1,3,5-Trisubstituted Hexahydrotriazines as Mannich Reagents. I. Preparation of Secondary Aminomethyl Sulfide Hydrochlorides

Delbert D. Reynolds and Bernard C. Cossar

Research Laboratories, Eastman Kodak Company
Rochester, N. Y. 14650

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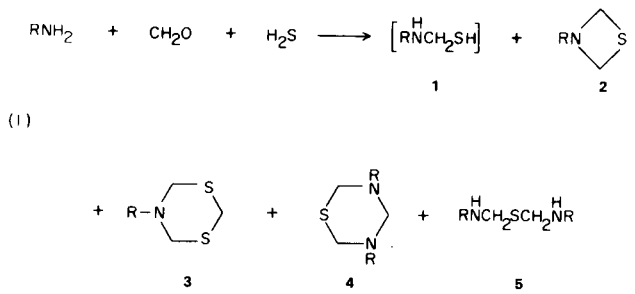
1,3,5-Trisubstituted hexahydrotriazines react with hydrogen chloride in the presence of anhydrous solvents to form useful intermediates for the introduction of the $RNHCH_2$- group into compounds which undergo the Mannich reaction. The effectiveness of the new aminomethylating agent has been demonstrated by the preparation of secondary aminomethyl sulfide hydrochlorides.

The Mannich reaction has been defined as the condensation of ammonia, a primary or a secondary amine with formaldehyde and a compound having at least one hydrogen of pronounced activity (1). This definition is broad, but the practical applications have been limited mainly to the use of secondary amines. This fact becomes immediately obvious when one examines the comprehensive tabulation of aminomethylation products compiled by Hellmann and Opitz (2). The reason for this limitation is that ammonia and primary amines yield initial products which may undergo further reactions resulting in a mixture of products (3-6).

When hydrogen sulfide is the material being aminomethylated, the reaction is further complicated since the intermediate **1** (eq. 1) has an -SH group which is extremely susceptible to attack by aminomethylating reagents. These facts may be used to explain the variety of products that have been derived from the reaction of primary amines and formaldehyde with hydrogen sulfide (eq. 1) (7-10).



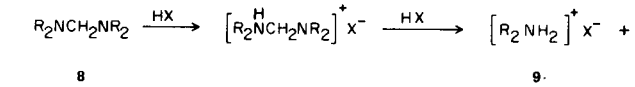
(1)

Although compounds of type **1** have not been isolated, it is reasonable to assume that products **2**, **3**, **4** and **5** result from the reaction of the intermediate **1** with the starting materials. Compounds **5** have been isolated only when R is aryl. It is also significant that in only one instance (11) has a compound of type **6** been reported as having been formed by the aminomethylation of a mercaptan by a primary amine and formaldehyde. In contrast, the reaction of mercaptans with secondary amines and formaldehyde to yield the tertiary aminomethyl sulfides **7** is well documented (12).

We have found that the 1,3,5-trisubstituted hexahydrotriazines **11** react with hydrogen chloride in anhydrous solvents to form useful intermediates for the introduction of the RNH-CH_2- group into compounds which undergo the Mannich reaction. Thus, the potential scope of the Mannich reaction has been broadened, since it can now become more applicable to the preparation of secondary aminomethyl derivatives.

This paper discusses the nature of this reagent, the conditions under which it is formed, and its use in the aminomethylation of hydrogen sulfide and mercaptans. Good yields of secondary aminomethyl sulfide hydrochlorides of types **5** and **6** are formed.

In 1958, Boehme (13) described the cleavage of bis-



(2)

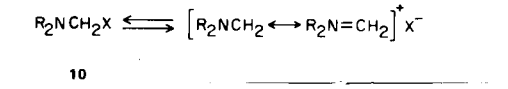
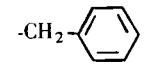
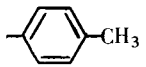


TABLE I

Products of the *n*-Propylaminomethylation of Mercaptans

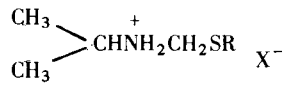
$$CH_3CH_2CH_2\overset{+}{N}H_2CH_2SR \quad Cl^-$$

