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A five-step sequence has been established for the room temperature reaction of sulfur with benzylamine. Benzylamine polysulfides and benzylidenimine polysulfides occur as interconverting intermediates in this system. The final products are benzylammonium polysulfides, ammonia, and N-benzylidene benzylamine.

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Primary amines have been successfully employed in the Willgerodt-Kindler reaction (1, 2) where, in addition to the usual products, they can lead to novel types of compounds. Thus, acetophenone at elevated temperatures gives thioamides (1, 2) but at room temperature (in the presence of 0.25 g atoms of sulfur per mol of ketone) gives a Schiff's base (3). When the quantity of sulfur is increased, the yield of Schiff's base decreases, and at a sulfur to ketone ratio of 8:1 the heterocyclic compound 8-alkylamino-8-phenyl-1,2,3,4,5,6-hexathiocane-7thione (1) results (4, 5). Primary amines are



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known to catalyze various reactions of sulfur with organic substrates. Aniline, for example, shows an accelerating effect on the rate of vulcanization of natural rubbers (6–8). Mercaptans, unreactive toward elemental sulfur at low temperatures, readily evolve hydrogen sulfide in the presence of butylamine (9, 10) providing a convenient route to alkyl disulfides. By adjusting the molar ratio of mercaptan to sulfur, the sulfur chain length in the product can be changed fairly selectively up to the tetrasulfide (10). *n*-Butyl- and other amines may function as catalysts in the dehydrogenation of heterocyclic compounds with elemental sulfur (11, 12).

The mechanism of the Willgerodt-Kindler reaction remains unclear, notwithstanding a considerable amount of work. Most of the proposed mechanisms (1, 2, 9, 13–17) have considered the first step to be attack either by the amine at the carbonyl carbon or by sulfur at the α -carbon to the carbonyl group. This step is generally thought

to be followed by migration of the functional group or groups along the carbon chain with eventual irreversible oxidation at the end of the chain giving the final product. These mechanisms remain rather speculative, and none has considered the possibility of any reaction between sulfur and the amine. More detailed information about the interaction of sulfur with amines, a reaction which is known to occur even at room temperature (18, 19), appears vital to any understanding of the Willgerodt-Kindler reaction and the various other reactions involving amines as catalysts in sulfur reactions. The work described herein was undertaken with the aim of establishing the nature of the room temperature reactions between sulfur and benzylamine.

Results and Discussion

A Proposed Reaction Scheme

Purified tertiary amines have been demonstrated to be inert to sulfur under normal conditions (18, 20, 21) but to give trialkylammonium polysulfides when hydrogen sulfide is added (22). Primary and secondary amines also lead to alkylammonium polysulfides with hydrogen sulfide and sulfur (22) although here the same products result even in the absence of added hydrogen sulfide (23, 24). Levi (25) has proposed reactions 1 and 2 to account for these observations.

 $[1] \qquad 2R_2NH + S_{y+1} \rightarrow R_2N - S_y - NR_2 + H_2S$

[2] $H_2S + (x - 1)S + 2R_2NH \rightarrow (R_2NH_2^+)_2S_x^{2-1}$

Spectroscopic and conductometric measurements (18) have confirmed the presence of alkylammonium polysulfides in both the primary and secondary amine systems. The e.s.r. data have been interpreted (26) in terms of polythiobisamines, and these materials have been isolated from several secondary amine – sulfur reactions carried out in the presence of a hydrogen sulfide scavenger (25, 27). It therefore seems reasonable to assume that since primary amines form polysulfide ions, they should also form polythiobisamines. The product isolated from benzylamine (the only primary amine reported to lead to a well-defined product) and sulfur in the presence of lead(II) oxide was not the benzylamine polysulfide, however, but rather its oxidation product, benzylidenimine tetrasulfide (28, 29).

Benzylamine disulfide was consequently prepared and evaluated as a possible intermediate in this reaction. This material decomposed quite readily when exposed to small amounts of benzylamine at room temperature. Even in the absence of base it was stable for only a few hours. After an induction period $(5-5\frac{1}{2}h)$ with no change), it underwent fairly rapid ($\sim l$ h) 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 the autocatalytic decomposition was monitored by n.m.r., benzylamine and benzylidenimine tetrasulfide were observed to form, to increase to a maximum concentration, and then to decrease in amount as the concentration of N-benzylidene benzylamine increased. The ratio of benzylamine to benzylidenimine tetrasulfide formed in the early stages was near 4:1. These results suggested a base catalyzed redox type disproportionation of benzylamine disulfide as per eq. 3. The ben-

$$\begin{array}{c} H & H \\ \downarrow & \downarrow \\ 1 & 1 \\ 3 & 3C_6H_5CH_2N_5_2 - NCH_2C_6H_5 \rightarrow \\ H & H \\ 4C_6H_5CH_2NH_2 + C_6H_5C - N - S_4 - N - CC_6H_5 + 2S \end{array}$$

zylamine produced would be expected to catalyze further decomposition of the benzylamine disulfide leading to the observed autocatalysis. As described in the preceding paper (29), benzylidenimine tetrasulfide reacts with benzylamine to give benzylamine, and ammonia. This reaction would occur as the concentration of benzylidenimine tetrasulfide and benzylamine increased during the decomposition and would thus account for the observed products. Since benzylidenimine tetrasulfide was obtained from the decomposition of benzylamine *disulfide*, benzylamine polysulfides could be intermediates in the reaction of benzylamine with sulfur. When sulfur, benzylamine disulfide, or benzylidenimine tetrasulfide was dissolved in an excess of benzylamine, a reddish-brown solution formed, and ammonia was evolved. From all of these solutions benzylammonium polysulfides and *N*-benzylidene benzylamine were isolated. Thus, these possible intermediates all lead to the same final products.

