UDC 547.829.07

112. **Yoshio Ban, Osamu Yonemitsu, Takeshi Oishi, Susumu Yokoyama, and Masako Nakagawa** : Reaction of 1-Phenethyl-2(1*H*)-pyridones with Phosphoryl Chloride. Formation of 1-Phenethyl-2-chloropyridinium Salts.[*2]

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As preliminary experiments to clarify the conformation at C-11b of emetine (I), attempt was made to synthesize 1,2,3,4,6,7-hexahydro-11b*H*-benzo[*a*]quinolizines (IIa,b,c), to examine the oxidation of these compounds with mercuric acetate, and to elucidate the stereochemical meaning of α- and β-isomers derived from methiodides of (IIa, b, c).

Recently, Ban and Oishi[1] reported a convenient preparation of phenethyl alcohols which are very useful starting materials for synthesizing (IIa, b, c) in Sugasawa's way, which is shown in Chart 1.

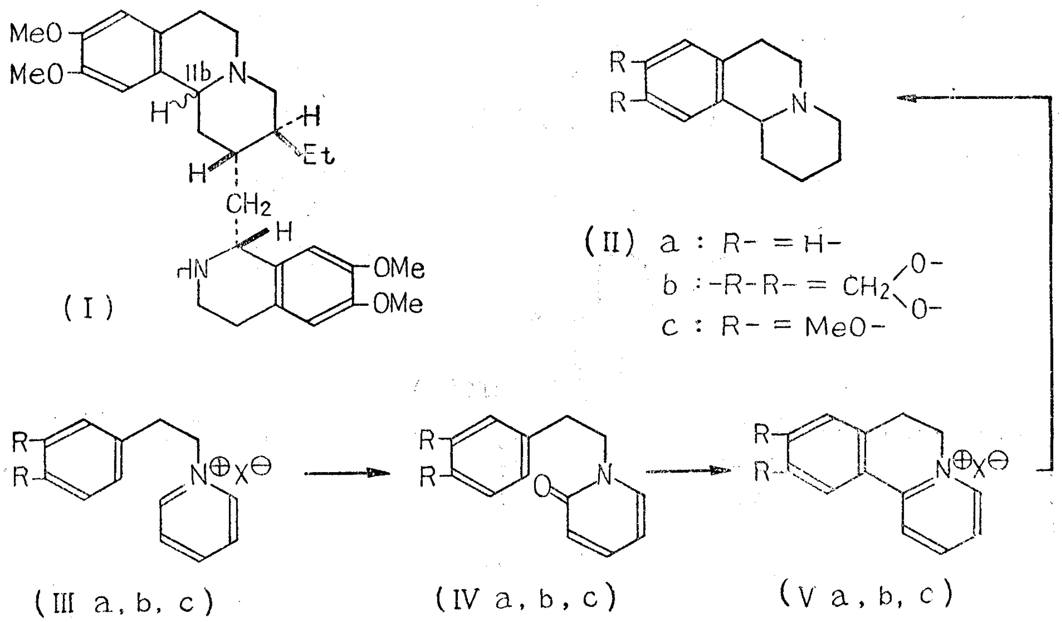

Chart 1.

Thus the authors had the recourse to this way and obtained the unexpected results partially different from that of the previous workers.[2~5]

1-Phenethylpyridinium bromide (IIIa), which had been easily obtained by heating an equimolar mixture of pyridine and phenethyl bromide, was oxidized with alkaline potassium ferricyanide to yield the corresponding pyridone (IVa) in the usual fashion.

Then the pyridone (IVa) was heated with phosphoryl chloride under reflux for 2 hours to give a quaternary iodide, m.p. 191°(decomp.), consistent with the previously

