employed as extractants in the work-up that was analogous to that for the cupric bromide reaction. Distillation of the concentrated organic residue provided 8.08 g. of 1,1,3-trimethoxypropane, b.p. 53–54° (24 mm.), 149° (760 mm.), $n^{23.5}$D 1.3993 (lit.[29] b.p. 148°, n^{25}D 1.4000). The infrared spectrum showed characteristic acetal and ether linkage in the 1050–1175-cm.$^{-1}$ region. A second fraction, 4.69 g. (104%), of 2-chloro-1,3,3-trimethoxypropane, b.p. 41–43° (0.8 mm.), was obtained. The substance showed one peak on gas chromatography. The infrared spectrum was very similar to that of the corresponding bromide.

Anal. Calcd. for $C_6H_{13}ClO_3$: C, 42.76; H, 7.71; Cl, 21.04. Found: C, 42.98; H, 7.84; Cl, 20.63.

Propargaldehyde with Cupric Bromide.—A mixture of 4.10 g. (0.076 mole) of propargaldehyde and 89.3 g. (0.40 mole) of $CuBr_2$ in 400 ml. of methanol stirred and refluxed for 16 hr. afforded upon work-up 39.2 g. (90%) of cuprous bromide and 14.7 g. (63%) of tribromoacrolein dimethyl acetal having b.p. 89–91° (2 mm.). The infrared spectrum showed C=C at 1580 cm.$^{-1}$ and acetal at 1140–1070 cm.$^{-1}$. The n.m.r. spectrum consisted of two singlets at 5.08 (acetal H) and 3.38 p.p.m. (OCH_3) (tetramethylsilane reference) having peak areas in the approximate ratio of 1:6.

Anal. Calcd. for $C_5H_7Br_3O_2$: C, 17.67; H, 2.06; Br, 70.65. Found: C, 17.96; H, 2.25; Br, 70.30.

A 2,4-dinitrophenylhydrazone had m.p. 235–237°.

With Cupric Chloride.—In similar fashion, 5.40 g. (0.10 mole) of propargaldehyde and 53.8 g. (0.40 mole) of $CuCl_2$ in 175 ml. of methanol yielded, after 6.5 hr. at reflux, 21.9 g. (55%) of cuprous chloride and 5.53 g. (49%) of trichloroacrolein dimethyl acetal having b.p. 58–60° (2.8 mm.). The infrared spectrum showed C=C at 1595 cm.$^{-1}$ and acetal bands at 1150–1060 cm.$^{-1}$. The n.m.r. spectrum consisted of two singlets at 5.26 and 3.35 p.p.m. with peak areas in the ratio of 1:6.

Anal. Calcd. for $C_5H_7Cl_3O_2$: Cl, 51.76. Found: Cl, 51.86.

A 2,4-dinitrophenylhydrazone had m.p. 228.5–229° (lit.[30] m.p. 229–230°).

Anal. Calcd. for $C_9H_5Cl_3N_4O_4$: C, 32.13; H, 1.49. Found: C, 32.23; H, 1.73.

The Oxidative Bromination of Ethanol.—A solution of 44.7 g. (0.2 mole) of cupric bromide in 250 ml. of absolute ethanol refluxed for 49 hr. yielded 20.64 g. (72.4%) of cuprous bromide and 5.9 g. (90%) of 1,1-dibromo-2,2-diethoxyethane having b.p. 71–74° (2.5 mm.), n^{25}D 1.4808 (lit.[31] n_D 1.4802). A small amount of lower boiling material was not investigated. The dibromo acetal emerged as one peak when gas chromatographed and its infrared spectrum exhibited the characteristic acetal 1060–1150-cm.$^{-1}$ bands. The n.m.r. spectrum consisted of doublets at 5.60 and 4.60, a quartet at 3.65, and a triplet at 1.20 p.p.m.

Anal. Calcd. for $C_7H_{12}Br_2O_2$: C, 26.10; H, 4.35. Found: C, 26.07; H, 4.68, 4.52.

Acrylonitrile with Cupric Bromide in Ethanol.—A solution of 5.3 g. (0.10 mole) of acrylonitrile and 89.4 g. (0.4 mole) of cupric bromide in 500 ml. of absolute ethanol stirred and refluxed for 89 hr. yielded 40.1 g. (70%) of cuprous bromide. Distillation of the organic product afforded 7.81 g. of a fraction having b.p. 52–57.5° (0.85 mm.). A very small higher boiling fraction (57–68° at 0.6 mm.) was not investigated. Gas chromatography (10-ft. column, DC-710, 152°) of the major fraction indicated the presence of three constituents. The first peak (19.8 min.) accounted for 24% (1.9 g.) of the mixture. This substance was trapped from the column and found to have an identical infrared spectrum and emergence time with authentic ethyl α-bromo-β-ethoxypropionate. The latter was prepared by treating ethyl α,β-dibromopropionate with 2 moles of sodium ethoxide.[32]

The other, later emerging constituents were not well resolved. The shouldered peaks were trapped and their infrared spectrum accorded with a mixture of 1,1-dibromo-2,2-diethoxyethane and ethyl α,β-dibromopropionate. Gas chromatography of the authentic mixture closely resembled the unknown chromatogram, and spiking the unknown with either constituent shifted the shoulder. The n.m.r. spectrum of the unknown mixture exhibited bands characteristic of the authentic mixture. When ethyl acrylate was the substrate the yield of dibromo ester was greatly increased.

Cupric Bromide with Methanol.—A solution of 22.35 g. (0.10 mole) of cupric bromide in 200 ml. of absolute methanol refluxed for 12 hr. afforded upon titration 0.41 g. of cuprous bromide (2.1%).

Cupric Chloride with Ethanol.—A solution of 53.8 g. (0.40 mole) of cupric chloride in 250 ml. of absolute ethanol refluxed for 25 hr. provided no detectable cuprous chloride by titration.

(29) R. Voet, *Bull. soc. chim. France*, [4] **41**, 1313 (1927).

(30) A. Roedig and E. Degner, *Ber.*, **86**, 1469 (1953).

(31) S. M. McElvain and P. M. Watters, *J. Am. Chem. Soc.*, **64**, 1964 (1942).

(32) A. Michael, *J. prakt. Chem.*, **60**, 413 (1889); J. L. Wood and V. DuVigneaud, *J. Biol. Chem.*, **134**, 414 (1946).

