droxide solution. Filtration of the flocculent precipitate was very tedious.

In two cases the azostyrene in the product was found to be 1.7% and 1.2% of the I used.

Infrared spectra were obtained with a Perkin–Elmer "Infracord," Model 137. All solids were run in potassium bromide pellets. *p*-Vinylaniline was run neat between sodium chloride plates.

Acknowledgment.—This work is part of a program of research that has been supported by the Robert A. Welch Foundation, the National Science Foundation (grant no. G-14551), and Texas Technological College (grant no. 1654). We wish to thank these donors for their support.

Organic Sulfur Compounds. I. Synthesis of *sec*-Mercaptoalkylamine Hydrochlorides[1a,b]

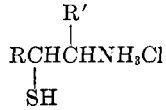
F. I. CARROLL, J. D. WHITE, AND MONROE E. WALL

The Natural Products Laboratory, Research Triangle Institute, Durham, North Carolina

Received September 28, 1962

Methods for the preparation of *sec*-mercaptoalkylamine hydrochlorides are presented. The scheme used for the preparation of these compounds involves the preparation of *sec*-benzylthionitroalkanes, followed by reduction of the nitro group with lithium aluminum hydride and reductive debenzylation with sodium in liquid ammonia to free the mercaptan. Several procedures for preparing the requisite *sec*-benzylthionitroalkanes involving isolation of nitroölefins followed by the addition of benzyl mercaptan or reaction of the latter with nitroölefins formed *in situ* are discussed.

The synthesis of mercaptoalkylamines is a subject of current interest because of the antiradiation activity of some of these compounds.[2,3] Although there are numerous reports of the synthesis of compounds in which the mercapto group is attached to a primary carbon atom, there is a paucity of data concerning the synthesis of mercaptoalkylamines bearing sulfur on secondary or tertiary carbon atoms. This paper describes the preparation of a group of new *sec*-mercaptoalkylamine hydrochlorides of type I or II shown below. In addition, improved procedures for preparing nitroolefins and *sec*-benzylthionitroalkane precursors are described.



I. R = alkyl, R′ = H
II. R = alkyl, R′ = CH_3 or C_2H_5

We initially planned to use the reaction scheme outlined in Chart A for the preparation of the *sec*-mercaptoalkylamine hydrochlorides.

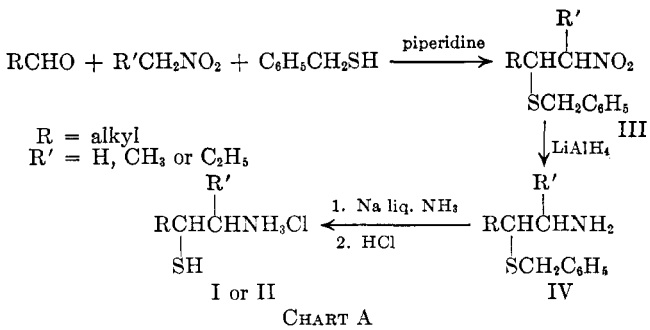


CHART A

Parham and Ramp[4] reported that nitromethane, propionaldehyde and benzyl mercaptan mixed in the absence of solvent and a catalytic amount of piperidine added, reacted exothermically to give 2-benzylthio-1-nitrobutane in nearly quantitative yield. These authors suggested that the 2-benzylthio-1-nitrobutane was apparently formed by the addition of benzyl mercaptan to 1-nitrobutene formed *in situ*. Our initial attempts to extend this method to longer chain aldehydes were unsatisfactory. The reaction products were impure and because of decomposition could not be distilled without undue losses. Therefore, we turned our attention to the route shown in Chart B.

