# Stable Carbonium Ions. XLVI.[1] Protonated Acetyl- and Benzoylpyridinium Ions

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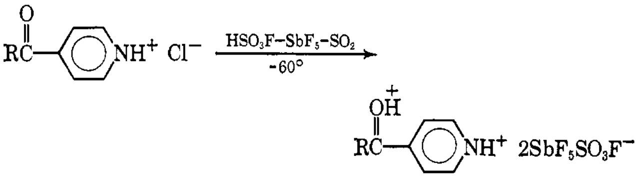
**Abstract:** Protonated 2-, 3-, and 4-acetyl- and -benzoylpyridinium ions were investigated with nmr spectroscopy at −60° in $FSO_3H–SbF_5–SO_2$ solution. Analysis of the spectra allowed the elucidation of the structure of protonated acetyl- and benzoylpyridinium ions.

In searching for model compounds for organic dications, we felt it of interest to carry out an investigation of the protonated isomeric (2-, 3-, and 4-) acetyl- and benzoylpyridinium ions. These model compounds were considered of added interest because it was expected that the isomeric ions would yield some information on the proximity effect of the two positive charges. Whereas nmr spectral studies of pyridinium ions and alkyl-substituted pyridinium ions are known,[3] no similar studies on acetyl- and benzoylpyridinium ions are available. Thus we included these ions in our investigation, even more so because they helped in the structural assignments of the diprotonated species.

## Results and Discussion

The isomeric (2-, 3-, and 4-substituted) acetyl- an benzoylpyridines were commercially available and wer purified before use. The acetyl- and benzoylpyridiniu ions were investigated as the hydrochloride salts i sulfur dioxide solution at −60°. Investigation of tl protonated acetyl- and benzoylpyridinium ions w carred out at −60° in sulfur dioxide solution using t strong acid system $HSO_3F–SbF_5$ as protonating age



The assignment of pyridine and pyridinium ring hydrogens was made according to the analyzed spectra of 2-acetylpyridine[4] and 3-acetylpyridine.[5] The chemical shifts are approximate since the spectra of the pyridinium ions were not fully analyzed and the assignments were made on the basis of a first-order interpretation. We assume that the error introduced by this method of analysis is within 0.05 ppm, which is sufficient for our purpose. The isomeric (2-, 3-, or 4-) acetyl- and benzoylpyridinium hydrochlorides give well-resolved nmr spectra in sulfur dioxide at −60°.

The chemical shifts summarized in Tables I and II show a large low-field shift compared with those of the free bases. It is, however, important to be aware that a solvent effect may very likely contribute to some extent to the low-field shifts. The proton on nitrogen is observed in sulfur dioxide solution at −60° and appears at −14.5 to −14.8 ppm and −14.7 to −15.1 ppm for acetyl- and benzoylpyridinium, respectively. The appearance of the proton on nitrogen at very low field is caused by the absence of paramagnetic effects in protonated species[3c] which accounts also for the higher shifts of $\gamma$ and $\beta$ hydrogens as compared with those of $\alpha$ protons. The methyl hydrogens of acetylpyridinium are slightly shifted to low field in $SO_2$ solution. The hydrogens of the pyridinium ring are differently affected by protonation and this depends on the position of the substituent in the ring.

In 4-acetyl- and 4-benzoylpyridine, protonation of the nitrogen deshields the 3 and 5 positions more than the 2 and 6 positions. In the 2 and 3 isomers the effect of protonation is complicated by a solvent effect. The comparative displacements observed are summarized in Tables I and II.

Protonation of 2-, 3-, and 4-acetyl- and -benzoylpyridinium was shown to occur in the strong acid system, $FSO_3H–SbF_5–SO_2$. The protons on nitrogen and on oxygen were observed at low field in the nmr spectra at −60°. The existence of stereoisomers was confirmed by the observation of two OH peaks for the diprotonated 3- and 4-substituted pyridines. These isomers are explained by the assumption that the proton on oxygen of an asymmetrically substituted ketone[6] is in two magnetically nonequivalent environments depending on its relationship to the substituents. An equilibrium of two isomers is shown in Figures 1–4. Further evidence of the presence of two isomers was found in the coupling of the proton on oxygen with the methyl hydrogens in the diprotonated 3-acetyl- and 4-acetylpyridines. The low-field peak of the $=OH^+$ in these isomers is split into a quartet by the neighboring methyl which appears as a doublet. The coupling is of the allylic type with the *cis* coupling constant bigger than the *trans*. The upfield peak of the $=OH^+$ in the diprotonated 3-acetyl- or 4-acetylpyridines is a singlet where no *trans* allylic coupling is observable.

