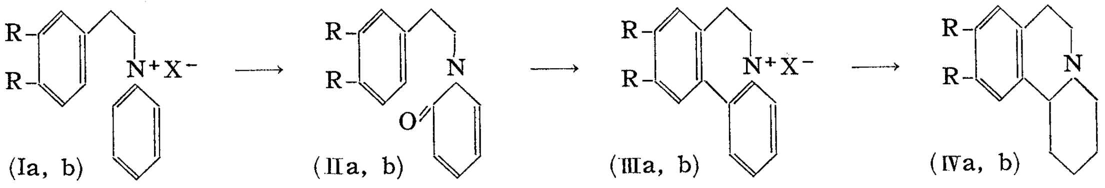
UDC 547.829.07

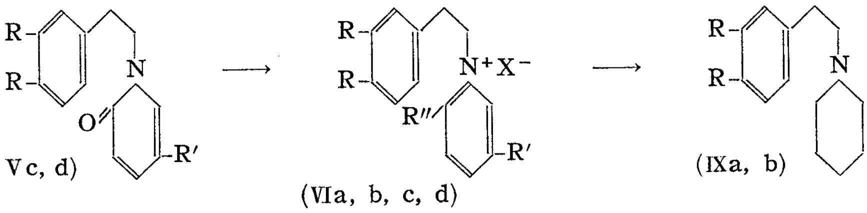
Reaction of 1-(Phenethyl)-2(1*H*)-pyridones with Phosphoryl Chloride.* Formation of 1-(Phenethyl)-2-chloropyridinium Salts.

Previously, Sugasawa, *et al.* and Govindachari, *et al.* described a synthesis of 1,2,3,4,6,7-hexahydro-11b*H*-benzo[*a*]quinolizine(IVa)[1,2] and its 9,10-methylenedioxy derivatives (IVb),[3] which were obtained by the route shown below.



a : R=H
b : -R + R- = -O-CH$_2$-O-

Recently, it was reported that 1-phenethylpyridones (Vc and Vd), when treated with phosphoryl chloride, gave the corresponding 2-chloro- (VIc)[4] and 2-ethoxy-pyridinium (VId)[5] derivatives, respectively, but not the cyclized products.



a : R=H, R'=H, R''=Cl
b : -R + R- = -O-CH$_2$-O-, R'=H, R''=Cl
c : R=H, R'=C$_2$H$_5$, R''=Cl
d : R=H, R'=COOH(Et), R''= -OC$_2$H$_5$

Thus, the cyclization of pyridones (IIa and IIb) with phosphoryl chloride was reinvestigated.

On being heated with phosphoryl chloride for 2 hours and then treated with potassium iodide, the pyridones (IIa and IIb) gave colorless needles (VIa) of m.p. 192~193° (decomp.), and yellow plates (VIb) of m.p. 194~195° (decomp.), in good yields, which had been assigned respectively to (IIIa) and (IIIb) in previous papers.[1,3] Both gave correct analysis for (VIa) (*Anal.* Calcd. for $C_{13}H_{13}NClI$: C, 45.17; H, 3.79; N, 4.05. Found : C, 45.43; H, 4.00; N, 4.25) and (VIb) (*Anal.* Calcd. for $C_{14}H_{13}O_2NClI$: C, 43.16; H, 3.39; N, 3.59. Found : C, 43.36; H, 4.03; N, 3.53).

The picrates of the compounds (VIa) and (VIb) were easily obtained as yellow granules, m.p. 136~137° (*Anal.* Calcd. for $C_{19}H_{15}O_7N_4Cl$: C, 51.06; H, 3.35; N, 12.54. Found : C, 51.19; H, 3.46; N, 12.47), and yellow plates, m.p. 150~151° (*Anal.* Calcd. for $C_{20}H_{15}O_9N_4Cl$: C, 48.95; H, 3.08; N, 11.46. Found : C, 49.09; H, 3.04; N, 11.35), which had also been described previously as picrates of (IIIa) and (IIIb).

