur was dissolved in an amine solvent. In order to explain the species present in sulfur-amine solutions, Levi(83) proposed the following scheme:

$$2RR'NH + (x+1)S \longrightarrow RR'N\text{—}S_x\text{—}NRR' + H_2S \tag{22}$$

XX

$$H_2S + 2RR'NH + yS \longrightarrow (RR'NH_2)_2S_{y+1} \tag{23}$$

Equation (23) is essentially the same as (21). Evidence for (22) was obtained for secondary amines by adding a hydrogen sulfide scavenger to the sulfur-amine solution. N,N'-polythiodiamines, XX,(83,84), were isolated under these conditions. Levi(83) obtained a tetrasulfide and a trisulfide for piperidine and a trisulfide and a disulfide for both dimethylamine and diethylamine using lead(II) oxide as the hydrogen sulfide scavenger. Jenne and Becke-Goehring(84) obtained a tetrasulfide and a trisulfide for dimethylamine and a tetrasulfide, trisulfide and disulfide for diethylamine using mercuric oxide as the hydrogen sulfide scavenger. They proposed the reaction scheme as shown below (24):

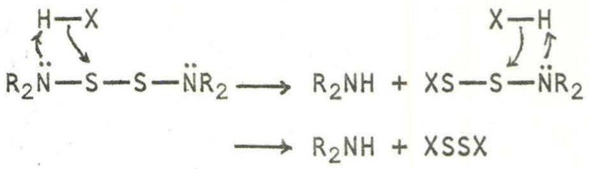


(24)

The last step of (24) was analogous to the known decomposition of N,N'-tetrathiobisdimethylamine to the trisulfide and sulfur on heating:(84)

$$(CH_3)_2N{-}S_4{-}N(CH_3)_2 \xrightarrow{120^\circ C} (CH_3)_2N{-}S_3{-}N(CH_3)_2 + S \qquad (25)$$

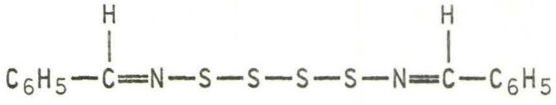
Saville(85) showed that N,N'-polythiobisamines decomposed with acid, HX (where X = SH, Cℓ, SO_3H and RS), as shown in equation (26).



$$R_2\ddot{N}{-}S{-}S{-}\ddot{N}R_2 \longrightarrow R_2NH + XS{-}S{-}\ddot{N}R_2 \longrightarrow R_2NH + XSSX \qquad (26)$$

Therefore, equation (22) must be an equilibrium.

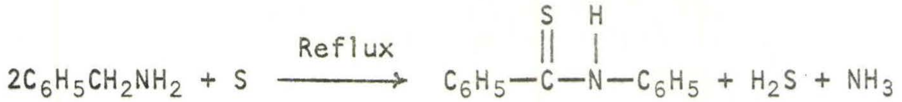
Subsequently, Levi(19) tried to establish equation (22) for primary amines by adding a sulfide ion scavenger. From ethylamine and sulfur mixed with lead(II) oxide, he obtained a pitchy material from which no definite compound could be isolated. When benzylamine was reacted with sulfur in the presence of lead(II) oxide at room temperature, a yellow crystalline material was isolated in quite good yield. He assigned the structure of this compound incorrectly, but as described in Part I, it was benzylidenimine tetrasulfide XIV.



$$C_6H_5-\overset{H}{C}=N-S-S-S-S-N=\overset{H}{C}-C_6H_5$$

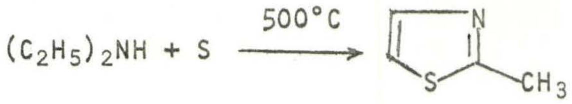
XIV

The above reactions concerned sulfur with an amine at room temperature. When sulfur was heated with an amine, however, different types of products (thioamides) were obtained. For example, when sulfur was refluxed in excess benzylamine, N-benzyl thiobenzamide was obtained in high yield (27).(39) The same compound also resulted when dibenzylamine



$$2C_6H_5CH_2NH_2 + S \xrightarrow{\text{Reflux}} C_6H_5-\overset{S}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-C_6H_5 + H_2S + NH_3 \qquad (27)$$

and sulfur were heated together.(85)* When diethylamine and sulfur were reacted at quite high temperatures, thiazole was obtained (28).(86)



(28)

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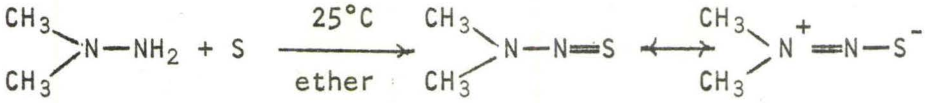
[*] Thioamides are also typical products of the so-called Willgerodt-Kindler reaction which will be discussed in the following section.

A new class of organic compounds containing the thionitroso function, -N═S, has also been prepared by the reaction of 1,1-dimethylhydrazine with sulfur (29).(87)



(29)

Ultraviolet spectra and conductivity measurements of sulfur-amine solutions have been reported.(88) The ultraviolet spectrum of sulfur in a tertiary amine was only slightly different from that of sulfur in an inert solvent such as hexane. In contrast, sulfur in primary and secondary amines showed quite different spectra which resembled the spectrum of sulfur in tertiary amines to which hydrogen sulfide had been added. Therefore, it was concluded that open chain polysulfide ions, S_x^{2-}, were formed.

The conductivity of sulfur in primary and secondary amines confirmed the suggestion that ions were present.(88) The conductivity was comparable to that of salts such as potassium iodide and tetra-n-butylammonium perchlorate at comparable concentration. However, since the mobilities of the ions in the amines were not determined, an accurate estimate of the number of ions could not be made.

An ESR study of sulfur in amines(89) showed that free radicals were present. In ethylenediamine, tetramethylguanidine and piperidine, at least 10^{-4} moles of free radicals per mole of sulfur (S_8) were observed. For n-butylamine, n-heptylamine, ethanol amine and morpholine, the weaker signal corresponded to about 10^{-5} moles of radicals per mole of sulfur (S_8). For pyridine, diethylamine, aniline and triethylamine, no signal was detected. On the basis of g-values and the observed resonance at -196°C, the radicals were inferred to have the free spins localized on sulfur atoms. Hodgeson, Buckler and Peters(89) suggested that polythiobisamines might (by homolytic sulfur-sulfur bond cleavage(30)) be responsible for these radicals.

$$RR'N{-}S_x{-}NRR' \longrightarrow RR'N{-}Sy\cdot + RR'NS_{x-y}\cdot \qquad (30)$$

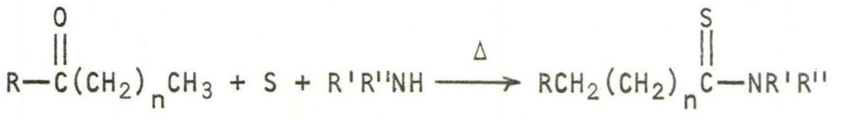
In summary then, conductivity measurements showed sulfur-amine solutions to contain ions, and the UV spectrum indicated these ions to be polysulfide ions for both secondary and primary amines. While the reaction scheme shown in (22) and (23) seems quite reasonable for secondary amines (i.e., XX was isolatable), it is not established for primary amines. Indeed, benzyl amine, the only primary amine to give a characterized product is inconsistent with this scheme.

3. REACTIONS OF SULFUR AND AMINES WITH ORGANIC COMPOUNDS

Many reactions are known in which organic substrates react with sulfur in the presence of amines. The most important of these is the so-called Willgerodt-Kindler reaction.

The original Willgerodt reaction was the reaction of alkyl-aryl ketones with aqueous ammonium polysulfide above 200°C in a sealed tube. The most important preparative modification of this reaction was introduced by Kindler.(90) Since then the Willgerodt-Kindler reaction has been taken to mean the reaction of ketones with sulfur and primary or secondary anhydrous amines at elevated temperatures.

The major reaction product is a thioamide as shown in equation (31).



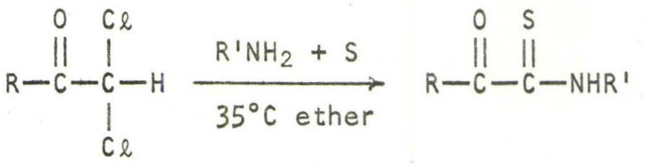
$$R-\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_nCH_3 + S + R'R''NH \xrightarrow{\Delta} RCH_2(CH_2)_n\overset{\overset{\displaystyle S}{\|}}{C}-NR'R'' \qquad (31)$$

The product thioamides have the same carbon chain length as the starting ketone without skeletal rearrangement. The reaction formally involves the reduction of the carbonyl group in combination with the oxidation of the terminal methyl group.

In these reactions amines served as a solvent, and the ketone to sulfur ratio was approximately 1:1 ∿ 1.5. The reaction temperature was normally about 130° - 200°C. The side chain could not be too long since the yield decreased as the chain became longer. This reaction has a very considerable synthetic importance; carboxylic acids can be obtained on hydrolysis of the thioamide, and amines can be obtained by reduction. Several good reviews of these reactions have appeared,(91,92,93,94) and many mechanisms have been proposed.(91,92,94,95,96,97,98,99) These mechanisms have considered the primary attack to occur either at the carbonyl group (by the amine) or at the α-position relative to the carbonyl group (by sulfur). Migration of the functional group or groups along the carbon chain and eventual irreversible oxidation at the end of the chain then provides the final products. These mechanisms are still quite speculative and rather surprisingly none have considered the possibility of any reactions between sulfur and the amine.

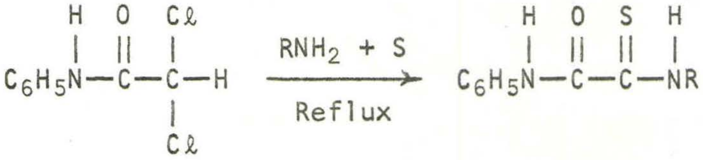
Many other organic substrates give thioamides when reacted with sulfur and amines under Willgerodt-Kindler conditions. Examples of these include: aldehydes, alcohols, thiols, olefins, acetylenes, and imines. Many of these compounds have consequently been proposed as intermediates in the Willgerodt-Kindler reactions.

It has been shown that α,α-dichloroketones react with sulfur and amines at much lower temperatures than the normal Willgerodt-Kindler conditions (32).(100) The carbonyl group remained unaltered



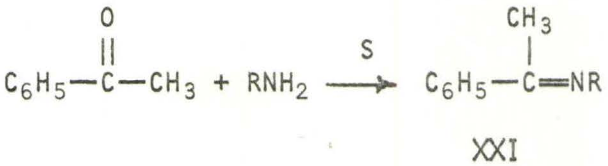
$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{C\ell}{|}}{\overset{\overset{C\ell}{|}}{C}}-H \xrightarrow[35°C\ \text{ether}]{R'NH_2\ +\ S} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{S}{\|}}{C}-NHR' \qquad (32)$$

in (32); this was also true when dichloroacetanilide was heated with sulfur in cyclohexylamine (33).(101)



$$C_6H_5\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{C\ell}{|}}{\overset{\overset{C\ell}{|}}{C}}-H \xrightarrow[\text{Reflux}]{RNH_2\ +\ S} C_6H_5\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{S}{\|}}{C}-\overset{\overset{H}{|}}{N}R \qquad (33)$$

Although acetophenone reacted with sulfur and amines under Willgerodt-Kindler conditions (*elevated temperature*) to form thioamides, it has also been shown to react at *room temperature* with primary amines in the presence of elemental sulfur (0.25 g atom of sulfur per mole of ketone) to give a Schiff's base XXI (34).(102)

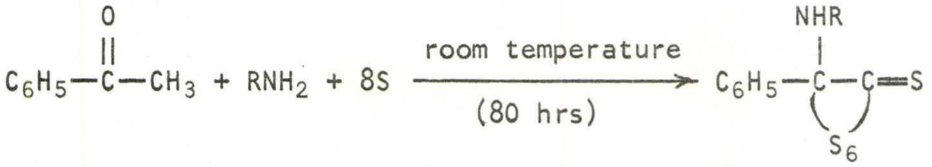


$$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 + RNH_2 \xrightarrow{S} C_6H_5-\overset{\overset{CH_3}{|}}{C}=NR \qquad (34)$$

XXI

$R = n\text{-}C_4H_9$

When the quantity of sulfur was increased, the yield of Schiff's base decreased. A further increase in the quantity of sulfur (molar ratio, ketone:amine:sulfur = 1:2:8, methanol as solvent) gave a novel compound, XXII, 8-alkylamino-8-phenyl-1,2,3,4,5,6-hexathiocane-7-thione (35).(103)



(35)

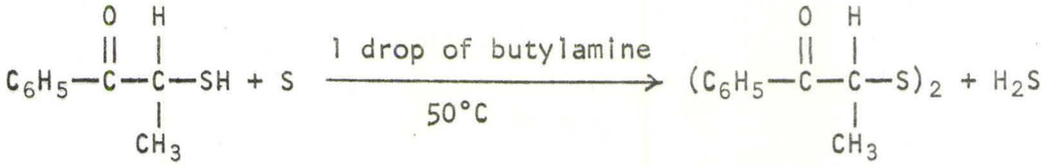
R = methyl, ethyl,
n-butyl, cyclohexyl

XXII

When acetophenone imine, XXI, was used in place of acetophenone (molar ratio, imine:amine:sulfur = 1:2:8), the yield of XXII was higher. Therefore, XXI was proposed to be an intermediate in (35).(103)

Amines are also known to catalyze reactions of sulfur with organic substrates. For example, amines showed an accelerating effect on the rate of vulcanization of natural rubber. Several workers have suggested that this is due to "thermal liberation of active sulfur".(104,105)

Mercaptans do not react with elemental sulfur at low temperatures, but addition of traces of primary or secondary amines has been shown to result in rapid formation of alkyl disulfides and hydrogen sulfide (36).(97,106) By altering the molar ratio of mercaptan to sulfur, the



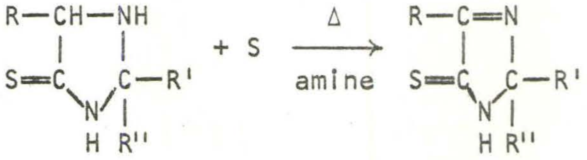
$$C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-SH + S \xrightarrow[50°C]{\text{1 drop of butylamine}} (C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-S)_2 + H_2S \qquad (36)$$

sulfur chain length in the product sulfide could be changed fairly selectively (up to the tetrasulfide) (37).(107)

$$RSH + 3S \xrightarrow{\text{Butylamine}} RS_4R\ (90\%) + RS_3R\ (10\%) \qquad (37)$$

R = t-butyl and t-pentyl

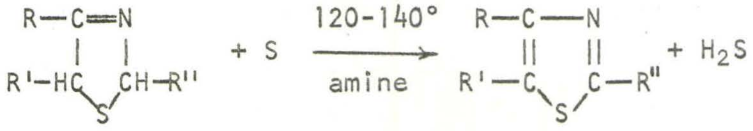
Amines are also known to catalyze the dehydrogenation of heterocyclic compounds by sulfur. For example, 2,2,5-trisubstituted imidazoline-4-thiones, XXIII, with elemental sulfur in the presence of amines gave good yields of 3-imidazoline-4-thione, XXIV (38).(108)



(38)

XXIII XXIV

3-Thiazoline, XXV, was also dehydrogenated by elemental sulfur with a drop of butylamine giving thiazole, XXVI (39).(106) 3-Thiazoline



(39)

XXV XXVI

is, however, dehydrogenated even in the absence of amine in the same temperature range.(109) The role of the amine in this reaction is obviously not established.

In summary then, many organic substrates react with sulfur-amine solutions at elevated temperature to give Willgerodt-Kindler products. Many react at lower temperatures to give other products. Amines are also known to catalyze the reaction of sulfur with organic substrates. In these reactions the mechanisms are not well understood; all of these mechanisms overlook the possibility of any direct interaction of sulfur with the amine and emphasize rather the interaction of either sulfur or the amines with the organic substrate.

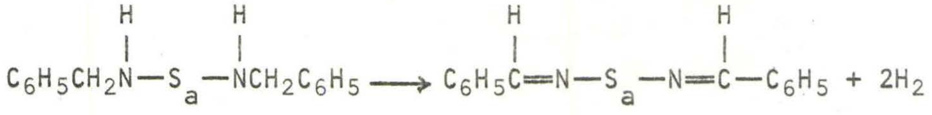
4. AIMS OF THE PRESENT WORK

In Part I of this thesis it was shown that sulfur with benzylamine gives benzylidenimine polysulfides which further react with benzylamine to give N-benzylidene benzylamine and benzylammonium polysulfides. In this section the details of the reaction of benzylamine with sulfur will be investigated with the aim of establishing a reaction scheme and identifying the more important intermediates. In view of the ease with which sulfur and amines react, this information appears vital to any understanding of the Willgerodt-Kindler reaction and the various other reactions involving a primary amine and sulfur. Also, the sulfur-ammonia system might well be more readily rationalized if the sulfur-primary amine system were understood.

CHAPTER VI. RESULTS AND DISCUSSION

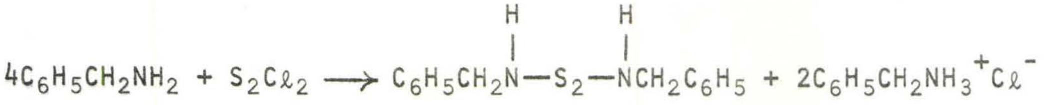
1. QUALITATIVE OBSERVATIONS LEADING TO A PROPOSED REACTION SCHEME

Since secondary amines react with sulfur to give tetraalkylamine polysulfides and alkylammonium polysulfides, it seemed quite reasonable to assume that primary amines should also react with sulfur to give dialkylamine polysulfides and alkylammonium polysulfides. When benzylamine was reacted with sulfur in the presence of lead (II) oxide, however, the product was not a benzylamine polysulfide, XXVII, but rather a benzylidenimine polysulfide, XXVIII. The latter is an oxidation product of the benzylamine polysulfide (40). The possibility that benzylamine polysulfide was formed and then either decomposed (by redox disproportionation) or was oxidized by benzylamine was consequently considered. A sample of benzylamine disulfide,* XXIX, was therefore prepared. The benzylamine disulfide (obtained as a white solid from sulfur monochloride and benzylamine in ether (41)) decomposed quite readily when exposed to small amounts of base, e.g., benzylamine, at room temperature. Even in the absence of base it was stable for only



$$C_6H_5CH_2\overset{H}{N}-S_a-\overset{H}{N}CH_2C_6H_5 \longrightarrow C_6H_5\overset{H}{C}{=}N-S_a-N{=}\overset{H}{C}-C_6H_5 + 2H_2 \qquad (40)$$

XXVII XXVIII



$$4C_6H_5CH_2NH_2 + S_2Cl_2 \longrightarrow C_6H_5CH_2\overset{H}{N}-S_2-\overset{H}{N}CH_2C_6H_5 + 2C_6H_5CH_2NH_3{}^{+}Cl^{-} \qquad (41)$$

XXIX

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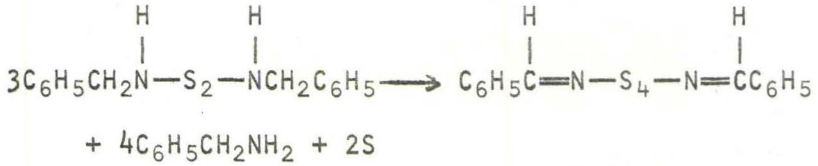
*Also called dithiobisbenzylamine or N,N'-dibenzylamine disulfide.

a few hours at room temperature. After an induction period (5 hours with no change), it underwent rapid (∿1 hour half life) autocatalytic decomposition. The products of these decompositions were N-benzylidene benzylamine and ammonia along with smaller amounts of benzylidenimine tetrasulfide, benzylammonium polysulfides and sulfur. When this autocatalytic decomposition was monitored by NMR, benzylamine and benzylidenimine tetrasulfide were observed to form and to increase to a maximum concentration in the early stages of the decomposition, and then to decrease in amount as the concentration of N-benzylidene benzylamine increased. The ratio of benzylamine to benzylidenimine tetrasulfide formed was near 4:1. All this indicated a base catalyzed decomposition of benzylamine disulfide (redox type disproportionation) as per equation (42). The benzylamine produced from the benzylamine disulfide would be expected to catalyze further decomposition of the benzylamine disulfide leading to the observed autocatalysis. As mentioned in Part I, benzylidenimine tetrasulfide reacts with benzylamine to give benzylammonium polysulfides and N-benzylidene benzylamine. This reaction would occur as the concentration of benzylidenimine tetrasulfide and benzylamine increased during the autocatalytic decomposition and thus would account for the observed final products. As benzylidenimine tetrasulfide was obtained from the decomposition of benzylamine disulfide, it is quite reasonable to assume that a

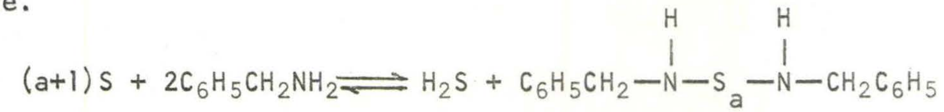


$$3C_6H_5CH_2\overset{\overset{H}{|}}{N}-S_2-\overset{\overset{H}{|}}{N}CH_2C_6H_5 \longrightarrow C_6H_5\overset{\overset{H}{|}}{C}=N-S_4-N=\overset{\overset{H}{|}}{C}C_6H_5 + 4C_6H_5CH_2NH_2 + 2S \qquad (42)$$

benzylamine polysulfide is an intermediate in the reaction of benzylamine with sulfur.

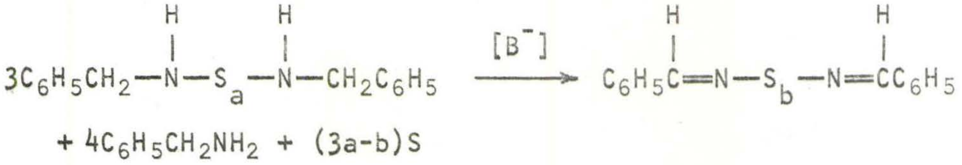
When sulfur was dissolved in an excess of benzylamine in the absence of lead (II) oxide, it immediately formed a reddish brown solution, and gaseous ammonia was evolved. From this solution benzylammonium polysulfide* and N-benzylidene benzylamine were isolated. Thus, with excess benzylamine sulfur serves, in an overall sense, as an oxidizing agent.

With this information, equations (43) to (47) were proposed where (45) is base catalyzed and (46) is apparently catalyzed by sulfide ion. The latter point seems justified since only traces of N-benzylidene benzylamine and ammonia were produced from benzylidenimine tetrasulfide and benzylamine in the presence of the sulfide scavenger, lead (II) oxide.



$$(a+1)S + 2C_6H_5CH_2NH_2 \rightleftharpoons H_2S + C_6H_5CH_2-\overset{H}{\overset{|}{N}}-S_a-\overset{H}{\overset{|}{N}}-CH_2C_6H_5 \qquad (43)$$

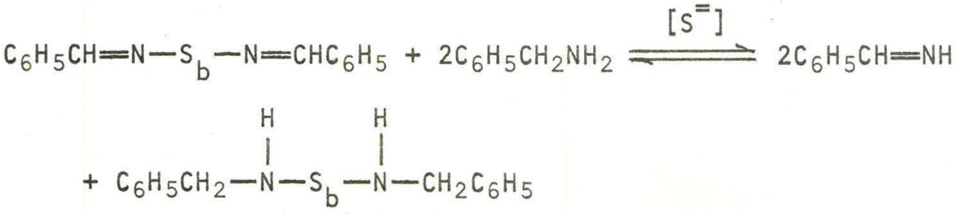
$$(x-1)S + 2C_6H_5CH_2NH_2 + H_2S \longrightarrow (C_6H_5CH_2NH_3)_2S_x \qquad (44)$$



$$3C_6H_5CH_2-\overset{H}{\overset{|}{N}}-S_a-\overset{H}{\overset{|}{N}}-CH_2C_6H_5 \xrightarrow{[B^-]} C_6H_5\overset{H}{\overset{|}{C}}=N-S_b-N=\overset{H}{\overset{|}{C}}C_6H_5$$
$$+ 4C_6H_5CH_2NH_2 + (3a-b)S \qquad (45)$$

---

*Although Levi(38) suggested that benzylammonium hexasulfide was produced by the addition of hydrogen sulfide to a sulfur-benzylamine solution, this material was most likely a mixture of varying chain length polysulfides averaging about 6-7, as described in Part I.



$$C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + 2C_6H_5CH_2NH_2 \overset{[S^{=}]}{\rightleftharpoons} 2C_6H_5CH{=}NH$$

$$+ C_6H_5CH_2{-}\overset{\overset{H}{|}}{N}{-}S_b{-}\overset{\overset{H}{|}}{N}{-}CH_2C_6H_5 \qquad (46)$$

$$C_6H_5CH{=}NH + C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}N{-}CH_2C_6H_5 + NH_3 \qquad (47)$$

(a, b and x represent the number of sulfur atoms in the sulfur chain).

