28. Tanezo Taguchi and Seiki Kasuga*¹: Heteroalicyclic
Aminoalkanol. II. Reactions of DL-2-Piperi-
dinemethanol involving the Formation
of DL-1-Azabicyclo[4,1,0]heptane.*²

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For the purpose described in the first paper of this series,¹⁾ DL-2-piperidinemethanol (I) was exposed to a variety of reactions. I was converted to DL-1-benzoyl-2-piperidine-methanol (II) by the Schotten-Baumann method with 1 equiv. of benzoyl chloride. The benzoyl group in II migrated from N to O on treatment with 2% aqueous hydrochloric acid forming DL-2-piperidinemethanol benzoate (III) hydrochloride and the group reverted from O to N on treatment of III·HCl with 5% aqueous sodium hydroxide regenerating II. DL-1-Benzoyl-2-piperidinemethanol benzoate (IV) was prepared from either I or II by the Schotten-Baumann benzoylation where I needed 2 equiv. of benzoyl chloride and II did 1 equiv.

The condensation of I with benzaldehyde catalysed by acetic acid was effected by removal of water formed as an azeotropic mixture with benzene added and yielded DL-3-phenyl-hexahydro-3H-oxazolo[3,4-a]pyridine (V). The structure of V was supported by a couple of specific absorption bands due to the oxazolidine ring,²⁾ $\lambda_{\max}^{\text{Nujol}} \mu$: 8.71, 8.88, 9.10, and also by findings that V suffered acidic hydrolysis to give I and oxidation with bromine to give III·HBr probably passing through the oxazolopyridinium salt (VI).

DL-2-(2-Piperidylmethyl)-2-thiopseudourea dihydrochloride (VIII·2HCl) was prepared by the action of thiourea on DL-2-(chloromethyl)piperidine hydrochloride (VII·HCl) which was yielded by the reaction of thionyl chloride on I.³⁾ In the reaction, a small amount of

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DL-3-imino-hexahydrothiazolo[3,4-*a*]pyridine hydrochloride (K·HCl) was also formed with ammonium chloride, suggesting that VIII·2HCl formed cyclized to K·HCl by heat, splitting NH_4Cl . Thus, the source of K·HCl was proven to be VIII·2HCl in an attempt where VIII·2HCl was boiled in butanol. To effect transguanylation,⁴⁾ VIII·2HCl was treated with an ethanolic solution containing 1 equiv. potassium hydroxide. The reaction mixture was positive in the nitroprusside test for thiol and afforded DL-1-(2,4-dinitrophenylamidino)-2-(2,4-dinitrophenylthiomethyl)piperidine (XI) by reaction with 2,4-dinitro-chlorobenzene. This indicates that the essential product of the reaction might be DL-1-amidino-2-piperidinemethanethiol hydrochloride (X·HCl). These findings about VIII·2HCl are analogous to the results obtained by Doherty, *et al.*⁴⁾ in the same treatments of 2-(2-aminoethyl)thiopseudourea dihydrobromide.

Recently, Taguchi and co-workers⁵⁾ revealed that methyl 2-dialkylaminoalkyl xanthates rearrange quantitatively to the corresponding dithiolcarbonates by distillation. Thus the rearrangement is against the Chugaev reaction rule⁶⁾ and requires the anti-parallel coplanarity of the dialkylamino and the xanthate groups, where the anchimeric power of the former group to the latter works in such a mechanism as has been discussed in the other paper.⁷⁾ For the same purpose, here was prepared methyl DL-(1-methyl-2-piperidylmethyl)xanthate (XIII) in the usual way⁵⁾ from DL-1-methyl-2-piperidinemethanol (II) which was obtained by methylation of I with formic acid and formaldehyde.⁸⁾ The xanthate (XIII) was characterized from an infrared spectral determination, $\lambda_{\text{max}}^{\text{Nujol}} \mu$: 8.21, 9.36, and also from the finding that alkaline hydrolysis gave XII. By distillation, the xanthate (XIII) was transformed to DL-S-(1-methyl-2-piperidylmethyl) S'-methyl dithiolcarbonate (XIV) in a yield as high as 87.6%. This seems a reasonable result because the molecule (XIII) as well as acyclic analogues can be spacially arranged to meet the steric requirement proposed for the rearrangement.^{5,7)} The structure of XIV was supported by infrared spectral data, $\lambda_{\text{max}}^{\text{Nujol}} \mu$: 5.73, 6.07, 11.63, and also by the following observation. Alkaline hydrolysis followed by oxidation with air converted XIV to DL-1,1'-dimethyl-2,2'-dithiodimethyldipiperidine (XVI) which was identical with an authentic sample prepared from DL-1-methyl-2-chloromethylpiperidine (XVII) through DL-2-(1-methyl-2-piperidylmethyl)-2-thiopseudourea (XVIII). The Hofmann exhaustive

