of benzene was added slowly 1.88 g (7.6 mmol) of tris(diethylamino)phosphine (2). After 10 min, the benzene was removed under vacuum and the residue chromatographed over silica gel. Elution with 10% chloroform in hexane afforded 50 mg (7%) of 6H,12H-dibenzo[*b*,*f*][1,5]dithioocin as colorless crystals, mp 172–178°, which after crystallization from ethanol afforded colorless needles, mp 173–175° (lit.[24] mp 174–176°).

2-Phenyl-1,3-propanedithiol (10).—A solution of 4.6 g (10 mmol) of 2-phenyl-1,3-propanediol ditosylate[25] and 10 g (130 mmol) of thiourea in 50 ml of ethanol was refluxed for 4 hr; the ethanol was removed under vacuum and the residue refluxed under nitrogen with 10 g of sodium hydroxide in 50 ml of water for 12 hr. After careful acidification, the mixture was extracted with chloroform and the extract washed well with water, dried, and evaporated to dryness. The crude oil was fractionally distilled under vacuum to afford 1.0 g (55%) of a pale yellow oil: bp 76–78° (0.005 mm); nmr ($CDCl_3$) τ 2.70 (mulitplet, 5 H, aromatic), 6.0–7.4 (multiplet, 5 H), 8.7 (multiplet, 3 H, S–H). This crude dithiol was used without further purification.

4-Phenyl-1,2-dithiolane (12).—A solution of 1.4 g (7.6 mmol) of the dithiol 10 and 1.8 g (1.8 mmol) of triethylamine in 20 ml of methanol was added dropwise with stirring in a nitrogen atmosphere to a solution of 1.95 g (8 mmol) of iodine in 50 ml of methanol. The resulting solution was rapidly filtered and the filtrate cooled in dry ice until crystals formed. The crystals were filtered and washed well with cold methanol to afford 1.0 g (73%) of yellow crystals, mp 77–83°. Sublimation at 75° and 25-μ pressure afforded 488 mg of yellow crystals: mp 82–84°; ir (KBr) 1600, 1490, 1460, 775, and 705 cm^{-1} (aromatic); $\lambda_{max}^{benzene}$ 335 mμ (ϵ 143); nmr ($CDCl_3$) τ 2.66 (multiplet, 5 H, aromatic), 6.5 (multiplet, 5 H).

Anal. Calcd for $C_9H_{10}S_2$: C, 59.29; H, 5.53; S, 35.18. Found: C, 59.09; H, 5.50; S, 34.83.

3-Phenylthietane (14).—A solution of 400 mg (2.2 mmol) of 12 and 600 mg (2.4 mmol) of tris(diethylamino)phosphine (2) in 10 ml of benzene was refluxed 4 hr during which time the yellow color was discharged. The reaction mixture was evaporated to dryness and the residue chromatographed over silica gel. Elution with 1:1 hexane–chloroform afforded 280 mg (87%) of a colorless oil, homogeneous on thin layer and gas chromatography (LAC column at 190°): $n^{25}D$ 1.5895; ir (film) 1610, 1500, 1465, 760, 705 cm^{-1} (aromatic); nmr (CCl_4) τ 2.78 (5 H), 5.50 (multiplet, 1 H), 6.62 (multiplet, 4 H).

This material was characterized as its sulfone (H_2O_2, AcOH): mp 101–101.5°; ir (KBr) 1320, 1140 cm^{-1} (SO_2).

Anal. Calcd for $C_9H_{10}SO_2$: C, 59.29; H, 5.53; S, 17.59. Found: C, 59.67; H, 5.60; S, 17.84.

1α,5α-Epidithioandrostane-3,17-dione (22).—The method used was a modification of the procedure of Tweit and Dodson[12] in that triphenylphosphine was used to remove occluded sulfur from the crude product. This material was crystallized from acetone (33% yield): mp 210–214° (lit.[12] mp 210–214°); ir (KBr) 1730 (C_{17} C=O), 1710 cm^{-1} (C_3 C=O); λ_{max}^{MeOH} 364 mμ (ϵ 51), 280 sh (650), 262 (730); nmr[11] ($CDCl_3$) (100 MHz) τ 6.15 (quartet, 1 H, $J_{AX} + J_{BX} = 7$ Hz, $J_{AX} - J_{BX} = 1$ Hz), 9.10 (singlet, 3 H), 8.59 (singlet, 3 H), and a multiplet centered at about τ 7.5–6.9.