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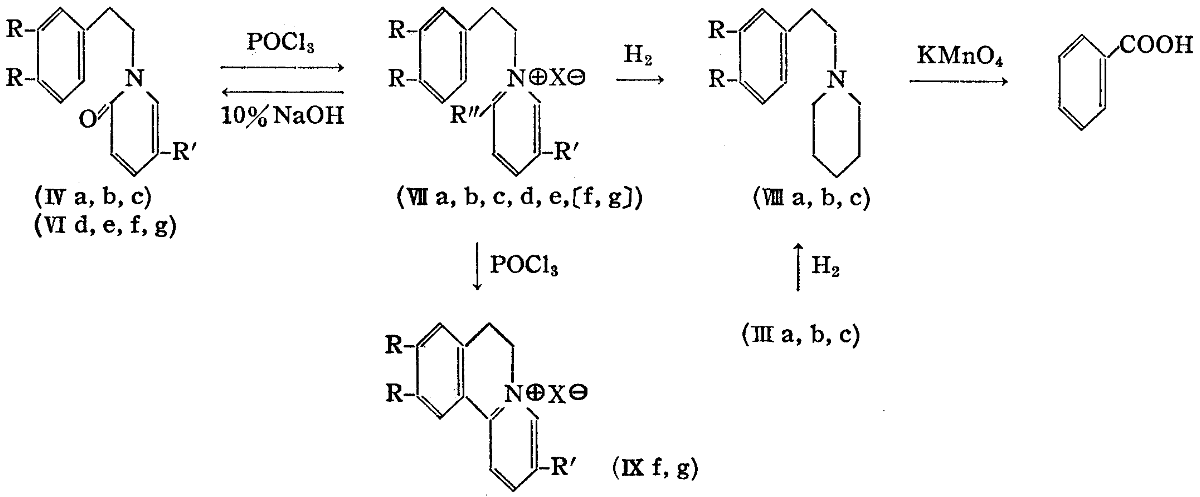
[*2] The preliminary report of this paper was published as a communication by S. Sugasawa, S. Akaboshi, and Y. Ban (This Bulletin **7**, 263(1959)). S. Akaboshi and others will publish their results separately from this paper.

1) Y. Ban, T. Oishi : This Bulletin, **6**, 574(1958).
2) S. Sugasawa, N. Sugimoto : Ber., **72**, 979(1939).
3) a) S. Sugasawa, S. Akaboshi, M. Suzuki : Yakugaku Zasshi, **72**, 1273(1952). b) S. Akaboshi : *Ibid.*, **72**, 1277(1952).
4) T. Govindachari, B. Thyagarajan : Proc. Indian Acad. Sci., **39**A, 232(1954) (C.A., **49**, 9653(1955)).
5) C. Tani, K. Ishibashi : Yakugaku Zasshi, **77**, 324(1957).

described iodide of m.p. 191~192°(decomp.), to which had been assigned benzo[*a*]quinolizinium iodide (Va; $X=I$).3) Surprisingly, however, the picrate (m.p. 136.5~137.5°) derived from this iodide clearly showed a positive reaction in Beilstein test. If it were benzo[*a*]quinolizinium picrate (Va; X=picrate anion), it should be negative to this test.

On the other hand, Sugasawa and Tomisawa6) obtained 9,10-methylenedioxy-3-ethoxycarbonyl-6,7-dihydrobenzo[*a*]quinolizinium iodide (IXf; $X=I$) by cyclization of the corresponding pyridone (VIf) with phosphoryl chloride. Later, Wiley and his co-workers7) reported that although 1-(3,4-methylenedioxyphenethyl)-5-carboxy-2(1*H*)-pyridone (VIf) and 1-(3,4-dimethoxyphenethyl)-5-carboxy-2(1*H*)-pyridone (VIg) underwent cyclization to quinolizinium salts (IXf, g) with phosphoryl chloride in xylene, 1-phenethyl-5-carboxy-2-(1*H*)-pyridone (VIe) failed to give any cyclized product and was merely converted to 2-ethoxypyridinium salt (VIIe) when the reaction mixture was treated with alcohol.



a : R=H, R′=H, R″=Cl
b : -R-R-=-O-CH$_2$-O-, R′=H, R″=Cl
c : R=MeO, R′=H, R″=Cl
d : R=H, R′=Et, R″=Cl
e : R=H, R′=COOH(Et), R″=OC$_2$H$_5$
f : -R-R-=-O-CH$_2$-O-, R′=COOH(Et), R″=Cl
g : R=MeO, R′=COOH(Et), R″=Cl

Chart 2.

Moreover, Berson and Cohen8) pointed out that 1-phenethyl-5-ethyl-2(1*H*)-pyridone (VId) reacted with phosphoryl chloride in benzene to give only the corresponding 2-chloropyridinium salt (VIId) and not a cyclized product.

