VI VII

Experimental Section

Materials. Samples of cyclopropanone and cyclopropanone hydrate were kindly given by Professor N. J. Turro whom we thank for his help. All the other alicyclic ketones were reagent grade commercial chemicals and used without further purification.

Nmr Spectra. A Varian Associates Model A-56-60A nmr spectrometer with 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.

Preparation of Protonated Alicyclic Ketones. Samples of protonated ketones were prepared by dissolving 1.5 ml of SbF_5–FSO_3H (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling to −78°. The ketone (0.2–0.3 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −78°, and with vigorous agitation dropwise added to the acid solution. The cyclopropanone was used as 0.5 *M* solution in methylene chloride. The excess of acid was always indicated in the spectra by the intense peak at −10.9 ppm. This peak and that of H_3O^+ at about −10.5 ppm were deleted from the spectra (Figures 1–11) for simplicity.

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Stable Carbonium Ions. LVI.[1a] Diphenylpyridinyl- and Phenylmethylpyridinylcarbonium Ions

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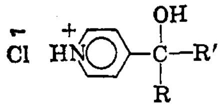
Abstract: As model compounds for the study of dication systems, the isomeric diphenyl-2-, -3-, and -4-pyridinyl- and phenylmethylpyridinylcarbonium ions were investigated by nmr spectroscopy in SbF_5–FSO_3H–SO_2 solution at −30°. The *p*-tolylmethyl-4-pyridinylcarbonium ion was also investigated in the same acid system.

The stability of dicarbonium ions is known to be related to the distance and the type of separation of the positive charges. We have recently observed simple alkyldicarbonium ions[2] and alkylenedioxodicarbonium ions.[3] Looking for model compounds in the investigation of dication systems we felt it of interest to extend our studies to the isomeric diphenylpyridinyl- and phenylmethylpyridinylcarbonium ions. In the isomeric diphenyl- and phenylmethyl-2-, -3-, and -4-pyridinylcarbonium ions the proximity effects of the two positive charges can be compared. The behavior of diphenyl-2-pyridylmethanol and diphenyl-4-pyridylmethanol in 100% sulfuric acid has been studied by their vibrational spectra and by cryoscopy of the systems.[4] We wish to report now a systematic nmr investigation of isomeric diphenyl-2-, -3-, and -4-pyridyl- as well as phenylmethylpyridylmethanols in the extremely strong acid system fluorosulfonic acid–antimony pentafluoride (1:1 *M*).

Results and Discussion

In order to gain a better understanding of the pyridinylcarbonium ions to be investigated, first we studied the corresponding monocations (pyridinylmethanols). The isomeric diphenyl- and phenylmethyl-2-, -3-, and -4-pyridinylmethanols were investigated as the hydrochloride salts in sulfur dioxide solution at −60°.



R = phenyl or methyl

It was found that they give well-resolved nmr spectra with the rate of exchange of the proton on nitrogen slow enough to observe this resonance peak as a broad singlet. Comparison of the chemical shifts of the free bases with those of the conjugated acids (pyridinium hydrochlorides) helps to understand the charge distribution in the pyridinium ring systems. For any given pyridine isomer, the deshielding effect of N-protonation is generally independent of substituents on the pyridine ring (data summarized in Table I and II).

The nmr spectra of the N-protonated phenylmethylpyridylmethanols show a significant deshielding of the pyridinium ring hydrogens. The effect on the pyridine ring hydrogens is smaller for the C-2 and C-6 hydrogens than for the C-3, C-4, and C-5 hydrogens. The same observation can be made from the nmr study of diphenylpyridinylmethanol. The methyl and phenyl hydrogens are not deshielded (compared with the starting phenylmethyl- and diphenylpyridylmethanols), and their resonance position changes only within the limits of the solvent effect.

The NH^+ proton is observable in the nmr spectra only at low temperature and is at a rather low field. The significance of the deshielding effect was discussed for the pyridinium ion itself,[5] as were deshielding effects on

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(1) (a) Part LV: G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 938 (1968); (b) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

(2) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

(3) G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 3313 (1966).

(4) H. A. Smith and L. W. Holley, *ibid.*, **80**, 3714 (1958).

(5) W. M. S. Gil and J. N. Murell, *Trans. Faraday Soc.*, **60**, 248 (1964).

