Nucleophilic Substitution on S_4N_4. Reactions with Benzylamines

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Received May 29, 1970

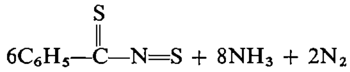
Reactions of benzylamines with tetrasulfur tetranitride lead to benzylidenimine polysulfides, ammonia, *N*-benzylidene benzylamines, and some free sulfur. The stoichiometric equation has been established. The reaction is quite sensitive to structural changes and appears limited to ring substituted benzylamines. The benzylidenimine polysulfides undergo thermal decomposition to sulfur and triphenyl-*s*-triazine and react with benzylamine to give benzylammonium polysulfides, ammonia, and *N*-benzylidene benzylamine. The benzylammonium polysulfides decompose in air to sulfur, hydrogen sulfide, and benzylammonium thiosulfate.

Canadian Journal of Chemistry, 49, 271 (1971)

Tetrasulfur tetranitride is quite reactive toward nucleophilic substitution. Reactions with phosphines (1–3), Grignard reagents (4, 5), ammonia (6, 7), amines (8), cyanide ion (1), and diazomethanes (9) have been reported. Although the products differ considerably from one reaction to another, they generally arise from attack of the nucleophile on sulfur with destruction of the sulfur nitrogen ring system. Formulas of products from a few of these reactions are supported by both elemental analysis and molecular weight determinations, but for some only an elemental analysis is reported; in a few cases there is neither. Seldom is the structure of the product unambiguously determined with both. Overall stoichiometries have only rarely been investigated and, not surprisingly, a composite picture of nucleophilic substitution on tetrasulfur tetranitride has not emerged.

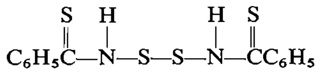
Closely related nucleophiles often appear to behave differently. Although ammonia (6, 7) is reported to give an ammoniate of composition $S_2N_2 \cdot NH_3$, generally formulated as $H_2N{-}S{-}\overset{-}{N}{-}\overset{+}{S}{=}NH$, secondary amines are reported to give thiobisamines. Thus, dimethylamine gave bisdimethylamine monosulfide and piperidine gave bispiperidine monosulfide (8). Benzylamine on the other hand was reported by Schenck (8) to give ammonia, sulfur, and triphenyl-*s*-triazine when reacted on a steam bath but the thioamide of thiobenzoic acid, **1**, at room temperature. The stoichiometry given in eq. 1 was proposed. A material identical to **1** was subsequently isolated from the reaction of sulfur with benzylamine in the presence of lead(II) oxide (10). Based on a molecular weight determination, structure **1** was discarded in favor of **2** or possibly **3**. An authentic sample of **3** subsequently prepared from benzylamine and sulfurmonochloride, however, had different properties (11). The structure of Schenck's material remains in doubt (11*b*). A reaction between tetrasulfur tetranitride and phenylhydrazine was reported to lead to sulfur, nitrogen, and ammonia. The stoichiometry given in eq. 2 was proposed although benzene was not isolated.

[1] $6C_6H_5CH_2NH_2 + 3S_4N_4 \rightarrow$



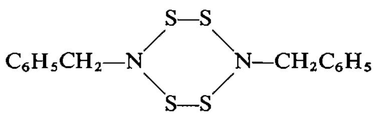
$$6C_6H_5{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}N{=}S + 8NH_3 + 2N_2$$

1



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

2



3

[2] $12C_6H_5NHNH_2 + 3S_4N_4 \rightarrow$

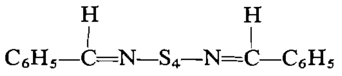
$$12S + 8NH_3 + 12C_6H_6 + 14N_2$$

The work described herein was undertaken with the aims of clarifying the structure of the benzylamine tetrasulfur tetranitride product, of establishing the overall stoichiometry for the reaction, and of determining if this reaction was applicable to other primary amines or to phenylhydrazine.

Results and Discussion

Characterization of Products

When tetrasulfur tetranitride and benzylamine were mixed as described by Schenck (8) [about 1 mol of tetrasulfur tetranitride to 7 mol of amine], an exothermic reaction was observed. This was accompanied by several color changes and the evolution of ammonia. Yellow needles which appeared to be identical to the material described by Schenck were obtained on washing the product with ice cold methanol and constituted the major crystalline product. The elemental analysis corresponded quite closely to the composition $(C_7H_6NS_2)_x$, and the molecular weight (osmometric in benzene) showed x to be 2 in agreement with Levi's observations (10) on the material isolated from 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, **2** and **3**, and also with **1**. It should have been formulated as benzylidenimine tetrasulfide, **4**, based on the following evidence.



$$C_6H_5-\overset{H}{\overset{|}{C}}=N-S_4-N=\overset{H}{\overset{|}{C}}-C_6H_5$$

4

The n.m.r. spectrum, Fig. 1, showed a sharp singlet at −7.87 p.p.m. and a multiplet at −7.05 to −7.48 p.p.m. Integration indicated one proton for the singlet and five protons for the multiplet (phenyl group). This eliminated structures **1** and **3** but did not rule out **2** although it would be rather surprising to have found such a sharp singlet for a thioamide proton (usually at least 0.5 p.p.m. wide). The i.r. spectrum showed no N—H stretching absorption (nothing above 3100 cm^{-1}) thus eliminating **2**. There was, however, a weak band at 1630 cm^{-1} assignable to a C═N stretch, *i.e.* structure **4**.

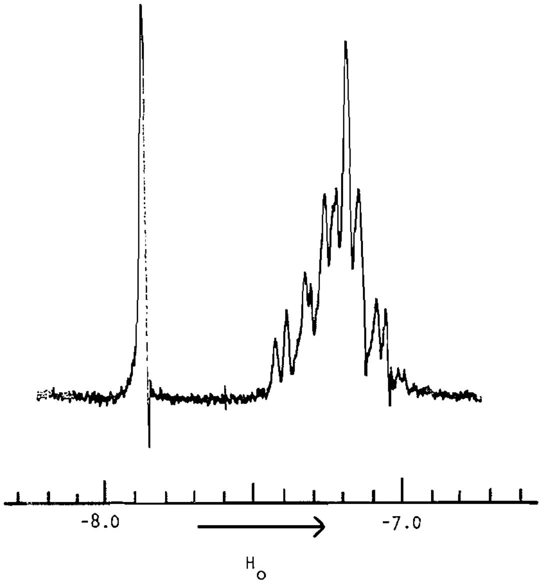
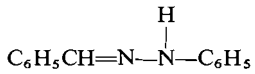
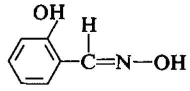


FIG. 1. The n.m.r. spectrum of benzylidenimine tetrasulfide.

