a determination for percentage hydroxyl indicated two hydroxyl groups in the molecule.

1,2-Cyclohexanedione Phenylosazone (IX).—Compound VIII (1.0 g.) was suspended in a solution of 3 g. of glacial acetic acid in 20 ml. of water and 5.0 g. of phenylhydrazine was added slowly with stirring. An exothermic reaction took place with the formation of a yellow solid. The reaction mixture was then heated gently on a steam-bath for 10 minutes, cooled and filtered. The product was recrystallized from ethanol; yield 2.2 g. (92%), m.p. 151–152° dec.

Anal. Calcd. for $C_{18}H_{20}N_4$: C, 73.94; H, 6.91; N, 19.16. Found: C, 73.61; H, 6.91; N, 19.24.

Treatment of 1,2-cyclohexanedione (X)[9] with phenylhydrazine in acetic acid in the same manner as VIII was treated also gave the phenylosazone IX[13] (m.p. 152–153° dec.). The infrared spectra of the two samples of the phenylosazone IX, which were prepared from VIII and the diketone X, were identical when run as Nujol mulls. The strong bands in these spectra appeared at 6.27, 6.42, 6.67, 8.05 and 13.35 μ.

6-Oxocyclohexen-1-yl Benzoate (XI).—Compound VIII (2.0 g.) was suspended in 12 ml. of dry pyridine and 3.0 ml. of benzoyl chloride was added dropwise with stirring. An exothermic reaction occurred with the formation of a white precipitate. The mixture was then heated on a steam-bath for 5 minutes, cooled to room temperature, and poured into 25 ml. of ice-water with stirring. A yellow oily mass precipitated. The supernatant liquid was decanted, and the yellow mass was treated twice with 20 ml. of 5% sodium carbonate solution. The residue was then dissolved in 10 ml. of pyridine and poured on ice. The precipitate was filtered and recrystallized from isopropyl alcohol; yield 2.5 g. (70%), m.p. 89–90°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59; mol. wt., 216. Found: C, 71.87; H, 5.76; mol wt., 221 (in acetone by the Menzies ebullioscopic method).

When the diketone X[9] was caused to react with benzoyl chloride in pyridine in the same manner as compound VIII was treated, the resulting product melted at the same temperature as the benzoate XI which was prepared from VIII (89–90°). A mixed melting point of the two substances gave no depression. Also, the infrared spectra of the two materials ($CHCl_3$ solution) were identical and fully agreed with the postulated structure. The monoconjugated ketone functional band appeared at 5.93 μ. A band at 5.78 μ indicated an aryl ester. Bands at 6.26 and 6.68 μ indicated the phenyl ring.

1,2-Cyclohexanedione (X) from VIII.—Compound VIII (1.0 g.) was stirred and heated at 60° in 15 ml. of 10% hydrochloric acid for 3 hours. The resulting yellow-green solution was cooled, saturated with sodium chloride, and extracted with ether. After drying the ether extract over sodium sulfate and evaporating the ether, there remained 0.6 g. of a yellow-green oil which contained about 80% of the diketone X based on infrared analysis (2% $CHCl_3$ solution) as compared with the spectrum of a pure sample of the diketone X.[9] This represents a yield of about 53%.

The infrared spectrum of X in chloroform solution shows that the compound exists to a considerable extent in its monoenolic form. Strong sharp monoconjugated ketone and hydroxyl bands appear at 5.99 and 2.89 μ, respectively.

Nitric Acid Oxidation of VIII.—Fifteen ml. of 35% nitric acid was heated to 80° with stirring. A small quantity of VIII was added, whereupon the reaction mixture turned yellow-green and then dark red-brown. The exothermic reaction, which liberated NO_2 fumes, caused the temperature to rise to 100°. This temperature was maintained while a total of 2.0 g. of compound VIII was slowly added. After all of VIII was introduced, the reaction solution was heated at 100° for 15 minutes. The solution was then submitted for chromatographic analysis[8] in order to determine the acidic components which were formed. The analysis revealed that 0.81 g. of succinic acid, 0.25 g. of glutaric acid and 0.08 g. of adipic acid were formed.