S-Bis(diethylamino)phosphino-1α-thioandrostan-4-ene-3,17-dione (25).—A suspension of 348 mg (1 mmol) of 1α,5α-epidithioandrostan-3,17-dione (22) in 5 ml of dry benzene containing 1.0 g (4 mmol) of tris(diethylamino)phosphine (2) was stirred overnight. The solvent was removed under vacuum and the residue chromatographed over silica gel. After elution of tris(diethylamino)phosphine sulfide with 95:5 dichloroethane–acetone, the product was eluted with 85:15 dichloroethane–acetone. Crystallization from hexane afforded 100 mg (20%) colorless crystals: mp 201–202°; ir (KBr) 1740 (C_{17} C=O), 1670 cm^{-1} (C=C—C=O); λ_{max}^{MeOH} 228 mμ (ϵ 6450), 280 (1470); mass spectrum, parent ion at *m/e* 492.2960 (Calcd for $C_{27}H_{45}N_2O_2PS$: 492.2939) with a fragment ion at *m/e* 284.1785 [$P^+ - (Et_2N)_2PSH$] (calcd for $C_{19}H_{24}O_2$: 284.1776).

Anal. Calcd for $C_{27}H_{45}N_2O_2PS$: C, 65.81; H, 9.21; N, 5.69. Found: C, 65.75; H, 9.02; N, 5.61.

Registry No.—**3,** 25636-58-2; **4,** 25636-59-3; **5,** 1027-31-2; **6,** 25636-60-6; **10,** 25636-61-7; **12,** 6133-92-2; **14,** 25636-63-9; **14** (sulfone), 25636-64-0; **16,** 25636-65-1; **22,** 25632-08-0; **25,** 25631-60-1.

Acknowledgement.—We wish to thank the National Research Council of Canada and the Petroleum Research Fund administered by the American Chemical Society for support of this work.

(24) G. W. Stacy, F. W. Villaescusa, and T. E. Wollner, *J. Org. Chem.*, **30**, 4074 (1965).

(25) C. Beard and A. Burger, *ibid.*, **27**, 1649 (1962).

Aralkyl Hydrodisulfides.[1] XI. The Reaction with Amines

JITSUO TSURUGI, YASUO ABE, TAKESHIGE NAKABAYASHI, SHUNICHI KAWAMURA, TEIJIRO KITAO,[2] AND MITSUO NIWA[3]

Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka, Japan

Received October 6, 1969

Aralkyl hydrodisulfides were allowed to react with several amines at room temperature. The amines (morpholine, mono-, di-, and tri-*n*-butylamine, and piperidine) having pK_a values greater than 8.36 behave as bases. The products from 10 mmol of hydrodisulfide consisted of nearly 5 mmol of each hydrogen sulfide and diaralkyl disulfide, and 5 mg-atoms of sulfur, or, alternatively, nearly 5 mmol of hydrogen sulfide and fluctuating amounts of sulfur, diaralkyl disulfide, and polysulfides, the last of which were formed at the expense of the disulfide and sulfur. These results are satisfactorily explained by the basic mechanism reported previously and modified here. The amines (aniline, N,N-dimethylaniline, and pyridine) having pK_a values less than 5.17 behave as nucleophiles and gave hydrogen sulfide, arylalkanethiol, diaralkyl polysulfides, and disulfide, the last of which was formed at the expense of the thiol. These results are explained by the nucleophilic mechanism. 2,4-Lutidine having pK_a value of 6.79 seems to behave as a nucleophile.

It has been well known that amines behave as nucleophiles[4] toward octatomic sulfur or organic sulfur compounds. However, amines could behave as bases rather than nucleophiles in the presence of aralkyl hydrodisulfides which are weakly acidic. Our previous works have shown that nucleophiles such as phosphines,[5,6] phosphites[7] and arsines[8] attack aralkyl hydro-

(1) Part X: S. Kawamura, Y. Abe, and J. Tsurugi, *J. Org. Chem.*, **34**, 3633 (1969).

(2) Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka, Japan.

(3) University of Osaka Prefecture, undergraduate, 1959–1963.

