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

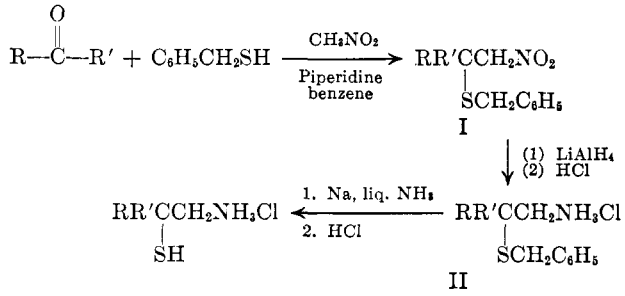
F. I. CARROLL, J. D. WHITE, AND MONROE E. WALL

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

Received November 30, 1962

A general method for the preparation of *tert*-mercaptoalkylamine hydrochlorides is presented. The method involves the preparation of a *tert*-benzylthionitroalkane by allowing a mixture of ketone, nitromethane, and benzyl mercaptan in benzene to react in the presence of piperidine followed by reduction of the nitro group with lithium aluminum hydride and reductive debenzylation with sodium in liquid ammonia. Other possible methods for the preparation of *tert*-benzylthionitroalkanes are discussed.

The previous article in this series[2] described the synthesis of a number of new *sec*-mercaptoalkylamine hydrochlorides. In this paper we will discuss the preparation of analogous *tert*-mercaptoalkylamine hydrochlorides both in the aliphatic and alicyclic series and some of the particular problems which occur in the synthesis of cyclic *exo*-nitroölefins and the corresponding cyclic *tert*-benzylthionitroalkanes. The general scheme used for the preparation of these *tert*-mercaptoalkylamine hydrochlorides is shown in Chart A.



III. R = R′ = CH_3—
IV. R = CH_3—, R′ = C_2H_5
V. R,R′ = $(CH_2)_n$; n = 3, 4, 5, and 6

CHART A

The crude *tert*-benzylthionitroalkanes (I) were reduced to the *tert*-benzylthioalkylamines (II) in good over-all yield. The debenzylation of II using the same procedure previously described[2] proceeded in high yield and afforded nice crystalline compounds of excellent purity.

The intermediates II [R, R′ = $(CH_2)_4$] and [RR′ = $(CH_2)_5$] were also prepared by the scheme outlined in Chart B.

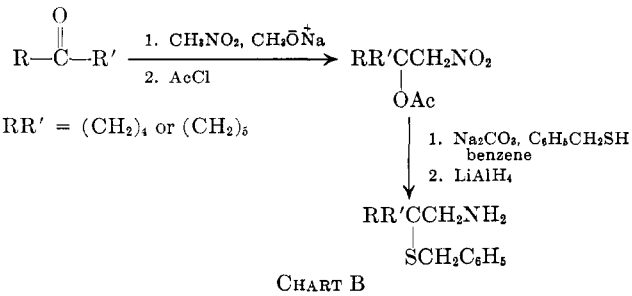


CHART B

The products obtained by this procedure were identical to those obtained by the scheme outlined in Chart A.

In order to substantiate the structures of the *tert*-benzylthioalkylamines, methyl ethyl ketone and cyclohexanone were converted to II *via* the scheme shown in Chart C.

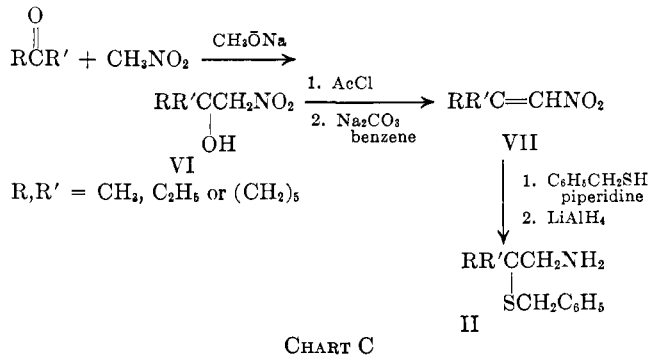


CHART C

The *tert*-benzylthioalkylamines obtained by isolation of the nitroölefin followed by addition of benzyl mercaptan and reduction with lithium aluminum hydride were identical to the products obtained *via* the modified Parham and Ramp procedure, Chart A, or by the nitroacetate procedure, Chart B. 1-Aminomethylbenzylthiocyclohexane obtained *via* the modified Parham and Ramp procedure decomposed on attempted vacuum distillation and was isolated as the hydrochloride.