Acknowledgment.—We wish to thank Dr. R. H. Munch, Dr. W. E. Koerner, Dr. W. R. Deason, Mr. O. E. Kinast, Mr. L. O. Jessen and Mr. A. Bybell for their assistance with the numerous infrared analyses and other analytical data. We are also indebted to Dr. N. J. Leonard, Dr. R. B. Woodward and Dr. Robert Levine for valuable advice and to Dr. O. J. Weinkauff, Associate Director of Research, whose interest and coöperation made this work possible.

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(13) No reference could be found of the preparation of IX directly from the diketone X; however, H. Sen and S. K. Ghosh, *Quart. J. Indian Chem. Soc.*, **4**, 477 (1927), reported the melting point of IX to be 153–154° when prepared from 1,2-cyclohexanedione monophenylhydrazone. Other references to IX give melting points which range from 150 to 154°.

[CONTRIBUTION FROM THE PHARMACEUTICAL INSTITUTE, MEDICAL FACULTY, UNIVERSITY OF KYUSHU]

Preparation and Stereochemistry of *dl*-2-Aminocyclohexane Thiols[1]

BY TANEZO TAGUCHI AND MASAHARU KOJIMA

RECEIVED AUGUST 2, 1955

dl-trans-2-Aminocyclohexanethiol was obtained from either *dl-trans-* or *dl-cis*-2-benzoylaminocyclohexyl tosylate with, respectively, retention or inversion of configuration by treatment with thiourea in absolute ethanol, and alkaline hydrolysis of the resulting *dl-trans*-2-benzoylaminocyclohexylisothiuronium tosylate. The mechanisms and assignment of configurations are discussed. The mechanism is supported by the fact that *meso-cis*-cyclohexenimine upon treatment with thiobenzoic acid gives the N-benzoyl derivative of the same *dl*-2-aminocyclohexanethiol. *dl-cis*-2-Aminocyclohexanethiol was obtained by fusion of *dl-trans*-2-thiobenzoylaminocyclohexanol with phosphorus pentoxide, followed by hydrolysis. Fusion of *dl-cis*-2-phenyl-4,5-cyclohexanoöxazoline with phosphorus pentasulfide gave a racemic 2-phenyl-4,5-cyclohexanothiazoline which was converted to *dl-trans*-2-aminocyclohexyl thiobenzoate hydrochloride by treatment with hydrochloric acid and thus designated as *trans*. Fusion of *dl-trans-* or *dl-cis*-2-benzoylaminocyclohexanol with phosphorus pentasulfide resulted in mixtures of *dl-trans-* and *dl-cis*-2-phenyl-4,5-cyclohexanothiazolines. The *cis*-thiazoline was much more stable to mineral acid than the *trans* isomer.

It seemed valuable to seek information on the stereochemistry of aminothiols, particularly in comparison with diastereoisomeric aminoalcohols. For this reason an investigation of the 2-aminocyclonexanethiols was undertaken.

Treatment of either the *trans*-I, or *cis*-II form of *dl*-2-benzoylaminocyclohexyl tosylate with thiourea in absolute ethanol gave a *dl*-2-benzoylaminocyclohexylisothiuronium tosylate, which upon alkaline hydrolysis yielded a *dl*-2-benzoylaminocyclohexanethiol of m.p. 161–162° (V). This suggests that the reaction proceeds by different mechanisms for the *cis* and the *trans* starting material.