A New Synthetic Route to Substituted Mercaptoethylamines. Hydroxyl Displacement by Thiols[1a]

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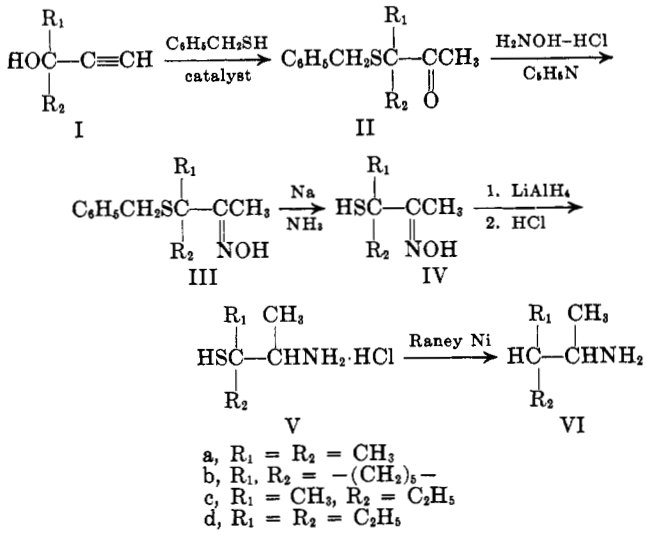
A catalytic displacement reaction of the hydroxyl group of ethynyl carbinols (I) by thiols has been discovered. The displacement is accompanied by internal hydration of the acetylenic function of I. These developments have made possible a new synthetic approach to substituted mercaptoethylamines (V). The β-keto sulfide II is converted to an oxime III. The protecting benzyl group of III is then removed by reaction with sodium in liquid ammonia to give an α-thiol oxime (IV). This intermediate is reduced with lithium aluminum hydride to yield a substituted mercaptoethylamine V, wherein the thiol group is located on a tertiary carbon atom and the amino group, on a secondary carbon atom.

The synthesis of substituted mercaptoethylamines has been of value in the correlation of structure with the activity of prospective antiradiation agents.[2] Until recently[3] few mercaptoethylamines containing a tertiary thiol group had been synthesized. We now wish to report a new synthetic approach for substituted mercaptoethylamines (V) which contain a tertiary thiol group and an amino group on an adjacent secondary carbon atom. This synthesis involves a novel displacement of a hydroxyl group of an ethynylcarbinol (I) with concomitant transformation of the acetylenic linkage to a methyl ketone function (II). Additional

(1) (a) Presented on sabbatical leave (G. W. S.) at various universities in Australia and New Zealand, 1963, and before the Division of Organic Chemistry at the 148th Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964. (b) In part from the Ph.D. Thesis of B. F. Barnett, Washington State University, June 1963. (c) National Defense Education Act Fellow, 1961–1964.

(2) (a) "Symposium on Radiation-Protective Agents," Abstracts, Division of Medicinal Chemistry, 141st Meeting of the American Chemical Society, Washington, D. C., March 1962, p. 28N. (b) J. F. Thomson, "Radiation Protection in Mammals," Reinhold Publishing Corp., New York, N. Y., 1962, p. 66.

(3) F. I. Carroll, J. D. White, and M. E. Wall, *J. Org. Chem.*, **28**, 1236, 1240 (1963).

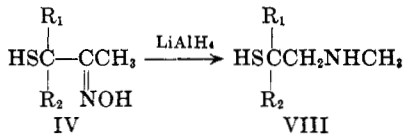


a, $R_1 = R_2 = CH_3$
b, $R_1, R_2 = -(CH_2)_5-$
c, $R_1 = CH_3, R_2 = C_2H_5$
d, $R_1 = R_2 = C_2H_5$

comment on this key reaction of the synthesis is made subsequently.

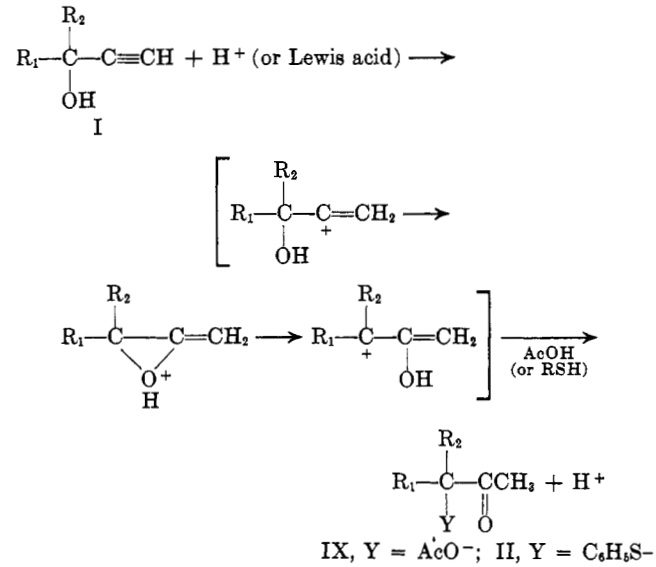
The oximes III were formed in the usual manner in yields of 62–88%. Where the product was a solid, it was purified by recrystallization from aqueous alcohols; however, the oximes IIIc and IIId were oils, which were fractionally distilled. It was thought that it might be possible to remove the benzyl group with simultaneous reduction of the oxime group to an amino group using lithium aluminum hydride. However, IIIa, c, and d all formed the corresponding amino sulfide VII, the benzylthio group remaining intact throughout the reduction. To remove the benzyl group, the well-known procedure involving sodium and liquid ammonia was employed[3,4]; it was interesting to note, however, that on y the benzyl group was removed under these conditions and no reduction of the oxime group took place. Thus a series of α-thiol oximes (IV) was obtained in yields of 70–75% after purification by either distillation (some of the oximes were liquids) or crystallization.

Reduction of the α-thiol oximes to the final products (V), isolated as hydrochlorides, was carried out with lithium aluminum hydride in ether. In several instances, the mercaptoethylamine hydrochlorides (V) were treated with a carbonyl reagent to form expected thiazolidine hydrochlorides. This conversion confirmed the presence of adjacent thiol and amino groups. However, the possibility of a Beckmann-type rearrangement of the oxime function during reduction with lithium aluminum hydride,[5] which would yield a secondary amine also capable of forming a thiazolidine prompted a closer investigation of these products (V). To this end, the n.m.r. spectra were consistent with V rather than VIII. And further, desulfurization of



Va with Raney nickel gave 2-amino-3-methylbutane (VIa), which would be expected to result from Va rather than VIIIa. The product VIa was identified as a hydrochloride and a *p*-nitrobenzoyl derivative; the infrared spectra of these derivatives were identical with those of similar derivatives derived from VIa, prepared by hydrogenation of 3-methyl-2-butanone oxime.