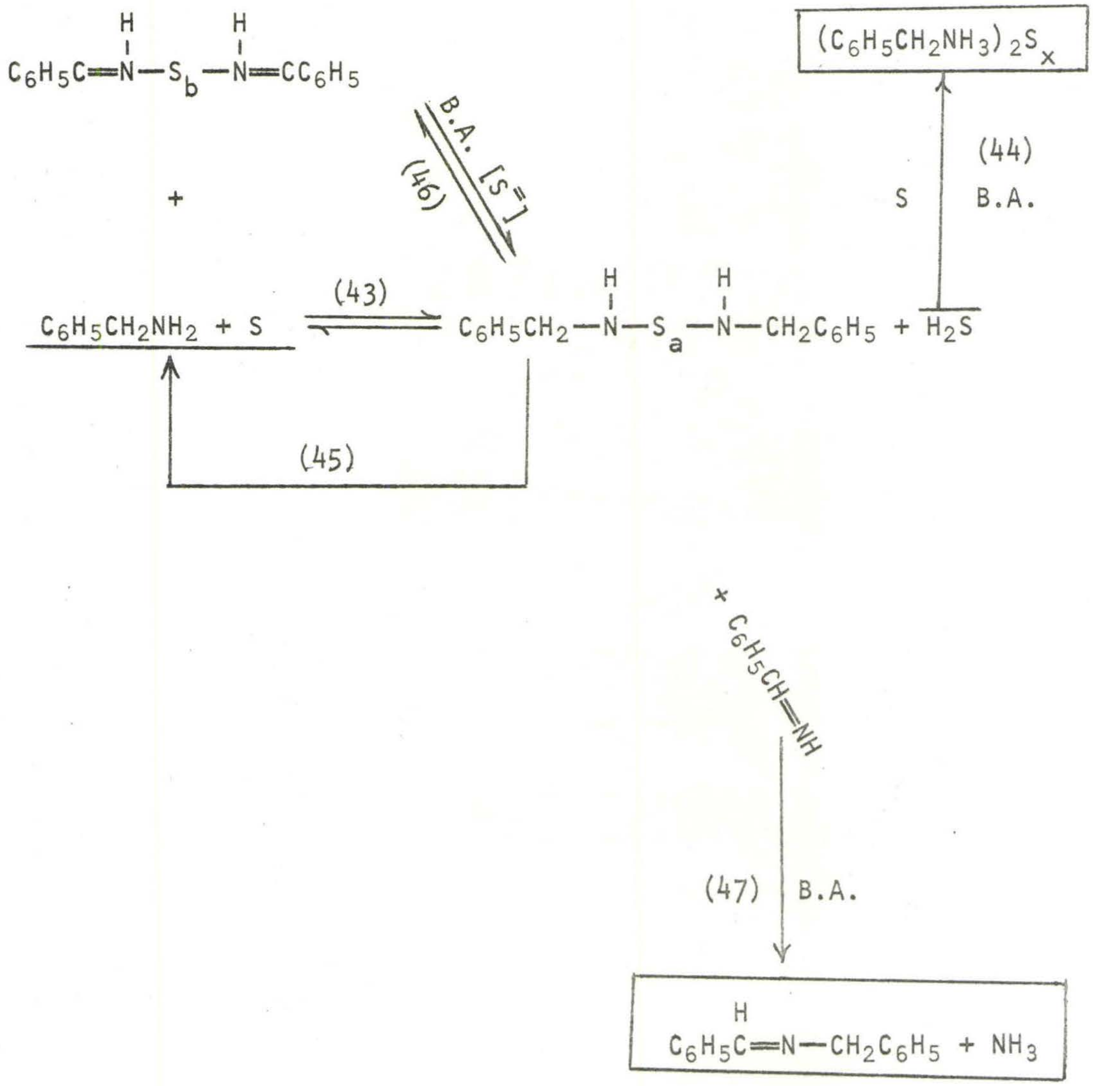
This scheme is rather complicated. Benzylamine polysulfides, $C_6H_5CH_2{-}\overset{H}{N}{-}S_a{-}\overset{H}{N}{-}CH_2C_6H_5$, and benzylidenimine polysulfides, $C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5$, appear repeatedly as cyclical intermediates until all the sulfur present is used up as benzylammonium polysulfides. Fig. 21 shows a schematic diagram indicating the relationships between the various compounds.

The various catenated sulfur species do not necessarily have a uniform chain length. The isolated benzylammonium polysulfides had an average of 6 ∿ 7 sulfur atoms per molecule, while the benzylidenimine polysulfides appeared mainly with four sulfurs and somewhat less commonly with three or two. No estimate of the sulfur chain length in the benzylamine polysulfides is available.

In (43) benzylamine reacts with sulfur to give a benzylamine polysulfide and hydrogen sulfide. This is written as an equilibrium since tetraalkylamine polysulfides, $R_2N{-}S_2{-}NR_2$, are known to react with hydrogen sulfide to give amines and elemental sulfur(85) as shown in equation (48). In (44) the hydrogen sulfide formed in (43) reacts with

$$R_2N{-}S_2{-}NR_2 + H_2S \longrightarrow 2R_2NH + 3S \qquad (48)$$

Fig. 22. REACTION SCHEME FOR SULFUR WITH BENZYLAMINE



where: B.A. is benzylamine.

Underlined compounds are starting materials.

Squared compounds are final products.

Other compounds are intermediates.

Numbers in parentheses correspond to equation numbers.

sulfur and benzylamine to give benzylammonium polysulfides (one of the final products). Both (43) and (44) are based on analogy with secondary amines. In (45) the benzylamine polysulfides decompose to benzylamine, sulfur and benzylidenimine polysulfides as observed experimentally for benzylamine *di*sulfide. Since sulfur and benzylamine are produced in this step, (43), (44) and (45) will be repeated. In (46) the benzylidenimine polysulfides produced in (45) are proposed to react with benzylamine in the presence of sulfide ion to give benzylamine polysulfides and benzylidenimine, $C_6H_5CH{=}NH$. This represents an exchange of imine for amine. The exchange of one amine for another has been previously observed in alkylamine polysulfides. Thus, when N-methylaniline disulfide, XXX, was mixed with aniline or when aniline disulfide, XXXI, was mixed with N-methylaniline, exchange occurred quite rapidly to give the five species shown in equations (49) and (50).(110)

$$C_6H_5\overset{\overset{CH_3}{|}}{N}-S_2-\overset{\overset{CH_3}{|}}{N}C_6H_5 + C_6H_5NH_2 \rightleftharpoons C_6H_5\overset{\overset{CH_3}{|}}{N}-S_2-\overset{\overset{H}{|}}{N}C_6H_5 + C_6H_5\overset{\overset{CH_3}{|}}{N}H \qquad (49)$$

XXX

$$C_6H_5\overset{\overset{CH_3}{|}}{N}-S_2-\overset{\overset{H}{|}}{N}C_6H_5 + C_6H_5NH_2 \rightleftharpoons C_6H_5\overset{\overset{H}{|}}{N}-S_2-\overset{\overset{H}{|}}{N}C_6H_5 + C_6H_5\overset{\overset{CH_3}{|}}{N}-H \qquad (50)$$

XXXI

Therefore, it is expected that an imine-amine exchange will occur with benzylidenimine tetrasulfide in the presence of the excess benzylamine. The benzylidenimine formed in this exchange is known and is quite reactive toward nucleophiles.(111) It has been previously proposed(112) to react with benzylamine to give N-benzylidene benzylamine and ammonia as per equation (47). Equation (46) is shown as being catalyzed by sulfide ion. Catalysis by sulfide ion is not uncommon in sulfur-amine reactions. The reaction of triphenyl phosphine with sulfur in trimethylamine is reported to be catalyzed by ∿10^{-5} mole of hydrogen sulfide per mole of sulfur.(81) Also, the reaction of triethylamine with S_6 to give S_8 is catalyzed by 10^{-8} M/liter sulfide ion.(82)

Since benzylamine polysulfides are produced in (46), steps (45), (43), (44) and (46) will be repeated. Thus, until all the sulfur is used up to give benzylammonium polysulfides or all the benzylamine is used up to give N-benzylidene benzylamine, benzylammonium polysulfides and ammonia, the key steps (45) and (46) continue to occur in a cyclical sense.

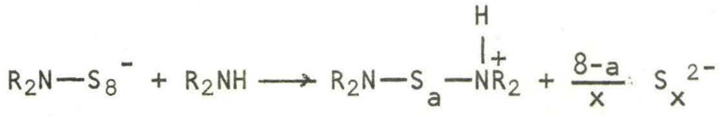
Davis(113) has proposed a different reaction scheme (51-52) for the initial steps in the interaction of sulfur with an amine in which no free hydrogen sulfide is involved. His proposal is quite reasonable.

$$R_2NH + S_8 \rightleftharpoons R_2\overset{\overset{H}{|}}{N}{}^{+}—S_8^{-} \qquad (51)$$

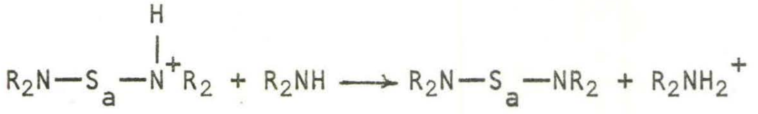
$$R_2\overset{\overset{H}{|}}{N}{}^{+}—S_8^{-} + R_2NH \xrightleftharpoons{\text{fast}} R_2NH_2^{+} + R_2N—S_8^{-} \qquad (52)$$

XXXII

Although equations (43) and (44) show free hydrogen sulfide, it need not necessarily be present. XXXII could well be present as an intermediate which reacts with more amine to give the benzylamine polysulfide, XXVII, and alkylammonium polysulfides as per (53) and (54).

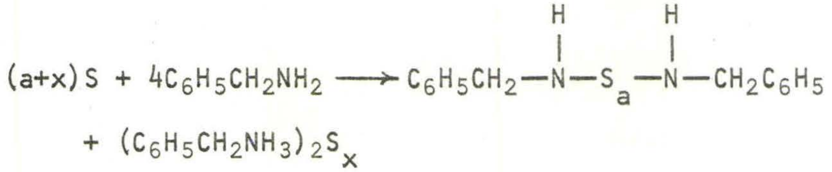


$$R_2N{-}S_8^- + R_2NH \longrightarrow R_2N{-}S_a{-}\overset{\overset{H}{|}}{N}{}^{+}R_2 + \frac{8-a}{x}\,S_x^{2-} \qquad (53)$$



$$R_2N{-}S_a{-}\overset{\overset{H}{|}}{N}{}^{+}R_2 + R_2NH \longrightarrow R_2N{-}S_a{-}NR_2 + R_2NH_2^+ \qquad (54)$$

The sum of equations (51), (52), (53) and (54), given by (55), is the same as the sum of equations (43) and (44). It is not possible at present to distinguish between them. For simplicity, the scheme formulated here will be based on equations (43) and (44), but it should be borne in mind that equations (51) - (54) offer equally good alternatives.



$$(a+x)S + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2{-}\overset{\overset{H}{|}}{N}{-}S_a{-}\overset{\overset{H}{|}}{N}{-}CH_2C_6H_5 + (C_6H_5CH_2NH_3)_2S_x \qquad (55)$$

2. QUANTITATIVE ASSESSMENT OF THE PROPOSED REACTION SEQUENCE

The proposed scheme (43 - 47) accounts for the observed intermediates and products, and each of the steps is based on analogy with a known reaction in a similar system. The intricate relationship between the compounds makes it impossible, however, to study any one step independently of all of the others. Nevertheless, a number of quantitative predictions result from this scheme which are subject to experimental tests.

A. STOICHIOMETRY OF OVERALL REACTION OF SULFUR WITH EXCESS BENZYLAMINE

Combination of equations (43) - (47) produces equation (56).*

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*Equation (56) is derived on page 150.

$$S + \frac{4}{x} C_6H_5CH_2NH_2 \longrightarrow \frac{1}{x} C_6H_5CH{=\!=}N{-}CH_2C_6H_5 + \frac{1}{x} NH_3 + \frac{1}{x} (C_6H_5CH_2NH_3)S_x \quad (56)$$

The four coefficients (on benzylamine, N-benzylidene benzylamine, ammonia and benzylammonium polysulfide) are given in terms of x, the number of sulfurs in the benzylammonium polysulfide chain. Since this is known by elemental analysis [see Part I] to be between 6-7, an "acceptable range" for each coefficient is predicted.

A known quantity of sulfur was reacted with a known excess of benzylamine. The ammonia evolved was collected in an acid trap and determined by back titration. The benzylammonium polysulfide precipitated was filtered, dried in a dry box and weighed. The molar ratio of N-benzylidene benzylamine to residual benzylamine was determined by integration of the NMR spectrum of the remaining oil. This along with the total weight of oil gave the absolute quantity of N-benzylidene benzylamine formed and also the benzylamine consumed. Table 16 shows the molar ratios of starting materials consumed and of products obtained along with experimental and calculated coefficients of equation (56) for x = 6 and 7. The experimentally obtained coefficients for the four species are in good agreement with those calculated based on equation (56).

B. SULFUR AND BENZYLAMINE IN THE PRESENCE OF LEAD (II) OXIDE

Steps (43) and (45) together were examined independently of the others by adding a sulfide scavenger, lead (II) oxide, to suppress the sulfide catalyzed reaction (46). Combination of equation (43) and (45) gives the stoichiometric equation (57) * where the hydrogen

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* Equation (57) is derived on page 152.

Table 16. STOICHIOMETRY FOR EXCESS BENZYLAMINE WITH SULFUR

Compounds (used or obtained)		No. of mmoles	Coefficients for (56) Found	Calcd. x = 6	Calcd. x = 7
Benzylamine		13.4	0.670	0.667	0.573
Sulfur		20.0*	1.00	1.00	1.00
N-benzylidene benzylamine		3.26	0.163	0.167	0.143
Ammonia		3.00	0.150	0.167	0.143
Benzylammonium polysulfide	if x=6	3.22	0.161	0.167	0.143
	x=7	2.99	0.150		

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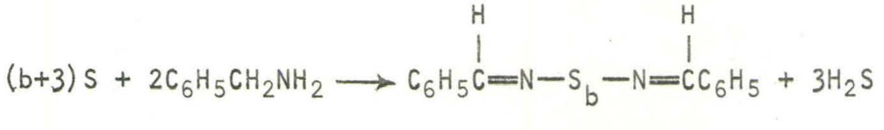
*mg atoms.



$$(b+3)S + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5\overset{H}{\overset{|}{C}}{=}N{-}S_b{-}N{=}\overset{H}{\overset{|}{C}}C_6H_5 + 3H_2S \qquad (57)$$

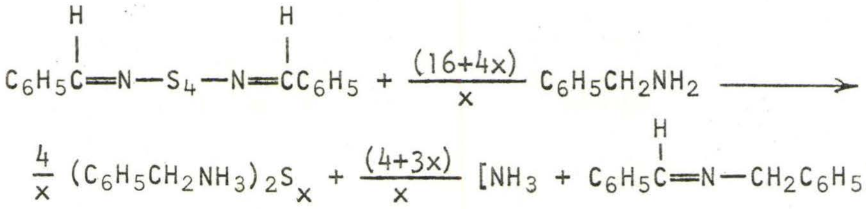
sulfide produced is removed by the lead (II) oxide to give lead (II) sulfide and water as shown in (58). When sulfur and benzylamine were

$$H_2S + PbO \longrightarrow PbS + H_2O \qquad (58)$$

allowed to react in triethylamine in the molar ratio of 7 to 2 (b = 4), the yield of benzylidenimine polysulfides isolated was 90.2% based on this equation. The products consisted of benzylidenimine tetra-, tri-, di- and monosulfides in molar ratios of 8.5:1.0:1.0:0.5. The same reaction in benzene gave a similar yield, but the reaction time was almost ten fold longer. When the sulfur to benzylamine ratio was lowered, the average sulfur content of the benzylidenimine polysulfides formed decreased although the total yield of polysulfides remained high based on (57). Thus, equation (57) remains valid, and changing the ratio of sulfur to benzylamine leads to variation in the numerical value of (b).

C. STOICHIOMETRIC REACTION OF BENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE

The reaction of benzylidenimine tetrasulfide with excess benzylamine was studied quantitatively in the absence of lead (II) oxide. Here, all 5 equations (43 - 47) contribute to the overall scheme, and suitable combination (where b = 4) leads to the stoichiometric equation (59).*



$$C_6H_5\overset{H}{\overset{|}{C}}{=}N{-}S_4{-}N{=}\overset{H}{\overset{|}{C}}C_6H_5 + \frac{(16+4x)}{x}\, C_6H_5CH_2NH_2 \longrightarrow \frac{4}{x}\,(C_6H_5CH_2NH_3)_2S_x + \frac{(4+3x)}{x}\,[NH_3 + C_6H_5\overset{H}{\overset{|}{C}}{=}N{-}CH_2C_6H_5] \qquad (59)$$

The coefficients are again determined by the average sulfur chain length of the benzylammonium polysulfide produced.

A known quantity of benzylidenimine tetrasulfide was reacted with a known excess of benzylamine. The benzylammonium polysulfides precipitated on dilution with anhydrous ether and were removed by filtration. An integrated NMR spectrum of the mother liquor gave the ratio of N-benzylidene benzylamine to the residual benzylamine. This, along with the total weight after removal of the solvent, gave the absolute quantity of N-benzylideninimine benzylamine produced and the quantity of benzylamine consumed. The ammonia evolved was collected in an acid

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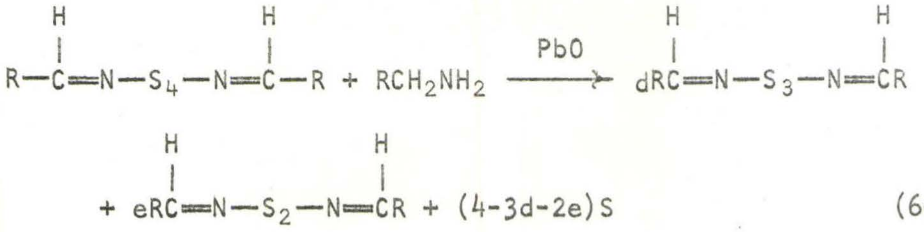
*Equation (59) is derived on page 152.

trap and was determined by back titration. Table 17 shows the experimental coefficients for N-benzylidene benzylamine, ammonia and benzylammonium polysulfide along with those calculated from equation (59) for x = 6 and x = 7. These results show equation (59) to provide a good quantitative description of the experimental facts.

Table 17. STOICHIOMETRY FOR BENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE

Compounds	Coefficients		
	Found	Calculated	
		x = 6	x = 7
Benzylidenimine tetrasulfide	1	1	1
Benzylamine	6.67	6.67	6.28
N-benzylidene benzylamine	3.57	3.67	3.58
Ammonia	3.37	3.67	3.58

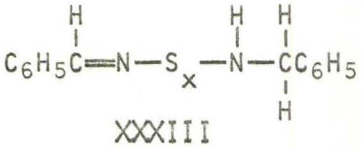
Benzylidenimine tetrasulfide exposed to benzylamine in the presence of lead oxide gave only equilibration of the sulfur chain length (60),



$$R{-}\overset{H}{\overset{|}{C}}{=}N{-}S_4{-}N{=}\overset{H}{\overset{|}{C}}{-}R + RCH_2NH_2 \xrightarrow{PbO} dR\overset{H}{\overset{|}{C}}{=}N{-}S_3{-}N{=}\overset{H}{\overset{|}{C}}R + eR\overset{H}{\overset{|}{C}}{=}N{-}S_2{-}N{=}\overset{H}{\overset{|}{C}}R + (4-3d-2e)S \qquad (60)$$

where R = C_6H_5-

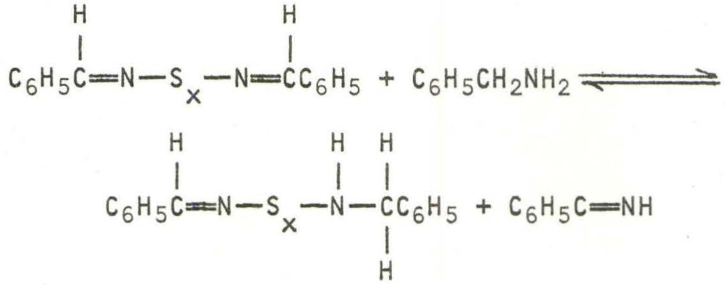
as well as small amounts of unsymmetrical mixed amine-imine polysulfides, XXXIII. The latter are most likely intermediates in the exchange



$$C_6H_5\overset{H}{\overset{|}{C}}{=}N{-}S_x{-}\overset{H}{\overset{|}{N}}{-}\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}C_6H_5$$

XXXIII

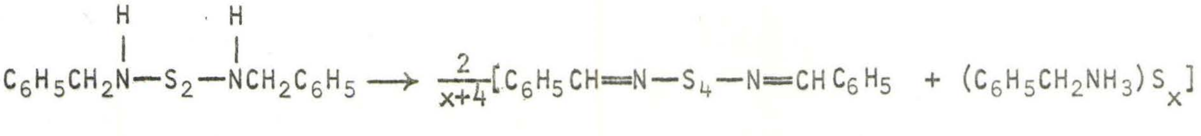
reaction (46) as shown in equation (61).



$$C_6H_5\overset{H}{C}{=}N{-}S_x{-}N{=}\overset{H}{C}C_6H_5 + C_6H_5CH_2NH_2 \rightleftharpoons C_6H_5\overset{H}{C}{=}N{-}S_x{-}\overset{H}{N}{-}\underset{H}{\overset{H}{C}}C_6H_5 + C_6H_5\overset{H}{C}{=}NH \qquad (61)$$

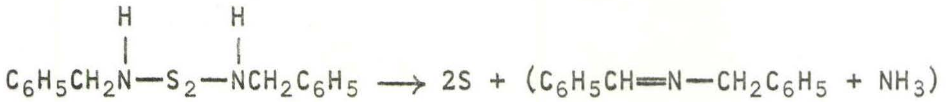
D. AUTOCATALYTIC DECOMPOSITION OF BENZYLAMINE DISULFIDE

In the autocatalytic decomposition of benzylamine disulfide, the final products were N-benzylidene benzylamine and ammonia (molar ratio 1:1), a smaller quantity of benzylammonium polysulfide and benzylidenimine tetrasulfide (again in molar ratio of 1:1) and some elemental sulfur (38% of the total sulfur). The ratio of the sum of N-benzylidene benzylamine plus ammonia to the sum of benzylammonium polysulfide plus benzylidenimine tetrasulfide was (10±3):1. Combination of equations (43) to (47) predicts the stoichiometric equations (62)* and (63)* for the decomposition of benzylamine disulfide. Equation (62)



$$C_6H_5CH_2\overset{H}{N}{-}S_2{-}\overset{H}{N}CH_2C_6H_5 \longrightarrow \frac{2}{x+4}[C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 + (C_6H_5CH_2NH_3)S_x]$$

$$+ \frac{x}{x+4}[C_6H_5CH{=}N{-}CH_2C_6H_5 + NH_3] \qquad (62)$$



$$C_6H_5CH_2\overset{H}{N}{-}S_2{-}\overset{H}{N}CH_2C_6H_5 \longrightarrow 2S + (C_6H_5CH{=}N{-}CH_2C_6H_5 + NH_3) \qquad (63)$$

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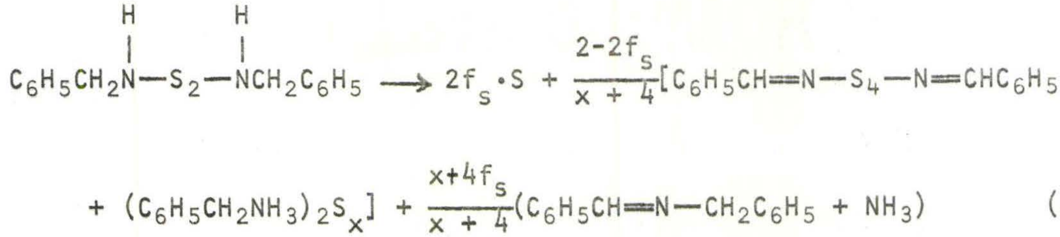
*Equations (62) and (63) are derived on pages 153 and 155, respectively.

is obtained by making the assumption that sulfur reacts with benzylamine much faster than benzylamine reacts with benzylidenimine tetrasulfide, while equation (63) is obtained from the assumption that benzylidenimine tetrasulfide reacts with benzylamine much faster than sulfur reacts with benzylamine. Therefore, (62) and (63) represent two limiting cases. If sulfur reacts with benzylamine much faster than benzylidenimine tetrasulfide, then there is no sulfur obtained as a product. If the benzylidenimine tetrasulfide reacts much faster with benzylamine than sulfur, then all of the sulfur in the benzylamine disulfide is changed to elemental sulfur. Therefore, the amount of sulfur obtained can be taken as a measure of the relative importance of equation (62) and (63) and reflects the relative rates of (43) and (46). Since the free sulfur obtained represents 38% of the total sulfur, the reaction rate of (43) (sulfur + benzylamine) is approximately 50% faster than (46) (benzylidenimine + benzylamine).

