The crude oil (21 g), obtained subsequent to removal of phenylmercuric chloride (99% yield), was shown to contain no N-methyl-N-phenyl-1,2,2-trichlorovinylamine[5] by analysis using thin layer chromatography (silica gel, 20% benzene–petroleum ether, bp 60–68°, ceric sulfate–phosphoric acid developer).

The crude mixture was not resolved. Attempts to distil the product at a bath temperature of 130° resulted in extensive decomposition. A small amount of oil [~1 g, bp 45–70° (0.01 mm)] was obtained which was purified by chromatography on alumina using petroleum ether as eluent. This product was not identified; the nmr spectrum shows two different allyl groups.

Reaction of N-Methyl-N-(3-methyl-2-butenyl)aniline with Phenyl(tribromomethyl)mercury.—A solution of **1b** (5.25 g, 0.03 mole) and phenyl(tribromomethyl)mercury[19] (31.8 g, 0.06 mole) in benzene (100 ml) was heated at reflux temperature for 1.75 hr. Analysis of 90 ml of benzene which was then distilled showed 2.3% yield of isoprene. The oil (8.5 g) obtained subsequent to removal (see procedure for **1b**) of phenylmercuric bromide (91% yield) had an infrared spectrum very similar to the crude product obtained when phenyl(trichloromethyl)mercury was used (*i.e.*, to crude **3b**). Tribromovinylamine **11** was thermally unstable and was not obtained pure. Hydrolysis occurred when crude **11** was chromatographed on alumina (200 g). Elution of the column with petroleum ether and benzene gave 2.1 g of glassy material which was not characterized, and elution with ethyl acetate gave 3.10 g (34% yield) of crude 2,2-dibromo-N-methylacetanilide (mp 94–103°), the expected hydrolysis product[5] of **11**. The amide was purified to mp 109–110° by recrystallization from petroleum ether.

Anal. Calcd for $C_9H_9Br_2NO$: C, 35.21; H, 2.95; N, 4.56. Found: C, 35.41; H, 2.76; N, 4.52.

The nmr spectrum of 2,2-dibromo-N-methylacetanilide showed aromatic *H* (complex, τ 2.4–2.8, wt 5), *CH*Br_2 (singlet, τ 4.22, wt 1), and *CH*$_3$N (singlet, τ 6.67, wt 3).

Reaction of γ,γ-Dimethylallyl Phenyl Sulfide (13) with Phenyl(trichloromethyl)mercury.—A solution of **13**[6] (8.9 g, 0.05 mole) and phenyl(trichloromethyl)mercury (19.8 g, 0.05 g-atom) in benzene (125 ml) was heated for 41 hr. The conditions and processing were similar to those described for **1b** (procedure A). No isoprene was detected in the benzene distillate. The crude black oil (10.1 g), obtained subsequent to removal of phenylmercuric chloride, had infrared and nmr spectra similar to, but not identical with, those of the product[6] when ethyl trichloroacetate and sodium methoxide were used as the carbene source. The oil was placed on silica gel (250 g) and evolution of hydrogen chloride was noted.[6] Elution with 33% benzene–petroleum ether (bp 60–68°) gave 3.6 g of uncharacterized oil which decomposed upon standing. Further elution of the column with benzene gave 2.8 g (27% yield) of thiolphenyl ester of 2,2-dimethyl-3-butenoic acid, the infrared spectrum of which was essentially identical with that reported.[6] The ester was further purified by distillation [bp 75–79° (0.07 mm), n^{20}D 1.5552] [lit.[6] bp 56–57° (0.01 mm), $n^{22.5}$D 1.5550] and the product was identical (infrared and nmr) with authentic ester.

(19) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

Nucleophilic Displacement Reactions of β-Amino Mercaptans

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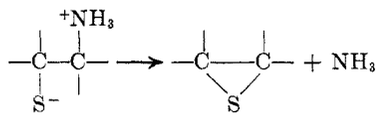
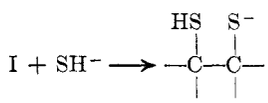
β-Amino mercaptans have been found to undergo intramolecular nucleophilic displacement of the amino group by the neighboring mercaptide group. Reaction of episulfides formed *in situ* with bisulfide or mercaptides offers a novel route to polythiols and mercapto thio ethers.