We wish now to return to the new reaction which makes this synthesis convenient, the conversion of ethynylcarbinols I to β-keto sulfides II. Several investigators[6] have observed that ethynylcarbinols I react with glacial acetic acid in the presence of mercuric ion and boron trifluoride to give acetylacyloins (IX). It seemed that this reaction might proceed by way of a neighboring group mechanism. Cram and Hammond[7] have suggested a similar mechanism for the Rupe



IX, Y = AcO^-; II, Y = C_6H_5S-

rearrangement.[8] In line with this reasoning, it was thought that it might be possible to substitute a thiol as nucleophile in this system and obtain a β-keto sulfide (II) rather than acetylacyloin (IX). With a catalyst prepared from mercuric acetate and concentrated sulfuric acid in glacial acetic acid, this objective was indeed realized, initially with 3-methyl-1-butyn-3-ol (Ia). The ethynylcarbinol (Ia) and α-toluenethiol were added simultaneously to the catalyst preparation, and the reaction mixture was heated at 70–80° under nitrogen; the desired product IIa was obtained along with a small amount of acetylenic sulfide X. When this reaction was carried out using boron trifluoride in glacial acetic acid rather than the catalyst of choice (procedure B), none of the desired β-keto sulfide IIa was obtained, but instead only the acetylenic sulfide Xa. Of course, it was possible to convert Xa to the desired β-keto sulfide IIa in the presence of mercuric sulfate and dilute sulfuric acid.[9] Also, in the case of benzyl 1-ethynylcyclohexyl sulfide (Xb), which is derived from 1-ethynylcyclohexanol (Ib), conversion to the corresponding β-keto sulfide IIb in an excellent yield (80%) was accomplished by the same catalytic conditions which bring about the over-all change of Ib to IIb. These facts suggest that the re-

(4) W. H. Hartung and R. Simonoff, *Org. Reactions*, **7**, 263 (1953).

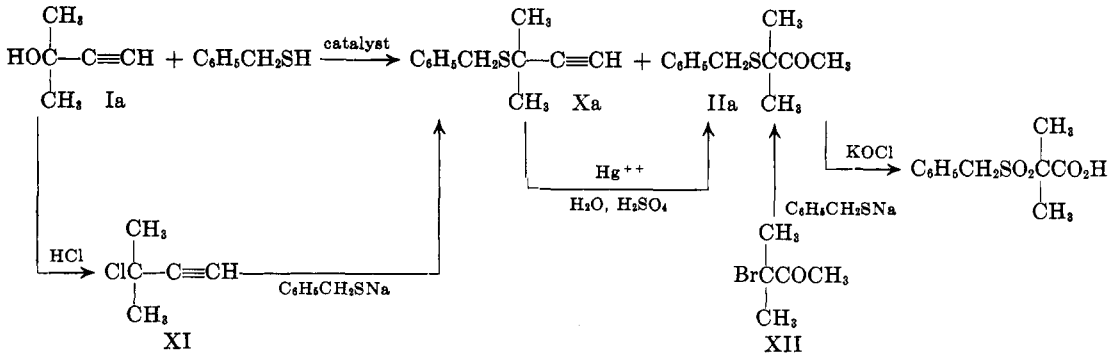
(5) R. E. Lyle and H. J. Troscianiec, *J. Org. Chem.*, **20**, 1757 (1955); we are indebted to a referee of our manuscript for calling this possibility to our attention.

(6) (a) J. F. Froning and G. F. Hennion, *J. Am. Chem. Soc.*, **62**, 653 (1940); (b) R. McGill, U. S. Patent 2,198,172 (1940); *Chem. Abstr.*, **34**, 5463 (1940).

(7) D. J. Cram and G. W. Hammond, "Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p. 504.

(8) *Cf.* M. F. Ansell, J. W. Hancock, and W. J. Hickinbottom, *J. Chem. Soc.*, 911 (1956).

(9) G. W. Stacy and R. A. Mikulec, *Org. Syn.*, **35**, 1 (1955).



action, in part at least, may not proceed by a neighboring group mechanism, but rather first by the formation of an acetylenic sulfide such as X followed by hydration to a β-keto sulfide II. The formation of a sulfide by displacement of a hydroxyl group has precedent in a similar reaction with tertiary alcohols investigated by Gregg, Iddles, and Stearns.[10] These authors found that α-toluenethiol would react with triphenylcarbinol in the presence of boron trifluoride to give an excellent yield of the corresponding sulfide.

In the current work, it was found that other ethynylcarbinols I gave corresponding β-keto sulfides II in yields of 74–78%. Experimentation with components of the catalytic mixture reflected the importance of the role which each assumed. For example, in the case of 3-methyl-1-pentyn-3-ol (Ic) a 75% yield of β-keto sulfide IIc was obtained under optimum conditions. However, if the mercuric acetate was omitted from the catalyst preparation, the yield was reduced to 36%. Further, concentrated sulfuric acid proved itself to be of critical importance, for if it were not included, no product was obtained.

Returning to the formation of the acetylenic sulfide Xa and the corresponding β-keto sulfide IIa, one might comment on the characterization of these substances. In addition to direct formation from the ethynylcarbinol Ia, the acetylenic sulfide Xa was also obtained from the chloroalkyne XI. In like manner, the β-keto sulfide IIa was alternately obtained from 3-bromo-3-methyl-2-butanone (XII). Further, IIa was degraded by the haloform reaction; not only was the carboxyl group produced as expected, but also the sulfide function was oxidized to a sulfone group.

In addition to the benzyl sulfide, the preparation of a thioacetate XIII was attempted from 3-methyl-1-butyn-3-ol (Ia), since this also seemed a likely source of a masked thiol group. A product could not be isolated, although the infrared spectrum revealed a trace in the reaction mixture as identified with a sample prepared from 3-bromo-3-methyl-2-butanone and sodium thioacetate. Because of the success of the benzyl sulfide formation, this approach was discontinued.

Biological Evaluation.—Both the 1,1,2-trialkylmercaptoethylamine hydrochlorides V and the precursor α-thiol oximes IV were tested as prospective antiradiation agents, but none of these substances showed appreciable activity.

Experimental

All melting points are corrected. Boiling points at reduced pressures are uncorrected. The microanalytical work was performed by the Galbraith Laboratories, Knoxville, Tenn., and Dr. G. Weiler and Dr. F. B. Strauss, Microanalytical Laboratories, Oxford, England. The infrared spectra were determined on a Beckman IR-5 spectrophotometer. The spectra of liquids were run as thin films between two rock-salt plates. N.m.r. spectra were determined on a Varian Model A-60 spectrometer.

Reaction of 3-Methyl-1-butyn-3-ol (Ia) and α-Toluenethiol. Procedure A.—A catalytic mixture was prepared under an atmosphere of nitrogen. Mercuric acetate (6.40 g., 0.02 mole) was dissolved in 150 ml. of glacial acetic acid. To this was added 5.00 g. (0.04 mole) of α-toluenethiol, which resulted in the formation of a heavy, white precipitate, which interfered with the process of stirring. The precipitate partially dissolved when the mixture was heated to about 70°, and at this point 4 ml. of concentrated sulfuric acid was added. A solution of 42.0 g. (0.50 mole) of 3-methyl-1-butyn-3-ol (Ia) and 62.0 g. (0.50 mole) of α-toluenethiol was added dropwise to the catalytic mixture at such a rate to maintain the temperature at 70–80°. After the addition had been completed, the mixture was stirred for 24 hr. at room temperature and then poured slowly into 500 ml. of sodium carbonate (200 g.) solution.

