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89. Sanya Akaboshi[*1] and Shiro Ikegami[*2] : Synthesis of the Heterocyclic Compounds by Pschorr Cyclization. III.[*3] Syntheses of 10, 11-Methylenedioxy-7, 8-dihydro-6*H*-benzo[*c*]pyrid-[1, 2-*a*]azepinium Salts and Their Derivatives.

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*2])

In the preceding papers[*3,*4] of this series, the new synthetic method of benzo[*a*]-quinolizinium salts and their derivatives by Pschorr cyclization was reported.

In general, the intramolecular cyclization of the Pschorr reaction is widely adapted to the formation of a five- or six-membered ring in a good yield.[1] However, the application of this reaction to the formation of a seven-membered ring has not been hitherto found in literature.

In the present paper, the authors wish to report the successful application of the intranuclear cyclization of the Pschorr type reaction to the preparation of a seven-membered heterocyclic compounds containing a nitrogen atom at a bridge head.

It was shown in Part II[*3] of this series that, when 4 and 5 positions of the benzene ring in the starting materials were substituted with the methylenedioxy group, Pschorr cyclization took place smoothly and a cyclized product was obtained in a good yield

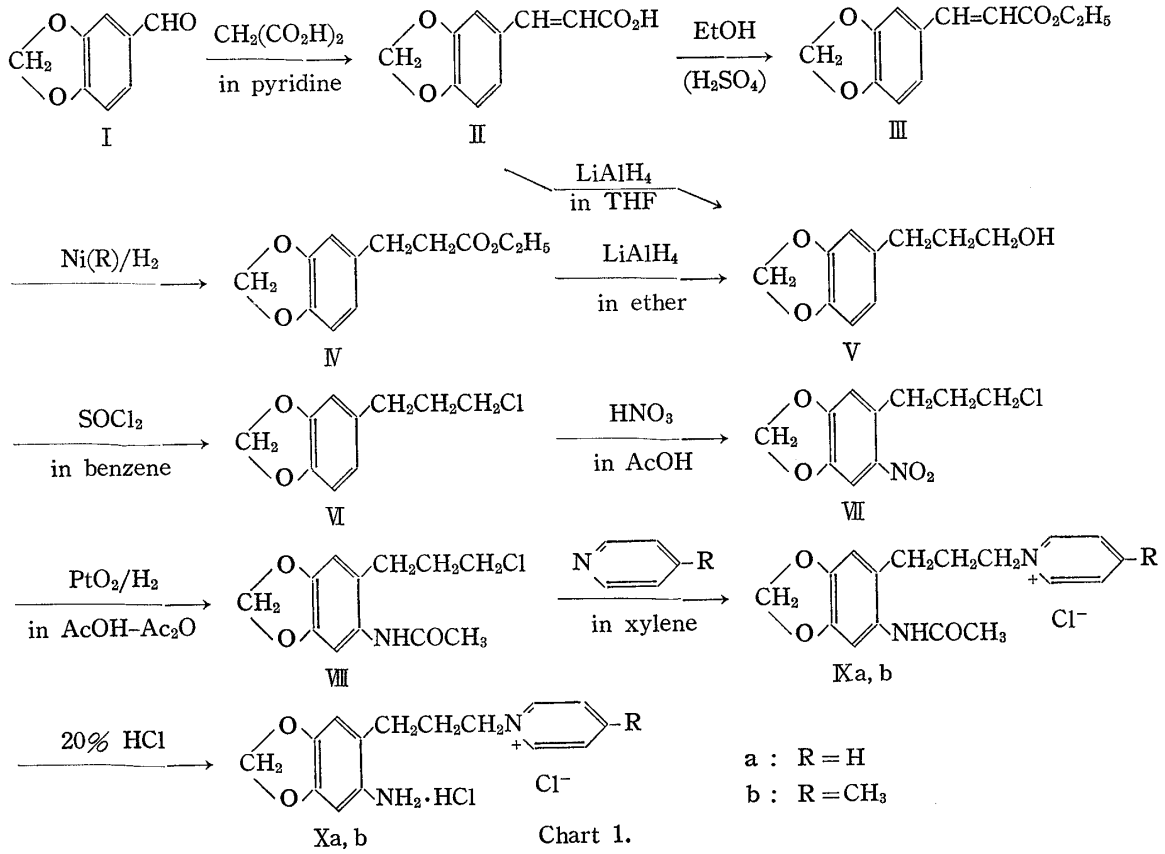

Chart 1.