Several aspects of the reaction schemes given under Charts A, B, and C require further comment. In our previous paper[2] we have shown that the reaction of aldehydes with nitromethane to give nitro alcohols proceeds in good yield. In contrast, the reaction equilibrium in the case of the same reaction with simple aliphatic and alicyclic ketones lies on the side of the reactants. Thus, acetone gives about a 50% yield of the nitro alcohol, methyl ethyl ketone about 15% and diethyl ketone a negligible yield. Similarly, cyclohexanone gives a 47% yield of the nitro alcohol, whereas cyclopentanone and cycloheptanone gave very low yields. Hence, the procedure given under Chart C is of poor preparative significance. In addition, in the alicyclic series the *exo*-olefins VIII (n = 2 and 4) cannot be isolated. All elimination procedures tested have given the corresponding *endo*-olefins IX (n = 2 and 4.)[3,4]

(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) F. I. Carroll, J. D. White, and Monroe E. Wall, Part I, *J. Org. Chem.*, **28**, 1236 (1963).

(3) H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934).

(4) Z. Eckstein, A. Sacha, and T. Urbański, *Bull. Acad. Polon. Sci., Class III*, **5**, 213 (1957); *Chem. Abstr.*, **51**, 16318 (1957).

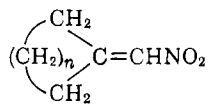
TABLE I

tert-BENZYLTHIOALKYLAMINES

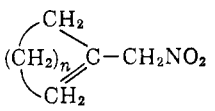
$$RR'CCH_2NH_2$$
$$|$$
$$SCH_2C_6H_5$$

RR'	% Yield[a]	$n^{25}D$	d^{25}	B.p. (mm.) or m.p., °C.	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3, CH_3	50[b]			118–119[c]	$C_{11}H_{18}NSCl$[d]	57.00	56.69	7.83	7.82
CH_3, C_2H_5	76.5	1.5512	1.0148	110 (0.08)	$C_{12}H_{19}NS$	68.84	69.17	9.15	9.17
C_2H_5, C_2H_5	46	1.5548	1.0158	109 (0.05)	$C_{13}H_{21}NS$	69.89	69.79	9.48	9.40
$(CH_2)_3$	60.3	1.5699	1.0684	116–119 (0.07–0.05)	$C_{12}H_{17}NS$	69.51	69.49	8.27	8.14
$(CH_2)_4$	52.7	1.5692	1.0698	126–130 (0.05–0.1)	$C_{13}H_{19}NS$	70.53	70.53	8.65	8.38
$(CH_2)_5$	52.2[b]			182–183	$C_{14}H_{22}NSCl$[d]	61.85	61.77	8.16	8.00
$(CH_2)_6$	42.2[b]			171–173	$C_{15}H_{24}NSCl$[d]	63.02	62.90	8.46	8.47

[a] Over-all yield from the ketone. [b] Isolated as the hydrochloride. [c] H. M. Crooks, Jr., "Penicillamine, Its Analogs and Homologs in the Chemistry of Penicillin," H. T. Clark, J. R. Johnson, and Sir R. Robinson, Princeton University Press, 1949, p. 649, reported m.p. 116–117°. [d] Analysis on amine hydrochloride.



VIII. n = 2, 3 and 4



IX. n = 2, 3 and 4

It has been reported[5] that acetic acid could be eliminated from 1-nitromethylcyclohexanol acetate with sodium carbonate to give the *exo*-olefin VIII (n = 3). When this experiment was performed in our laboratory, the *exo*-olefin VIII (n = 3) was formed. However, the main product obtained was the *endo*-olefin IX (n = 3). The condensation of nitromethane with cyclobutanone has not been reported.