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* This paper concerns a correction of the erroneous description of 1,2,3,4,6,7-hexahydro-11b*H*-benzo[*a*]quinolizine and its 9,10-methylenedioxy derivative published by Sugasawa and his co-workers in Yakugaku Zasshi, **72**, 1273(1953) and Ber., **72**, 979(1939).

) S. Sugasawa, S. Akaboshi, M. Suzuki : Yakugaku Zasshi, **72**, 1273(1952).

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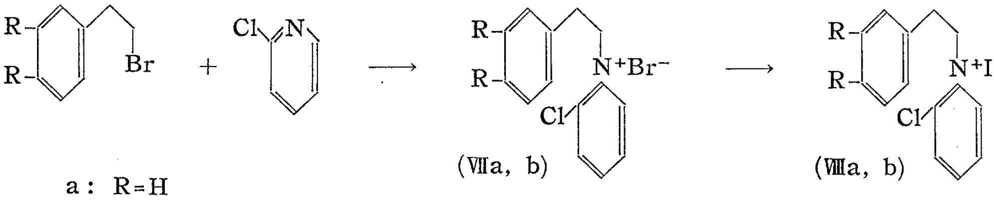
5) R. Wiley, N. Smith, L. Knabeschuh : J. Am. Chem. Soc., **75**, 4482(1953).

In order to prove the chemical structure of the iodides (VIa and VIb), phenethyl and 3,4-methylenedioxyphenethyl bromide were each heated with 2-chloropyridine in ethanol or acetone solution and the corresponding bromides (VIIa), m.p. 188°(decomp.), and (VIIb), m.p. 171~173°, were obtained though in poor yields.



(VIIa, b) (VIIIa, b)

a: R=H
b: -R + R- = -O-CH$_2$-O-

When these bromides (VIIa and VIIb) were treated with potassium iodide in aqueous solution, the corresponding iodides (VIIIa), m.p. 192~193°(decomp.), and (VIIIb), m.p. 192~194°, were obtained.

Both of these iodides (VIIIa and VIIIb) and their picrates were found to be identical with the iodides of (VIa) and (VIb) and their picrates, by the mixed melting point tests, and UV and IR determinations. Thus, the structures of (VIa) and (VIb) were established.

When the compounds (VIa) and (VIb : X = Cl) were hydrogenated over Adams' catalyst in hydrous ethanol, there were obtained the corresponding reduced compounds (IXa and IXb). Hydrochloride of (IXa)6) : Colorless plates, m.p. 225~226° (*Anal.* Calcd. for $C_{13}H_{20}NCl$: C, 69.16; H, 8.93; N, 6.20. Found : C, 69.18; H, 8.61; N, 5.96). Picrate: Yellow needles, m.p. 148~149° (*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). Hydrochloride of (IXb) : Colorless plates, m.p. 214~215° (*Anal.* Calcd. for $C_{14}H_{20}O_2NCl$: C, 62.33; H, 7.47; N, 5.19. Found : C, 62.35; H, 7.37; N, 5.08). Picrate : Yellow needles, m.p. 163~164° (*Anal.* Calcd. for $C_{20}H_{22}O_9N_4$: C, 51.95; H, 4.80; N. 12.12. Found : C, 52.11; H, 4.92; N, 12.59). All of these compounds had been described as the derivatives of (IVa) and (IVb) in previous papers.

The compounds (Ia) and (Ib) were also hydrogenated by the same means, to give the corresponding piperidine derivatives, which formed hydrochlorides of m.p. 224~225° 6) and of m.p. 214~215°, respectively. These derivatives and their picrates were proved to be identical with those of (IXa) and (IXb) by mixed melting point tests and IR identifications.

The synthesis of hexahydro-11b*H*-benzo[*a*]quinolizine (IVa) and its 9,10-methylenedioxy derivative (IVb) are now being studied and the details will be reported in the near future.

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6) F. Kröhnke : Ber., **84**, 388(1951).