(4) (a) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959); (b) R. E. Davis and N. F. Nakshbendi, *J. Amer. Chem. Soc.*, **84**, 2085 (1962); (c) J. Tsurugi, *Rubber Chem. Technol.*, **31**, 773 (1958); (d) E. Ciuffarin and G. Guaraldi, *J. Amer. Chem. Soc.*, **85**, 543 (1963).

(5) J. Tsurugi, T. Nakabayashi, and T. Ishihara, *J. Org. Chem.*, **30**, 2707 (1965).

(6) T. Nakabayashi, S. Kawamura, T. Kitao, and J. Tsurugi, *ibid.*, **31**, 861 (1966).

(7) T. Nakabayashi, J. Tsurugi, S. Kawamura, T. Kitao, M. Ui, and M. Nose, *ibid.*, **31**, 4174 (1966).

(8) J. Tsurugi, T. Horii, T. Nakabayashi, and S. Kawamura, *ibid.*, **33**, 4133 (1968).

TABLE I

PRODUCTS (mmol) OF ARALKYL HYDRODISULFIDES (10 mmol) WITH AMINES UNDER NITROGEN ATMOSPHERE AT ROOM TEMPERATURE

Run	R in RSSH	Amine	pK_a	Molar ratio of amine/RSSH	Procedure[a]	Products (mmol or mg-atoms) H_2S	RSH	RS_xR $x = 2$	$x = 3,4,5$	Mean value of x	S
1	$C_6H_5CH_2$	Aniline	4.58	10	A	4.4	0	1.3	3.6	3.1	0
2	$C_6H_5CH_2$	N,N-Dimethylaniline	5.06	10	A	2.4	4.7	0.2	2.5	3.4	0
3	$C_6H_5CH_2$	Pyridine	5.17	10	A	4.1	0	1.1	3.9	3.0	0
4	$C_6H_5CH_2$	*n*-Butylamine	10.43	10	B	4.6	0	3.7	1.1	2.4	3.0
5	$C_6H_5CH_2$	Di-*n*-butylamine	11.25	10	A	4.7	0	3.0	2.3	2.8	1.0
6	$C_6H_5CH_2$	Piperidine	11.25	10	B	4.8	0	3.4	1.6	2.6	2.0
7	$(C_6H_5)_2CH$	Aniline	4.58	10	A	3.4	2.6	0	3.5	3.8	0
8	$(C_6H_5)_2CH$	N,N-Dimethylaniline	5.06	10	A	2.3	3.3	0.1	2.9	3.9	0
9	$(C_6H_5)_2CH$	Pyridine	5.17	3	C	3.6	1.5	0	4.4	3.2	0
10	$(C_6H_5)_2CH$	2,4-Lutidine	6.79	10	A	4.2	0	1.1	3.7	3.1	0
11	$(C_6H_5)_2CH$	Morphorine	8.36	10	A	4.0	0	5.0	0		4.8
12	$(C_6H_5)_2CH$	*n*-Butylamine	10.43	10	B	4.8	0	4.6	0		5.0
13	$(C_6H_5)_2CH$	Tri-*n*-butylamine	10.89	10	A	3.0	0	3.9	1.0	2.4	3.0
14	$(C_6H_5)_2CH$	Di-*n*-butylamine	11.25	10	A	4.0	0	5.0	0		5.1
15	$(C_6H_5)_2CH$	Piperidine	11.25	6	B	4.3	0	5.0	0		5.6
16	$(C_6H_5)_3C$	Aniline	4.58	10	A	2.8	4.1	...[b]	...[b]	...[b]	...[b]

[a] See the Experimental Section. [b] Not determined.

disulfides both on sulfhydryl and sulfenyl sulfur atoms, and that hydroxide ion[9] abstracts proton from hydrodisulfides, allowing the resulted aralkyl disulfide ions (RSS^-) to react further with hydrodisulfides. Now it seems interesting to examine whether amines behave as bases or as nucleophiles toward hydrodisulfides.