It is well known that substitution reactions of the *trans* isomer I proceed with a neighboring group effect of the acyl group through the intermediate *dl-cis*-2-phenyl-4,5-cyclohexanoöxazoline (IIIa), while

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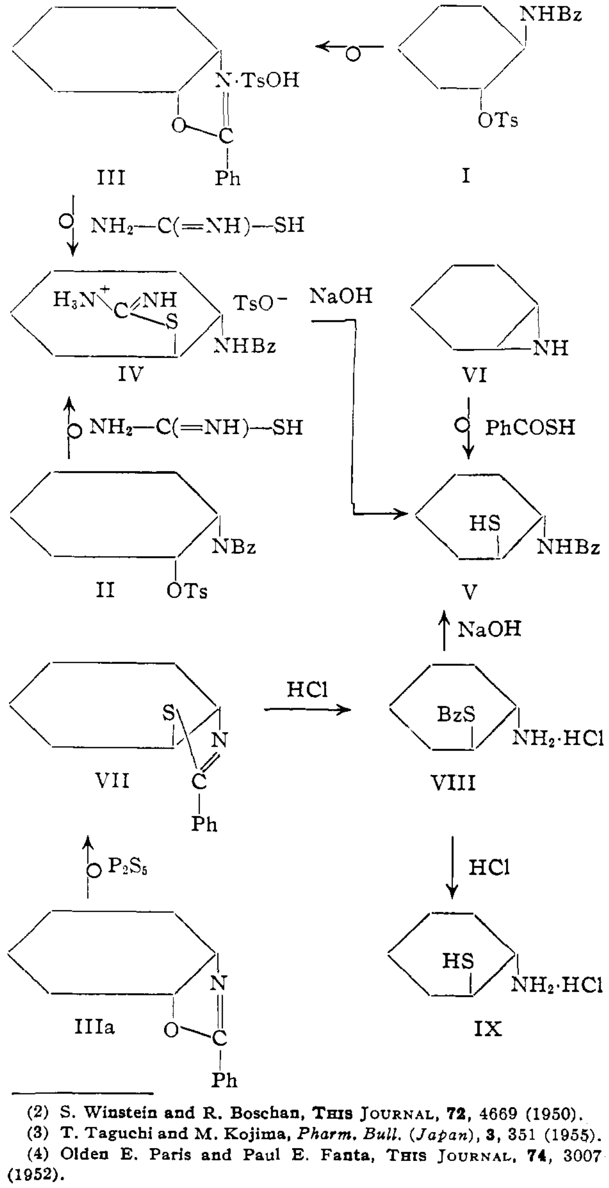
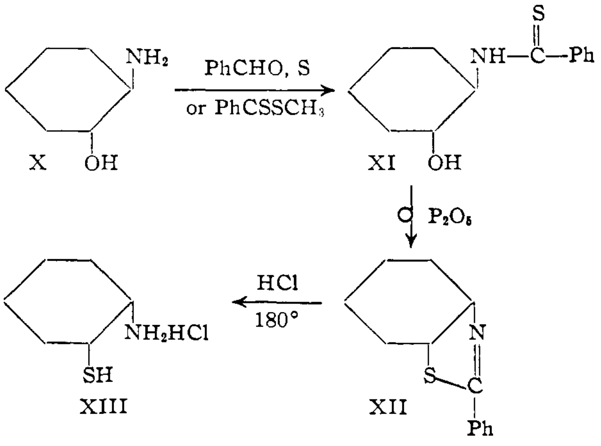
(1) Studies in Stereochemistry, VII.

there is no such effect with the *cis* isomer II.[2,3] Thus, it may be considered that the *trans* compound I gives rise by the anichimeric property of the benzoyl group to the *dl-cis*-oxazoline III, which is then attacked by thiourea from the back side at C_5 giving *dl-trans*-2-benzoylaminocyclohexylisothiuronium tosylate (IV) with over-all retention of configuration (I → III → IV). On the other hand, the *cis* compound II gives IV by simple SN2 reaction with inversion. On this basis the racemic isothiuronium tosylate formed in the above-mentioned reactions was designated as *trans*. Formation of the *dl-cis*-oxazoline III as the intermediate is further supported by the fact that heating this compound with thiourea and ethanol also gives the *dl-trans* compound IV. Additional evidence for the *trans* configuration of IV is provided by the fact that *meso-cis*-cyclohexenimine gives the same epimer IV on treatment with thiobenzoic acid; it has been generally recognized that the *cis*-imine opens in the *trans* manner.[4]