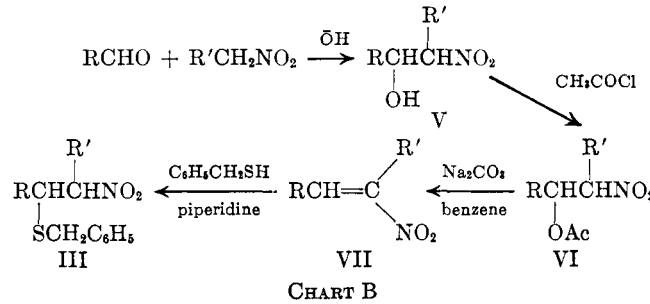


CHART B

Each of the four steps in Chart B is reported to occur in good yield. The major disadvantage was that several distillations were required. We overcame this difficulty, however, by preparing the desired nitroölefin from the appropriate aldehyde and nitroalkane without purification of either the nitro alcohol or the nitro acetate. The nitro alcohol was prepared by allowing the aldehyde and the nitroalkane to condense in the presence of aqueous alcoholic sodium hydroxide according to the method of Sprang and Degering.[5] The progress of the reaction was followed by the disappearance of the carbonyl band of the aldehyde and the appearance of a strong hydroxyl absorption at 3560–3600 cm.$^{-1}$. The nitro acetates could be obtained directly from the crude nitro alcohols. The simplest procedure was to add acetyl chloride directly to the

(1) (a) This investigation was supported by the Department of the Army and the U. S. Army Medical Research and Development Command, contract no. DA-49-193-MD-2164; (b) part of this material was presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(2) Proposed Anti-Radiation Drug Program, Part 2 and 3, Department of Radiobiology, Walter Reed Army Institute of Research, Walter Reed Army Medical Center.

(3) T. P. Johnston and A. Gallagher *J. Org. Chem.*, **26**, 3780 (1961).

(4) W. E. Parham and F. L. Ramp, *J. Am. Chem. Soc.*, **73**, 1293 (1951).

(5) C. A. Sprang and E. F. Degering, *ibid.*, **64**, 1063 (1942).

nitro alcohol without solvent. The completion of the reaction was determined by the disappearance of the hydroxyl absorption and the appearance of a strong carbonyl peak at 1725–1735 cm.$^{-1}$. The crude nitro acetate was converted to the desired nitroölefin using the method of Hass, Susie, and Heider[6] which uses a suspension of anhydrous sodium carbonate as the base in refluxing dry benzene. The progress of the reaction was readily determined by the disappearance of the acetate carbonyl absorption and the appearance of a strong carbon–carbon double bond peak at 1630–1640 cm.$^{-1}$. The relatively low boiling nitroölefins could be easily separated in high yield and good purity by one distillation (Table I). The desired *sec*-benzylthio-nitroalkanes (III) were prepared by the addition of benzyl mercaptan in benzene, catalyzed by piperidine, to the nitroölefin. Using this procedure the *sec*-benzylthionitroalkanes were prepared in high yield and excellent purity (Table II). The infrared spectra of these compounds show typical peaks at 3030, 3065, and 3085 cm.$^{-1}$ due to aromatic C—H stretching and strong bands at 1550 and 1360 cm.$^{-1}$ attributable to the nitro group. The crude *sec*-benzylthionitroalkane (III) (R′ = H; R = C_3H_7, C_4H_9, and C_5H_{11}) could be purified by distillation under reduced pressure. However, III (R′ = H; R = C_6H_{13}, C_7H_{15}, and ) and III (R = C_3H_7; R′ = CH_3, and C_2H_5) obtained in 93–100% yield decomposed on attempted distillation. These compounds as crude undistilled products were sufficiently pure to be reduced to the corresponding *sec*-benzylthioalkylamines which could be easily purified by distillation or conversion to the hydrochlorides followed by recrystallization.

TABLE I

NITROÖLEFINS

$RCH{=}C(R')NO_2$

R	R′	% Yield from RCH₂O	B.p., °C. (mm.)	B.p., °C. (mm.) reported
n-C_3H_7	H	67.9	27–29 (0.1–0.15)	69–70 (12)[a]
n-C_4H_9	H	42.4	44–47 (0.25–0.3)	54–55 (1.5)[b]
n-C_5H_{11}	H	65.3	96–99 (0.08)	57 (1)[c]
n-C_6H_{13}	H	49.2	73–74 (0.2)	112 (9)[a]
n-C_7H_{15}[d]	H	60.9	91–95 (0.2–0.3)	
 [e]	H	61.1	99–100 (0.1)	
n-C_3H_7	CH_3	55.2	42–45 (0.05)	53 (1)[c]
n-C_3H_7	C_2H_5	38.9	61–65 (0.7–0.8)	84.4 (10)[f]

