

Tautomer Chemistry of Thiazolidines.

1-Thia-4-azaspiro[4,5]decane (1)

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The thiazolidine, 1-thia-4-azaspiro[4,5]decane (Ia), which is derived from cyclohexanone and 2-aminoethanethiol (X), forms a thiazolidone (VIII) with mercaptoacetic acid more slowly and in lower yield than with 2-phenylthiazolidine, a case reported previously. A thiazolidine which is related to a non-conjugate chain tautomer such as Ic, might be expected to behave in this way. Alkylation, as another possible example of tautomer chemistry, was studied, and *N*-, *S*-, and *C*-alkylation were all observed under varying circumstances. Thus, thiazolidine Ia undergoes alkylation with methyl iodide in ethanol to form the *N*-methylthiazolidine (IIa), and in sodium-liquid ammonia to give the *S*-methyl derivative (III). In the latter case, alkylation occurs with reductive cleavage. Although no trace of other tautomer derivatives (IV, V) was to be found in the methyl iodide alkylation, I with acrylonitrile did in fact give *C*-alkylation. An analytically pure mixture of tautomers was obtained, from which 2-oxocyclohexanepropionitrile (VI) was isolated on hydrolysis. In a manner similar to the formation of III, IIa was *S*-alkylated by treatment with sodium-liquid ammonia followed by benzyl chloride to give a saturated product (XVII). Although such a process might be identified with a chain tautomer (IIb), the evidence is to the contrary, since the intermediate (XIV), which might be involved in such a process, fails to undergo a similar reduction with sodium-liquid ammonia. A greatly improved procedure for the preparation of thiazolidine (XI, 86% yield) is also reported.

The possibility is apparent that the aryl group in previously studied 2-phenylthiazolidine might have some effect in influencing the formation of tautomer derivatives [whether the reaction course proceeds by way of a chain tautomer or an alternative mechanism (3)]. Therefore, it was of interest to determine if a thiazolidine with alkyl or spiro-alkyl substitution would behave similarly. An interesting thiazolidine of the latter type is the cyclohexanone-derived 1-thia-4-azaspiro[4,5]decane (Ia) (4). In agreement with our suspicion, we indeed found that Ia on being heated with mercaptoacetic acid reacted sluggishly to give only a 24% yield of the thiazolidone (VIII), whereas thiazolidone formation had occurred with 2-phenylthiazolidine in 75% yield (3).

Another chemical tautomeric reaction of interest was alkylation of Ia. Accordingly, if Ia were heated with methyl iodide and sodium carbonate in ethanol (sealed tube), *N*-alkylation occurred to give the corresponding *N*-methylthiazolidine (IIa) (5); no other products (*i.e.* IV, V) were observed.

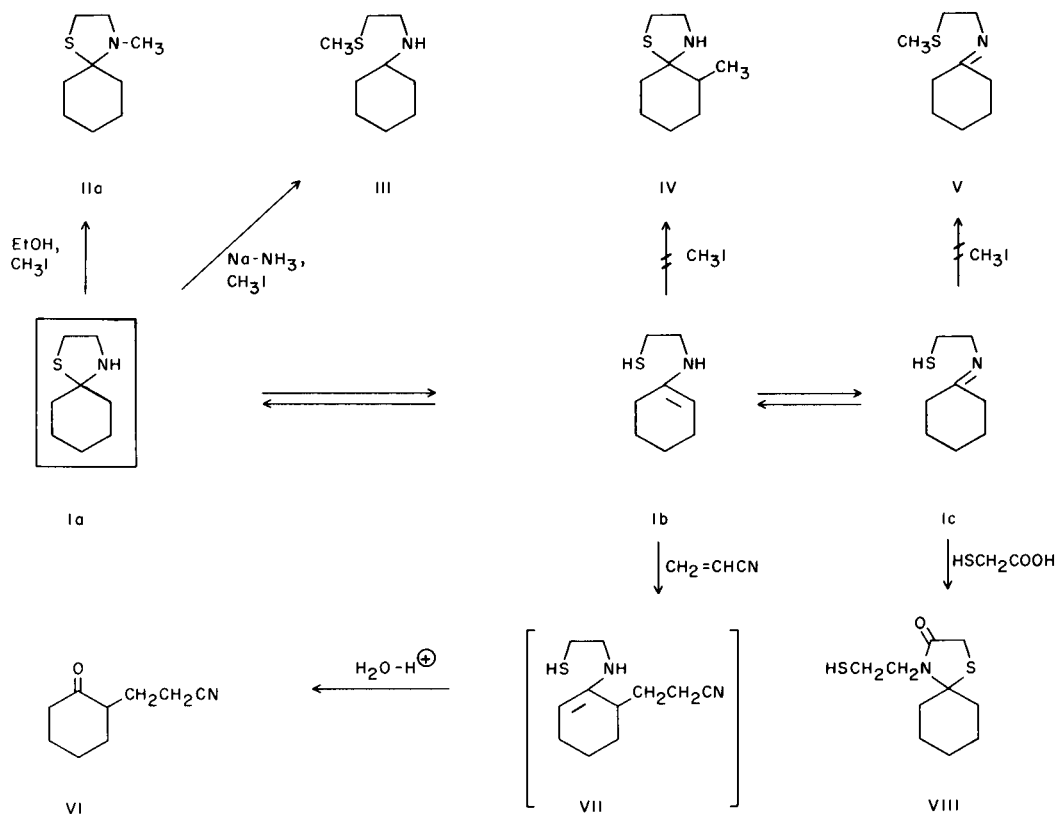
In contrast to aryl-substituted thiazolidines, dialkyl- or spiro-substituted derivatives very interestingly possess an additional tautomeric form involving an enamine function (Ib). An alkylation experiment of Ia with acrylonitrile (6) suggests the validity of this relationship. Although a