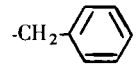
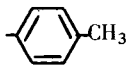
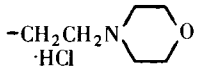
Compound No.	-R	M.p., °C	Yield %	Analyses Calcd. C	H	Cl	N	S	Found C	H	Cl	N	S
29	$-CH_3$	168-169 (a)	93	38.6	9.1	22.8	9.0	20.6	38.7	9.2	22.6	9.1	20.2
30	$-C_3H_7$-*n*	158-159 (a)	93	45.8	9.9	19.3	7.6	17.5	45.7	10.0	19.4	7.9	17.6
31	$-C_{10}H_{21}$	157-158 (a)	97	--	--	12.6	5.0	11.4	–	–	12.2	5.4	11.5
26	$-\overset{O}{\overset{\|}{C}}CH_3$	123-124 (a)	66	39.2	7.7	19.3	7.6	17.5	38.9	7.9	19.0	7.8	17.7
32	$-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$	94-95 (b)	82	–	–	15.6	6.2	14.1	–	–	16.0	6.5	14.5
33	$-CH_2CH_2COOH$	108-109 (a)	92	39.3	7.6	–	6.6	15.0	38.9	7.8	–	6.7	15.4
34		137-138 (a)	88	57.0	7.8	15.3	6.0	13.8	56.8	7.6	14.9	6.1	13.8
35		117-118 (b)	--	55.2	7.4	16.3	–	14.7	55.6	7.5	15.7	–	15.0
36		75-76 (a)	--	–	–	15.3	6.0	13.8	–	–	15.4	6.0	13.8

Analytical samples recrystallized from (a) acetonitrile; (b) ethyl acetate.

TABLE II

Product of the Isopropylaminomethylation of Mercaptans



Compound No.	-R	M.p., °C	Yield %	Analyses (a) Calcd. C	H	Cl	N	S	Found C	H	Cl	N	S
37	$-CH_3$	161-162	93	38.6	9.1	22.8	9.0	20.6	38.3	8.9	22.3	9.1	20.2
38	$-C_3H_7$-*n*	117-118	90	45.8	9.9	19.3	7.6	17.5	45.8	9.8	19.0	8.0	17.6
39	$-C_{10}H_{21}$	107-108	95	59.6	11.4	12.6	5.0	11.4	60.0	11.8	12.6	5.2	11.6
40		147-148	77	39.2	7.7	19.3	7.6	17.5	38.9	7.9	19.0	7.9	17.4
41		169-170	78	57.0	7.8	15.3	6.0	13.8	57.2	8.1	15.5	6.3	14.2
42		134-135	87	57.0	7.8	–	6.0	13.8	56.8	7.9	–	5.8	14.1
43		171-172	95	41.2	8.3	24.3	9.6	11.0	41.1	8.0	24.6	9.5	10.9

(a) Analytical samples recrystallized from acetonitrile.

TABLE III

Products of the *n*-Butylaminomethylation of Mercaptans

$CH_3CH_2CH_2CH_2\overset{+}{N}H_2CH_2SR\ Cl^-$

Compound No.	-R	M.p., °C	Yield %	Calcd. C	Calcd. H	Calcd. Cl	Calcd. N	Calcd. S	Analyses Found C	Found H	Found Cl	Found N	Found S
44	$-CH_3$	167-168 (a)	94	42.5	9.5	20.9	8.3	19.0	42.4	9.3	20.6	8.3	18.6
45	$-C_3H_7$-*n*	167-168 (a)	90	48.6	10.2	17.9	7.1	16.2	48.3	10.1	17.5	7.1	16.2
46	$-C_{10}H_{21}$	163-164 (a)	97	60.9	11.6	12.0	4.7	10.8	60.6	11.5	12.4	5.0	10.8
47	$-CH_2CH_2COOH$	126-127 (a)	89	42.2	7.9	15.6	6.2	14.1	42.1	8.2	16.0	5.9	14.1
24		153-154 (a)	79	58.6	8.2	14.4	5.7	13.0	58.3	8.2	14.8	5.6	13.4
48		114-115 (b)	–	57.0	7.8	15.3	–	13.8	57.4	8.0	15.1	–	14.1

Analytical samples recrystallized from (a) acetonitrile; (b) ethyl acetate.

(dialkylamino)methanes (**8**) by halogen acids in aprotic solvents. The cleavage yielded two products, each having saltlike properties. One was the amine hydrochloride **9** and the second was designated as an α-halogenated amine (**10**), which, because of its physical and chemical properties, was represented as shown in equation 2. A variety of compounds of type **10** were prepared and shown to act as aminoalkylating agents.