Furthermore, two analogous compounds were isolated from the same reaction mixture whose n.m.r. spectra were quite similar to **4**. They both had one sharp singlet of area one downfield from a phenyl multiplet of area five. Elemental analyses and molecular weights along with n.m.r. confirmed that these compounds had the same organic component as **4** but that three and two sulfur atoms replaced the four in **4**. Table 1 lists n.m.r. chemical shifts in various known compounds with a benzylidenimine group. The benzylidenic protons in these compounds lie between −7.73 and −8.61 p.p.m. The chemical shifts of the low field singlets for the three compounds isolated from the reaction of tetrasulfur tetranitride with benzylamine, Table 2, also lie in this region. Thus, the chemical shifts are in good agreement with the benzylidenimine structure. The last compound in Table 2, an analogous monosulfide prepared from *p*-chlorobenzylamine and tetrasulfur tetranitride, is of particular interest. Its n.m.r. spectrum is very similar to that of **4** with a sharp singlet downfield of the phenyl multiplet (areas 1:4). The elemental analysis showed only one sulfur atom per two nitrogen atoms. With a molecular weight near 322, the n.m.r. spectrum requires this compound to have equivalent organic components. There is only one possible symmetrical structure with one sulfur which satisfies all of the requirements: *p*-chlorobenzylidenimine monosulfide. The similarity in n.m.r. spectra then requires similar structures for the other materials. Pyrolysis of benzylidenimine tetrasulfide to elemental sulfur, benzonitrile, and triphenyl-*s*-triazine also supports structure **4**.

A similar arylimine disulfide (but disubstituted on both benzylidene carbons) has been previously prepared (14) by reaction of sulfur monochloride with the phenyl magnesium bromide – benzonitrile adduct. The assignment of structure was based mainly on chemical evidence including the method of synthesis and the observed hydrolysis to benzophenoneimine hydrochloride and sulfur monochloride with concentrated hydrochloric acid.

TABLE 1. The n.m.r. chemical shifts for various known compounds with benzylidenimine protons

Compounds	C_6H_5— (p.p.m.)	$\overset{\displaystyle H}{\overset{|}{-C}}{=}N-$ (p.p.m.)	Solvents
$C_6H_5CH{=}N{-}N{=}CHC_6H_5$	−7.30 to −7.90	−8.52	CCl_4 (12*a*)
 $C_6H_5CH{=}N{-}\overset{\displaystyle H}{\overset{|}{N}}{-}C_6H_5$	−6.50 to −7.70	−7.73	Acetone (12*b*)
$CH_3OC_6H_4CH{=}N{-}N{=}CHC_6H_4OCH_3$	−6.83 to −7.82	−8.61	$CDCl_3$ (12*c*)
	−6.75 to −7.45	−8.18	$CDCl_3$ (13)
$C_6H_5CH{=}N{-}CH_2C_6H_5$	−7.16 to −7.80	−8.22	CCl_4*
p-$ClC_6H_4CH{=}N{-}CH_2C_6H_4Cl$-*p*	−7.32 to −7.92	−8.44	$CDCl_3$*
p-$CH_3OC_6H_4CH{=}N{-}CH_2C_6H_4OCH_3$-*p*	−6.58 to −7.80	−8.10	$CDCl_3$*

*This work.

TABLE 2. Selected constants for arylimine polysulfides $Y{-}C_6H_4CH{=}N{-}S_x{-}N{=}CHC_6H_4{-}Y$

		Infrared (cm^{-1})			Nuclear magnetic resonance	
Y	*x*	C=N	S—N	Thin-layer chromatography* R_f	$-N{=}\overset{\displaystyle H}{\overset{|}{C}}-$	Phenyl
H	4	1630	853	0.46†	−8.02§	−7.12 to −7.55
					−7.87‖	−7.05 to −7.48
	3	1658	850	0.40†	−8.42‖	−7.32 to −7.88
	2	1655	853	0.36†	−8.14‖	−7.24 to −7.84
	1			(0.24)†	(−8.61)‖	
p-CH_3O	4	1670	863	0.73‡	−7.95§	−6.67 to −7.95¶
	3			(0.68)‡		
p-Cl	4	1640	853	0.49†	−7.98§	−7.23
	1	1640	852	0.28†	−8.65§	−7.44 to −7.87

*( ) Not fully characterized.
†Carbon disulfide.
‡Methylene chloride.
§Deuterochloroform.
‖Carbon tetrachloride.
¶Methoxy at −3.85.

Stoichiometry of the Reaction

Schenck's (8) proposed reaction, corrected to the benzylidenimine tetrasulfide structure, is given in eq. 3. When a five-fold excess of acid

$$[3]\quad S_4N_4 + 2C_6H_5CH_2NH_2 \rightarrow N_2 + C_6H_5CH{=}N{-}S_x{-}N{=}CHC_6H_5 + (4 - x)S + 2NH_3$$

($5\ HCl/S_4N_4$) was used to trap the ammonia, the acid solution was basic at the end of the reaction. More than 5 mol of ammonia per mol of nitride was evolved rather than the 2 required by eq. 3. Formation of benzylidenimine tetrasulfide from benzylamine represents oxidation; taking nitrogen to retain its −3 oxidation state in ammonia, sulfur must be reduced. The change in formal oxidation state for sulfur is from +3 in S_4N_4 to $+\frac{1}{2}$ in benzylidenimine tetrasulfide, a change of $2\frac{1}{2}\ e^-$/sulfur, or $10\ e^-/S_4N_4$. Oxidation of benzylamine represents a $2\ e^-$ change or $4\ e^-$/benzylidenimine tetrasulfide. An additional $6\ e^-$ oxidation product is required. Schenck's scheme used the conversion of two nitrogen atoms of S_4N_4 to elemental nitrogen for this purpose. It seems quite likely from the large quantity of ammonia evolved, however, that *all* of the nitrogen of S_4N_4 goes to ammonia. Since 80–85% of the sulfur has been accounted for already, the additional oxidized product must arise from the benzylamine. Column chromatography gave this product, *N*-benzylidene benzylamine. The latter is formally derivable from benzylamine by a 2 e^- oxidation to benzylidenimine and subsequent elimination of ammonia between this product and benzylamine. Thus, 3 mol of *N*-benzylidene benzylamine would be required to account for the missing 6 e^- oxidation. One might then formulate the overall reaction as eq. 4 where the three *N*-benzylidene

$$[4]\quad S_4N_4 + 8C_6H_5CH_2NH_2 \rightarrow C_6H_5CH{=}N{-}S_x{-}N{=}CHC_6H_5 + 7NH_3 + 3C_6H_5CH{=}N{-}CH_2C_6H_5 + (4 - x)S$$