Table I. Pmr Data of Diphenylpyridylmethanols and Their Mono- and Dications

	C_5H_5N and $C_5H_5N^+H$	C_6H_5	OH	N^+H
Diphenyl-2-pyridylmethanol[b]	−7.05 to −8.60	−7.28	−6.16	
Diphenyl-2-pyridinylmethanol[c]	−7.65 to −8.72	−7.23	−4.70	−13.78[a]
Diphenyl-2-pyridinylcarbonium ion[d]	−8.70 to −9.80	−8.10 to −9.30		−12.90[a]
Diphenyl-3-pyridylmethanol[b]	−7.00 to −8.35	−7.23	−4.93	
Diphenyl-3-pyridinylmethanol[c]	−7.85 to −8.93	−7.36	−4.65	−14.73[a]
Diphenyl-3-pyridinylcarbonium ion[d]	−8.90 to −9.80	−8.20 to −9.30		−13.20[a]
Diphenyl-4-pyridylmethanol[b]	−7.20 to −8.30	−7.20	−5.10	
Diphenyl-4-pyridinylmethanol[c]	−8.05, −8.50	−7.28	−4.18	−14.23[a]
Diphenyl-4-pyridinylcarbonium ion[d]	−8.96, −9.50	−8.15 to −8.65		−13.30[a]

[a] At −80°. [b] At room temperature in $CDCl_3$ with TMS as internal reference. [c] At −60° in SO_2. [d] At −30° in $SbF_5–FSO_3H–SO_2$.

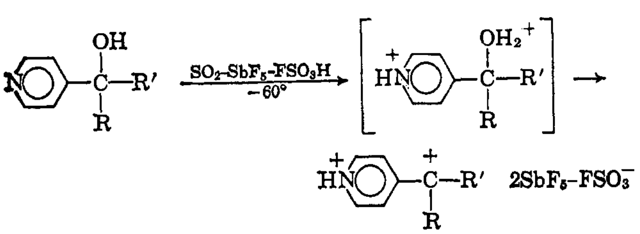
Table II. Pmr Data of Phenylmethylpyridylmethanols and Their Mono- and Dications

	C_5H_5N or $C_5H_5N^+H$	C_6H_5	p-CH_3	CH_3	OH	N^+H
Phenylmethyl-2-pyridylmethanol[b]	−6.80 to −7.62	−6.80 to −7.20 C-6: −8.40		−1.86	−5.75	
Phenylmethyl-2-pyridinylmethanol[c]	−7.50 to −7.90	−7.90 to −9.05		−1.96	−4.70	−13.41[a]
Phenylmethyl-2-pyridinylcarbonium ion[d]	−8.30 to −9.10	−9.10 to −9.60		−4.03		−13.10[a]
Phenylmethyl-3-pyridylmethanol[b]	−6.86 to −7.50	−6.86 to −8.60		−1.83	−6.08	
Phenylmethyl-3-pyridinylmethanol[c]	−7.20 to −7.60	−7.85 to −8.95		−1.95	−4.51	−14.43[a]
Phenylmethyl-3-pyridinylcarbonium ion[d]	−8.43 to −9.35	−9.35 to −9.74		−4.21		−13.30[a]
Phenylmethyl-4-pyridylmethanol[b]	−7.33	−7.33, −8.35		−1.91	−4.45	
Phenylmethyl-4-pyridinylmethanol[c]	−7.25	−7.90, −8.43		−1.83	−3.80	−14.15[a]
Phenylmethyl-4-pyridinylcarbonium ion[d]	−8.20 to −8.60	−9.00 to −9.50		−4.00		−13.30[a]
p-Tolylmethyl-4-pyridylmethanol[b]	−7.23	−7.33, −8.40	−2.33	−1.90	−3.97	
p-Tolylmethyl-4-pyridinylmethanol[c]	−7.20	−8.50, −8.03	−2.06	−1.88	−4.08	−14.08[a]
p-Tolylmethyl-4-pyridinylcarbonium ion[d]	−8.00 to −8.44	−8.50 to −9.30	−3.08[e]	−3.70[e]		−13.10[a]

[a] At −80°. [b] At room temperature in $CDCl_3$ with TMS as internal reference. [c] At −60° in SO_2. [d] At −30° in $SbF_5–FSO_3H–SO_2$. [e] Quartet; $J_{CH_3-CH_3} = 1.4$ Hz.