[a] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928). [b] Ref. 12. [c] D. Nightingale and J. R. Janes, *J. Am. Chem. Soc.*, **66**, 352 (1944). [d] *Anal.* Calcd. for $C_9H_{17}NO_2$: C, 63.12; H, 10.01. Found: C, 63.07; H, 10.05. $n^{25}D$ 1.4620; d^{25} 0.9424. [e] *Anal.* Calcd. for $C_8H_{11}NO_2$: C, 62.73; H, 7.24. Found: C, 62.92; H, 7.25. $n^{25}D$ 1.5195, d^{25} 1.0721. [f] Ref. 6.

During the course of our investigation we found that the requisite benzylthionitroalkanes could be prepared by a route which eliminates the necessity for isolating the nitroölefin. We found that 2-benzylthio-1-nitrohexane and 3-benzylthio-2-nitroheptane could be obtained in good yield by refluxing the corresponding nitroacetate with benzyl mercaptan in a suspension of anhydrous sodium carbonate in benzene. See Chart C.

(6) H. B. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

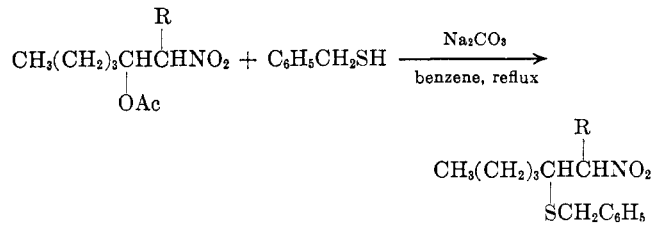


CHART C

The 2-benzylthio-1-nitrohexane was distilled to afford an 82.6% yield of pure product. No attempt was made to distill the 3-benzylthio-2-nitroheptane. It was reduced directly to 3-benzylthio-2-heptylamine which was obtained in a 69% over-all yield from the starting nitroacetate.

Finally we turned our attention to a reinvestigation of the Parham and Ramp procedure. We found, by the simple modification of carrying out the reaction in benzene,[7] that the crude benzylthio-1-nitroalkane thus formed was now sufficiently pure to be directly reduced with lithium aluminum hydride to the corresponding crude amine. The latter could be then purified by distillation. In this manner, 2-benzylthio-1-hexylamine could be prepared in a 44% over-all yield from valeraldehyde. The compound was identical to the product obtained by lithium aluminum hydride reduction of the benzylthionitrohexane obtained by direct addition of benzyl mercaptan to pure 1-nitrohexene.

Although the Parham and Ramp method provides the simplest sequence for obtaining the 2-benzylthio-1-alkylamines, it cannot be used for the preparation of pure 2-benzylthio-1-nitroalkanes. If the latter are required, it is necessary to prepare them *via* the nitroolefin as outlined in Chart B or *via* the nitroacetate as outlined in Chart C.

The requisite *sec*-benzylthioalkylamines were best prepared by lithium aluminum hydride reduction of the corresponding nitro derivatives, using sodium potassium tartrate to decompose the alumino complex. One distillation afforded analytically pure amines in 58–84% yield. See Table III.

The *sec*-benzylthioalkylamines were converted to their hydrochlorides which were debenzylated with sodium in liquid ammonia to afford the desired *sec*-mercaptoalkylamine. The procedure used for the debenzylation was modified somewhat from that reported by Baddiley and Thain[8] (see Experimental section). The *sec*-mercaptoalkylamine hydrochlorides, which were obtained in 22–88% yield, showed –SH absorption at 2495–2550 cm.$^{-1}$ in the infrared and analyzed 98–100% pure by a N-ethylmaleimide sulfhydryl analysis.[9]

The *sec*-mercaptoalkylamines recorded in Table IV have been tested as possible anti-radiation agents by the Department of Radiobiology, Walter Reed Institute of Research, Walter Reed Army Medical Center, Washington, D. C. The compounds of general structure II were tested as a mixture of racemates. None of the compounds showed any protection to mice against ionizing radiation.