The spectrum of protonated 2-acetyl- and 2-benzoylpyridinium ions does not show the presence of two stereoisomers. It seems likely that the influence of the

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[1] Part XLV: C. A. Cupas, J. M. Bollinger, and G. A. Olah, *J. Am. Chem. Soc.*, in press.

[2] National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

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**Table I.** Nmr Chemical Shifts of 2-, 3-, and 4-Acetylpyridines, -pyridinium Ions, and Protonated -pyridinium Ions

| | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | $CH_3$ | $=OH^+$ | $NH^+$ |
|---|---|---|---|---|---|---|---|---|
| 2-Acetylpyridine[a] | | −8.0 | −7.8 | −7.5 | −8.7 | −2.7 | | |
| 2-Acetylpyridinium ion[b] | | −8.9 | −8.7 | −8.3 | −9.2 | −2.8 | | −14.5[h] |
| | | $\Delta\delta_4 \equiv \Delta\delta_3 > \Delta\delta_5 > \Delta\delta_6$ | | | | | | |
| Protonated 2-acetylpyridinium ion[c] | | −9.7 | −9.7 | −9.4 | −9.7 | −4.0 | −17.4 | −13.9[h] |
| | | $\Delta\delta_5 > \Delta\delta_4 > \Delta\delta_3 > \Delta\delta_6$ | | | | | | |
| 3-Acetylpyridine[a] | −9.2 | ... | −7.5 | −8.2 | −8.8 | −2.7 | | |
| 3-Acetylpyridinium ion[b] | −9.1 | ... | −8.2 | −8.8 | −9.0 | −2.7 | | −14.8[h] |
| | | $\Delta\delta_4 > \Delta\delta_5 > \Delta\delta_6 > \Delta\delta_2$ | | | | | | |
| Protonated 3-acetylpyridinium ion[c] | −10.0 | ... | −9.0 | −9.7 | −10.0 | −4.0[d] | −16.0[e]<br>−15.0 | −13.2[h] |
| | | $\Delta\delta_6 > \Delta\delta_5 \equiv \Delta\delta_2 > \Delta\delta_4$ | | | | | | |
| 4-Acetylpyridine[a] | −8.5 | −7.4 | ... | −7.4 | −8.5 | −2.4 | | |
| 4-Acetylpyridinium ion[b] | −8.8 | −8.4 | ... | −8.4 | −8.8 | −2.7 | | −14.8[h] |
| | | $\Delta\delta_3 \equiv \Delta\delta_5 > \Delta\delta_2 \equiv \Delta\delta_6$ | | | | | | |
| Protonated 4-acetylpyridinium ion[c] | −9.6 | −9.4 | ... | −9.4 | −9.6 | −4.0[f] | −16.5[g]<br>−16.3 | −13.3[h] |
| | | $\Delta\delta_3 \equiv \Delta\delta_5 > \Delta\delta_2 \equiv \Delta\delta_6$ | | | | | | |

[a] In $CDCl_3$ at room temperature. [b] In $SO_2$ at −60°. [c] In $SO_2$-$SbF_5$-$FSO_3H$ at −60°. [d] Doublet, $J_{CH_3\text{-}OH} = 0.9$ Hz. [e] Quartet, $J_{OH\text{-}CH_3} = 0.9$ Hz. [f] Doublet, $J_{CH_3\text{-}OH} = 1.0$ Hz. [g] Quartet, $J_{OH\text{-}CH_3} = 1.0$ Hz. [h] Broad peak.