benzylamines are needed to complete the reduction of sulfur. Four moles of ammonia would arise from the four nitrogens of the nitride and the remaining three would result from formation of the 3 mol of *N*-benzylidene benzylamine. This equation was tested by reacting benzylamine and tetrasulfur tetranitride in an 8:1 molar ratio and attempting quantitative isolation of all products. The coefficients from eq. 4 (1:8:1:7:3) were found experimentally to be 1.0:8.0:1.0:6.8:2.8. The stoichiometry given in eq. 4 was therefore quite closely approximated. With a large excess of benzylamine (22:1 molar ratio), benzylidenimine polysulfides were not obtained. The yield of *N*-benzylidene benzylamine increased considerably, and an orange solid identified as benzylammonium polysulfide was obtained in addition to a small amount of benzylammonium thiosulfate. These products were also observed when benzylidenimine polysulfides were reacted with benzylamine. With less than 8 mol of amine per mol of nitride, eq. 4 was still observed, but the quantity of arylimine polysulfides produced decreased in proportion to the quantity of amine used. When the 8:1 stoichiometric reaction was followed by n.m.r. spectroscopy, the final products were found to be present along with the starting materials even in the very early stages of the reaction (5 min). The concentration of the final products increased, and the concentration of the reactants decreased as time passed; the reaction was completed in about 15 h at room temperature. No peaks were observed at any time other than those corresponding to products and reactants, and notwithstanding several color changes, it appears unlikely that any *long-lived* intermediates are present between the starting tetrasulfur tetranitride and benzylidenimine polysulfides. Therefore, the reaction as represented by eq. 4 describes the course of nucleophilic substitution on tetrasulfur tetranitride by benzylamine and offers a synthetic route to arylimine polysulfides with mono substituted α-carbons.[1] The mechanism is not clear, but all of the nitrogen of the tetrasulfur tetranitride goes to ammonia, and the nucleophile becomes bound only to sulfur. Clearly several steps are required with an early step being partially ionic since the reaction is at least ten fold slower in non polar solvents (see next section). The reaction might be better thought of as a redox process than as a nucleophilic substitution.

Synthetic Application

Since the reaction as run was heterogeneous and would not be useful for solid amines, the effect of various solvents was investigated. Benzene resulted in a very slow reaction (if any); only unreacted starting materials were present after 24 h. Acetone resulted in rapid consumption of tetrasulfur tetranitride and amine; however, this appeared to be a Willgerodt–Kindler reaction (15, 16).[2] Several amine solvents were found to give benzylidenimine polysulfides, but the yields were lower than in the absence of solvent. Yields of benzylidenimine polysulfides were 52% in dimethylformamide, 60% in pyridine, and 91% in triethylamine compared to the quantitative reaction observed in the absence of these solvents. Triethylamine, therefore, appears usable when necessary but offers no advantage over the *neat* reaction. Both *p*-methoxy and *p*-chlorobenzylamine were found to undergo a reaction analogous to eq. 4. With the former, the sulfur containing species were *p,p'*-dimethoxybenzylidenimine tetrasulfide in 77% yield and the apparent trisulfide in about 5% yield. The yield of *N*-(*p*-methoxybenzylidene)*p*-methoxybenzylamine was quantitative. With *p*-chlorobenzylamine the yield of polysulfides and of *N*-(*p*-chlorobenzylidene)-

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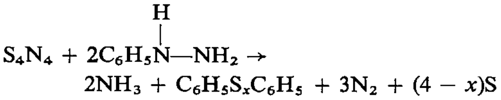
[1] See however following paper.

[2] Although tetrasulfur tetranitride has not previously been examined as a sulfur source under Willgerodt-Kindler conditions, its reactivity in this sense is probably not too surprising (17).

p-chlorobenzylamine was 79%, and some mono sulfide was isolated along with the tetrasulfide. An additional 14% of elemental sulfur was also obtained. Free sulfur could arise by decomposition of the tetrasulfide to the observed monosulfide or by decomposition of some precursor. *p*-Nitrobenzylamine gave approximately 48% of elemental sulfur and no other tractable product. The *p*-nitro group is most likely involved directly in a competing reaction[3] of some sort since both *p*-chloro and *p*-methoxybenzylamines gave acceptable yields of aryliminepolysulfides. α-Methylbenzylamine did not lead to an analogous arylimine polysulfide while allylamine resulted in an apparent polymer. The reaction is therefore quite sensitive to small structural changes, and its synthetic usefulness appears limited to the reactions of ring substituted benzylamines.

With phenylhydrazine (8:1 molar ratio) the products were diphenyl disulfide, diphenyl monosulfide, elemental sulfur, and ammonia. In this reaction approximately 2 mol of ammonia per mol of tetrasulfur tetranitride were evolved. Thus, nitrogen gas must have been formed directly from tetrasulfur tetranitride to complete reduction of the sulfur. Had a reaction analogous to that with benzylamine occurred to give $C_6H_5N{=}N{-}S_x{-}N{=}NC_6H_5$, followed by breakdown of this product to the observed phenylsulfides and nitrogen, 7 mol of ammonia per mol of tetrasulfur tetranitride should still have been evolved. The phenylhydrazine reaction is therefore quite different from that with benzylamine and appears best formulated as in eq. 5. The yield of diphenyl-

[5] 

$$S_4N_4 + 2C_6H_5\overset{\overset{H}{|}}{N}{-}NH_2 \rightarrow 2NH_3 + C_6H_5S_xC_6H_5 + 3N_2 + (4-x)S$$

polysulfides isolated in the presence of triethylamine based on eq. 5 was 74% (55% disulfide and 19% monosulfide). Here also the nucleophile becomes bonded only to sulfur, but the nitrogen is obtained in a different oxidation state than in the benzylamine reaction.

Reactions of Benzylidenimine Tetrasulfide

A mass spectrum of benzylidenimine tetrasulfide failed to show the parent peak. Instead, fragments such as S_x^+ ($x = 1$–8) and $C_6H_5CN^+$ were observed. The sulfur species with $x > 4$ must come from thermal decomposition and subsequent reactions rather than fragmentation, and the whole mass spectrum therefore probably represents pyrolysis products. Schenck (8) reported triphenyl-*s*-triazine as a product from the reaction of tetrasulfur tetranitride with benzylamine at steam bath temperature. Levi (10) was unable to reproduce this work in refluxing benzene. Consequently, the thermal decomposition of benzylidenimine tetrasulfide was investigated. Benzylidenimine tetrasulfide, heated to 105 °C (just above the m.p.) *in vacuo*, gave triphenyl-*s*-triazine, hydrogen sulfide, elemental sulfur, and benzonitrile as the main products along with a basic gas presumed to be ammonia. Thus, the main decomposition is described by eq. 6. The yield of sulfur based on eq. 6 was 82%,

$$[6]\quad C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 \rightarrow H_2S + 2/x(C_6H_5CN)_x + 3S$$

and 67% of the total nitrogen was isolated in the form of either triphenyl-*s*-triazine or benzonitrile. Ammonia must arise from another reaction in competition with eq. 6. This decomposition was not observed in refluxing benzene and appeared to occur only at or above the m.p.

Photolysis of benzylidenimine tetrasulfide resulted in decomposition to lower polysulfides and elemental sulfur as shown in eq. 7. Benzylidenimine monosulfide is very likely produced in this reaction. Although not isolated and fully characterized, the presence of this material is fairly certain from n.m.r. spectra (benzylidenimine type proton at −8.61 p.p.m.) and t.l.c. (R_f of 0.24, color observed when sprayed with silver nitrate solution was nearly identical to the other three benzylidenimine polysulfides and developed at the same rate) of the photolysis mixture.

$$[7]\quad C_6H_5CH{=}N{-}S_4{-}N{=}CHC_6H_5 \xrightarrow{h\nu} C_6H_5CH{=}N{-}S_{4-x}{-}N{=}CHC_6H_5 + xS \quad (x = 1\text{–}3)$$

Since benzylidenimine tetrasulfide was not isolated from tetrasulfur tetranitride in the presence of excess benzylamine, the reaction of the polysulfide with benzylamine was investigated. Benzylidenimine tetrasulfide reacted readily with benzylamine to give a deep reddish solution. Addition of anhydrous ether precipitated an orange solid which resembled the benzylammonium hexasulfide prepared by Levi (19) from sulfur, benzylamine, and hydrogen sulfide.