(7) The use of a Stark–Bidwell tube to Collect the water formed provides a convenient method for following the course of the reaction.

(8) J. Baddiley and E. M. Thain, *J. Chem. Soc.*, 800 (1952).

(9) N. M. Alexander, *Anal. Chem.*, **30**, 1292 (1958).

TABLE II

2-BENZYLTHIO-1-NITROALKANES

$$RCHCH(R')NO_2$$
$$|$$
$$SCH_2C_6H_5$$

R	R′	% Yield	$n^{25}D$	d^{25}	B.p., °C. (mm.)	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-C_3H_7	H	80.1	1.5404	1.0964	137 (0.1)	$C_{12}H_{17}NO_2S$	60.22	60.40	7.16	7.15
n-C_4H_9	H	81.3	1.5329	1.084	131–132 (0.15)	$C_{13}H_{19}NO_2S$	61.62	61.81	7.56	7.55
n-C_5H_{11}	H	91.9	1.5304	1.0619	135 (0.1)	$C_{14}H_{21}NO_2S$	62.88	63.08	7.92	7.74

TABLE III

sec-BENZYLTHIOALKYLAMINES

$$RCHCH(R')NH_2$$
$$|$$
$$SCH_2C_6H_5$$

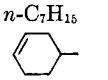
R	R′	% Yield	$n^{25}D$	d^{25}	B.p., °C. (mm.)	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-C_3H_7	H	84.6	1.5468	1.0106	113 (0.05)	$C_{12}H_{19}NS$	68.84	68.93	9.15	8.99
n-C_4H_9	H	78.3	1.5404	0.9987	100 (0.1)	$C_{13}H_{21}NS$	69.89	69.56	9.48	9.22
n-C_5H_{11}	H	65	1.5350	0.9826	132 (0.1)	$C_{14}H_{23}NS$	70.83	70.81	9.76	9.63
n-C_6H_{13}	H	65[a]	1.5303	0.9761	139 (0.06)	$C_{15}H_{25}NS$	71.65	71.60	10.02	9.93
n-C_7H_{15}	H	58.5[a]	1.5265	0.9637	132 (0.09)	$C_{16}H_{27}NS$	72.39	72.51	10.25	10.15
	H	62.5[a,b]			151–153[c]	$C_{15}H_{22}NSCl$[d]	63.46	63.39	7.81	7.86
n-C_3H_7	CH_3	74[a]	1.5381	0.9917	97–102 (0.05)	$C_{13}H_{21}NS$	69.90	69.86	9.47	9.46
n-C_3H_7	C_2H_5	64.3[a]	1.5338	0.9826	110–114 (0.05)	$C_{14}H_{23}NS$	70.83	70.71	9.76	9.44

[a] Yields calculated from the crude 2-benzylthio-1-nitroalkanes. [b] Obtained as the hydrochlorides. [c] Melting point of the hydrochloride. [d] Analysis of the hydrochloride.

TABLE IV

sec-MERCAPTOALKYLAMINE HYDROCHLORIDES

$$RCHCH(R')NH_3Cl$$
$$|$$
$$SH$$

R	R′	% Yield	M.p., °C.	% pure by SH analysis	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
n-C_3H_7	H	88.1	*a*	100	$C_5H_{14}NSCl$	38.57	38.92	9.06	9.02	9.00	8.70	20.60	20.72
n-C_4H_9[a,b]	H	40	*a*	99.8	$C_6H_{16}NSCl$	42.46	42.46	9.50	9.34	8.25	8.00	18.89	18.65
n-C_5H_{11}	H	59.2	*a*	99	$C_7H_{18}NSCl$	45.75	45.78	9.87	9.82	7.62	7.47	17.45	17.46
n-C_6H_{13}	H	75	*a*	99.4	$C_8H_{20}NSCl$	48.58	48.85	10.19	10.05	7.08	6.94	16.21	16.06
n-C_7H_{15}	H	49.9	*a*	100	$C_9H_{22}NSCl$	51.03	51.44	10.47	10.51	6.62	6.74	15.14	14.69
	H	22	*a*	100	$C_8H_{16}NSCl$	49.59	49.40	8.33	8.22	7.23	7.14	16.55	16.26
n-C_3H_7	CH_3	57.5	136–138	99.4	$C_6H_{16}NSCl$	42.46	42.31	9.50	9.29	8.25	8.05	18.89	18.73
n-C_3H_7	C_2H_5	66.6	124–127	100	$C_7H_{18}NSCl$	45.75	45.62	9.87	9.67	7.62	7.47	17.45	17.25
n-C_4H_9	CH_3	55	143–147	100	$C_7H_{18}NSCl$	45.75	45.51	9.87	9.71	7.62	7.88	17.45	17.18