The solution was filtered, and the filtrate was extracted with ether (three 150-ml. portions). The combined ether extracts were washed with 10% hydrochloric acid (three 100-ml. portions) and finally with a saturated sodium chloride solution. After it had been dried over anhydrous sodium sulfate, the ether was removed by flash distillation. Distillation of the residue yielded 4.40 g. of an initial fraction consisting principally of benzyl 1,1-dimethyl-2-propynyl sulfide (Xa), b.p. 60–68° (0.1 mm.), and 43.9 g. (45%) of 3-(benzylthio)-3-methyl-2-butanone (IIa), b.p. 100–105° (0.2 mm.). The infrared spectra of these substances were identical with the spectra of samples prepared from XI and XII.

Procedure B.—A catalytic mixture was prepared by heating 4.00 g. of red mercuric oxide, 2 ml. of absolute methanol, 1.00 g. of trichloroacetic acid, and 2 ml. of freshly distilled boron trifluoride etherate, at which point the mixture turned a pasty white.[11] To this mixture was added dropwise a solution of 50.0 g. (0.40 mole) of α-toluenethiol and 42.0 g. (0.50 mole) of 3-methyl-1-butyn-3-ol (Ia). After addition had been completed, the mixture was stirred for 3 hr. at room temperature and then poured slowly into 200 ml. of saturated sodium carbonate solution.

The resulting mixture was extracted with ether (three 100-ml. portions). The combined ether extracts were dried over anhydrous potassium carbonate, and the ether then was removed. The residue was distilled to yield 47.7 g. of a dark orange oil, b.p. 90–100° (0.3 mm.); redistillation gave 28.0 g. (30%) of a pale yellow oil, b.p. 90–92° (0.3 mm.), $n^{20}D$ 1.5559. The infrared absorption spectrum established that this substance was the acetylenic sulfide Xa described in procedure A and in the sequel as prepared by an alternate method.

Benzyl 1,1-Dimethyl-2-propynyl Sulfide (Xa).—A mixture of 8.00 g. (0.20 mole) of sodium hydroxide and 12.0 g. (0.10 mole) of α-toluenethiol in 100 ml. of absolute ethanol was stirred and heated to the reflux temperature at which point 1.00 g. of sodium bicarbonate was added. Then 10.25 g. (0.10 mole) of 3-chloro-3-methyl-1-butyne (XI)[12] was added dropwise as stirring and heating under reflux were continued. When the addition had been completed, the mixture was heated further under reflux for 3 hr. The flask then was fitted for distillation, and the ethanol

(10) D. C. Gregg, H. A. Iddles, and P. W. Stearns, Jr., *J. Org. Chem.*, **16**, 246 (1951).

(11) G. F. Hennion and W. S. Murray, *J. Am. Chem. Soc.*, **64**, 1220 (1942).

(12) Prepared by the method of Hennion and Boisselle in 55% yields [B. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, **26**, 725 (1961)].

was removed. Benzene then was added, and the ethanol–benzene–water azeotrope was distilled.

The benzene solution left as residue was washed with 10% sodium hydroxide solution (twice), distilled water, and saturated sodium chloride solution, and was dried over anhydrous sodium sulfate. The benzene was removed by flash distillation under reduced pressure (aspirator). The residue was distilled to yield a pale yellow oil, b.p. 85–90° (1.5 mm.); redistillation gave 7.20 g. (38% yield) of Xa: b.p. 74–75° (0.08 mm.); $n^{20}D$ 1.5555; d^{25}_4 0.870; ν_{max} (cm.$^{-1}$) C≡CH 3300 (s), 2120 (w); identical with that of procedure B above.

Anal. Calcd. for $C_{12}H_{14}S$: C, 75.75; H, 7.41; S, 16.85. Found: C, 75.83; H, 7.44; S, 16.60.

3-(Benzylthio)-3-methyl-2-butanone (IIa).—A solution of the sodium salt of 24.0 g. (0.20 mole) of α-toluenethiol was prepared in the same manner as previously described from 8.00 g. (0.20 mole) of sodium hydroxide and 200 ml. of absolute ethanol. To the refluxing mixture a solution of 33.0 g. (0.20 mole) of 3-bromo-3-methyl-2-butanone[13] in 50 ml. of absolute ethanol was added dropwise over a period of 1 hr. The mixture was stirred overnight at room temperature. After the addition of 200 ml. of thiophene-free benzene, the flask was fitted for distillation. The ethanol and water were removed by distillation, and the benzene phase was washed with water and dried over anhydrous sodium sulfate. Distillation yielded 35.5 g. of a yellow oil, b.p. 100–102° (0.6 mm.). Redistillation through a helice-packed column (14 mm. × 12 cm.) afforded 30.4 g. (75%) of IIa as a light yellow oil: b.p. 105–106° (1.0 mm.); $n^{25}D$ 1.5405; d^{25}_4 1.046; ν_{max} (cm.$^{-1}$) C=O 1730 (s).

Anal. Calcd. for $C_{12}H_{16}OS$: C, 69.17; H, 7.74; S, 15.39. Found: C, 69.25; H, 7.79; S, 15.55.

A **2,4-dinitrophenylhydrazone** was obtained as orange, needle-like crystals after two recrystallizations from ethanol and ethyl acetate, m.p. 119–120°.

Anal. Calcd. for $C_{18}H_{20}N_4O_4S$: C, 55.65; H, 5.19; N, 14.42. Found: C, 55.90; H, 5.63; N, 14.19.

By way of hydration,[9] a sample of IIa was also obtained through heating under reflux for 1 hr. a mixture of 5.00 g. (0.026 mole) of the acetylenic sulfide Xa, 25 ml. of methanol, 8 ml. of water, 5 ml. of concentrated sulfuric acid, and 3.00 g. of red mercuric oxide. After the usual work-up,[9] 2.20 g. (51%) of the β-keto sulfide IIa, b.p. 91–94° (0.4 mm.), was obtained, identical with that from 3-bromo-3-methyl-2-butanone (XII) above (infrared spectrum).

Benzyl 1-Ethynylcyclohexyl Sulfide (Xa).—A solution of 24.8 g. (0.20 mole) of α-toluenethiol in 25 ml. of absolute ethanol was added to a mixture of 4.60 g. (0.20 g.-atom) of sodium in 50 ml. of absolute ethanol. After the addition was completed, 2.0 g. sodium bicarbonate was added. To this mixture was added 28.5 g. (0.20 mole) of 1-ethynylcyclohexyl chloride[12] in 50 ml. of ethanol. After stirring for 2 hr., the ethanol was removed under reduced pressure. The residue was triturated with ether and filtered. The residue from the ether solution was distilled to give 8.40 g. (18%) of the product Xa: b.p. 92–95° (0.06 mm.); $n^{25}D$ 1.5976; d^{25}_4 1.070.

