Anal. Calcd. for $C_{16}H_{18}NO_2I$ (*erythro*-XIV·HI): C, 50.14; H, 4.94; N, 3.65. Found: C, 49.79; H, 4.91; N, 3.59.

The picrate melted at 188–189° alone and on admixture with *erythro*-XIV·picrate.[18] When solution of the hydroiodide was made alkaline, DL-*erythro*-N-benzoyl-norephedrine[17] (m.p. 143–144°) was obtained.

Decomposition of *threo*-XII in Aqueous Sodium Hydroxide.—A solution of 0.20 g. of *threo*-XII in 10 ml. of water was boiled until it became turbid; an oily layer appeared after ten minutes. After cooling, the mixture was extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate and evaporated to dryness to give an oil, yield 0.12 g., which was converted to the picrate, yield 0.18 g. Recrystallization from absolute ethanol gave colorless plates; m.p. 142–143° alone and on admixture with *threo*-XIII·picrate.[17]

(18) T. Taguchi and M. Kojima, *Pharm. Bull. (Tokyo)*, **3**, 4 (1955).

Anal. Calcd. for $C_{22}H_{18}N_4O_8$: C, 56.62; H, 3.89; N, 12.01. Found: C, 56.79; H, 3.89; N, 11.97.

Decomposition of *threo*-XII in an Aqueous Silver Oxide Suspension.—To a solution of 0.20 g. of *threo*-XII was added about the mole equivalent of silver oxide. The silver iodide was filtered and the filtrate boiled for 10 minutes until an oil appeared. After cooling, the mixture was extracted with ether. The extract was dried over anhydrous sodium sulfate and evaporated to dryness to leave 0.10 g. of an oil from which a picrate was prepared; yield 0.14 g. m.p. 141–142° alone and on admixture with *threo*-XIII·picrate.

Acknowledgments.—The authors are indebted to the Microanalytical Section of this Institute and the Center of Microanalyses of this University for microanalyses.

KATAKASU, FUKUOKA, JAPAN

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

Reaction of 2-Aminoalkyl Sulfates or Halides with Sodium Disulfide in the Presence of Cyclohexanone. A New Synthesis of Thiazolidines and 2-Aminoalkane Thiols[1]

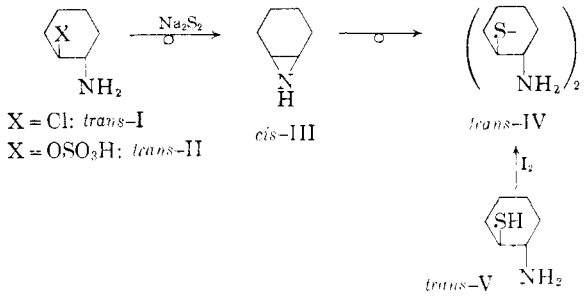
BY TANEZO TAGUCHI, MASAHARU KOJIMA AND TOMIO MURO

RECEIVED AUGUST 11, 1958

DL-*trans*-2-Aminocyclohexyl chloride (*trans*-I) or sulfate (*trans*-II) reacted with sodium disulfide to yield a compensated *trans-trans*-bis-(2-aminocyclohexyl) disulfide (IV). The *cis* epimer (*cis*-I) gave cyclohexanone (VI), *trans*-IV and DL-*trans*-spiro[cyclohexane-1,2′-(4′,5′-cyclohexano)-thiazolidine] (VII). Compound VII, which yielded VI and DL-*trans*-2-aminocyclohexane thiol (*trans*-V) upon hydrolysis, was also prepared by the condensation of VI and *trans*-V. Thus, the formation of VII was probably due to the secondary condensation of VI and *trans*-V formed in the disulfide reaction. This finding suggested a new method for the synthesis of thiazolidines by the reaction of 2-aminoalkyl halides or sulfates with sodium disulfide in the presence of aldehydes or ketones.