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product. Thus all reactions pursued for the confirmation of the structure (XXIV) support its correctness. In conclusion, the reactions tried in this study indicate that I behaves just like an acyclic β -aminoalcohol, as be stereochemically well-convinced.

Experimental*4

DL-1-Benzoyl-2-piperidinemethanol (II)—To a solution of 5 g. of DL-2-piperidinemethanol (I) in 5 ml. of ether were added simultaneously 6 g. of benzoyl chloride dissolved in 20 ml. of ether and 20 ml. of aqueous sodium hydroxide under chilling at 0° and stirring. The charge was agitated for 1 hr. at room temperature, ether layer removed, extracted with benzene, dried over anhyd. sodium sulfate and evaporated to dryness. The residue was combined with a crop yielded from evaporation of the ether layer. Recrystallization of the residue from ether gave colorless granules of m.p. 94~95°, yield 7.2 g. (75.7%). *Anal.* Calcd. for $C_{13}H_{17}O_2N$ (II): C, 71.20; H, 7.82; N, 6.34. Found: C, 71.24; H, 7.74; N, 6.09.

DL-2-Piperidinemethanol Benzoate Hydrochloride (III·HCl)—A half gram of II was dissolved in 20 ml. of 2% aqueous hydrochloric acid and concentrated *in vacuo* and ethanol added to cause the precipitation of crystals. Filtration followed by recrystallization from methanol-ethanol furnished colorless pillars of m.p. 243~244°, yield 0.53 g. (91%). *Anal.* Calcd. for $C_{13}H_{17}O_2N \cdot HCl$ (III·HCl): C, 61.05; H, 7.09; N, 5.48. Found: C, 61.08; H, 7.22; N, 5.52.

DL-2-Piperidinemethanol Benzoate Hydrobromide (III·HBr)—Treatment of II with 2% aqueous hydrobromic acid was carried out just as the preparation of III·HCl. Recrystallization from ethanol gave

*4 All melting and boiling points were uncorrected.

colorless needles, m.p. 233~234°(decomp.), yield 91%. *Anal.* Calcd. for $C_{13}H_{17}O_2N \cdot HBr$ (III·HBr): C, 52.01; H, 6.04; N, 4.67. Found: C, 52.10; H, 5.98; N, 4.96.

The Formation of II from III·HCl through O→N Acyl Migration—To 10 ml. of 5% aqueous sodium hydroxide was added 0.2 g. of III·HCl and the mixture went into a clear solution after stirring for a half hour. The solution was extracted with benzene, dried over anhyd. sodium sulfate and evaporated to dryness. Recrystallization of the residue from ether gave colorless granules, yield 0.15 g. (88%), m.p. 74° alone and on admixture with a sample of II.

DL-1-Benzoyl-2-piperidinemethanol Benzoate (IV)

a) **From I**—To 10 ml. of an ethereal solution containing 1.15 g. of I were added 9 ml. of aqueous sodium hydroxide and then 3 g. of benzoyl chloride in drops. The reaction proceeded evolving a bit of heat. After stirring for 3 hr. the ether layer was separated from the aqueous layer and the aqueous layer was extracted with ether. The combined ether solution was washed with 2*N* aqueous hydrochloric acid and then water. The ether solution was dried over anhyd. sodium sulfate and evaporated to dryness. The residue was dissolved in ethanol and water added to cause the precipitation of crystals. After filtration, recrystallization from ether-ligroin gave colorless granules of m.p. 65~67°, yield 2.8 g. (87.3%). *Anal.* Calcd. for $C_{20}H_{21}O_3N$ (IV): C, 74.29; H, 6.55; N, 4.33. Found: C, 74.13; H, 6.73; N, 4.01.

b) **From II**—To 0.5 g. of II dissolved in 5 ml. of benzene were added 5 ml. of 10% aqueous sodium hydroxide and then 0.4 g. of benzoyl chloride in drops under stirring. The reaction mixture was treated analogously to procedure (a) and furnished colorless granules, yield 0.66 g. (89%), m.p. 65° alone and on admixture with a sample of IV prepared by procedure (a).