In the course of another study, a quantity of 1-amino-2,3-propanedithiol was required.[1] An attempt to prepare this compound by Stocken's procedure[2] (heating a methanolic solution of 2,3-dibromopropylamine hydrobromide and excess ammonium bisulfide for 16 hr at 90°, then isolating product by adding ammonium hydroxide and extracting with benzene) gave 1,2,3-propanetrithiol instead of the aminodithiol. By modifying the work-up procedure, both 1-amino-2,3-propanedithiol and 1,2,3-propanetrithiol were isolated from the reaction mixture (Table I). We assumed that the propanetrithiol was derived through reaction of initially formed 1-amino-2,3-propanedithiol with ammonium bisulfide. Further investigation has established that this synthesis is an example of a general reaction involving episulfide formation through the nucleophilic displacement of a β-amino group by a mercaptide group. Snyder and Stewart[3] speculated that an episulfide might be formed in the thermal decomposition of N-substituted β-amino mercaptans upon attempted distillation; however, to our knowledge, our synthesis is the first established example of displacement of the amino group with episulfide formation. We believe that the amino mercaptan exists as a zwitterion, and that elimination of ammonia occurs as shown in eq 1.



(1)



(2)

That this displacement reaction is applicable to simple β-aminomercaptans was demonstrated by the preparation of 1,2-propanedithiol in 58% yield by treating 1-amino-2-propanethiol with excess ammonium bisulfide at 90°. To facilitate isolation, water was used as solvent in this and other examples involving β-amino mercaptans.

The β-amino mercaptans can also be formed *in situ* and treated further with ammonium bisulfide (Table II). Reaction of propylenimine with excess ammonium bisulfide in water at 125° led to formation of 1,2-propanedithiol in 42% yield. Since the intermediate 2-amino-1-propanethiol possesses the amino group on a secondary carbon, a higher temperature was required to displace the amino group than in the case of the isomeric 1-amino-2-propanethiol. At 90°, less than 2% propanedithiol was obtained. Similarly, reaction of ethylenimine and ammonium bisulfide at 125° produced 1,2-ethanedithiol in 38% yield.

The modest yields presumably are the result of by-product formation from the reaction of the intermediate

(1) This work was done in part under Contract DA-49-193-MD-2069 with U. S. Army Medical Research and Development Command.

(2) L. A. Stocken, *J. Chem. Soc.*, 592 (1947).

(3) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2672 (1947).

TABLE I

SYNTHESIS OF 1-AMINO-2,3-PROPANEDITHIOL AND 1,2,3-PROPANETRITHIOL

$BrCH_2CH(Br)CH_2NH_2HCl + NH_3 + H_2S \longrightarrow$
II
$HSCH_2CH(SH)CH_2NH_2 + HSCH_2CH(SH)CH_2SH$
III IV

II, g	H_2S, g	NH_3, g	Reacn cond	Yield, % III	Yield, % IV
40	80	40	*a*	17	33[b]
80	100	50	*c*	44[d]	*e*
40	*f*	*f*	*a*	*g*	28
40	80	40	*h*		27[i]

[a] For 16 hr at 90°; methanol solvent. [b] Extraction with benzene was not carried out prior to treatment with liquid ammonia. Both products were removed by toluene extraction. After removal of toluene the two products codistilled, and III separated from IV on cooling. [c] For 48 hr at ambient temperature; methanol solvent. [d] Compound III had mp 112–119°. Attempted distillation of III gave considerable decomposition; a small amount which sublimed had mp 120–122°. [e] Some IV was detected by gas–liquid partition chromatographic analysis of the benzene extract. [f] Preformed ammonium bisulfide (120 g) was employed. [g] The toluene extract gave a gummy precipitate from which pure III could not be obtained. [h] For 16 hr at 90°; water solvent. [i] The aqueous mixture from the reactor was extracted with ether; distillation of the dried ether extract gave IV.