Anal. Calcd. for $C_{15}H_{18}S$: C, 79.21; H, 7.88; S, 12.91. Found: C, 79.61; H, 7.92; S, 12.75.

1-(Benzylthio)cyclohexyl Methyl Ketone (IIb).—A solution of 50.0 g. (0.40 mole) of 1-ethynylcyclohexanol (Ib) and 50.0 g. (0.40 mole) of α-toluenethiol was added slowly to a catalytic mixture consisting of 150 ml. of glacial acetic acid, 6.40 g. of mercuric acetate, 3 ml. of concentrated sulfuric acid, and 5 ml. of α-toluenethiol which was prepared in the same manner as previously described. After the reaction mixture had been worked up, the residue gave 70.0 g. of crude product when passed through a thin-film molecular still at *ca.* 60° (0.1 mm.). The infrared spectrum indicated a mixture of the acetylenic sulfide Xb and the product. Distillation yielded 62.5 g. (78% considering recovered starting material) of IIb: b.p. 98° (0.03 mm.); 1.5628; d^{25}_4 1.095; ν_{max} (cm.$^{-1}$) C=O 1720 (s).

Anal. Calcd. for $C_{15}H_{20}OS$: C, 72.50; H, 8.12; S, 12.90. Found: C, 72.51; H, 8.18; S, 13.14.

The **2,4-dinitrophenylhydrazone** from 500 mg. of the ketone after crystallization from ethanol–ethyl acetate yielded 550 mg. (64%) of product as fine red-orange crystals, m.p. 185–186° dec.

Anal. Calcd. for $C_{21}H_{24}N_4O_4S$: C, 58.86; H, 5.65; N, 13.08. Found: C, 58.71; H, 5.34; N, 13.35.

Product IIb was also obtained from benzyl 1-ethynylcyclohexyl sulfide by heating at 75° (nitrogen) with a mixture of 1 ml. of α-toluenethiol, 25 ml. of glacial acetic acid, 0.64 g. of mercuric acetate, and 0.50 ml. of concentrated sulfuric acid. The carbonaceous mixture was allowed to cool slowly to room temperature and then was stirred for 24 hr. The reaction mixture was worked up in the usual manner and yielded 1.1 g. of starting material, b.p. 70–85° (0.05 mm.), and 3.0 g. (80%) of IIb, b.p. 100–102° (0.04 mm.), identical with that above prepared from 1-ethynylcyclohexanol (Ib) (infrared spectrum).

3-(Benzylthio)-3-methyl-2-pentanone (IIc).—By a procedure virtually identical with those for IIa and b, IIc (78.0 g.) was obtained in a 73% yield from 49.0 g. (0.50 mole) of 3-methyl-1-pentyn-3-ol (Ic): b.p. 86–88° (0.04 mm.); $n^{20}D$ 1.5470; d^{25}_4 1.027; ν_{max} (cm.$^{-1}$) C=O 1720 (s). If mercuric acetate is omitted, the yield of IIc is 36%.

Anal. Calcd. for $C_{13}H_{18}OS$: C, 70.23; H, 8.16; S, 14.42. Found: C, 70.44; H, 8.25; S, 14.52.

3-(Benzylthio)-3-ethyl-2-pentanone (IId).—From 56.0 g. (0.50 mole) of 3-ethyl-1-pentyn-3-ol (Id) and 62.0 g. (0.50 mole) of α-toluenethiol was obtained 41.0 g. of IId (66% considering recovered starting material): b.p. 82–84° (0.06 mm.); $n^{25}D$ 1.5391; d^{25}_4 1.080; ν_{max} (cm.$^{-1}$) C=O 1720 (s).

Anal. Calcd. for $C_{14}H_{20}OS$: C, 71.13; H, 8.53; S, 13.57. Found: C, 71.33; H, 8.13; S, 13.36.

2-(Benzylsulfonyl)-2-methylpropanoic Acid.—A solution of 15.0 g. (0.072 mole) of IIa in 10 ml. of methanol was added to *ca.* 500 ml. of potassium hypochlorite solution.[14] The resulting mixture was heated to 70° and stirred for 3 hr. The excess hypochlorite was destroyed by the addition of sodium bisulfite until the solution did not give a positive test with starch–iodide paper. The solution was made strongly acidic with the addition of 60 ml. of concentrated hydrochloric acid and was extracted with ether. The ether was washed with 10% sodium hydroxide solution. The basic extracts were combined and made strongly acidic with concentrated hydrochloric acid and re-extracted with ether. The combined ether extractions were dried over anhydrous sodium sulfate and, after filtration, evaporated to yield 12.2 g. (68% crude) of colorless crystals. Recrystallization of this crude material from cyclohexane yielded 10.0 g. (57%) of colorless crystals, m.p. 119–120°, lit.[15] m.p. 124°.

Anal. Calcd. for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82; S, 13.24. Found: C, 54.50; H, 5.65; S, 13.28.

A mixture of 2.00 g. (8.20 mmoles) of 2-(benzylsulfonyl)-2-methylpropanoic acid and 10 ml. of thionyl chloride was heated under reflux for 0.5 hr. and was poured into 40 ml. of ice-cold concentrated ammonium hydroxide. The crude material was recrystallized from cyclohexane to yield 1.60 g. (80%) of **2-(benzylsulfonyl)-2-methylpropanamide** as white, flaky crystals, m.p. 115–116°.

Anal. Calcd. for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; S, 13.29. Found: C, 54.96; H, 6.32; S, 13.28.

S-1,1-Dimethylacetonyl Thioacetate (XIII).—To a mixture of 37.0 g. (0.35 mole) of anhydrous sodium carbonate in 100 ml. of absolute ethanol, 25.0 g. (0.33 mole) of thioacetic acid dissolved in an equal volume of ethanol was added dropwise over a period of 20 min., and the solution was heated to reflux temperature. A solution of 55.0 g. (0.33 mole) of 3-bromo-3-methyl-2-butanone (XII)[13] in 50 ml. of ethanol was added dropwise over a period of 0.5 hr. After the mixture had been refluxed for 2 hr., it was cooled, and the flask was fitted for distillation. Thiophene-free benzene (600 ml.) was added, and the mixture was filtered. After the water, ethanol, and benzene were removed by azeotropic distillation of the filtrate through a helice-packed column (12 mm. × 15 cm.), the residue yielded 25.6 g. (49%) of product as a pale yellow oil: b.p. 56–57° (1.0 mm.); $n^{20}D$ 1.4779; d^{25}_4 1.051; ν_{max} (cm.$^{-1}$) C=O 1710 (s), CH_3COS 1695 (s).