The equation for the intermediate case (64)[*] can be obtained by



$$C_6H_5CH_2\overset{H}{\overset{|}{N}}-S_2-\overset{H}{\overset{|}{N}}CH_2C_6H_5 \longrightarrow 2f_s\cdot S + \frac{2-2f_s}{x+4}[C_6H_5CH{=}N-S_4-N{=}CHC_6H_5 + (C_6H_5CH_2NH_3)_2S_x] + \frac{x+4f_s}{x+4}(C_6H_5CH{=}N-CH_2C_6H_5 + NH_3) \qquad (64)$$

combining (62) and (63) and taking the fraction of sulfur obtained as a product (f_s = mg atom of elemental sulfur/mg atom of the total sulfur) as a measure of the relative importance of these two extreme cases.

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[*] Equation (64) is derived on page 156.

Equation (64) predicts the ratio of benzylidenimine tetrasulfide to benzylammonium polysulfide to be 1:1 and the ratio of N-benzylidene benzylamine to ammonia to be 1:1. This is in excellent agreement with the experimental data. The ratio of N-benzylidene benzylamine plus ammonia to benzylammonium polysulfide plus benzylidenimine tetrasulfide is predicted to be $(x + 4f_s/2(1 - f_s)$. Experimentally, 38% of free sulfur was isolated (i.e., f_s equals 0.38). Therefore, this ratio is calculated to be 6.6 for $x = 6$, 7.5 for $x = 7$ and 8.4 for $x = 8$. The ratio obtained experimentally was 10 ± 3. The experimental error is large, but the agreement is acceptable.*

E. p-METHOXYBENZYLIDENIMINE TETRASULFIDE WITH BENZYLAMINE

Additional evidence for a benzylidenimine polysulfide - benzylamine polysulfide "cyclical" mechanism was obtained by reacting p-methoxybenzylidenimine tetrasulfide with unsubstituted benzylamine. Suitable combination of equations (43) to (47) predicts the stoichiometric equation to be as shown in (65).** Two kinds of N-benzylidene

$$CH_3O{-}C_6H_4CH{=}N{-}S_4{-}N{=}CHC_6H_4{-}CH_3O + \frac{16+4x}{x} C_6H_5CH_2NH_2$$

$$\longrightarrow \underset{\text{XXXIV}}{2CH_3O{-}C_6H_4CH{=}N{-}CH_2C_6H_5} + \frac{4+x}{x} \underset{\text{XXXV}}{C_6H_5CH{=}N{-}CH_2C_6H_5}$$

$$+ \frac{4+3x}{x} NH_3 + \frac{4}{x} (C_6H_5CH_2NH_3)_2S_x \qquad (65)$$

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*The 38% sulfur is more apt to be too low than too high (since S has some solubility in N-benzylidene benzylamine). If this number is increased, the agreement improves.

**Equation (65) is derived on page 157.

benzylamines, XXXIV and XXXV, are expected as products. The ratio of XXXIV to XXXV should be $2:\frac{4+x}{x}$ or 1.20 - 1.27:1.00 where x = 6-7. The products, obtained after removal of the benzylammonium polysulfides, were hydrolyzed with dilute hydrochloric acid. As required by equation (65), the benzylammonium polysulfides and all of the benzylamine formed by hydrolysis of the N-benzylidene benzylamines were unsubstituted; all of the p-methoxy substituent was present in the aldehydes formed from the N-benzylidene benzylamines. Not all of the aldehyde was substituted, however; the ratio of anisaldehyde to benzaldehyde was 1.3:1.0 in excellent agreement with the 1.20 - 1.27 predicted in equation (65).

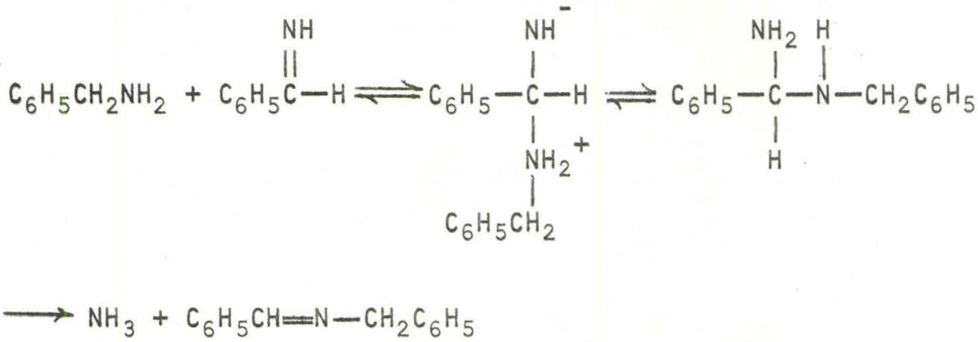
Thus, with a polysulfide chain length of ~6 - 7 as established for the benzylammonium polysulfides in Part I, all aspects of each of the 5 equations (56,57,59,64,65) derived from the proposed scheme (43) to (47) have been quantitatively confirmed experimentally. The reaction scheme with a benzylidenimine polysulfide - benzylamine polysulfide "cycle" is therefore considered to provide a satisfactory explanation of the reaction of sulfur with benzylamine.

CHAPTER VII. CONCLUSIONS

1. AMINE - SULFUR

The scheme given by equations (43) - (47) and shown in Fig. 21 has been established only for benzylamine. Nevertheless, it seems reasonable to expect that other primary amines might follow a similar overall reaction scheme. It has been previously(80) shown that sulfur with a few primary amines, such as butylamine and ethylenediamine, give alkylammonium polysulfides. Sulfur is therefore reduced by these amines, and the amines must be oxidized either to alkylamine polysulfides, alkyledenimine polysulfides or the Schiff's bases.

A detailed reaction mechanism can not be formulated for each step in equations (43) - (47) at this time, but an early step is probably ionic since the rate of formation of benzylidenimine tetrasulfide from benzylamine and sulfur in the presence of a sulfide scavenger was faster in polar solvents than in non-polar solvents. Step (44) is obviously ionic. Step (43) is probably an equilibrium since alkylamine polysulfides have been previously observed to react with hydrogen sulfide to give sulfur and an amine.(85) Step (45) is apparently base catalyzed, a reaction which could involve the weakly acidic N-H protons. This is consistent with the isolation of tetraalkylamine polysulfides from sulfur and secondary amines where the absence of a second N-H would prevent step (45). Step (46) is catalyzed by sulfide ion since benzylidenimine tetrasulfide does not react with benzylamine in the presence of a sulfide scavenger. Without a scavenger, reaction (46) is quite fast. The autocatalytic decomposition of benzylamine disulfide which produced a limited amount of benzylamine in addition to sulfur, and benzylidenimine polysulfide provides some indication of the relative rates of steps (43) and (46) since the latter two materials compete for the limited amount of benzylamine formed. Apparently step (43) is about 50% faster than (46). The final step (47) is probably a nucleophilic addition of benzylamine to the imine carbon followed by a proton shift and elimination of ammonia to give N-benzylidene benzylamine as per equation (66).



$$C_6H_5CH_2NH_2 + C_6H_5\overset{\overset{\displaystyle NH}{\|}}{C}{-}H \rightleftharpoons C_6H_5{-}\overset{\overset{\displaystyle NH^-}{|}}{\underset{\underset{\underset{\displaystyle C_6H_5CH_2}{|}}{\underset{\displaystyle NH_2^+}{|}}}{C}}{-}H \rightleftharpoons C_6H_5{-}\overset{\overset{\displaystyle NH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}CH_2C_6H_5$$

$$\longrightarrow NH_3 + C_6H_5CH{=}N{-}CH_2C_6H_5 \qquad (66)$$

The reaction of benzylamine with sulfur in the presence of lead (II) oxide has some synthetic importance in the preparation of imine polysulfides. Sulfur is a much cheaper starting material than tetrasulfur tetranitride. The reaction conditions are quite mild, and the rate is quite fast. If this synthesis is applicable to other primary amines, it could provide a convenient route for the conversion of primary amines to aldehydes or ketones which could be readily obtained by hydrolysis of the imine polysulfides. This reaction (amine to aldehyde or ketone) is of some current interest.(114)

2. AMMONIA - SULFUR

Since the formation of alkylamine polysulfides is now established as the first step in the reaction of sulfur with both primary and secondary amines, it seems reasonable to attempt to extend the reaction to the sulfur-ammonia system. The products of dissolving sulfur in ammonia might then be expected to be ammonium polysulfides and amine polysulfides, $H_2N{-}S_x{-}NH_2$, or their ionization products, $H_2N{-}S_x{-}NH^-$, as per equation (67). Since (67) is expected to be

$$(x+y)S + 4NH_3 \rightleftharpoons H_2N{-}S_x{-}NH_2 + (NH_4)_2S_y \qquad (67)$$

an equilibrium by analogy with the secondary amine-sulfur systems, evaporation of the ammonia would lead to the recovery of sulfur (as observed). Equation (67) is consistent with the conductivity data since ions are present ($S_y^=$) and a substantial part of the sulfur is in a nonconducting form. It is also consistent with the spectroscopic data since at least two different species are present in equilibrium. [Ionization of the amine polysulfides and changes in x and y with changing sulfur concentration would be expected to result in deviations from Beer's law.] Finally, it should be noted that, while the spectroscopic data has eliminated <u>sulfide</u> ion as a significant species in the liquid ammonia-sulfur system, this data does not rule out <u>polysulfide</u> ions as proposed in (67). The UV spectra of polysulfide ion will, of course, be different from that of the parent monosulfide ion. Thus, equation (67) appears to be consistent with the physical data* and is not necessarily inconsistent

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*The phase diagrams which establish $S:NH_3$ of 3:1 and 6:1 as "stable" compositions would reflect both reactions and <u>solvation</u> of the resulting species.

with the recovery$^{(115)}$ of S_7NH (elimination of NH_3 from the x = 7 species) or of $S_4N_4$$^{(71)}$ when a sulfide scavenger is added.

CHAPTER VIII. EXPERIMENTAL

1. GENERAL

Instruments, solvents and chromatography are as described in Part I.

2. SULFUR WITH BENZYLAMINE IN THE PRESENCE OF LEAD (II) OXIDE

A. RATIO OF SULFUR TO BENZYLAMINE, 3:2

(i) LONG REACTION TIME

Sulfur (1.018 g, 31.8 mg atoms), along with 7.528 g (32.3 mmoles) of lead (II) oxide and 3 ml of benzene, was placed in a 100 ml round-bottomed flask with a magnetic stirring bar. The flask was flushed with dry nitrogen, and 2.2 ml (20.1 mmoles) of benzylamine was added with stirring. The exothermic reaction proceeded smoothly, and the yellow color of the pasty reaction mixture became completely black quite soon. Further color changes could not be observed due to the presence of the lead sulfide. Evolution of a basic gas was observed for 2 ∿ 3 hours. Stirring was continued for about 50 hours at room temperature. The black pasty reaction mixture was filtered, and the filter cake was washed with ether and benzene to give a yellow filtrate. The solvent was removed in vacuo leaving 2.30 g of a deep yellow oil. This was dissolved in about 80 ml of methanol and chilled to give 970 mg of a yellow solid. The NMR spectrum of this solid showed three sharp singlet peaks downfield from a complex phenyl multiplet. The ratio of these three peaks was 2 (-7.87 ppm):5.5 (-8.14 ppm):1 (8.42 ppm). A TLC of this solid showed 3 components with R_f values of 0.46, 0.40 and 0.36 (silica gel - carbon disulfide, with 0.80 for sulfur). This solid was, therefore, a mixture of benzylidenimine tetrasulfide, benzylidenimine trisulfide and benzylidenimine disulfide in molar ratio of 2:1:5.5, respectively. From these ratios the weights of each component were calculated (Table 18).

The solvent (from the mother liquor) was removed in vacuo to give 1.29 g of oil. The TLC and NMR spectra of this oil showed the presence of only two materials identified as N-benzylidene benzylamine [R_f = 0.06 in CS_2; -4.68 ppm (a broad singlet), -8.22 ppm (a broad singlet) and -7.16 ∿ -7.80 ppm (a multiplet) in $CC\ell_4$] and unsymmetrical amine-imine monosulfide* [R_f = 0.15 in CS_2; -3.66 ppm (a broad triplet), -4.30 ppm (a doublet), -7.07 ∿ -7.67 ppm (a multiplet) and -7.77 ppm (a singlet) in $CC\ell_4$]. The molar ratio of N-benzylidene benzylamine to unsymmetrical amine-imine monosulfide was 7:2. Table 18 summarizes the yields of all products.

Table 18. SULFUR WITH BENZYLAMINE (3:2)

	Weight (mg)	No. of mmoles
$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$	263	0.783
$C_6H_5CH{=}N{-}S_3{-}N{=}CHC_6H_5$	119	0.392
$C_6H_5CH{=}N{-}S_2{-}N{=}CHC_6H_5$	588	2.16
$C_6H_5CH{=}N{-}CH_2{-}C_6H_5$	955	4.88
$C_6H_5CH{=}N{-}S{-}\overset{H}{N}{-}CH_2C_6H_5$	336	1.39

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*Complete identification of this material is described on page 125.

(ii) SHORT REACTION TIME

The reaction was repeated with the same molar ratio of reactants but with larger quantities and a shorter reaction time. Sulfur (20.2 g, 632 mg atoms), lead (II) oxide (150 g, 644 mmoles) and benzylamine (40.8 ml, 375 mmoles) were stirred with 60 ml of benzene under a nitrogen atmosphere for 4 hours. The reaction mixture was worked up as described above to give 18.26 g of yellow solid identified as benzylidenimine tetrasulfide (54.4 mmoles) by NMR and TLC. The mother liquor contained N-benzylidene benzylamine and a small amount of the unsymmetrical amine-imine monosulfide. Benzylidenimine tri- and disulfides were not present under these conditions.

B. RATIO OF SULFUR TO BENZYLAMINE, 1:1

Sulfur (984 mg, 30.7 mmoles), lead (II) oxide (9.10 g, 39.0 mmoles) and 10 ml of benzene were placed in a 100 ml three-necked flask with a water cooled condenser. A serum rubber stopper was placed at one of the necks, and the other was connected to a cylinder of dry nitrogen gas. The top of the condenser was connected to a gas washing bottle containing 250 ml of aqueous hydrochloric acid solution (containing 50.0 mg equivalents of acid). The benzylamine used was degassed under vacuum in order to remove any free ammonia which might have been present due to hydrolysis. 3.4 ml (31.2 mmoles) of benzylamine was introduced through the serum stopper by syringe. The reaction mixture was stirred for about 20 hours with a continuous (slow) flow of dry nitrogen.

The acid solution was diluted to 500 ml, and an aliquot was titrated with 0.100 N sodium hydroxide.* 5.00 ml of this acid required 4.535 ml

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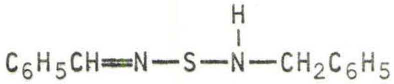
*Prepared from a Concentrated Volumetric Solution produced by British Drug House, Toronto, Ont.

of standard sodium hydroxide solution. 45.35 mg equivalents of acid, therefore, remained unused, and 4.65 mmoles of ammonia was evolved. The reaction mixture was filtered, and the black lead sulfide was washed with ether and benzene. After the removal of solvent, 3.64 g of oil was obtained. The NMR spectrum of the oil showed the following components: benzylidenimine tetrasulfide (molar ratio of 2.83), benzylidenimine disulfide (molar ratio of 1.00), N-benzylidene benzylamine (molar ratio of 6.00), unsymmetrical amine-imine monosulfide (molar ratio of 3.00), unreacted benzylamine (molar ratio of 1.00) and a small amount of solvent ether (molar ratio of 1.83). From the total weight and these molar ratios the yields of products were calculated and are shown in Table 19.

Table 19. SULFUR WITH BENZYLAMINE (1:1)

	Weight (mg)	No. of mmoles
$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$	915	2.72
$C_6H_5CH{=}N{-}S_2{-}N{=}CHC_6H_5$	262	0.965
 $C_6H_5CH{=}N{-}S{-}\overset{\overset{\displaystyle H}{\vert}}{N}{-}CH_2C_6H_5$	698	2.89
$C_6H_5CH{=}N{-}CH_2C_6H_5$	1120	5.75
$C_6H_5CH_2NH_2$ (unreacted)	103	0.965
NH_3	-	4.65

The above data rests on the assumed structure of the unsymmetrical amine-imine monosulfide. This material was isolated and its structure was confirmed as follows. The crude oil was taken up in about 50 ml of methanol and chilled. About 850 mg of benzylidenimine tetrasulfide precipitated and was collected by filtration. Then, a total of 260 mg of benzylidenimine disulfide precipitated in several successive parts. After this, the solution was kept for a few days in a freezer. 350 mg of a white crystalline material precipitated. After recrystallization from methanol, this white solid had a melting point of 58.5 - 59°C. The NMR spectrum of this material in carbon tetrachloride (shown in Fig. 23) consisted of 4 absorptions: a singlet at -7.77 ppm (1.0 H), a multiplet at -7.07 ∿ -7.67 ppm (10.2 H), a doublet at -4.30 ppm (2.0 H; coupling constant, 5.5 cps) and a broad triplet at -3.66 ppm (1.0 H). The infrared spectrum of this solid in carbon tetrachloride is shown in Fig. 24. Bands assignable to -NH stretching at 3360 cm^{-1}, C=N stretching at 1645 cm^{-1} and S-N stretching absorption at 853 cm^{-1} are apparent. The R_f value of this material was 0.154 (silica gel - carbon disulfide, with 0.80 for sulfur). The molecular weight and elemental analysis were also consistent with the structure, $C_6H_5CH{=\!=}N{-}S{-}\overset{H}{N}{-}CH_2C_6H_5$. Anal. Calc. for $C_{14}H_{14}N_2S$: C, 69.39; H, 5.82; N, 11.56; S, 13.23, Mol. Wt. 242. Found: C, 69.92; H, 5.30; N, 11.74; S, 13.65, Mol. Wt. 249.

C. RATIO OF SULFUR TO BENZYLAMINE, 1:2

Sulfur (1.291 g, 40.4 mmoles), 9.10 g (39.0 mmoles) of lead (II) oxide, 8.7 ml (79.8 mmoles) of benzylamine and 15 ml of benzene were stirred in a round-bottomed flask under nitrogen for about 15 hours. Vigorous evolution of ammonia was noted. The products were separated from the lead sulfide in the usual manner. After evaporation of the solvent, 7.48 g of oil was obtained. The NMR spectrum and TLC showed

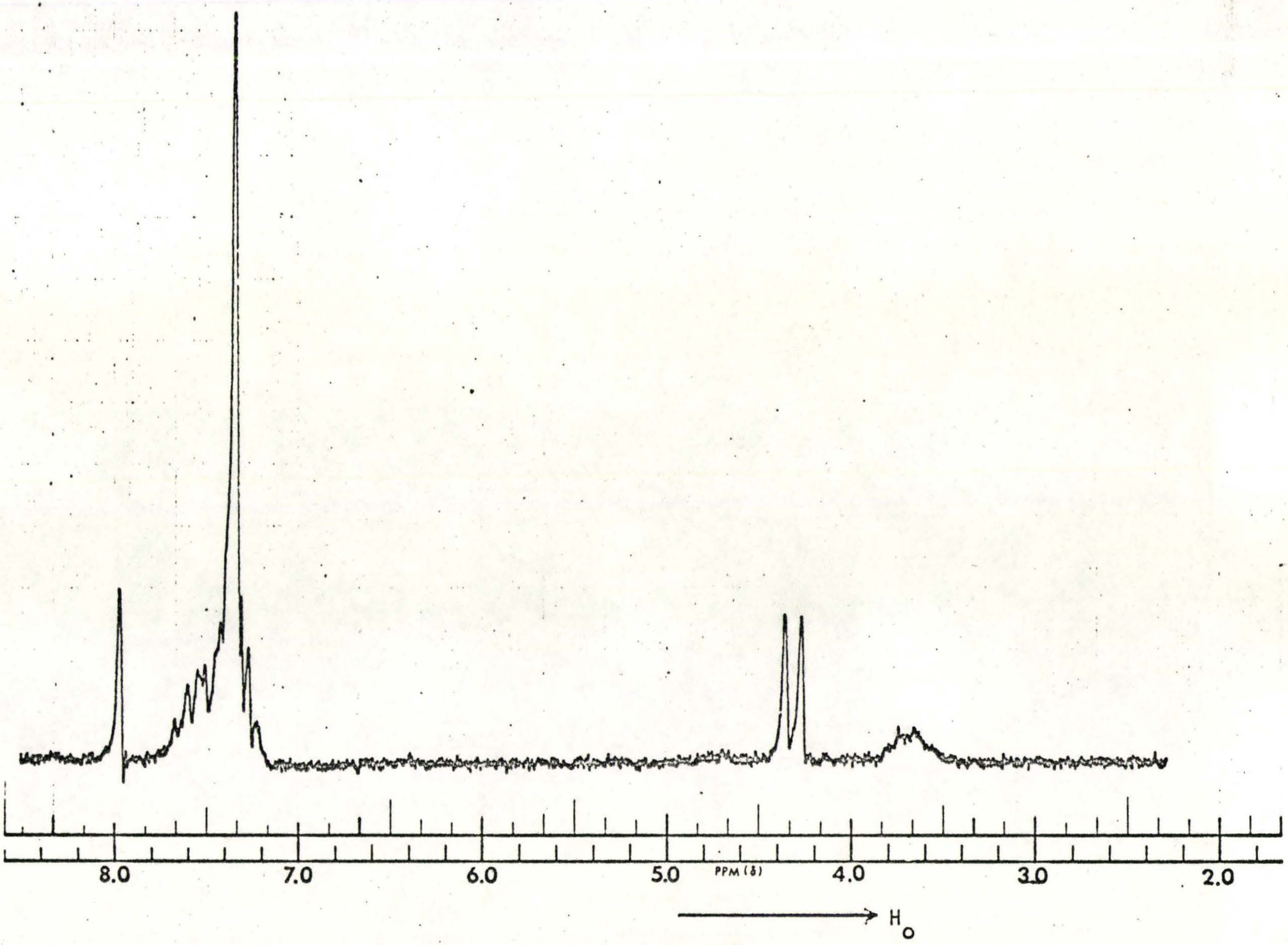


Fig. 23. NMR SPECTRUM OF UNSYMMETRICAL AMINE-IMINE MONOSULFIDE (IN CCl_4)

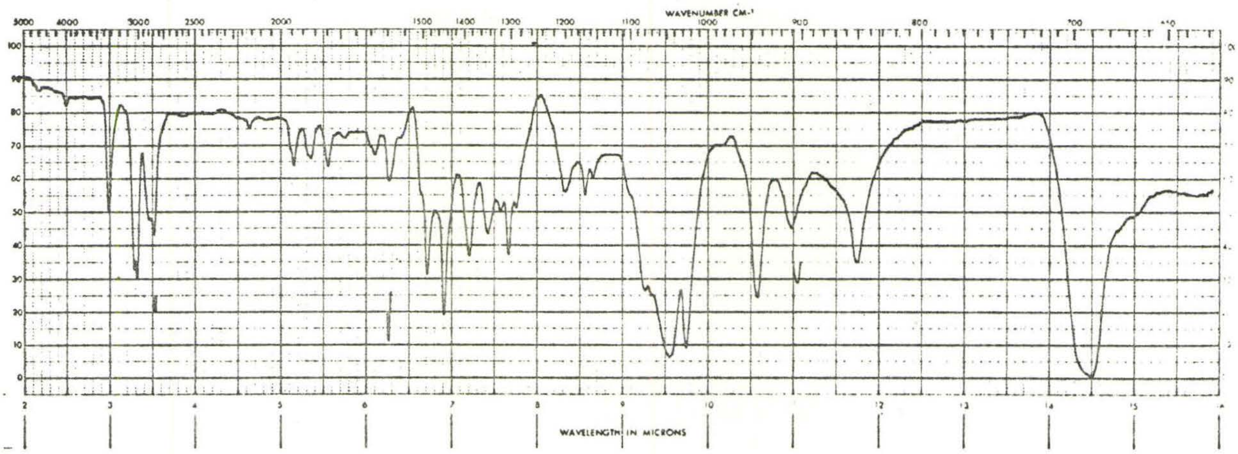


Fig. 24. IR SPECTRUM OF UNSYMMETRICAL AMINE-IMINE MONOSULFIDE (IN $CC\ell_4$)

this oil to consist of 3 components: N-benzylidene benzylamine (molar ratio of 4.0), unsymmetrical monosulfide (molar ratio of 1.0) and unreacted benzylamine (molar ratio of 8.0). From this data, yields of products were calculated as shown in Table 20.*

D. RATIO OF SULFUR TO BENZYLAMINE, 7:2

(i) IN TRIETHYLAMINE

Sulfur (1.034 g, 32.3 mmoles), 3.486 g (15.0 mmoles) of lead (II)

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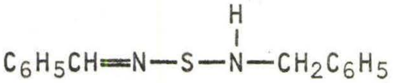
*When this reaction mixture was dissolved in acetone, a reaction occurred and the odor of the solution became very vile. Although the products were not characterized, it was assumed that a Willgerodt-Kindler type reaction had occurred.