Results and Discussion

The pK_a values of amines used in this work range from 4.58 to 11.25 including primary, secondary, and tertiary amines and both aromatic and aliphatic ones. The aralkyl hydrodisulfide (benzyl, benzhydryl, or triphenylmethyl hydrodisulfide) in benzene was added dropwise to an excess amine in a stream of nitrogen at room temperature. The results are shown in Table I. Comparatively good material balance is observed for each run, in spite of the different molar ratios of amine/hydrodisulfide and different procedures. Product distributions in Table I indicate distinctive feature depending on pK_a values of amines used. Our results show that amines of stronger basicity (pK_a values > 8.36) give a different product distribution from that of amines of weaker basicity (pK_a values < 5.17).

Basic Attack of Amines.—Table I indicates that the reaction products of 10 mmol of benzhydryl hydrodisulfide with amines of stronger basicity are nearly 5 mmol of each hydrogen sulfide and benzhydryl disulfide, and 5 mg-atoms of elemental sulfur for runs 11, 12, 14, and 15. This product distribution reminds us of our previous work[9] on the reaction of hydrodisulfides with concentrated potassium hydroxide. The reaction sequence is cited again here in eq 1–3. Eq 3 shows that

$$RSSH + OH^- \longrightarrow RSS^- + H_2O \quad (1)$$

$$RSSH + RSS^- \longrightarrow RSSR + HS_2^- \quad (2)$$

$$HS_2^- \xrightarrow{H^+} H_2S + \frac{1}{8}S_8 \quad (3)$$

hydrogen sulfide evolves and sulfur precipitates after the neutralization. In the present work, sulfur precipitated after addition of hydrochloric acid. Hydrogen sulfide evolved during the reaction at room temperature in the case of runs 11 (with morpholine), 13 (with tri-*n*-butylamine) and 14 (with di-*n*-butylamine). In the case of runs 12 (with *n*-butylamine) and 15 (with piperidine) hydrogen sulfide evolved only after addition of hydrochloric acid. This difference may come from different stabilities of amine–hydrogen sulfide salts, which depend on basicity and steric hindrance of amines.

A supplementary nmr experiment indicated that dibenzhydryl trisulfide was formed besides the disulfide at an earlier stage of the reaction with piperidine. The trisulfide was found by nmr analysis to be desulfurated with piperidine during the reaction. As shown in run 15, Table I, it disappeared at the end of the reaction. Therefore, eq 5 may be considered to compete with eq

$$RSSH + R'_3N \longrightarrow RSS^- + [R'_3NH]^+ \quad (4)$$

$$RSS^- + RSSH \longrightarrow RSSSR + SH^- \quad (5)$$

2. As to the reaction sequence[9] with concentrated alkali, the similar situation (competition of eq 5 with 2) is conceivable. A nmr reexamination revealed that benzhydryl hydrodisulfide in dioxane-d_8 reacted with a concentrated sodium deuteroxide in deuterated water, giving a 4:1 ratio of disulfide–trisulfide. After neutralization followed by extraction, the disulfide alone was detected. This suggests that the reaction sequence with alkali is not so simple as indicated in eq 1–3.

Regarding the basic attack of amines, we propose that anion RSS^- formed in eq 4 reacts with hydrodisulfide by eq 2 or 5. The cation $[R'_3NH]^+$ from eq 4 combines with anion HS^- from eq 5 or HS_2^- from eq 2, as indicated in eq 6, where x is 1 or 2. The

$$[R'_3NH]^+ + HS_x^- \longrightarrow [R'_3NH]^+HS_x^- \quad (6)$$

(9) S. Kawamura, T. Kitao, T. Nakabayashi, T. Horii, and J. Tsurugi, *J. Org. Chem.*, **33**, 1179 (1968).

succeeding steps, eq 7–8, may explain the results of runs 11, 12, 14, and 15. Eq 8, desulfuration step with

$$\left.\begin{aligned}[R'_3NH]^+HS_x^- + HCl &\longrightarrow [R'_3NH]^+Cl^- + HS_xH\\ [R'_3NH]^+HS_x^- &\longrightarrow R'_3N + HS_xH\\ HS_xH &\longrightarrow H_2S + \frac{x-1}{8}S_8\end{aligned}\right\} \quad (7)$$

$$RS_xR + R'_3N \longrightarrow RSSR + R'_3N^+S_{x-2}^- \quad (8)$$

amines, is quite analogous to the desulfuration with trivalent phosphorus compounds.[8,10] The resulted amine sulfide $R'_3N^+S_x^-$ is quite analogous to the product from the reaction of amine with octatomic sulfur.[4b] The constitution of this product and recovery of octatomic sulfur from the product have been discussed[4b] in detail. The amine sulfide resulted from eq 8 must be less stable than phosphine sulfide which can make use of d orbitals of both sulfur and phosphorus atoms to form a strong bond.[11] The amine sulfide may decompose in contact with acid as shown in eq 9. The