Equations 4 to 8 are consequently proposed to account for the benzylamine-sulfur system¹ where [6] is base catalyzed and [7] is catalyzed by sulfide ion. The latter point seems justified since only small amounts of *N*-benzylidene benzylamine and ammonia were produced from benzylidenimine tetrasulfide and benzylamine in the presence of lead(II) oxide, a sulfide ion scavenger.

$$[4] \quad (a + 1)S + 2C_{6}H_{5}CH_{2}NH_{2} \rightleftharpoons H H H H_{2}S + C_{6}H_{5}CH_{2}N-S_{a}-NCH_{2}C_{6}H_{5}$$

$$[5] \quad H_{2}S + (x - 1)S + 2C_{6}H_{5}CH_{2}NH_{2} \rightarrow (C_{6}H_{5}CH_{2}NH_{2} \rightarrow (C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2-} H H H_{5}$$

$$[6] \quad 3C_{6}H_{5}CH_{2}N-S_{a}-NCH_{2}C_{6}H_{5} \rightarrow 4C_{6}H_{5}CH_{2}NH_{2} + C_{6}H_{5}CH=N-S_{b}-N=CHC_{6}H_{5} + (3a - b)S$$

$$[7] \quad C_{\delta}H_{5}CH=N-S_{b}-N=CHC_{6}H_{5} + 2C_{6}H_{5}CH_{2}NH_{2} \rightleftharpoons 2C_{6}H_{5}CH=NH H H_{4} + C_{6}H_{5}CH_{2}NH_{2} \rightarrow NCH_{2}C_{6}H_{5}$$

$$[8] \quad C_{6}H_{5}CH=NH + C_{6}H_{5}CH_{2}NH_{2} \rightarrow NH_{3} + C_{6}H_{5}CH=N-CH_{2}C_{6}H_{5}$$

In [4], benzylamine reacts with sulfur to give a benzylamine polysulfide and hydrogen sulfide. This is written as an equilibrium since tetraalkylamine polysulfides are known (30) to react with hydrogen sulfide to give amines and elemental sulfur. In eq. 5, the hydrogen sulfide formed in [4] reacts with more sulfur and benzylamine to give benzylammonium polysulfides (one of the final products). Both eqs. 4 and 5 are based on analogy with Levi's (25) work on secondary amines. Davis and Nakshbendi (18)

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¹In eqs. 4–8 *a*, *b*, and *x* represent the number of sulfur atoms in the various polysulfide chains; *b* is generally 4 and less commonly 3, 2, or 1; *x* is generally 6–7; no estimate for *a* is available.

have proposed an alternative mechanism (reactions 9 and 10) for the initial steps in the interaction of sulfur with a secondary amine which does not involve free hydrogen sulfide. The primary amine analogue of 2 could well be present

$$[9] \qquad \begin{array}{c} H \\ R_2NH + S_8 \rightarrow R_2N \longrightarrow S_8^- \\ H \\ [10] \quad R_2N \longrightarrow S_8^- + R_2NH \rightarrow R_2NH_2^+ + R_2N \longrightarrow S_8^- \\ \end{array}$$

in our system as an intermediate which could react with more amine to give benzylamine polysulfide and alkylammonium polysulfides as per eqs. 11 and 12. The sum of eqs. 9 to 12, given by [13], is the same as the sum of [4] and [5].

$${}_{2}N - S_{8}^{-} + R_{2}NH \rightarrow H$$

$$\stackrel{i}{R_{2}}N - S_{c} - \stackrel{N}{}_{+}R_{2} + \frac{8 - a}{x}S_{x}^{-2}$$

$$H$$

[12]
$$R_2N \rightarrow S_a \rightarrow NR_2 + R_2NH \rightarrow R_2N \rightarrow R_$$

[11]² R

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[13]
$$(a + x)S + 4C_6H_5CH_2NH_2 \rightarrow$$

H H
 $C_6H_5CH_2N-S_a-NCH_2C_6H_5$
 $+ (C_6H_4CH_2NH_3^+)_2S_2^{-2}$

For simplicity only, since it is not possible to distinguish between these two mechanisms on the basis of the work described here, the scheme will be based on eqs. 4 and 5. It should be emphasized, however, that eqs. 9-12 offer an equally good alternative to [4] and [5] (see also reference 31). In eq. 6, the benzylamine polysulfides formed in [4] are proposed to decompose to benzylamine, sulfur, and benzylidenimine polysulfides as observed experimentally for benzylamine disulfide. Since sulfur and benzylamine are produced in this step, eqs. 4-6 will be repeated. In eq. 7, the benzylidenimine polysulfides produced in [6] are proposed to react with benzylamine in the presence of sulfide ion to give benzylamine polysulfides and benzylidenimine. Exchange of one amine for another has been previously

²From the charge balance it is apparent that (8 - a)/x must equal 1 in this particular equation (*i.e.*, a + x = 8).

observed in alkylamine polysulfides. Thus, when N-methylaniline disulfide is mixed with aniline or when aniline disulfide is mixed with N-methylaniline, exchange occurs quite rapidly at room temperature³ to give the five species shown in eq. 14. By analogy, exchange of imine for amine in the presence of the excess benzylamine is

$$\begin{array}{cccccc} CH_{3} & CH_{3} & H \\ & & & | \\ [14] & C_{6}H_{5}N-S-S-NC_{6}H_{5} + 2C_{6}H_{5}-N-H \rightleftharpoons \\ CH_{3} & CH_{3} & H \\ C_{6}H_{5}-N-H + C_{6}H_{5}NH_{2} + C_{6}H_{5}N-S-S-NC_{6}H_{5} \rightleftharpoons \\ CH_{3} & H & H \\ 2C_{6}H_{5}N-H + C_{6}H_{5}N-S-S-NC_{6}H_{5} \end{array}$$

expected to occur here with the benzylidenimine polysulfides. The benzylidenimine proposed as a product in this exchange is known (32) and is quite reactive toward nucleophiles. It has been previously proposed (33) to react with benzylamine to give N-benzylidene benzylamine and ammonia as per [8]. Catalysis by sulfide ion as proposed in eq. 7 appears to be fairly common in sulfur-amine reactions (20, 21). Since benzylamine polysulfides are produced in [7], all steps will be repeated until all the sulfur is converted to benzylammonium polysulfides or all the benzylamine is converted to N-benzylidene benzylamine and ammonia. The proposed scheme is obviously complex with benzylamine polysulfides and benzylidenimine polysulfides involved in a cyclical catalytic sense. The interrelationship between the various compounds is shown in Fig. 1.