The **2,4-dinitrophenylhydrazone** was obtained as yellow-orange crystals after recrystallization from ethanol and water, m.p. 139–141°.

Anal. Calcd. for $C_{13}H_{16}N_4O_5S$: C, 45.87; H, 4.74; N, 16.46. Found: C, 45.77; H, 4.45; N, 16.40.

3-(Benzylthio)-3-methyl-2-butanone Oxime (IIIa).—A mixture of 10.6 g. (0.05 mole) of 3-(benzylthio)-3-methyl-2-butanone

(13) This compound was prepared by the method of Favorsky in 75% yields [A. Favorsky, *J. prakt. Chem.*, [2] **88**, 660 (1913)].

(14) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1962, p. 441.

(15) Y. Iskander and R. Tewfik, *J. Chem. Soc.*, 2050 (1951).

(IIa), 7.08 g. (0.10 mole) of hydroxylamine hydrochloride, and 20 ml. of pyridine was stirred for 13 hr. at room temperature. The cloudy mixture then was poured into 50 ml. of 10% hydrochloric acid and was extracted with ether (three 50-ml. portions). The combined ether extracts were washed with two 50-ml. portions of saturated sodium chloride solution. The ether solution was dried over anhydrous magnesium sulfate and was evaporated under reduced pressure to give 11.8 g. of crude oxime, m.p. 72–76°, which was recrystallized from 110 ml. of 45% aqueous ethanol to yield 10.0 g. (88%) of colorless crystals: m.p. 79–80°; ν_{max} (cm.$^{-1}$) C=NOH 3300(s).

Anal. Calcd. for $C_{12}H_{17}NOS$: C, 64.53; H, 7.69; S, 14.39. Found: C, 64.81; H, 7.68; S, 14.18.

1-(Benzylthio)cyclohexyl Methyl Ketone Oxime (IIIb).—By the same method employed for IIIa, 43.0 g. (0.17 mole) of IIb yielded 41.0 g. of a pale yellow oil, which crystallized upon standing overnight; recrystallization from methanol–water gave 40.0 g. (88%) of needle-like crystals: m.p. 126–127°; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) C=NOH 3230 (s).

Anal. Calcd. for $C_{15}H_{21}NOS$: C, 68.40; H, 8.04; S, 12.17. Found: C, 68.55; H, 7.75; S, 12.10.

3-(Benzylthio)-3-methyl-2-pentanone Oxime (IIIc).—From 10.0 g. (0.045 mole) of IIc, was obtained an oil which upon distillation yielded 9.20 g. (82%) of IIIc: b.p. 110–116° (0.03 mm.); $n^{25}D$ 1.5728; d^{25}_4 1.225; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) C=NOH 3280 (s).

Anal. Calcd. for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; S, 13.51. Found: C, 65.94; H, 7.99; S, 13.58.

3-(Benzylthio)-3-ethyl-2-pentanone Oxime (IIId).—In the same way, 24.0 g. (0.089 mole) of the ketone IId, yielded 20.2 g. (62%) of the oxime as a pale yellow oil: b.p. 125–128° (0.1 mm.); $n^{25}D$ 1.5552; d^{25}_4 1.225; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) C=NOH 3260 (s).

Anal. Calcd. for $C_{14}H_{21}NOS$: C, 65.89; H, 8.42; N, 5.57. Found: C, 66.06; H, 8.26; N, 5.91.

2-Amino-3-(benzylthio)-3-methylbutane (VIIa).—A solution of 15.0 g. (0.67 mole) of IIIa in 50 ml. of anhydrous ether was added to a stirred slurry of 8.40 g. (0.22 mole) of lithium aluminum hydride in 120 ml. of anhydrous ether at such a rate to maintain a slow reflux.[16] The mixture was heated under reflux for 3 hr., cooled in an ice bath, and decomposed by the slow addition of 20 ml. of water. This was followed by the addition of a solution consisting of 250 ml. of 20% potassium sodium tartrate and 50 ml. of 10% sodium hydroxide. The resulting slurry was placed in a continuous ether extractor and extracted for 24 hr. The ether extract was dried over anhydrous potassium carbonate and concentrated *in vacuo*. The resulting oil, when treated with 40 ml. of 10% hydrochloric acid solution, yielded, after filtration, 10.2 g. of starting material, m.p. 68–74°. The acidic filtrate was extracted with ether, then was made strongly basic with a 50% sodium hydroxide solution, and was re-extracted with ether. The ether, after drying over sodium sulfate, was removed under reduced pressure. Distillation of the residue yielded 3.40 g. (88% considering recovered starting material) of VIIa as a pale yellow oil: b.p. 81–83° (0.08 mm.); ν_{max} (cm.$^{-1}$) NH_2 3360 (w), 3300 (w).

Dry hydrogen chloride was passed into a solution of 1.00 g. (4.80 mmoles) of VIIa in 20 ml. of anhydrous ether, and the 2-amino-3-(benzylthio)-3-methylbutane hydrochloride which was precipitated was collected by filtration, yield 900 mg. (77%), m.p. 111–112°.[17]

Anal. Calcd. for $C_{12}H_{20}ClNS$: C, 58.63; H, 8.20; S, 13.05. Found: C, 58.36; H, 8.17; S, 13.21.

A mixture of 500 mg. (2.40 mmoles) of the amine VIIa, 10 ml. of pyridine, and 0.5 ml. of benzoyl chloride was allowed to stand at room temperature overnight and poured into 100 ml. of ice water with vigorous stirring. The crude **2-benzoylamino-3-(benzylthio)-3-methylbutane**, m.p. 98–102°, was recrystallized twice from cyclohexane to yield 650 mg. (86%) of colorless crystals, m.p. 108–109°.

Anal. Calcd. for $C_{19}H_{23}NOS$: C, 72.80; H, 7.39; S, 10.23. Found: C, 72.54; H, 7.24; S, 10.19.

2-Amino-3-(benzylthio)-3-methylpentane (VIIc).—By the same procedure employed for VIIa, 34.0 g. (0.14 mole) of the oxime IIIc yielded 8.00 g. (36%) of the amine: b.p. 87–90° (0.06 mm.); $n^{25}D$ 1.5032; ν_{max} (cm.$^{-1}$) NH_2 3340 (w), 3290 (w).

Anal. Calcd. for $C_{13}H_{21}NS$: C, 69.90; H, 9.48; S, 14.36. Found: C, 70.22; H, 9.45; S, 14.57.

2-Amino-3-(benzylthio)-3-ethylpentane (VIId).—As for VIIa, 16.0 g. (0.064 mole) of the oxime IIId yielded 7.1 g. (47%) of VIId as a pale yellow yellow oil: b.p. 60–65° (0.05 mm.); n^{25}_4 1.5304; d^{25}_4 1.003; ν_{max} (cm.$^{-1}$) NH_2 3320 (w), 3240 (w).