The *dl*-N-benzoyl thiol V is also designated as *trans*, because the formation reaction from the *dl-trans*-isothiuronium salt (IV) involves no breaking of bonds to ring atoms. This compound V was also obtained by fusion of the *dl-cis*-oxazoline IIIa with phosphorus pentasulfide to give a *dl*-2-phenyl-4,5-cyclohexanothiazoline (VII), followed by treatment with hydrochloric acid to give *dl-trans*-2-aminocyclohexyl thiobenzoate hydrochloride (VIII), and treatment of VIII with sodium hydroxide. Since in the reaction sequence III → VII → VIII → V there seems to be no possibility of inversion except in III → VII, the thiazoline VII is designated as *trans*. *dl-trans*-2-Aminocyclohexanethiol hydrochloride (IX) was obtained by boiling the S-benzoyl hydrochloride VIII in 10% aqueous hydrochloric acid; IX is also considered to be *trans* because the reaction involves no breaking of bonds to ring atoms. *dl-cis*-2-Phenyl-4,5-cyclohexanothiazoline (XII) was obtained by treatment of *dl-trans*-2-aminocyclohexanol (X) with benzaldehyde and sulfur or with methyl dithiobenzoate, and fusion of the resulting *dl-trans*-2-thiobenzoylaminocyclohexanol (XI) with phosphorus pentoxide. This result is analogous to the formation of the *dl-cis*-oxazoline III from the O-analog of XI by similar treatment and suggests that the *cis*-thiazoline XII might be derived from replacement of the OH group by the S of the thiobenzoyl group by SN2 reaction at C_1. The *cis*-thiazoline XII was, in contrast to the *trans*-isomer, so stable that boiling in concentrated acid did not affect it. The thiazoline ring was opened to give *dl-cis*-aminocyclohexanethiol hydrochloride and benzoic acid only by heating with hydrochloric acid at 180° in a sealed tube.



Fusion of *dl-trans*-2-benzoylaminocyclohexanol (XIV) with phosphorus pentasulfide gave a mixture of the *dl-trans*- and *cis*-thiazolines VII and XII which could be separated by conversion to picrates and recrystallization from methanol. A more convenient method of separation utilizes the difference in stability of the two isomers to 5% aqueous hydrochloric acid; the *trans* isomer VII is converted to the hydrochloride VIII by heating, while the *cis* isomer is unchanged. These are easily separated by difference of solubility in water. Yields calculated on the basis of this separation method were 9% of the *trans* isomer and 52% of the *cis* isomer. Similar treatment of *dl-cis*-2-benzoyla-

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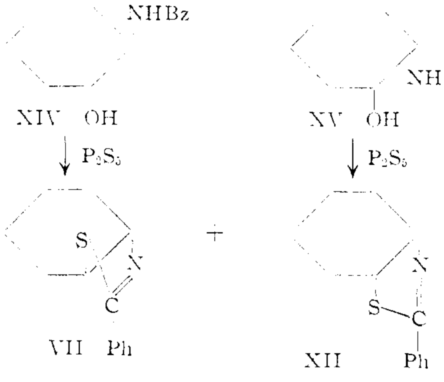
[2] S. Winstein and R. Boschan, This Journal, **72**, 4669 (1950).

[3] T. Taguchi and M. Kojima, *Pharm. Bull.* (*Japan*), **3**, 351 (1955).

[4] Olden E. Paris and Paul E. Fanta, This Journal, **74**, 3007 (1952).

minocyclohexanol (XV) gave 10% *trans*- and 4.5% *cis*-thiazolines. The lower yields in this case were caused by contamination by a reddish gummy material which could not be characterized.