Quantitative Assessment of the Proposed Reaction Scheme

The proposed scheme described by Fig. 1 (reactions 4-8) accounts for the observed products using intermediates which are known independently to lead to these products. 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 the others. Nevertheless, a number of quantitative predictions can be derived from this scheme which are subject to experimental test. Before deriving these predic-

³J. C. Barrick and F. P. Olsen, unpublished observations.

tions, three useful relationships are noted. First, all hydrogen sulfide formed in the presence of benzylamine (since hydrogen sulfide is formed only from benzylamine, it cannot be formed in the absence of benzylamine) goes immediately to benzylammonium polysulfides. Therefore, in the absence of a sulfide scavenger, eqs. 4 and 5 may always be combined (added) to eliminate hydrogen sulfide as in [13]. Second, since benzylidenimine was neither isolated nor detected, it must react with benzylamine fairly rapidly compared to the various other reactions in the system. Here again, benzylidenimine is formed only from benzylamine and hence cannot be formed in the absence of benzylamine (alternatively and equally good, equilibrium [7] may lie fairly far to the left). Equations 7 and 8 may consequently be combined to eliminate benzylidenimine (twice [8] added to [7]) to give [15]. Finally, it should be noted that the benzylamine polysulfides formed in [7] have

[15]
$$C_6H_5CH=N-S_b-N=CHC_6H_5$$

+ $4C_6H_5CH_2NH_2 \rightarrow$
H H
 $|$ |
 $C_6H_5CH_2N-S_b-NCH_2C_6H_5 + 2NH_3$
+ $2C_6H_5CH_2N-CH_2C_6H_5$

a different sulfur chain length than those formed in [4]. Since the chain length is variable in both places, this does not pose a chemical problem. However, the combination of equations is very much simpler if these two materials can be related. Equation 16 is postulated for this purpose. This equation is solely a computational

$$\begin{array}{cccc}
H & H \\
\mid & \mid \\
[16] & C_6H_5CH_2N - S_b - NCH_2C_6H_5 \rightarrow \\
H & H \\
& & | \\
C_6H_5CH_2N - S_g - NCH_2C_6H_5 + (b - a)S_g
\end{array}$$

artifact and need not reflect a real chemical process. Indeed, free sulfur could be formed or consumed in eqs. 6 or 7. 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 four processes. The result is the same and is accounted for by [16].

Stoichiometry of the Overall Reaction of Sulfur with an Excess of Benzylamine

An overall equation for the reaction of sulfur with excess benzylamine may be obtained by

BITS

$$+$$
 BA
 $+$ BA



combining eqs. 4 through 8 to eliminate all intermediates. Benzylamine polysulfides may be eliminated by adding eq. 6 to three times [13] to give [17]. The benzylidenimine polysulfides may

[17]
$$(3x + b)S + 8C_6H_5CH_2NH_2 \rightarrow C_6H_5CH=N-S_b-N=CHC_6H_5 + 3(C_6H_5CH_2NH_3^+)_2S_x^{2-}$$

now be eliminated from [17] by the following procedure. First, eq. 15 is combined with [16] to correct the sulfur chain lengths and then (after multiplying by three) combined with [6] to give (after dividing by a common factor of 2) [18]. Equation 18 when combined with [17] gives

[18]
$$C_6H_5CH=N=S_b=N=CHC_6H_5$$

+ $4C_6H_5CH_2NH_2 \rightarrow 3NH_3$
+ $3C_6H_5CH=NCH_2C_6H_6$ + bS

. .

(after dividing by 3x) the predicted overall stoichiometric reaction, [19]. The quantities of

^[19] S +
$$\frac{4}{x}C_{6}H_{5}CH_{2}NH_{2} \rightarrow$$

 $\frac{1}{x}C_{6}H_{5}CH = NCH_{2}C_{6}H_{5} + \frac{1}{x}NH_{3}$
 $+ \frac{1}{x}(C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{3}^{2-}$

benzylamine, N-benzylidene benzylamine, ammonia, and benzylammonium polysulfide required to react with or formed from one gram atom of sulfur are functions of x, the number of sulfurs in the benzylammonium polysulfide chain. Since this is known (29) to be between 6 and 7, an "acceptable range" for each coefficient is predicted. A known quantity of sulfur was therefore reacted with a known excess of benzylamine. The ammonia evolved was collected in an acid trap and determined by back titration. The

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TABLE 1. Test of eq. 19

Compounds	Coefficients		
	Found*	Calculated	
		x = 6	x = 7
Sulfur Benzylamine	(1.00) 0.670	(1.00) 0.667	(1.00) 0.573
Ammonia Benzylammonium polysulfide	0.165	0.167	0.143
if x = 6 x = 7	0.161 0.150	0.167	0.143

benzylammonium polysulfides were precipitated by addition of ether, dried, and weighed. The total combined weight of *N*-benzylidene benzylamine and residual benzylamine was determined, and the molar ratio of these two materials was obtained by integration of an n.m.r. spectrum to give the absolute quantities of *N*-benzylidene benzylamine formed and of benzylamine consumed. Thus, each of the four coefficients in [19] is experimentally measurable. Table 1 compares the experimental values with those calculated for x = 6 and 7. The results for all four materials are in quite good agreement with those predicted based on eq. 19.

Reaction of Sulfur with Benzylamine in the Presence of a Sulfide Scavenger

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Steps 4 and 6 together should be subject to examination independently of the others by adding a sulfide scavenger to suppress the sulfide catalyzed reaction 7. Combination of [4] and [6] (three times [4] added to [6]) gives the stoichiometric eq. 20 where the hydrogen sulfide produced is removed by the lead oxide to give lead sulfide and water rather than reacting as per [5]. When

$$[20] \quad (b+3)S + 2C_6H_5CH_2NH_2 \rightarrow H \qquad H \\ \downarrow \\ C_6H_5C = N - S_b - N = CC_6H_5 + 3H_2S$$

sulfur and benzylamine were allowed to react in triethylamine in the molar ratio of 7 to 2 (*i.e.*, b = 4), the yield of benzylidenimine polysulfides isolated was 90 \pm 2% based on [20]. The products consisted of benzylidenimine tetra-, tri-, di-, and monosulfides in molar ratios of approximately 16:2:2:1. The balance of the starting material was converted to N-benzylidene benzylamine along with some benzylidenimine benzylamine sulfide (the unsymmetrical mixed amine imine monosulfide). The same reaction in benzene gave a similar yield and distribution of products, but the reaction time was almost ten fold longer. When the benzylamine to sulfur ratio was increased, the average sulfur content of the benzylidenimine polysulfides formed decreased, and the total yield of polysulfides based on [20] decreased somewhat. The decrease appeared to be due to incomplete blocking of reaction 7 since *N*-benzylidene benzylamine formation was increased considerably as was the quantity of benzylidenimine benzylamine monosulfide. The latter is most likely an intermediate in the exchange reaction as shown in eq. 21. Thus,

$$H H$$

$$[21] C_{6}H_{5}C=N-S_{b}-N=CC_{6}H_{5}$$

$$+ C_{6}H_{5}CH_{2}NH_{2} \rightleftharpoons$$

$$H H$$

$$C_{6}H_{5}C=N-S_{b}-NCH_{2}C_{6}H_{5} + C_{6}H_{5}CH=NH$$

eq. 20 appears to remain valid. Changing the molar ratio of sulfur to benzylamine leads mainly to variation in the numerical value of b.