*1 Present address : National Institute of Radiological Sciences, Anagawa-cho, Chiba (赤星三弥).

*2 Hongo, Tokyo (池上四郎).

*3 Part II : S. Akaboshi, T. Kato, A. Saiga : This Bulletin, **11**, 1446 (1963).

*4 Part I : S. Akaboshi, T. Kato : Yakugaku Zasshi, **83**, 1067 (1963).

1) D. F. DeTar, "Organic Reactions," Vol. IX, p. 409 (1957), John-Wiley & Sons, Inc., New York.

with none of by-product. Therefore, 1-[3-(2-amino-4,5-methylenedioxyphenyl)propyl]-pyridinium chloride hydrochloride (Xa) and its 4-methyl derivative (Xb) were chosen as the most reactive substrates for the formation of seven-membered ring by Pschorr cyclization.

For the synthesis of pyridinium salts (Xa and Xb), at first, 3,4-methylenedioxycinnamic acid (Ⅱ) was prepared by the condensation and decarboxylation of piperonal and malonic acid in pyridine in the presence of a little of piperidine as a catalyst with slight modification according to the method of Pearl and Beyer[2]. 3-(3,4-Methylenedioxyphenyl)propanol (Ⅴ) was readily preparable from the acid (Ⅱ) thus obtained by the following two methods. 1) The acid (Ⅱ) was directly reduced with lithium alminum hydride in tetrahydrofuran at refluxing temperature to give the saturated alcohol (Ⅴ) in a good yield. 2) The acid (Ⅱ) was esterified in a good yield (93%) by refluxing in ethanol with a small amount of conc. sulfuric acid and subsequently, the corresponding ethyl ester (Ⅲ) was catalytically hydrogenated in ethyl acetate by using freshly prepared Raney nickel as catalyst under 60~80 atmospheric pressures at 50~60°. The ethyl propionate derivative (Ⅳ) obtained in a yield of 97% was reduced with lithium aluminum hydride in ether to afford the corresponding alcohol (Ⅴ) in a good yield (92.6%).

The alcohol (Ⅴ) was chlorinated with thionyl chloride in absolute benzene in the usual manner and then nitration of the resulting chloride (Ⅵ) with concentrated nitric acid in glacial acetic acid proceeded smoothly to give 1-(3-chloropropyl)-2-nitro-4,5-methylenedioxybenzene (Ⅶ) in an excellent yield. As mentioned in the previous paper,*[3] when the nitro derivative (Ⅶ) was catalytically hydrogenated in a mixture of acetic acid and acetic anhydride in the presence of Adams catalyst, the amine derivative generated was immediately acetylated to give the corresponding acetamide (Ⅷ), which was then converted into the corresponding quaternary salts (Ⅸa and Xb) by refluxing with pyridine or 4-picoline in xylene. Warming the acetamide-quaternary salts in 20% aqueous hydrochloric acid yielded the hydrolyzed products, 1-[3-(2-amino-4,5-methylenedioxyphenyl)propyl]pyridinium chloride hydrochloride (Xa) and its 4-methyl derivative (Xb), which served as the valuable substrates for the following cyclization procedure.

Decomposition of an aqueous solution of the diazonium chloride obtained by treatment of Xa with a slight excess of sodium nitrite was carried out merely by