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[3] See for example ref. 18.

Its n.m.r. spectrum supported this structure. A sample left in the air for a few days decomposed slowly with the evolution of hydrogen sulfide to sulfur and benzylammonium thiosulfate. The thiosulfate presumably arose by air oxidation of either the polysulfide or of one of its intermediate hydrolysis products. Thiosulfates have been previously isolated from sulfur with butylamine and from sulfur with ethylenediamine (20). In these cases the thiosulfates were thought to form concurrently with, rather than from, the polysulfides. Our results demonstrate that in the benzylamine system thiosulfates are a simple air oxidation/hydrolysis product of the benzylammonium polysulfides.

When a sample of benzylammonium polysulfide was dissolved in methanol, it decomposed quite rapidly to hydrogen sulfide, benzylamine and sulfur. The molar ratio of benzylamine to sulfur was 1:3.2 requiring an average sulfur chain length between 7 and 8. Levi's designation (19) of a similar material as a *hexa*sulfide was based on this type of quantitative decomposition to hydrogen sulfide, sulfur, and benzylamine.[4] Similar orange solids were prepared by Levi's (19) method and were also found to result from the reaction of either sulfur or heptasulfurimide with benzylamine. Heptasulfurimide has been previously (21) found to react with a large number of amines. In the case of propylamine, Richter (21) was able to demonstrate the presence of the propylammonium cation in solution although the anion was not identified. Our results would suggest that the anion was a polysulfide or possibly a thiosulfate if the solutions were not kept free of air. (Reactions between sulfur and benzylamine form the basis of the following paper.)

Sulfur chain lengths obtained by analysis of the products from the sulfur–amine, heptasulfurimide–amine, and benzylidenimine tetrasulfide – amine routes tended to vary from one preparation to another. In general, values ranged between 6 and 7 although values as high as 8–9 were occasionally obtained. Several samples of these materials were subjected to pyrolysis and in all cases gave hydrogen sulfide, sulfur, thiobenzamide, 3,5-diphenyl-1,2,4-thiadiazole, and dibenzyl polysulfides. Occasionally, 1,2-diphenyl ethane or *N*-benzylthiobenzamide was also isolated. The ratio of these materials tended to vary from one benzylammonium polysulfide preparation to another with sulfur rich species (free sulfur and dibenzylpolysulfides) predominating by a greater amount compared to sulfur-poor species (diphenylethane, *N*-benzylthiobenzamide, and 3,5-diphenyl-1,2,4-thiadiazole) in those cases where analysis suggested longer sulfur chains. While we cannot be certain that the starting material is free of *uncombined* sulfur in all cases, we favor a variable chain length polysulfide formulation with an average sulfur chain length of between 6 and 7 being most common for the product from the sulfur–benzylamine route in the absence of added hydrogen sulfide and also from the benzylidenimine polysulfide – benzylamine route. The polysulfides when heated with excess benzylamine gave *N*-benzylthiobenzamide. This material has also been obtained in high yield by heating sulfur in benzylamine directly (22). Its formation by heating polysulfides in benzylamine could well arise indirectly by this route, *i.e.*, decomposition to hydrogen sulfide, benzylamine, and free sulfur and subsequent reactions of the latter.

Spectra of Benzylidenimine Polysulfides

The chemical shift in the proton n.m.r. spectra of the methylene group in alkyl polysulfides, $RCH_2S_xCH_2R$, has been reported to be quite sensitive to sulfur chain length (23, 24). For dimethyl-di-*t*-butyl- and dibenzylpolysulfides the absorption moves to lower field as the number of sulfur atoms in the chain increases while for methyl chloro polysulfides, CH_3S_xCl, the methyl absorption moves to higher field as the number of sulfurs increases (23, 24). The difference in chemical shifts between two members of a series generally tended to become smaller as the sulfur chain length increased in all series although the tetra- and pentasulfides appeared closer than expected in the methyl series. For the unsubstituted benzylidenimine polysulfides, the chemical shifts of the benzylidene protons (Table 2) did not vary with sulfur chain length in a consistent manner. The tetrasulfide was at highest field,

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[4] Elemental analysis leading to percent composition does not distinguish between a benzylammonium polysulfide (chain length 6–7) and a benzylammonium hydrogen sulfide (with a chain length of 3–3.5); however, a polysulfide on thermal decomposition would lead to hydrogen sulfide and benzylamine in molar ratios of 1:2 while a benzylammonium hydrogensulfide would give these materials in a 1:1 molar ratio. Levi's (19) observed values of 1:1.97 and 1:2.07 eliminate this latter possibility.

followed by the disulfide, the trisulfide, and at lowest field the (presumed) monosulfide. It is apparent that estimating sulfur chain lengths from relative chemical shifts alone is dangerous where these shifts have not been independently established by some other method. The R_f values (Table 2) appear to be a better criterion for this purpose. These increase monotonously as the number of sulfurs increase in all cases.

The i.r. spectra of the benzylidenimine polysulfides were complex; however, all showed weak absorption between 1640 and 1670 cm^{-1} as well as fairly strong absorption between 850–865 cm^{-1}. These regions, summarized in Table 2, represent C=N and N—S stretching frequencies. The intensity of the C=N absorption is known to be quite variable (25). Oximes generally give very weak C=N stretching absorptions.[5] For all benzylidenimine polysulfides prepared, the C=N stretching absorptions were observed to be weak. The sulfur–nitrogen stretching frequencies have been found (27) to be related to the sulfur–nitrogen bond lengths by the empirical eq. 8,

$$r_{NS} = 0.0483\mu_{NS} + 1.099 \quad [8]$$

where μ_{NS} = i.r. stretch in μ; r_{NS} = bond length. The sulfur–nitrogen bond lengths estimated from this equation are fairly constant at 1.66 Å for all of the imines prepared. This is somewhat shorter than the normal single bond length of 1.76 Å found in sulfamic acid (28) or the single bond covalent radii sum of 1.74 Å (29) but is longer than the N—S bond in tetrasulfur tetranitride (1.62 Å) (30). These data suggest that the N—S bond in the benzylidenimine polysulfides has at least some double bond character. The bond order is estimated as about 1.5 from the empirical relationship between i.r. stretching frequency and bond order given by Chapman and Waddington (31). If these empirical relationships hold for the benzylidenimine polysulfides, the suggested increase in bond order could be interpreted as evidence for dπ–pπ double bonding between the Schiff's base and the adjacent sulfur.