TABLE II

PREPARATION OF DITHIOLS

V, VI, or VII[a] + H_2S + NH_3 ⟶ VIII or IX[b]

Reactant, g	NH_3,[c] g	H_2S, g	Product	Yield, %	Bp, °C	$n^{20}D$
V, 59.1	80	171[d]	IX	58	143–147	1.5317
V, 47.7	84	169[e]	IX	35	146–149	1.5303
VII, 29.4	80	189[f]	IX	5		
VII, 28.7	80	187[g]	IX	42	149–151	1.5312
VI, 22.3	80	189[g]	VIII	38	140–143	1.5567

[a] V, 1-amino-2-propanethiol; VI, ethylenimine; VII, propylenimine. [b] VIII, ethanedithiol; W. P. Hall and E. E. Reid [*J. Am. Chem. Soc.*, **65**, 1466 (1943)] reported bp 146–146.5°, $n^{25}D$ 1.5558. IX, 1,2-propanedithiol; P. S. Fitt and L. N. Owen [*J. Chem. Soc.*, 2250 (1957)] reported bp 52–56° (25 mm), $n^{20}D$ 1.527–1.531. [c] Ammonia was introduced as concentrated ammonium hydroxide in runs employing water as solvent. Reactions were carried out in water with a solvent volume of 500 ml unless otherwise noted. [d] Solvent volume 600 ml; reacted at 90° for 16 hr. [e] Methanol solvent; reacted at 90° for 19 hr. [f] Run at 90° for 16 hr. [g] Run at 125° for 16 hr.

episulfide with the thiol group of the starting material or of the product, rather than with the bisulfide or mercaptide reagent. No attempt was made to isolate byproducts or unreacted starting material.

Mercaptide ions also react with the intermediate episulfide (Table III). When 1-amino-2-propanethiol was heated in the presence of excess propyl mercaptan and aqueous ammonia, 1-propylthio-2-propanethiol was obtained in 30% yield. This structure is consistent with ring opening at the least substituted carbon atom.

TABLE III

SYNTHESIS OF 1-PROPYLTHIO-2-PROPANETHIOL

V or X[a] + $CH_3CH_2CH_2SH$ + NH_3 ⟶
$CH_3CH(SH)CH_2SCH_2CH_2CH_3$

Reactant, g	NH_3,[b] g	C_3H_7SH, g	Yield, %
V, 50.7	80	380[c]	30
V, 46.2	90	473[d]	9
X, 11.1	39	167[e]	19

[a] V, 1-amino-2-propanethiol; X, 2-amino-1-propanethiol. [b] Ammonia was introduced as concentrated ammonium hydroxide in runs employing water as solvent. [c] Run in 600 ml of water at 90° for 17 hr. [d] Run in 600 ml of 1-propanol at 125° for 16 hr. [e] Run in 300 ml of water at 125° for 41 hr.

The reaction of mercaptans and β-amino mercaptans offers further evidence of an episulfide intermediate, since reaction of the isomeric 2-amino-1-propanethiol and propyl mercaptan in aqueous ammonia also led to 1-propylthio-2-propanethiol in 22% yield. Formation of the same product from the two isomeric amino mercaptans indicates that a common intermediate, propylene sulfide, is involved. Further evidence of the importance of a neighboring-group effect is the fact that neither ethylenediamine nor 3-amino-1-propanethiol reacted with ammonium bisulfide under the usual reaction conditions.

Reaction of 2,3-dibromopropylamine hydrochloride with ammonium bisulfide at room temperature (to minimize episulfide formation) gave 3-amino-1,2-propanedithiol. This compound is an unstable solid, mp 120–122°, which decomposes slowly on standing. The hydrochloride salt, mp 99–100°, was prepared and its infrared spectrum was identical with that of an authentic sample prepared by hydrolysis of the corresponding ethyl urethan (eq 3). 3-Amino-1,2-propanedithiol hydrochloride, prepared from 1,2-dibromopropylamine and potassium bisulfide, has been reported to melt at 245° dec.[4] Although the reported carbon–hydrogen analyses agreed with theory, no mercaptan analysis was given. Apparently, a higher molecular weight amino sulfide was actually obtained. In the present study, 3-amino-1,2-propanedithiol was also characterized by reaction of the bissodium mercaptide derivative with benzyl chloride. Treatment with hydrochloric acid gave 3-amino-1,2-bis(benzylthio)-propane hydrochloride, mp 90–92° (eq 4).