Reactions of Benzylidenimine Tetrasulfide with Excess Benzylamine

This situation is nearly covered by eq. 18 above. The bS formed in [18] should react in the presence of the excess benzylamine according to [19]. Adding [18] to [19] multiplied by b eliminates the sulfur to give [22]. Since the starting material is the tetrasulfide, b = 4 and the overall stoichiometric eq. 23 results. The coefficients based

$$[22] \quad C_{6}H_{5}CH=N-S_{b}-N=CHC_{6}H_{5} \\ + \frac{4(b+x)}{x}C_{6}H_{5}CH_{2}NH_{2} \rightarrow \\ \frac{b}{x}(C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2-} \\ + \frac{3x+b}{x}(C_{6}H_{5}CH=N-CH_{2}C_{6}H_{5} + NH_{3}) \\ [23] \quad C_{6}H_{5}CH=N-S_{4}-N=HCC_{6}H_{5} \\ + \frac{(16+4x)}{x}C_{6}H_{5}CH_{2}NH_{2} \rightarrow \\ \frac{4}{x}(C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2-} \\ + \frac{4+3x}{x}[NH_{3}^{+} + C_{6}H_{5}CH=N-CH_{2}C_{6}H_{5}] \\ \end{cases}$$

on the reaction of 1 mol of benzylidenimine tetrasulfide with excess amine are determined by the average sulfur chain length of the benzylammonium polysulfide produced. The products

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	Coefficients			
		Calculated		
Compounds	Found*	x = 6	<i>x</i> = 7	
Benzylidenimine tetrasulfide Benzylamine V-Benzylidene	(1.00) 6.67	(1.00) 6.67	(1.00) 6.28	
benzylamine Ammonia	3.57 3.37	3.67 3.67	3.58 3.58	

*±5% of values shown.

were separated as described for the reaction of sulfur with excess amine. Table 2 shows the experimental coefficients for *N*-benzylidene benzylamine, ammonia, benzylammonium polysulfide, and benzylamine along with those predicted from eq. 23 for x = 6 and 7. These results show eq. 23 to provide a good quantitative description of the experimental facts.

Benzylidenimine tetrasulfide exposed to benzylamine in the presence of lead(II) oxide gave only equilibration of the sulfur chain length as well as small amounts of several benzylidenimine benzylamine polysulfides again presumably via reaction 21.

Autocatalytic Decomposition of Benzylamine Disulfide

In the autocatalytic decomposition of benzylamine disulfide, the final products are N-benzylidene benzylamine and ammonia along with smaller quantities of benzylammonium polysulfides, benzylidenimine tetrasulfide, and elemental sulfur. Two assumptions are inherent in the derivation of the previous equations. Equations 4-8 must of course hold, and there must be an excess of benzylamine (not necessary for [20] only). In the decomposition of benzylamine disulfide, benzylidenimine polysulfides, and sulfur are produced in the presence of 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 processes, a factor which is not relevant to the previous derivations. Two limiting cases can be imagined: (i) where benzylamine reacts with sulfur very much faster than with benzylidenimine polysulfides, and (ii) where benzylidenimine polysulfides react much faster than sulfur.

Case (i) Following decomposition according

to [6], the reaction of (3a - b) sulfurs with 4 benzylamines according to [13] must be considered. For the values of a, b, and x relevant to this case (a = 2 since the starting material is the disulfide, $b \sim 4$ and x = 6-7), it is apparent that 3a - b < a + x. Therefore, reaction 13 is limited by the quantity of sulfur present and not by the quantity of benzylamine. Multiplying [13] by (3a - b)/(a + x) and adding this result to [6] eliminates the sulfur and leads to [24].

$$\begin{array}{c} H & H \\ \begin{array}{c} H & H \\ \downarrow & \downarrow \\ a + x \\ C_{6}H_{5}CH_{2}N - S_{a} - NCH_{2}C_{6}H_{5} \rightarrow \\ C_{6}H_{5}CH = N - S_{b} - N = CHC_{6}H_{5} \\ + \frac{4x - 8a + 4b}{a + x} C_{6}H_{5}CH_{2}NH_{2} \\ + \frac{3a - b}{a + x} (C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2^{-1}} \end{array}$$

The remaining benzylamine will now react with the benzylidenimine polysulfides. This should be according to [15]. However, it is first necessary to correct for the differing sulfur chain lengths, *i.e.*, eq. 15 is added to [16] to give [25].

However, this equation is not consistent with the assumption that reaction of sulfur with benzylamine is rapid. Since sulfur is formed in the presence of benzylamine, eq. 25 must be modified to allow for reaction of the sulfur with benzylamine. This can be done by multiplying [13] by (b - a)/(a + x) and then adding [25]. The result, [26], now gives the fate of the remaining benzylamine present in [24].

$$[26] \quad C_{6}H_{5}CH=N-S_{b}-N=CHC_{6}H_{5}$$

$$+\frac{4(x+b)}{a+x}C_{6}H_{5}CH_{2}NH_{2} \rightarrow$$

$$2(NH_{3}+C_{6}H_{5}CH=NCH_{2}C_{6}H_{5})$$

$$H \qquad H$$

$$+\frac{x+b}{a+x}C_{6}H_{5}CH_{2}N-S_{a}-NCH_{2}C_{6}H_{5}$$

$$+\frac{b-a}{a+x}(C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2}$$

Equations 26 and 24 may now be combined to eliminate benzylamine by multiplying [26] by (x - 2a + b)/(x + b) and adding this to [24] to

[

give (after dividing out a common factor of 2) eq. 27. Since the starting material is the disulfide,

$$H H H$$

$$[27] C_{6}H_{5}CH_{2}N-S_{a}-NCH_{2}C_{6}H_{5} \rightarrow$$

$$\frac{a}{b+x}C_{6}H_{5}CH=N-S_{b}-N=CHC_{6}H_{5}$$

$$+\frac{a}{b+x}(C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2-}$$

$$+\frac{x-2a+b}{b+x}(NH_{3}+C_{6}H_{5}CH=NCH_{2}C_{6}H_{5})$$

a = 2, and since only benzylidenimine tetrasulfide was observed experimentally among the products in this reaction, b = 4. Substituting these for a and b in [27] gives [28] as the predicted overall stoichiometric reaction for case (i).

$$\begin{array}{ccccc}
H & H \\
| & | \\
[28] & C_{6}H_{5}CH_{2}N - S_{2} - N - CH_{2}C_{6}H_{5} \rightarrow \\
& \frac{2}{x + 4} \left[C_{6}H_{5}CH - N - S_{4} - N - CHC_{6}H_{5} + (C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2^{-}}\right] \\
& + \frac{x}{x + 4} \left(C_{6}H_{5}CH - NCH_{2}C_{6}H_{5} + NH_{3}\right)
\end{array}$$

Case (ii) Returning to eq. 6, the benzylamine produced now reacts exclusively with the benzylidenimine polysulfides according to [15]. The latter must be modified (added to [16]) to correct the sulfur chain length and may then be added to [6] to give (after dividing out a common factor of 2) eq. 29.