**Table II.** Nmr Chemical Shifts of 2-, 3-, and 4-Benzoylpyridines, -pyridinium Ions, and Protonated -pyridinium Ions

| | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | Ph | $=OH^+$ | $NH^+$ |
|---|---|---|---|---|---|---|---|---|
| 2-Benzoylpyridine[a] | ... | −8.2 | −8.0 | −7.9 | −8.6 | −7.4 | | |
| 2-Benzoylpyridinium ion[b] | ... | −8.6 | −8.2 | −8.1 | −8.9 | −7.4 | | −14.7[d] |
| | | $\Delta\delta_3 > \Delta\delta_6 > \Delta\delta_4 \equiv \Delta\delta_5$ | | | | | | |
| Protonated 2-benzoylpyridinium ion[c] | ... | −9.5 | −9.3 | −9.2 | −9.8 | −8.7 | −14.7 | −13.5[d] |
| | | $\Delta\delta_4 \equiv \Delta\delta_5 > \Delta\delta_3 \equiv \Delta\delta_6$ | | | | | | |
| 3-Benzoylpyridine[a] | −9.0 | ... | −7.1 | −8.1 | −8.8 | −7.6 | | |
| 3-Benzoylpyridinium ion[b] | −8.9 | ... | −8.2 | −8.8 | −8.9 | −7.6 | | −15.2[d] |
| | | $\Delta\delta_4 > \Delta\delta_5 > \Delta\delta_6 > \Delta\delta_2$ | | | | | | |
| Protonated 3-benzoylpyridinium ion[c] | −9.6 | ... | −9.0 | −9.6 | −9.6 | −8.6 | −14.2<br>−13.9 | −13.2[d] |
| | | $\Delta\delta_4 \equiv \Delta\delta_5 > \Delta\delta_2 \equiv \Delta\delta_6$ | | | | | | |
| 4-Benzoylpyridine[a] | −8.7 | −7.7 | ... | −7.7 | −8.7 | −7.5 | | |
| 4-Benzoylpyridinium ion[b] | −8.9 | −8.2 | ... | −8.2 | −8.9 | −7.6 | | −15.1[d] |
| | | $\Delta\delta_3 \equiv \Delta\delta_5 > \Delta\delta_2 \equiv \Delta\delta_6$ | | | | | | |
| Protonated 4-benzoylpyridinium ion[c] | −9.6 | −8.9 | ... | −8.9 | −9.6 | −8.7 | −14.5<br>−14.1 | −13.4[d] |
| | | $\Delta\delta_3 \equiv \Delta\delta_5 \equiv \Delta\delta_2 \equiv \Delta\delta_6$ | | | | | | |

[a] In $CDCl_3$ at room temperature. [b] In $SO_2$ at −60°. [c] In $SO_2$-$SbF_5$-$FSO_3H$ at −60°. [d] Broad peak.

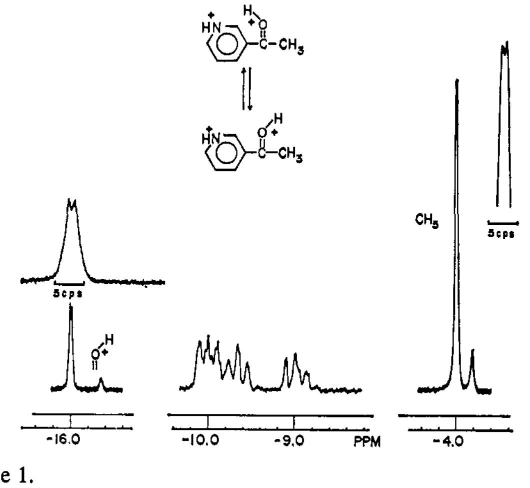

Figure 1.

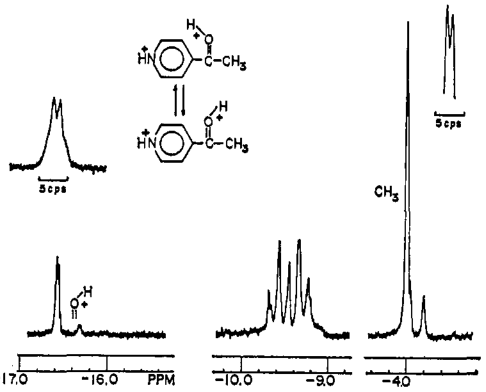

Figure 2.

near positive charge on the nitrogen stabilizes the conformation shown in Figures 5 and 6. The proximity of the positive charge also highly deshields the proton on oxygen which appears at very low field, −17.4 ppm, for diprotonated 2-acetylpyridine. The positive charge in this case is necessarily located on the oxygen atom and not on the carbon atom of the carbonyl group. Diprotonated 2-benzoylpyridine shows the proton on oxygen at higher field. The smaller deshielding observed could be explained by the phenyl substituent effect in which a part of the positive charge is now strongly delocalized. The methyl shifts in the isomeric, diprotonated acetylpyridines are about equal, whereas the phenyl shifts in diprotonated 2-phenylpyridine are 0.3 and 0.2 ppm downfield from the 3- and 4-benzoyl isomers, respectively. The effect of the positive charge on oxygen on the chemical shifts of the pyridinium ring hydrogens is generally greater on the *para* than the *ortho* and *meta* positions relative to the substituent. The comparative displacements are summarized in Tables I and II.