Experimental[5]

dl-trans-**2-Aminocyclohexanol (X)**.—Prepared by usual method, b.p. 105° (10 mm.), m.p. 66–68°, its hydrochloride, m.p. 173°.

dl-trans-**2-Benzoylaminocyclohexanol (XIV)**.—The general method of Leffler and Adams[6] was applied, m.p. 169–170°.

dl-trans-**2-Benzoylaminocyclohexyl Tosylate (I)**: *prepared* by the author's improved procedure reported previously,[7] m.p. 123°.

dl-cis-**2-Benzoylaminocyclohexanol (XV)**: prepared by detosylation[8] of *dl-trans*-N-benzoyl-O-tosylate (I), m.p. 184–185°.

dl-cis-**2-Benzoylaminocyclohexyl Tosylate (II)**: prepared by the author's improved procedure,[3] m.p. 174–175° (listed as 163–165° by McCasland[8] and 162–163° by Winstein[2]).

dl-cis-**2-Phenyl-4,5-cyclohexanoöxazoline (IIIa)** was prepared by the adaptation of Winstein's procedure,[2] m.p. 46–47°, its tosylate III, m.p. 159–160°.

meso-cis-**Cyclohexenimine (VI)**: The procedure of Paris and Fanta[4] was used; m.p. 20°, b.p. 149–150°.

dl-trans-**2-Benzoylaminocyclohexylisothiuronium Tosylate (IV)**. **(a)**.—A mixture of 2.4 g. of *dl-trans*-2-benzoylaminocyclohexyl tosylate (I) and 4 g. of thiourea in 16 ml. of absolute ethanol was refluxed on a water-bath for ten hours. After cooling, the precipitated thiourea was filtered and the ethanolic mother liquor evaporated to dryness. On dissolving the residue in 5 ml. of water, crystals soon appeared. After filtration the crude product weighed 2.5 g., melted at 134–136° dec. and recrystallized from methanol to give colorless cubes of m.p. 138° dec. *Anal.* Calcd. for $C_{20}H_{27}N_3S_2O_4$: C, 54.87; H, 6.22; N, 9.60. Found: C, 54.40; H, 6.34; N, 9.65.

(b).—A mixture of 1 g. of *dl-cis*-2-benzoylaminocyclohexyl tosylate (II) and 1 g. of thiourea in 20 ml. of absolute ethanol was refluxed on a water-bath for 23 hours. The reaction mixture was treated as described under (a) except that the residue from the ethanolic mother liquor was crystallized on addition of 4 ml. of water and 4 ml. of ether. The resulting crystals weighed 0.55 g. and melted at 138° dec. alone and on admixture with the *dl-trans*-isothiuronium tosylate (IV).

(c).—To 1 g. of *dl-cis*-2-phenyl-4,5-cyclohexanoöxazoline tosylate (III) and 1.2 g. of thiourea was added 14 ml. of absolute ethanol and the mixture refluxed on a water-bath for five hours. Working up exactly as in (a) resulted in colorless cubes of m.p. 138° dec. which were identical with the *dl-trans*-isothiuronium tosylate (IV) by a mixed m.p. determination; weight 0.66 g. To the aqueous filtrate from removal of IV was added 8 ml. of water and 5 ml. of 10% aqueous sodium hydroxide. The resulting precipitate, after filtration and recrystallization, melted at 182–183° and was identical with *dl-cis*-2-benzoylaminocyclohexanol; weight 0.22 g.

dl-trans-**2-Benzoylaminocyclohexanethiol (V) (a)**.—One gram of the *dl-trans*-isothiuronium tosylate (IV) in 10 ml. of 10% aqueous sodium hydroxide was boiled for five minutes. To the mixture, after cooling, was added 10 ml. of water and a small amount of undissolved substance was removed by filtration. The filtrate was acidified with 10% aqueous hydrochloric acid and chilled. The precipitate was filtered, 0.5 g., melting at 161–162°. Recrystallization from 50% aqueous ethanol gave colorless needles, m.p. 161–162°, which gave a positive sodium nitroprusside test for the mercapto group. *Anal.* Calcd. for $C_{13}H_{17}NSO$: C, 66.32; H, 7.28; N, 5.95. Found: C, 66.90; H, 6.95; N, 6.26.