The 1,3,5-trisubstituted hexahydrotriazines (**11**), which can be prepared in high yields by the reaction of primary amines with formaldehyde, bear a structural similarity to the bis(dialkylamino)methanes (**8**). When a given 1,3,5-trisubstituted hexahydrotriazine is treated with three moles of anhydrous hydrogen chloride in an aprotic solvent such as acetonitrile or ether, a quantitative yield of a product can be isolated which has saltlike properties. In an experiment in which 1,3,5-triethylhexahydrotriazine was allowed to react with three moles of hydrogen chloride in anhydrous acetonitrile at -30° the product was isolated, quickly transferred to a vacuum desiccator and thoroughly dried. Elemental analysis of this compound was in good agreement with structure **13** or its trimer **12** (R = C_2H_5). Mass spectra and nmr spectra do not differentiate between these structures. The infrared spectrum of the isolated product showed no absorption in the 1680 cm^{-1} region; compounds possessing the $\geq C=\overset{+}{N}-$ group do show absorption in this region (14). This suggests that our intermediate is the salt **12** at low temperature and not the cleavage product **13**. The nature of this intermediate will be the subject of further study. From a preparative standpoint, it

11

12

13

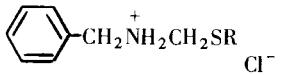
is preferable not to isolate these aminomethylation intermediates since they are deliquescent and therefore must be isolated and handled under anhydrous conditions.

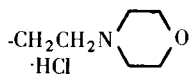
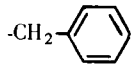
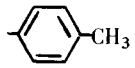
It is not required that an aprotic solvent be used for the aminomethylation reactions. When alcohols are used, intermediate alkoxymethylamine hydrochlorides are formed, as indicated by isolation and analysis by nmr spectroscopy. In instances where the aminomethylation reaction is very fast, as is true for hydrogen sulfide, one may use methyl ketones as the reaction medium although they are known to take part in the Mannich reaction, but at a much slower rate.

As a general rule, the reactions are begun at low temperature, *e.g.*, -30°, and then allowed to proceed as the reaction temperature gradually rises. The products usually separate as crystalline hydrochlorides before the reaction

TABLE IV

Products of the Benzylaminomethylation of Mercaptans



Compound No.	-R	M.p., °C	Yield %	Analyses Calcd. C	H	Cl	N	S	Found C	H	Cl	N	S
49	$-CH_3$	162-163 (a)	91	53.1	6.9	17.4	6.9	15.7	53.0	6.9	17.0	7.3	15.8
50	$-C_3H_7$-*n*	154-155 (a)	86	57.0	7.8	15.3	6.0	13.8	56.8	8.2	15.0	6.2	13.8
51	$-C_{10}H_{21}$	160-161 (a)	98	65.5	9.8	10.8	4.3	9.7	65.6	9.6	11.2	4.2	9.7
52	$-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$	142-143 (a)	97	52.3	6.6	–	5.1	–	52.7	6.7	–	5.3	–
53	$-CH_2CH_2COOH$	151-152 (a)	82	50.5	6.2	–	5.4	12.2	50.3	6.0	–	5.2	12.1
54	 ·HCl	178-179 (b)	96	49.6	7.1	20.9	8.3	9.5	49.7	7.1	21.2	8.0	9.2
23		170-171 (a)	89	64.4	6.5	12.7	5.0	11.5	64.1	6.7	12.5	4.9	11.8
55		139-141 (a)	91	64.4	6.5	–	5.0	–	64.4	6.5	–	5.3	–

Analytical samples recrystallized from (a) acetonitrile; (b) methanol-acetonitrile

TABLE V

Bis(aminomethyl) Sulfide Dihydrochlorides

$RNHCH_2SCH_2NHR \cdot 2HCl$

Compound No.	-R	M. p., °C Yield %	Analyses Calcd. C	H	Cl	N	S	Found C	H	Cl	N	S	Chemical Shifts of (δ) $-NCH_2S-$ Protons (a)
25	$-C_2H_5$	137-138 82	32.6	8.2	32.1	12.7	14.5	32.3	8.2	32.2	13.1	14.2	4.53
19	$-CH_2CH_2CH_3$	147-148 56	38.5	8.9	28.5	11.3	12.9	38.4	8.7	28.4	11.3	13.2	4.58
56	$-CH(CH_3)_2$	140-141 48	38.5	8.9	28.5	11.3	12.9	38.5	9.2	28.7	11.1	12.6	4.56
57	$-CH_2CH_2CH_2CH_3$	149-150 63	43.3	9.5	25.6	10.1	11.6	43.3	9.3	26.0	9.8	11.5	4.56
58	$-CH_2CH{=}CH_2$	139-140 84	39.1	7.4	28.5	11.4	13.1	39.1	7.4	28.5	11.7	13.5	4.58