The modified Parham–Ramp procedure adopted for the preparation of *tert*-benzylthioalkylamines[2] gives excellent yields, ranging from 42–76.5% (Table I). Several mechanisms can be formulated to account for the formation of the *tert*-benzylthioalkylnitroalkanes obtained *via* the Parham and Ramp[6] procedure. Our data, however, are most consistent with the mechanism originally proposed by the above authors who suggested that the reaction proceeds *via* the addition of benzyl mercaptan to a nitroölefin formed as an intermediate in the reaction.[7] Although as we have indicated, the equilibrium for the formation of nitro alcohols is unfavorable, the reaction can be driven forward because of the elimination of water giving the nitroölefin which is irreversibly trapped by immediate reaction with benzyl mercaptan. This is clearly shown in the case of methyl ethyl ketone which on base-catalyzed reaction with nitromethane affords a 15% yield of nitro alcohol but a 76% yield of benzylthioalkylamine when treated by the modified Parham–Ramp procedure. Similarly, diethyl ketone gives only a negligible yield of nitro alcohol but affords a 46% yield of benzylthioalkylamine *via* the modified Parham–Ramp procedure.

In the case of the alicyclic series as exemplified by cyclohexanone the results have particular mechanistic significance. As shown in Chart D, 1-nitromethylbenzylthiocyclohexane (XII) can be prepared in three ways. Since XII decomposes on distillation, it is converted to XIII which can be purified easily. The most direct route to XII is *via* the Parham and Ramp reaction. The data indicates that this reaction involves formation of an intermediate nitroölefin, which in this case is the less stable *exo*-olefin VIII (n = 3). Olefin VIII (n = 3) is readily converted to the *endo*-olefin IX (n = 3). However, IX (n = 3) does not react with benzyl mercaptan, whereas VIII (n = 3) in the presence of piperidine reacts rapidly under mild conditions to give XII. Treatment of the nitro acetate XI under the same conditions which yields the olefin mixture VIII (n = 3) and IX (n = 3) but in the presence of added benzyl mercaptan affords, after lithium aluminum hydride reduction, a high yield of XIII. This experiment indicates that the reactive *exo*-olefin VIII (n = 3) is indeed formed and is trapped by added benzyl mercaptan before it can isomerize to the *endo* form IX (n = 3). The data presented in conjunction with the previous results obtained by Parham and Ramp[7] indicate that the reaction of cyclohexanone with nitromethane and benzyl mercaptan in the presence of a base such as piperidine is probably a special case of the

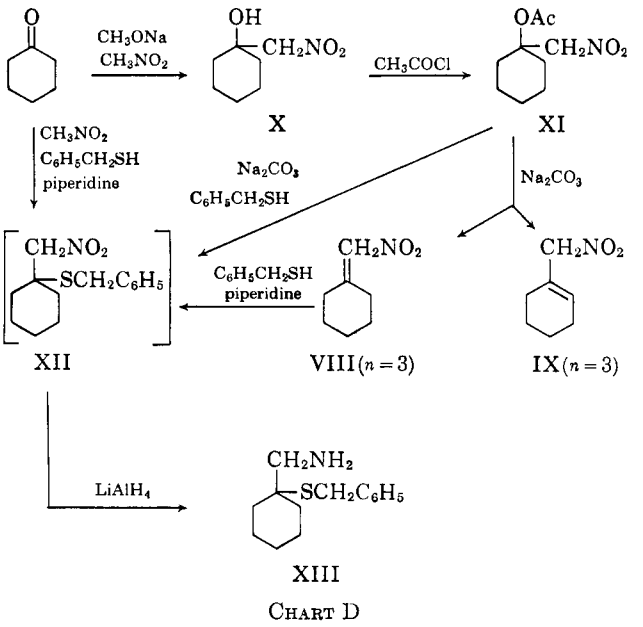


CHART D

(5) Z. Eckstein, T. Urbański, and H. Wojnowska, *Roczniki Chem.*, **31**, 1177 (1957); *Chem. Abstr.*, **52**, 9971 (1958).