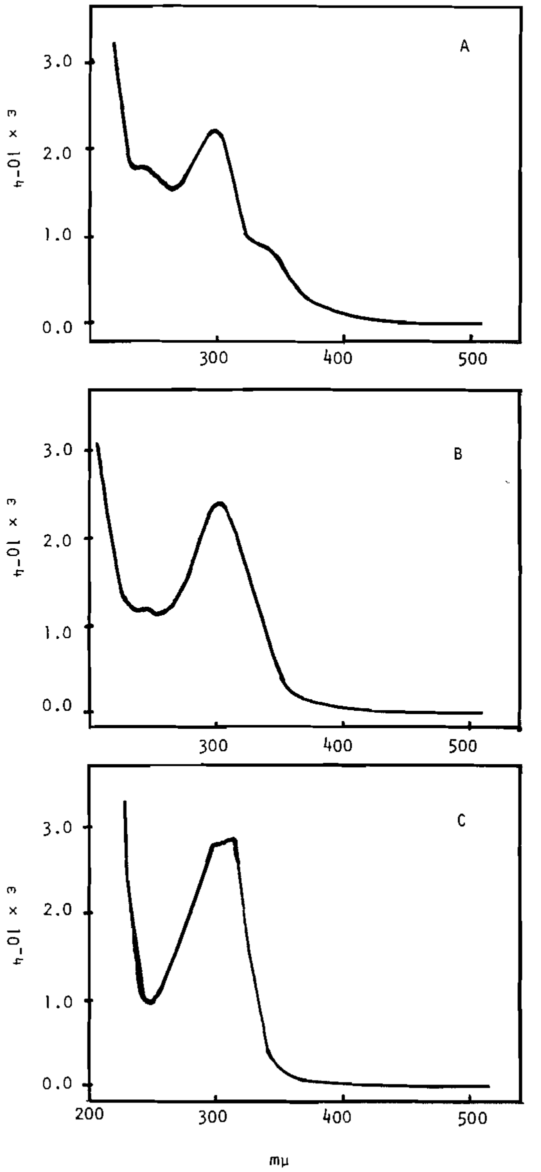

FIG. 2. Electronic absorption spectra of benzylidenimine polysulfides in methanol; (A) tetrasulfide; (B) trisulfide; (C) disulfide.

Ultraviolet absorption spectra for the unsubstituted benzylidenimine polysulfides are shown in Fig. 2. The tetrasulfide showed three maxima at 243 ($\varepsilon = 1.8 \times 10^4$), 303 ($\varepsilon = 2.3 \times 10^4$), and 333 mμ ($\varepsilon = 1.0 \times 10^4$). The trisulfide showed only two obvious maxima at 242 ($\varepsilon = 1.3 \times 10^4$) and 309 mμ ($\varepsilon = 2.4 \times 10^4$) while the disulfide had maxima at 294 ($\varepsilon = 2.8 \times 10^4$) and 304 mμ ($\varepsilon = 2.9 \times 10^4$). These spectra do not closely resemble those of either typical alkyl polysulfides (32, 33) or typical Schiff's bases (34). Judging from the increase in extinction coefficients in the 300 mμ region for the

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[5] Acetophenoneoxime shows a C=N stretching absorption whose molar extinction coefficient is almost 1/20 the value in the corresponding Schiff's base (26).

lower sulfides, it appears likely that three absorptions occur in each compound becoming more clearly separated as the sulfur chain length increases. It does not seem profitable to speculate on the probable origin of these transitions at this time.

Experimental

General

Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. Proton n.m.r. spectra were recorded on a Varian Model T-60 spectrometer and are relative to internal tetramethyl silane. Elemental analyses were performed by Schwarzkopf Microanalytic Laboratories, Woodside, New York. Molecular weight measurements were carried out on a Mechrolab Model 301A Vapor Pressure Osmometer with dibenzyl disulfide as reference and benzene as solvent. The i.r. spectra were recorded on a Beckman IR5 spectrometer and u.v. spectra on a Cary Model 14 using methanol as solvent. The dry box was a Vacuum Atmospheres Corporation Dry Lab Model HE-43 equipped with Dry Train Model HE-93B. The t.l.c.'s were obtained on 0.1 mm air dried silica gel plates using carbon disulfide or methylene chloride as eluent and sulfur as a reference. Chromatography grade silica gel (100–200 mesh) was used for column chromatography keeping the weight of absorbent to that of the mixture near 50:1.

Materials

Tetrasulfur tetranitride was prepared from sulfur monochloride and ammonia as previously described (35). Recrystallization from benzene afforded pure material of m.p. 178 °C dec. *p*-Nitrobenzylamine was prepared from potassium phthalimide and *p*-nitrobenzylbromide as previously described (36, 37). Its n.m.r. spectrum in deuterochloroform showed three absorptions: -1.72 p.p.m. (broad singlet, 2.2 H, —NH_2), -4.05 p.p.m. (singlet, 2.0 H, —CH_2—), and -7.36 to -8.34 p.p.m. (multiplet, 4.1 H, —C_6H_4—). The m.p. of the hydrochloride salt was 249–250 °C [lit. 250 (38) and 256 °C (39)]. Solvents used for chromatography were U.S.P. grade, and sulfur was "precipitated" grade. Other materials were reagent grade and were used without further purification.

Reactions of Sulfur with Benzylamine; Identification of Products

Tetrasulfur tetranitride (1.99 g, 10.8 mmol) 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 containing 50.0 mg equiv of hydrochloric acid in about 250 ml of water. Benzylamine was degassed under vacuum, and 8.0 ml (73 mmol) was introduced through the rubber serum stopper by syringe. The reaction was stirred at room temperature while a continuous flow of nitrogen was maintained through the apparatus. The tetrasulfur tetranitride dissolved in the benzylamine to give an orange solution which gradually changed to dark green and after 30 min to yellow-brown. These color changes were accompanied by evolution of heat and ammonia, the latter continuing for at least 5 h. After 14 h the reaction mixture solidified to a yellow chunk. At this point the hydrochloric acid solution was found to be basic. The reaction mixture was separated by chromatography. Hexane eluted about 20 mg of sulfur identified by its m.p. and R_f value. Pure benzylidenimine tetrasulfide (about 2.5 g), obtained from the column by elution with 13% benzene in hexane, was recrystallized from hot methanol to give yellow needles of m.p. 100.5–102 °C.

Anal. Calcd. for $C_{14}H_{12}N_2S_4$ (mol. wt.: 336): C, 49.97; H, 3.59; N, 8.32; S, 38.11. Found (332): C, 49.54; H, 3.67; N, 8.70; S, 37.70.

Benzylidenimine tri- and disulfides were also eluted by 13% benzene in hexane but were not cleanly separated on the column. Appropriate enriched fractions were combined and were further purified by fractional recrystallization from methanol. The trisulfide (about 200 mg) gave white needles of m.p. 125–126 °C.

Anal. Calcd. for $C_{14}H_{12}N_2S_3$ (mol. wt.: 304): C, 55.23; H, 3.97; N, 9.20; S, 31.59. Found (306): C, 55.07; H, 4.12; N, 8.98; S, 32.04.

The disulfide (about 400 mg) was recrystallized from methanol to give nearly colorless white needles of m.p. 100–100.5 °C.

Anal. Calcd. for $C_{14}H_{12}N_2S_2$ (mol. wt.: 272): C, 61.74; H, 4.44; N, 10.28; S, 23.54. Found (271): C, 61.16; H, 4.20; N, 10.41; S, 23.74.