$$HSCH_2CH(SH)CH_2NHCO_2C_2H_5 \xrightarrow{H_2O,\ HCl} HSCH_2CH(SH)CH_2\overset{+}{N}H_3\bar{C}l \quad (3)$$

$$BrCH_2CH(Br)CH_2\overset{+}{N}H_3\bar{C}l \xrightarrow[2.\ HCl]{1.\ NH_4SH} HSCH_2CH(SH)CH_2\overset{+}{N}H_3\bar{C}l$$

$$HSCH_2CH(SH)CH_2NH_2 \xrightarrow[2.\ RCl\ \ 3.\ HCl]{1.\ NaOCH_3} RSCH_2CH(SR)CH_2\overset{+}{N}H_3\bar{C}l \quad (4)$$

$$BrCH_2CH(Br)CH_2NHCO_2C_2H_5 \xrightarrow[2.\ RSH\ \ 3.\ HCl]{1.\ NaOCH_3} RSCH_2CH(SR)CH_2\overset{+}{N}H_3\bar{C}l$$

R = $C_6H_5CH_2$

Experimental Section

Boiling points and melting points are not corrected. Propyl mercaptan was a product of Matheson Coleman and Bell, ethylenimine and propylenimine were obtained from Interchemical Corp., and hydrogen sulfide and ammonia were secured from the Matheson Co. Preparation of other starting materials is given below.

(4) V. M. Fedoseev, *Dokl. Akad. Nauk. SSSR*, **148**, 871 (1963).

2,3-Dibromopropylamine Hydrochloride.—A stirred solution of 114.5 g (2 moles) of allylamine in 150 ml of water was cooled to 5° and 184 ml of concentrated hydrochloric acid was added, maintaining a temperature of 20° by the rate of addition. The reaction mixture was heated to 50° and 319.6 g (2 moles) of bromine was added dropwise, maintaining a temperature of 65°. After completion of bromine addition, 1 l. of 2-propanol was added, and the volatile material was removed on a rotary evaporator at room temperature and aspirator pressure. The residual oil was crystallized from a 1:1 mixture (v/v) of 1-propanol and 2-propanol to give 348 g of product, mp 138° (69% yield).

Anal. Calcd for $C_3H_8Br_2ClN$: C, 14.22; H, 3.18; Br, 63.08; Cl, 13.99; N, 5.53. Found: C, 14.45; H, 3.4; Br, 61.3; Cl, 16.6; N, 5.4.

1-Amino-2-propanethiol.—This compound was made by the addition of hydrogen sulfide to allylamine.[5]

2-Amino-1-propanethiol.—A 1400-ml stainless steel bomb was purged with nitrogen and charged with 44.4 g (0.78 mole) of propylenimine and 400 ml of methanol. After sealing and subsequent cooling of the reactor in a Dry Ice–acetone bath, 196 g (5.8 moles) of hydrogen sulfide was added. After the mixture reached room temperature, it was heated at 90° for 16 hr. The reactor was vented, the residue was transferred to a 1-l. flask, and solvent was removed on a steam bath. The residual solid was recrystallized from benzene to yield 26.5 g of 2-amino-1-propanethiol, mp 69–72° (26.7% yield). Admixture with 1-amino-2-propanethiol, mp 63–67°, lowered the melting point to 54–57°.

Ammonium Bisulfide.—Ammonia and hydrogen sulfide were bubbled into an ether solution cooled in a Dry Ice–acetone bath. To ensure bisulfide formation, the rate of hydrogen sulfide flow was greater than that of ammonia, and its addition was continued for 15 min after addition of ammonia was stopped. The resultant precipitate was pressed on a filter to yield a moist solid.