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

(7) When Parham and Ramp[6] allowed 2-nitropropane to react with formaldehyde and butyl mercaptan in the presence of piperidine, the only product isolated was 2-nitro-2-methylpropanol. The latter compound lacks an alpha hydrogen adjacent to the nitro group and hence cannot form a nitroölefin. Parham and Ramp suggested that the failure to isolate a β-nitro sulfide in this case indicated that their general reaction proceeds *via* a nitroölefin intermediate.

$$(CH_3)_2CHNO_2 + CH_2O + C_4H_9SH \xrightarrow{\text{piperidine}} (CH_3)_2\overset{NO_2}{\overset{|}{C}}CH_2OH$$

TABLE II

tert-MERCAPTOALKYLAMINE HYDROCHLORIDES

$RR'CCH_2NH_3Cl$

|

SH

RR'	% Yield	M.p.,[a] °C.	% Pure by SH analysis	Molecular formula	—Carbon, %— Calcd.	Found	—Hydrogen, %— Calcd.	Found	—Nitrogen, %— Calcd.	Found	—Sulfur, %— Calcd.	Found
CH_3, CH_3	97	220–222[b]	100	$C_4H_{12}NSCl$	33.91	33.92	8.54	8.49	9.89	9.76	22.64	22.38
CH_3, C_2H_5	60.2	208–209	99.2	$C_5H_{14}NSCl$	38.57	38.65	9.06	8.96	9.00	8.90	20.60	20.68
$(CH_2)_3$	92	227.5–228.5	100	$C_5H_{12}NSCl$	39.07	39.05	7.87	7.74	9.12	8.95	20.87	20.95
$(CH_2)_4$	96.4	224.5–225.5	100	$C_6H_{14}NSCl$	42.97	43.19	8.41	8.22	8.35	8.10	19.12	19.15
$(CH_2)_5$	55	194–196	100	$C_7H_{16}NSCl$	46.26	46.23	8.88	8.77	7.71	7.59	17.65	17.68
$(CH_2)_6$	62	192–195	100	$C_8H_{18}NSCl$	49.08	49.03	9.27	9.39	7.17	7.03	16.38	16.35

[a] These m.p. values were done in a sealed capillary tube. The compounds sublimed without melting in an open capillary. [b] Reported m.p. 202–203°. See footnote *c* from Table I.

simpler reaction of 1-nitromethylcyclohexanol acetate (XI) described previously.

The purity of the *tert*-mercaptoalkylamine hydrochlorides was determined by a sulfhydryl analysis using the N-ethylmaleimide method reported by Alexander.[8] The success of this method depends on the reaction shown in Chart E. It was of some interest that the *tert*-mercaptoalkylamine hydrochlorides required thirty minutes to an hour to reach equilibrium, whereas equilibrium was obtained instantaneously in the case of all the *sec*-mercaptoalkylamine hydrochlorides.[2]

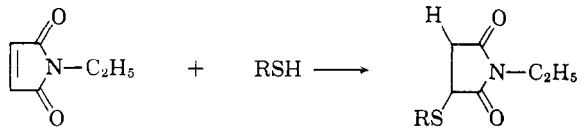


CHART E

Tests for the ability of the *tert*-mercaptoalkylamine hydrochlorides to protect mice against ionizing radiation have been carried out by the Department of Radiobiology, Walter Reed Army Institute of Research, Walter Reed Army Medical Center, Washington 12, D. C. None of the compounds showed protection.

Experimental[9]

Preparation of *tert*-Benzylthioalkylamines *via* the *tert*-Benzylthionitroalkanes Obtained from the Modified Parham and Ramp Procedure.—A mixture of ketone (0.2 mole), nitromethane (0.2 mole), benzylmercaptan (0.2 mole), piperidine (4 ml.), and 75 ml. of benzene (dried over calcium hydride) was refluxed under a water separator until water ceased coming off (12–15 hr.).[10] The reaction mixture was taken up in benzene, washed with dilute acid, washed with water, and then dried over magnesium sulfate. Removal of the benzene afforded an 87 to 100% yield of the product. The infrared spectra of these compounds showed no carbonyl peak and contained strong aromatic and nitro peaks.