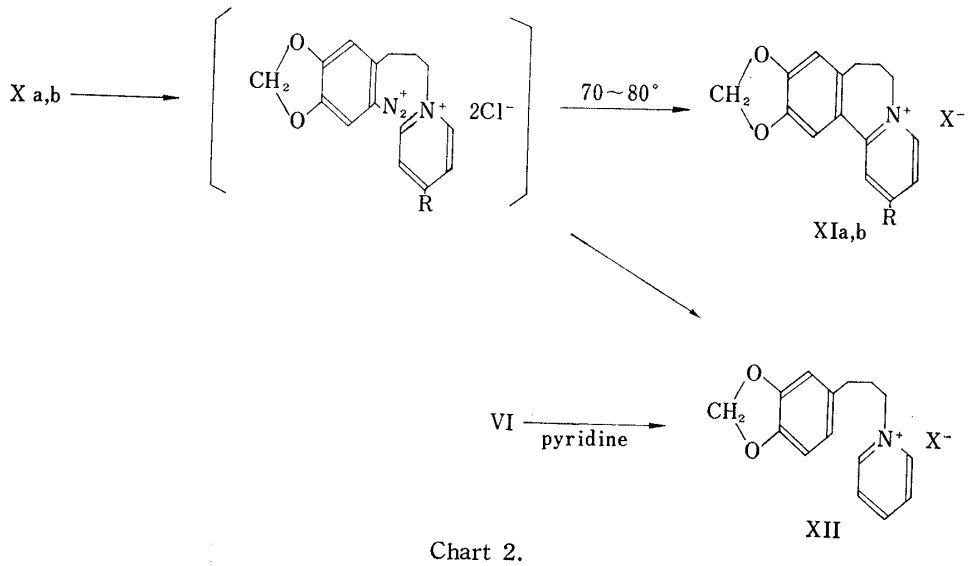

Chart 2.

2) I. A. Pearl, D. L. Beyer : J. Org. Chem., **16**, 216 (1951).

warming (70~80°) and resulted in the formation (59.1% yield) of the cyclized product (XIa) which was isolated as the quaternary iodide. In the cyclization procedure of Xa, a different decomposition condition of the corresponding diazonium salt, that is, gradual application of heat, led to the formation of a by-product isolated as the picrate, which was shown to be identical by direct comparison of their physical properties (mixed melting point and infrared spectra) with 1-[3-(3,4-methylenedioxyphenyl)propyl]pyridinium salt (XII) prepared from VI and pyridine.

Similarly, Pschorr reaction of 1-[3-(2-amino-4,5-methylenedioxyphenyl)propyl]-4-methylpyridinium chloride (Xb) afforded the corresponding benzopyridazepinium salt in a yield of 44.2%. In this case, the cyclized product was isolated as the picrate because of failure of solidification of its iodide.

In addition, better result was not obtained by using freshly prepared Gattermann's copper in the decomposition of these cold diazonium salt solutions.

The structure of these cyclized products was elucidated by the analytical data which were in accordance with the values calculated for XIa and XIb respectively and by the ultraviolet spectra of these compounds. The ultraviolet spectra of XIa and XIb showed the bands which should be expected to these cyclized compounds (Fig. 1) and also were similar to those of 9,10-methylenedioxy-6,7-dihydrobenzo[*a*]-quinolizinium salt and its 2-methyl derivative. Moreover, in further confirmation of the structure of these products, XIa was converted into the corresponding chloride with silver chloride in aqueous ethanol and the chloride submitted to catalytic hydrogenation in the presence of Adams catalyst in ethanol to furnish the octahydro-derivative (XIII). The synthesis of the hydrogenated product, 10,11-methylenedioxy-1,2,3,4,6,7,8,12*b*-octahydrobenzo[*c*]pyrid[1,2-*a*]azepine hydrochloride (XIII) thus obtained was tried by the route as shown in Chart 3. The cyclization by Bischler-Napieralski reaction of 1-[3-(3,4-methylenedioxyphenyl)propyl]-2-piperidinone(XV) synthesized *via* the oxidation of XII with potassium ferricyanide, followed by the catalytic hydrogenation of 2(1*H*)-pyridone derivative (XIV) over Raney nickel, failed even by the use of the various dehydrating agents such as phosphoryl chloride, phosphorus pentoxide and polyphosphoric acid and an unidentified product was obtained instead of the expected cyclized product. Recently, Minami, *et al.*[3,4] reported that Bischler-Napieralski reaction of the formamide derivatives with phosphorus pentoxide and polyphosphoric acid had afforded the corresponding seven-membered heterocyclic compounds in a poor yield. But, no report for the formation of seven-membered ring by the application of Bischler-Napieralski reaction in a field of 2-piperidinone has been hitherto published. The result as mentioned above gave support to be difficult for a preparation of a compound such as XVI by Bischler-Napieralski reaction.