Reaction of 2,3-Dibromopropylamine Hydrochloride with Ammonium Bisulfide.—In a 1400-ml stainless steel bomb was placed the 2,3-dibromopropylamine hydrochloride and 600 ml of solvent and the bomb was purged with nitrogen for 5 min. After sealing and subsequent cooling of the reactor in a Dry Ice–acetone bath, weighed amounts of hydrogen sulfide and then ammonia were added. The reaction vessel was heated to the desired temperature at autogenous pressure and shaken on a platform rocker for a given period of time. After cooling, the reactor was vented and nonvolatile materials were removed. Solvent and excess ammonium bisulfide were removed on a rotary evaporator at aspirator pressure, with a bath temperature not exceeding 40°. The semisolid residue was extracted several times with 100-ml portions of benzene and the solid residue was dissolved in 500 ml of liquid ammonia. After the ammonia had evaporated, the solid was extracted with several 100-ml fractions of hot toluene. 1-Amino-2,3-propanedithiol crystallized from the toluene on cooling. The benzene extract was distilled to yield 1,2,3-propanetrithiol. Results are summarized in Table I. A redistilled sample of the 1,2,3-propanetrithiol had bp 64° (0.25 mm), $n^{20}D$ 1.6112 [lit.[6] bp 80° (2 mm), $n^{22}D$ 1.6105].

Anal. Calcd for $C_3H_8S_3$: C, 25.68; H, 5.75; S, 68.57. Found: C, 25.7; H, 5.76; S, 69.4.

1-Amino-2,3-propanedithiol Hydrochloride. A. From the Free Base.—Crude 1-amino-2,3-propanedithiol (17.0 g) was dissolved in 1-propanol and concentrated hydrochloric acid was added during stirring and cooling. The solvent was removed by a rotary evaporator at aspirator pressure and a temperature not exceeding 40°. The residual solid was redissolved in hot 1-propanol and one-half the equivalent volume of tetrahydrofuran was added. The solution was then placed in a refrigerator. Initial gummy precipitates were removed until the material crystallized as an amorphous, white solid. The yield was 3.2 g, mp 99–101°. The infrared spectrum of this material was identical with that of 1-amino-2,3-propanedithiol hydrochloride prepared from ethyl 2,3-dimercaptopropylurethan.

B. From Ethyl 2,3-Dimercaptopropylurethan.—A solution of 39.0 g (0.2 mole) of ethyl 2,3-dimercaptopropylurethan[7] in 100 ml of concentrated hydrochloric acid was heated under reflux for 16 hr in a nitrogen atmosphere. Solvent was removed by a rotary evaporator, and the residue was crystallized from a 1:2 mixture (v/v) of 1-propanol and tetrahydrofuran. Recrystallization from a 2:1 mixture (v/v) of 1-propanol and tetrahydrofuran gave 10 g of 3-amino-1,2-propanedithiol hydrochloride, mp 99.5–100.5° (31% yield).

Anal. Calcd for $C_3H_{10}ClNS_2$: C, 22.56; H, 6.31; N, 8.77; S, 40.16. Found: C, 22.75; H, 6.3; N, 8.4; S, 40.2; SH, 36.6.

3-Amino-1,2-bis(benzylthio)propane Hydrochloride. A. From 3-Amino-1,2-propanedithiol.—Crude 3-amino-1,2-propanedithiol, mp 93–118° (5.2 g, 0.04 mole), was added to a solution of 0.11 mole of sodium methoxide in 300 ml of methanol cooled in an ice bath. After 15 min, 13.9 g (0.11 mole) of benzyl chloride was added in one portion. The solution was allowed to warm to room temperature. Upon standing for 15 hr, much solid had formed. Solvent was removed at room temperature by a rotary evaporator with aspirator pressure and 250 ml of water was added to the wet solid. The mixture was extracted with four 100-ml portions of ether and 10 ml of concentrated hydrochloric acid was added to the combined extracts. The resultant solid was removed and dissolved in 75 ml of warm tetrahydrofuran. 3-Amino-1,2-bis(benzylthio)propane hydrochloride crystallized as a fibrous, white solid, mp 84–90°. The product was obtained in 36% yield (5.6 g). When recrystallized from chloroform, a sample melted at 92–95°.

Anal. Calcd for $C_{17}H_{22}ClNS_2$: C, 60.06; H, 6.52; N, 4.13. Found: C, 59.6; H, 7.0; N, 4.0.

Admixture with 3-amino-1,2-bis(benzylthio)propane hydrochloride prepared from ethyl 2,3-dibromopropylurethan (see below) caused no depression of melting point. Infrared spectra of the two samples were identical and were in agreement with the assigned structure.