$$R'_3N^+S_x^- + HCl \longrightarrow [R'_3NH]^+Cl^- + \frac{x}{8}S_8 \quad (9)$$

formation of dibenzhydryl polysulfides in run 13 (with tri-*n*-butylamine) can be explained by assuming that desulfuration (eq 8) is not complete under the reaction conditions, because of steric hindrance of tri-*n*-butylamine. The product distribution of the reaction of benzyl hydrodisulfide (runs 4, 5, and 6) resembles that of run 13. This result may be explained by the incomplete desulfuration of benzyl polysulfides. Supplementary nmr experiments under similar conditions indicated that dibenzyl tetrasulfide and trisulfide were desulfurated with piperidine more slowly than the corresponding dibenzhydryl compounds.

Nucleophilic Attack of Amines.—The products of runs 7, 8, and 9 are hydrogen sulfide, diphenylmethanethiol and dibenzhydryl polysulfides, and resemble those with nucleophiles (phosphines,[5,6] phosphites,[7] and arsines[8]). If we apply the mechanisms of both the sulfenyl and sulfhydryl sulfur attacks by nucleophiles[8] to the present study, we can explain the product formation for runs 7–9. From the analogy to the mechanism of sulfhydryl sulfur attack, we may write the following equation. The amine sulfides produced in eq 10 are

$$RSSH + R'_3N \longrightarrow RS^-\left[\begin{matrix}SH\\ |\\ NR'_3\end{matrix}\right]^+ \longrightarrow RSH + R'_3N^+S^- \quad (10)$$

considered less stable than the ones from amines of stronger basicity and to react further as indicated in eq 11, in contrast to eq 9. The mechanism of hydrogen

$$R'_3N^+S^- + 2\,RSSH \longrightarrow RSSSSR + R'_3N + H_2S \quad (11)$$

$$R'_3N^+S^- + [R'_3NH]^+SH^-$$

sulfide formation could be different depending on the basicity of amines (*cf.* eq 7).

(10) C. G. Moore, and B. R. Treggo, *J. Appl. Polymer Sci.*, **5**, 299 (1961); **8**, 1957 (1964).

(11) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, London, 1965, p 67.

For sulfenyl sulfur attack, we propose the following steps by analogy with other nucleophiles. The for-

$$RSSH + R'_3N \longrightarrow \left[\begin{matrix}RS\\ |\\ NR'_3\end{matrix}\right]^+ + SH^- \quad (12)$$

$$SH^- + RSSH \longrightarrow RSS^- + H_2S \quad (13)$$

$$\left[\begin{matrix}RS\\ |\\ NR'_3\end{matrix}\right]^+ + RSS^- \longrightarrow RSSSR + R'_3N \quad (14)$$

mation of polysulfides in runs 7–9 was satisfactorily explained by eq 11 and 14, if the desulfuration of polysulfides does not proceed under these conditions by amines of weaker basicity.

The results from benzyl hydrodisulfide with amines of weaker basicity (runs 1 and 3) make a clear contrast in the point that dibenzyl disulfide is formed at the expense of thiol as compared with the corresponding results from benzhydryl hydrodisulfide. Benzyl hydrodisulfide, which suffers less steric hindrance than benzhydryl compound,[5-8] is considered to be attacked predominantly on sulfenyl sulfur, and hence reacts predominantly *via* eq 12, 13, and 14. The thiol produced as a minor product *via* eq 10 must have reacted with SH^- produced in eq 12, just as the hydrodisulfide reacts with SH^- as indicated in eq 13. The resulted RS^- anion also must have reacted with $[RSNR'_3]^+$ quite similarly to eq 14. Thus the formation of dibenzyl disulfide for runs 1 and 3 are explained by eq 15 and 16. On the other hand, the almost quantitative

$$RSH + SH^- \longrightarrow RS^- + H_2S \quad (15)$$

$$\left[\begin{matrix}RS\\ |\\ NR'_3\end{matrix}\right]^+ + RS^- \longrightarrow RSSR + NR'_3 \quad (16)$$

yield of the thiol and the negligible amount of the disulfide for run 2 with N,N-dimethylaniline can be interpreted by overwhelming sulfhydryl sulfur attack, because of the steric hindrance of the nucleophile, N,N-dimethylaniline. The persistence of the thiol cited in runs 7–9 may be explained also by the same reason; that is, benzhydryl hydrodisulfide is sterically more hindered than benzyl hydrodisulfide.