(b).—To 0.5 g. of *meso-cis*-cyclohexenimine (VI)[4] dissolved in 4 ml. of benzene was added a solution of 0.7 g. of thiobenzoic acid in 5 ml. of benzene. On standing crystals appeared which were collected; weight 1.05 g. Recrystallization from 50% aqueous ethanol gave colorless needles which showed m.p. 161–162° alone and on admixture with a sample of *dl-trans*-N-benzoylthiol V.

(c).—A small amount of *dl-trans*-2-aminocyclohexylthiobenzoate hydrochloride (VIII) was dissolved in 5% sodium hydroxide and the solution was acidified with 5% aqueous hydrochloric acid. The precipitated crystals were filtered and recrystallized from 50% aqueous ethanol, m.p. 161–162° alone and also on admixture with an authentic sample.

dl-trans-**2-Phenyl-4,5-cyclohexanothiazoline (VII)**.—A well-ground mixture of 3 g. of *dl-cis*-oxazoline (IIIa) and 3 g. of phosphorus pentasulfide was fused at 150–180° in an oil-bath till hydrogen sulfide gas ceased to evolve. On heating in 30 ml. of 10% aqueous sodium hydroxide the fused mass went into solution, leaving an oily layer which was extracted with ether, washed with water and then shaken with 10 ml. of 5% aqueous hydrochloric acid three times. On neutralizing with sodium bicarbonate an oily substance separated. The oily layer was extracted with ether, dried over fused sodium sulfate and evaporated to dryness. The remaining light yellowish oil boiled at 157–159° (3 mm.), melted at 51–52° and yielded 1.92 g.

The picrate when recrystallized from methanol gave yellow needles, m.p. 195–196°. *Anal.* Calcd. for $C_{14}H_{18}N_4SO_7$: C, 51.10; H, 4.06; N, 12.55. Found: C, 51.09; H, 4.06; N, 12.54.

dl-trans-**2-Aminocyclohexyl Thiobenzoate Hydrochloride (VIII)**.—To 1 g. of the *trans*-thiazoline VII was added 5 ml. of 5% aqueous hydrochloric acid and heated on a boiling water-bath for an hour. On cooling, colorless needles precipitated, m.p. 221° dec., weight 0.9 g. Recrystallization from 3% aqueous hydrochloric acid[9] gave colorless needles, m.p. 223° dec. *Anal.* Calcd. for $C_{13}H_{18}NSOCl$: C, 57.42; H, 6.67; N, 5.15. Found: C, 57.39; H, 6.45; N, 5.25. **The picrate** was recrystallized from 70% methanol as yellow needles, m.p. 167–168°. *Anal.* Calcd. for $C_{19}H_{20}N_4SO_8$: N, 12.07. Found: N, 12.34.

dl-trans-**2-Aminocyclohexanethiol Hydrochloride (IX)**.—To 1 g. of the *dl-trans*-S-benzoylaminothiol hydrochloride (VIII) was added 10 ml. of 10% aqueous hydrochloric acid and the mixture boiled for three hours. After cooling, the precipitated benzoic acid was filtered and the mother liquor was evaporated to dryness under reduced pressure. The residue was recrystallized from methanol to give colorless plates, m.p. 225°, weight 0.5 g., which gave a positive sodium nitroprusside test for the mercapto group. *Anal.* Calcd. for $C_6H_{14}SCl$: C, 42.94; H, 8.41; N, 8.35. *Found*: C, 43.15; H, 8.00; N, 8.36.