[a] These compounds had indefinite melting points. [b] Debenzylation done on free amine.

Experimental[10]

Preparation of the Nitroölefins *via* the Nitro Alcohol and Nitro Acetate.—One mole each of the aldehyde and nitroalkane in ethanol were treated at 10° with 1 mole of sodium hydroxide according to the method of Sprang and Degering.[5] On acidification, an almost quantitative yield of the crude nitro alcohol was obtained. The infrared spectrum shows hydroxyl absorption at 3560–3600 cm.$^{-1}$ and typical nitro peaks at 1360 and 1550 cm.$^{-1}$. The nitro alcohol was converted to the nitro acetate by adding an excess of acetyl chloride directly to the crude nitro alcohol under anhydrous conditions. The excess acetyl chloride was removed at 50° under reduced pressure. The infrared spectrum showed absence of hydroxyl absorption and a strong acetate carbonyl peak at 1725–1735 cm.$^{-1}$. The nitroölefins were obtained from the crude nitro acetates using the method of Hass, Susie, and Heider[6] by refluxing 0.5 mole of anhydrous sodium carbonate with the crude nitro acetates dissolved in 400 ml. of benzene previously dried over calcium hydride. The nitroölefins obtained are recorded in Table I. The infrared spectra show absence of acetate peaks and contain a strong C=C peak at 1630–1640 cm.$^{-1}$.

Preparation of *sec*-Benzylthionitroalkanes.—To a mixture of 0.4 mole of benzyl mercaptan and 3 ml. of piperidine in 100 ml. of benzene was added dropwise 0.4 mole of the nitroölefin in 75 ml. of benzene. The reaction mixture usually was left at room temperature from 2–15 hr. but essentially the same yield was obtained if the reaction was worked up immediately after the addition. The solution was washed with dilute hydrochloric acid, water and dried over magnesium sulfate. Removal of the benzene afforded 90–100% of the crude product. The crude products could be purified readily by one distillation through a 4-in. Vigreux column under reduced pressure. The infrared spectrum shows typical peaks at 3030, 3065, and 3085 cm.$^{-1}$ due to aromatic C–H absorption and strong bands at 1365 and 1550 cm.$^{-1}$ attributable to the nitro group. See Table II for analysis and yields. The higher molecular weight products decomposed on attempted distillation. These products were reduced in crude form to the *sec*-benzylthioalkylamines which could be purified by distillation or conversion to the hydrochloride followed by recrystallization.

Preparation of the *sec*-Benzylthioalkylamines.—A solution of 0.3 mole of the 2-benzylthio-1-nitroalkanes in 200 ml. of anhydrous ether (dried over sodium) was added dropwise to an ice-cooled stirred solution–suspension of 34.1 g. (0.9 *M*) of lithium aluminum hydride in 1600 ml. of anhydrous ether. The reaction was very exothermic, and the addition usually required 1 hr. or longer. The reaction mixture was refluxed for 1 hr. after the addition was completed. The excess lithium aluminum hydride was decomposed with water and 2 l. of 20% sodium potassium tartrate

(10) Boiling points and melting points are uncorrected. Elemental analyses are by Micro-Tech Laboratories, Skokie, Ill.

solution was added. The reaction mixture was stirred until all the solids dissolved. The ether layer was decanted, and the aqueous layer was extracted three times with 150-ml. portions of ether. The ether layers were combined and dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure afforded an almost quantitative yield of the crude amines. One distillation through a 4-in. Vigreux column under reduced pressure afforded pure amines showing only one peak on a vapor phase chromatogram.[11] The yields and analysis are recorded in Table III. The infrared spectra shows N–H absorption at 3380 cm.$^{-1}$. The hydrochlorides of these amines were prepared by bubbling dry hydrogen chloride gas into an ethereal solution of the amine. Removal of the ether under vacuum afforded the crude amine hydrochloride in 98–100% yield. The crude products were used for the preparation of the *sec*-mercaptoalkylamine hydrochlorides.