Anal. Calcd. for $C_{14}H_{23}NS$: C, 68.83; H, 9.76; S, 15.51. Found: C, 68.56; H, 9.63; S, 15.41.

3-Mercapto-3-methyl-2-butanone Oxime (IVa).—To a solution of 55.0 g. (0.25 mole) of IIIa in 1 l. of liquid ammonia was added with stirring small pieces of sodium metal until a permanent blue color was developed (14.5 g., 0.63 g.-atom, of sodium was required). The excess sodium was destroyed by the addition of a small piece of Dry Ice. The ammonia was permitted to evaporate overnight under a nitrogen atmosphere to give a tan-colored residue. The residue was dissolved in 500 ml. of water and was extracted with ether. The aqueous phase was made acidic with concentrated hydrochloric acid and adjusted to pH 7 with sodium carbonate. The oily, cloudy solution was cooled overnight in a refrigerator to yield 30.0 g. of crude material, m.p. 50–55°. Recrystallization from methanol–water yielded 26.0 g. (73%) of IVa as pale green crystals: m.p. 55–56°; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) C=NOH 3300 (s), SH 2560 (w).

Anal. Calcd. for $C_5H_{11}NOS$: C, 45.08; H, 8.33; S, 24.07. Found: C, 45.03; H, 8.36; S, 24.10.

1-Mercaptocyclohexyl Methyl Ketone Oxime (IVb).—By the same procedure employed for IVa, 46.0 g. (0.17 mole) of the oxime IIIb yielded 19.0 g. of crude product. Recrystallization from methanol–water gave 17.1 g. (57%) of colorless crystals: m.p. 99–100°; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) C=NOH 3280 (s), SH 2560 (w).

Anal. Calcd. for $C_8H_{15}NOS$: C, 55.46; H, 8.73; S, 18.50. Found: C, 55.57; H, 8.46; S, 18.41.

3-Mercapto-3-methyl-2-pentanone Oxime (IVc).—As for IVa, 31.0 g. (0.13 mole) of IIIc yielded 14.2 g. (74%) of IVc as a colorless oil: b.p. 69–70° (0.05 mm.); $n^{25}D$ 1.4921; d^{25}_4 0.993; $\nu_{max}^{10\%\ CCl}$ (cm.$^{-1}$) C=NOH 3280 (s), SH 2560 (w).

Anal. Calcd. for $C_6H_{13}NOS$: C, 48.94; H, 8.89; S, 21.78. Found: C, 48.75; H, 8.74; S, 21.60.

3-Mercapto-3-ethyl-2-pentanone Oxime (VId).—As for IVa, 50.0 g. (0.20 mole) of IIId yielded 18.0 g. (55%) of the product: b.p. 68–69° (0.06 mm.); $n^{25}D$ 1.5002; d^{25}_4 1.045; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) C=NOH 3240 (s), SH 2550 (w).

Anal. Calcd. for $C_7H_{15}NOS$: C, 52.14; H, 9.37; S, 19.88. Found: C, 52.15; H, 9.10; S, 20.10.

3-Amino-2-methyl-2-butanethiol Hydrochloride (Va).—A solution of 10.0 g. (0.075 mole) of IVa in 150 ml. of anhydrous ether was added at such a rate as to maintain a slow rate of reflux to a stirred slurry of 3.00 g. (0.079 mole) of lithium aluminum hydride in 50 ml. of ether. After the mixture had been heated under reflux for 18 hr., it was decomposed by the dropwise addition of 20 ml. of water. The solution was acidified with dilute sulfuric acid, and the pH was adjusted to 8 with sodium carbonate. After the addition of 100 ml. of a 25% Rochelle salt solution, the slurry was placed in a continuous extractor and extracted for 24 hr. with ether. The ether extract was dried over potassium carbonate and, after filtration, dry hydrogen chloride was passed into the solution. The hydrochloride was collected by filtration to yield 6.50 g. (73%), m.p. 235–236°.

Anal. Calcd. for $C_5H_{14}ClNS$: C, 38.57; H, 9.06; Cl, 22.77; S, 20.59. Found: C, 38.55; H, 8.96; Cl, 22.70; S, 20.82.

A mixture of 5 ml. of cyclohexanone and 200 mg. (1.3 mmoles) of Va hydrochloride was heated until a homogeneous solution was obtained. Cooling yielded 250 mg. (76%) of **4′,5′,5′-trimethylspiro[cyclohexane-1,2′-thiazolidine] hydrochloride** as fine, colorless, needle-like crystals, m.p. 262–264°.

Anal. Calcd. for $C_{11}H_{22}ClNS$: C, 56.02; H, 9.40; Cl, 15.06. Found: C, 56.22; H, 9.22; Cl, 14.88.

Desulfurization of 3-Amino-2-methyl-2-butanethiol Hydrochloride (Va) to 2-Amino-3-methylbutane Hydrochloride (VIa).—To a mixture of one teaspoon of Raney nickel (W-2, 2 days old) in 15 ml. of water was added 330 mg. (2.12 mmoles) of Va.[18] The mixture was stirred for 3 days at room temperature and filtered, after which the Raney nickel was washed with 100 ml. of water and the washings were added to the filtrate. The combined filtrates were acidified with 0.1 equiv. of 20% sulfuric acid and steam distilled until 80 ml. of distillate was collected. This

(16) D. R. Smith, M. Maienthal, and J. Tipton, *J. Org. Chem.*, **17**, 294 (1952).

(17) In this instance and subsequently, analytically pure hydrochlorides were obtained by recrystallization from ethanol or by merely washing with ether.

(18) R. Chatterjee, A. H. Cook, I. Heilbron, and A. L. Levy, *J. Chem. Soc.*, 1337 (1948).

distillate was discarded, and the residue then was made basic with 0.2 equiv. of 20% sodium hydroxide, after which the mixture again was steam distilled until 70 ml. of distillate possessing an amine-like odor had been collected. The distillate was extracted with ether (three 50-ml. portions) and, after the ether extracts had been dried over anhydrous magnesium sulfate, anhydrous hydrogen chloride was introduced to yield 88 mg. (33%) of 2-amino-3-methylbutane hydrochloride (VIa): m.p. 182–184°; a mixture melting point with an authentic specimen[19] showed no depression; ν_{max}^{KBr} (cm.$^{-1}$) $CNH_3^+Cl^-$ 1605 (m), 2000 (m); identical with that of the authentic sample.

Anal. Calcd. for $C_5H_{14}ClN$: C, 48.58; H, 11.42; Cl, 28.69. Found: C, 48.38; H, 11.33; Cl, 28.84.