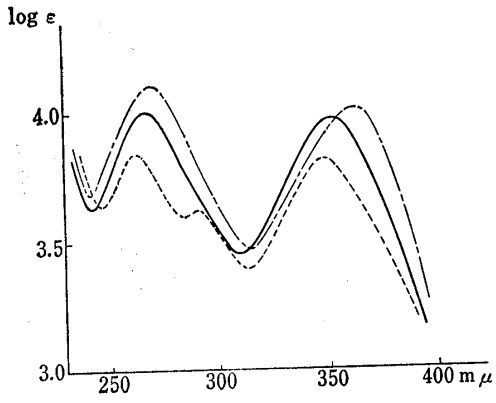

Fig. 1. Ultraviolet Absorption Spectra (in EtOH)

——— 10,11-Methylenedioxy-7,8-dihydro-6*H*-benzo[*c*]pyrid[1,2-*a*]azepinium perchlorate (XIa, X=ClO_4)

– – – – – 2-Methyl-10,11-methylenedioxy-7,8-dihydro-6*H*-benzo[*c*]pyrid[1,2-*a*]azepinium perchlorate (XIb, X=ClO_4)

—·—·— 9,10-Methylenedioxy-6,7-dihydrobenzo[*a*]quinolizinium iodide

On the mechanism of the Pschorr cyclization, recently, Abramovitch, *et al.*[5,6]

3) M. Tomita, S. Minami: Yakugaku Zasshi, **83**, 1022 (1963).
4) S. Minami, S. Uyeo: This Bulletin, **12**, 1012 (1964).
5) R. A. Abramovitch, W. A. Hymers, J. B. Rajan, R. Wilson: Tetrahedron Letters, **1963**, 1507 and related references cited herein.
6) R. A. Abramovitch, G. Tertzakian: *Ibid.*, **1963**, 1511 and related references cited herein.

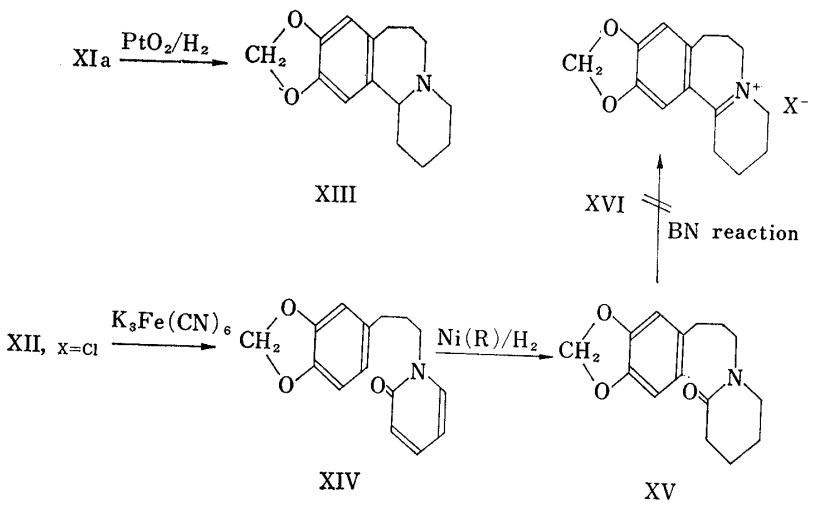

Chart 3.

pointed out that the participation of radical intermediates in the transition state would be best interpreted to explain some aspects of the uncatalyzed thermal decomposition of diazonium salts. The radical mechanism also would be much favored in the cyclization of the pyridinium derivatives described above.

Experimental*5

3-(3,4-Methylenedioxyphenyl)propanol (V)——Reduction of 3,4-methylenedioxycinnamic acid with $LiAlH_4$ in tetrahydrofuran (THF): To a suspension of 11.7 g. of $LiAlH_4$ in 300 ml. of THF, a muddy mixture of 40 g. of 3,4-methylenedioxycinnamic acid and 100 ml. of THF was added in small portions with stirring. The reaction was vigorously exothermic with evolution of hydrogen and the color changed pale yellow. After the addition of the acid (II), the reaction mixture was refluxed for 3 hr. with stirring. About 250 ml. of the solvent was distilled and 13 ml. of H_2O was added dropwise to the reaction mixture for decomposition of the complex. The resultant mixture was filtered off and the residue was extracted with THF. The filtrate and the THF extract were combined and dried over anhyd. K_2CO_3. After removal of the solvent, the residue was distilled to give colorless liquid, b.p_2 132~135°.[7] Yield, 30 g. or 80%. IR $\nu_{max}^{cap.}$ cm^{-1}: 3400 (OH).