Preparation of 3-Acetoxy-2-nitroheptane.—Nitroethane (150.2 g., 2 moles) was allowed to condense with *n*-valeraldehyde (172.3 g., 2 moles) at 10° using 2 moles of sodium hydroxide in aqueous alcohol as the base.[5] From the work-up 265.9 g. (82.4%) of crude product was obtained. The crude 3-hydroxy-2-nitroheptane was converted to the acetate using the procedure reported by Tindall.[12] 3-Hydroxy-2-nitroheptane (161.2 g., 1 mole) and concentrated sulfuric acid (0.98 g., 0.01 mole) were placed in a flask and acetic anhydride (102 g., 1 mole) was added; the temperature was kept at about 60°. The acetic acid was removed on a rotary evaporator, and the remaining liquid was distilled under reduced pressure to afford 157.9 g. (77%) of a liquid, b.p. 85–90° at 0.5 mm., n^{25}D 1.4353.

Anal. Calcd. for $C_9H_{17}NO_3$: C, 53.18; H, 8.43. Found: C, 53.11; H, 8.31.

Preparation of 3-Benzylthio-2-heptylamine.—A stirred mixture of 3-acetoxy-2-nitroheptane (101.6 g., 0.5 mole), benzyl mercaptan (62.1 g., 0.5 mole), sodium carbonate (26.5 g., 0.25 mole), and 400 ml. of benzene (dried over calcium hydride) was refluxed for 46 hr. The sodium acetate was filtered from the benzene and dissolved in water. The aqueous solution was extracted with benzene and after drying over magnesium sulfate was combined with the benzene filtrate. Removal of the benzene afforded 133 g. of crude 3-benzylthio-2-nitroheptane.

The reduction of the crude 3-benzylthio-2-nitroheptane was conducted in the manner described for the general reduction of *sec*-benzylthionitroalkanes using lithium aluminum hydride. A 69% yield of a colorless liquid, b.p. 108–115° at 0.07–0.08 mm., was obtained, n^{25}D 1.5321.

Anal. Calcd. for $C_{14}H_{23}NS$: C, 70.83; H, 9.76. Found: C, 70.61; H, 9.50.

Preparation of 2-Acetoxy-1-nitrohexane.—To a solution of 36.5 g. (0.249 mole) of crude 1-nitro-2-hexanol (prepared by the method of Sprang and Degering[5] in a 98.5% yield) in 100 ml. of chloroform was added 22 g. (0.28 mole) of acetyl chloride. The reaction mixture was left at room temperature for 2 hr. and then refluxed for 30 min. The reaction mixture was diluted with 100 ml. of chloroform, washed with water, and dried over magnesium sulfate. Removal of the chloroform afforded 43.1 g. of crude nitroacetate. Distillation under reduced pressure afforded 34.36 g. (74.3%) of liquid, b.p. 84–85 at 0.1 mm. Reported[13] b.p. 105 at 3 mm., n^{25}D 1.4385; reported[13] n^{25}D 1.4337.

Preparation of 2-Benzylthio-1-nitrohexane *via* 2-Acetoxy-1-nitrohexane.—A mixture of 2-acetoxy-1-nitrohexane (18.9 g., 0.1 mole), benzyl mercaptan (12.4 g., 0.1 mole), sodium carbonate (5.3 g., 0.05 mole), and benzene (25 ml.) was refluxed for 3 hr. The reaction mixture was worked up as described for the preparation of 3-benzylthio-2-nitroheptane to afford 26.2 g. of crude product. Distillation under reduced pressure yielded 20.9 g. (82.6%) of product, b.p. 140° at 0.1 mm., n^{25}D 1.5335 as compared to n^{25}D 1.5329 when prepared by the addition of benzyl mercaptan to 1-nitrohexene (Table II). The infrared spectra of the two compounds were superimposable, and both had the same retention time on a vapor phase chromatogram.[11]