Elution with 20% ether in benzene gave *N*-benzylidene benzylamine (about 1.9 g) as an oil with a b.p. near 105 °C at 0.1 mm Hg. The n.m.r. and i.r. spectra were identical to those of an authentic sample prepared from benzylamine and benzaldehyde (40). Benzaldehyde (about 2.0 g) was eluted by 40% ether in benzene and was identified by comparison of its n.m.r. and i.r. spectra with those of an authentic sample. A quantity of benzylamine was obtained from the column on elution with 50% methanol in ether. Since an n.m.r. spectrum of the crude reaction mixture prior to chromatography did not indicate the presence of either benzylamine or benzaldehyde, these materials must form by hydrolysis of *N*-benzylidene benzylamine on the column.

Quantitative Reaction at a Molar Ratio of 1:8

The reaction was repeated as above using 922 mg (5.01 mmol) of tetrasulfur tetranitride and 4.4 ml (40.3 mmol) of benzylamine. The gas washing bottle contained 50.0 mg equiv of hydrochloric acid. After 20 h of stirring the hydrochloric acid was diluted to 500 ml. A 25.0 ml aliquot required 8.20 ml of 0.100 *N* sodium hydroxide solution for neutralization. The products were separated by washing with ice cold methanol to give 1.21 g of benzylidenimine tetrasulfide contaminated with small amounts of sulfur and benzylidenimine tri- and disulfides. The methanol was removed *in vacuo* to give 3.26 g of oil. The t.l.c. indicated this oil to be mainly *N*-benzylidene benzylamine with a small amount of benzylidenimine tetrasulfide. An n.m.r. spectrum gave the molar ratio of these two as 9.1 to 1.0. Total yields of products were therefore: ammonia, 33.6 mmol; *N*-benzylidene benzylamine, 2.74 g (14.0 mmol); sulfur and benzylidenimine polysulfides together expressed as tetrasulfide, 1.73 g (5.15 mmol).

Excess Benzylamine

Tetrasulfur tetranitride (500 mg, 2.72 mmol) and 6.4 ml of benzylamine (59 mmol) were stirred under a dry nitrogen atmosphere. The solution went through the orange and green stages, became orange and then blood red. After 24 h it was reddish brown and quite viscous. Upon addition of anhydrous ether a reddish solution containing an orange solid was obtained; some hydrogen sulfide was evolved. The orange solid was filtered, and the red ether solution was evaporated to give 5.75 g of material which when chromatographed yielded *N*-benzylidene benzylamine (1.78 g), sulfur (130 mg), benzaldehyde (1.95 g), benzylammonium thiosulfate (210 mg), and a quantity of benzylamine. The orange solid melted with decomposition at 90–97 °C in an evacuated sealed tube and decomposed continuously in air with evolution of hydrogen sulfide. After several days in air it was a mixture of sulfur and a white solid which after recrystallization from methanol had a m.p. of 173–174 °C. This material in aqueous solution gave a white precipitate with lead acetate; with silver nitrate it gave a yellowish precipitate which soon turned brown; with barium chloride it gave a white precipitate which was soluble in dilute hydrochloric acid but not in acetic acid; it readily discolored permanganate and was therefore identified as a thiosulfate. The n.m.r. spectrum in deuterium oxide showed three peaks consistent in chemical shift and areas with those expected for the phenyl, ammonium (exchanging with water), and methylene peaks of a benzylammonium ion. Its i.r. spectrum showed a strong NH stretch at 3280 cm^{-1}. Calcd. for benzylammonium thiosulfate 8.80% N, found 8.53% N.

Reactions with p-Chlorobenzylamine; Identification of Products

Tetrasulfur tetranitride (533 mg, 2.90 mmol) and 2 ml of *p*-chlorobenzylamine (16 mmol) were reacted as above. After 24 h the thick yellow paste was separated by chromatography. Hexane eluted about 70 mg of sulfur. Elution with 20% benzene in hexane gave about 570 mg of *p*-chlorobenzylidenimine tetrasulfide which was recrystallized from methanol to give yellow needles of m.p. 114.5–116 °C.

Anal. Calcd. for $C_{14}H_{10}N_2S_4Cl_2$ (mol. wt.: 405): C, 41.48; H, 2.49; N, 6.91; Cl, 17.49; S, 31.64. Found (395): C, 41.56; H, 2.65; N, 6.91; Cl, 17.38; S, 31.80.

p-Chlorobenzylidenimine monosulfide (about 240 mg) was eluted by 50% benzene in hexane and after recrystallization from methanol gave yellow needles of m.p. 146.2–146.8 °C.

Anal. Calcd. for $C_{14}H_{10}N_2SCl_2$ (mol. wt.: 309): C, 54.38; H, 3.26; N, 9.06; Cl, 22.93; S, 10.37. Found (322): C, 54.15; H, 3.25; N, 9.56; Cl, 22.86; S, 10.88.

N-(*p*-Chlorobenzylidene)-*p*-chlorobenzylamine was eluted by 100% benzene and was recrystallized from methanol to give thin white plates of m.p. 62–65 °C.

Anal. Calcd. for $C_{14}H_{11}NCl_2$ (mol. wt.: 264): C, 63.66; H, 4.20; N, 5.30; Cl, 26.84. Found (281): C, 63.57; H, 4.18; N, 5.31; Cl, 26.58.

At Molar Ratio of 1:8

When 344 mg (1.87 mmol) of tetrasulfur tetranitride was reacted with 2.11 g (14.9 mmol) of *p*-chlorobenzylamine, the products obtained were sulfur, 33 mg (1.03 mmol), *p*-chlorobenzylidenimine tetrasulfide, 598 mg (1.48 mmol), and *N*-(*p*-chlorobenzylidene)-*p*-chlorobenzylamine, 1.17 g (4.43 mmol). *p*-Chlorobenzylidenimine monosulfide was found in only trace amounts along with two other materials which appeared to be the di- and trisulfides based on their R_f values of 0.38 and 0.30 *vs.* 0.49 and 0.25 for the tetra- and monosulfides, respectively.

Reactions with p-Methoxybenzylamine; Identification of Products

Tetrasulfur tetranitride (542 mg, 2.94 mmol) and 2.0 ml (16 mmol) of *p*-methoxybenzylamine were reacted as above. After 24 h the solidified product was washed with ice cold methanol to give 710 mg (1.79 mmol) of *p*-methoxybenzylidenimine tetrasulfide which on recrystallization from absolute ethanol gave yellow plates of m.p. 112–113 °C.

Anal. Calcd. for $C_{16}H_{16}N_2S_4O_2$ (mol. wt.: 396): C, 48.46; H, 4.07; N, 7.06; S, 32.34. Found (391): C, 48.59; H, 4.24; N, 7.10; S, 32.66.

The methanol solution was concentrated, and the products were dissolved in chloroform from which 93 mg of a white solid of m.p. 230 °C precipitated. This material was identified as *p*-methoxybenzylammonium thiosulfate based on n.m.r. and chemical analyses as described for benzylammonium thiosulfate. The remaining yellow oil was purified by column chromatography to give an additional 140 mg of *p*-methoxybenzylidenimine tetrasulfide (eluted by 5% ether in benzene), 620 mg of anisaldehyde (eluted by 100% ether) identified by comparison of its n.m.r. and i.r. spectra with those of an authentic sample, and *p*-methoxybenzylamine (eluted by 80% methanol in ether) which was identified by its n.m.r. spectrum.