dl-cis-**2-Phenyl-4,5-cyclohexanothiazoline (XII)**.—One gram of phosphorus pentasulfide and 0.85 g. of *dl-trans*-2-thiobenzoylaminocyclohexanol were ground well and mixed, avoiding moisture. The mixture was fused at 150° in an oil-bath. After cooling, 7 ml. of 10% aqueous sodium hydroxide was added and the mixture heated on a boiling water-bath. The separated oily layer was extracted with ether, washed with water, dried over fused sodium sulfate and evaporated to dryness. The residue weighed 0.64 g. and boiled at 155–157° (3 mm.). **Picrate**: yellow plates (from methanol), m.p. 131–132°. *Anal.* Calcd. for $C_{19}H_{18}N_4SO_7$: C, 51.10; H, 4.06; N, 12.55. Found: C, 51.09; H, 3.98; N, 12.38.

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(5) All melting points are uncorrected.

(6) M. T. Leffler and Roger Adams, THIS JOURNAL, **59**, 2256 (1937).

(7) T. Taguchi and M. Nakayama, *ibid.*, **73**, 5679 (1951).

(8) G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, *ibid.*, **71**, 637 (1949).

(9) Recrystallization from water was partially accompanied by hydrolysis to give *dl-trans*-2-benzoylaminocyclohexanethiol (V).

***dl-cis*-2-Aminocyclohexanethiol Hydrochloride (XIII).**—To 1 g. of *dl-cis*-2-phenyl-4,5-cyclohexanothiazoline (XII) was added 4 ml. of 20% aqueous hydrochloric acid and the mixture heated at 160–180° for three hours. To the mixture was added 5 ml. of water and undissolved benzoic acid was filtered off. The filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from methanol giving colorless plates, m.p. 245–247° dec., weight 0.45 g., which gave a positive sodium nitroprusside test for the mercapto group. *Anal.* Calcd. for $C_6H_{14}SCl$: C, 42.94; H, 8.41; N, 8.35. Found: C, 42.49; H, 8.01; N, 8.05.

***dl-trans*-2-Thiobenzoylaminocyclohexanol (XI).**—(a) A well-ground mixture of 1.5 g. of *dl-trans*-2-aminocyclohexanol (X), 0.92 g. of benzaldehyde and 0.4 g. of sulfur was heated on a boiling water-bath. After three hours the mixture converted to a reddish sirupy substance. The substance, after cooling, was dissolved in 5 ml. of ethanol, unreacted sulfur filtered off and ethanol distilled off. Addition of 6 ml. of carbon tetrachloride to the residue afforded yellow crystals, m.p. 115–118°, weight 1.63 g. Recrystallization from carbon tetrachloride gave light yellow cubes or silky needles, m.p. 120–121°. *Anal.* Calcd. for $C_{13}H_{17}NSO$: C, 66.32; H, 7.28; N, 5.95. Found: C, 66.13; H, 7.36; N, 5.70.

(b) A uniform mixture of 0.5 g. of *dl-trans*-2-aminocyclohexanol (X) and 0.7 g. of methyl dithiobenzoate was heated on a boiling water-bath till methyl mercaptan ceased to evolve. During the reaction, the mixture changed to a sirupy substance which became reddish and then brownish. On standing at room temperature the sirup solidified gradually. After washing with ether, recrystallization from carbon tetrachloride gave light yellow cubes, m.p. 115–117° alone and on admixture with a sample obtained in procedure (a).