The product distribution of run 10 (the reaction of benzhydryl hydrodisulfide with 2,4-lutidine) quite resembles that of run 3 (benzyl hydrodisulfide with pyridine). If the disulfide would arise from the desulfuration of the polysulfides, elemental sulfur would be found among the products as indicated in eq 8 and 9. The absence of sulfur for 2,4-lutidine ($pK_a = 6.79$) can be attributed to the nucleophilic mechanism.

Predominance of sulfhydryl sulfur attack by steric hindrance is visualized in run 16, where aniline was allowed to react with triphenylmethyl hydrodisulfide. Owing to the absence of H atom, by which a mixture of polysulfides was conveniently analyzed by nmr, the result of run 16 shows only the amounts of hydrogen sulfide and the thiol. The amount of the latter clearly indicates the predominance of sulfhydryl sulfur attack.

Consideration from Equilibrium Viewpoint.—From the viewpoint of acid–base theory, eq 4 should be written as a reversible step. The equilibrium constant

$$RSSH + R'_3N \rightleftarrows RSS^- + R'_3NH^+$$

K is calculated from definition of pK_a as follows. Eq 17 suggests that amines having far less pK_a than

$$\log K = pK_{a_{amine}} - pK_{a_{RSSH}} \quad (17)$$

$pK_{a_{RSSH}}$ cannot be expected to behave as bases toward aralkyl hydrodisulfides which are weak acids. In such cases amines will behave as nucleophiles rather than bases as our results indicate.

Experimental Section

Benzyl hydrodisulfide, benzhydryl hydrodisulfide, and triphenylmethyl hydrodisulfide were prepared and purified by the method reported elsewhere.[12,13] Amines (CP grade) were dehydrated over sodium hydroxide and distilled before use. Benzene (CP grade) was used without further purification. General features of the apparatus have been described previously.[9] Nmr spectra were taken on a JNM 3H-60 spectrometer, with tetramethylsilane as an internal standard. Dibenzhydryl disulfide, when isolated from other products (in runs 11 and 15), was weighed and identified by mixture melting points. Amount of alkanethiol and each amount of diaralkyl disulfide, trisulfide, and tetrasulfide in mixture were determined by nmr spectra.[1,8,9] τ value of –SH in authentic triphenylmethanethiol $(C_6H_5)_3CSH$ was 7.10 (7% in CCl_4). The amount of hydrogen sulfide was estimated by iodometric method,[5] and that of elemental sulfur was determined iodometrically using triphenylphosphine in the same manner as described elsewhere,[5] after identification by mixture melting points. In runs 4, 5, and 6, amounts of elemental sulfur were calculated by substracting those of nmr data (polysulfidic sulfur S_{x-2} in RS_xR) from titrating values ($S_{x-2} + S_8$). We adopted procedures A, B, and C, taking account of behavior of hydrogen sulfide evolution.

Reactions of Aralkyl Hydrodisulfides with Amines. Procedure A (Run 1, 2, 3, 5, 7, 8, 10, 11, 13, 14, and 16).—A solution of 10 mmol of aralkyl hydrodisulfide in 20 ml of benzene and 100 mmol of amine were separately deaerated by bubbling with nitrogen gas for 30 min. The output of nitrogen stream was introduced into a trap (acetone–Dry Ice) for removal of benzene and amine, and then into the absorbing bottles of hydrogen sulfide. The solution of aralkyl hydrodisulfide was added, with stirring, to amine at room temperature. After 2 days, the amount of hydrogen sulfide evolved was estimated. For analysis of the other products, the reaction mixture was chilled on an ice–salt bath. To this mixture was added with stirring 30 ml of 5 N hydrochloric acid for neutralization of the amine. Then the mixture was extracted with benzene, and each component in the dried extract was estimated by nmr spectra (CCl_4) using 1,1,2,2-tetrachloroethane as an internal standard for determination of each amount.