At Molar Ratio of 1:8

When 2.00 g (10.8 mmol) of tetrasulfur tetranitride was reacted with 10.9 ml (87 mmol) of *p*-methoxybenzylamine and the product was washed with ice cold methanol, 3.13 g of *p*-methoxybenzylidenimine tetrasulfide remained. Upon cooling to about −20 °C, 372 mg of a yellow solid precipitated. This material was a roughly equal mixture of *p*-methoxybenzylidenimine tetrasulfide and a new *p*-methoxybenzylidenimine polysulfide of $R_f = 0.68$ *vs.* 0.73 for the tetrasulfide. Attempted recrystallization of this material led to a mixture of these two materials with a third, *p*-methoxybenzylidenimine polysulfide. The original solvent from which these solids were obtained was removed *in vacuo* to give 8.45 g of oil. A part of this material when chromatographed gave mainly anisaldehyde and *p*-methoxybenzylamine. The n.m.r. spectrum before chromatography did not show any aldehyde, however. When the balance was distilled under reduced pressure, a yellow oil was obtained at 175–180 °C and 0.1 mm Hg which crystallized to a solid of m.p. 36.5–37.5 °C, lit. (41) 37–38 °C for *N*-(*p*-methoxybenzylidene)-*p*-methoxybenzylamine. The n.m.r. spectrum (a singlet at −3.62, 3.0 H, CH_3O—; a broad singlet at −4.58, 4.1 H, —CH_2—; a multiplet at −6.58 to −7.80, 4.1 H, —C_6H_4—; and a broad singlet at −8.10 p.p.m., 1.0 H, H—C═N) was consistent with that expected for this material. Total yields were therefore

3.32 g (8.37 mmol) of *p*-methoxybenzylidenimine tetrasulfide, 180 mg (0.49 mmol) of *p*-methoxybenzylidenimine trisulfide[6] and 8.45 g (33.1 mmol) of *N*-(*p*-methoxybenzylidene)-*p*-methoxybenzylamine.

p-Nitrobenzylamine

Tetrasulfur tetranitride (500 mg, 2.72 mmol) was reacted as above with 2.0 g (13 mmol) of *p*-nitrobenzylamine. The reaction mixture became very viscous, and 2 ml of dimethylformamide (the minimum amount to allow the mixture to be stirred) was added. After 12 h 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) precipitated. The mother liquor contained a viscous tar whose n.m.r. spectrum showed no peaks downfield from the phenyl multiplet. Characterization of this material was not undertaken.

d,l-α-Methylbenzylamine

Tetrasulfur tetranitride (656 mg, 3.56 mmol) was reacted as above with 2 ml of α-methylbenzylamine (16 mmol). The reaction mixture became brownish red, and a basic gas was evolved. After stirring for 24 h, the viscous product was dissolved in methanol and cooled to 0 °C whereupon 160 mg (5.0 mg atoms) of sulfur precipitated. Attempted chromatographic separation led to a number of fractions of viscous dark brown materials but none had the singlet methyl peak required for a benzylidenimine type of product. Distillation, recrystallization and preparative scale t.l.c. failed to give tractable, single component products.

Allylamine

Tetrasulfur tetranitride (501 mg, 2.72 mmol) was reacted as above with allylamine (2 ml, 27 mmol). Ammonia was evolved fairly rapidly, and the color passed through orange to dark brown; after 6 h it had become very viscous. The excess allylamine was removed *in vacuo* leaving a dark brown tar which was insoluble in ether, benzene, hexane, and alcohol. This was assumed to be polymeric and was not further characterized.

Phenylhydrazine

Tetrasulfur tetranitride, 514 mg (2.80 mmol), was placed in a flask equipped as in the benzylamine reaction and cooled to 0 °C. The gas washing bottle contained 7.00 mg equiv of hydrochloric acid in about 70 ml of water. Phenylhydrazine (2.15 g, 19.9 mmol) was added to the flask and immediately solidified. On warming to about 20 °C it remelted, and the temperature of the exothermic reaction which ensued was maintained below 25 °C by periodic cooling. The solution became orange, then brilliant yellow-orange, and eventually yellow. After 6 h gas evolution had ceased. After 12 h the reaction was stopped, and the solution in the acid trap was diluted to 100 ml. A 50 ml aliquot required 4.45 ml of 0.075 *N* potassium hydroxide solution for neutralization. The products were separated by column chromatography. Hexane eluted 221 mg (6.90 mg atoms) of elemental sulfur. Elution with 15% benzene in hexane gave 196 mg of a white solid which was recrystallized from methanol to give diphenyl disulfide of m.p. 59–60 °C, lit. (42) 60–61 °C, and molecular weight by mass spectrum of 218 (Calcd. for $C_{12}H_{10}S_2$, 218). The n.m.r. and i.r. spectra were identical to those of authentic diphenyldisulfide. Elution with 20% benzene in hexane gave 122 mg of diphenyl monosulfide as a colorless oil. The mass spectrum showed an apparent molecular ion of mass 186 (Calcd. for $C_{12}H_{10}S$, 186). The n.m.r. and i.r. spectra were identical to those of the authentic material. Elution with more polar solvents gave considerable amounts of multicomponent mixtures of viscous red materials which were not characterized. A similar reaction of 504 mg (2.74 mmol) of tetrasulfur tetranitride and 2 ml (20.4 mmol) of phenylhydrazine in 5 ml of triethylamine for 30 h at 0 °C with work-up as above led to 95 mg (2.97 mg atoms) of elemental sulfur, 326 mg (1.49 mmol) of diphenyl disulfide, and 99 mg (0.53 mmol) of diphenyl monosulfide

Pyrolysis of Benzylidenimine Tetrasulfide

Benzylidenimine tetrasulfide (711 mg, 2.12 mmol) was placed in a 100 ml flask, evacuated to 7×10^{-4} mm Hg, sealed, and heated in an oil bath to 105 °C. As the solid fused, some gas evolution was observed, and an oil boiled off and condensed on the walls of the flask above the oil bath level. After 7 h the mixture was cooled, the flask was opened, and a basic gas was detected by p*H* paper. Hydrogen sulfide was also detected by wet lead acetate paper. The non-volatile products were separated by column chromatography. Pure hexane eluted 222 mg (6.6 mg atoms) of elemental sulfur. Elution with 13% benzene in hexane gave 45 mg of unreacted benzylidenimine tetrasulfide (0.13 mmol). Elution with 20% benzene in hexane gave 234 mg (0.76 mmol) of triphenyl-*s*-triazine (R_f 0.14, silica gel – carbon disulfide with sulfur = 0.80). Recrystallization from a hexane–benzene mixture gave colorless needles of m.p. 234.5–235 °C [lit. (43) 235–235.4 °C]. The i.r. spectrum of this material was identical to that of authentic triphenyl-*s*-triazine (43). A 1:1 mixture of benzene and hexane eluted 59 mg (0.57 mmol) of benzonitrile identified by comparison of its i.r. and n.m.r. spectra with those of an authentic sample.