mixture of cyanoethyl tautomer derivatives was observed, it was obtained in a state of analytical purity. Hydrolytic treatment of this mixture gave a low yield (15%) of the *C*-alkyl derivative, 2-oxocyclohexanepropionitrile (VI). This result might also be explained by direct *C*-alkylation of the thiazolidine (Ia) rather than its chain tautomer, a consideration which remains currently unanswered.

Although *N*- and *C*-alkylation under different conditions had both now been noted in the preceding experiments, *S*-alkylation producing a derivative of either Ib or Ic, respectively, had not been observed. But a development relevant to this question resulted from the reinvestigation of a report of *N*-alkylation of thiazolidine (XI) by methyl iodide in sodium-liquid ammonia (7). In our hands, these conditions applied to Ia led instead to an *S*-alkyl derivative (III) with simultaneous reductive cleavage of the carbon-sulfur bond. By reduction of the double bond, III could be related to either of the tautomers (Ib or Ic), but the evidence to be presented subsequently favors reductive cleavage.

To further pursue the speculation of possible enamine tautomer involvement, we wished to study alkylation of the *N*-methyl derivative (IIa). A more practical synthetic route to this required substance than *N*-methylation of Ia (as already discussed) originated with 2-(methylamino)-ethanethiol (XII) (8).

SCHEME I



Synthesis of such *N*-alkylated aminothiols had been reported by lithium aluminum hydride reduction of appropriate thiazolidines, and in the current instance, parent thiazolidine (XI) (9). In route to this objective, we experienced difficulties in preparing XI by the known method (10), so that it was necessary to develop modifications, which have greatly improved the procedure. Attempted application of the original procedure (10) gave yields of the free base XI as high as 40%. However, the method was unreliable and although the hydrochloride of XI was readily obtained, subsequent formation of the free base (XI) usually occurred in poor yield. The main limitation was the formation of large quantities of a solid by-product (uncharacterized). It was determined that a critical factor was maintenance of an excess concentration of aqueous sodium carbonate. This was accomplished by addition of a solution of the hydrochloride of XI to an equimolar amount of sodium carbonate. To a lesser degree, continuous ether extraction of the highly polar product from the aqueous reaction mixture was also helpful in giving maximum yields of thiazolidine (XI) (80-86%).

2-(Methylamino)ethanethiol (XII) was then formed in yields of 68-70% by lithium aluminum hydride reduction

of XI (9); under conditions of the reaction, oxidation of XII to a disulfide occurred quite readily if a nitrogen atmosphere was not employed. The conversion may be another example of reductive cleavage of a carbon-sulfur bond, although reduction via a Schiff base tautomer is also a possibility. The *N*-methylthiazolidine, 4-methyl-1-thia-4-azaspiro[4,5]decane (IIa), was then obtained in an 85% yield as a colorless oil by heating XII with cyclohexanone.