Procedure B (Run 4, 6, 12, and 15).—This procedure was adopted in such a case that hydrogen sulfide was not released before neutralizing the reaction solution which involved amines of large pK_a value. Thus, it was ambiguous to know from the evolution of hydrogen sulfide only whether hydrodisulfides disappeared completely. Therefore, the reaction mixture was acidified after 3 days (1 day longer than in procedure A). Hydrogen sulfide was evolved immediately after the addition of acid. The succeeding treatment of the acidified mixture was identical with that described for procedure A.

Procedure C (Run 9).—To a solution of 10 mmol of benzhydryl hydrodisulfide in 15–20 ml of benzene was added, with stirring, 30 mmol of pyridine under nitrogen atmosphere at room temperature. When hydrogen sulfide almost escaped out, the reaction vessel was heated to 50° in order to sweep out hydrogen sulfide which remained in the reaction mixture. Neutralization was not carried out in this case. The products were extracted with benzene, and diphenylmethanethiol was estimated iodometrically using an aliquot of the dried extract. After the thiol in the remaining extract was oxidized with an excess of alcoholic iodine solution to the corresponding disulfide, dibenzhydryl polysulfides were analyzed by desulfuration with potassium cyanide.[14]

Nmr Spectroscopic Studies. A.—The reaction mixture of benzhydryl hydrodisulfide (5.2 mmol) with piperidine (5.6 mmol), in benzene (20 ml), was analyzed by nmr spectra, which showed the ratio of dibenzhydryl disulfide/trisulfide to be *ca.* 2. Extraction of the mixture changed the ratio to *ca.* 8. Finally, according to procedure A, no dibenzhydryl trisulfide was found.

B.—The reaction of benzhydryl hydrodisulfide (0.7 mmol) in dioxane-d_8 (1 ml) with sodium deuterioxide (5 mmol) in deuterated water (0.5 ml) was traced for 45 min, starting from the time when the reactants were mixed, under the same condition as described previously.[9] In this case the ratio of disulfide/trisulfide was 4 and was almost unchanged as time proceeded.

C.—Preliminary experiments showed that piperidine clearly converts dibenzhydryl trisulfide or tetrasulfide to dibenzhydryl disulfide, since from a mixture of the former and the amine white needles of dibenzhydryl disulfide precipitated (mp 151–152°). Similar treatments of benzyl derivatives, however, did not afford clean dibenzyl disulfide. To a solution of dibenzyl trisulfide, dibenzyl tetrasulfide, dibenzhydryl trisulfide, or dibenzhydryl tetrasulfide (252 μmol) in benzene-d_6 containing dichloromethane or 1,2-dibromoethane (588 or 266 μmol, as internal standard) was added piperidine (1260 μmol). The amount of benzene-d_6 was adjusted so that the total weight was 1 g. Desulfuration of the trisulfide or tetrasulfide in the above solution was traced by nmr spectroscopy. Such experiments showed that the desulfuration is not a simple reaction and that disproportionation occurs, *viz.*, the tetrasulfides, for example, once gave mixtures of polysulfides which gradually change to the disulfides. Therefore, the time required for the absorption of a starting material to diminish to one-half of its original value was determined. For dibenzyl trisulfide and tetrasulfide, and dibenzhydryl trisulfide and tetrasulfide, $t_{1/2}$ values were about 40, 10, 20, and <10 min, respectively. In the case of measurements of benzhydryl compounds, rapid formation of crystalline disulfide made the experiments difficult; hence the half times were roughly estimated.

Registry No.—Benzyl hydrodisulfide, 3492-66-8; benzhydryl hydrodisulfide, 3492-67-9; triphenylmethyl hydrodisulfide, 3492-71-5; aniline, 62-53-3; N,N-dimethylaniline, 121-69-7; pyridine, 110-86-1; 2,4-lutidine, 108-47-4; morpholine, 110-91-8; *n*-butylamine, 109-73-9; tri-*n*-butylamine, 102-82-9; di-*n*-butylamine, 111-92-2; piperidine, 110-89-4.

(12) J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).
(13) T. Nakabayashi, J. Tsurugi, and T. Yabuta, *ibid.*, **29**, 1236 (1964).
(14) S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *ibid.*, **30**, 2711 (1965).