Diprotonation of the acetyl- and benzoylpyridines shifts the resonance position of the hydrogens on nitro-

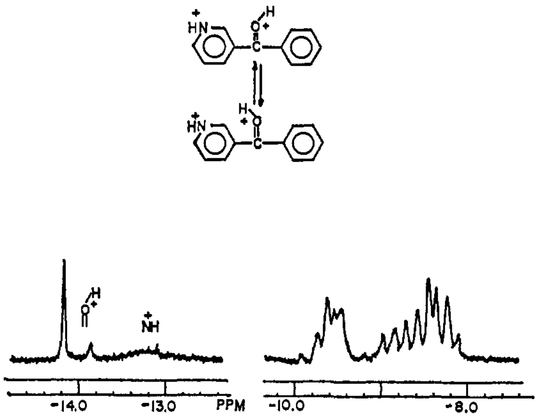

Figure 3.

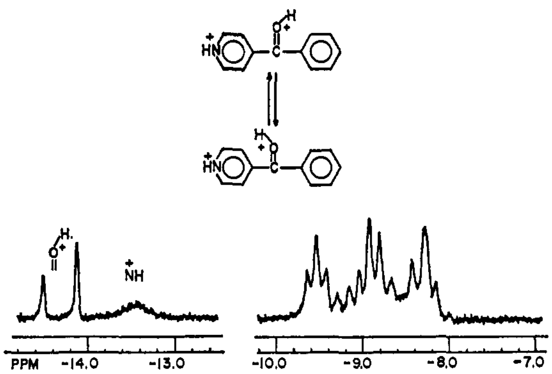

Figure 4.

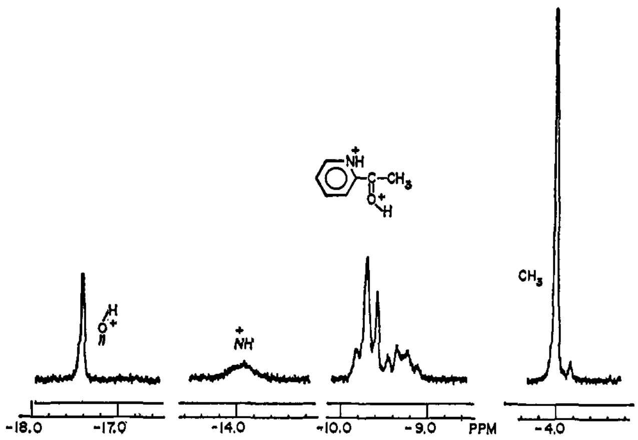

Figure 5.

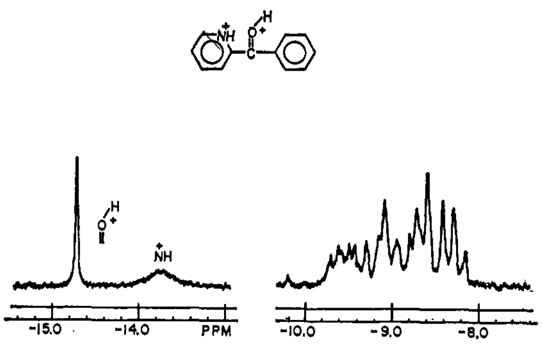

Figure 6.

gen upfield slightly compared with those of monoprotonated species in the same solvent at −60° (Tables I and II).

## Experimental Section

**Materials.** The 2-, 3-, and 4-acetyl- and -benzoylpyridines were commercially available and were distilled or recrystallized before use. The acylpyridinium hydrochloride salts were prepared by bubbling a stream of dry hydrogen chloride through a chloroform solution of free base. The melting points of the salts recrystallized from chloroform agree with the literature values: I, 2-acetylpyridinium hydrochloride, 184–185°;[7] II, 3-acetylpyridinium hydrochloride, 178°;[8] III, 4-acetylpyridinium hydrochloride, 155°; IV, 2-benzoylpyridinium hydrochloride, 128°;[9] V, 3-benzoylpyridinium hydrochloride, 161°;[9] and VI, 4-benzoylpyridinium hydrochloride, 197°.[9]

**Nmr Spectra.** A Varian Associates Model A-56-60 A spectrometer with a variable-temperature probe was used for all spectra. External TMS was used as reference (sealed capillary tube). The coupling constants are accurate to within 0.1 Hz.

Samples of protonated acetyl- and benzoylpyridinium were prepared by dissolving 0.2–0.3 g of the acylpyridinium hydrochloride in 1.5 ml of sulfur dioxide held at −76°. This solution was added dropwise to 1.5 ml of $HSO_3F$–$SbF_5$ (1:1 *M* solution) dissolved in 1 ml of cold sulfur dioxide. The excess of acid was always indicated in the spectra by the intense peak at −10.9 ppm. This peak and that of the $H_3O^+$ at about −10.5 ppm were deleted from the spectra (Figures 1–6) for simplicity.

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