[29] $C_6H_5CH_2N-S_a-NCH_2C_6H_5 \rightarrow C_6H_5CH=NCH_2C_6H_5 + NH_3 + aS$

Н

H

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In the decomposition of benzylamine disulfide a = 2; therefore, [29] reduces to [30], the predicted stoichiometric equation for this case.

$$[30] \quad \begin{array}{c} H & H \\ \downarrow & \downarrow \\ 1 \\ C_6H_5CH_2N \\ S_2 \\ -NCH_2C_6H_5 \\ \rightarrow \\ 2S + C_6H_5CH \\ = NCH_2C_6H_5 + NH_3 \\ \end{array}$$

Equation 28 does not contain sulfur as a final product while in [30], elemental sulfur is the *only* sulfur-containing species. Experimentally, 38% of all the sulfur present went to elemental sulfur. Therefore neither of these two limiting cases holds. The intermediate case may be approximated by combining eqs. 28 and 30 and taking the fraction of sulfur obtained as a product ($f_s = mg$ atoms of elemental sulfur produced/ total mg atoms of sulfur present in all forms) as

a measure of the relative importance of these two extreme cases (*i.e.*, $f_{\rm S}[30]$ added to $(1 - f_{\rm S})[28]$) as in [31]. Equation 31 predicts the ratio of benzylidenimine tetrasulfide to benzylammonium polysulfide as well as the ratio of benzylidenimine

$$\begin{array}{r} H & H \\ | & | \\ [31] & C_6H_5CH_2N - S_2 - NCH_2C_6H_5 \rightarrow 2f_8S \\ &+ \frac{2(1 - f_8)}{x + 4} \left[C_6H_5CH = N - S_4 - N = CHC_6H_5 \\ &+ (C_6H_5CH_2NH_3^+)_2S_x^{2-1} \right] \\ &+ \frac{x + 4f_8}{x + 4} \left(C_6H_5CH = NCH_2C_6H_5 + NH_3 \right)
\end{array}$$

benzylamine to ammonia to be 1:1. Experimentally these two ratios were found to be 0.99 ± 0.05 and 1.02 ± 0.05 in excellent agreement with [31]. The ratio of *N*-benzylidene benzylamine *plus* ammonia to benzylammonium polysulfide *plus* benzylidenimine tetrasulfide is predicted by [31] to be $(x + 4f_s)/2(1 - f_s)$. Since experimentally $f_s = 0.38$, this ratio should be 6.1 for x = 6 and 6.9 for x = 7. The experimental value was $\sim 10 \pm 3$. The probable error is quite large, but the agreement appears acceptable.⁴

p-Methoxybenzylidenimine Tetrasulfide with Amine

Two kinds of *N*-benzylidene benzylamines are expected as products from the reaction of *p*-methoxybenzylidenimine tetrasulfide with unsubstituted benzylamine according to eqs. 4–8. When eq. 7 is written for the reaction of *p*-methoxybenzylidenimine polysulfide with unsubstituted benzylamine and added to twice [8] (*p*-methoxybenzylidenimine reacting with unsubstituted benzylamine), the result is [32]. All

32]
$$CH_3OC_6H_4CH=N-S_b-N=CHC_6H_4OCH_3$$

+ $4C_6H_5CH_2NH_2 \rightarrow$
 $2CH_3OC_6H_4CH=NCH_2C_6H_5$
H H
+ $2NH_2 + C_6H_5CH_2N-S_b-NCH_2C_6H_5$

the *p*-methoxy substituent has now been converted to final products and the newly formed unsubstituted benzylamine polysulfides decompose via [6]. After correcting for the sulfur chain

 $^{{}^{4}}$ The 38% of sulfur isolated is apt to be too low rather than too high since sulfur has some solubility in *N*-benzylidene benzylamine. If the quantity of sulfur isolated were to be increased (as it probably should be) by only a few milligrams, the agreement would improve considerably.

length in [6] by adding three times [16], three times [32] may be added leading to the situation shown in [33]. Since there is an excess of benzyl-

[33]
$$3CH_3OC_6H_4CH=N-S_b-N=CHC_6H_4OCH_3$$

+ $8C_6H_5CH_2NH_2 \rightarrow$
 $C_6H_5CH=N-S_b-N=CHC_6H_5 + 2bS$
+ $6NH_3 + 6CH_3OC_6H_4CH=NCH_2C_6H_5$

amine, the sulfur in [33] reacts as per [19], and the benzylidenimine polysulfides as per [23]. Adding eq. 22 to 33 and this in turn to 2b times eq. 19 gives (after dividing out a common factor of 3) the predicted overall stoichiometric equation as in [34]. Since the starting material is the tetra-

- $[34] CH_{3}OC_{6}H_{4}CH=N-S_{b}-N=CHC_{6}H_{4}OCH_{3}$ $+\frac{4(b+x)}{x}C_{6}H_{5}CH_{2}NH_{2} \rightarrow$ $\frac{b}{x}(C_{6}H_{5}CH_{2}NH_{3}^{+})_{2}S_{x}^{2-}+\frac{3x+b}{x}NH_{3}$ $+\frac{x+b}{x}C_{6}H_{5}CH=NCH_{2}C_{6}H_{5}$ $+2CH_{3}OC_{6}H_{4}CH=NCH_{2}C_{6}H_{5}$ sulfide, b = 4, and [34] reduces to [35]. $[35] CH_{3}OC_{6}H_{4}CH=N-S_{4}-N=CHC_{6}H_{4}OCH_{3}$
 - $+ \frac{(16 + 4x)}{x} C_6 H_5 CH_2 NH_2 \rightarrow$ $2CH_3 OC_6 H_4 CH = NCH_2 C_6 H_5$ $+ \frac{4 + x}{x} C_6 H_5 CH = NCH_2 C_6 H_5 + \frac{4 + 3x}{x} NH_3$ $+ \frac{4}{x} (C_6 H_5 CH_2 NH_3^+)_2 S_x^{2-}$

The ratio of N-(p-methoxybenzylidenimine) benzylamine to N-benzylidenimine benzylamine should be 2:[(4 + x)/x] or 1.20 to 1.27 where x = 6 to 7. The products, obtained after removal of the benzylammonium polysulfides, were hydrolyzed with dilute hydrochloric acid. As required by eq. 35 the benzylammonium polysulfides and all of the benzylamine formed by hydrolysis of the N-benzylidene benzylamine 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 1.29 ± 0.10 in excellent agreement with that predicted in eq. 35.