Returning now to the central point, we can only report that initial experiments for the purpose of observing *S*- or *C*-alkylation derivatives of an enamine tautomer (IIb) have been unencouraging. Thus, attempted alkylation of IIa with acrylonitrile (6) showed no reaction, (recovery of the starting material, 89%). This result is to be compared with the small yield of cyanoethyl derivative obtained by reaction of I with acrylonitrile, as described above. Attempts to alkylate IIa with benzyl chloride under strongly basic conditions were also negative, except in the case of a sodium-liquid ammonia experiment. In this instance, however (as for Ia), reductive cleavage of the thiazolidine ring is thought to have occurred prior to the *S*-alkylation. Structural assignment of the product (XVII) was based on the n.m.r. spectrum, which was consistent

4-Methyl-1-thia-4-azaspiro[4,5]decane (IIa).

A. By Alkylation of 1-Thia-4-azaspiro[4,5]decane (Ia) with Methyl Iodide.

In a sealed tube was placed a solution of 3.00 g. (0.019 mole) of Ia in 10 ml. of absolute ethanol and to this was added 2.02 g. (0.019 mole) of anhydrous sodium carbonate followed by 2.71 g. (0.019 mole) of methyl iodide; the mixture was heated at 110° for 1 day in a Parr bomb. After the reaction mixture had been dissolved in 50 ml. of water and extracted with ether (4 x 25 ml.), the usual work-up produced 2.80 g. of a pale yellow oil, which was distilled to give 1.56 g. (48%) of a colorless oil (IIa); b.p. 50-52° (0.03 mm.); n^{25} 1.5334. The infrared absorption spectrum was identical to that of the sample of the product obtained from XII and which is described in B as follows.

B. From 2-(Methylamino)ethanethiol (XII).

To 8.00 g. (0.088 mole) of molten XII (nitrogen) was added 8.65 g. (0.088 mole) of cyclohexanone. The mixture was swirled and allowed to stand until the exothermic reaction had subsided (20 minutes). The colorless oil was distilled to give 12.8 g. (85%) of a colorless oil (IIa); b.p. 58-60° (0.1 mm.); n^{25} 1.5320 [lit. b.p. 133-135° (22 mm.); n^{25} 1.5360 (9)]; δ 2.60-3.38 (SCH₂CH₂N), 2.23 (NCH₃), 0.85-1.94 (cyclohexyl), ratio of 4:3:10.

Cyanoeethyl-Substituted 1-Thia-4-azaspiro[4,5]decane. (Mixture of VII and Related Tautomer Derivatives).

To a solution of 10.0 g. (0.0636 mole) of 1-thia-4-azaspiro[4,5]decane (Ia) in 40 ml. of absolute ethanol was added 5.30 g. (0.10 mole) of acrylonitrile. After the yellow solution had been stirred under reflux for 3 days and the ethanol removed under reduced pressure, the residue was distilled to give 5.26 g. of starting thiazolidine Ia, b.p. 55-57° (0.1 mm.) followed by 5.14 g. (73%, allowing for recovered starting material) of the cyanoethyl-substituted product (probably a mixture of the *N*-, *S*-, and *C*-alkylated products) as an orange oil; b.p. 108-110° (0.1 mm.); n^{25} 1.5413; ν max (chloroform), 3310 (w, NH), 2250 (m, C≡N), 1655 cm⁻¹ (m, C=N).

Anal. Calcd. for C₁₁H₁₈N₂S: C, 62.82; H, 8.63; S, 15.25. Found: C, 62.57; H, 8.73; S, 15.05.

Hydrolysis of Cyanoethyl-Substituted 1-Thia-4-azaspiro[4,5]decane. 2-Oxocyclohexanepropionitrile (VI).

The tautomer-derivative mixture resulting from cyanoethylation of 1-thia-4-azaspiro[4,5]decane [5.00 g. (0.024 mole)] was added to 50 ml. of 10% hydrochloric acid solution. The reaction mixture was then continuously extracted with ether for 2 days, and after the solution had been dried over magnesium sulfate and the ether removed, the residual oil was distilled to give 0.48 g. (15%) of 2-oxocyclohexanepropionitrile (VI) as a colorless oil (b.p. 59-60°) (0.08 mm.). The infrared absorption spectrum was identical with that of an authentic sample (6).

N-[2-(Methylthio)ethyl]cyclohexylamine (III). From Reductive Cleavage-Alkylation of 1-Thia-4-azaspiro[4,5]decane (Ia).