Table 20. SULFUR WITH BENZYLAMINE (2:1)

	Weight (mg)	No. of mmoles
$C_6H_5CH{=}N{-}CH_2C_6H_5$	3070	15.7
$C_6H_5CH_2NH_2$	3340	31.2
 $C_6H_5CH{=}N{-}S{-}\overset{\overset{H}{\vert}}{N}{-}CH_2C_6H_5$	2740	3.91

oxide, 1 ml (9.17 mmoles) of benzylamine and 10 ml of triethylamine were stirred together under a dry nitrogen atmosphere at room temperature. After one to two hours the reaction mixture became very black. After 24 hours of stirring, it was filtered, and the lead sulfide washed thoroughly with ether and benzene. As the filtrate was concentrated, a solid precipitated. This was filtered and washed with ether to give 338 mg of a yellow solid identified as pure benzylidenimine tetrasulfide by its TLC and NMR spectra. After the rest of the solvent had been removed, 1.13 g of solid remained. This was dissolved in carbon disulfide, and its NMR spectrum obtained. Five materials were observed: benzylidenimine tetrasulfide (molar ratio of 5.0), benzylidenimine trisulfide (molar ratio of 0.8), benzylidenimine disulfide (molar ratio of 1.0), N-benzylidene benzylamine (molar ratio of 1.0) and an additional small peak[*] at 4.5 cps downfield from benzylidenimine trisulfide (-8.48 ppm). From the molar ratio and the total weight, the quantity of each component was calculated as shown in Table 21.

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[*] This peak is very likely benzylidenimine monosulfide as described in Part I. See page 29.

Table 21. SULFUR WITH BENZYLAMINE (7:2) IN TRIETHYLAMINE

	Weight (mg)	No. of mmoles
$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$	1060	3.17
$C_6H_5CH{=}N{-}S_3{-}N{=}CHC_6H_5$	114	0.375
$C_6H_5CH{=}N{-}S_2{-}N{=}CHC_6H_5$	110	0.405
$C_6H_5CH{=}N{-}S{-}N{=}CHC_6H_5$	43	0.179
$C_6H_5CH{=}N{-}CH_2C_6H_5$	80	0.410

(ii) IN BENZENE

Sulfur (1.030 g, 32.3 mmoles), 3.498 g (15.0 mmoles) of lead (II) oxide, 1 ml (9.17 mmoles) of benzylamine and 10 ml of benzene were stirred together under a nitrogen atmosphere at room temperature for a week. The reaction proceeded much slower than the reaction in triethylamine where sulfur was completely consumed in less than 20 hours as demonstrated by TLC. In benzene, sulfur remained (by TLC) for almost a week at room temperature.

The reaction mixture was filtered, and the lead sulfide was washed thoroughly with ether and benzene. After the solvent was removed, 1.52 g of solid remained. The products were identified, and yields were calculated as before. These are shown in Table 22.

3. SULFUR WITH EXCESS BENZYLAMINE IN THE ABSENCE OF LEAD (II) OXIDE

Sulfur (640 mg, 20.0 mmoles) was placed in a three-necked flask equipped as described on page 123. The wash bottle contained 7.50 mg equivalents of hydrochloric acid. 2.90 g (27.1 mmoles) of benzylamine

Table 22. SULFUR WITH BENZYLAMINE (7:2) IN BENZENE

	Molar Ratio	Weight (mg)	No. of mmoles
$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$	34.0	1128	3.36
$C_6H_5CH{=}N{-}S_3{-}N{=}CHC_6H_5$	4.6	138	0.454
$C_6H_5CH{=}N{-}S_2{-}N{=}CHC_6H_5$	1.0	26.8	0.0985
$C_6H_5CH{=}N{-}S{-}N{=}CHC_6H_5$	3.0	71.1	0.296
$C_6H_5CH{=}N{-}CH_2C_6H_5$	6.5	125	0.642

(degassed under vacuum) was introduced into the reaction flask and stirred at room temperature under a nitrogen atmosphere. Sulfur gradually dissolved giving a brownish-red solution. Stirring was continued for four hours with a relatively rapid flow of nitrogen gas. The reaction mixture was a viscous red solution; no solid was visible. Anhydrous ether was added, and the mixture was stirred for two hours. An orange solid precipitated which was filtered and washed with anhydrous ether. The orange solid was dried in air, and evolution of hydrogen sulfide was noted. After the ether was gone, the orange solid weighed approximately 960 mg. (The weight was not accurate due to continuous decomposition with evolution of H_2S--about 30 $\sim$ 40 mg loss of weight per twenty minutes). The melting point was 90-96°C d in an evacuated sealed tube. After two days it had decomposed into sulfur and benzylammonium thiosulfate. It was, therefore, identified as benzylammonium polysulfide. The ether extract was evaporated under reduced pressure at about 35 - 40°C to give 2.27 g of reddish oil. The NMR spectrum was integrated in the usual manner and led to the data in Table 23.

Table 23. SULFUR WITH EXCESS BENZYLAMINE IN THE ABSENCE OF LEAD (II) OXIDE

	Weight (mg)	No. of mmoles	Ratio
S (reacted)	640	20.0	6.66
$C_6H_5CH_2NH_2$ (consumed)	1430	13.4	4.1
$C_6H_5CH{=}N{-}CH_2C_6H_5$	636	3.26	1.0
NH_3	-	3.00	0.922
$(C_6H_5CH_2NH_3)_2S_x$	1314	3.22(x=6) 3.29(x=7)	0.989 1.01

The acid solution in the gas washing bottle was diluted to 500 ml, and a 50.0 ml aliquot was titrated with 0.100 N sodium hydroxide solution. 4.50 ml of base was required for neutralization. Therefore, 4.50 mg equivalents of acid remained, and 3.00 mg equivalents of ammonia was evolved.

4. BENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE

Benzylidenimine tetrasulfide (1.016 g, 3.03 mmoles) was placed in a 100 ml three-necked flask equipped with a water cooled condenser, a nitrogen inlet, a rubber serum stopper and a washing bottle containing 250 ml of aqueous hydrochloric acid (15.00 mg equivalents of hydrochloric acid). Benzylamine (6.6 ml, 60.5 mmoles) was introduced into the flask through the serum stopper. Benzylidenimine tetrasulfide dissolved immediately in the benzylamine to give a brownish-red solution. The reaction mixture was stirred for about 6 hours with a continuous (slow) flow of nitrogen.

The hydrochloric acid solution in the gas washing bottle was diluted to 500 ml. A 50.0 ml aliquot required 4.82 ml of 0.100 N sodium hydroxide solution for neutralization. Therefore, 4.82 mg equivalents of acid remained, and 10.18 mg equivalents of ammonia were evolved. The reaction mixture was a reddish oil to which 50 ml of anhydrous ether was added. An orange solid precipitated which was filtered and washed with anhydrous ether. This orange solid decomposed fairly rapidly in air with evolution of H_2S to give sulfur and benzylammonium thiosulfate. The melting point of the orange solid in an evacuated sealed tube was 95-97°C. Therefore, this material was identified as benzylammonium polysulfide, $(C_6H_5CH_2NH_3)_2S_x$.

The solvent from the ether solution was removed in vacuo at 40-50°C to give 6.42 g of a reddish oil. The NMR spectrum of this solid indicated the presence of N-benzylidene benzylamine (molar ratio of 1.0) and unreacted benzylamine (molar ratio of 3.73). The yields of products were calculated in the usual manner and are shown in Table 24.

5. BENZYLIDENIMINE TETRASULFIDE WITH BENZYLAMINE IN THE PRESENCE OF LEAD (II) OXIDE

Benzylidenimine tetrasulfide (1.001 g, 3.00 mmoles), 2.714 g (11.6 mmoles) of lead (II) oxide and 15 ml of benzene were placed in a three-necked flask equipped as described above. The gas washing

Table 24. BENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE

	Weight (mg)	No. of mmoles	Ratio
$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$ (used)	1.02	3.03	1.00
$C_6H_5CH_2NH_2$ (used)	3.76	20.2	6.14
$C_6H_5CH{=}N{-}CH_2C_6H_5$	2.10	10.8	3.57
NH_3	-	10.2	3.37
$(C_6H_5CH_2NH_3)_2S_x$	-	-	-

bottle contained 25.00 mg equivalents of hydrochloric acid. Benzylamine (3.9 ml, 35.18 mmoles) was introduced into the flask and stirred for 24 hours. The reaction proceeded slowly, and the mixture became completely black.

After 5 hours the acid solution was diluted to 500 ml. Titration of a 5.0 ml aliquot required 2.26 ml of a 0.100 N sodium hydroxide solution for neutralization. Therefore, 22.6 mg equivalents of hydrochloric acid remained, and only 2.4 mmoles of ammonia were evolved.

The reaction mixture was worked up in the usual way to give 35.9 g of a viscous oil. TLC in carbon disulfide showed benzylidenimine di-, tri- and tetrasulfides along with several other materials of very low R_f values. The NMR spectrum showed a large quantity of unreacted benzylamine, along with benzylidenimine di-, tri- and tetrasulfides and several other unknown peaks.

The reaction products were separated by column chromatography using about 200 g of silica gel. After evaporation of solvents, each fraction was weighed individually, and its TLC was examined. Fractions were combined according to their R_f values. The NMR spectra of the combined fractions were obtained. Products were identified from R_f values and chemical shifts. The integration of the NMR spectra combined with the weights of the fractions gave the yields of products shown in Table 25.

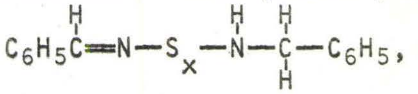
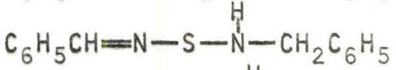
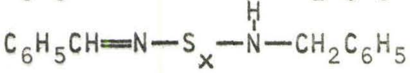
Fractions eluted by ether contained about 75 mg of a mixture of two unfamiliar materials. The NMR spectrum of the mixture indicated that these were probably unsymmetrical amine-imine polysulfides,  $C_6H_5\overset{H}{C}{=}N{-}S_x{-}\overset{H}{N}{-}\underset{H}{\overset{H}{C}}{-}C_6H_5$, with x > 1. Thus, both had a doublet near -4.3 ppm (coupling constant ∿5.5 cps), a broad peak (probably a triplet) near -3.6 ppm and a complex phenyl absorption near -7 ∿ -7.9 ppm, along with a singlet downfield from the phenyl absorption (at -8.3 ppm and at -8.5 ppm).*

Table 25. BENZYLIDENIMINE TETRASULFIDE WITH BENZYLAMINE IN THE PRESENCE OF LEAD (II) OXIDE

	Weight (mg)	No. of mmoles
S	37	1.15†
$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5$	171	0.509
$C_6H_5CH{=}N{-}S_3{-}N{=}CHC_6H_5$	111	0.366
$C_6H_5CH{=}N{-}S_2{-}N{=}CHC_6H_5$	89	0.329
 $C_6H_5CH{=}N{-}S{-}\overset{H}{N}{-}CH_2C_6H_5$	∿ 25	0.10
 $C_6H_5CH{=}N{-}S_x{-}\overset{H}{N}{-}CH_2C_6H_5$	∿ 75	-
$C_6H_5CH{=}N{-}CH_2C_6H_5$	480	2.46
$C_6H_5CH_2NH_2$ (unreacted)	large quantity	
NH_3		2.40

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*Compare with Fig. 22.

†mg atoms.

6. p-METHOXYBENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE

p-Methoxybenzylidenimine tetrasulfide was prepared from p-methoxybenzylamine and S_4N_4 as described in Part I and purified by recrystallization from methanol to give m.p. 112-113°C. 734 mg (1.85 mmoles) was placed in a 100 ml round-bottomed flask with a magnetic stirring bar, and 1.4 ml (12.8 mmoles) of benzylamine was added. The reaction mixture was stirred under a nitrogen atmosphere. After 5 hours, a TLC showed the absence of p-methoxybenzylidenimine tetrasulfide and the presence of new materials whose R_f values were 0.73, 0.38, 0.24 and 0.00 (in $CH_2C\ell_2$). Sulfur, p-methoxybenzylidenimine tetrasulfide, N-benzylidene benzylamine, p-methoxy-N-benzylidene benzylamine and benzylamine have R_f values of 0.73, 0.53, 0.38, 0.24 and 0.00, respectively. These spots, therefore, most probably represent sulfur, p-methoxy-N-benzylidene benzylamine, N-benzylidene benzylamine, and unreacted benzylamine.

About 60 ml of anhydrous ether was introduced into the reaction mixture and stirred for one hour. An orange solid, which was filtered and washed with anhydrous ether, precipitated from the yellowish solution. It had a melting point of 95-97°C d, and when kept in the air for a few days, it decomposed to sulfur and benzylammonium thiosulfate with evolution of hydrogen sulfide. An NMR of the thiosulfate, taken in D_2O, showed three absorptionscorresponding to a benzyl CH_2 group, an NH_3^+ group and a phenyl complex. No evidence for any p-CH_3O group was detected. The orange solid was, therefore, identified as unsubstituted benzylammonium polysulfide.

The ether was removed in vacuo, and an NMR spectrum of the resulting oil was taken (Neat). It showed a complicated phenyl region between

-6.85 ppm ∿ -8.04 ppm, a broad NH_2 peak at -1.87 ppm, a methoxy methyl group at -3.47 ppm, the CH_2 group of benzylamine at -3.87 ppm, an unresolved CH_2 peak for the mixed N-benzylidene benzylamines at -4.74 ppm and the unresolved CH singlets for the mixed N-benzylidene benzylamines at -8.21 ppm.

This reaction mixture was then refluxed for 4 hours with about 50 ml of 5% hydrochloric acid. After cooling, the mixture was extracted with ether.

The aqueous layer was neutralized with base and extracted by ether. The ether layer was dried and evaporated to give a large quantity of oil. The NMR spectrum of this material, taken in deuterochloroform, showed only benzylamine (phenyl peak at -7.38 ppm, CH_2 peak at -3.87 ppm and NH_2 peak at -1.87 ppm). No trace of a methoxy methyl group could be observed.

The ether extract was dried, and the ether was removed in vacuo to give an oil. The NMR spectrum (Neat) of this oil showed 2 aldehyde peaks, anisaldehyde at -9.87 ppm and benzaldehyde at -10.00 ppm, as well as the p-methoxy methyl absorption at -3.74 ppm and a complex phenyl region. The ratio of the two aldehyde peaks, anisaldehyde: benzaldehyde, was approximately 1.5:1. This ratio is higher than the ratio of p-methoxy-N-benzylidene benzylamine to unsubstituted benzylamine since, when the solvent was removed, the more volatile benzaldehyde was more easily lost than p-methoxybenzaldehyde. This ratio changed with the time of stripping solvents and is not considered very accurate. Therefore, to get a better ratio, the NMR spectrum of the crude reaction mixture (before hydrolysis) was examined. This NMR spectrum showed the overlapping CH_2 peak for the two kinds of N-benzylidene benzylamines at -4.74 ppm (peak ratio of 20), and a methoxy methyl peak at -3.47 ppm (peak ratio of 17). The ratio of p-methoxy-N-benzylidene benzylamine to unsubstituted benzylidene benzylamine was calculated as follows:

The relative amount of p-CH_3O BBA* is:

$\frac{1}{3} \times$ (peak ratio of p-CH_3O group) $= \frac{1}{3} \times 17 = 5.67$ (a)

Total amount of BBA* is: $\frac{1}{2} \times$ (molar ratio of CH_2 peak for the two kinds of BBA*) =

$\frac{1}{2} \times 20 = 10.$ (b)

$\therefore$ The relative amount of unsubstituted BBA* is: (b) - (a) = 4.33

Therefore, $\frac{\text{p-CH}_3\text{O BBA}^*}{\text{BBA}^*} = \frac{5.7}{4.3} = 1.3$

7. PREPARATION OF BENZYLAMINE DISULFIDE

A. PRELIMINARY

Freshly distilled sulfur monochloride (1.84 ml, 22.9 mmoles) in 100 ml of anhydrous ether was added dropwise to 10 ml (91.7 mmoles) of benzylamine in 500 ml of anhydrous ether in a 1 liter three-necked flask equipped with a stirrer and calcium chloride drying tube. The flask was kept in an ice bath during the reaction period. A white precipitate (benzylammonium chloride) formed immediately. After about one hour the solution was filtered, and the solvent was removed in vacuo to give a very creamy pale yellow oil. This oil was kept in

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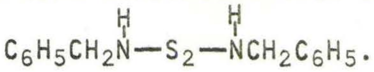
*BBA is an abbreviation of N-benzylidene benzylamine.

the refrigerator for several hours whereupon it solidified. The NMR spectrum in carbon tetrachloride consisted of peaks at -2.75 ppm (broad N-H peak), -4.09 ppm (singlet, CH_2-) and -7.05 ppm (singlet, phenyl-) in the approximate ratio of 1:2:5, respectively. There were some minor additional peaks at -4.00, -4.08 and -4.58 ppm. The major bands were consistent with those expected for benzylamine disulfide,  $C_6H_5CH_2\overset{H}{N}{-}S_2{-}\overset{H}{N}CH_2C_6H_5$.

During the time the NMR spectrum was taken, the crude reaction mixture was left on the bench top at room temperature (30 minutes). During this period a very vigorous exothermic reaction occurred with the evolution of ammonia, and the reaction mixture became reddish. Hexane precipitated a yellow solid which, after filtration, was found to be a mixture of benzylidenimine tetrasulfide and sulfur. The hexane solution contained N-benzylidene benzylamine.

B. TRIMETHYLAMINE AS ACID SCAVENGER

The preparation of benzylamine disulfide was repeated using trimethylamine as an acid scavenger. This time evaporation of the filtrate gave a yellow oil whose NMR spectrum showed many peaks. A TLC showed benzylidenimine tetrasulfide as a major product. In this reaction the amount of trimethylamine is in substantial excess. It may have led to the decomposition of the products.

C. CHARACTERIZATION OF BENZYLAMINE DISULFIDE.

The preparation was repeated under almost identical conditions (as in A) but with a slight excess (2 $\sim$ 3%) of sulfur monochloride. Evaporation of the filtrate from 10.0 ml (91.7 mmoles) of benzylamine and 1.9 ml of sulfur monochloride (23.6 mmoles) gave a creamy pale

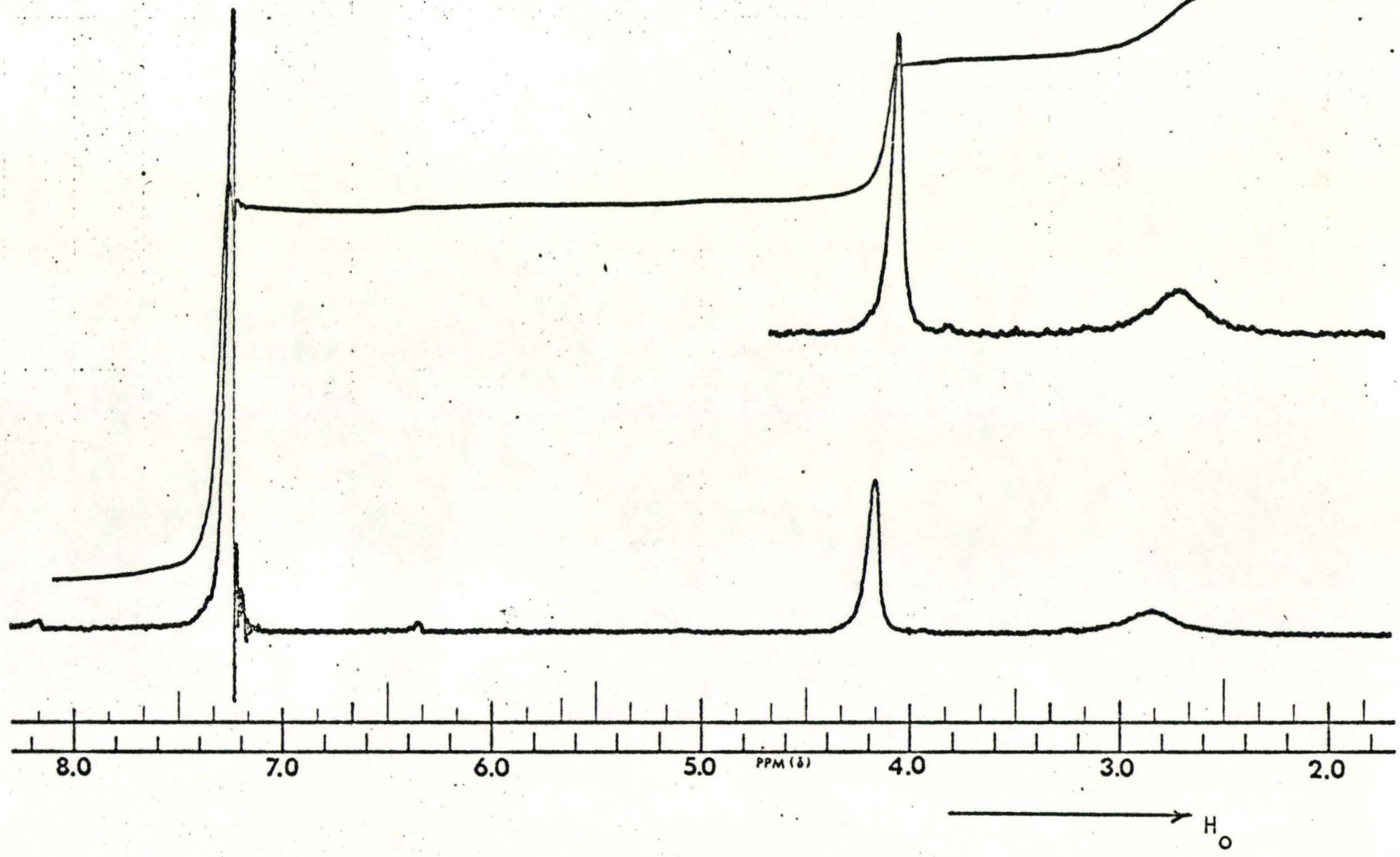
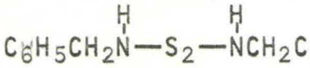


Fig. 25. NMR SPECTRUM OF BENZYLAMINE DISULFIDE (IN $CDCl_3$)

yellow oil. This oil was dissolved in hexane at 30-40°C. On cooling to ice temperature, a white solid of m.p. 50-51°C was obtained. Further recrystallization from pentane gave 1.68 g of white solid of m.p. 52.5-53°C. The NMR spectrum shown in Fig. 25 consisted of bands at -2.75 ppm (broad, -NH), -4.09 ppm (singlet, $-CH_2$) and at -7.05 ppm (singlet, phenyl-) in the ratio of 1.00:1.91:4.92, respectively. The IR spectrum (Fig. 26) showed an N-H stretching absorption at 3334 cm^{-1} and an S-N stretching frequency at 850 cm^{-1}. An R_f value could not be obtained accurately since this compound decomposed on the silica gel plate to give a streak (R_f = ∿0.05). This compound was consequently identified as benzylamine disulfide,  $C_6H_5CH_2\overset{H}{N}—S_2—\overset{H}{N}CH_2C_6H_5$. Anal. Calcd. for $C_{14}H_{16}N_2S_2$: C, 60.83; H, 5.83; N, 10.13; S, 23.20; Mol. Wt. 276. Found: C, 60.93; H, 5.53; N, 9.93; S, 23.42; Mol. Wt. 270.