Conclusions

Using a polysulfide chain length of 6–7 as established independently (29) for the benzylammonium polysulfides, all aspects of each of the five eqs. 19, 20, 23, 31, and 35, derived from the proposed scheme (reactions 4-8), 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 reactions of sulfur with benzylamine. Although the scheme has been established only for benzylamine, it nevertheless seems reasonable to expect that other primary amines might follow a similar overall reaction sequence. It has been previously shown (23, 24) that sulfur with a few primary amines, such as butylamine and ethylenediamine, gives alkylammonium polysulfides. Since sulfur is reduced by these amines, the amines must be oxidized, presumably to either the alkylamine polysulfides, alkylidenimine polysulfides, or Schiff's bases.

A detailed mechanistic interpretation cannot be formulated for each of the steps (eqs. 4-8) 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 the sulfide scavenger was considerably faster in polar solvents than in non-polar solvents. Step 5 is obviously ionic as is the analogous step 9 in the Davis (18) mechanism. The observed base catalysis in step 6 most probably involves the weakly acidic N-H protons. This is consistent with the isolation (25, 27) of tetraalkylamine polysulfides from sulfur and secondary amines where the absence of a second N-H would block step 6. The autocatalytic decomposition of benzylamine disulfide which produced a limited amount of benzylamine in addition to sulfur and benzylidenimine polysulfides provides some indication of the relative rates of steps 4 and 7 (because these appear to be equilibria, steps 5, 6, and 8 may also contribute, however) since the latter two materials compete for the limited amount of benzylamine formed. Apparently, step 4 (along with 5 and 6) is about 50%faster than 7 (along with 8). The final step, 8, is very likely a reversible nucleophilic addition of benzylamine to the imine carbon followed by a proton shift and elimination of ammonia.

The reaction of primary amines with sulfur in the presence of lead(II) oxide has some potential synthetic importance in the preparation of imine polysulfides. Sulfur is obviously a more convenient starting material than tetrasulfur tetranitride (29). The reaction conditions are quite

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mild, and the rate is reasonably rapid. 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.

Experimental

Instrumentation, solvents and chromatography were as previously described (29).

Benzylamine Disulfide

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Freshly distilled sulfur monochloride (1.9 ml, 23.6 mmol) in 100 ml of anhydrous ether was added dropwise to 10.0 ml (91.7 mmol) of benzylamine in 500 ml of anhydrous ether in a 1 l three-necked flask equipped with a stirrer and calcium chloride drying tube. A white precipitate of benzylammonium chloride formed rapidly and was separated by filtration. The solvent was removed *in vacuo* to give a pale yellow, creamy oil. This oil was dissolved in hexane at 30-40 °C and on cooling to ice temperature precipitated a white solid. Further recrystallization from pentane gave pure benzylamine disulfide of m.p. 52.5–53 °C.

Anal. Calcd. for $C_{14}H_{16}N_2S_2$ (mol. wt.: 276): C, 60.83; H, 5.83; N, 10.13; S, 23.20. Found (270): C, 60.93; H, 5.53; N, 9.94; S, 23.42.

Evaporation of the mother liquor gave 3.0 g of oil whose n.m.r. spectrum indicated the presence of benzylamine disulfide, *N*-benzylidene benzylamine, and other unidentified materials.

The n.m.r. spectrum of benzylamine disulfide showed absorptions at -2.75 (broad, -NH), -4.09 (singlet, $-CH_2$ ---), and -7.05 p.p.m. (singlet, phenyl-) with relative areas of 1.00:1.91:4.92, respectively. The i.r. spectrum showed N-H stretching at 3334 cm⁻¹ and S—N stretching at 850 cm⁻¹. An R_f value could not be obtained since the material decomposed on the silica gel plate. Pure benzylamine disulfide kept under vacuum in a drying apparatus at room temperature for 5-6 h decomposed to a mixture of benzylidenimine polysulfides, N-benzylidene benzylamine, and sulfur. It could be stored at -20 °C for several weeks, but decomposition eventually began even at this temperature. The impure material could be kept for a much longer period. When benzylamine disulfide was heated in a m.p. capillary to 75 °C and cooled, the oil solidified and remelted at 53 °C. When it was heated above 100 °C, however, decomposition occurred with evolution of gas. A t.l.c. of the decomposition product showed sulfur, benzylidenimine tetra-, tri-, and disulfides, and N-benzylidene benzylamine.

The course of the room temperature decomposition of benzylamine disulfide was monitored by n.m.r. spectroscopy. Approximately 260 mg of pure material was stirred under a nitrogen atmosphere. Periodically a 25–30 mg aliquot was withdrawn, dissolved in 0.5 ml of deuterochloroform and an n.m.r. spectrum was taken. After 3 h no change was apparent. After 5 h some benzylamine was visible (about 5%). After 6 h approximately 85% of the disulfide remained. After an additional $\frac{1}{2}$ h (total elapsed time: $6\frac{1}{2}$ h) nearly 95% of the disulfide was decomposed, and benzylamine and benzylidenimine tetrasulfide were prominent in molar ratios of approximately 4:1. A small amount of *N*-benzylidene benzylamine was also observable at this time. After 8 h the n.m.r. showed mainly *N*-benzylidene benzylamine, small amounts of benzylidenimine tetrasulfide and the benzylammonium cation (presumably the polysulfides). A spectrum after 13 h was unchanged from that at 8 h.