(a) Spectra were obtained in DMSO solution on a Varian A-60 spectrometer. TMS was the internal standard.

has reached room temperature. The high yields (see Tables I-IV) of the aminomethyl sulfide hydrochlorides **14** (eq. 3) may be related to a variety of factors including the

(3)

11 **14**

R = alkyl or alkaryl

R' = alkyl, aryl or alkaryl

very reactive nature of the aminomethylating agent, which allows the reaction to proceed at low temperature, thus minimizing side reactions. Moreover, protonation of the amino-nitrogen atom (**14**) decreases its nucleophilic character and hence renders it less susceptible to attack by the aminomethylating agent.

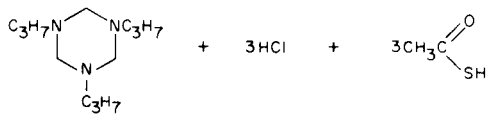
We had hoped to isolate the unknown mercaptomethylamine salt **15**. However, we obtained only the bis(secondary aminomethyl) sulfide hydrochlorides **16** in good to excellent yields (eq. 4). (See Table V). At first, the

(4)

11 **15** **16**

formation of **16** was thought to result from a secondary reaction of **15** with the aminomethylating reagent. In an attempt to minimize this type of reaction, a continuous reactor (15) was devised which consisted of an 18-inch x 1-inch glass column filled with glass helices and attached to a receiving flask. An aminomethylating solution was then prepared by the reaction of 1,3,5-triethylhexahydrotriazine with three equivalents of hydrogen chloride in a mixture of acetonitrile and methanol. This solution was introduced slowly at the top of the column and allowed to flow downward against a countercurrent of hydrogen sulfide. It was hoped that compound **15** (where $R = C_2H_5$) would form rapidly and move down the column, thus avoiding subsequent aminomethylation. Such was not the case. The sole product was the bis compound **16** ($R = C_2H_5$). This result suggested the possibility that the initially formed compound **15** ($R = C_2H_5$) was reacting with itself since it can function as both an aminomethylating agent and the compound to be aminomethylated. This self-reaction concept was substantiated by an experiment

in which thioacetic acid was aminomethylated as indicated in equation 5 and the isolated thioester **17** was then



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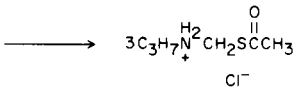

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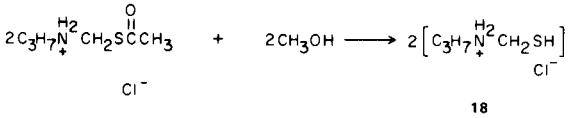
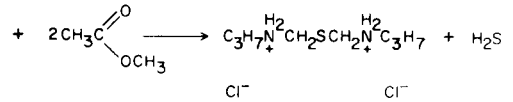
cleaved by a methanol-HCl solution (eq. 6). Product **19**



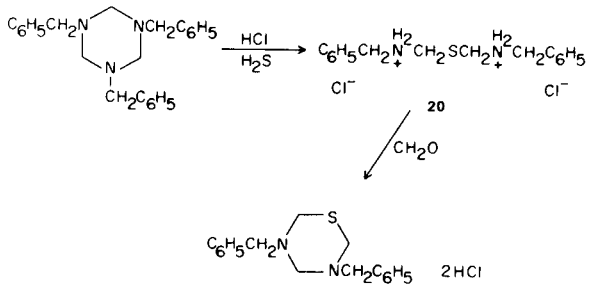
(6)



19

was isolated in high yield.

The reaction of hydrogen chloride with 1,3,5-tribenzylhexahydrotriazine in methyl ethyl ketone followed by subsequent reaction with hydrogen sulfide gave 3,5-dibenzyltetrahydro-1,3,5-thiadiazine (**21**) instead of the expected sulfide **20**. This result may be explained by the reaction of **20** with formaldehyde to yield **21** (eq. 7). The nmr



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spectrum of the free base prepared from **21** was identical with that of 3,5-dibenzyltetrahydro-1,3,5-thiadiazine prepared by the method of Braithwaite and Graymore (16).

EXPERIMENTAL

The 1,3,5-trisubstituted hexahydrotriazines were prepared according to the general procedure given below. General references have been listed by Smolin and Rapport (17). Melting points are uncorrected. An A-60 Varian spectrometer was used for the nmr determination, with tetramethylsilane as the reference standard. A Perkin-Elmer 137 instrument was used to obtain the infrared spectra.