Mousseron and his co-workers[2] have reported the preparation of a compensated bis-(2-aminocyclohexyl) disulfide by the treatment of DL-2-aminocyclohexyl chloride (I) with sodium disulfide. The present work was undertaken to determine the configuration of this compound. DL-*trans*-2-Aminocyclohexyl chloride (*trans*-I) was treated with sodium disulfide to yield an oil which was converted to the hydrochloride. This hydrochloride was identical with a compensated *trans-trans*-bis-(2-aminocyclohexyl) disulfide (*trans*-IV) hydrochloride[3] obtained by the oxidation of DL-*trans*-2-amino-cyclohexane thiol[4] (*trans*-V) with iodine, followed by salt formation. The *trans* configuration was assigned to IV because its formation by the oxidation of *trans*-V does not involve the breaking of bonds at asymmetric centers. Therefore, it is presumed that the disulfide reaction first gave the intermediate *meso-cis*-cyclohexenimine (*cis*-III) from which *trans*-IV was formed; thus the reaction as a whole involved double inversion; see Chart 1.

CHART 1



cis-I reacted with sodium disulfide to yield cyclohexanone (VI), *trans*-IV and a basic substance which was shown to be *trans*-VII. The hydrochloride of this basic substance was hydrolyzed to give cyclohexanone (VI) and the *trans*-aminothiol (*trans*-V) hydrochloride. We then prepared the epimers of DL-spiro[cyclohexane-1,2′-(4′,5′-cyclohexano)-thiazolidine] (VII) hydrochloride by the condensation of cyclohexanone (VI) and the *trans*- or *cis*-aminothiol V; the *trans* epimer (*trans*-VII) hydrochloride was identical with the hydrochloride under consideration.

The results of the treatment of *cis*-I with sodium disulfide may be interpreted as follows: since the reaction medium becomes alkaline due to hydrolysis of sodium disulfide,[5] some of the *cis*-I undergoes elimination of hydrochloric acid to give cyclohexanone (VI) *via* 1-aminocyclohex-2-ene. Also *cis*-I gives *trans*-IV *via* *Sn*2 reaction at C_1; participation of the amino group in a reaction at C_1 is not favored by the *cis*-relationship. Then the reduction of *trans*-IV in the reaction medium gives *trans*-V which condenses with VI to yield *trans*-VII; see Chart 2. Since *trans*-IV was not reduced by sodium disulfide under similar conditions in the

(1) Studies in Stereochemistry, XXIV; paper XXIII, THIS JOURNAL, **81**, 4318 (1959).

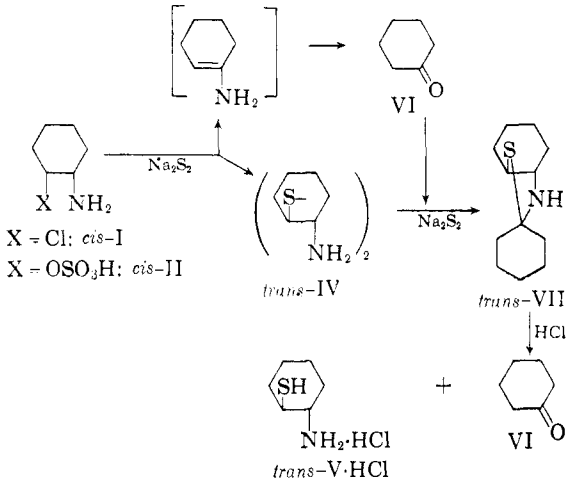
(2) M. Mousseron, H. Bousquet and G. Marret, *Bull. soc. chim. France*, 84, (1948).

(3) There are theoretically two compensated *trans-trans* diastereoisomers, one of which is racemic and the other *meso*, but it is not clear which is the product (*trans*-IV).

(4) T. Taguchi and M. Kojima, THIS JOURNAL, **78**, 1684 (1956).