The crude *tert*-benzylthionitroalkanes were reduced with lithium aluminum hydride using the method reported by Carroll, White, and Wall.[2] The amines (II) [R = R' = CH_3; R = CH_3, R' = C_2H_5; and R, R' = $(CH_2)_3$ and $(CH_2)_4$] were purified by distillation. The amines (II) [R, R' = $(CH_2)_5$ and $(CH_2)_6$] decomposed on attempted distillation. These amines were converted to their hydrochlorides by adding a cold saturated ethereal solution of hydrogen chloride to a cold ethereal solution of the amine and purified by recrystallization from isopropyl alcohol. The amine or amine hydrochlorides were obtained in 42.2 to 76.5% over-all yield from ketone.

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

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

(10) In the case of diethyl ketone seven days reflux was required.

Preparation of 1-Nitromethylcyclohexanol Acetate.—Sodium methoxide (12.5 g.) was added to a mixture of cyclohexanone (590 g., 6 moles) and nitromethane (122 g., 2 moles). After stirring in the deep freeze for 48 hr. the reaction mixture was neutralized with dilute hydrochloric acid, extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the ether and excess cyclohexanone followed by distillation under reduced pressure afforded 150 g. (47.2%) of liquid, b.p. 81–85° at 0.1–0.15 mm.; reported[11] 93–95° at 2 mm., $n^{25}D$ 1.4900; reported[11] $n^{20}D$ 1.4875.

The 1-nitromethylcyclohexanol was converted to the acetate with acetyl chloride in chloroform. Distillation under reduced pressure afforded a 98% yield of 1-nitromethylcyclohexanol acetate, b.p. 98–101° at 0.2–0.25 mm.; reported[12] b.p. 116° at 1 mm., $n^{25}D$ 1.4687; reported[12] $n^{20}D$ 1.4669.

Preparation of 1-Aminomethylbenzylthiocyclohexane *via* 1-Nitromethylcyclohexanol Acetate.—A mixture of nitromethylcyclohexanol acetate (20.1 g., 0.1 mole), benzyl mercaptan (12.4 g., 0.1 mole), sodium carbonate (5.3 g., 0.05 mole), and 25 ml. of benzene was refluxed for 27 hr. The sodium acetate was filtered from the benzene and dissolved in water. The aqueous solution was extracted with benzene and after drying was combined with the benzene filtrate. Removal of the benzene afforded 23.7 g., 89.5% (crude yield) of product. The infrared spectrum of this liquid showed almost no acetate absorption at 1735 cm.$^{-1}$, and contained strong nitro peaks at 1545 and 1370 cm.$^{-1}$.

The crude 1-nitromethylbenzylthiocyclohexane was reduced to 1-aminomethylbenzylthiocyclohexane with lithium aluminum hydride.[2] Distillation under reduced pressure afforded 15.77 g. (74.8%) of pure product, b.p. 133–137° at 0.05 mm., $n^{25}D$ 1.5700, d^{25} 1.0683.

Anal. Calcd. for $C_{14}H_{21}NS$: C, 71.43; H, 8.99. Found: C, 71.36; H, 8.95.

A small sample of the amine was converted to the hydrochloride by adding a cold saturated ethereal solution of hydrogen chloride to a cold solution of the amine in ether. Recrystallization of the solid obtained from isopropyl alcohol afforded white crystals. M. p. 182–183°. A m.m.p. with the 1-aminomethylbenzylthiocyclohexane hydrochloride obtained *via* the modified Parham and Ramp procedure (Table I) was not depressed. The infrared spectra of the two compounds were identical.

Preparation of 1-Nitromethylcyclopentanol Acetate.—1-Nitromethylcyclopentanol was prepared using the same conditions as described for the preparation of 1-nitromethylcyclohexanol. From 168 g. (2 moles) of cyclopentanol and 122 g. (2 moles) of nitromethane 31.8 g. (10.8%) of product was obtained, b.p. 112–113° at 11 mm.; reported[13] 120–121° at 14 mm.

1-Nitromethylcyclopentanol was converted to 1-nitromethylcyclopentanol acetate with acetyl chloride in chloroform. Distillation under reduced pressure afforded a yield (50.8%) of liquid, b.p. 85° at 0.15 mm.; reported[14] b.p. 121–123° at 13 mm., $n^{25}D$ 1.4622.