General Procedure: Preparation of 1,3,5-Trialkylhexahydrotriazines.

To a 12 l., three-necked flask equipped with a stirrer, thermometer, and a dropping funnel, two l. of water and 300 g. of sodium hydroxide were added. After the sodium hydroxide had dissolved, two l. of benzene were introduced. With external cooling, 40 moles of the appropriate amine was added and the mixture cooled to 20-25°. Formaline (35-40%) (3600 g.) was added slowly while maintaining the temperature below 25°. When the formalin addition was complete salt and additional benzene were added when necessary to ensure two distinct layers. The benzene layer was separated, dried over magnesium sulfate and the benzene removed under vacuum. Products **11** having the following properties were obtained after distillation through a 24-inch column packed with glass helices.

R	B. p. °C.	n_D^{25}	% Yield
C_2H_5-	53/0.3	1.4565	73
n-C_3H_7-	94/0.7	1.4570	83
i-C_3H_7-	87/0.6	1.4625	70
n-C_4H_9-	112/0.4	1.4585	54
CH_2=CH-CH_2-	92/0.4	1.4875	83

Isolation of Aminomethylating Intermediate.

Anhydrous hydrogen chloride (12.0 g.) was absorbed in 250 ml. of anhydrous acetonitrile at -30°. To this was added 17.1 g. (0.1 mole) of 1,3,5-triethylhexahydrotriazine. The temperature of the reaction mixture was kept at about -20°. A white gelatinous precipitate formed immediately. The reaction mixture was allowed to warm to room temperature, during which time the precipitate became crystalline. It was filtered quickly, washed with anhydrous ether, and dried under vacuum, yield, 26.5 g. (94.6%).

Anal. Calcd. for C_3H_8ClN: C, 38.5; H, 8.6; N, 15.0. Found: C, 38.5; H, 8.4; N, 14.7.

β-Carboxyethyl Ethylaminomethyl Sulfide Hydrochloride **22**.

Reaction of Isolated Intermediate.

The isolated intermediate (9.0 g.) prepared in the above experiment was added to a solution of 12.0 g. of β-mercaptopropionic acid in 50 ml. of acetonitrile. The temperature rose exothermically to 45° and a crystalline product separated. After 30 minutes, 100 ml. of ether was added, the product was filtered, washed with ether, and dried to give 15.5 g. (77.8%) of the sulfide **22**, m.p. 104-109°. One recrystallization from 2-propanol yielded 13.5 g., m.p. 113-115°; nmr (deuterium oxide) δ, 1.30 center (T, 3H, CH_3), 2.53-3.33 (M, 6H, S-CH_2CH_2- and -CH_2N), 4.17 ppm (S, 2H, -CH_2S-).

Anal. Calcd. for $C_6H_{14}ClNO_2S$: C, 36.2; H, 7.0; Cl, 17.8; N, 7.0; S, 16.0. Found: C, 36.1; H, 6.9; Cl, 17.8; N, 6.7; S, 16.0.

Reaction of Intermediate Prepared *in situ*.

Anhydrous hydrogen chloride (4.0 g.) was absorbed in 100 ml. of acetonitrile at -30°. To this was added 5.7 g. (0.033 mole) of 1,3,5-triethylhexahydrotriazine and 10.6 g. (0.1 mole) of β-mercaptopropionic acid. The temperature was kept at about -20°

during this addition. Within a few minutes a white crystalline product separated. After 30 minutes 100 ml. of ether was added, the product was separated by filtration and dried to give 19.0 g. (95.4%) of compound **22**, m.p. 100-107°. One recrystallization from 2-propanol raised the m.p. to 113-115°. The nmr and ir spectra were identical with those of the compound prepared from the isolated intermediate.

General Procedure for Aminomethylation of Mercaptans (Acetonitrile as Reaction Medium) (Tables I-IV).

Anhydrous hydrogen chloride (4.0 g.) was absorbed in an anhydrous acetonitrile solution (100 ml.) of 1,3,5-trisubstituted hexahydrotriazine (0.033 mole) which was maintained at about -30°. A mercaptan (0.1 mole) was dissolved in acetonitrile (50 ml.) and added slowly to the above solution. The reaction mixture was allowed to remain at room temperature for 15 hours, cooled, and poured into 400 ml. of cold ether. The crystalline salt was isolated by filtration, washed with ether, and dried in vacuum. Analytical samples were recrystallized as noted in Tables I-IV.