(5) O. E. Paris and P. E. Fanta, *ibid.*, **74**, 3007 (1952).

CHART 2



absence of cyclohexanone (VI), it is presumed that VI participates in the reduction, but the mechanism of this step is not clear.

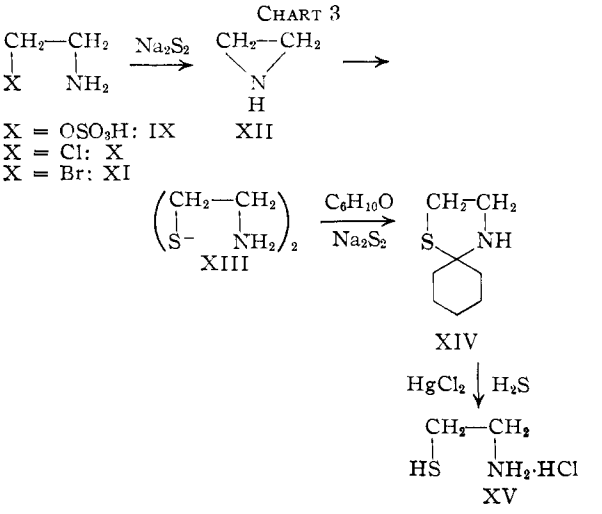
Similar results were obtained with DL-2-aminocyclohexyl sulfates (II) instead of the chlorides in the reactions mentioned above except that in the case of *cis*-II no *trans*-VII was isolated.

The formation of *trans*-VII suggested that thiazolidines might be synthesized by the reaction of 2-aminoalkyl chlorides or sulfates with sodium disulfide in the presence of aldehydes or ketones. In fact both *trans*-I and *trans*-II reacted with sodium disulfide and cyclohexanone to give *trans*-VII which was then converted to *trans*-V. As a starting material *trans*-II is preferable because it is easier to prepare than *trans*-I.

This method was also used for the preparation of spiro[cyclohexane-1,2-thiazolidine] (XIV) from 2-aminoethyl sulfate (IX), 2-aminoethyl chloride (X) and 2-aminoethyl bromide (XI); XIV was hydrolyzed by the usual method using mercuric chloride to form the cysteamine–mercuric chloride complex which upon treatment with hydrogen sulfide yielded cysteamine hydrochloride (XV). The reaction mechanism for the formation of XIV has not been elucidated. However, if the mechanism is analogous to that suggested above for *trans*-I and *trans*-II, the reaction should proceed through the intermediates XII and XIII, as shown in Chart 3.

The use of aldehydes and ketones other than cyclohexanone in this preparative method is being investigated; formaldehyde and acetone did not give the desired thiazolidines.

CHART 3



Experimental[6]

DL-*trans*-**2-Aminocyclohexyl Sulfate** (*trans*-**II**).—To a solution of 105 g. of DL-*trans*-2-aminocyclohexanol in 210 ml. of water was added dropwise 94.5 g. of 95% sulfuric acid with cooling. After distillation of the water under reduced pressure, the mixture was evaporated to dryness on an oil-bath at 100–200° under reduced pressure. After cooling, a small amount of methanol–water was added to the gray residue which was broken up and filtered. The remainder was recrystallized from water to give cubes (yield 115 g.) which carbonized at 303–310° and were identical with a sample of *trans*-II prepared by the Paris procedure.[5] The mother liquor of recrystallization, on concentration and addition of methanol, yielded a further crop of crystals, 32 g.

(6) Melting and boiling points are uncorrected.

DL-*cis*-**2-Aminocyclohexyl sulfate** (*cis*-**II**) was prepared as above from 9.5 g. of DL-*cis*-2-aminocyclohexanol, yield 14.0 g. Recrystallization from 50% ethanol gave colorless needles, m.p. 289–290° dec.