Judging from these papers, it was considered that the quaternary iodide obtained by the authors would not be quinolizinium iodide (Va; $X=I$) as had been described in the previous papers3) but would be 2-chloropyridinium iodide (VIIa, $X=I$). Thus the determination of halogen atom (Carius method) in the derived picrate was carried out and proved the value of chlorine to be consistent with the value calculated for (VIIa; X=picrate anion).

The UV absorption spectrum of the iodide is shown in Fig. 1 (1), which was in reasonable accordance with that of 2-chloropyridine hydrobromide (Fig. 1 (3), in 4.4*N* HBr-EtOH), and its IR absorption spectrum showed the bands at 760 and 700 cm^{-1} which were considered to be due to the CH out-of-plane bending vibration of mono-substituted benzene or C-Cl stretching vibration.

To confirm this assumption, the iodide was converted to the corresponding chloride

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6) S. Sugasawa, H. Tomisawa : Yakugaku Zasshi, **72**, 804(1952).
7) R. Wiley, N. Smith, L. Knabeschuh : J. Am. Chem. Soc., **75**, 4482(1953).
8) J. Berson, T. Cohen : *Ibid.*, **78**, 416(1956).

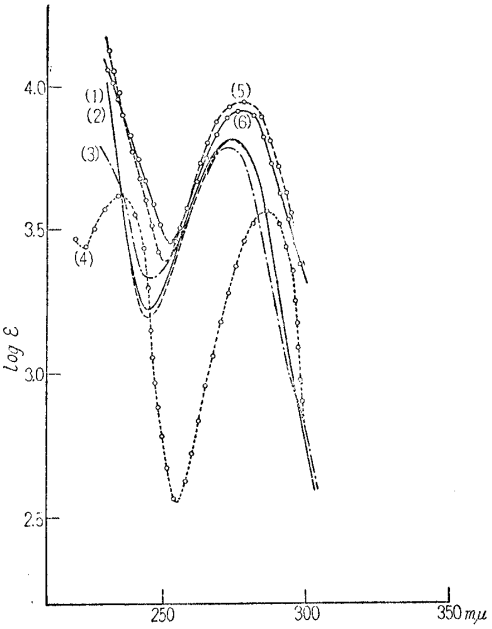

Fig. 1.

(1) ———— 1-Phenethyl-2-chloropyridinium iodide (VIIa, X=I)
(2) ------ 1-Alkyl-2-chloropyridinium salt
(3) —·—·— 2-Chloropyridine hydrobromide (in 4.4N HBr-EtOH)
(4) ---○---○--- 3,4-Methylenedioxyphenethyl alcohol
(5) -○--○-- (2) + (4)
(6) —○—○— 1-(3,4-Methylenedioxyphenethyl)-2-chloropyridinium iodide (VIIb, X=I)

in the usual way and subjected to hydrogenation over Adams catalyst in hydrous ethanol containing several drops of 10% hydrochloric acid. Four molar equivalents of hydrogen was taken up very smoothly and the liberated base, after the usual treatment, had a piperidine-like characteristic odor and was negative to Beilstein reaction before purification. This showed that this base would be 1-phenethylpiperidine (VIIIa) and not a quinolizine derivative (IIa).

The methiodide, m.p. 180~181°, and picrate, m.p. 147~148°, of this base were consistent with the previously described[3a] methiodide, m.p. 179~180°, and picrate, m.p. 148~148.5°, which had been assigned to derivatives of (IIa).

Thus, these derivatives were identified through the mixed melting point test and IR spectra with those of authentic 1-phenethylpiperidine (VIIIa)[9,10] which had been prepared by hydrogenation of 1-phenethylpyridinium bromide (IIIa).

In addition, oxidation of the methiodide of (VIIIa) with potassium permanganate yielded pure benzoic acid contrary to the previous description[3a] and the structure of (VIIIa) was unequivocally established.

Therefore, it was proved that this reaction sequence proceeded as (IVa)→(VIIa)→(VIIIa), as shown in Chart 2, and not as (IVa)→(Va)→(IIa).