Benzyl Benzylaminomethyl Sulfide Hydrochloride **23** (Ether as Reaction Medium).

Anhydrous hydrogen chloride (4.0 g.) was dissolved in 150 ml. of anhydrous ether at -20°. An ether solution (50 ml.) of 1,3,5-tribenzylhexahydrotriazine (11.9 g.) was added to the cold solution. Benzyl mercaptan (13.0 g.) was then added. There was an immediate separation of crystalline product. After 4 hours at room temperature it was separated by filtration and dried to give 14.9 g. (89%) of a compound which was shown by infrared and nmr to be identical with the product obtained by the above general procedure. See compound **23**, Table IV.

Benzyl *n*-butylaminomethyl Sulfide Hydrochloride **24** (Methanol as Reaction Medium).

Methanol (40 ml.) containing 17.0 g. of 1,3,5-tri-*n*-butylhexahydrotriazine was cooled to -20° and 8.2 g. of anhydrous hydrogen chloride dissolved therein. A solution of 25.0 g. of benzylmercaptan in 50 ml. of methanol was then added. A slight exotherm ensued and within a few minutes benzyl *n*-butylaminomethyl sulfide hydrochloride began to crystallize. After 4 hours, the product was separated and dried; yield, 35.8 g. (73%); nmr and ir spectra showed it to be identical with compound **24**, Table III.

General Procedure for the Aminomethylation of Hydrogen Sulfide (Methyl Ethyl Ketone as Reaction Medium) (Table V).

A methyl ethyl ketone solution (400 ml.) of 1,3,5-trisubstituted hexahydrotriazine (0.2 mole) was cooled to -30°, while 21.0 g. of hydrogen sulfide was absorbed therein. With continued cooling, 12.0 g. of anhydrous hydrogen chloride was passed into the solution. After 15 hours at room temperature, the crystalline product was separated by filtration and dried. Analytical samples were recrystallized from methanol-acetonitrile mixtures.

Bis(ethylaminomethyl) Sulfide Dihydrochloride (**25**) via Continuous Reactor.

An anhydrous acetonitrile (300 ml.) solution of 34.2 g. (0.2 mole) of 1,3,5-triethylhexahydrotriazine was cooled to -30° and treated with 21.0 g. of hydrogen chloride. The reaction mixture was allowed to reach room temperature. The crystalline product was dissolved by the addition of 30 ml. of methanol. This solution was then introduced at the top of an 18-in. x 1-in. glass column packed with glass helices and attached to a receiving flask. The solution was allowed to flow downward countercurrent to the flow of hydrogen sulfide. The addition of the aminomethylating agent was continued over a 1-hour period. The crystalline reaction product formed in both the receiver and the lower part of the column. Infrared and nmr spectra proved this product to be identical with compound **25**, Table V.

Cleavage of *n*-Propylaminomethylthioacetate Hydrochloride (**26**) to Form bis(*n*-Propylaminomethyl) Sulfide Dihydrochloride (**27**).

A methanol solution (200 ml.) of 18.3 g. (0.001 mole) of compound **26** was treated with 2.0 g. of hydrogen chloride and refluxed for 4 hours. The cooled reaction mixture was poured into cold ether with vigorous stirring. The crystalline product **27** (20.0 g., 81%) was recrystallized from a methanol-acetonitrile mixture. Infrared and nmr spectra and a mixture melting point showed that this product was identical with compound **19**, Table V.

3,5-Dibenzyltetrahydro-1,3,5-thiadiazine and the Dihydrochloride (**28**).

Two-tenths of a mole (71.4 g.) of 1,3,5-tribenzylhexahydrotriazine was dissolved in 400 ml. of methyl ethyl ketone. The solution was cooled to -30° and allowed to react successively with 21.0 g. of hydrogen sulfide and 12.0 g. of hydrogen chloride. After 15 hours at room temperature the crystalline product was separated and dried to yield 56.0 g. (54%) of the thiadiazine hydrochloride **28**, m.p. 259-261°. An aliquot of **28** was neutralized by aqueous sodium bicarbonate and recrystallized from methanol, m.p. 92-93°. This free base is identical with that prepared by Braithwaite and Graymore (15) by the reaction of 1,3,5-tribenzylhexahydrotriazine with hydrogen sulfide; nmr (deuteriochloroform), δ 7.39 (S, 10, Ar); 4.25 (S, 4, $-SCH_2N-$); 4.11 (S, 4, $ArCH_2N$); 4.04 ppm (S, 2, $-NCH_2N-$).

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