Anal. Calcd. for $C_6H_{13}NO_4S$: C, 36.91; H, 6.70; N, 7.07. Found: C, 37.31; H, 6.81; N, 7.08.

meso-cis-**Cyclohexenimine** (*cis*-**III**).—(a) A solution of 50 g. of *trans*-II in 200 ml. of 20% aqueous sodium hydroxide was boiled for 1.5 hours and then steam distilled. The distillate was saturated with sodium hydroxide and extracted with ether. The ether was removed from the extract, and the residue distilled under diminished pressure. The product (yield 17.5 g., b.p. 60–62° (35 mm.), m.p. 20°) was converted to the picrate; m.p. 120–122° alone and on admixture with a sample of *cis*-III prepared by Paris' procedure.[5]

(b) A reaction mixture, containing 3 g. of *trans*-I·HCl (see below) dissolved in 10 ml. of water and 40 ml. of 10% aqueous sodium hydroxide, was treated as in (a) except that the final distillation was carried out over an oil-bath at 180–200°. The oily distillate was not crystallized and converted to the picrate, yield 250 mg., which melted at 120–122° alone and on admixture with a sample prepared under (a).

DL-*trans*-**2-Aminocyclohexyl Chloride Hydrochloride** (*trans*-**I·HCl**).—To 40 ml. of 20% ethanolic hydrochloric acid was slowly added an ethanolic solution of 5 g. of *cis*-III with cooling, and the mixture evaporated to dryness on a water-bath, yield 6 g. Recrystallization from ethanol–ether gave colorless plates, m.p. 205–207° dec., reported[7] m.p. 205–207°.

Anal. Calcd. for $C_6H_{13}NCl_2$: N, 8.23. Found: N, 7.99.

DL-*cis*-**2-Aminocyclohexyl chloride hydrochloride** (*cis*-**I·HCl**) was prepared by McCasland's procedure[8] as colorless needles, m.p. 185–186°.

DL-*trans*-**2-Aminocyclohexane thiol** (*trans*-**V**) was prepared by Winternitz' procedure,[7] m.p. 78–80°; hydrochloride, m.p. 225° dec. It was also prepared by the authors' method[4]; hydrochloride, m.p. 225° dec.

A Compensated *trans-trans*-**(2-Aminocyclohexyl) Disulfide** (*trans*-**IV**).—To a solution of 2 g. of *trans*-V·HCl in 15 ml. of water was added an aqueous iodine–potassium iodide solution until the color of iodine remained. After the addition of 8 ml. of 20% aqueous sodium hydroxide, the mixture was extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, freed from ether and distilled; b.p. 164–168° (4 mm.), accompanied by partial sublimation of *trans*-V, m.p. 79–80°. The hydrochloride was recrystallized as colorless cubes from methanol–ether; m.p. 271–272° dec., m.p. 284–289° reported by Winternitz, *et al.*[9]

(7) F. Winternitz, M. Mousseron and R. Dennilauler, *Bull. soc. chim. France*, 382 (1956).

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

(9) F. Winternitz, M. Mousseron and R. Dennilauler, *Bull. soc. chim. France*, 1228 (1956).

Anal. Calcd. for $C_{12}H_{26}N_2S_2Cl_2$: C, 43.23; H, 7.86; N, 8.40. Found: C, 43.15; H, 7.75; N, 8.13.

Treatment of *trans*-I with Sodium Disulfide. The Formation of *trans*-IV.—To a solution of 3 g. of *trans*-I·HCl in 6 ml. of water, which had been neutralized with 1.5 ml. of water containing 0.71 g. of sodium hydroxide, was added 18 ml. of 50% ethanol containing 4.3 g. of $Na_2S_2·9H_2O$ and 0.57 g. of sulfur. The mixture was boiled for 2 hours on a water-bath, freed from ethanol, and extracted with ether. The extract was treated as in the preceding procedure to give an oil, yield 0.95 g., which boiled at 160–165° (3 mm.) accompanied by partial sublimation of *trans*-V, m.p. 79–80°. The hydrochloride melted at 271–272° dec. alone and on admixture with a sample of *trans*-IV·HCl.