Benzylidenimine Benzylamine Monosulfide

Sulfur (984 mg, 30.7 mg atoms), lead(II) oxide (9.10 g, 40.7 mmol), and 10 ml of benzene were placed in a 100 ml three-necked flask equipped with a water condenser, a serum rubber stopper, a cylinder of dry nitrogen gas, and an outlet to a gas washing bottle with about 250 ml of aqueous hydrochloric acid solution (containing 50.0 mg equiv of acid). The benzylamine used was degassed under vacuum, and 3.4 ml (31.2 mmol) was introduced through the serum stopper by syringe. The reaction mixture was stirred for about 20 h with a continuous slow flow of dry nitrogen. The acid solution was diluted to 500 ml, and a 5.00 ml aliquot required 4.53 ml of 0.100 N sodium hydroxide for neutralization. Ammonia (4.7 mmol) had therefore been evolved. The lead sulfide was removed by filtration and was thoroughly washed with ether and benzene. The combined solvents were removed, the remaining oil was weighed, and an n.m.r. spectrum integrated. This led to the following distribution of materials: benzylidenimine tetrasulfide, 910 mg (2.7 mmol); benzylidenimine disulfide, 260 mg (1.0 mmol); benzylidenimine benzylamine monosulfide, 700 mg (2.9 mmol); N-benzylidene benzylamine, 1.12 g (5.7 mmol); and unreacted benzylamine, 100 mg (0.9 mmol). These data rest on the assumed structure of benzylidenimine benzylamine 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. Benzylidenimine tetrasulfide precipitated (850 mg) and was discarded. Then, 260 mg of benzylidenimine disulfide (contaminated with some tetrasulfide) precipitated in several successive fractions which were collected and discarded. After several days at -20 °C, 350 mg of a white crystalline material precipitated. This material was recrystallized from methanol to give benzylidenimine benzylamine monosulfide of m.p. 58.5-59 °C.

Anal. Calcd. for $C_{14}H_{14}N_2S$ (mol. wt.: 242): C, 69.39; H, 5.82; N, 11.56; S, 13.23. Found (249): C, 69.6; H, 5.30; N, 11.74; S, 13.65.

An n.m.r. spectrum in carbon tetrachloride showed four absorptions: a singlet at -7.77 (1.0 H, benzylidene proton), a multiplet at -7.07 to -7.67 (10.2 H, phenyl rings), a doublet at -4.30 (2.0 H, J = 5.5 c.p.s., methylene protons), and a broad triplet at -3.66 p.p.m. (1.0 H, proton on nitrogen). The i.r. spectrum in carbon tetrachloride showed bands assignable to N—H stretching at 3360 cm⁻¹, C=N stretching at 1645 cm⁻¹, and S-N stretching at 853 cm⁻¹. The R_t value on silica gel with carbon disulfide as eluent was 0.15 vs. 0.80 for sulfur. This material was also formed when benzylidenimine tetrasulfide and benzylamine were mixed in the presence of lead(II) oxide. For example, 1.00 g (2.98 mmol) of benzylidenimine tetrasulfide stirred for 5 h with 3.9 mI (35.7 mmol) of benzylamine and 2.71 g (12.2 mmol) of lead(II) oxide in 15 ml of benzene led on chromatography to: 37 mg (1.2 mg atom) of sulfur, 170 mg (0.51 mmol) of benzylidenimine tetrasulfide, 110 mg (0.37 mmol) of benzylidenimine trisulfide, 90 mg (0.33 mmol) of benzylidenimine disulfide, 25 mg (0.10 mmol) of benzylidenimine benzylamine sulfide, 75 mg of two other unsymmetrical amine-imine polysulfides which were not fully characterized, and 480 mg (2.5 mmol) of *N*-benzylidene benzylamine. Ammonia (2.4 mmol) was evolved.

Quantitative Experiments; Sulfur with Excess Benzylamine Sulfur (640 mg, 20.0 mg atoms) was placed in a threenecked flask equipped with a stirrer, gas washing bottle, nitrogen inlet, and rubber serum stopper. The gas washing bottle contained 7.50 mg equiv of hydrochloric acid. Benzylamine (2.90 g, 27.1 mmol) was introduced through the serum stopper, and the flask was stirred at room temperature under a slow continuous flow of nitrogen. After 4 h the reaction was complete, and anhydrous ether was added. The mixture was stirred for 2 h, and the orange solid which precipitated was filtered and washed with anhydrous ether. When this solid was dried in air, evolution of hydrogen sulfide was observed. When the solid was free of ether, it weighed approximately 960 \pm 30 mg. The weight was not accurate due to continuous decomposition with evolution of hydrogen sulfide, about 35 mg weight loss per 20 min. The m.p. was 90-96 °C dec. in an evacuated sealed tube. After 2 days in air, it had decomposed into sulfur and benzylammonium thiosulfate. The combined ether extract was evaporated under reduced pressure at about 35-40 °C to give 2.42 g of oil containing benzylamine, N-benzylidene benzylamine, and benzylammonium polysulfide. The integrated n.m.r. spectrum led to the following distribution of products: benzylamine, 1.47 g (therefore 1.43 g, 13.4 mmol, consumed); N-benzylidenebenzylamine, 640 mg (3.26 mmol); benzylammonium polysulfides, 1.31 g (total; 3.22-2.98 mmol for x = 6 and 7, respectively). The acid solution in the gas washing bottle was diluted to 500 ml, and a 50.0 ml aliquot required 4.50 ml of 0.100 N sodium hydroxide solution for neutralization. Therefore, 3.00 mg equiv of ammonia were evolved.

Sulfur and Benzylamine in the Presence of a Sulfide Scavenger

Sulfur (1.03 g, 32.2 mg atoms), 3.49 g (15.6 mmol) of lead(II) oxide, 1 ml (9.17 mmol) of benzylamine, and 10 ml of triethylamine were stirred together under a dry nitrogen atmosphere at room temperature. Within 2 h the reaction mixture had become quite black. After 24 h it was filtered, and the lead sulfide was washed thoroughly with ether and benzene. The combined filtrate was concentrated to give 1.41 g of solid. This was dissolved in carbon disulfide, and its n.m.r. spectrum was recorded. Integration gave the relative amounts of the five components (whose identities were verified by t.l.c.) and led to the following data: benzylidenimine tetrasulfide, 1.06 g (3.16 mmol); benzylidenimine trisulfide, 0.11 g (0.37 mmol); benzylidenimine disulfide, 0.11 g (0.41 mmol); benzylidenimine monosulfide,⁵ 0.043 g (0.18 mmol); N-benzylidene benzylamine, 0.080 g (0.41 mmol). An analogous reaction in benzene using identical quantities required 1 week for complete reaction of the sulfur and led to the following data: tetrasulfide, 1.13 g (3.36 mmol); trisulfide, 0.14 g (0.46 mmol); disulfide, 0.027 g (0.10 mmol); monosulfide,⁵ 0.071 g (0.30 mmol); *N*-benzylidene benzylamine, 0.125 g (0.64 mmol).