DL-3-Phenyl-hexahydro-3*H*-oxazolo[3,4-*a*]pyridine (V)—To a mixture of 1 g. of I, 0.88 ml. of benzaldehyde and 10 ml. of benzene was added 1 ml. of glacial acetic acid and boiled removing water formed by an azeotropic mixture with benzene. The removal of water was repeated by adding benzene further. The reaction mixture was washed with 5% aqueous sodium bisulfite, dried over anhyd. sodium sulfate, freed of solvent and distilled *in vacuo*, b.p.s 134~136°, yield 1.3 g. (73.6%). *Anal.* Calcd. for $C_{13}H_{17}ON$ (V): C, 76.80; H, 8.44; N, 6.90. Found: C, 76.49; H, 8.56; N, 6.70. Hydrolysis of V in conc. hydrochloric acid gave I and benzaldehyde.

Oxidation of V with Bromine. The Formation of III·HBr—To a solution of 0.5 g. of V dissolved in 2 ml. of chloroform was dropped 2 ml. of chloroform containing 0.4 g. of bromine under ice-chilling and stirring. The reaction mixture was agitated with 2 ml. of 10% aqueous sodium hydroxide and the chloroform layer was separated from the aqueous layer. The chloroform layer was dried over anhyd. sodium sulfate, evaporated to dryness and ether added to cause crystallization. Recrystallization from ethanol gave colorless needles, yield 0.67 g. (90%), m.p. 233° alone and on admixture with an authentic sample of III·HBr.

DL-2-(2-Piperidylmethyl)-2-thiopseudourea Dihydrochloride (VIII·2HCl)—Four grams of VII³⁾ and 2 g. of thiourea were dissolved in 12 ml. of ethanol and refluxed for 10 hr. Evaporation of ethanol left a liquid containing a small quantity of crystals (NH_4Cl). After filtration, the filtrate was mixed with acetone and allowed to stand overnight, during which time crystals precipitated. The crystals were collected by filtration and recrystallized from ethanol-acetone and then from ethanol yielding colorless needles of m.p. 182~184°, yield 2.5 g. (43%). *Anal.* Calcd. for $C_7H_{16}N_3S \cdot 2HCl$ (VIII·2HCl): C, 34.15; H, 6.96; N, 17.07. Found: C, 34.47; H, 7.39; N, 16.67. The mother liquor deposited crystals by concentration. Recrystallization from butanol gave colorless pillars, yield 0.8 g. (17.6%), m.p. 186~188° alone and on admixture with a sample of DL-3-imino-hexahydro-3*H*-thiazolo[3,4-*a*]pyridine·HCl (K·HCl) described below.

DL-3-Imino-hexahydro-3*H*-thiazolo[3,4-*a*]pyridine·HCl (IX·HCl)—A solution of 0.2 g. of VIII·HCl in 2 ml. of butanol was refluxed for 1 hr. Precipitating ammonium chloride was filtered off and the filtrate was concentrated till crystals appeared. Filtration followed by recrystallization from butanol gave colorless needles of m.p. 186~188°, yield 0.18 g. (79.5%). *Anal.* Calcd. for $C_7H_{12}N_2S \cdot HCl$ (IX·HCl): C, 43.63; H, 6.86; N, 14.54. Found: C, 43.27; H, 7.10; N, 14.44.

Picrate: recrystallized from water, m.p. 158~160°

DL-1-(2,4-Dinitrophenylamidino)-2-(2,4-dinitrophenylthiomethyl)piperidine (XI)—To 2 ml. of an ethanolic solution containing 50 mg. of VIII·2HCl was added 0.57 ml. of 2% ethanolic potassium hydroxide. In a little while, to the solution were added 41 mg. of 2,4-dinitrochlorobenzene dissolved in 2 ml. of ethanol and then 1.14 ml. of 2% ethanolic potassium hydroxide. The solution colored orange and crystals of potassium chloride appeared. After setting aside overnight, the reaction mixture was filtered and the filtrate was evaporated to dryness. Recrystallization of the residue gave brownish yellow granules of m.p. 185~187°(decomp.), yield 25 mg. (24.3%). *Anal.* Calcd. for $C_{19}H_{19}O_8N_7S$ (XI): C, 45.14; H, 3.79; N, 19.40. Found: C, 45.09; H, 3.78; N, 19.33.