Preparation of 2-Benzylthio-1-hexylamine *via* 2-Benzylthio-1-nitrohexane Obtained from the Parham and Ramp Procedure.[4]—A mixture of 17.2 g. (0.2 mole) of *n*-valeraldehyde, 12.2 g. (0.2 mole) of nitromethane, 24.8 g. (0.2 mole) of benzyl mercaptan, 4 ml. of piperidine, and 75 ml. of benzene was refluxed for 20 hr. using a water separator. The product was taken up in benzene, washed with dilute acid, washed with water, and dried over magnesium sulfate. Removal of the benzene afforded 53 g. of crude product. An attempt was made to distil a small sample of the liquid at reduced pressure; however, the liquid decomposed on heating and no product could be forced over by heating the bath to 221°.

The remainder of the product was reduced to 2-benzylthio-1-hexylamine using the general procedure described for the reduction of *sec*-benzylthionitroalkanes with lithium aluminum hydride. A 42% yield of liquid, b.p. 114–116° at 0.07–0.10 mm., was obtained, n^{25}D 1.5404. When 2-benzylthio-1-hexylamine was obtained *via* 1-nitrohexene (Table III) the n^{25}D was 1.5404. The infrared spectra of these two compounds were identical, and both had the same retention time on a vapor phase chromatogram.[11]

Preparation of *sec*-Mercaptoalkylamine Hydrochlorides.—The above compounds were prepared according to the method of Baddiley and Thain[8] using the following modified procedure. The *sec*-benzylthioalkylamine hydrochloride[14] (0.1 mole) was placed in a 1-l. three-necked flask equipped with a stirrer, gas inlet tube, and Dry Ice condenser and the complete system was protected against moisture with a soda lime drying tube. Ammonia (300 ml.) was introduced into the flask and in the case of high molecular weight *sec*-benzylthioalkylamine hydrochlorides, 100 ml. of dry ether was added. Sodium metal in small pieces was added to the solution until a permanent blue color remained for 45 min. The sodium (0.20–0.22 g.-atom) was added while nitrogen was blown over the solution. The excess sodium was decomposed by adding a little ammonium chloride and the ammonia allowed to evaporate under nitrogen to a small volume. Anhydrous ether (200 ml.) was added, and the remainder of the ammonia was boiled out of the solution by heating the solution on a hot water bath. The stirred ether suspension was cooled, and 100 ml. of ether saturated with dry hydrogen chloride gas was added to the mixture and the contents were stirred rapidly for 2 hr. The solids were filtered, washed well with dry ether, transferred to a 1-l. flask, extracted three times with 200-ml. portions of isopropyl alcohol, and the total filtrate was concentrated under nitrogen. Ether was added and the solution allowed to crystallize in the ice box. The crude solids obtained were purified by recrystallization from an isopropyl alcohol and ether mixture or by vacuum sublimation. The products obtained showed —SH absorption at 2495–2550 cm.$^{-1}$ in the infrared and analyzed 99–100% pure by a N-ethylmaleimide sulfhydryl assay.[9] See Table IV for yields and elemental analysis.

Acknowledgment.—We are indebted to Dr. Richard G. Hiskey, University of North Carolina, and Dr. Samuel G. Levine for helpful discussions.

(11) Vapor phase chromatograms were obtained on an F and M Model 300 vapor fractometer using a 24-in., 0.25-in. aluminum column packed with 60/80-mesh acid-washed Chromosorb P containing 5% Carbowax 20 M.

(12) J. B. Tindall, *Ind. Eng. Chem.*, **33**, 65 (1941).

(13) N. L. Drake and A. B. Ross, *J. Org. Chem.*, **23**, 717 (1958).

(14) In the case of 2-benzylthio-1-hexylamine the free amine was used in place of its hydrochloride. However, this led to a low yield, and the blue end point due to excess sodium was extremely difficult to detect.