To a solution of 2.30 g. (0.10 g.-atom) of sodium in liquid ammonia was added 15.7 g. (0.10 mole) of Ia in 50 ml. of ether. After 10.7 g. (0.11 mole) of methyl iodide was added from a dropping funnel, the solution was allowed to evaporate overnight, and then additional ammonia was removed under reduced pressure (aspirator). The oil remaining was dissolved in 100 ml. of ether, extracted with 10% hydrochloric acid (3 x 50 ml.). After further work-up, the residual oil was distilled to yield 5.83 g. (34%) of colorless oil; b.p. 61-63° (0.15 mm.); n^{25} 1.5005; ν max

(chloroform), 3330 cm⁻¹ (w, NH); δ 2.34-2.89 (SCH₂CH₂N), 2.02 (SCH₃), 0.83-1.93 (cyclohexyl NH), ratio 4:3:12. The spectra differed from those of the *N*-methyl derivative (II).

Anal. Calcd. for C₉H₁₉NS: C, 62.41; H, 11.06; S, 18.51. Found: C, 62.17; H, 11.18; S, 18.29.

1-Cyclohexyl-1-[2-(methylthio)ethyl]-3-phenyl-2-thiourea.

A sample of III was converted to the phenylthiourea derivative in 66% yield by reaction with phenylisothiocyanate; the crude product was triturated with petroleum ether, and recrystallized from methanol; m.p. 84-85°; ν max (potassium bromide) 3160 (m, NH), 605, 1450, 696 cm⁻¹ (m, s, s, C₆H₅).

Anal. Calcd. for C₁₆H₂₄N₂S₂: C, 62.29; H, 7.84; S, 20.79. Found: C, 62.62; H, 8.04; S, 20.66.

Thiazolidine (XI).

To a solution of 57.2 g. (0.50 mole) of 2-aminoethanethiol hydrochloride (X) in 300 ml. of water was added 40.6 g. of 37% formaldehyde solution (0.50 mole of formaldehyde). The solution was allowed to stand 20 hours with occasional swirling (nitrogen) and then added as rapidly as possible to a solution of 53.2 g. (0.50 mole) of sodium carbonate in 300 ml. of water. The clear colorless solution was then saturated with potassium chloride and extracted with ether (4 x 400 ml.). After the combined ether extracts were dried over anhydrous magnesium sulfate and evaporated under reduced pressure, the residual oil was distilled to give 33.0 g. (75%) of XI as a colorless liquid; b.p. 60-62° (10 mm.); n^{25} 1.5427 [lit. (10) b.p. 164-165°; n^{30} 1.551]; ν max (chloroform), 3260 cm⁻¹ (s, NH); δ 4.06 (SCH₂N), 2.42-3.23 (SCH₂CH₂NH), ratio 2:5. Continuous ether extraction of the original aqueous solution gave an additional 6.00 g. (total yield 86%).

2-(Methylamino)ethanethiol (XII).

To a solution of 22.0 g. (0.25 mole) of thiazolidine (XI) in 800 ml. of anhydrous ether was added 100 ml. of 1 *M* solution of lithium aluminum hydride in ether over a 0.75-hour period (nitrogen), after which the mixture was heated under reflux for an additional hour. To decompose unreacted reagent, 10 ml. of water was carefully added, and the mixture was filtered using Celite. After the ether had been dried over anhydrous magnesium sulfate and removed by distillation, 13.0 g. (57%) of a white solid was obtained; m.p. 52-53° [lit. (13) m.p. 52-53°]; ν max (chloroform), 3315 (w, NH), 2840 cm⁻¹ (w, SH). Distillation did not change the melting point; b.p. 140-146° [lit. (8) b.p. 134-137°]. Continuous extraction of the lithium and aluminum salts with ether resulted in an additional 3.00 g. (total yield, 70%).

Attempted Reaction of 4-Methyl-1-thia-4-azaspiro[4,5]decane (IIa) with Acrylonitrile.

A mixture of 5.00 g. (0.029 mole) of IIa and 1.70 g. (0.032 mole) of acrylonitrile in 25 ml. of absolute ethanol was heated under reflux for 3 days in a flask protected with a calcium chloride tube. The ethanol was removed under reduced pressure, and the residue was distilled to give 4.45 g. (89% recovery) of starting thiazolidine (IIa).

N-[2-(Benzylthio)ethyl]-*N*-methylcyclohexylamine (XVII). From Reductive Cleavage-Alkylation of 4-Methyl-1-thia-4-azaspiro[4,5]decane (IIa).