Anal. Calcd. for $C_{12}H_{26}N_2S_2Cl_2$: C, 43.23; H, 7.86. Found: C, 43.31; H, 7.72.

Treatment of *cis*-I with Sodium Disulfide. The Formation of Cyclohexanone (VI), *trans*-IV and DL-*trans*-Spiro[cyclohexane-1,2′-(4′,5′-cyclohexano)-thiazolidine] (*trans*-VII).—*cis*-I·HCl (3 g.) was treated with sodium disulfide as described for *trans*-I·HCl. After reaction, 12 ml. of ethanol was distilled. A 2,4-dinitrophenylhydrazone (yield 0.26 g.) was isolated from the distillate, m.p. 157–158° alone and on admixture with an authentic sample of the VI 2,4-dinitrophenylhydrazone. The residual mixture was extracted with ether, and the extract washed with water and extracted with 10% aqueous hydrochloric acid. The aqueous layer which separated from the ether layer was combined with the wash water and steam distilled. From the distillate additional VI was isolated as the 2,4-dinitrophenylhydrazone, 50 mg.

When the hydrochloric acid solution was cooled and allowed to stand, crystals separated which were filtered; an additional crop was obtained by concentration of the filtrate to half its volume, total yield 0.20 g. Recrystallization from ethanol–ether gave colorless plates, m.p. 221–222° dec. alone and on admixture with a sample of *trans*-VII·HCl described below.

Anal. Calcd. for $C_{12}H_{22}NSCl$: C, 58.50; H, 8.92; N, 5.68. Found: C, 58.26; H, 8.78; N, 5.42.

The mother liquor of the concentrated hydrochloric acid solution was neutralized with 10% aqueous sodium hydroxide and extracted with ether. The extract was washed with water, the ether removed and the residue dissolved in ethanolic hydrochloric acid. When ether was added, crystals separated (yield 0.20 g.) which were recrystallized; m.p. 272–273° dec. alone and on admixture with a sample of *trans*-IV·HCl.

DL-*trans*-**Spiro[cyclohexane-1,2′-(4′,5′-cyclohexano)-thiazolidine]** (*trans*-**VII**).—To a solution of *trans*-V·HCl in 7 ml. of water were added 0.9 g. of cyclohexanone (VI) and 3 ml. of 10% aqueous sodium hydroxide. The mixture was warmed till an oily layer appeared. The cooled mixture was extracted with ether and the extract treated in the usual manner. The product (yield 0.70 g., b.p. 132–135° (8 mm.)) was converted to the hydrochloride, m.p. 220–222° dec.

Anal. Calcd. for $C_{12}H_{22}NSCl$: C, 58.50; H, 8.92; N, 5.68. Found: C, 58.72; H, 8.92; N, 5.70.

DL-*cis*-**Spiro[cyclohexane-1,2′-(4′,5′-cyclohexano)-thiazolidine]** (*cis*-**VII**),—*cis*-V·HCl[4] (1 g.), treated as described for *trans*-V·HCl, gave 1.36 g. of an oil. The hydrochloride melted at 202–203°.

Anal. Calcd. for $C_{12}H_{22}NSCl$: C, 58.50; H, 8.92; N, 5.68. Found: C, 58.61; H, 8.86; N, 5.70.

Treatment of *trans*-II with Sodium Disulfide. The Formation of *trans*-IV.—To a solution of 4.9 g. of *trans*-II in 10 ml. of 10% aqueous sodium hydroxide was added an aqueous sodium disulfide solution (6 g. of $Na_2S_2·9H_2O$), 0.8 g. of sulfur and 25 ml. of water. The reaction mixture was heated on a water-bath for 4 hours, cooled and extracted with ether. The ethereal solution was washed with water and extracted with 10% aqueous hydrochloric acid. The extract was evaporated to dryness. The residue to which a small quantity of methanol had been added was filtered, yield 2.0 g., and recrystallized from methanol–ether as colorless cubes, m.p. 271–272° dec. alone and on admixture with a sample of *trans*-IV·HCl.