Pure benzylamine disulfide (m.p. 52.5-53°C) and less pure material (m.p. 51-52°C) were kept under vacuum in a drying apparatus at room temperature for 5 ∿ 6 hours. The pure material decomposed into a mixture of benzylidenimine polysulfides, N-benzylidene benzylamine and sulfur. The impure material also decomposed but more slowly. Pure benzylamine disulfide could be stored at -20°C for several weeks, but eventual decomposition occurred even at this temperature. The impure material could be kept for a much longer period.

Benzylamine disulfide in a melting point capillary was heated to 75° and cooled down. The oil solidified and remelted at 53°C. When it was heated above 100°C, however, decomposition occurred with evolution of gas. A TLC of this decomposed material showed sulfur,

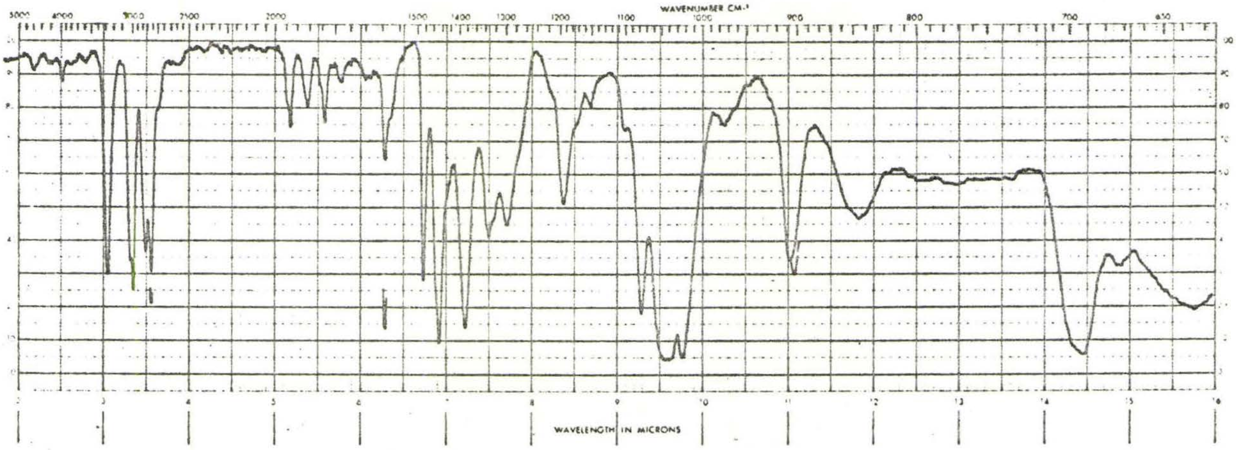


Fig. 26. IR SPECTRUM OF BENZYLAMINE DISULFIDE

benzylidenimine tetra-, tri- and disulfides and N-benzylidene benzylamine. Evaporation of the mother liquor gave 3.0 g of oil whose NMR spectrum indicated the presence of benzylamine disulfide, N-benzylidene benzylamine and other unidentified materials.

8. REACTION OF BENZYLAMINE DISULFIDE WITH BENZYLAMINE

Benzylamine disulfide (60 mg, 0.22 mmoles) in 1 ml of benzene was stirred with two drops (∿35 mg, ∿0.33 mmoles) of benzylamine under a nitrogen atmosphere. The color became greenish, then pale yellow and in 15-30 minutes rather reddish. The solvent was removed in vacuo, and an NMR spectrum of the mixture was taken in $CDC\ell_3$.

Peaks corresponding to benzylamine, N-benzylidene benzylamine and benzylidenimine tetrasulfide were observed. The presence of these materials was confirmed by TLC.

9. DECOMPOSITION OF BENZYLAMINE DISULFIDE

A. DECOMPOSITION

Benzylamine disulfide (248 mg, 0.894 mmoles) was stirred under a (slow) flow of nitrogen gas. The outlet was connected to a gas washing bottle containing aqueous hydrochloric acid (1.00 mg equivalent of hydrochloric acid). The white solid slowly changed color, and in about 2 hours it became pasty. After 5 hours the reaction mixture was a yellow oil which contained a precipitate. The precipitate was filtered and washed with small amounts of anhydrous ether to give 22 mg of elemental sulfur. The solvent was removed in *vacuo* to give 196 mg of oil whose NMR spectrum showed 3 materials: benzylidenimine tetrasulfide, N-benzylidene benzylamine and benzylammonium polysulfide in the ratio of 2:20.5:2, respectively. From these data the yields of products were calculated (Table 26).

Table 26. DECOMPOSITION OF BENZYLAMINE DISULFIDE

	Weight (mg)	No. of mmoles
S	22	0.688*
$C_6H_5CH{=}N-S_4-N{=}CHC_6H_5$	23.8**	0.071**
$C_6H_5CH{=}N-CH_2C_6H_5$	142**	0.729**
$(C_6H_5CH_2NH_3)_2S_x$	31.3**	0.072**
NH_3	-	0.715***

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* mg atoms.

** Obtained from NMR with the assumption of $x = 7$. The molar ratio of ammonia plus N-benzylidene benzylamine to benzylidenimine tetrasulfide plus benzylammonium polysulfide does not change more than 3% if x is assumed to be 6 or 8.

*** 2.08 ml of 0.100 N NaOH was required for 1/5 of acid solution.

B. NMR STUDY

The course of the decomposition of benzylamine disulfide to benzylidenimine tetrasulfide, N-benzylidene benzylamine and sulfur was monitored by NMR spectroscopy. 262 mg (0.964 mmoles) of pure benzylamine disulfide (m.p. 52-53°C) was stirred under a nitrogen atmosphere. After 2 hours, no change was observed. After three hours, the solid had become slightly pale yellow and very slightly sticky. After five hours, although there was still no big change, about 25 mg of solid was removed, dissolved in 0.5 ml of $CDC\ell_3$ and an NMR spectrum taken (Fig. 27). In addition to peaks for benzylamine disulfide (-2.75 ppm, -4.09 ppm and -7.05 ppm), an additional new peak at -3.81 ppm appeared.

The yellow color of the solid became more intense and pasty. After 6 hours (total time), another 25 mg sample was withdrawn, dissolved in 0.5 ml of $CDC\ell_3$ and an NMR spectrum taken (Fig. 28). In addition to peaks for benzylamine disulfide, several new peaks were observed. The most important aspect of the spectra was that the peak at -3.85 ppm had increased and a broad peak appeared near -1.80 ppm. These two peaks were benzylamine.

After 6.5 hours (total time), the reaction mixture had become less viscous and appeared to be a reddish oil. Another 25 mg aliquot was treated as before (Fig. 29). During this 30 minute period very drastic changes had occurred. Benzylamine disulfide had decomposed completely. Two peaks at -1.42 ppm and -3.87 ppm assigned to benzylamine were present along with two peaks at -4.78

ppm and -8.20 ppm assigned to N-benzylidene benzylamine (see Table 1, page 19). A peak at -7.85 ppm assigned to benzylidenimine tetrasulfide was also present. In addition, peaks at -4.24 ppm (doublet) and -8.30 ppm due to an unsymmetrical imine-amine sulfide were observed. A TLC of this solution showed sulfur (R_f = 0.80, silica gel - carbon disulfide), benzylidenimine tetrasulfide (R_f = 0.375), N-benzylidene benzylamine (R_f = 0.07) and other materials of very small R_f value.

After 8 hours, the reaction mixture was a yellowish oil with a small amount of precipitate. A 25 mg aliquot treated as above gave Fig. 30. Benzylammonium ions (CH_2- group at -3.92 ppm and $-NH_3^+$ peak at -1.77 ppm, ratio of 2:2.75, respectively), N-benzylidene benzylamine ($-CH_2$ group at -4.85 ppm and CH=N group at -8.21 ppm) and benzylidenimine tetrasulfide (-CH= group at -8.21 ppm) were identified in the NMR spectrum.

After 13 hours, a final NMR spectrum was taken. The species observed were the same as after 8 hours, but the ratio was somewhat different. N-benzylidene benzylamine had increased while benzylamine and benzylidenimine tetrasulfide had decreased.

10. DERIVATION OF EQUATIONS

In this section the proposed relationships (43) to (47) are combined into a set of overall equations which predict the consequences of mixing the various intermediates or starting materials in the benzylamine-sulfur system. These are the stoichiometric equations subjected to experimental verification in Chapter VI. Before deriving these equations, three useful relationships are noted. First, all hydrogen sulfide formed in the

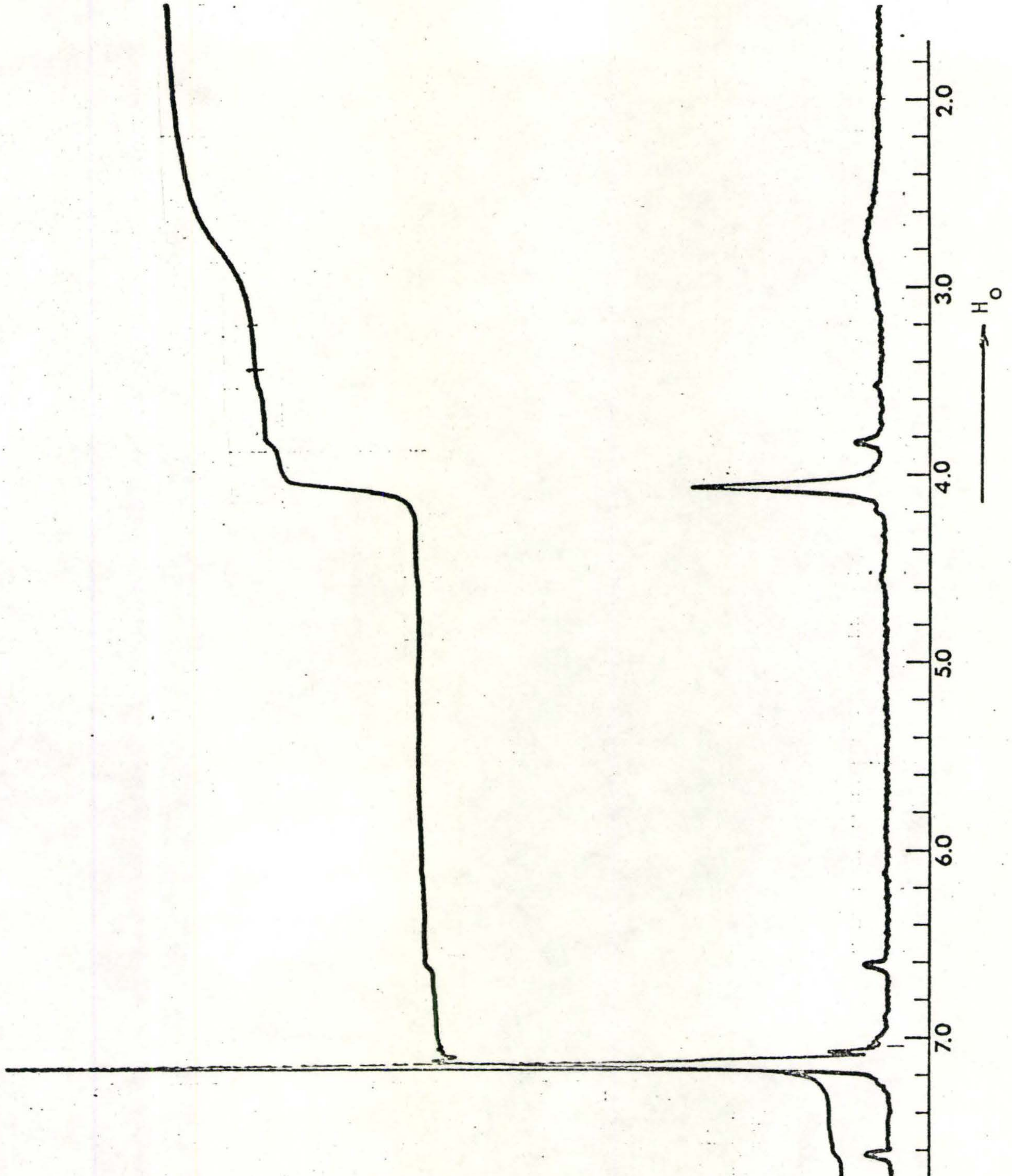


Fig. 27. DECOMPOSITION OF BENZYLAMINE DISULFIDE AT 5 HOURS (IN $CDCl_3$)

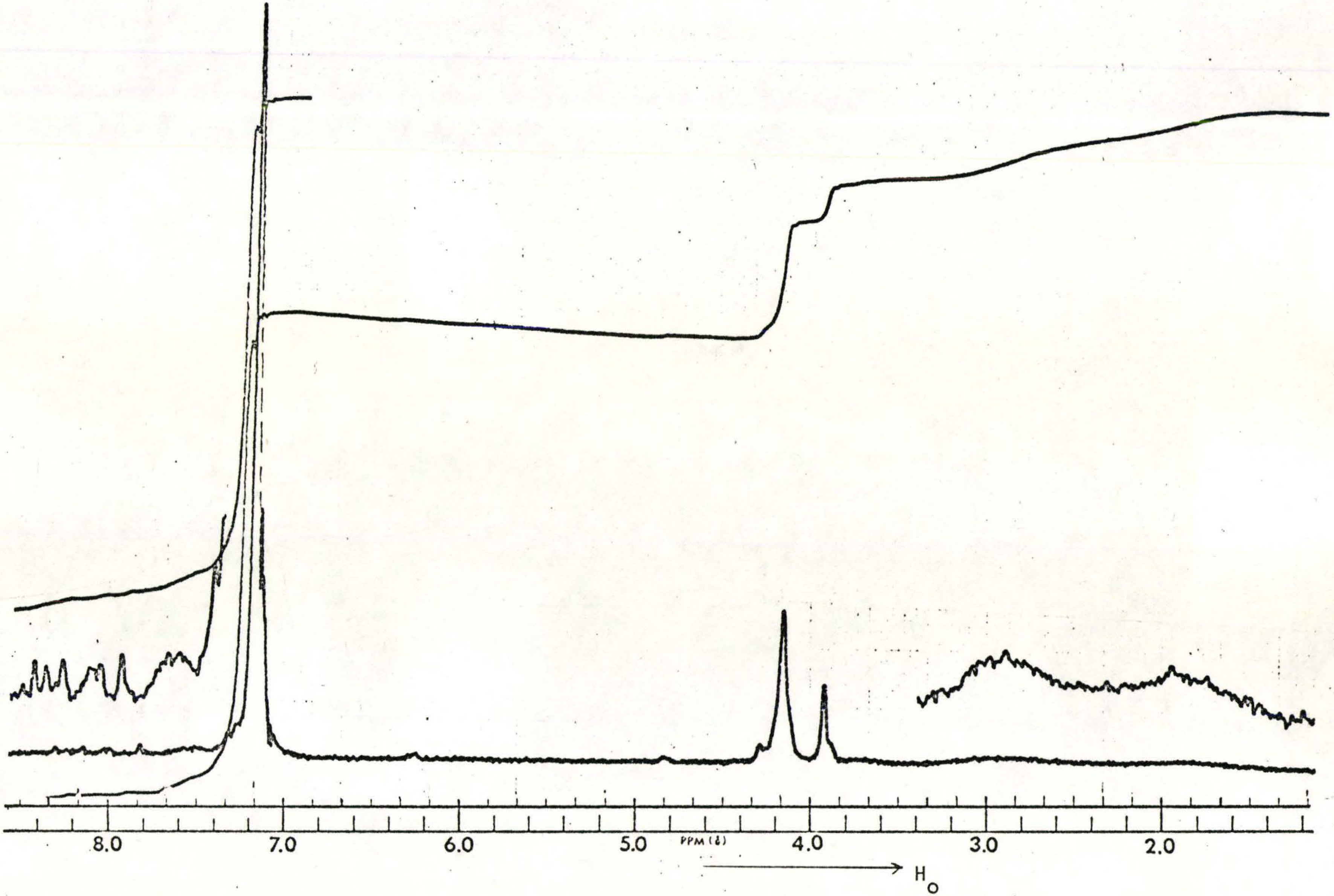


Fig. 28. DECOMPOSITION OF BENZYLAMINE DISULFIDE AT 6 HOURS (IN $CDC\ell_3$)

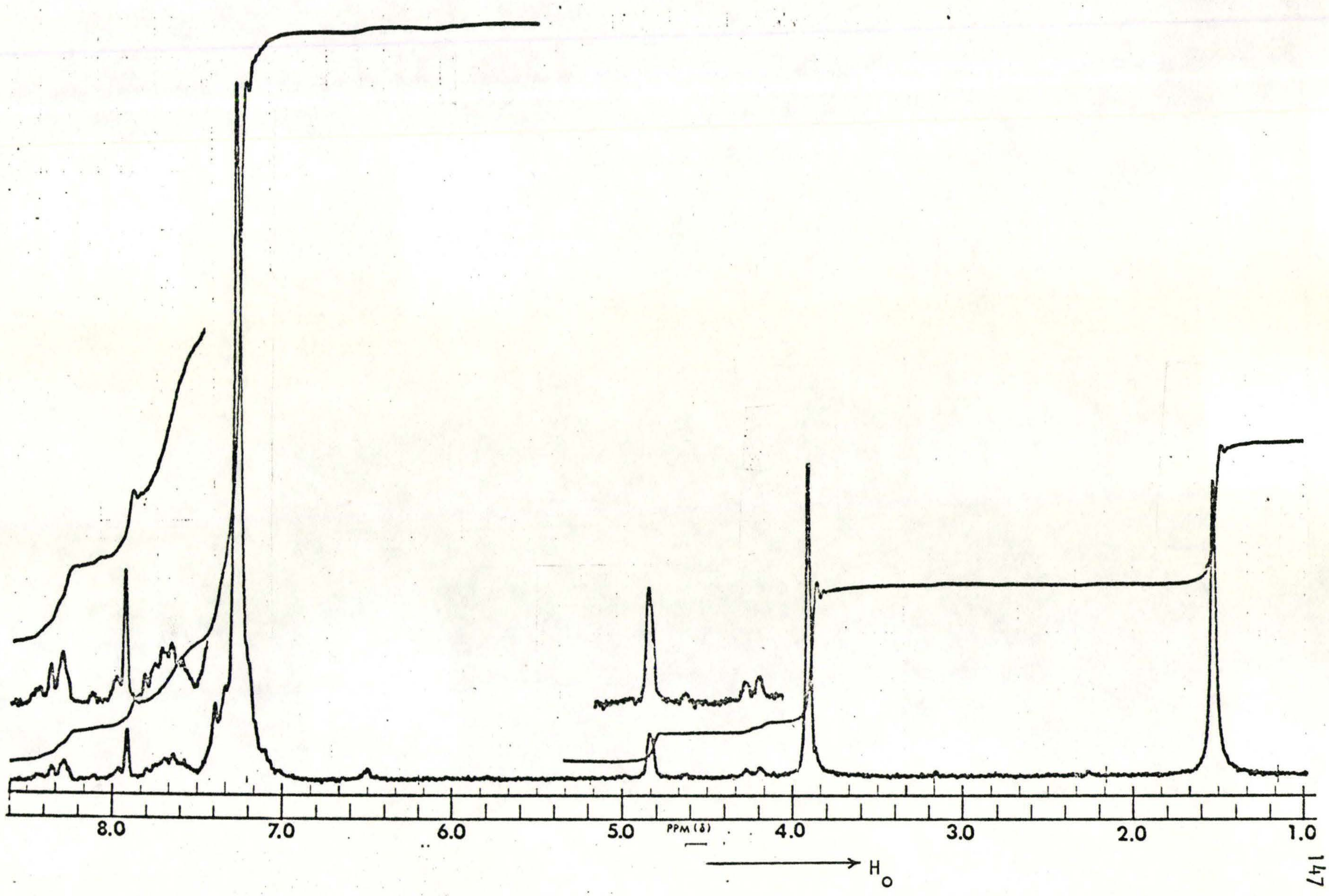


Fig. 29. DECOMPOSITION OF BENZYLAMINE DISULFIDE AT 6.5 HOURS (IN CDCℓ_3)

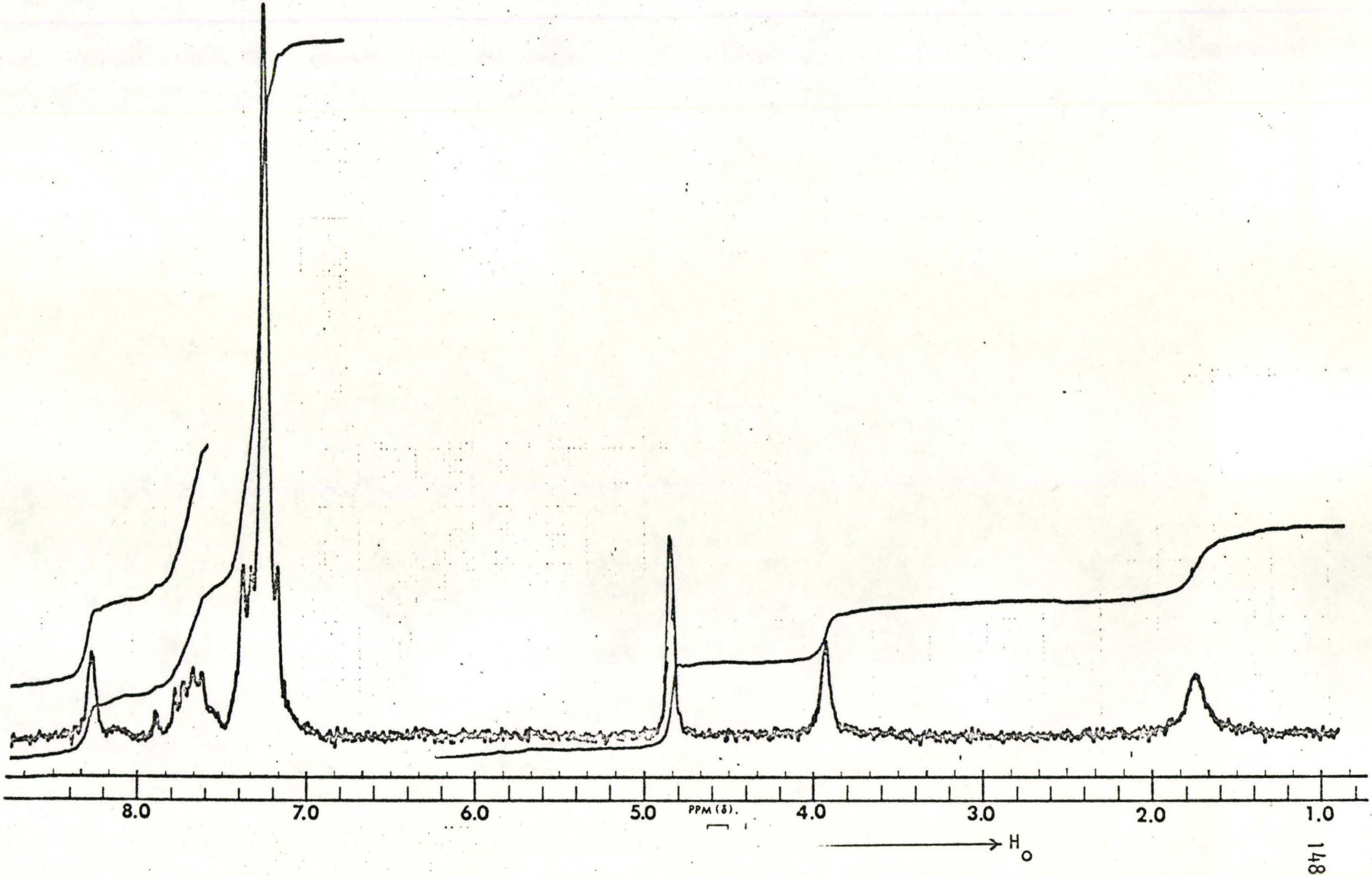
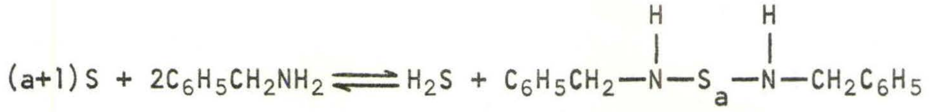


Fig. 30. DECOMPOSITION OF BENZYLAMINE DISULFIDE AT 8 HOURS (IN $CDCl_3$)

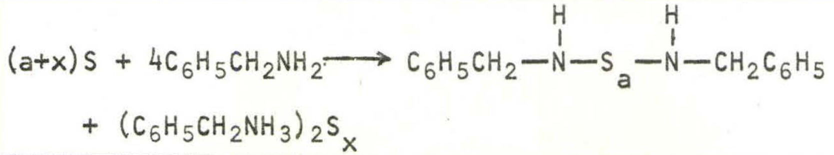
presence of benzylamine (since hydrogen sulfide is formed only from benzylamine, it cannot be formed in the <u>absence</u> of benzylamine) goes immediately to benzylammonium polysulfides. Therefore, (43) and (44)



$$(a{+}1)\mathrm{S} + 2\mathrm{C_6H_5CH_2NH_2} \rightleftharpoons \mathrm{H_2S} + \mathrm{C_6H_5CH_2}-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{S}_a-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2C_6H_5} \qquad (43)$$

$$(x{-}1)\mathrm{S} + 2\mathrm{C_6H_5CH_2NH_2} + \mathrm{H_2S} \longrightarrow (\mathrm{C_6H_5CH_2NH_3})_2\mathrm{S}_x \qquad (44)$$

may be combined (added) so as to eliminate H_2S and give equation (68).