Phenylurethan: white needles (from *n*-hexane), m.p. 99~100°. *Anal.* Calcd. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.85. IR ν_{max}^{KBr} cm^{-1}: 3340 (NH), 1700 (CO).

1-(3-Chloropropyl)-3,4-methylenedioxybenzene (VI)——To a solution of 80 g. of V in 300 ml. of abs. benzene and 37 ml. of pyridine, a solution of 64 ml. of thionyl chloride in 100 ml. of abs. benzene was added dropwise at 5~10° with stirring. The mixture was allowed to stand with continuous stirring for 2 hr. after the addition had been completed. After cooling, 200 ml. of water was added to the reaction mixture in order to dissolve pyridine hydrochloride and the benzene layer was shaken with saturated aqueous $NaHCO_3$ solution to remove excess thionyl chloride and dried over anhyd. Na_2SO_4. The solvent was removed *in vacuo* and the residue was distilled to afford compound (VI) as a colorless oil of b.p_2 116~118°. Yield, 80.8 g. or 90%. IR spectrum did not show any characteristic bands in the OH region.

1-(3-Chloropropyl)-6-nitro-3,4-methylenedioxybenzene (VII)——To a solution of 80 g. of VI in 320 ml. of glacial AcOH, a mixture of 96 ml. of conc. HNO_3 (S. G., 1.42) and 110 ml. of glacial AcOH was added dropwise at 5° with vigorous stirring to give a pale green solution. After the addition of one-fourth volume of the mixture of HNO_3 and glacial AcOH had finished, temperature of the reaction mixture was gradually raised until the vigorous reaction began with sudden rising of temperature. As soon as the reaction became suddenly vigorous, a beautiful green colored solution changed reddish brown with evolution of a gas. After the addition of the HNO_3-AcOH mixture had been completed below 20°, the reaction mixture was allowed to stand for 1 hr. at room temperature with efficient stirring and then poured into ca. 1 L. of ice-water. The precipitate was collected by filtration, washed several times with cold water and dissolved in 700 ml. of benzene. The benzene solution was washed with saturated aq. $NaHCO_3$ solution to remove excess of HNO_3,

*5 All melting points and boiling points are uncorrected.

7) M. T. Bogert, G. Powell: J. Am. Chem. Soc., **53**, 2747 (1931), report b.p_5 149~150° for 3-(3,4-methylenedioxyphenyl)propanol.

dried over anhyd. Na_2SO_4 and the solvent was evaporated to give yellow crystals of m.p. 49~50.5°. Yield, 87.5 g. or 88.2%. These cryatals were recrystallized from benzene-*n*-hexane to give yellow needles of m.p. 50.5~51.5°. On considering the case of nitration of 1-(2-chloroethyl)-3,4-methylenedioxybenzene by the similar method,*3 the position of the nitro group would be the para position to the methylenedioxy group. *Anal.* Calcd. for $C_{10}H_{10}O_4N_2Cl$: C, 49.29; H, 4.13; N, 5.75. Found : C, 49.58; H, 4.30; N, 5.76. IR ν_{max}^{Nujol} cm^{-1} : 1515, 1350 (NO_2).

2-(3-Chloropropyl)-4,5-methylenedioxyacetanilide (VIII)——The nitro derivative (VII : 3 g.) was dissolved in a mixture of 12 ml. of Ac_2O and 15 ml. of AcOH and hydrogenated in the presence of PtO_2 (100 mg.) at room temperature under an atmospheric pressure of hydrogen. After taking up nearly 3 mole equivalents (830 ml.) of hydrogen, the hydrogenation came to stop. The catalyst was removed by filtration and the filtrate was evaporated to dryness. The resultant mass was recrystallized from benzene-*n*-hexane to give VII as white needles of m.p. 146~147°. Yield, 1.5 g. or 48.4%. *Anal.* Calcd. for $C_{12}H_{14}O_3NCl$: C, 56.36; H, 5.51; N, 5.47. Found : C, 56.08; H, 5.40; N, 5.57. IR ν_{max}^{Nujol} cm^{-1} : 3300 (NH), 1660 (CO).