Based upon this result, the compounds which were described as (Va) and (IIa) by Govindachari, *et al.*[4] and by Tani, *et al.*,[5] should be corrected to (VIIa) and (VIIIa), respectively.

Further, examination was made on the products when each of 1-(3,4-methylenedioxyphenethyl)-2(1*H*)-pyridone (IVb) and 1-(3,4-dimethoxyphenethyl)-2(1*H*)-pyridone (IVc) was reacted with phosphoryl chloride, and it was found that, although these pyridones containing activated benzene ring were expected to cyclize much easier than (IVa), they gave only the corresponding 2-chloropyridinium salts (VIIb and VIIc), and not the cyclized products, at least under the above-described condition.

The curve shown in Fig. 1 (2), which is obtained by subtracting the absorption of phenethylamine hydrochloride from the UV absorption spectrum of (VIIa; X=I) shown in Fig. 1 (1), corresponds to the chromophore of 1-alkyl-2-chloropyridinium salt. When

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[9] F. Kröhnke: Ber., 84, 388(1951).
[10] C. Bahner, M. Frielden, L. Rives, M. Pickens: J. Am. Chem. Soc., **73**, 4455(1951).

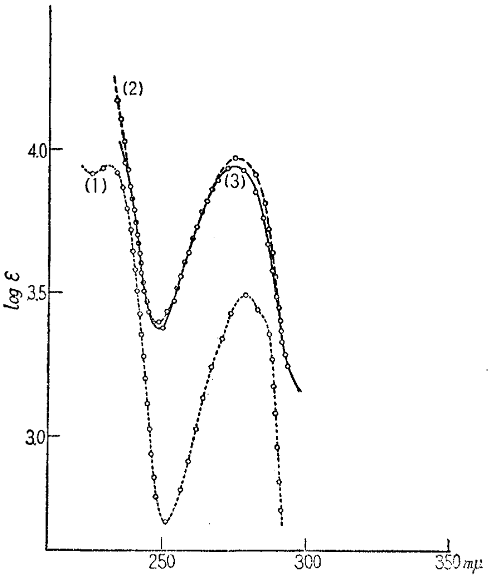

Fig. 2.

(1) ---○---○--- 3,4-Dimethoxyphenethylamine hydrochloride

(2) -○--○-- (1) + Fig. 1 (2)

(3) —○—○— 1-(3,4-Dimethoxyphenethyl)-2-chloropyridinium iodide (VIIc, X=I)

the absorption of 3,4-methylenedioxyphenethyl alcohol (Fig. 1 (4)) and of 3,4-dimethoxyphenethylamine hydrochloride (Fig. 2 (1)) is respectively added to this curve, there are obtained the curves (Fig. 1 (5) and Fig. 2 (2)) which predict the similarity of absorption spectra of (VIIb) and (VIIc).

The actual absorption spectra of quaternary iodides obtained are shown in Fig. 1(6) and Fig. 2 (3), which are approximately in accordance with the above-predicted curves. The analytical data of the iodides and picrates were equivalent to the values calculated for those of (VIIb) and (VIIc), and both picrates showed positive reaction in Beilstein test.

One of them, 1-(3,4-methylenedioxyphenethyl)-2-chloropyridinium iodide, m.p. 190~191°(decomp.)(VIIb; X=I), is consistent with the previously described iodide of m.p. 191° (decomp.) which has been assigned to (Vb; X=I).[2,3b] Therefore, these descriptions should be corrected now.

The structure of the iodide (VIIc; X=I) was unequivocally established in a similar way with the establishment of (VIIa).

The iodide, after being converted to the corresponding chloride, was hydrogenated to a single base, which had a faint piperidine-like odor and formed a perchlorate, m.p. 149~150°, and picrate, m.p. 155~156°. On the other hand, authentic 1-(3,4-dimethoxyphenethyl)piperidine (VIIIc) was prepared by hydrogenation of 1-phenethylpyridinium bromide (IIIc), and gave a perchlorate, m.p. 146~148°, and a picrate, m.p. 155~156°, both of which were identified with the above-mentioned derivatives through the mixed melting point test and IR spectra. These derivatives are quite different from those of (IIc) which was prepared by cyclization of the corresponding piperidone as described by Sugasawa and Mizukami.[11]

On being treated with diluted aqueous sodium hydroxide solution at a room temperature, the iodides (VIIa, b, c; X=I) yielded the corresponding pyridones (IVa, b, c) very readily, which had been described as the ring cleavage of benzo[*a*]quinolizinium salts (Va, b, c) induced by various basic reagents.[3] It was also observed that 1-methyl-2-chloropyridinium methosulfate yielded 1-methyl-2(1*H*)-pyridone under a similar condition.