Methyl DL-1-Methyl-2-piperidylmethyl Xanthate (XIII)—To a suspension of 0.46 g. of powdered metallic sodium in 25 ml. of anhyd. ether were dropped 3 g. of DL-1-methyl-2-piperidinemethanol⁸⁾ (XII) dissolved in 30 ml. of anhyd. ether and then 1.8 ml. of carbon disulfide while ice-cooling and stirring. The mixture became viscous. Furthermore, 1.24 ml. of methyl iodide dissolved in 5 ml. of anhyd. ether was added and stirred under ice-cooling. During the time, the viscous state disappeared and sodium

iodide deposited. After filtration, the filtrate was evaporated to dryness under reduced pressure at room temperature and the remaining yellow oil, yield 3.1 g. (60%), was converted to the picrate. Recrystallization from ethanol gave yellow needles of m.p. 124~126°. *Anal.* Calcd. for $C_9H_{17}ONS_2 \cdot C_6H_3O_7N_3$ (XIII·picrate): C, 40.17; H, 4.49; N, 12.49. Found: C, 40.43; H, 4.78; N, 12.77.

Hydrochloride: The precipitate resulted from mixing an ethereal solution of XIII and ethereal hydrogen chloride was recrystallized from ethanol-ether, m.p. 134~135°. The alkaline hydrolysis of XIII gave the starting material (XII).

DL-S-(1-Methyl-2-piperidylmethyl) S'-Methyl Dithiolcarbonate (XIV)—Four grams of XIII was heated at 130° for a half hour and then distilled *in vacuo* yielding 3.5 g. (87%) of a light yellow oil, b.p. 119~120°. Picrate: recrystallized from ethanol, m.p. 164~165°. *Anal.* Calcd. for $C_9H_{17}ONS_2 \cdot C_6H_3O_7N_3$ (XIV·picrate): C, 40.17; H, 4.49; N, 12.49. Found: C, 39.91; H, 4.74; N, 12.61.

DL-1-Methyl-2-chloromethylpiperidine Hydrochloride (XVII·HCl)—To 7 g. of XII⁸⁾ dissolved in 20 ml. of anhyd. chloroform was dropped 6 ml. of thionyl chloride while stirring and then refluxed for 3 hr. The reaction mixture was poured on ice and the aqueous layer was evaporated to dryness *in vacuo*. The residue was dissolved in ethanol and ether added to deposit crystals. Recrystallization from acetone gave colorless needles of m.p. 159~161°, yield 7.1 g. (71%). *Anal.* Calcd. for $C_7H_{14}NCl \cdot HCl$ (XVII·HCl): C, 45.66; H, 8.21; N, 7.61. Found: C, 45.91; H, 8.21; N, 7.68. Picrate: recrystallized from acetone, m.p. 167~168°.

DL-2-(1-Methyl-2-piperidylmethyl)-2-thiopseudourea Dihydrochloride (XVIII·2HCl)—Three grams of XVII·HCl and 1.23 g. of thiourea were dissolved in 10 ml. of ethanol and refluxed for 4 hr. Evaporation to dryness left a viscous substance which crystallized after dissolved in ethanol followed by adding ether. Recrystallization from butanol gave colorless needles of m.p. 192~193°, yield 2.8 g. (66%). *Anal.* Calcd. for $C_8H_{17}N_3S \cdot 2HCl$ (XVIII·2HCl): C, 36.92; H, 7.36; N, 16.15. Found: C, 36.95; H, 7.44; N, 16.18.