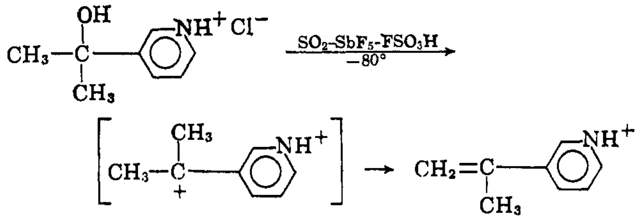
N-acyl groups in N-acetyl- and N-benzoylpyridinium ions.[6] The difference in chemical shifts of the NH protons of differently substituted pyridinium isomers is significant in the limits of concentration dependence and solvent effects on these shifts. Generally the N–H⁺ resonance peak of the 3 isomers appears at lower field than that of 2 isomers and even lower than that of the 4 isomers.

N-Protonation and ionization of phenylmethylpyridylmethanols and diphenylpyridylmethanols to the corresponding dications was complete at −60° in the strong acid system $SbF_5–FSO_3H$ (1:1) diluted with SO_2.



The stability of the dications is sufficient to permit the observation of their pmr spectra at room temperature. The proton on nitrogen at this temperature exchanges rather rapidly, and it cannot be observed. The stability of diphenyl-substituted dications is higher than that of the phenylmethyl dications. Dimethylpyridylmethanols under the same conditions ionize rapidly to the dications which are highly unstable and eliminate protons to give the isopropenylpyridinium ions, the only species observed even at −80°.

The diphenylpyridinylcarbonium ions can be isolated as crystalline stable salts. For all protonated isomers the spectral patterns are similar to those of free bases.



The spectra of the dications which are shown in Figures 1–6 are completely different from those of the monocations. The pyridinium and phenyl ring proton shifts of the dications were assigned on the basis of first-order interpretation with the assumption that the resonances of the pyridinium ring hydrogens are at lower field than those of the phenyl ring hydrogens. The introduction of a second positive charge into these systems was expected to affect at a higher degree the phenyl or methyl substituents attached to the electron-deficient carbon atom than the pyridinium ring hydrogens.

The nmr spectra of phenylmethylpyridinylcarbonium ions, Figures 1–3, show the phenyl hydrogens and pyridinium hydrogens as complex multiplets. Although the pyridinium ring hydrogens are more deshielded at lower field than those of the phenyl ring, some overlapping of the resonances is observed for the 2- and 3-pyridinium isomers. The phenylmethyl-4-pyridinylcarbonium ion shows two resonance multiplets, one of the pyridinium ring hydrogens from −9.00 to −9.50 ppm and the other of the phenyl ring hydrogens from −8.20 to −8.60 ppm. Comparison of these chemical shifts with those of the monocations (phenylmethylpyridinylmethanol) shows a larger low-field shift for the phenyl ring hydrogens than for the pyridinium ring hydrogens. Although the pyridinium ring already has a positive charge, the shifts of the resonance positions

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(6) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **89**, 4736 (1967).

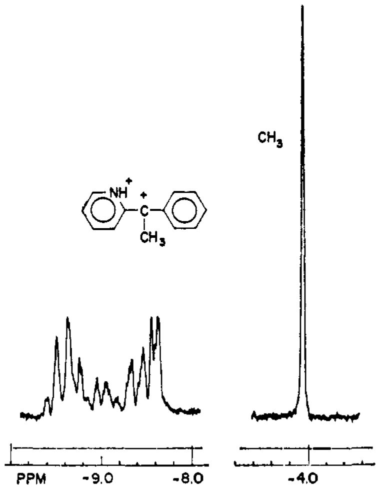

Figure 1.

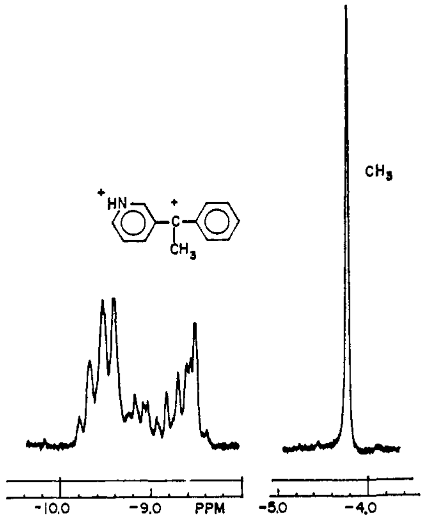

Figure 2.