The successful reports in cyclization of (VIf, g) by Sugasawa[6] and by Wiley[7] are doubtless due to the fact that the ring-substituted chlorine of (VIIf, g) is subject to activation by electron-attracting carboxyl group, as Wiley and others have pointed out, and since the electron density at 6-position of benzene ring of (IVb, c or VIIb, c) is much higher than in

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[11] S. Sugasawa, K. Mizukami: This Bulletin, **6**, 359(1958).

(IVa or VIIa), it is expected that these compounds will be cyclized under more vigorous conditions. This point will therefore be examined in the near future.

The authors are grateful to Prof. S. Sugasawa for his kind advice and encouragement throughout this work, and also to Mr. Yoshio Shimizu for his technical co-operation in this work. Thanks are also due to Mrs. F. Hisamichi and Mr. T. Yoda, Tokyo Research Laboratory, Tanabe Seiyaku Co. Ltd., for microanalytical data.

Experimental*3

1-Phenethyl-2-chloropyridinium Iodide (XVIIa, X=I)—To 1.2 g. of 1-phenethyl-2(1*H*)-pyridone, 5 g. of $POCl_3$ was added and the mixture was refluxed in an oil bath kept at 120~130° for 2 hr. After the excess $POCl_3$ was evaporated *in vacuo*, petr. ether was added to the residue, which solidified on standing in an ice-box over night. The solid was separated by decantation, dissolved in a small amount of water, treated with charcoal, and then saturated with solid KI. The precipitate was collected, washed with water, and recrystallized from acetone-MeOH to white needles, m.p. 191° (decomp., with efferv.). Yield, 2.0 g. (95.7%). *Anal.* Calcd. for $C_{13}H_{13}NClI$: C, 45.17; H, 3.79; N, 4.05. Found : C, 45.15; H, 3.66; N, 3.84. UV λ_{max}^{EtOH} 273 mμ(log ε 3.82). IR ν_{max}^{KBr} 760, 700 cm^{-1} (for monosubstituted benzene or C-Cl). The iodide was treated with 10% NaOH at room temperature to give very readily the starting pyridone (λ_{max}^{EtOH} 302 mμ), m.p. 103~105°, showing no depression on admixture with the authentic specimen.

Picrate : Obtained from the foregoing iodide in the usual way and recrystallized from MeOH as yellow blades, m.p. 136.5~137.5°. *Anal.* Calcd. for $C_{19}H_{15}O_7N_4Cl$: C, 51.06; H, 3.35; N, 12.54; Cl, 7.95. Found : C, 50.80, H, 3.29; N, 12.00; Cl, 8.01.

1-Phenethylpiperidine (VIIIa)—a) A solution of the foregoing iodide (VIIa, 1.80 g.) in 50 cc. of EtOH was mixed with AgCl freshly prepared from 1.8 g. of $AgNO_3$ and heated under reflux on a steam bath for 2 hr. In the course of this reaction, the silver halide was occassionally pulverised with a glass rod. The AgI produced and excess AgCl were filtered off and EtOH was evaporated *in vacuo* to leave yellow crystals (1.18 g. or 89%).

A mixture of the chloride obtained and 50 mg. of the Adams catalyst in 50 cc. of 50% EtOH was subjected to hydrogenation at room temperature (25°) in atmospheric pressure of hydrogen and 4 molar equivalents of H_2 (455 cc., 102% of the theoretical amount) was absorbed very smoothly in 2 hr. After removal of the catalyst and solvent, the residual hygroscopic solid was dissolved in a small amount of water, basified with conc. KOH solution, separating an oily substance. This oil was taken up in ether, dried over solid KOH, and the solvent was evaporated to leave an almost colorless liquid having a piperidine-like characteristic odor, and negative to Beilstein reaction before purification. The crude oil was distilled to colorless liquid, $b.p_{10}$ 145~150°(9) (710 mg. or 81%), which was characterized as its picrate and methiodide.