A similar reaction with 1.02 g (31.9 mg atoms) of sulfur, 7.53 g (33.8 mmol) of lead oxide, and 2.2 ml (20.1 mmol) of benzylamine in 3 ml of benzene led to the data below: tetrasulfide, 0.26 g (0.77 mmol); trisulfide, 0.12 g (0.39 mmol); disulfide, 0.59 g (2.2 mmol); benzylidenimine benzylamine monosulfide, 0.34 g (1.4 mmol); and *N*-benzylidene benzylamine, 0.95 g (4.9 mmol).

Benzylidenimine Tetrasulfide with Excess Benzylamine

Benzylidenimine tetrasulfide (1.02 g, 3.03 mmol) was placed in a 100 ml three-necked flask equipped as described above. The gas washing bottle contained 15.00 mg equiv of hydrochloric acid. Benzylamine (6.6 ml, 60.5 mmol) was introduced through the serum stopper. After 6 h the reaction was complete. The acid solution was diluted to 500 ml, and a 50.0 ml aliquot required 4.82 ml of 0.100 N sodium hydroxide solution for neutralization. Therefore, 10.2 mg equiv of ammonia were evolved. The reaction mixture was diluted with 50 ml of anhydrous ether, and the orange solid which precipitated was filtered and washed with anhydrous ether. The combined ether solutions were concentrated in vacuo at 40-50 °C to give 6.41 g of oil containing only N-benzylidene benzylamine and unreacted benzylamine. The weight and integrated n.m.r. spectrum indicated the amounts of these two products to be: benzylamine, 4.32 g (therefore 2.15 g, 20.2 mmol, consumed) and N-benzylidene benzylamine, 2.10 g (10.8 mmol).

Decomposition of Benzylamine Disulfide

Benzylamine disulfide (248 mg, 0.90 mmol) was stirred under a slow flow of nitrogen gas. The outlet was connected to a gas washing bottle containing 1.00 mg equiv of aqueous hydrochloric acid. The white solid changed slowly to a yellow oil which contained a solid. The precipitate was filtered and washed with small amounts of anhydrous ether to give 22 mg (0.69 mg atoms) of elemental sulfur. The solvent was removed in vacuo to give 196 mg of an oil whose n.m.r. spectrum showed three materials: benzylidenimine tetrasulfide, N-benzylidene benzylamine, and benzylammonium ion (presumably the polysulfide) in molar ratios of 2.0:20.5:2.0. respectively. From these data the yields of products were calculated to be:6 benzylidenimine tetrasulfide, 24 mg (0.071 mmol); N-benzylidene benzylamine, 142 mg (0.73 mmol); benzylammonium polysulfide, 31 mg (0.071 mmol). The acid solution was diluted to 500 ml, and a 200 ml aliquot required 1.14 ml of 0.100 N sodium hydroxide for neutralization. Therefore, 0.715 mmol of ammonia was evolved.

p-Methoxybenzylidenimine Tetrasulfide

p-Methoxybenzylidenimine tetrasulfide was prepared from *p*-methoxybenzylamine and tetrasulfur tetranitride as previously described (29). After recrystallization from methanol it had a m.p. of 112-113 °C. A 734 mg (1.85 mmol) sample was placed in a 100 ml round-bottom flask with a magnetic stirring bar, and 1.4 ml (12.8 mmol)

⁵Not fully characterized, see ref. 29.

⁶Benzylammonium polysulfide was assumed to be the heptasulfide. These numbers do not change more than 5% if the hexa- or octasulfide is assumed.

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of benzylamine was added. The reaction mixture was stirred under a nitrogen atmosphere for 5 h whereupon a t.l.c. showed the absence of p-methoxybenzylidenimine tetrasulfide. About 60 ml of anhydrous ether was introduced into the reaction mixture and stirred for 1 h. An orange solid precipitated from the yellowish solution which was filtered and washed with anhydrous ether. It melted at 95-97 °C dec. and, when kept in the air for a few days, decomposed to sulfur and a thiosulfate with the evolution of hydrogen sulfide. An n.m.r. spectrum of the thiosulfate taken in deuterium oxide showed three absorptions corresponding to a benzyl CH₂ group, an NH_3^+ group, and a phenyl complex. No absorption corresponding to a p-methoxy methyl group was detected. The orange solid was, therefore, unsubstituted benzyl-ammonium polysulfide. The combined ether extracts were concentrated in vacuo, and the n.m.r. spectrum of the resulting oil showed a complicated phenyl region between -6.85 and -8.04 p.p.m., a broad NH₂ peak at -1.87p.p.m., a methoxy methyl group at -3.47 p.p.m., the CH₂ of benzylamine at -3.87 p.p.m., an unresolved CH2 doublet for mixed N-benzylidene benzylamine at -4.74 p.p.m., and the unresolved CH triplets for mixed *N*-benzylidene benzylamine at -8.21 p.p.m. This mixture was refluxed for 4 h with 50 ml of 5% hydrochloric acid. After cooling the mixture was extracted with ether (ether extract I). The aqueous layer was neutralized with base and extracted with ether (ether extract II). Ether extract II was dried and concentrated to give a large quantity of oil. The n.m.r. spectrum of this material, taken in deuterochloroform, showed only benzylamine. No trace of a methoxy methyl group could be detected. Ether extract I was dried and the ether removed in vacuo to give an oil whose n.m.r. spectrum showed two aldehyde peaks: anisaldehyde at -9.87 p.p.m. and benzaldehyde at -10.00 p.p.m. as well as the p-methoxy methyl absorption at -3.74 p.p.m. and a complex phenyl region. The ratio of the two aldehyde peaks, anisaldehyde to benzaldehyde, was approximately 1.5 to 1. However, the ratio increased with the time of evaporation (of the ether) presumably due to selective loss of the more volatile benzaldehyde. A more accurate ratio was obtained from the n.m.r. spectrum of the crude reaction mixture (before hydrolysis). Integration of the combined overlapping CH₂ peaks for the two kinds of N-benzylidene benzylamines at -4.74 p.p.m. relative to the methoxy methyl peak at -3.47 p.p.m. gave 40.3:34.0. The relative amount of the p-methoxy derivative was therefore 1/3 of 34.0 or 11.3, and the total relative amount of both kinds of Schiff's bases was 1/2 of 40.3 or 20.1. The relative amount of the unsubstituted material was therefore 20.1 less 11.3 or 8.8. The ratio of p-methoxy substituted to unsubstituted N-benzylidene benzylamine was therefore 11.3/8.8 or 1.29 ± 0.10 .

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