Also, a **p-nitrobenzoyl derivative** was prepared from 26 mg. (0.23 mmole) of 2-amino-3-methylbutane hydrochloride (VIa) and 43 mg. (0.25 mmole) of *p*-nitrobenzoyl chloride: yield 7 mg. (14%) after recrystallization from cyclohexane; m.p. 119–120°, lit.[20] m.p. 114–115°; a mixture melting point with a sample prepared from the alternate route showed no depression; ν_{max}^{KBr} (cm.$^{-1}$) NH 3280 (s), CONH 1642 (s); identical with that of the authentic sample.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 60.99; H, 6.83; N, 11.86. Found: C, 61.02; H, 7.12; N, 12.08.

1-(1-Aminoethyl)cyclohexanethiol Hydrochloride (Vb).—By the same procedure employed for Va, 35.0 g. (0.20 mole) of IVb yielded 22.0 g. (69%) of Vb as a colorless oil, b.p. 85–90° (0.06 mm.), which solidified upon cooling, m.p. 84–88°. Dry hydrogen chloride was passed through 20 ml. of anhydrous ether solution containing 1.00 g. (6.30 mmoles) of Vb to precipitate 960 mg. (77%) of the amine hydrochloride, m.p. 135–136°.

Anal. Calcd. for $C_8H_{18}ClNS$: C, 49.11; H, 9.27; Cl, 18.11. Found: C, 48.95; H, 9.39; Cl, 17.93.

A mixture of 1.00 g. (5.10 mmoles) of Vb and 10 ml. of cyclohexanone was heated until a homogeneous solution was obtained. After cooling to room temperature, the reaction mixture was poured slowly into 50 ml. of anhydrous ether to precipitate 750 mg. (53%) of **4′-methyldispiro[cyclohexane-1,2′-thiazolidine-5′,1″-cyclohexane] hydrochloride** as a white hygroscopic material, m.p. 155–157°.

Anal. Calcd. for $C_{14}H_{26}ClNS$: C, 60.95; H, 9.51; Cl, 12.86. Found: C, 60.62; H, 9.46; Cl, 12.65.

In like manner, 1.00 g. (5.10 mmoles) of Vb and 10 ml. of benzaldehyde gave 825 mg. (56%) of **4′-methyl-2-phenylspiro-[cyclohexane-1,5′-thiazolidine] hydrochloride**, m.p. 89–90°.

(19) A sample of this substance was prepared from 2-amino-3-methylbutane obtained by hydrogenation of 3-methyl-2-butanone oxime [D. C. Iffland and T. Yen, *J. Am. Chem. Soc.*, **76**, 4180 (1954)].

(20) A. Michael and G. H. Carlson, *J. Org. Chem.*, **4**, 169 (1939).

Anal. Calcd. for $C_{15}H_{22}ClNS$: C, 63.70; H, 7.49; Cl, 12.54. Found: C, 63.41; H, 7.76; Cl, 12.83.

2-Amino-3-methyl-3-pentanethiol (Vc).—As for Va, 15.0 g. (0.10 mole) of IVc yielded 6.50 g. (66%) of Vc: b.p. 55–58° (0.06 mm.); $n^{25}D$ 1.5003; d^{25}_4 0.998; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) NH_2 3340 (w), 3290 (w), SH 2560 (w).

Anal. Calcd. for $C_6H_{15}NS$: C, 54.08; H, 11.35; N, 10.15. Found: C, 53.95; H, 11.61; N, 10.23.

3-Mercapto-3-ethyl-2-aminopentane (Vd).—As for Va, 8.00 g. (0.05 mole) of IVd yielded 4.50 g. (62%) of IXd: b.p. 40–45° (0.03 mm.); $n^{25}D$ 1.5149; d^{25}_4 1.015; $\nu_{max}^{10\%\ CCl_4}$ (cm.$^{-1}$) NH_2 3350 (w), 3280 (w), SH 2560 (w).

Anal. Calcd. for $C_7H_{14}NS$: C, 57.09; H, 11.64; S, 21.77. Found: C, 57.28; H, 11.51; S, 22.04.

The **hydrochloride** was formed from 1.00 g. (6.8 mmoles) of Vd in 25 ml. of anhydrous ether, yield 990 mg. (79%), m.p. 175–176°, which was placed in a vacuum desiccator immediately following the filtration.

Anal. Calcd. for $C_7H_{18}ClNS$: C, 45.76; H, 9.87; Cl, 19.28. Found: C, 45.92; H, 9.94; Cl, 19.09.

From 1.00 g. (5.40 mmoles) of Vd and 10 ml. of cyclohexanone was obtained **5′,5′-diethyl-4′-methylspiro[cyclohexane-1,2′-thiazolidine] hydrochloride** as colorless crystals, m.p. 232–234°.

Anal. Calcd. for $C_{13}H_{26}ClNS$: C, 59.16; H, 9.57; S, 12.16. Found: C, 59.02; H, 9.46; S, 12.25.

From 1.00 g. (5.40 mmoles) of the Vd and 10 ml. of benzaldehyde was obtained **5,5-diethyl-4-methyl-2-phenylthiazolidine hydrochloride**, m.p. 220–222°.

Anal. Calcd. for $C_{14}H_{22}ClNS$: C, 61.88; H, 8.13; S, 11.80. Found: C, 62.01; H, 8.03; S, 11.84.

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The Effects of Metallic Ions on the Autoxidation of Phenylhydroxylamine to Azoxybenzene in Methanol

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The effects of metallic ions on the autoxidation of phenylhydroxylamine have been studied kinetically by estimating consumed oxygen. Cupric ion showed the strongest acceleration, some other ions had weaker effects in the order ferric > manganous > nickel ≅ chromium > cobaltous ion, while stannous and silver ions have no effect. The kinetics was studied more extensively on cupric ion catalysis. The rate was expressed as follows (p = partial pressure of oxygen): $v = k_M[C_6H_5NHOH]p + k_C[C_6H_5NHOH][Cu^{+2}]p$. The rate was retarded by the addition of a high concentration of methyl methacrylate or styrene but not by the addition of hydroquinone or diphenylamine. A mechanism involving the coupling of a radical, $C_6H_5\dot{N}OH$, produced from a complex between phenylhydroxylamine and cupric ion is postulated and discussed.

In our previous paper[1] it has been reported that the autoxidation of phenylhydroxylamine to form azoxybenzene in methanol follows the stoichiometry in eq. 1.

$$4C_6H_5NHOH + O_2 \longrightarrow 2C_6H_5NO{=}NC_6H_5 + 4H_2O \quad (1)$$

The rate was expressed as

$$v = k[C_6H_5NHOH]p$$

where p is the partial pressure of oxygen and the reaction was accelerated by base and retarded by acid, but was not affected by the addition of radical initiators or inhibitors.

(1) Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, *J. Am. Chem. Soc.*, **86**, 3854 (1964).