B. From Ethyl 2,3-Dibromopropylurethan.—To a solution of 130 g (1.05 moles) of α-toluenethiol, 300 ml of methanol, and 42 g (1.05 moles) of sodium hydroxide maintained at 5° was added a solution of 145 g (0.5 mole) of ethyl 2,3-dibromopropylurethan in 300 ml of methanol. The solution was stirred for 3 hr at 5°, for 2 hr at 35°, and finally for 0.5 hr at 60°. The reaction solution was cooled to room temperature, 700 ml of water was added, and the product was extracted with two 250-ml portions of chloroform. The combined chloroform extracts were washed with 150 ml of water, dried over anhydrous sodium sulfate, and stripped on a rotary evaporator at room temperature and aspirator pressure to give 183.5 g (98% yield) of ethyl 2,3-bis(benzylthio)propylurethan. A sample of the crude product, $n^{20}D$ 1.5736, decomposed on attempted distillation.

A stirred mixture of 37.6 g (0.1 mole) of the above urethan, 100 ml of concentrated hydrochloric acid, and 50 ml of water was heated at reflux temperature for 20 hr. Addition of 75 ml of ether to the cooled mixture dissolved unhydrolyzed starting material. The residual white, crystalline solid was collected on a filter, washed with ether, and dried to give 4.8 g (14% yield) of 3-amino-1,2-bis(benzylthio)propane hydrochloride, mp 90–95°.

Alkyl Dithiols.—A 1400-ml stainless steel bomb was charged with the mercaptoamine or aziridine, water, and ammonium hydroxide and purged with nitrogen. The vessel was then cooled and hydrogen sulfide was added under pressure. The reactor was heated to the desired temperature and shaken on a platform rocker for a given period. After cooling, the reactor was vented, and the liquid contents were transferred to a separatory funnel where they were extracted several times with 100-ml portions of ether. Removal of solvent and distillation yielded the desired product. When methanol was employed as solvent, the reaction mixture was treated with aqueous sodium hydroxide. After removal of the alcohol, the aqueous solution was made acidic and extracted with ether. Results are given in Table II.

1-Propylthio-2-propanethiol.—The procedure for the preparation of dithiols was followed except that the mercaptan was added before sealing the reaction vessel, and no hydrogen sulfide was added. Elemental analysis was made on a purified sample [bp 102–103° (35 mm), $n^{20}D$ 1.5051]. Identity of products in all runs was established by gas–liquid partition chromatography using a 10-ft column of 10% G.E. SE 30 silicon rubber on 60–80 mesh Gas-Chrom P. The temperature was programmed from 100 to 300° at 30°/min and the helium carrier flow was 60 ml/min. In all cases, a minor product of somewhat shorter retention time was also formed, presumably 2-propylthio-1-propanethiol. Results are given in Table III.

(5) S. D. Turk, R. P. Louthan, R. L. Cobb, and C. R. Bresson, *J. Org. Chem.*, **27**, 2846 (1962).

(6) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2943 (1950).

(7) A. A. Pavlic, W. A. Lazier, and F. K. Signaigo, *J. Org. Chem.*, **14**, 59 (1949).

Anal. Calcd for $C_6H_{14}S_2$: C, 47.94; H, 9.39; S, 42.67; SH, 21.33. Found: C, 47.95; H, 9.3; S, 39.4; SH, 20.5.

Treatment of Ethylenediamine with Ammonium Bisulfide.—The general procedure used with 1-amino-2-propanethiol was followed. Heating 30 g of ethylenediamine, 80 g of ammonia, and 203 g of hydrogen sulfide in 600 ml of water led to no discernible formation of 1,2-ethanedithiol.

Treatment of 3-Amino-1-propanethiol with Ammonium Bisulfide.—The general procedure was followed. Heating 49 g of 3-amino-1-propanethiol, 80 g of ammonia, and 184 g of hydrogen sulfide in 600 ml of water yielded only some black polymeric material. Extraction with ether and inspection of both the extract and aqueous phases by gas–liquid partition chromatography indicated that neither 1,3-propanedithiol nor trimethylenesulfide had been formed.