Picrate : Yellow needles (from MeOH), m.p. 147~148°. *Anal.* Calcd. for $C_{19}H_{22}O_7N_4$: C, 54.54; H, 5.30; N, 13.39. Found : C, 54.45; H, 5.01, N, 13.75.

Methiodide : The free base was mixed with an excess of MeI to produce a white crystalline solid under evolution of heat in several minutes and the solid was recrystallized from MeOH to colorless minute needles, m.p. 180~181°.(10) *Anal.* Calcd. for $C_{14}H_{22}NI$: C, 50.76; H, 6.69. Found : C, 50.45; H, 6.38. IR ν_{max}^{KBr} 758, 695 cm^{-1} (CH out-of-plane bending vibration for monosubstituted benzene).

b) A solution of 3.47 g. of 1-phenethylpyridinium bromide (IIIa, m.p. 124~125°; λ_{max}^{EtOH} 259 mμ(log ε 3.70)), in 100 cc. of 50% EtOH was hydrogenated over 50 mg. of pre-reduced Adams catalyst in atmospheric pressure of hydrogen (25°). After 3 molar equivalents of H_2 (1000 cc., 103% of the calculated amount) was absorbed smoothly, the whole was treated in the same way as in (a) to give the free base, $b.p_{10}$ 145~150°,(9) having a piperidine-like odor. Yield, 2 g. or 80.5%.

Picrate : Yellow needles (from MeOH), m.p. 148~149°. No m.p. depression was observed when this sample was mixed with the picrate obtained by (a) method, and IR spectra of the two samples were quite consistent in all respects.

Methiodide : Colorless small needles (from MeOH), m.p. 180~181°,(10) which was identified with the methiodide prepared by method (a) through a mixed m.p. test and IR identification.

These derivatives had been described as those of (IIa) previously.(3a)

Oxidation of 1-Phenethylpiperidine with $KMnO_4$—The foregoing methiodide (850 mg.) was suspended in a small amount of water, mixed with Ag_2O freshly prepared from 850 mg. of $AgNO_3$, and

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*3 A Koken Model DS-301 double-beam spectrophotometer equipped with two NaCl prisms was used for the determination of IR spectra, and samples were run as Nujol mulls or as KBr disks. A Beckman Model DK-2 spectrophotometer was used for the determination of UV spectra. All m.p.s are uncorrected.

the hydroxide solution obtained was oxidized in the following way:

A solution of 5 g. of $KMnO_4$ in 200 cc. of water was added dropwise after recognizing that each drop was consumed, to the above-mentioned hydroxide solution under mechanical stirring at a room temperature for 10 hr., during which time the consumption of the oxidizing reagent was very slow. The mixture was kept standing over night, and then warmed and stirred on a steam bath at 50~60° for 8 hr. At the beginning of this period, a piperidine-like odor was detected and this was probably due to the partial Hofmann degradation of the methohydroxide of (VIIIa). After standing over night at room temperature, remainder of the oxidizing reagent was added to the reaction mixture, and the mixture was again warmed and stirred at 50~60° for 5 hr. Then the excess of $KMnO_4$ was decomposed by adding a small amount of oxalic acid solution, the precipitated MnO_2 was filtered off by suction, and washed thoroughly with boiling water twice. The combined filtrate was neutralized with 20% H_2SO_4, concentrated to about 10 cc., cooled, and the separated inorganic substance was filtered off.

When the filtrate was acidified with 10% HCl, there was produced a white solid having m.p. 120° before purification, which showed no depression of m.p. on admixture with authentic benzoic acid, and IR spectra of the two were consistent in all respects.