1-[3-(2-Acetamido-4,5-methylenedioxyphenyl)propyl]pyridinium Chloride (IXa)——A solution of 1.0 g. of the acetanilide (VIII) in a mixture of 30 ml. of dehyd. xylene and 3.2 ml. of pyridine was refluxed for 30 hr. The crystalline mass which separated gradually was filtered while hot and washed with benzene and then ether. The crude product of m.p. 192.5~193.5°(decomp.) was obtained in 1.2 g. or 92% yield and recrystallized from EtOH-ether to give white prisms, m.p. 195.5~196°(decomp.). The analytical sample was dried at 70~80° overnight. *Anal.* Calcd. for $C_{17}H_{19}O_3N_2Cl\cdot\frac{1}{2}H_2O$: C, 59.38; H, 5.86; N, 8.14. Found : C, 58.95; H, 5.80; N, 8.08. IR ν_{max}^{KBr} cm^{-1} : 3300 (NH), 1675 (CO), 1633 ($C=\overset{+}{N}$), 772 (pyridine).

1-[3-(2-Acetamido-4,5-methylenedioxyphenyl)propyl]-4-methylpyridinium Chloride (IXb)——Crude IXb (2.54 g.) was obtained from 2.0 g. of VIII and excess 4-picoline by the similar method as described in the preparation of IXa. This crude product of m.p. 124~126°(decomp.) was obtained in 93.1% yield and recrystallized from EtOH-ether to give white prisms, m.p. 127~128°(decomp.). *Anal.* Calcd. for $C_{18}H_{21}O_3N_2Cl\cdot H_2O$: C, 59.47; H, 6.32; N, 7.64. Found : C, 59.22; H, 6.32; N, 7.69. IR ν_{max}^{Nujol} cm^{-1} : 3430 (NH), 1693 (CO), 1643 ($C=\overset{+}{N}$).

1-[3-(2-Amino-4,5-methylenedioxyphenyl)propyl]pyridinium Chloride Hydrochloride (Xa)——The acetamido-quaternary salt (IXa : 2.0 g.) was dissolved in 20 ml. of 20% HCl and the solution was gently refluxed for 3 hr. After evaporation of the solvent, the residue was dissolved in MeOH (10 ml.) and the solution was treated with charcoal and evaporated to dryness. The brownish white crystals were obtained in 85.2% yield and recrystallized twice from MeOH-ether to give white needles, m.p. 252~253°(decomp.). *Anal.* Calcd. for $C_{15}H_{18}O_2N_2Cl_2$: C, 54.71; H, 5.54; N, 8.51. Found : C, 54.23; H, 5.39; N, 8.73. IR ν_{max}^{KBr} cm^{-1} : 2780, 2510 ($\overset{+}{N}H_3$), 1630 ($C=\overset{+}{N}$), 775 (pyridine).

1-[3-(2-Amino-4,5-methylenedioxyphenyl)propyl]-4-methylpyridinium Chloride Hydrochloride (Xb)——Crude Xb (1.7 g.) was obtained from 2.0 g. of IXb by hydrolysis in the similar procedure described above. Yield, 86.7%. White needles (from MeOH-ether), m.p. 245.5~246.5°(decomp.). The analytical sample was dried at 70~80° overnight. *Anal.* Calcd. for $C_{16}H_{20}O_2N_2Cl_2\cdot H_2O$: C, 53.19; H, 6.13; N, 7.75. Found : C, 53.61; H, 6.06; N, 7.87. IR ν_{max}^{KBr} cm^{-1} : 2800, 2570, 2370 ($\overset{+}{N}H_3$), 1640 ($C=\overset{+}{N}$).