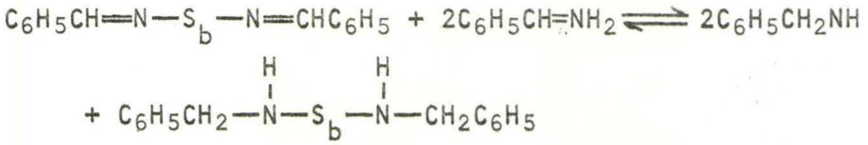


$$\boxed{\begin{gathered}(a{+}x)\mathrm{S} + 4\mathrm{C_6H_5CH_2NH_2} \longrightarrow \mathrm{C_6H_5CH_2}-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{S}_a-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2C_6H_5} \\ + (\mathrm{C_6H_5CH_2NH_3})_2\mathrm{S}_x \qquad (68)\end{gathered}}$$

Second, since benzylidenimine was neither isolated nor detected, it must react with benzylamine (47) fairly rapidly compared to the various other reactions in the system. Here again, it should be noted that

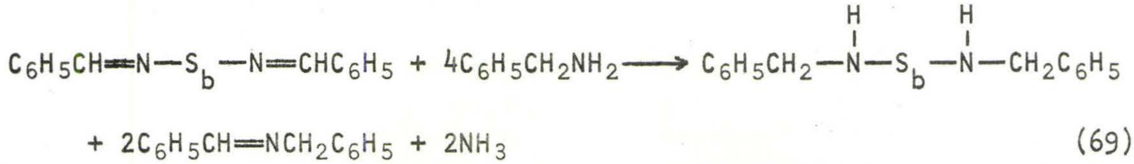
$$\mathrm{C_6H_5CH{=}NH} + \mathrm{C_6H_5CH_2NH_2} \longrightarrow \mathrm{C_6H_5CH{=}N{-}CH_2C_6H_5} + \mathrm{NH_3} \qquad (47)$$

benzylidenimine is formed only from benzylamine (46) and hence cannot



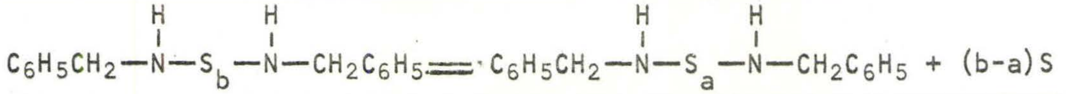
$$\begin{gathered}\mathrm{C_6H_5CH{=}N}-\mathrm{S}_b-\mathrm{N{=}CHC_6H_5} + 2\mathrm{C_6H_5CH{=}NH_2} \rightleftharpoons 2\mathrm{C_6H_5CH_2NH} \\ + \mathrm{C_6H_5CH_2}-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{S}_b-\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2C_6H_5} \qquad (46)\end{gathered}$$

be formed in the absence of benzylamine. (Alternately and equally good, the equilibrium represented by equation (46) lies far to the left.) Since benzylidenimine is never a final product, (46) and (47) may be combined to eliminate benzylidenimine [twice (47) added to (46)] as in (69). Finally, it should be noted that the benzylamine



$$C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2{-}\overset{H}{N}{-}S_b{-}\overset{H}{N}{-}CH_2C_6H_5 + 2C_6H_5CH{=}NCH_2C_6H_5 + 2NH_3 \qquad (69)$$

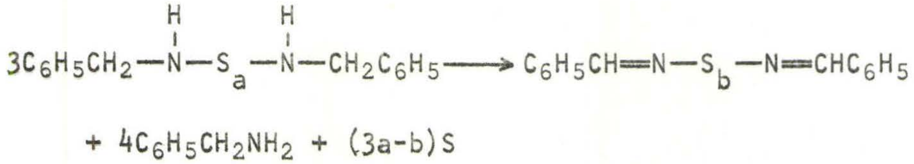
polysulfides formed in (43) have a different sulfur chain length than those formed in (46). Since the chain length is variable in both places, this does not pose a chemical problem. However, the derivation of equations is very much simpler if these two benzylamine polysulfides can be related. Equation (70) is proposed for this purpose. This equation is solely a computational artifact and need not reflect a real chemical process. Indeed, free sulfur could be formed or consumed in (45) or (46). It could also be formed by decomposition of (or consumed by addition to) either benzylamine polysulfides or benzylidenimine polysulfides or by any combination of these processes. The result is the same and is accounted for by equation (70).



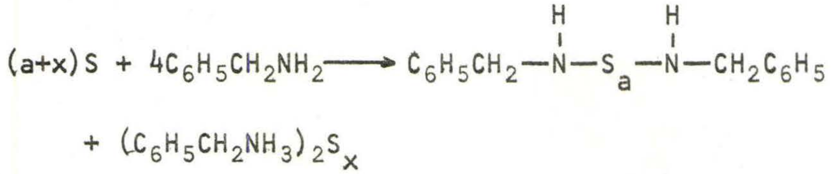
$$C_6H_5CH_2{-}\overset{H}{N}{-}S_b{-}\overset{H}{N}{-}CH_2C_6H_5 \rightleftharpoons C_6H_5CH_2{-}\overset{H}{N}{-}S_a{-}\overset{H}{N}{-}CH_2C_6H_5 + (b-a)S \qquad (70)$$

A. SULFUR WITH EXCESS BENZYLAMINE: EQUATION (56)

To derive the overall equation for the reaction of sulfur with excess benzylamine, it is necessary to eliminate both benzylamine polysulfides and benzylidenimine polysulfides. The former may be eliminated by adding (45) to three times (68) to give equation (71).



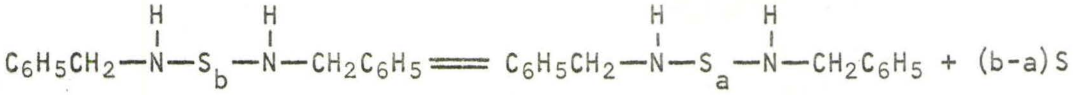
$$3C_6H_5CH_2{-}\overset{H}{N}{-}S_a{-}\overset{H}{N}{-}CH_2C_6H_5 \longrightarrow C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 + (3a-b)S \qquad (45)$$



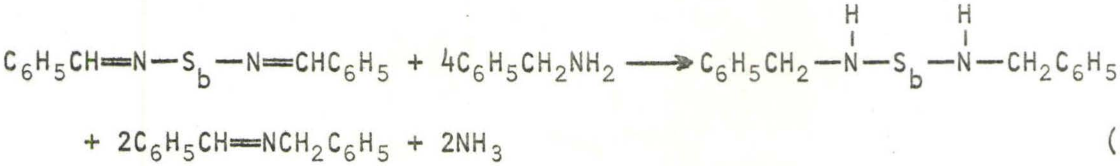
$$(a+x)S + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2-\overset{\overset{H}{|}}{N}-S_a-\overset{\overset{H}{|}}{N}-CH_2C_6H_5 + (C_6H_5CH_2NH_3)_2S_x \qquad (68)$$

$$(3x+b)S + 8C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 3(C_6H_5CH_2NH_3)_2S_x \qquad (71)$$

The benzylidenimine polysulfides can now be eliminated from (71) by the following procedure. First, equation (70) is combined with (69)

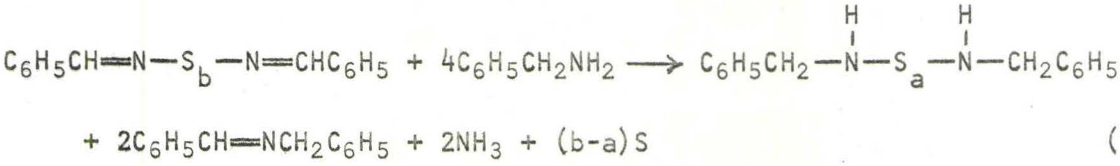


$$C_6H_5CH_2-\overset{\overset{H}{|}}{N}-S_b-\overset{\overset{H}{|}}{N}-CH_2C_6H_5 =\!=\!= C_6H_5CH_2-\overset{\overset{H}{|}}{N}-S_a-\overset{\overset{H}{|}}{N}-CH_2C_6H_5 + (b-a)S \qquad (70)$$



$$C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2-\overset{\overset{H}{|}}{N}-S_b-\overset{\overset{H}{|}}{N}-CH_2C_6H_5 + 2C_6H_5CH{=}NCH_2C_6H_5 + 2NH_3 \qquad (69)$$

to give equation (72). The benzylamine polysulfides in (72) are now



$$C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2-\overset{\overset{H}{|}}{N}-S_a-\overset{\overset{H}{|}}{N}-CH_2C_6H_5 + 2C_6H_5CH{=}NCH_2C_6H_5 + 2NH_3 + (b-a)S \qquad (72)$$

the same benzylamine polysulfides which appeared in (45) and may be eliminated by adding (45) to three times (72) to give (73). Equation

$$2C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 8C_6H_5CH_2NH_2 \longrightarrow 6(NH_3 + C_6H_5CH{=}NCH_2C_6H_5) + 2bS \qquad (73)$$

(73) is reducible by a factor of 2; this, when combined with equation (71), gives (after rearranging the coefficients--dividing by 3x) the overall reaction as in equation (56).

$$\boxed{\begin{aligned}&S + \frac{4}{x}\, C_6H_5CH_2NH_2 \longrightarrow \frac{1}{x}\, NH_3 + \frac{1}{x}\, C_6H_5CH{=}N{-}CH_2C_6H_5\\ &\qquad + \frac{1}{x}\, (C_6H_5CH_2NH_3)_2S_x \qquad\qquad (56)\end{aligned}}$$

B. SULFUR WITH BENZYLAMINE IN THE PRESENCE OF A SULFIDE SCAVENGER: EQUATION (57)

In the presence of lead (II) oxide (46) is blocked. Reaction (44) cannot occur since any hydrogen sulfide formed is converted to lead sulfide. Thus, it is only necessary to eliminate the benzylamine polysulfides from equations (43) and (45). This is done by adding (45) to three times (43) to give (57).

$$\boxed{(3{+}b)S + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + 3H_2S \qquad (57)}$$

C. BENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE: EQUATION (59)

This situation is nearly covered by (73) derived above. The 2bS

$$\begin{aligned}&2C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + 8C_6H_5CH_2NH_2 \longrightarrow 6(NH_3 + C_6H_5CH{=}NCH_2C_6H_5)\\ &\qquad + 2bS \qquad\qquad (73)\end{aligned}$$

formed in (73) will react in the presence of the excess benzylamine according to equation (56). Dividing equation (73) by 2 and adding it to equation (56) multiplied by (b) eliminates the sulfur to give equation (74). Since the starting material is the tetrasulfide, b = 4. Rewriting

$$\begin{aligned}&C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + \frac{4b+4x}{x}\, C_6H_5CH_2NH_2 \longrightarrow \frac{b}{x}\, (C_6H_5CH_2NH_3)_2S_x\\ &\qquad + \frac{3x+b}{x}\, (C_6H_5CH{=}NCH_2C_6H_5 + NH_3) \qquad\qquad (74)\end{aligned}$$

equation (74) with b = 4 gives equation (59).

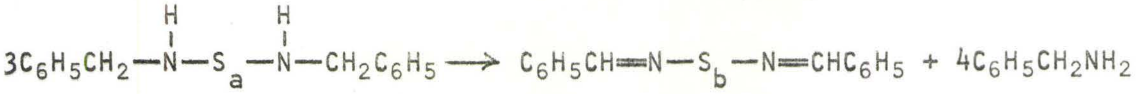
$$C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 + \frac{16+4x}{x}\, C_6H_5CH_2NH_2 \longrightarrow \frac{4}{x}\,(C_6H_5CH_2NH_3)_2S_x + \frac{3x+4}{x}\,(C_6H_5CH{=}NCH_2C_6H_5 + NH_3) \qquad (59)$$

D. DECOMPOSITION OF BENZYLAMINE DISULFIDE

Two assumptions are inherent in the derivation of the previous equations. First, equations (43) - (47) must hold, and second there must be an excess of benzylamine [not necessary for equation (57) only]. In the decomposition of benzylamine disulfide benzylidenimine polysulfides and sulfur are produced with a limited amount of benzylamine. Since the latter reacts with both of the former, it is necessary to consider the relative rates of the two reactions--a factor which is not relevant to the previous derivations. Two limiting cases will be considered; the first where benzylamine reacts with sulfur much faster than it does with the benzylidenimine polysulfides, and the second where the benzylidenimine polysulfides react much faster than the sulfur.

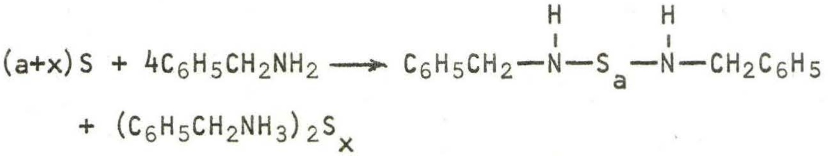
(i) LIMITING CASE 1: SULFUR REACTS VERY FAST (EQUATION 62)

Benzylidenimine polysulfides decompose according to equation (45)



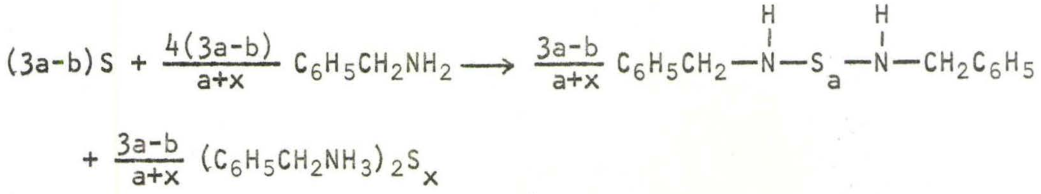
$$3C_6H_5CH_2{-}\overset{H}{N}{-}S_a{-}\overset{H}{N}{-}CH_2C_6H_5 \longrightarrow C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 + (3a-b)S \qquad (45)$$

to give benzylamine, sulfur and benzylidenimine polysulfides. The reaction of (3a-b) sulfurs with 4 benzylamines must now be considered. This reaction is given by equation (68). For the values of a, b and x relevant to this case [a = 2 since the starting material is the

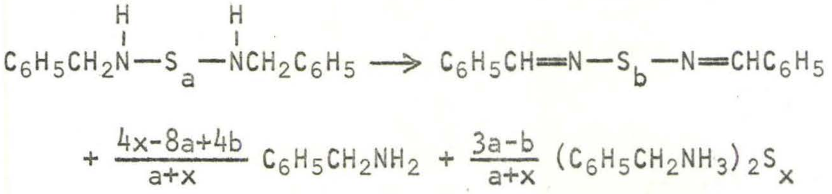


$$(a+x)S + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2-\overset{H}{N}-S_a-\overset{H}{N}-CH_2C_6H_5 + (C_6H_5CH_2NH_3)_2S_x \qquad (68)$$

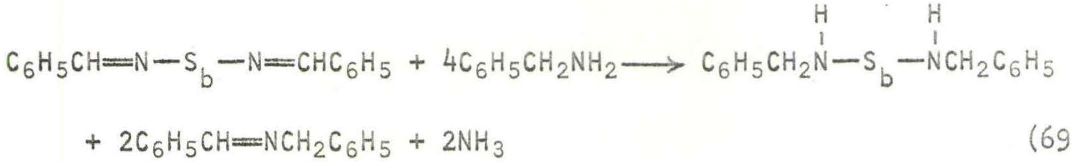
disulfide, b ≈ 4 and x = 6 - 7], it is apparent that $3a-b < a+x$. Therefore, reaction (68) is limited by the quantity of sulfur present not by the quantity of benzylamine. Multiplying (68) by $(3a-b)/(a+x)$ gives equation (75) which can then be added to (45) to eliminate the sulfur as in equation (76). The excess benzylamine can now react with the benzylidenimine polysulfides. This should be according to (69).



$$(3a-b)S + \frac{4(3a-b)}{a+x} C_6H_5CH_2NH_2 \longrightarrow \frac{3a-b}{a+x} C_6H_5CH_2-\overset{H}{N}-S_a-\overset{H}{N}-CH_2C_6H_5 + \frac{3a-b}{a+x} (C_6H_5CH_2NH_3)_2S_x \qquad (75)$$

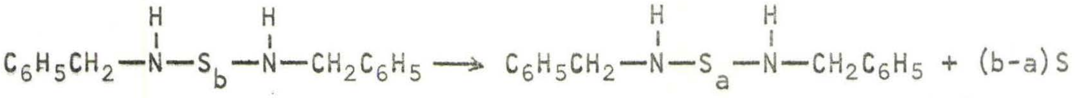


$$C_6H_5CH_2\overset{H}{N}-S_a-\overset{H}{N}CH_2C_6H_5 \longrightarrow C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + \frac{4x-8a+4b}{a+x} C_6H_5CH_2NH_2 + \frac{3a-b}{a+x} (C_6H_5CH_2NH_3)_2S_x \qquad (76)$$

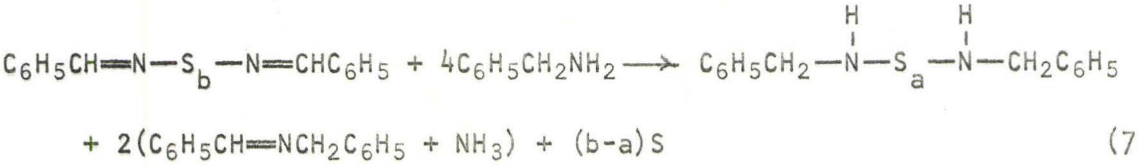


$$C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2\overset{H}{N}-S_b-\overset{H}{N}CH_2C_6H_5 + 2C_6H_5CH{=}NCH_2C_6H_5 + 2NH_3 \qquad (69)$$

However, this equation cannot be combined with (76) since the benzylamine polysulfides have different chain lengths. Therefore, it is first necessary to modify (69) by adding (70) to give equation (77). Unfortun-

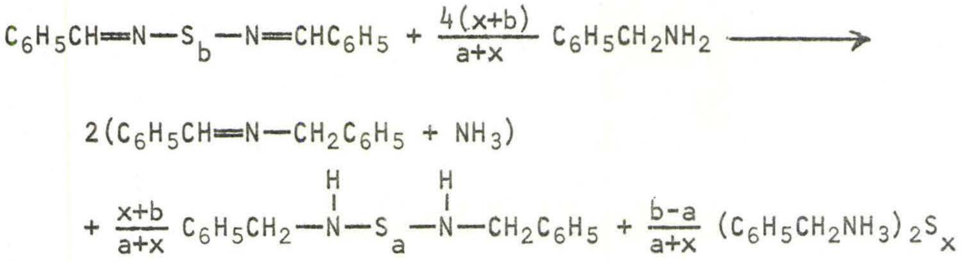


$$C_6H_5CH_2-\overset{H}{N}-S_b-\overset{H}{N}-CH_2C_6H_5 \longrightarrow C_6H_5CH_2-\overset{H}{N}-S_a-\overset{H}{N}-CH_2C_6H_5 + (b-a)S \qquad (70)$$



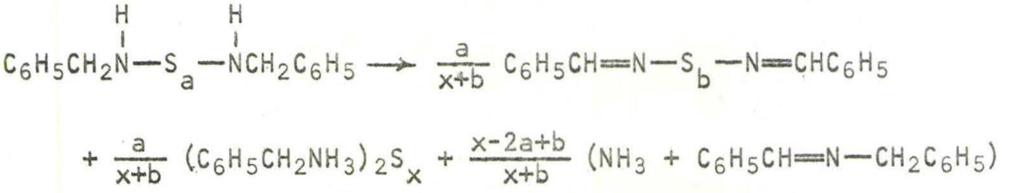
$$C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2-\overset{H}{N}-S_a-\overset{H}{N}-CH_2C_6H_5 + 2(C_6H_5CH{=}NCH_2C_6H_5 + NH_3) + (b-a)S \qquad (77)$$

ately, (77) is not valid since sulfur is formed in the presence of benzylamine; (77) must be modified to eliminate sulfur as a product. This can be done by multiplying equation (68) by (b-a/a+x) and then adding it to (77) to give equation (78). Equation (78) now gives