To a solution of 5.00 g. (0.030 mole) of IIa in 500 ml. of liquid ammonia was added approximately 1.2 g. (0.05 g.-atom) of sodium until a permanent blue color appeared. After excess sodium had been destroyed by addition of a small piece of dry ice,

3.82 g. (0.030 mole) of benzyl chloride was added dropwise. The mixture was allowed to stand overnight for evaporation of ammonia; the residue was taken up in 50 ml. of water, which was then extracted with 100 ml. of ether. The ether phase was separated and washed with additional water (2 x 50 ml.). After final work-up, a residue of 6.17 g. of an orange oil was obtained and was distilled to give 5.24 g. (66%) of a colorless oil; b.p. 110-112° (0.03 mm.); n_D^{25} 1.5458, d_4^{25} 1.0973; ν max (chloroform), 1640, 1500, 1450, 700 cm^{-1} (w, m, s, s, C_6H_5); δ 7.08-7.22 (C_6H_5), 3.60 ($\text{C}_6\text{H}_5\text{CH}_2$), 2.32-2.56 ($\text{SCH}_2\text{CH}_2\text{N}$), 2.13 (NCH_3), 0.83-1.97 (cyclohexyl), ratio 5:2:4:3:11.

Anal. Calcd. for $\text{C}_{16}\text{H}_{25}\text{NS}$: C, 72.95; H, 9.57; S, 12.17. Found: C, 73.09; H, 9.61; S, 11.97.

N-[2-(Benzylthio)ethyl]-*N*-methylcyclohexylamine (XVII) Hydrochloride.

Introduction of anhydrous hydrogen chloride into a solution of 200 mg. (0.76 mmole) of XVII in 30 ml. of anhydrous ether gave 153 mg. (67%) of the hydrochloride as a white crystalline solid after thorough washing with the ether; m.p. 133-135°; ν max (potassium bromide), 2630 cm^{-1} (s, NH_3^+Cl^-).

Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{ClNS}$: C, 64.07; H, 8.74; Cl, 11.82. Found: C, 63.85; H, 8.90; Cl, 12.01.

2-(Benzylthio)-*N*-cyclohexylideneethylamine (XV).

A solution of 14.7 g. (0.15 mole) cyclohexanone and 25.0 g. (0.15 mole) of 2-(benzylthio)ethylamine (IX) (14) in 100 ml. of dry benzene under nitrogen was heated under reflux until the theoretical amount of water was removed by azeotropic distillation (3 hours). After the benzene had been removed under reduced pressure, 39.0 g. of a residual orange oil was obtained and distilled to give 30.4 g. (82%) of a light yellow oil; b.p. 130-135° (0.05 mm.); n_D^{25} 1.5684; d_4^{25} 1.3021; ν max (chloroform), 1655 cm^{-1} (m, C=N). Although this material proved to be analytically impure, it was suitable for conversion to the sequential intermediate in the series (XVI).

Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{NS}$: C, 72.82; H, 8.56; S, 12.95. Found: C, 69.79; H, 8.46; S, 14.54.

N-[2-(Benzylthio)ethyl]cyclohexylamine (XVI).

Dropwise to a solution of 24.7 g. (0.10 mole) of XV in 800 ml. of anhydrous ether (nitrogen) was added a solution of 50 ml. of 1 *M* lithium aluminum hydride in ether (50 mmole) at such a rate as to maintain slow reflux (10 minutes). After the mixture was heated for an additional hour, 5 ml. of water was cautiously added. The mixture was filtered through Celite and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to give 25.2 g. of residue, which on distillation afforded 22.3 g. (90%) of a colorless liquid; b.p. 108-112° (0.05 mm.); n_D^{25} 1.5562; d_4^{25} 1.0714; ν max (chloroform), 3250 cm^{-1} (w, NH); δ 7.14 (C_6H_5), 3.52-3.60 ($\text{C}_6\text{H}_5\text{CH}_2$), 1.10 ($\text{SCH}_2\text{CH}_2\text{N}$, NH); 0.68-2.85 (cyclohexyl), ratio 5:2:16.

Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{NS}$: C, 72.23; H, 9.29; S, 12.86. Found: C, 71.99; H, 9.08; S, 12.64.

N-[2-(Benzylthio)ethyl]-*N*-methylcyclohexylamine (XVII). By the Eschweiler-Clarke Reaction on *N*-[2-(Benzylthio)ethyl]cyclohexylamine (XVI).