10,11-Methylenedioxy-7,8-dihydro-6*H*-benzo[*c*]pyrid[1,2-*a*]azepinium Salt (XIa)——To a solution of 500 mg. of Xa in 8 ml. of 10% HCl was added dropwise 3 ml. of aq. solution containing 90 mg. of $NaNO_2$ with stirring at 5°. Temperature of the reaction mixture was kept at 5° for 30 min. and then a few crystals of urea were added to the solution for the decomposition of excess HNO_2. After 10 min. the solution was warmed on a water bath at 70~80° to complete the reaction, as shown by a negative coupling reaction with alkaline β-naphthol. After removal of solvent *in vacuo*, the residue was dissolved in anhyd. EtOH (3 ml.) and the solution was treated with charcoal. The viscous oil obtained by the evaporation of the solvent was dissolved in H_2O (3 ml.) and to the solution were added KI crystals and the suspended solution was extracted with $CHCl_3$. Drying and evaporation of the $CHCl_3$ solution left an orange-viscous oil. The orange crystals obtained by trituration with a few drops of acetone were recrystallized from H_2O to give pale orange needles, m.p. 272~273°(decomp.). Yield, 280 mg. or 59.1%. *Anal.* Calcd. for $C_{15}H_{14}O_2NI$: C, 49.06; H, 3.84; N, 3.81. Found : C, 49.45; H, 4.27; N, 4.03. IR ν_{max}^{Nujol} cm^{-1} : 1620 ($C=\overset{+}{N}$). UV $\lambda_{max}^{90\%\,EtOH}$ mμ (log ε) : 352 (3.97), 267 (4.21).

Picrate : yellow needles (from acetone-EtOH), m.p. 173.5~174.5°. *Anal.* Calcd. for $C_{21}H_{16}O_9N_4$: C, 53.85; H, 3.44; N, 11.96. Found : C, 53.55; H, 3.73; N, 11.91.

Perchlorate : white prisms (from EtOH), m.p. 253~254°(decomp.). *Anal.* Calcd. for $C_{15}H_{14}O_6NCl$: C, 53.29; H, 4.15; N, 4.12. Found : C, 53.10; H, 4.38; N, 4.26. UV $\lambda_{max}^{90\%\,EtOH}$ mμ (log ε) : 352 (3.96), 267 (4.00).

When the decomposition of the diazonium salt was carried out according to the following condition, that is, successive warming at room temperature for 30 min., at 40° for 1 hr. and then at 70~80° for 1 hr., a by-product isolated as the picrate from the soluble part in acetone was obtained in a poor yield and besides, the cyclized product was obtained in 45% yield as an insoluble material in acetone. This by-product was identical with XII (X=$C_6H_3O_7N_3$) by direct comparison of physical properties (mixed m.p. and IR spectra).

2-Methyl-10,11-methylenedioxy-7,8-dihydro-6*H*-benzo[*c*]pyrid[1,2-*a*]azepinium Salts (XIb)——The amino-quaternary salt (Xb : 500 mg.) was submitted to Pschorr reaction according to the similar method described above. To an EtOH solution of the cyclized product obtained after the diazotization of the amine and the decomposition of the diazonium compound, a few drops of picric acid dissolved in EtOH was added. The precipitate was collected by filtration and recrystallized from EtOH to give yellow needles, m.p. 233～234° (decomp.). Yield, 300 mg. or 44.2%. *Anal.* Calcd. for $C_{22}H_{18}O_9N_4$: C, 54.77; H, 3.76; N, 11.62. Found : C, 54.83; H, 3.92; N, 12.04.

Perchlorate : white prisms (from EtOH), m.p. 169～170°. *Anal.* Calcd. for $C_{16}H_{16}O_6NCl$: C, 54.32; H, 4.56; N, 3.96. Found : C, 54.08; H, 4.82; N, 3.85. IR ν_{max}^{KBr} cm^{-1} : 1632 ($C=\overset{+}{N}$). UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 345 (3.74), 289 (3.57), 263 (3.83).

10,11-Methylenedioxy-1,2,3,4,6,7,8,12*b*-octahydrobenzo[*c*]pyrid[1,2-*a*]azepine Hydrochloride (XIII)——Pyridinium chloride (Xa, X=Cl : 500 mg.) was hydrogenated in 20 ml. of EtOH in the presence of PtO_2 (100 mg.) as catalyst. After taking up 3 mole equivalents of hydrogen, the catalyst was removed by filtration and the solvent was evaporated *in vacuo*. The hydrogenated product was recrystallized from MeOH–iso-Pr_2O to give colorless needles of m.p. 265～266°(decomp.). Yield, 430 mg. or 84.1%. *Anal.* Calcd. for $C_{15}H_{20}O_2N$-Cl : C, 63.94; H, 7.15; N, 4.97. Found : C, 63.50; H, 6.82; N, 5.17. UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 290 (3.66), 244 (3.62).