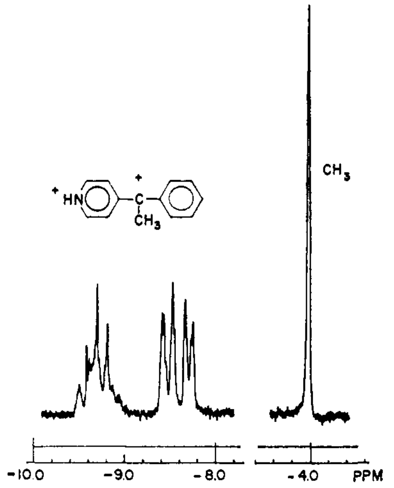

Figure 3.

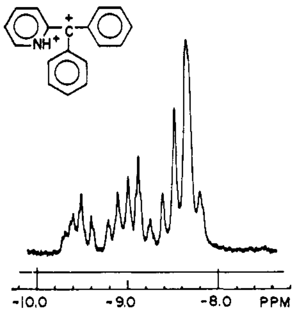

Figure 4.

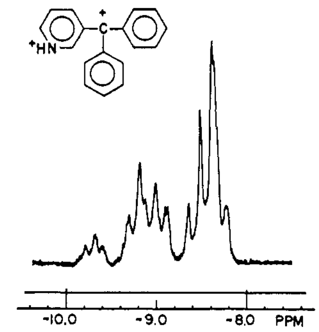

Figure 5.

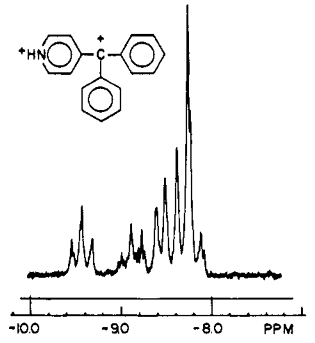

Figure 6.

can only be explained by the modification of the charge densities by the formation of the pyridiniumcarbonium ion. The most affected substituent is the methyl group directly attached to the carbonium carbon atom. The shift to lower field of the methyl hydrogens is 2.07, 2.26, and 2.17 ppm for 2-, 3-, and 4-pyridinyls, respectively. These shifts are comparable to the deshielding effects observed for α-hydrogens of alkylcarbonium ions. The proton on the nitrogen of the phenylmethylpyridinylcarbonium ion can be observed only at low temperatures. The resonance position measured at $-60°$ appears as a broad singlet at -13.10, -13.30, and -13.30 ppm for the 2-, 3-, and 4-pyridinyl isomers, respectively. The resonance is shifted 0.31, 1.13 and 0.75 ppm, respectively, upfield compared with those of monocations. The nmr spectra of diphenylpyridinylcarbonium ions investigated at $-30°$ show analogous spectral changes to those of the phenylmethylpyridinylcarbonium ions discussed previously. A first-order interpretation of the nmr spectra is generally less feasible because of the overlapping of the phenyl proton resonance with those of the pyridinium ring hydrogens. Nevertheless, the nmr spectra of the diphenyl-4-pyridinylcarbonium ion show the resonance of the pyridinium ring hydrogens at -8.96 and -9.50 ppm which can be assigned to the C-2, C-6, and C-3, C-5 hydrogens, respectively. It can be seen by comparing these shifts with those of the mono-

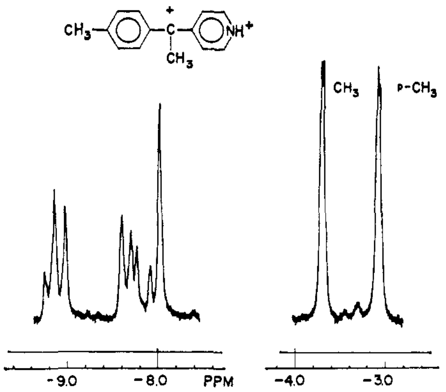

Figure 7.

cations that the influence of the carbonium ion center is slightly greater on the C-3 and C-5 hydrogens (being more deshielded) than on the C-2 and C-6 positions. The phenyl hydrogens appear as a multiplet from −8.15 to −8.65 ppm. The deshielding effects are larger for the phenyl hydrogens than for the pyridinyl hydrogens signifying that the positive charge of the carbonium ion is more delocalized into the phenyl ring than into the pyridinium ring. The protons on the nitrogen of the diphenylpyridinylcarbonium ions appear at −12.90, −13.20, and −13.30 ppm, respectively, for the 2-, 3-, and 4-pyridinyl isomers. They are shifted upfield in the same order as for phenylmethylpyridinylcarbonium ions, namely 0.88, 1.53, and 0.98 ppm. From these data it can be seen that in both series the 3-pyridinyl isomer shows the higher shift.