To 2.55 g. (0.05 mole) of 90% formic acid was added 5.00 g. (0.02 mole) of XVI with cooling of the mixture in a water bath (11). While the resulting orange solution was maintained at room temperature, 2.45 g. (0.03 mole) of (37%) formaldehyde was added, and the solution was heated on a steam bath. To control the frothing, which initially occurred to a considerable degree

(approximately 10 minutes), the flask was removed from the bath for a short period. After further heating for 1 day, a solution of 5.31 g. (0.05 mole) of sodium carbonate in 30 ml. of water was added carefully. The aqueous solution was extracted with ether (3 x 25 ml.), and the combined ether extracts were dried over anhydrous magnesium sulfate. After removal of the ether, the 5.88 g. of residual orange oil was distilled to give 5.02 g. (95%) of a colorless liquid; b.p. 115-117° (0.05 mm.).

The infrared spectrum of this substance was identical to that obtained by reductive cleavage-alkylation of IIa with sodium-liquid ammonia followed by benzyl chloride.

2-(Benzylthio)-*N*-methylethylamine (XIII).

To a solution of 5.00 g. (0.055 mole) of XII in 100 ml. of absolute ethanol (nitrogen) was added 1.27 g. (0.055 mole) of sodium in small pieces. The solution was stirred 15 minutes, and 7.00 g. (0.055 mole) of benzyl chloride was added dropwise over a 20-minute period. After the mixture had been stirred for 15 hours at room temperature and the ethanol had been subsequently removed, the residue was taken up in 50 ml. of water, which was then extracted with ether (3 x 50 ml.). After further work-up, the residue was distilled to give 8.54 g. (85%) of a colorless oil; b.p. 86° (0.1 mm.); n_D^{25} 1.5543; d_4^{25} 1.0572; ν max (chloroform), 3300 (m, NH); 1610, 1500, 1460, 702 cm^{-1} (m, s, s, s, C_6H_5); δ 7.07-7.20 (C_6H_5), 3.56 ($\text{C}_6\text{H}_5\text{CH}_2$), 2.39-2.60 ($\text{SCH}_2\text{CH}_2\text{N}$), 2.20 (NCH_3), 1.04 (NH), ratio 5:2:4:3:1.

Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{NS}$: C, 66.24; H, 8.34; S, 17.69. Found: C, 66.50; H, 8.47; S, 17.81.

N-[2-(Benzylthio)ethyl]-*N*-methyl-1-cyclohexen-1-ylamine (XIV).

A solution of 3.00 g. (0.017 mole) of XIII and 1.62 g. (0.017 mole) of cyclohexanone in 20 ml. of anhydrous benzene was heated under reflux for 26 hours (nitrogen) to give 83% of the theoretical amount of water by azeotropic distillation. Benzene was removed under reduced pressure leaving 4.61 g. of a residual orange oil which was distilled to give 730 mg. of starting XIII, b.p. 80-83° (0.03 mm.) and 3.08 g. (95%, considering recovered starting material) of the enamine (XIV) as a colorless oil, b.p. 116-118° (0.03 mm.); redistillation gave 2.51 g. (77%); b.p. 116-118° (0.03 mm.); n_D^{25} 1.5683; d_4^{25} 1.0856; ν max (chloroform), 1640 cm^{-1} (s, C=C); δ 6.93-7.32 (C_6H_5), 4.30 (t, $\text{CH}_2=\text{CH}$, J=7 c.p.s.) 3.57 ($\text{C}_6\text{H}_5\text{CH}_2$), 2.40 (NCH_3) 1.09-2.50 (cyclohexyl), ratio 5:1:2:16.

Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{NS}$: C, 73.51; H, 8.87; S, 12.27. Found: C, 73.52; H, 9.02; S, 12.52.

Attempted Reduction of *N*-[2-(Benzylthio)ethyl]-*N*-methyl-1-cyclohexen-1-ylamine (XIV) with Sodium-liquid Ammonia.

To a solution of 3.00 g. (0.011 mole) of XIV in 500 ml. of liquid ammonia was added approximately 1.0 g. (4 equivalents) of sodium in small pieces (until a permanent blue color appeared). After excess sodium had been destroyed by careful addition of a small piece of dry ice, 1.46 g. (0.011 mole) of benzyl chloride was added dropwise and the pale gray mixture was stirred 1 hour. The solution was allowed to stand overnight for evaporation of the ammonia, and the solid gray residue was washed with 200 ml. of ether. After filtration, the ether filtrate was evaporated to give 3.50 g. of yellow oil, which was distilled to yield 2.85 g. (95%) recovery of starting enamine, b.p. 116-118° (0.03 mm.).

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