Preparation of 1-Aminomethylbenzylthiocyclopentane *via* 1-Nitromethylcyclopentanol Acetate.—1-Nitromethylbenzylthio-

(11) T. F. Wood and R. J. Cadorin, *J. Am. Chem. Soc.*, **73**, 5504 (1951).

(12) W. Sobótka, Z. Eckstein, and T. Urbański, *Bull. Acad. Polon. Sci., Class III*, **5**, 653 (1957); *Chem. Abstr.*, **52**, 876 (1958).

(13) L. M. Kozlov, E. F. Fink, and G. B. Liorber, *Trudy Kazansk. Khim. Tekhnol. Inst.*, **23**, 148 (1957); *Chem. Abstr.*, **52**, 8933 (1958).

(14) L. M. Kozlov and B. G. Liorber, *Trudy Kazansk. Khim. Tekhnol. Inst.*, **26**, 48 (1959); *Chem. Abstr.*, **54**, 2448 (1960).

cyclopentane was prepared in the same manner as described for 1-nitromethylbenzylthiocyclohexane using 18.7 g. (0.1 mole) of 1-nitromethylcyclopentanol acetate, 12.4 g. (0.1 mole) of benzyl mercaptan, 5.3 g. (0.05 mole) of sodium carbonate, and 25 ml. of benzene. Removal of the benzene afforded 22.6 g. (89.6% crude yield) of sulfide. The infrared spectrum showed absence of acetate peaks and the expected aromatic and nitro peaks were present.

The crude 1-nitromethylbenzylthiocyclopentane was reduced with lithium aluminum[2] hydride to the desired 1-aminomethylbenzylthiocyclopentane. Distillation of the crude liquid obtained afforded (63.2%) of pure amine, b.p. 129° at 0.1 mm., $n^{25}D$ 1.5692, d^{25} 1.0698. $n^{25}D$ 1.5692 when obtained *via* the modified Parham and Ramp procedure (Table I).

Preparation of Nitromethylene Cyclohexane.—1-Nitromethylcyclohexanol, 142 g. (0.896 mole), was acetylated with excess acetyl chloride. After the addition the excess acetyl chloride was removed under reduced pressure. The crude nitro acetate which showed no hydroxyl absorption was refluxed with a suspension of anhydrous sodium carbonate, 47.5 g. (0.448 mole) in 400 ml. of benzene (dried over calcium hydride). The sodium acetate was filtered from the benzene. After drying over magnesium sulfate these extracts were added to the benzene filtrate and the benzene was removed under reduced pressure. The remaining liquid was distilled under reduced pressure through a 4-in. Vigreux column. The early fraction, 59 g., b.p. 53–58° at 0.07 mm., was 1-nitromethylcyclohexene; reported[15] b.p. 98–102° at 12 mm. The later fraction, 25.6 g., b.p. 65–73° at 0.1 mm., was a mixture of 1-nitromethylcyclohexene and nitromethylenecyclohexene. Redistillation of the latter fraction through a 22-in. spinning band column afforded 15 g. of liquid that was mainly nitromethylenecyclohexene, b.p. 105–106° at 12 mm.; reported[15] b.p. 108–110° at 12 mm., $n^{25}D$ 1.5065; reported[15] $n^{25}D$ 1.5079.

Preparation of 1-Aminomethylbenzylthiocyclohexane *via* Nitromethylenecyclohexane.—To a solution of 10.1 g. (0.0815 mole) of benzyl mercaptan and 0.5 ml. of piperidine in 5 ml. of benzene was added 11.5 g. (0.0815 mole) of nitromethylenecyclohexane in 5 ml. of benzene. After standing at room temperature for 3 hr. the reaction mixture was diluted with benzene, washed with dilute hydrochloric acid, washed with water, and dried over magnesium sulfate. Removal of the benzene afforded 16.4 g. (76%) of crude product.

The 1-nitromethylbenzylthiocyclohexane, 16.4 g. (0.062 mole) was reduced with lithium aluminum hydride (7.05 g., 0.186 mole).[2] Distillation of the crude product afforded 3.28 g. (22.6%) of a colorless product, b.p. 133° at 0.08 mm., $n^{25}D$ 1.5685. When 1-aminomethylbenzylthiocyclohexane was obtained *via* 1-nitromethylcyclohexanol acetate the b.p. was 129° at 0.1 mm., $n^{25}D$ 1.5692. The infrared spectra of the two compounds were identical.