In order to simplify the pattern of the nmr spectra, we prepared the mono- and dications of *p*-tolylmethyl-4-pyridylmethanol. The nmr spectrum of *p*-tolylmethyl-4-pyridinylmethanol shows no resonance shifts for the *p*-tolyl and methyl substituents as compared with the pyridyl alcohol. The pyridine ring is affected by protonation in the usual way with the C-3 and C-5 hydrogens being more deshielded than the C-2 and C-6 hydrogens. Although the nmr spectra of the monocations and those of the free bases show similar features, the spectrum of the dication is completely different (Figure 7). The two resonance multiplets between −8.00 to −8.50 ppm and −9.00 to −9.30 ppm cannot be assigned on the basis of a first-order interpretation. The methyl resonance of the *p*-tolylmethyl-4-pyridinylcarbonium ion appears at −3.70 ppm with a deshielding of 1.82 ppm and the *p*-methyl resonance appears at −3.08 ppm with a deshielding of 1.00 ppm. The delocalization of the positive charge into the phenyl ring is more important than for corresponding phenylmethyl-4-pyridinylcarbonium ion and can be explained in terms of stabilization by the *p*-methyl group with the tendency toward a quinoidal structure. Undoubtedly due to the peculiar structure of this carbonium ion we observe a long-range, eight-bond, spin-spin coupling of 1.4 Hz between the two methyl groups. Coupling through eight bonds is not present in the corresponding *p*-toylmethyl-4-pyridinylmethanol. Proof of this long-range coupling was found in decoupling experiments *via* double irradiation of the methyl resonances to give sharp singlets.

As a result of the nmr investigation it can be said that stable diphenylpyridinylcarbonium ions and phenylmethylpyridinylcarbonium ions can be obtained by protonation and ionization of the corresponding methanols. The diphenylpyridinylcarbonium ions are stable enough to be isolated as crystalline salts. The phenylmethylpyridinylcarbonium ions were only observed in acidic solutions. The structure of these dications is characterized by the delocalization of the positive charge by the substituents to different extents. It is noteworthy that the charge densities of the pyridinium ring are appreciable modified by the formation of a neighboring carbonium ion center. The *p*-methyl substituent in the *p*-tolylmethylpyridinylcarbonium ion changes the structure of the carbonium ion indicating a higher degree of positive charge delocalization into the phenyl ring. Increase of the delocalization is expected to be related to the substituent effect of the *p*-methyl group.

Attempts to prepare dimethylpyridinylcarbonium ions by ionization of dimethylpyridinylmethanols have failed, the only species observed even at −80° being the isopropenylpyridinium ions.

Experimental Section

Materials. The isomeric diphenylpyridinyl- and methylpyridinylmethanols were prepared by Grignard methods from the isomeric 2-, 3-, and 4-acetylpyridines or -benzoylpyridines. The hydrochloride salts were prepared by passing a stream of dry hydrogen chloride through a chloroform solution of free bases. The melting points and analytical data of all compounds recrystallized from alcohol solutions agree with the literature values.[7]

Preparation of Dications and Their Nmr Spectral Investigation. A Varian Associates Model A-56-60A spectrometer with a variable-temperature probe was used for all spectra. Decoupling experiments were carried out on a Varian Associates Model HA-60IL spectrometer. External TMS was used as reference (sealed capillary tube).

Samples of phenylmethyl- or diphenylpyridinylcarbonium ion were prepared by dissolving 0.3 g of the corresponding 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 for simplicity.

Acknowledgment. Support of this work by grants of the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

(7) H. L. Otto, J. P. Wibant, and G. W. J. M. Govenendaal, *Rec. Trav. Chim.*, 78, 446 (1959).