1-(3,4-Methylenedioxyphenethyl)-2-chloropyridinium Iodide (VIIb)—A mixture of 1.0 g. of 1-(3,4-methylenedioxyphenethyl)-2(1*H*)-pyridone (m.p. 147~148°; λ_{max}^{EtOH} mμ (log ε): 229.5(4.02), 289.5(3.91), 302(3.80)) and 5 cc. of $POCl_3$ was heated under reflux in an oil bath at 120~130° for 2 hr. The excess $POCl_3$ was evaporated *in vacuo*, the residue was taken up in cold water, the aqueous solution was treated with activated charcoal, and then saturated with solid KI. The precipitate (0.9 g. (56.3%)) was recrystallized from Me_2CO-MeOH to yellow needles, m.p. 190~191°(decomp.), which was consistent with that of the product previously assigned to (Vb, X=I). *Anal.* Calcd. for $C_{14}H_{13}O_2NClI$: C, 43.15; H, 3.36. Found: C, 43.15; H, 3.39. λ_{max}^{EtOH} 278 mμ (log ε 3.915) (Fig. 1 (6)). This absorption spectrum was almost in accordance with the added curve (Fig. 1 (5)) of two spectra depending upon the following chromophores: 3,4-Methylenedioxyphenethyl alcohol (Fig. 1 (4)) and 1-alkyl-2-chloropyridinium salt (Fig. 1 (2)).

This iodide was treated with dil. NaOH solution at a room temperature to give the corresponding pyridone (m.p. 147~148°) in nearly quantitative yield and identified through the mixed m.p. test and UV spectra.

Picrate: Obtained in the usual manner as yellow scales (from MeOH), m.p. 147~148°, positive to Beilstein test. *Anal.* Calcd. for $C_{20}H_{15}O_9N_4Cl$: C, 48.94; H, 3.08. Found: C, 49.04; H, 3.23.

1-(3,4-Dimethoxyphenethyl)-2-chloropyridinium Iodide (VIIc, X=I)—A mixture of 1 g. of 1-(3,4-dimethoxyphenethyl)-2(1*H*)-pyridone (IVc, m.p. 78~80°, λ_{max}^{EtOH} mμ(log ε): 229(4.23), 286(3.80), 305(3.79)), 2.5 g. of $POCl_3$, and 10 cc. of toluene was heated at reflux in an oil bath at 120° for 1.5 hr. In this case, when the bath temperature reached 100°, the oily substance separated with vigorous evolution of HCl. On cooling, the lower oily layer solidified, separated by decantation from the supernatant layer, and washed with petr. ether. To the supernatant layer petr. ether was also added, the separated solid was combined, and the whole was dissolved in a small amount of water.

The aqueous solution was treated with charcoal and then saturated with solid KI to give a yellow precipitate, which was recrystallized from MeOH to crystals of m.p. 164.5~165.5°(decomp., with efferv.). Yield, 1.14 g. (61.4%). *Anal.* Calcd. for $C_{15}H_{17}O_2NClI$: C, 44.41; H, 4.22; N, 3.45. Found: C, 44.48; H, 4.22; N, 3.61. UV λ_{max}^{EtOH} 274 mμ(log ε 3.95).

This UV absorption spectrum is shown in Fig. 2(3), which was almost in accordance with the added curve of two spectra depending upon the following chromophores: 3,4-Dimethoxyphenethylamine hydrochloride (Fig. 2(1), λ_{max}^{EtOH} mμ(log ε): 231(3.95), 279(3.49)) and 1-alkyl-2-chloropyridinium salt (Fig. 1(2), λ_{max}^{EtOH} 273 mμ(log ε 3.82)).

To the warm aqueous solution of the iodide (VIIc), 10% NaOH solution was added and it became turbid almost instantaneously and separated an oily substance, which was taken up in ether. The extract was washed, dried, and ether was evaporated leaving a nearly colorless syrup, which solidified on standing. Colorless needles as recrystallized from MeOH, m.p. 78~80°, which was identified with the starting pyridone through mixed m.p. test and UV spectra (λ_{max}^{EtOH} 229, 286, 305 mμ).