Treatment of *cis*-II with Sodium Disulfide. The Formation of VI and *trans*-IV.—*cis*-II (4 g.) was treated with sodium disulfide as described for *trans*-II, and the reaction mixture was steam distilled. From the distillate VI was isolated as the 2,4-dinitrophenylhydrazone, yield 2.9 g. The residue was extracted with ether. Treatment of the ether extract with dry hydrogen chloride yielded a gummy product which was separated by decantation and dissolved in a small quantity of ethanol. Upon the addition of ether, crystals separated; yield 0.09 g., m.p. 270° dec. alone and on admixture with *trans*-IV·HCl.

Reaction of *trans*-IV with Sodium Disulfide in the Presence of VI. The Formation of *trans*-VII.—A mixture of 1 g. of *trans*-IV, 4 ml. of a 10% sodium disulfide solution, 1.2 g. of VI and 8 ml. of water was warmed for 2 hours, cooled and extracted with ether. The washed and dried extract was distilled. The product (b.p. 132–135° (8 mm.), yield 0.07 g.) was converted to the hydrochloride which was recrystallized, m.p. 220–222° dec. alone and on admixture with a sample of *trans*-VII·HCl.

Reaction of *trans*-I with Sodium Disulfide in the Presence of VI. The Formation of *trans*-VII.—Compound VI (3 ml.) was included in the reaction mixture described under the treatment of *trans*-I with sodium disulfide. The mixture was boiled on a water-bath for 2 hours and distilled *in vacuo* until 8 ml. of distillate, which contained ethanol and unreacted VI, was obtained. Water was added to the residue which was extracted with ether. The extract was treated in the usual manner and distilled. The product (b.p. 115–117° (3 mm.), yield 1.8 g.) was isolated as the hydrochloride of *trans*-VII; m.p. and mixed m.p. 220–222°.

Reaction of *trans*-II with Sodium Disulfide in the Presence of VI. The Formation of *trans*-VII.—The reaction mixture given under the treatment of *trans*-II with sodium disulfide (double quantity), containing 7 ml. of VI, was heated for 7 hours, cooled and extracted with ether. The extract, treated in the usual way, gave a product (yield 7.5 g., b.p. 127–131° (6 mm.)) which was isolated as the hydrochloride, m.p. 221–222° dec. alone and on admixture with a sample of *trans*-VII·HCl.

Hydrolysis of *trans*-VII. The Formation of *trans*-V.—*trans*-VII (2 g.) in 20 ml. of 20% aqueous hydrochloric acid was boiled for 2 hours and evaporated to dryness to give crystals which were washed with ether (yield 1.08 g.) and recrystallized from methanol as colorless plates, m.p. 225° dec. alone and on admixture with a sample of *trans*-V.

Spiro[cyclohexane-1,2′-thiazolidine] (XIV).—(a) To 14.1 g. of 2-aminoethyl sulfate (IX),[10] which had been neutralized with 40 ml. of a 10% aqueous sodium hydroxide solution, were added 20 ml. of VI and a mixture containing 24 g. of $Na_2S_2·9H_2O$ and 3.2 g. of sulfur in 100 ml. of water. The reaction mixture was warmed for 2 hours. The ether extract, after the usual treatment, was distilled *in vacuo;* b.p. 91–92° (7 mm.), yield 7.3 g. Colorless needles of the hydrochloride were recrystallized from methanol-ether; m.p. 164–166°, reported[11] m.p. 154–155°.