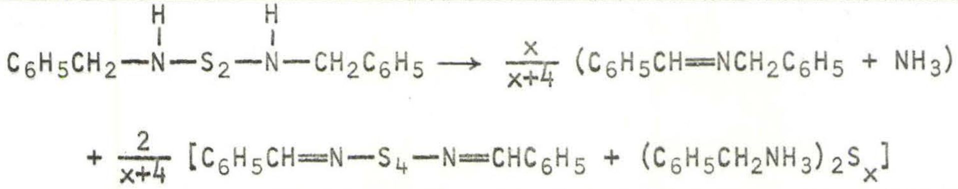
$$\mathrm{C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5} + \frac{4(x+b)}{a+x}\,\mathrm{C_6H_5CH_2NH_2} \longrightarrow 2(\mathrm{C_6H_5CH{=}N{-}CH_2C_6H_5} + \mathrm{NH_3}) + \frac{x+b}{a+x}\,\mathrm{C_6H_5CH_2{-}\overset{H}{N}{-}S_a{-}\overset{H}{N}{-}CH_2C_6H_5} + \frac{b-a}{a+x}\,(\mathrm{C_6H_5CH_2NH_3})_2\mathrm{S}_x \qquad (78)$$

the fate of the benzylamine present in limiting quantity in equation (76). These can be combined to eliminate the benzylamine by multiplying equation (78) by (x-2a+b)/x+b and adding the result to (76) to give equation (79).



$$\mathrm{C_6H_5CH_2\overset{H}{N}{-}S_a{-}\overset{H}{N}CH_2C_6H_5} \longrightarrow \frac{a}{x+b}\,\mathrm{C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5} + \frac{a}{x+b}\,(\mathrm{C_6H_5CH_2NH_3})_2\mathrm{S}_x + \frac{x-2a+b}{x+b}\,(\mathrm{NH_3} + \mathrm{C_6H_5CH{=}N{-}CH_2C_6H_5}) \qquad (79)$$

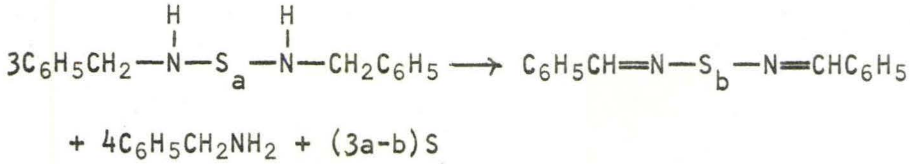
In the decomposition of benzylamine disulfide a = 2, and the benzylidenimine polysulfide obtained experimentally was the tetrasulfide only (b = 4). Substituting a = 2 and b = 4 in (79) gives equation (62).



$$\boxed{\mathrm{C_6H_5CH_2{-}\overset{H}{N}{-}S_2{-}\overset{H}{N}{-}CH_2C_6H_5} \longrightarrow \frac{x}{x+4}\,(\mathrm{C_6H_5CH{=}NCH_2C_6H_5} + \mathrm{NH_3}) + \frac{2}{x+4}\,[\mathrm{C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5} + (\mathrm{C_6H_5CH_2NH_3})_2\mathrm{S}_x] \qquad (62)}$$

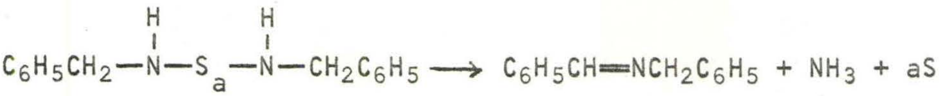
(ii) LIMITING CASE 2: BENZYLIDENIMINE POLYSULFIDES REACT VERY FAST (EQUATION 63)

Returning to equation (45) the benzylamine now reacts exclusively



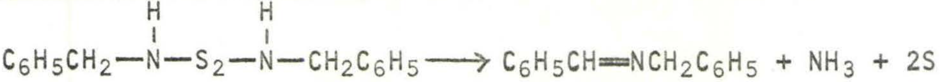
$$3C_6H_5CH_2-\overset{H}{\underset{}{N}}-S_a-\overset{H}{N}-CH_2C_6H_5 \longrightarrow C_6H_5CH{=}N-S_b-N{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 + (3a-b)S \qquad (45)$$

with the benzylidenimine polysulfides according to equation (69). The latter must be modified (by adding equation (70)) to correct the sulfur chain length before it can be added to equation (45) to give equation (80).



$$C_6H_5CH_2-\overset{H}{N}-S_a-\overset{H}{N}-CH_2C_6H_5 \longrightarrow C_6H_5CH{=}NCH_2C_6H_5 + NH_3 + aS \qquad (80)$$

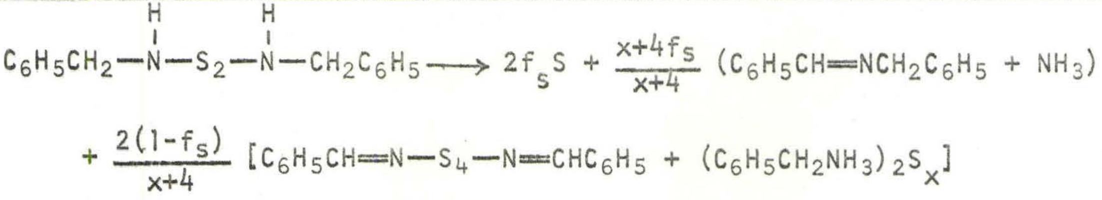
In the decomposition of benzylamine disulfide a = 2; therefore, equation (80) reduces to equation (63).



$$\boxed{C_6H_5CH_2-\overset{H}{N}-S_2-\overset{H}{N}-CH_2C_6H_5 \longrightarrow C_6H_5CH{=}NCH_2C_6H_5 + NH_3 + 2S \qquad (63)}$$

(iii) INTERMEDIATE CASE: EQUATION (64)

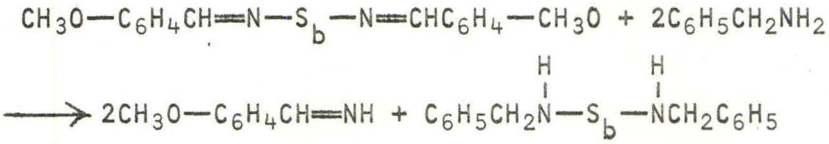
Equation (63) shows elemental sulfur as the only sulfur containing product. Equation (62) shows no free sulfur. Therefore, the elemental sulfur obtained from the decomposition reaction of benzylamine disulfide is a measure of the relative importance of reactions (62) and (63). Defining f_s as $\frac{\text{g atoms of elemental sulfur formed}}{\text{total g atoms of sulfur in the system}}$ leads to $f_s \times (63)$ as the total contribution from equation (63) and $(1-f_s) \times (62)$ as the total contribution from equation (62). The overall reaction is then $f_s(63) + (1-f_s)(62)$ as in equation (64).



$$\boxed{\begin{aligned}C_6H_5CH_2-\overset{H}{N}-S_2-\overset{H}{N}-CH_2C_6H_5 &\longrightarrow 2f_sS + \frac{x+4f_s}{x+4}(C_6H_5CH{=}NCH_2C_6H_5 + NH_3)\\ &+ \frac{2(1-f_s)}{x+4}[C_6H_5CH{=}N-S_4-N{=}CHC_6H_5 + (C_6H_5CH_2NH_3)_2S_x] \qquad (64)\end{aligned}}$$

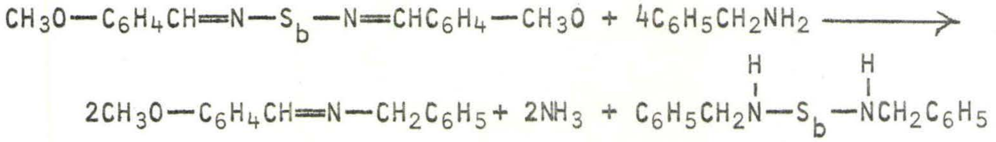
E. p-METHOXYBENZYLIDENIMINE TETRASULFIDE WITH EXCESS BENZYLAMINE: EQUATION (65)

Equation (46) written for p-methoxybenzylidenimine polysulfide gives equation (81):



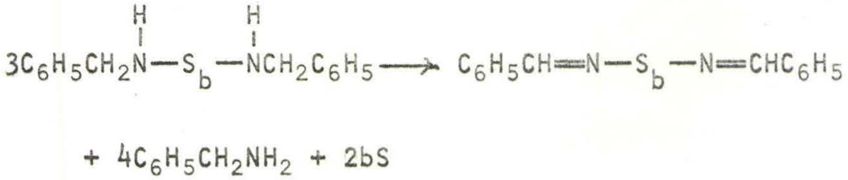
$$\begin{aligned}&CH_3O{-}C_6H_4CH{=}N{-}S_b{-}N{=}CHC_6H_4{-}CH_3O + 2C_6H_5CH_2NH_2\\&\longrightarrow 2CH_3O{-}C_6H_4CH{=}NH + C_6H_5CH_2\overset{H}{\overset{|}{N}}{-}S_b{-}\overset{H}{\overset{|}{N}}CH_2C_6H_5 \qquad (81)\end{aligned}$$

Adding (81) to twice (47) (p-methoxybenzylidenimine reacts with benzylamine) gives equation (82):



$$\begin{aligned}&CH_3O{-}C_6H_4CH{=}N{-}S_b{-}N{=}CHC_6H_4{-}CH_3O + 4C_6H_5CH_2NH_2 \longrightarrow\\&2CH_3O{-}C_6H_4CH{=}N{-}CH_2C_6H_5 + 2NH_3 + C_6H_5CH_2\overset{H}{\overset{|}{N}}{-}S_b{-}\overset{H}{\overset{|}{N}}CH_2C_6H_5 \qquad (82)\end{aligned}$$

All the p-methoxy substituent has now been converted to the final product, and the newly formed unsubstituted benzylamine polysulfide decomposes via equation (45). After correcting for the sulfur chain length as per equation (70), the products are as shown in (83). The products in (83) are sulfur and benzylidenimine polysulfides. Since there is an excess of benzylamine, the former reacts as per equation (56) and the latter,



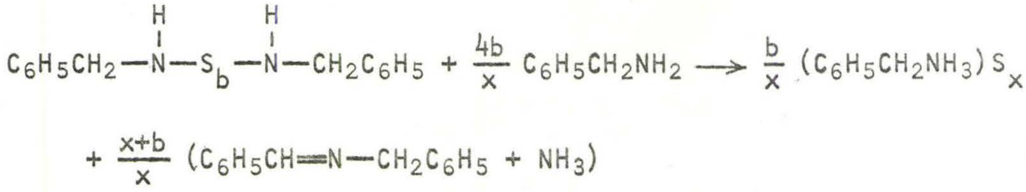
$$\begin{aligned}&3C_6H_5CH_2\overset{H}{\overset{|}{N}}{-}S_b{-}\overset{H}{\overset{|}{N}}CH_2C_6H_5 \longrightarrow C_6H_5CH{=}N{-}S_b{-}N{=}CHC_6H_5\\&\quad + 4C_6H_5CH_2NH_2 + 2bS \qquad (83)\end{aligned}$$

$$\begin{aligned}&S + \frac{4}{x}C_6H_5CH_2NH_2 \longrightarrow \frac{1}{x}(C_6H_5CH{=}N{-}CH_2C_6H_5 + NH_3)\\&\quad + \frac{1}{x}(C_6H_5CH_2NH_3)_2S_x \qquad (56)\end{aligned}$$

as per equation (74). When equation (74) is added to equation (83)

$$\begin{aligned} &C_6H_5CH{=\!=}N{-\!-}S_4{-\!-}N{=\!=}CHC_6H_5 + \frac{4b+4x}{x}\, C_6H_5CH_2NH_2 \longrightarrow \\ &\quad \frac{b}{x}\,(C_6H_5CH_2NH_3)_2S_x + \frac{3x+b}{x}\,(C_6H_5CH{=\!=}N{-\!-}CH_2C_6H_5 + NH_3) \end{aligned} \tag{74}$$

and this in turn is added to 2b times equation (56), equation (84) results (after dividing by a common factor of 3). Finally, equation



$$\begin{aligned} &C_6H_5CH_2{-\!-}\overset{\overset{\displaystyle H}{|}}{N}{-\!-}S_b{-\!-}\overset{\overset{\displaystyle H}{|}}{N}{-\!-}CH_2C_6H_5 + \frac{4b}{x}\, C_6H_5CH_2NH_2 \longrightarrow \frac{b}{x}\,(C_6H_5CH_2NH_3)S_x \\ &\quad + \frac{x+b}{x}\,(C_6H_5CH{=\!=}N{-\!-}CH_2C_6H_5 + NH_3) \end{aligned} \tag{84}$$

(84) can be added to equation (82) to give the overall expression (85) for p-methoxybenzylidenimine polysulfides reacting with excess benzyl-

$$\begin{aligned} &CH_3O{-\!-}C_6H_4CH{=\!=}N{-\!-}S_b{-\!-}N{=\!=}CHC_6H_4{-\!-}CH_3O + \frac{4(b+x)}{x}\, C_6H_5CH_2NH_2 \longrightarrow \\ &\quad \frac{b}{x}\,(C_6H_5CH_2NH_3)_2S_x + \frac{x+b}{x}\, C_6H_5CH{=\!=}N{-\!-}CH_2C_6H_5 \\ &\quad + 2CH_3O{-\!-}C_6H_4CH{=\!=}N{-\!-}CH_2C_6H_5 + \frac{3x+b}{x}\, NH_3 \end{aligned} \tag{85}$$

amine. Since the starting p-methoxybenzylidenimine polysulfide was the tetrasulfide, b = 4, and equation (85) reduces to equation (65).

$$\boxed{\begin{aligned} &CH_3O{-\!-}C_6H_4CH{=\!=}N{-\!-}S_4{-\!-}N{=\!=}CHC_6H_4{-\!-}CH_3O + \frac{16+4x}{x}\, C_6H_5CH_2NH_2 \longrightarrow \\ &\quad 2CH_3O{-\!-}C_6H_4CH{=\!=}NC_6H_5 + \frac{4+x}{x}\, C_6H_5CH{=\!=}NCH_2C_6H_5 \\ &\quad + \frac{4+3x}{x}\, NH_3 + \frac{4}{x}\,(C_6H_5CH_2NH_3)_2S_x \qquad (65) \end{aligned}}$$

F. OVERALL REACTION OF S_4N_4 WITH BENZYLAMINE: EQUATION (18)

The first step in the reaction of S_4N_4 with benzylamine was given on page 21 as equation (9). Since the benzylidenimine tetrasulfide

$$S_4N_4 + 8C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 + 3C_6H_5CH{=}NCH_2C_6H_5 + 3NH_3 \qquad (9)$$

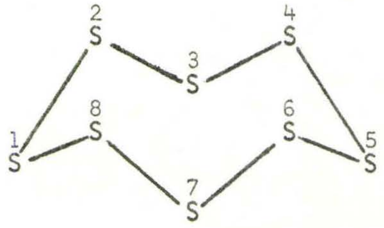
formed will react as per equation (74), the overall reaction is obtained by adding (9) to (74) to give equation (18).

$$\boxed{S_4N_4 + \left(\frac{12x+16}{x}\right) C_6H_5CH_2NH_2 \longrightarrow \left(\frac{6x+4}{x}\right) C_6H_5CH{=}N{-}CH_2C_6H_5 + \left(\frac{10x+4}{x}\right) NH_3 + \frac{4}{x}\,(C_6H_5CH_2NH_3)_2S_x \qquad (18)}$$

PART III. APPENDIX

CHAPTER IX. TETRASULFUR TETRAIMIDE, $S_4N_4H_4$, WITH STRONG BASE

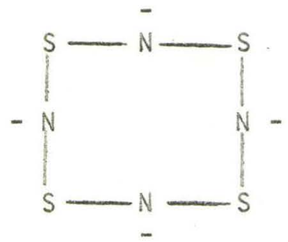
There are 7 eight membered cyclic sulfur imides known, i.e., S_7NH,(116) three isomers of $S_6(NH)_2$,(117,118,119) two isomers of $S_5(NH)_3$(120) and $S_4N_4H_4$.(121) The structures of these materials are very similar to that of the S_8 molecule (XXXVI); they are all puckered eight membered rings. In the three isomeric diimides, the 1-3, 1-4 and 1-5 atoms of the S_8 molecule (XXXVI) are replaced by the imino group, >NH.(122,123) In the two isomers of $S_5(NH)_3$, the 1-3-5 and 1-3-6 atoms of the S_8 molecule, XXXVI, are replaced(120) and in $S_4N_4H_4$, the 1-3-5-7 positions are substituted.(123,124) Cyclic sulfur imides with adjacent imino groups are not known. These cyclic sulfur imides, with the exception of $S_4N_4H_4$, are synthesized from the reaction of disulfur dichloride with ammonia in dimethyl formamide. $S_4N_4H_4$ has never been found in this reaction mixture; it is usually prepared by reduction of tetrasulfur tetranitride.



XXXVI

These sulfur imides are weakly acidic. For example, reaction with methyl magnesium iodide gave 1 mole of methane per mole of S_7NH

and 4 moles of methane per mole of $S_4N_4H_4$.(125) The hydrogens were also replaced by certain metal ions. Thus, $Hg(NS_7)_2$ and $Hg_2(NS_7)_2$ were obtained from S_7NH(126) while $Li[A\ell(SN)_4]$,(127) $[Cu(NS)]_4$,(128) $[Hg(NS)]_4$,(129), $Hg_2(NS)_4$(130) and $Hg_5(NS)_8$(130) were formed from $S_4N_4H_4$. The molecular weights of these metal compounds have not been established, and it is not known whether the ring system is still intact. In the case of $Li[A\ell(SN)_4]$, $S_4N_4H_4$ was recovered on careful hydrolysis.(127) The metals are thought to be bonded to nitrogen since addition of ethyl iodide to $[Ag(NS)]_4$ followed by hydrolysis gave ethylamine.(128) Alkyl metal salts of $S_4N_4H_4$ were also reported. Meuwsen reported that treatment of $S_4N_4H_4$ with KNH_2 probably formed $KNS \cdot KNH_2$.(25) Becke-Goehring and Schwarz(131) reacted $S_4N_4H_4$ with triphenyl methyl sodium, $(C_6H_5)_3C^-Na^+$, in ether and obtained an orange solid proposed to be $Na_4(S_4N_4)$, XXXVII.



XXXVII

This salt was quite unstable and detonated in moist air.

Chapman and Massey(131) observed that a series of color changes occurred when S_4N_4 was reduced with potassium in dimethoxy ethane. They observed a nine-line electron spin resonance spectrum which they assigned to the $S_4N_4^-$ anion. Reaction with more potassium caused this spectrum to increase in intensity to a maximum, after which it decreased to almost zero and then increased to a new nine-line spectrum. They proposed that this reflected the formation of more highly charged negative ions, $S_4N_4 \rightarrow S_4N_4^- \rightarrow S_4N_4^{2-} \rightarrow S_4N_4^{3-} \rightarrow S_4N_4^{4-}$. The two species, $S_4N_4^-$ and $S_4N_4^{3-}$, would be paramagnetic. The $S_4N_4^{4-}$ should be the same species as XXXVII.

Meinzer and Myers[132,133] found that reduction of S_4N_4 in tetrahydrofuran below 0°C yielded a nine-line spectrum different from that observed by Chapman and Massey. This new radical decomposed above 0°C to give fragments containing one and two nitrogens. On standing at room temperature these formed the four-nitrogen species of Chapman and Massey. The new four-nitrogen radical is believed to be the $S_4N_4^-$ radical ion. Therefore, Chapman and Massey must have observed some other species.

The existence of sulfur imide anions has been demonstrated only for heptasulfurimide, S_7NH,[134] and the hexasulfurdiimides, $S_6(NH)_2$.[135] The reaction of strong base with heptasulfurimide and the three isomeric hexasulfurdiimides led to proton abstraction in competition with addition of base to sulfur-sulfur and/or sulfur-nitrogen bonds. The sulfurimide anions obtained from all but the 1,3-$S_6(NH)_2$ were stable and effected nucleophilic substitution on alkyl halides to give various N-alkyl sulfurimides (86).

$$S_7NH + B^- \longrightarrow BH + S_7N^- \xrightarrow{RX} S_7NR + X^- \qquad (86)$$

Although heptasulfurimide and the 1,4- and 1,5-hexasulfurdiimides were alkylated without any rearrangement, alkylation of the supposed

1,3-hexasulfurdiimide anion was unsuccessful. This was found to result from instability of the anion (either $-\bar{N}-S-NH-$ or $-\bar{N}-S-\bar{N}-$)(135) due to the proximity of the two nitrogens.

There is no firm evidence for the existence of anions derived by proton abstraction from $S_4N_4H_4$. By analogy with the hexasulfurdiimides, it is expected that anions of $S_4N_4H_4$ would be unstable. The aim of this work was to show the presence or absence of anions derived from $S_4N_4H_4$. These were to be characterized as their alkyl derivatives.

Tetrasulfur tetraimide was reacted with a 40 fold excess of sodium hydride in THF in <u>vacuo</u> at room temperature. Several color changes were observed. The solution was at first pale yellowish orange but soon became deep bluish green. Soon a yellow precipitate formed which very slowly turned brownish red. The hydrogen evolved was collected and measured. When the color of the precipitate was yellow, the reaction was stopped by cooling in liquid nitrogen. 1.9 moles of hydrogen per mole of $S_4N_4H_4$ were observed. After the yellow precipitate turned red, 2.7 moles of hydrogen per mole of $S_4N_4H_4$ were observed. This is considerably less than that expected for quantitative abstraction of all four hydrogens. Anhydrous hydrochloric acid was added. A rapid reaction occurred with various color changes, but no $S_4N_4H_4$ was recovered (87). The red solid was also reacted with methyl

$$S_4N_4^{4-} + 4H^+ \longrightarrow S_4N_4H_4 \tag{87}$$

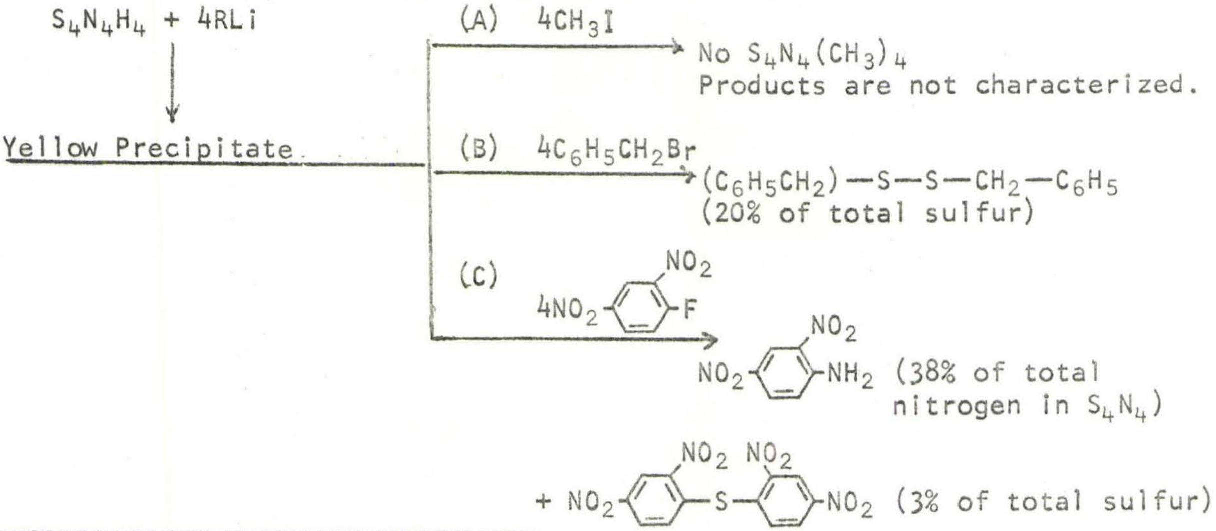
iodide, and a viscous red oil was obtained, but no $S_4N_4(CH_3)_4$(136) could be isolated. It is quite likely that the $S_4N_4H_4$ ring system was cleaved and that no stable $S_4N_4^{4-}$ ion was present.

In order to determine at which stage the ring system of $S_4N_4H_4$ was cleaved, a stoichiometric amount of base was added. The base used was a commercially available standard solution of an organo-lithium compound.* With one mole of organo-lithium compound per mole of $S_4N_4H_4$, two color changes occurred. At 0°C in THF, the solution rapidly became orange and after 30 minutes changed to greenish blue. With two or three moles of base, the same color changes occurred. With four moles of base the same sequence of color changes occurred followed by precipitation of a yellow solid. For each of

$$S_4N_4H_4 + RLi \xrightarrow{0^\circ C} \text{orange} \xrightarrow{30\ \text{min.}} \text{greenish blue} \xrightarrow{60\ \text{min.}} \text{yellow solid}$$

these steps, alkyl halide and/or water and/or dilute acid was added in an attempt to identify the species present. The experimental results are shown below.