Picrate : yellow needles (from EtOH–acetone), m.p. 190～191°. *Anal.* Calcd. for $C_{21}H_{22}O_9N_4$: C, 53.16; H, 4.67; N, 11.81. Found : C, 53.61; H, 4.41; N, 11.94.

Methiodide : pale yellow prisms (from EtOH), m.p. 261～262°(decomp.). *Anal.* Calcd. for $C_{16}H_{22}O_2NI$: C, 49.62; H, 5.72; N, 3.62. Found : C, 49.49; H, 5.28; N, 3.40.

1-[3-(3,4-Methylenedioxyphenyl)propyl]pyridinium Salts (XII)——A mixture of 10 g. of Ⅵ and 11 g. of pyridine was heated on a water bath at 90～95° for 6 hr. After removal of excess pyridine, the residue was washed several times with benzene and the solvent was evaporated to leave 14.7 g. of a pale brown viscous oil. This crude product was oxidized with $K_3Fe(CN)_6$ without further purification as the following description. A part of this crude product was converted into the corresponding iodide by the usual method.

Iodide : yellow prisms (from EtOH), m.p. 122～123°. *Anal.* Calcd. for $C_{15}H_{16}O_2NI$: C, 48.79; H, 4.37; N, 3.79. Found : C, 48.76; H, 4.54; N, 3.92. IR ν_{max}^{Nujol} cm^{-1} : 1630 ($C=\overset{+}{N}$). UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 287 (3.58), 266 (3.62), 260 (3.67).

Picrate : yellow needles (from acetone–EtOH), m.p. 119.5～120°. *Anal.* Calcd. for $C_{21}H_{18}O_9N_4$: C, 53.62; H, 3.86; N, 11.91. Found : C, 53.46; H, 4.07; N, 11.97.

1-[3-(3,4-Methylenedioxyphenyl)propyl]-2(1*H*)-pyridone (XIV)——To a solution of 11.7 g. of the crude Ⅻ in 60 ml. of H_2O, a solution of 41.5 g. of $K_3Fe(CN)_6$ dissolved in 140 ml. of H_2O was added dropwise below 10° with vigorous stirring. To the mixture 74 g. of granular KOH was added in small portions below 30° after the addition of $K_3Fe(CN)_6$ had completed. The reaction mixture was stirred at 30～40° for 2 hr. and extracted with benzene. The benzene extract was repeatedly washed with water and 3% HCl and dried over anhyd. Na_2SO_4. The solvent was evaporated to leave 6.2 g. of yellow crystals of m.p. 91.5～93°. These crystals were recrystallized from benzene–*n*-hexane to give pale yellow needles, m.p. 102～102.5°. *Anal.* Calcd. for $C_{15}H_{15}O_3N$: C, 70.02; H, 5.88; N, 5.44. Found : C, 70.22; H, 5.82; N, 5.43. IR ν_{max}^{Nujol} cm^{-1} : 1665 (CO).

1-[3-(3,4-Methylenedioxyphenyl)propyl]-2-piperidinone (XV)——The pyridone derivative (XⅣ : 5 g.) in 30 ml. of EtOH was hydrogenated using freshly prepared Raney nickel catalyst (from 2 g. of alloy) at an atmospheric pressure until 2 mole equivalents of hydrogen were absorbed. After removal of the catalyst and EtOH, the residue was distilled *in vacuo* to give colorless liquid of $b.p_1$ 195～200°. Yield, 4.2 g. or 82.8%. This liquid changed a semi-solid on standing overnight at room temperature, whose recrystallization was failed. The analytical data were those of the liquid. *Anal.* Calcd. for $C_{15}H_{19}O_3N$: C, 68.94; H, 7.33; N, 5.36. Found : C, 68.65; H, 7.40; N, 5.43. IR ν_{max}^{cap} cm^{-1} : 1630 (CO).

The authors express their deep gratitude to Prof. Emeritus S. Sugasawa and Prof. S. Yamada of the University of Tokyo for their interest and encouragement throughout the course of this work. Thanks are also due to the members of the Central Analysis Room of this Faculty for microanalytical, infrared and ultraviolet spectral data.

Summary

The Pschorr reaction of 1-[3-(2-amino-4,5-methylenedioxyphenyl)propyl]pyridinium chloride and its 4-methyl derivative was carried out and the corresponding cyclized product was obtained in a moderate yield respectively.

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