Anal. Calcd. for $C_8H_{16}NSCl$: C, 49.59; H, 8.32; N, 7.23. Found: C, 49.44; H, 8.28; N, 6.90.

(b) 2-Aminoethyl chloride (X) hydrochloride[12] (11.6 g.) was worked up as in (a) to give 9.55 g. of XIV; hydrochloride: m.p. 164–166°.

(c) 2-Aminoethyl bromide (XI) hydrobromide[13] (20.5 g.) was treated as in (a) to give 9.60 g. of XIV; hydrochloride m.p. 164–166°.

Cysteamine Hydrochloride (XV).—Compound XIV (8 g.) in 50 ml. of 20% hydrochloric acid was boiled for 2 hours to free VI as an oil. The yellow-brown mixture on evaporation to dryness gave a gummy residue which did not crystallize. The treatment was carried out under nitrogen. To the residue dissolved in 20 ml. of water was added mercuric chloride until precipitation ceased. The crystals were washed with water and then methanol; yield 19.1 g., m.p. 200° dec. Hydrogen sulfide was passed into a suspension of the crystals in 100 ml. of methanol. The mercuric sulfide was filtered and the filtrate was evaporated to dryness, yield 3.8 g. Recrystallization from ethanol gave colorless plates, m.p. 69–70° (hygroscopic).

(10) H. Wenker, THIS JOURNAL, **57**, 2328 (1935).

(11) S. V. Tsukerman, *Ukrain. Khim. Zhur.*, **19**, 523 (1953); *C. A.*, **49**, 8255e (1955).

(12) K. Ward, Jr., THIS JOURNAL, **57**, 915 (1935).

(13) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 91.

Anal. Calcd. for C_2H_8NSCl: C, 21.14; H, 7.09; N, 12.32. Found: C, 20.87; H, 7.08; N, 11.98.

The mercuric chloride complex of cysteamine (m.p. 200° dec., yield 15 g.) was also obtained when mercuric chloride was added directly to a solution of XIV (5 g.) in hydrochloric acid and the mixture, containing a gummy precipitate, was heated. After removal of mercuric sulfide, the filtrate was evaporated to dryness *in vacuo* to give 2.7 g. of crystals which were recrystallized— m.p. 69-70° (hygroscopic) alone and on admixture with a sample of XV prepared above.

Acknowledgments.—The authors are indebted to the Service Center of Microanalyses of the Kyushu University and also to the Microanalytical Section of this Institute for the microanalyses.

KATAKASU, FUKUOKA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF DELAWARE AND NORTHWESTERN UNIVERSITY]

The Preparation and Properties of 7,12-Dihydro-7-phenylpleiadene[1]

BY PETER T. LANSBURY*

RECEIVED JANUARY 2, 1959

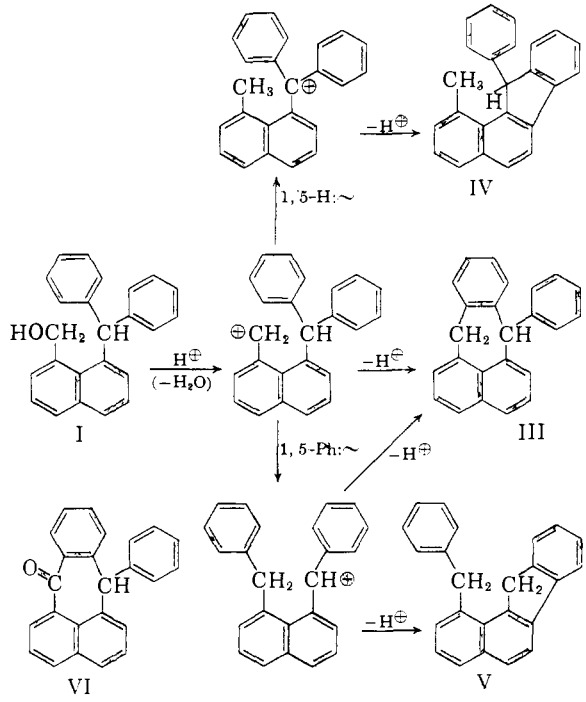
1-(8-Benzhydryl)-naphthylcarbinol (I) undergoes cyclodehydration in acidic media yielding 7,12-dihydro-7-phenylpleiadene (III) quantitatively. The structure of III was elucidated by means of ultraviolet and nuclear magnetic resonance spectroscopy, and by stereochemical considerations of the ring closure; III is a non-planar molecule and a weak donor for molecular complex formation.