Differential Thermal Analysis of Nitramines, Amine Salts, and Guanidine Derivatives

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A study of the thermal stability of a number of nitramines, amine nitrate salts, and guanidine derivatives by means of differential thermal analysis is presented. The position of the exotherms on the average is at about 260° for both cyclic nitramines and amine nitrate salts. In the open-chain nitramines the decomposition exotherms cover a very broad temperature range and the position of the peak maxima is apparently dictated by the electronegativity of the groups bonded to the amino nitrogens. In the case of the guanidine derivatives salts the decomposition exotherms would seem to depend on both the cation and anion structures and are possibly related to the hydrolysis constants of the salts.

The technique of differential thermal analysis (DTA) has aroused widespread interest for the study of the thermal behavior of numerous organic and polymeric compounds. The simplicity of manipulation and the small amounts of material required render this technique extremely valuable. However, as can be judged by the paucity of published data its potential value in the field of propellants had not been recognized until a few years ago.[1] This is particularly true of compounds of military interest such as nitramines, amine nitrate salts, and guanidine derivatives. Only a few of the latter have to this date been reported.[2] It is not surprising then that no serious efforts have as yet been made toward establishing some possible correlation between profiles of structural features and thermograms. Such an attempt based on the results obtained from 40 compounds is presented in this paper. These include cyclic and acyclic nitramines, their corresponding salts, and guanidine derivatives. Owing to the complex shape of many thermograms only the position of the exotherm maxima is discussed in relation to the structure of the compounds.

Results and Discussion

Cyclic Nitramines.—As shown in Table I, of the ten cyclic nitramines studied three boiled without decomposition (thermograms 1, 2, and 3). All the other nitramines gave exotherms, the average position of the maxima being at 265°. Throughout this series the exotherm maxima cover a rather broad temperature range (from 240 to 285°) and no clear relationship between structure and the decomposition temperature could be detected. In four of these nitramines (thermograms 6, 7, 8, and 10) it was observed that decomposition occurs near the melting point. With β-HMX (thermogram 10) an endotherm was observed at 185° and has been assigned to the crystal-phase transition from the β form to the metastable δ form in agreement with previous results obtained at other laboratories.[3,4] This assignment explains satisfactorily the behavior of the endotherm upon repeated heating of the sample to 200°. While immediate reheating results in the disappearance of the endotherm, reheating after a sufficiently long pause at room temperature leaves it unaffected.

Open-Chain Nitramines.—The positions of the exotherm maxima for this series of compounds are given in Table II. It is evident that the type of substitution on the amino nitrogen has a drastic influence on the thermal stability of these compounds. There is a strong indication that a direct relationship might exist between the electronic configuration of the nitramine function and its thermal stability. Replacement of the hydrogen atoms by electron-donating groups as in NN′-dinitro-NN′-dimethyl-1,2-diaminoethane (thermogram 14) shifts the exotherm to higher temperatures while the reverse is observed with electron-withdrawing groups such as carboxyethyl and acetyl (thermograms 15 and 16). Comparison of thermograms 14 and 17 in the open-chain series with those of the cyclic nitramines leads to the suggestion that whether the nitramine function is part of a ring or an open-chain structure apparently has very little bearing on its thermal stability.

In the open-chain series only two compounds (thermograms 12 and 13) incorporate into their structure a primary nitramino group and both compounds are characterized by a relatively low temperature exotherm (202 and 210°). Furthermore, the diammonium and guanidinium salts of the primary nitramine, NN′-dinitro-1,2-diaminoethane (thermograms 26 and 40), have exotherm maxima very close to that of the parent nitramine (191 and 215°). This raises the question as to whether the presence of the tautomeric *aci* form as

(1) P. G. Rivette and E. D. Besser, "Differential Thermal Analysis as a Research Tool in Characterizing New Propulsion Systems," NAVWEPS Report 7769, U. S. Naval Ordnance Test Station, China Lake, Calif., Oct 1961.

(2) M. I. Fauth, *Anal. Chem.*, **32**, 6, 655 (1960).

(3) Quarterly Progress Report No. 2, Walter C. McCrone Associates, Contract No. NOrd 18840, April 1962.

(4) Los Alamos Scientific Laboratory Report LAMS-2652, Contract W-7405-Eng., May 1962.