Benzylidenimine Tetrasulfide with Excess Benzylamine

Benzylidenimine tetrasulfide (510 mg, 1.52 mmol) was dissolved in 2.71 g (25 mmol) of benzylamine under a dry nitrogen atmosphere and stirred for 24 h.[7] The reaction mixture was placed in a dry box and anhydrous ether was introduced into the reaction mixture and stirred well. An orange solid precipitated which was filtered and washed with ether. This solid decomposed in air with the evolution of hydrogen sulfide and melted at 93–96 °C dec. in an evacuated sealed tube. Nitrogen analysis gave 6.67%. Calcd. for $C_{14}H_{10}N_2S_6$, 6.85 and for $C_{14}H_{10}N_2S_7$, 6.37%. An n.m.r. spectrum in dry dimethyl-d_6-sulfoxide showed three peaks: -3.96 (singlet, 1.7 H, $—CH_2—$), -6.32 (broad singlet, 3.4 H, $—NH_3$) and

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[6] The assignment of this material as the trisulfide rests on the R_f value and on the decomposition to tetrasulfide and a new material, probably the disulfide. Disproportionation of unsubstituted benzylidenimine trisulfide to di- and tetrasulfides was observed when samples were left in solution for long periods of time.

[7] A reaction run without a dry nitrogen atmosphere led to benzylammonium thiosulfate.

−7.00 p.p.m. (broad singlet, 5.0 H, C_6H_5—). The filtrate was concentrated to give an oily material. This was separated by column chromatography to give 55 mg of sulfur (1.7 mg atoms), 425 mg (2.2 mmol) of *N*-benzylidene benzylamine, 310 mg (2.9 mmol) of benzaldehyde, and a substantial quantity of benzylamine. A sample of the orange solid was placed in an evacuated sealed tube (weight not recorded) in the dry box and heated to 170–180 °C for 12 h. A strong odor of hydrogen sulfide (confirmed by wet lead acetate paper) was noted when the tube was cooled and opened. The non-volatile products were separated by column chromatography. Hexane eluted 73 mg (2.3 mg atoms) of elemental sulfur. Elution by 20–40% benzene in hexane gave 120 mg (about 0.4 mmol) of dibenzyl-polysulfides with sulfur chain lengths of 2–6 inclusive.[8] Elution with benzene gave 66 mg (0.27 mmol) of 3,5-diphenyl-1,2,3-thiadiazole which after recrystallization from ethanol had a m.p. of 89–90 °C [lit. (44) 89–90 °C]. This was further identified by mixed m.p. (undepressed) and comparison of its i.r. and n.m.r. spectra with those of an authentic sample prepared from thiobenzamide and iodine (44). Ether eluted 37 mg (0.16 mmol) of *N*-benzylthiobenzamide of m.p. 85 °C [lit. (45) 84–85 °C]. This was identified by mixed m.p. (undepressed) and comparison of its i.r. and n.m.r. spectra with those of the authentic material prepared from sulfur and benzylamine (45). Elution with 30% methanol in ether gave 72 mg (0.53 mmol) of thiobenzamide which was recrystallized from benzene to give a m.p. of 113–114 °C [lit. (46) 115–116 °C]. The mixed m.p. with an authentic sample prepared from benzonitrile and hydrogen sulfide (46, 47) was undepressed, and the i.r. and n.m.r. spectra were identical.

A sample of benzylammonium hexasulfide was prepared from benzylamine, sulfur, and hydrogen sulfide as previously described (19). It melted at 96 °C in an evacuated sealed tube and was an orange solid which decomposed slowly in air with evolution of hydrogen sulfide to give eventually elemental sulfur and benzylammonium thiosulfate. The n.m.r. spectrum of this material was virtually superimposable on that of the material obtained from the benzylidenimine tetrasulfide reaction.

Benzylamine with Sulfur

Benzylamine (5 ml, 45.8 mmol) was added to 1.08 g (33.8 mg atoms) of sulfur, and the mixture was stirred for 24 h under a nitrogen atmosphere. Anhydrous ether was added and stirred well. An orange solid remained undissolved (1.94 g) which melted at 93–94 °C in an evacuated sealed tube. Nitrogen analysis gave 6.54% (*i.e.*, between a hexa- and heptasulfide).

A sample was subjected to a Soxhlet extraction with anhydrous ether in the dry box for 24 h and was found to be completely decomposed into sulfur, benzylamine, and (presumably) hydrogen sulfide. A sample left in air evolved hydrogen sulfide and became a yellowish solid. This was dissolved in methanol to leave some elemental sulfur. The methanol solution was found to contain mainly benzylammonium thiosulfate. Another sample added to methanol evolved hydrogen sulfide and deposited 344 mg (10.7 mg atoms) of sulfur. The methanol solution contained 357 mg (3.3 mmol) of benzylamine. A sample (not weighed) was heated for 12 h at 170–180 °C in an evacuated sealed tube. The products obtained on chromatography were: sulfur, 188 mg (5.9 mg atoms); 1,2-diphenylethane, 74 mg (0.41 mmol); dibenzylpolysulfides (a mixture of tri-, tetra-, penta- and hexasulfides), 88 mg (about 0.35 mmol);[8] 3,5-diphenyl-1,2,3-thiadiazole, 127 mg (0.53 mmol); and thiobenzamide, 40 mg (0.29 mmol).

A sample of the benzylammonium polysulfide (568 mg) was dissolved in 8 ml of benzylamine and refluxed for 3 h during which time the dark reddish brown color slowly changed to pale yellow, and vigorous hydrogen sulfide evolution was observed. The reaction mixture was dissolved in hot hexane, and upon cooling 600 mg (2.7 mmol) of *N*-benzylthiobenzamide of m.p. 86 °C was obtained.

Heptasulfurimide with Benzylamine

Benzylamine (4.2 ml, 38.6 mmol) was added to 1.00 g (4.18 mmol) of heptasulfurimide under a dry nitrogen atmosphere. The solution immediately became blue and after a few minutes dull green and then reddish. After 10 h the dark red solution was placed in the dry box, and an aliquot was removed and heated in 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. The remainder was stirred with anhydrous ether in the dry box. About 400 mg of an orange solid precipitated. This was filtered and washed with anhydrous ether to give a material of m.p. 95–97 °C dec. Nitrogen analysis gave 5.82%; calculated for benzylammonium *octa*sulfide, 6.06 and for the *nona*sulfide, 5.67%. This material, in contrast to the previous samples, was not stable even in the dry box; it slowly became dark brown and looked "wet". In air it decomposed with the evolution of hydrogen sulfide to give sulfur and benzylammonium thiosulfate. A sample (not weighed) was pyrolyzed in an evacuated sealed tube as before and gave: sulfur, 174 mg (5.4 mg atoms); dibenzylpolysulfides (a mixture of di-, tetra- and pentasulfides), 214 mg (0.86 mmol);[8] 3,5-diphenyl-1,2,3-thiadiazole, 127 mg (0.53 mmol); and thiobenzamide, 40 mg (0.29 mmol).

This work was carried out under a grant from the National Research Council of Canada.

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[8] The chain length and average composition was estimated from n.m.r. spectra. See ref. 24.

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