(1) Yellow Stage



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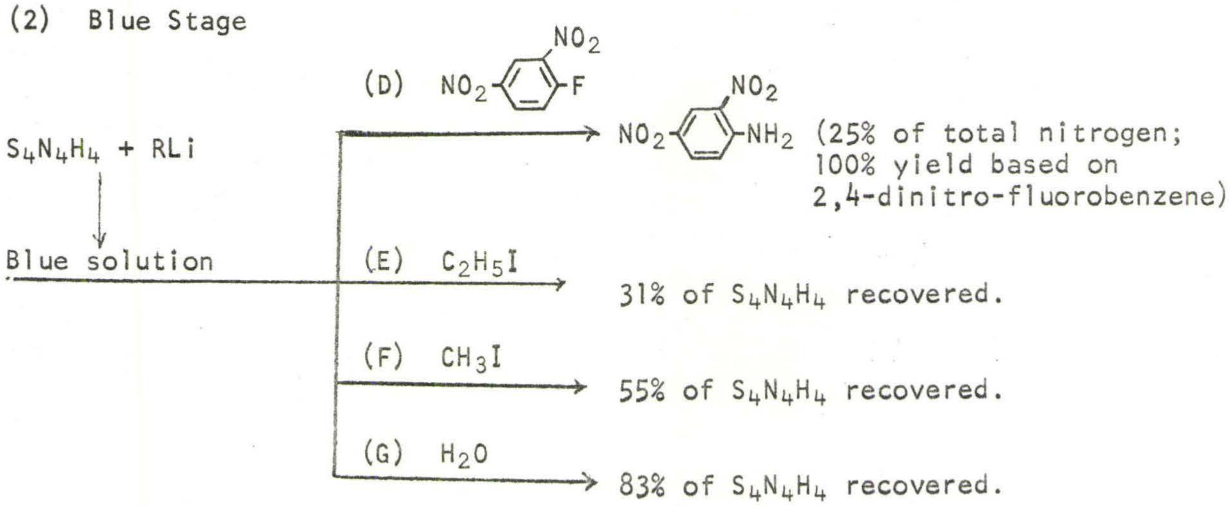
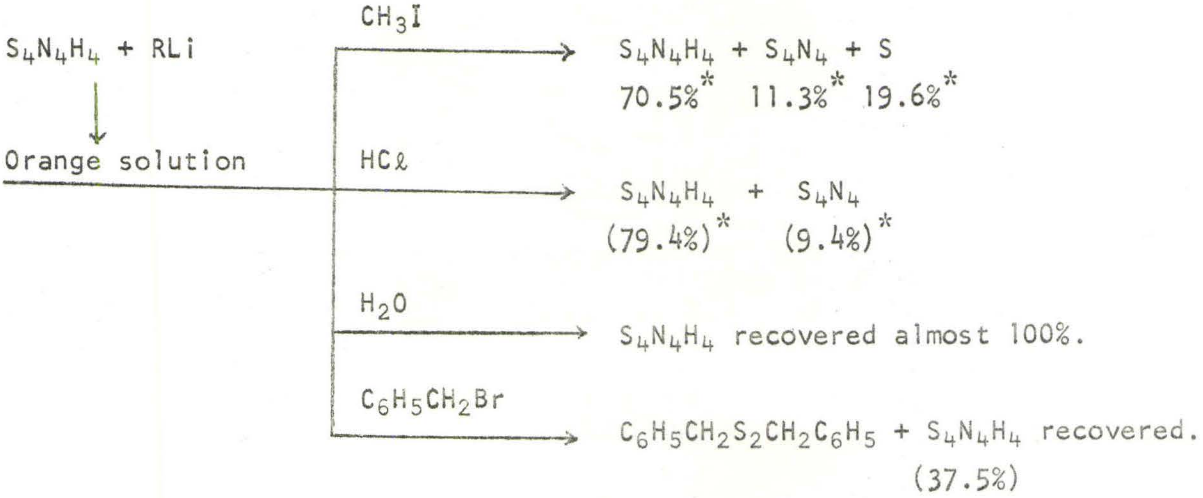
*Although S_7NH was reported(134) to be a strong enough acid to react with a non-aqueous solution of lithium hydroxide to give the sulfurimide anion, $S_4N_4H_4$ did not react similarly.

(2) Blue Stage



(3) Orange Stage



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*As % of total sulfur.

These results are not at all conclusive but suggest that perhaps at the blue stage the ring system of $S_4N_4H_4$ might remain intact. The orange stage could be a simple molecular complex, $(S_4N_4H_4)\cdot RLi$, since a large quantity of $S_4N_4H_4$ as well as S_4N_4 was obtained as product. The latter was found to be produced by the reaction of $S_4N_4H_4$ with methyl iodide according to equation (88). Other alkyl halides also

$$4S_4N_4H_4 + 4CH_3I \longrightarrow 3S_4N_4 + 4NH_4I + 2CH_3S_xCH_3 \qquad (88)$$

reacted with $S_4N_4H_4$ to form S_4N_4 but at a slower rate.

Since no stable derivative of the tetrasulfur tetraimide anion was isolated and since alkyl halides were found to react directly with $S_4N_4H_4$, this project was abandoned. $S_4N_4H_3^-$ could be present at the blue stage, but no firm evidence was obtained.

CHAPTER X. PYROLYSIS OF TETRASULFUR TETRAIMIDE

Meuwsen[(121)], while measuring the melting point of tetrasulfur tetraimide in an open capillary tube, observed decomposition. He then pyrolyzed a larger quantity in an open flask and observed the evolution of ammonia. Since a red material was formed, he proposed it to be a mixture of S_4N_4 and sulfur. Later, Fluck and Becke-Goehring found that $S_4N_4H_4$ was oxidized in air to give the red tetrameric thionylimide, $S_4N_4H_4O_4$.[(137)] Some ammonia was also observed to be formed in a competing reaction during the air oxidation. Therefore, the red material Meuwsen observed could well have been $S_4N_4H_4O_4$. The data reported below is a study of the thermal decomposition of $S_4N_4H_4$ in an oxygen free system.

The decomposition of tetrasulfur tetraimide was found to occur in <u>vacuo</u> at temperatures of 110-135°C. The reaction produced ammonia, sulfur, and tetrasulfur tetranitride (S_4N_4) in accord with equation (89). The stoichiometry of the decomposition was verified by isolation and

$$3S_4N_4H_4 \longrightarrow 2S_4N_4 + 4S + 4NH_3 \tag{89}$$

quantitative determination of the products. Equation (89) accounts for greater than 95% of the reacting tetrasulfur tetraimide. The coefficients of the species in (89) (based on 4.00 for ammonia) were experimentally determined to be 3.03 ($S_4N_4H_4$), 1.97 (S_4N_4), and 3.94 (sulfur). The remaining material (about 4%) was insoluble in all common solvents and appeared to be of high molecular weight. About

2% of the tetrasulfur tetraimide remained undecomposed well after the reaction had ended. This material was of extremely low density suggesting that the reaction may well proceed by intermolecular decomposition within the crystal lattice. A weak intermolecular hydrogen bond has been postulated in crystalline tetrasulfur tetraimide(123) in at least partial agreement with this suggestion.

EXPERIMENTAL

Tetrasulfur tetraimide was prepared by the stannous chloride reduction of tetrasulfur tetranitride as described by Meuwsen.(130) After recrystallization from methanol it had m.p. 152°C d (Lit.(138) 152°C d).

Tetrasulfur tetraimide, 1880 mg (10.0 mmoles), was placed in a sublimation apparatus and evacuated to a pressure of about 5×10^{-5} torr. The imide was then heated to 135°C for four hours. The volatile products were removed as formed and allowed to collect on the cool part of the sublimer (S_4N_4, sulfur, and some $S_4N_4H_4$) and in a liquid nitrogen trap (NH_3). The ammonia was then absorbed in 13.00 meq. of standard hydrochloric acid. The excess acid was back titrated and required 2.53 meq. of standard potassium hydroxide. A small amount (45 mg) of very bulky white powder remained in the reaction flask. After recrystallization from methanol, this material was identified as unreacted tetrasulfur tetraimide. The solid products collected on the cool part of the sublimer were extracted with benzene and then with methanol. They were separated by fractional recrystallization and identified as sulfur, 330 mg (10.3 mmoles) of m.p. 118-118.5°C (Lit.(139) 119°C); tetrasulfur tetranitride, 949 mg (5.16 mmoles) of m.p. 177.5-178°C (Lit$^{(71)}$ 178°C); and tetrasulfur tetraimide, 344 mg (1.83 mmoles) of 152°C d. Allowing for the tetrasulfur tetraimide recovered from both sources, 1491 mg (7.94 mmoles) of this material had reacted. The total weight of sulfur, ammonia, and tetrasulfur tetranitride obtained was 1459 mg. Of this the molar distribution was 40.5% ammonia, 39.7% sulfur and 19.8% tetrasulfur tetranitride, or 2:2:1. In addition, 78 mg of an unidentified black solid insoluble in a wide variety of solvents remained on the sublimer.

BIBLIOGRAPHY

1. Gregory, M., J. Pharm., 21, 315 (1835); ibid., 22, 301 (1835).

2. Barker, C. K., Cordes, A. W. and Mangrave, J. L., J. Phys. Chem., 69, 334 (1965).

3. Sharma, B. D. and Donohue, J., Acta Cryst., 16, 891 (1963).

4. Cotton, F. A. and Wilkinson, G., "Advanced Inorganic Chemistry", Interscience Publishers, New York, N.Y., 1967, pp. 115.

5. ibid., pp. 105.

6. Sass, R. L., Acta Cryst., 13, 320 (1960).

7. Mason, J. B., J. Chem. Soc. A, 1567 (1969).

8. Turner, A. G. and Mortimer, F. S., Inorg. Chem., 5, 906 (1966).

9. Braterman, P. S., J. Chem. Soc., 2297 (1965).

10. Chapman, D. and Waddington, T. C., Trans. Faraday Soc., 58, 1679 (1962).

11. Neubauer, D. and Weiss, J., Z. Anorg. Allg. Chem., 303, 28 (1960).

12. Wynne, K. J. and Jolly, W. L., Inorg. Chem., 6, 107 (1967).

13. Drew, M. G. B. and Templeton, G. H., ibid., 6, 1906 (1967).

14. MacDiarmid, A. G., Nature, 164, 1131 (1949).

15. Becke-Goehring, M., Prog. Inorg. Chem., 1, 207 (1959).

16. Banister, A. J. and Padley, J. S., J. Chem. Soc. A, 1437 (1967).

17. Banister, A. J., Dainty, P. J., Hazell, A. C., Hazell, R. G. and Lomborg, J. G., Chem. Commun., 1187 (1969).

18. Schenck, R., Ann., 290, 171 (1896).

19. Levi, T. G., Gazz. Chim. Ital., 61, 294 (1931).

20. Becke-Goehring, M. and Jenne, H., Chem. Ber., 92, 1149 (1959).

21. Ruff, O. and Geisel, E., ibid., 37, 1573 (1904).

22. Becke-Goehring, M. and Schwarz, R., Z. Anorg. Allg. Chem., 296, 3 (1958).

23. Fluck, E., *ibid.*, *312*, 195 (1961).

24. Weiss, V. J. and Piechaczek, H., Z. Naturforsch., *18B*, 1139 (1963).

25. Meuwsen, A., Chem. Ber., *64*, 2301 (1931).

26. Heal, H. G. in Nickless, G., "Inorganic Sulfur Chemistry", Elsevier Publishing Co., New York, N. Y., 1968, pp. 466.

27. Fluck, E., Becke-Goehring, M. and Dehoust, G., Z. Anorg. Allg. Chem., *312*, 60 (1961).

28. Kraus, V. H. L. and Jung, H., Z. Naturforsch., *16B*, 624 (1961).

29. Fluck, E. and Reinisch, R. M., Z. Anorg. Allg. Chem., *328*, 165 (1964).

30. Becke-Goehring, M., Fluck, E. and Lehr, W., Z. Naturforsch., *17b*, 126 (1962).

31. Becke-Goehring, M. and Lehr, W., Z. Anorg. Allg. Chem., *325*, 287 (1963).

32. Skoog, D. A. and Bartlett, J. K., Anal. Chem., *27*, 369 (1955).

33. (a) "NMR Spectra Catalog", Sadtler Research Laboratories, Philadelphia, Pa., 1967, Spectra No. 702.

    (b) *ibid.*, Spectra No. 3606.

    (c) *ibid.*, Spectra No. 4510M.

    (d) *ibid.*, Spectra No. 57.

    (e) *ibid.*, Spectra No. 1260.

    (f) *ibid.*, Spectra No. 286.

    (g) *ibid.*, Spectra No. 39.

    (h) *ibid.*, Spectra No. 184.

34. (a) "NMR" Spectra Catalog. Vol. 1", Varian Associates, Palo Alto, Calif., 1962, Spectra No. 156.

    (b) *ibid.*, Spectra No. 151.

35. Exner, O., Collect. Czech. Chem. Commun., *28*, 3150 (1963).

36. Jeffe, H. H., Chem. Rev., *53*, 191 (1953).

37. Cairns, T. L., Larchar, A. W. and McKusick, B. C., J. Am. Chem. Soc., 74, 5633 (1952).

38. Levi, T. G., Gazz. Chim. Ital., 60, 975 (1930).

39. McMillan, F. H., J. Am. Chem. Soc., 70, 868 (1948).

40. Grant, D. and Wazer, J. R. V., ibid., 86, 3012 (1964).

41. Wazer, J. R. V. and Grant, D., ibid., 86, 1450 (1964).

42. Tsurugi, J. and Nakabayashi, T., J. Org. Chem., 24, 807 (1959).

43. Nakabayashi, T., Tsurugi, J. and Yubata, T., J. Org. Chem., 29, 1236 (1954).

44. Fergson, L. N. and Branch, G. E. K., J. Am. Chem. Soc., 66, 1467 (1944).

45. Friedman, H. L. and Kerher, M., J. Colloid Sci., 8, 80 (1953).

46. Bellamy, L. J., "The Infra-red Spectra of Complex Molecules", John Wiley & Sons, Inc., New York, N.Y., 1962, pp. 271.

47. Banister, A. J., Moore, L. F. and Padley, J. S., Spectrochim. Acta, 23A, 2705 (1967).

48. Fabian, M. J. and Legrand, M., Bull. Soc. Chim. Fr., 1461 (1956).

49. Randerath, K., "Thin Layer Chromatography", Academic Press, New York, N. Y., 1964, pp. 21.

50. Rochow, E. G., "Inorganic Syntheses", Vol. VI, McGraw Hill Book Co. Inc., New York, N. Y., 1960, pp. 124.

51. Mason, A. T. and Winder, G. R., J. Chem. Soc., 65, 191 (1894).

52. (a) "Infra-red Spectra Catalog", Sadtler Research Laboratories, Philadelphia, Pa., 1965, Spectra No. 1946.

    (b) ibid., Spectra No. 7389.

    (c) ibid., Spectra No. 320.

    (d) ibid., Spectra No. 3203.

53. Juday, R. and Adkins, H., J. Am. Chem. Soc., 77, 4559 (1955).

54. Hammick, D. L. and Locket, G. H., J. Chem. Soc., 2362 (1922).

55. Gabriel, S., Chem. Ber., 20, 2224 (1887).

56. Brady, O. L. and Klein, L., J. Chem. Soc., 874 (1927).

57. Ing, H. R. and Manske, R. H. F., ibid., 2348 (1926).

58. Gross, F. R., Ingold, C. K. and Wilson, I. S., ibid, 2440 (1926).

59. Stenhouse, J., Proc. Royal Soc., London, 17, 62 (1868).

60. Shriner, R. L., Fuson, R. C. and Curtin, D. Y., "The Systematic Identification of Organic Compounds", John Wiley & Sons Inc., New York, N. Y., 1958, pp. 58.

61. Spencer, R. D. and Beggs, B. H., Anal. Chem., 35, 1633 (1963).

62. Kresze, G., Horn, A., Philippson, R. and Tredes, A., Chem. Ber., 98, 3401 (1965).

63. Hofmann, A. W. and Gabriel, S., Chem. Ber., 25, 1578 (1892).

64. Kindler, K., Ann., 431, 187 (1923).

65. Hofmann, A. W., Chem. Ber., 2, 645 (1869).

66. Buck, J. S. and Jenkkins, S., J. Am. Chem. Soc., 51, 2163 (1929).

67. Friedrich, F., J. Am. Chem. Soc., 35, 1866 (1913).

68. Franklin, E. C. and Kraus, C. A., ibid., 20, 820 (1898).

69. Ruff, O. and Hecht, L., Z. Anorg. Allg. Chem., 70, 49 (1911).

70. Moissan, H., Compt. Rend., 132, 510 (1901).

71. Ruff, O. and Geisel, E., Chem. Ber., 38, 2659 (1905).

72. Bergstrom, F. W., J. Am. Chem. Soc., 48, 2319 (1926).

73. Zipp, A. P. and Evers, E. C., Inorg. Chem., 8, 1746 (1969).

74. Nelson, J. T. and Lagowski, J. J., ibid., 6, 1292 (1967).

75. Bartlett, P. D., Lohaus, G. and Weiss, C. D., J. Am. Chem. Sco., 80, 5064 (1958).

76. Nelson, J. T. and Lagowski, J. J., Inorg. Chem., 6, 862 (1967).

77. Zipp, A. P., Dissertation Abstr., 26, 1909 (1969).

78. Becke-Goehring, M., Quart. Review, 10, 437 (1956).

79. Krebs, V. H., Weber, E. F. and Balters, H., Z. Anorg. Allg. Chem., 275, 417 (1954).

80. Voronkov, M. G. and Ledgzdyn, A. Y., Zh. Org. Khim., 3, 465 (1967).

81. Bartlett, P. D., Cox, E. F. and Davis, R. E., J. Am. Chem. Soc., 83, 103 (1961).

82. Bartlett, P. D., Davis, R. E. and Roderick, W. R., ibid., 83, 109 (1961).

83. Levi, T. G., Gazz. Chim. Ital., 61, 286 (1931).

84. Jenne, H. and Becke-Goehring, M., Chem. Ber., 91, 1950 (1958).

85. Saville, R. W., J. Chem. Soc., 2880 (1958).

86. Colebourne, N., Foster, R. G. and Robinson, E., ibid., 685 (1968).

87. Middleton, W. J., J. Am. Chem. Soc., 88, 3842 (1966).

88. Davis, R. E. and Nakshbendi, H. F., ibid., 84, 2085 (1962).

89. Hodgeson, W. G., Buckler, S. A., and Peters, G., ibid., 85, 543 (1963).

90. Kindler, K., Ann., 431, 193, 222 (1923).

91. Carmack, M. and Spielman, M. A., "Organic Reactions", Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 83.

92. Asinger, F. and Offermanns, H., "Synthesen mit Ketonen, Swefel und Ammoniak bzw. Aminen und chemisches Verhalten der Reactionprodukte", Westdeutscher Verlag, Köln und Opladen, (1966).

93. Ogata, Y. and Takagi, Y., Yuki Gosei Kagaku Kyokaishi, 16, 110 (1958).

94. Asinger, F., Angew. Chem. Int. Ed., 3, 19 (1964).

95. Asinger, F. and Offermanns, H., Monatsh. Chem., 100, 724 (1967).

96. King, J. A. and McMillan, F. H., J. Am. Chem. Soc., 68, 632 (1946).

97. McMillan, F. H. and King, J. A., J. Am. Chem. Soc., 70, 4143 (1948).

98. Behforouz, M., Diss. Abst., 26, 6365 (1966).

99. Dauben, W. G., Ciura, R. C. and Rogan, J. B., J. Org. Chem., 22, 362 (1957).

100. Asinger, F. and Offermanns, H., Angew. Chem. Int. Ed., 6, 907 (1967).

101. Milligan, B. and Swan, J. M., J. Chem. Soc., 1194 (1961).

102. Asinger, F. and Halcour, K., Monatsh. Chem., 95, 24 (1964).

103. Asinger, F., Becker, H. W., Schafer, W. and Sauss, A., ibid., 97, 301 (1966).

104. Kratz, G. D., Flower, A. H. and Coolidge, C., Ind. Eng. Chem., 12, 317 (1920).

105. Scott, W. and Bedford, C. W., ibid., 13, 126 (1921).

106. Asinger, F., Schäfer, W. and Triem, H., Monatsh. Chem., 97, 1510 (1966).

107. Vineyard, B. D., J. Org. Chem., 32, 3833 (1967).

108. Asinger, F., Schäfer, W., Meisel, H., Kersten, H. and Sauss, A., Monatsh. Chem., 98, 338 (1967).

109. Asinger, F., Thiel, M. and Schröder, L., Ann., 610, 49 (1959).

110. Barrick, J. C. and Olsen, F. P., Unpublished results.

111. Tolbert, T. L. and Houston, B., J. Org. Chem., 28, 695 (1963).

112. Pesez, M. and Bartos, J., Bull. Soc. Chim. Fr., 1122 (1963).

113. Davis, R. E., Reference (8) in Davis, R. E. and Nakshbendi, H. F. J. Am. Chem. Soc., 84, 2085 (1962).

[This reference is probably to Vol. III rather than Vol. II in Kharasch's series "Organic Sulfur Compounds". As of March 1970 it has not been published.]

114. Corey, E. J. and Achiwa, K., J. Am. Chem. Soc., 91, 1429 (1969).

115. Schenck, P. W. and Lautenback, D., Ger. Pat. 1,300,100 (July 31, 1969).

116. Becke-Goehring, M., Jenne, H. and Fluck, E., Chem. Ber., 91, 1947 (1958).

117. Weiss, J., Angew. Chem., 71, 246 (1959).

118. Heal, H. G., Nature, 199, 371 (1963).

119. Tavs, P., Schulze-Steinen, H. J. and Colchester, J. E., J. Chem. Soc., 2525 (1963).

120. Heal, H. G. and Kane, J., Nature, 203, 971 (1964).

121. Meuwsen, A., Chem. Ber., 62, 1959 (1929).

122. Weiss, J., Z. Anorg. Allg. Chem., 305, 190 (1960).

123. Sass, R. L. and Donohue, J., Acta Cryst., 11, 497 (1958).

124. Lund, E. W. and Svenson, S. R., Acta Chem. Scand., 11, 940 (1957).

125. Becke-Goehring, M., Herb, H. and Koch, W., Z. Anorg. Allg. Chem., 264, 137 (1951).

126. Meuwsen, A. and Schlossenagel, F., ibid., 271, 226 (1953).

127. Becke-Goehring, M., Weiss, J. and Zirker, G., Z. Naturforsh., 10b, 58 (1955).

128. Becke-Goehring, M., Weiss, J. and Zirker, G., Z. Anorg. Allg. Chem., 278, 1 (1955).

129. Becke-Goehring, M. and Zirker, G., ibid., 285, 70 (1956).

130. Meuwsen, A. and Lösel, M., ibid., 271, 217 (1953).

131. Chapman, D. and Massey, A. G., Trans. Faraday Soc., 58, 1291 (1962).

132. Jolly, W. L., in Tobolsky, A. V., "The Chemistry of Sulfides", Interscience Publishers, New York, N. Y., 1968, pp. 3.

133. Meinzer, R. A. and Myers, R. J., Am. Chem. Soc., Phys. Chem. Div., New York, Sept. 1966, paper No. V-155.

134. Olsen, B. A. and Olsen, F. P., Inorg. Chem., 8, 1836 (1969).

135. Tingle, E. M. and Olsen, F. P., ibid., 8, 1741 (1969).

136. Stone, B. D. and Nielson, M. L., J. Am. Chem. Soc., 81, 3580 (1959).

137. Fluck, V. E. and Becke-Goehring, M., Z. Anorg. Allg. Chem., 292, 229 (1957).

138. Wolbling, H., ibid., 57, 281 (1908).

139. Lewis, G. N. and Randall, M., J. Am. Chem. Soc., 36, 2468 (1914).