DL-1,1'-Dimethyl-2,2'-dithiodimethyldipiperidine (XVI)—a) To 0.7 g. of XVIII·2HCl was added 5 ml. of 2N aqueous sodium hydroxide, heated on a water bath for 1 hr. and air bubbled overnight. The reaction mixture was extracted with ether, dried over anhyd. potassium carbonate and evaporated to dryness. The remaining oil was converted to the picrate which was recrystallized from methanol, m.p. 153~155°, yield 0.68 g. (68.7%). *Anal.* Calcd. for $C_{14}H_{28}N_4S_2 \cdot 2C_6H_3O_7N_3$ (XVI·dipicrate): C, 41.71; H, 4.58; N, 14.97. Found: C, 41.66; H, 4.74; N, 14.67.

b) To 1 g. of XIV was added 40 ml. of 5% ethanolic sodium hydroxide and heated on a water bath for 1 hr. To the reaction mixture was dropwise added 10% ethanolic hydrochloric acid evolving gas which was absorbed in 15% ethanolic sodium hydroxide and identified as ethanethiol by conversion to 2,4-dinitroethylthiobenzene, m.p. 125° alone and on admixture with an authentic sample. The acidic reaction mixture was evaporated to dryness and the residue was mixed with an aqueous potassium carbonate. The mixture was oxidized by introducing air overnight, extracted with ether, dried over anhyd. potassium carbonate and evaporated to dryness. The resulting oil was converted to the picrate which was recrystallized from methanol, yield 0.8 g. (52%) m.p. 151~154° and showed no depression of melting point on admixture with an authentic sample (XVI·dipicrate) prepared by method (a).

The Hofmann Degradation of XII. The Formation of 6-Dimethylamino-1-hexanal (XXII)—To 50 ml. of a methanolic solution containing 8 g. of XII methiodide⁹⁾ was added a suspension of silver oxide prepared from 12 g. silver nitrate and 20 ml. of 10N aqueous sodium hydroxide. The mixture was stirred for 5 hr. and silver iodide was filtered off. The filtrate was evaporated to dryness under reduced pressure in the stream of N_2 and the residue was heated at 100° for 3 hr. under reduced pressure evolving gas. The remainder was distilled *in vacuo* and fractionated to two parts. The first fraction, b.p. 90~100°, yield 1 g. (29.4%), was redistilled and the distillate at b.p. 98~99° was collected. Its picrate was identical with XII·picrate, m.p. 158~159° alone and on admixture with an authentic sample. The second fraction, b.p. 160~170°, yield 1.1 g. (32.4%), was redistilled and the distillate, b.p. 168~170°, was collected. The product was positive in the aldehyde tests by the Tollens' reagent and fuchsin-sulfur dioxide. Picrate: recrystallized from water, m.p. 146~148°. *Anal.* Calcd. for $C_8H_{17}ON \cdot C_6H_3O_7N_3$ (XXII·picrate): C, 45.16; H, 5.41; N, 15.05. Found: C, 45.37; H, 5.58; N, 14.76.

DL-2-Piperidinemethanol Hydrogen Sulfate (XXIII)—To 5 g. of conc. sulfuric acid was slowly added 6 g. of I while ice-cooling. The mixture was gradually heated till temperature of a bath raised to 240°. After cooling, the solid mass remaining was crushed, washed with ethanol and recrystallized from methanol to give colorless pillars of m.p. 262~263° (decomp.), yield 7.4 g. (73%). *Anal.* Calcd. for $C_6H_{13}O_4NS$ (XXIII): C, 36.91; H, 6.71; N, 7.02. Found: C, 36.90; H, 6.71; N, 6.86.

DL-1-Azabicyclo[4.1.0]heptane (XXIV)—To 40 ml. of an aqueous solution containing 6 g. of XXIII was added 100 ml. of 10% aqueous sodium hydroxide and the mixture was distilled into a receiver which was well chilled with ice. Solid potassium hydroxide was added to the distillate under ice-cooling and the liberating oil was extracted with ether, dried over anhyd. potassium hydroxide and distilled *in vacuo* yielding an oil of b.p. 65°, yield 0.2 g. (6%). Immediately after distillation, the oil was converted to the picrate and recrystallized from ether-ethyl acetate, m.p. 151~152°. Whole treatment was carried out in a hurry and in the stream of N_2 gas. The free base (XXIV) polymerized completely within several hours even in the atmosphere of N_2 gas. *Anal.* Calcd. for $C_6H_{11}N \cdot C_6H_3O_7N_3$ (XXIV·picrate): C, 44.17; H, 4.33;

N, 17.18. Found: C, 44.17; H, 4.58; N, 17.00.