A small portion of the 1-aminomethylbenzylthiocyclohexane was dissolved in cold ether and treated with a saturated ethereal solution of hydrogen chloride. The solid obtained was recrystallized from isopropyl alcohol to afford crystals, m.p. 182–183°. A mixture melting point with 1-aminomethyl-1-benzylthiocyclohexane hydrochloride obtained *via* the modified Parham and Ramp procedure (Table I) was not depressed. The infrared spectra of the two compounds were identical.

Preparation of 1-Nitro-2-methyl-2-butanol.—A mixture of 2-butanone (2000 ml.), nitromethane (400 ml.) and sodium methoxide (60 g.) was allowed to stir at −20° for 4 days. The reaction mixture was neutralized to a Congo Red end point with 7% hydrochloric acid. The organic phase was decanted and the aqueous solution was extracted with ether. The ether extracts were mixed with the decanted organic layer and were washed with water. The ether solution was dried over magnesium sulfate and concentrated under vacuum. The remaining liquid was distilled under reduced pressure through a 4-in. Vigreux column. A 155.8-g. (15.8%) sample was collected; b.p. 112–115° at 23 mm.; reported[16] b.p. 96–97° at 18 mm. The infrared spectrum shows a strong hydroxyl peak at 3570 cm.$^{-1}$ and two strong nitro peaks at 1540 and 1385 cm.$^{-1}$.

Preparation of 1-Nitro-2-methylbutene.—In a 3-l. three-necked flask equipped with stirrer and dropping funnel and protected from moisture by a Drierite drying tube was placed (133.2 g., 1 mole) of 1-nitro-2-methyl-2-butanol. Acetyl chloride (85 g., 1.08 moles) was added dropwise at room temperature to the vigorously stirred nitro alcohol. The excess acetyl chloride was removed under reduced pressure. The infrared spectrum showed no -OH absorption and had a strong acetate peak at 1730 cm.$^{-1}$. Benzene (400 ml.) and anhydrous sodium carbonate (53 g., 0.5 moles) were added to the crude nitro acetate and the contents were refluxed for 24 hr. Work-up of the product as described by Hass, Susie, and Heider[17] afforded 105.6 g. of crude product. Distillation under reduced pressure through a 4-in. Vigreux column afforded 83.4 g. (72.5%) of 1-nitro-2-methylbutene, b.p. 41–43° at 0.08 mm.; reported[16] b.p. 62° at 11 mm. The infrared spectrum showed a strong C=C peak at 1635 cm.$^{-1}$ and the typical nitro peaks at 1510 and 1350 cm.$^{-1}$.

Preparation of 2-Benzylthio-2-methyl-1-butylamine *via* 1-Nitro-2-methylbutene.—This reaction was conducted in the same manner as described for the preparation of 1-aminomethylbenzylthiocyclohexane. The crude 2-benzylthio-2-methyl-1-butylamine was distilled under reduced pressure to afford a 76.5% yield of pure product from starting nitroölefin; b.p. 110° at 0.05 mm., $n^{25}D$ 1.5530. $n^{25}D$ was 1.5512 when prepared *via* the modified Parham and Ramp procedure. The infrared spectra of the two compounds were identical.

Perparation of *tert*-Mercaptoalkylamine Hydrochlorides.—The *tert*-mercaptoalkylamine hydrochlorides were prepared by the method of Carroll, White, and Wall.[2] The physical constants and elemental analysis are given in Table II.

The purity of the compounds were determined by a spectrophotometric assay for sulfhydryl groups using N-ethylmaleimide.[8] It was necessary to allow the *tert*-mercaptoalkylamine hydrochlorides to stand at room temperature from 30 min. to 1 hr. with the standard N-ethylmaleimide solution before equilibrium was obtained.

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

(15) G. D. Buckley and C. W. Scaife, British Patent, 595,282 (December 31, 1947); *Chem. Abstr.*, **42**, 3773 (1948).

(16) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

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