The Formation of *dl-trans*- and *dl-cis*-2-Phenyl-2,4-cyclohexanothiazolines (VII and XII) by Fusion of *dl-trans*-2-Benzoylaminocyclohexanol (XIV) with Phosphorus Pentasulfide.—Thirty-six grams of *dl-trans*-2-benzoylaminocyclohexanol (XIV) and 35 g. of phosphorus pentasulfide were well ground and mixed avoiding moisture. The mixture was heated at 150° till hydrogen sulfide gas ceased to evolve. After cooling, 300 ml. of 5% aqueous sodium hydroxide was added and the mixture warmed on a water-bath till the whole content dissolved leaving an oily product. The oily layer was extracted with 100 ml. of ether twice, washed with water and extracted with 100 ml. of 10% aqueous hydrochloric acid three times. The hydrochloric acid solution was washed with ether, neutralized with sodium bicarbonate and extracted with ether. The ether layer, dried over fused sodium sulfate and evaporated to dryness, yielded 26 g. of a yellowish oil. To a little of the material was added a saturated ethereal solution of picric acid and the precipitate was recrystallized from methanol to give two types of crystals, yellow needles of m.p. 195–196° and yellow plates of m.p. 131–132°. The former was identical with the *dl-trans*-thiazoline (VII) picrate and the latter with the *dl-cis*-thiazoline XII picrate by mixed m.p. determinations. To the remainder of the yellowish oil was added 100 ml. of 5% aqueous hydrochloric acid and the mixture warmed on a boiling water-bath. After cooling, the precipitated crystals were collected and the filtrate, on concentrating to 50 ml., yielded a further crop. After filtration the mother liquor, on adding acetone, gave a further crop, total weight 4.1 g. Recrystallization from 3% aqueous hydrochloric acid gave colorless needles of m.p. 223° dec. which were identical with the *dl-trans*-2-aminocyclohexyl thiobenzoate hydrochloride (VIII) by a mixed m.p. determination; **picrate**: recrystallization from 70% aqueous methanol gave yellow needles, m.p. 167–168° alone and on admixture with the *dl-trans*-2-aminocyclohexyl thiobenzoate (VIII) picrate.

The aqueous and acetonic mother liquors were combined and evaporated to dryness under reduced pressure. The residual gummy product was dissolved in water and on making alkaline with 10% aqueous sodium hydroxide an oil separated. The oil was extracted with ether, washed with water, dried over fused sodium sulfate and evaporated to dryness. The remaining oil weighed 18.5 g. and boiled at 156–159° (3 mm.); **picrate**, yellow plates (from methanol), m.p. 132–133°, which were identical with the *dl-cis*-thiazoline XII picrate by a mixed m.p. determination.

The Formation of *dl-trans*- and *dl-cis*-2-Phenyl-4,5-cyclohexanothiazolines (VII and XII) by Fusion of *dl-cis*-2-Benzoylaminocyclohexanol (XV) with Phosphorus Pentasulfide.—A well-ground mixture of 5 g. of *dl-cis*-2-benzoylaminocyclohexanol and 5 g. of phosphorus pentasulfide was heated at 150° in an oil-bath till hydrogen sulfide ceased to evolve. After cooling the fused mass was dissolved in 50 ml. of warm aqueous sodium hydroxide and a reddish oily product separated. The oily layer was extracted with ether and the ether solution was shaken with 20 ml. of 5% aqueous hydrochloric acid three times. On evaporation to dryness the ethereal solution yielded 0.73 g. of a reddish gummy product. The hydrochloric acid solution was neutralized with sodium bicarbonate yielding an orange-yellowish oil. The extraction of the oil with ether followed by the treatments with hydrochloric acid and then sodium bicarbonate was repeated. The oil was extracted with ether, dried over fused sodium sulfate, evaporated to dryness and boiled at 130–140° (2 mm.), weight 0.85 g. Henceforth, on treatment as above a little of the distilled oil was converted to picrates of *dl-trans*- and *dl-cis*-thiazolines. The remainder was separated into *dl-trans*-2-aminocyclohexyl thiobenzoate and the *dl-cis*-thiazoline (XII) which were identified as hydrochloride VIII and picrate, respectively, weight 0.58 and 0.52 g.

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KATAKASU, FUKUOKA, JAPAN