Reactions of XXIV*⁵ tried for Confirmation of its Structure

a) **Hydrolysis**—To an ethereal solution containing 0.1 g. of XXIV was added water and stirred for 1 hr. An aqueous solution saturated with potassium carbonate was added to the mixture while agitation and the aqueous layer was removed. The ether layer was dried over anhyd. potassium carbonate and an ethereal solution of picric acid was added to cause precipitation. After decantation of ether, the precipitate was recrystallized from ethanol-ether, m.p. 115°, and identified as I·picrate on a mixture melting point determination.

b) **With Hydrogen Chloride**—Ethereal solutions of XXIV (0.1 g.) and dry hydrogen chloride were placed in a sealed flask and set aside overnight. The precipitating crystals melted at 183~185° and at 183° on admixture with a sample of VII·HCl, m.p. 187~188°, ⁶ prepared by the Norton's procedure.³⁾ *Anal.* Calcd. for C₆H₁₂NCl·HCl (VII·HCl): C, 42.37; H, 7.70; N, 8.24. Found: C, 42.59; H, 7.77; N, 8.34.

c) **With Methyl Bromide**—An ethereal solution of XXIV (0.1 g.) was mixed with an ethereal solution of methyl bromide (0.1 g.) and allowed to stand overnight. The resulting precipitate was recrystallized from ethanol gave colorless granules of m.p. 230°, yield 0.16 g. (60%), which was identical with XXVII described below by a mixture melting point determination.

d) **With Thiourea**—An ethereal solution of 0.14 g. of XXIV was mixed with 0.1 g. of thiourea, 1.32 ml. of *N*-aqueous hydrochloric acid and 2 ml. of water while agitation. After a few minutes, 1.32 ml. of *N*-aqueous hydrochloric acid was added to the mixture and stirred for 1 hr. The ether layer was removed and the aqueous layer was evaporated to dryness *in vacuo*. The residue was dissolved in ethanol, undissolved substance removed and evaporated to dryness. The remainder was dissolved in butanol and refluxed for 1 hr. Precipitating ammonium chloride was filtered off and the filtrate was evaporated to dryness. The residue was converted to the picrate which was recrystallized from water, m.p. 152~154° and showed no depression of a mixture melting point with an authentic sample of X·picrate.

DL-2-Bromomethylpiperidine Hydrobromide (XXVI·HBr)¹⁴⁾—Three grams of I dissolved in 30 ml. of 48% aqueous hydrobromic acid was refluxed for 10 hr. and concentrated *in vacuo*. The residue crystallized after addition of ethanol and was filtered. Recrystallization from ethanol gave colorless needles of m.p. 188~190°, yield 4.1 g. (60.7%). *Anal.* Calcd. for C₆H₁₂NBr·HBr (XXVI·HBr): C, 27.82; H, 5.06; N, 5.41. Found: C, 28.08; H, 5.11; N, 5.63.

DL-2-Bromomethyl-1,1-dimethylpiperidinium Bromide (XXVII)—The free base liberated from 0.5 g. of XXVI·HBr was dissolved in 10 ml. of ether and to the solution was added 20 ml. of 10% ethereal solution of methyl bromide. After allowing to stand overnight, the resulting precipitate was filtered and recrystallized from ethanol to give colorless granules of m.p. 233~234° (decomp.), yield 0.47 g. (85%). *Anal.* Calcd. for C₈H₁₇NBr₂ (XXVII): C, 33.47; H, 5.97; N, 4.88. Found: C, 33.28; H, 6.25; N, 4.99.

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Summary

DL-2-Piperidinemethanol (I) was converted to O-acyl, 2-isothioureido and oxazolidine derivatives to be subjected to reactions such as acyl migration, transguanylation and oxidation with bromine respectively. The xanthate (XIII) derived from the *N*-methyl derivative of I (XII) was thermally rearranged to the corresponding dithiolcarbonate (XIV). In particular, I was converted to DL-1-azabicyclo[4,1,0]heptane (XXIV) *via* DL-2-piperidine-methanol hydrogen sulfate (XXIII). XXIV was easily polymerizable and therefore, stabilized in the form of picrate for identification. Structural proof for XXIV was provided from results of reactions to which it was subjected. In conclusion, the reaction sequences of I and XII were similar to those of acyclic analogues as be theoretically expected.

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*⁵ The material for every reaction was used immediately after preparation.

*⁶ 177~178° by Norton.³⁾

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