In the course of investigating acid-catalyzed rearrangement reactions of *peri*-substituted naphthalenes,[2] the possibility of encountering 1,5-phenyl shifts in the solvolysis of 1-(8-benzhydryl)-naphthylcarbinol (I) seemed quite promising because of the success realized in isomerizing 8-benzhydryl-1-naphthoic acid (II).[2] Other than forming carbonium ions of different geometry, both compounds I and II might be expected to rearrange in acid *via* a 1,5-phenyl group transfer from the proximal *peri*-benzhydryl substituent. This paper reports the preparation of I, its behavior in acidic media, and certain novel stereochemical aspects of the reaction product.

1-(8-benzhydryl)-naphthylcarbinol was prepared in 90% yield by reduction of ethyl 8-benzhydryl-1-naphthoate[2] with lithium aluminum hydride. Under a variety of acidic solvolysis conditions (see Experimental) compound I was quantitatively converted to a crystalline hydrocarbon, $C_{24}H_{18}$. When the infrared spectrum of this product showed that no oxygen-containing groups were present, it became obvious that a cyclodehydration had occurred at some stage of the solvolysis and, therefore, structures III, IV and V were entertained as possible formulations for $C_{24}H_{18}$.[3]

The dehydration product did not form either a solid picrate or a 1,3,5-trinitrobenzene derivative and reacted only feebly with tetracyanoethylene[4] (TCNE), suggesting a non-planar configuration, which would inhibit molecular complex formation.[5] The greatly reduced ratio of extinction coefficients for the charge transfer spectrum of III with TCNE as compared with naphthalene/TCNE[4] is of the same order of magnitude observed by Merrifield and Phillips[4] in comparing hexamethylbenzene/TCNE with the more hindered hexaethylbenzene complex.

Whereas the infrared spectrum of the dehydration product served mainly to indicate the absence of hydroxyl and ester groups, it seemed that the ultraviolet spectrum would provide some means of



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(1) The name "pleiadene" refers to the tetracyclic ring system, currently used in "Chemical Abstracts," as given in "The Ring Index" (A. M. Patterson and L. T. Capell, Reinhold Publishing Corp., New York, N. Y., 1940, p. 385).

(2) P. T. Lansbury and R. L. Letsinger, THIS JOURNAL, **81**, 940 (1959); **78**, 2648 (1956).

(3) Although III is the most obvious structure, and was selected as a working hypothesis, IV and V could readily arise, since after a 1,5-hydride or phenyl migration (ref. 2) the resultant carbonium ion would easily lead to a benzfluorene (for examples of acid-catalyzed dehydration of diphenyl-α-naphthylcarbinol and diphenyl-β-naphthylcarbinol to benzfluorenes see F. Ullmann and A. Mourawiew-Winigradoff, *Ber.*, **38**, 2213 (1905); M. Gomberg and W. E. Gordon, THIS JOURNAL, **57**, 119 (1935), and other references cited in "Elsevier's Encyclopedia of Organic Chemistry," Vol. 12B, Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp. 1095-1097).

(4) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(5) For some examples of steric effects in molecular complex formation between aromatic compounds and polynitro compounds, see (a) B. R. Brown and D. Ll. Hammick, *J. Chem. Soc.*, 1395 (1948); (b) M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951); and (c) M. S. Newman in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 472.