1-(3,4-Dimethoxyphenethyl)piperidine (VIIIc)—a) The above-mentioned iodide (1 g.) was converted to the corresponding chloride in the usual way. A mixture of the chloride, 50 mg. of pre-reduced Adams catalyst, and a few drops of 10% HCl in 60 cc. of 50% EtOH was subjected to hydrogenation at room temperature (25°) in atmospheric pressure of hydrogen. Four molar equivalents of H_2 (240 cc., 100.3% of the calculated amount) was absorbed in 3 hr. After filtration of the catalyst and evaporation of the solvent *in vacuo*, there remained a pale yellow oily substance, which was taken up in a small amount of cold water, the aqueous solution was washed with ether, and basified with $NaHCO_3$. This was extracted with benzene and yielded a pale yellow oil having a faint piperidine-like odor, which partially solidified on standing. The whole substance was dissolved in MeOH and converted into its perchlorate (670 mg. or 63.1%) of m.p. 149~150°(decomp.) as recrystallized from

MeOH. *Anal.* Calcd. for $C_{15}H_{24}O_6NCl$: C, 51.51; H, 6.91; N, 4.00. Found : C, 51.41; H, 6.89; N, 4.40.

This was identified with the authentic perchlorate obtained by direct hydrogenation of (IIIc) as described in (b) through the mixed m.p. test and IR spectra.

Picrate : Obtained from the above-mentioned perchlorate in the usual fashion and recrystallized from MeOH to yellow plates, m.p. 155～156°(decomp.), which was also identified with that obtained by method (b) through the mixed m.p. test and IR spectra. *Anal.* Calcd. for $C_{21}H_{26}O_9N_4$: C, 52.64; H, 5.47; N, 12.05. Found : C, 52.64; H, 5.28; N, 11.95.

b) A mixture of 500 g. of the bromide (IIIc, X=Br), 50 mg. of pre-reduced Adams catalyst, and several drops of 10% HCl, in 50 cc. of 50% EtOH was subjected to hydrogenation at room temperature (25°) in atmospheric pressure of hydrogen. At the end of 3 hr., 3 molar equivalents of H_2 (120 cc., 106% of the calculated amount) had been absorbed. After removal of the catalyst and solvent, the residual salt was dissolved in water, from which the base was liberated by adding solid NaOH. This was extracted with benzene, dried, and evaporated leaving the yellow oil with a piperidine-like odor. Yield, ca. 300 mg.

Perchlorate : Colorless plates (from EtOH), m.p. 146～148°.

Picrate : Yellow needles (from EtOH), m.p. 155～156°.

These salts are clearly different from those of the compound (IIc) prepared by Sugasawa and Mizukami9); free base, m.p. 57～59.5°; picrate, m.p. 171°; perchlorate, m.p. 180～183°.

1-Methyl-2-chloropyridinium Methylsulfate—To 1.2 g. of 2-chloropyridine 1.3 g. of dimethylsulfate was added dropwise resulting in evolution of heat. The clear solution was heated on a steam bath for 2 hr. to yield a reddish syrup, which solidified on standing over night. However, this solid did not show an accurate m.p. on account of its high hygroscopicity, and crystalline derivative, such as the iodide, perchlorate, or picrate, was not obtained for characterization except the chloroplatinate, which recrystallized from EtOH to orange blades, m.p. 219～220°(decomp.). *Anal.* Calcd. for $C_{12}H_{14}N_2Cl_2 \cdot Cl_6Pt$: C, 21.66; H, 2.12; N, 4.21; Pt, 29.33. Found : C, 21.91; H, 2.19; N, 4.33; Pt, 29.71.

To an aqueous solution of the above-mentioned methylsulfate, 10% NaOH was added and it became turbid and yellowish instantaneously, separating an oily substance. The whole was heated on a steam bath for 15 min. then extracted with *iso*-AmOH, and yielded an oil which distilled at 125～131°/12 mm. (127°/12.5 mm. in the literature).12) This was identified with 1-methyl-2(1*H*)-pyridone through the UV spectra.

Summary

It was proved that the reaction of each of 1-phenethyl-2(1*H*)-pyridone, 1-(3,4-methylenedioxyphenethyl)-2(1*H*)-pyridone, and 1-(3,4-dimethoxyphenethyl)-2(1*H*)-pyridone with phophoryl chloride gave the corresponding 2-chloropyridinium salt and not the cyclized product in every case.

On being treated with dilute aqueous sodium hydroxide solution at a room temperature, these 2-chloropyridinium salts yielded the corresponding pyridones, which had been described as the ring cleavage of benzo〔*a*〕quinolizinium salts induced with various basic reagents.

(Received January 28, 1959)

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12) Org. Syntheses, Coll. Vol. II, 419.