

NMR Spectra. The ^1H , ^{13}C , and ^{19}F spectra were recorded for the indicated solvents and conditions on a Varian XL-100 spectrometer. ^1H spectra were referred to internal CH_2Cl_2 (δ 5.35) as secondary standard, while the center of the CD_2Cl_2 multiplet in the ^{13}C spectrum was taken as + 53.6 ppm. ^{19}F spectra were referred to internal CFCl_3 .

Acknowledgments. Part of this work was conducted while one of us (W.K.) was a Visiting Professor in the Department of Chemistry, University of North Carolina at Chapel Hill. W.K. is indebted to the Department there for generous hospitality, and in particular to Professor Maurice Brookhart for advice and laboratory facilities, and to Dr. David Harris for his expertise with the Varian-XL-100 NMR spectrometer.

Note Added in Proof: Professor Volz (Universität

Karlsruhe) has kindly informed us that in ion series II, the one-bond ^{19}F - ^{13}C couplings decrease from 294.1 Hz ($\text{R} = \text{CH}_3$) through 282.38 Hz ($\text{R} = \text{C}_6\text{H}_5$) to 276.5 Hz ($\text{R} = \text{c-C}_3\text{H}_5$). This trend is in agreement with that reported herein for ion series II.

Registry No. 2-Naphthyl methyl ketone, 93-08-3; 6-fluoro-2-naphthyl methyl ketone, 33627-02-0; 1-(2-naphthyl)-1-methylethanol, 20351-54-6; 1-(6-fluoro-2-naphthyl)-1-methylethanol, 55831-07-7; 1-(2-naphthyl)-1-phenylethanol, 69726-39-2; 1-(6-fluoro-2-naphthyl)-1-phenylethanol, 69726-40-5; 1-(2-naphthyl)-1-cyclopropylethanol, 69726-41-6; 1-(6-fluoro-2-naphthyl)-1-cyclopropylethanol, 69745-65-9; 1-methyl-1-(2-naphthyl)ethylum, 25401-60-9; 1-cyclopropyl-1-(2-naphthyl)ethylum, 69726-42-7; 1-phenyl-1-(2-naphthyl)ethylum, 69726-43-8; 1-(6-fluoro-2-naphthyl)-1-methylethylum, 69726-44-9; 1-cyclopropyl-1-(6-fluoro-2-naphthyl)ethylum, 69726-45-0; 1-(6-fluoro-2-naphthyl)-1-phenylethylum, 69726-46-1.

Halogen Complexes of Pyridines. A Proton and Carbon-13 Nuclear Magnetic Resonance Study^{1a}

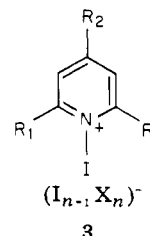
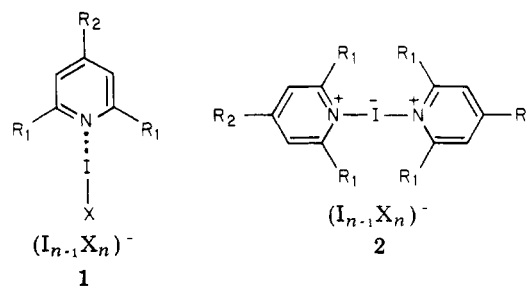
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Solutions of iodine and iodine chloride with pyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine were studied by ^1H and ^{13}C NMR. Support is deduced for the reported formation of three species: the charge-transfer complex $\text{B}\cdot\text{X}\cdot\text{I}$, the 1:1 complex $^+\text{B}\cdot\text{I}[\text{X}_n\text{I}_{n-1}]^-$, and the *N*-iododipyridinium salt $^+\text{B}_2\text{I}[\text{X}_n\text{I}_{n-1}]^-$. The ease of formation of each species appears to be a function of pyridine basicity, the Lewis acidity of the halogen (I_2 or ICl), the solvent polarity, and the relative donor-acceptor concentrations. The complexes derived from α -methyl-substituted pyridines can be distinguished by the magnitudes and directions of their ^{13}C "iodination" shifts.

Studies of complexes between IX ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}$) and pyridines have involved spectroscopic methods, measurements of the electrical conductivities of their solutions, and X-ray analyses of the more stable forms in the solid state.² There is ample evidence that charge-transfer complexes, 1, are formed in dilute solutions when solvents of low dielectric constant are used. In polar media, the formation of an ionic species is favored, the cation³ of which has been variously assigned structures 2 and 3 by different groups of workers.⁴⁻⁸ The crystal structures of solids corresponding to 1 and 2 have been determined for



$\text{R}_1 = \text{R}_2 = \text{H}$ or CH_3

some IX complexes of pyridines. Formation of both 1 and 2 in solution has been postulated by Larsen and Allred⁹

(1) (a) Supported by the National Science Foundation and by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences. (b) On sabbatical leave from Pennsylvania State University, Ogontz Campus, 1977-1978.

(2) For reviews see: Andrews, L. J.; Keefer, R. M. *Adv. Inorg. Chem. Radiochem.* 1961, 3, 91-133. Briegleb, G. "Elektronen-Donator-Acceptor-Komplexe"; Springer Verlag: Berlin, 1961. Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

(3) The nature of the anions 2 and 3 appears to be solvent and concentration dependent. For 2 ($\text{X} = \text{I}$), species ranging from I_3^- to I_9^- have been proposed.

(4) Ginn, S. G. W.; Wood, J. L. *Trans. Faraday Soc.* 1966, 62, 777-87.

(5) Reid, C.; Mulliken, R. S. *J. Am. Chem. Soc.* 1954, 76, 3869-74.

(6) Zingaro, R. A.; Tolberg, W. E. *J. Am. Chem. Soc.* 1959, 81, 1353-7.

(7) Haque, I.; Wood, J. L. *Spectrochim. Acta, Part A* 1967, 23a, 959-67.

(8) Popov, A. I.; Pflaum, R. T. *J. Am. Chem. Soc.* 1957, 79, 570-572.

(9) Larsen, D. W.; Allred, A. L. *J. Am. Chem. Soc.* 1965, 87, 1219-25.

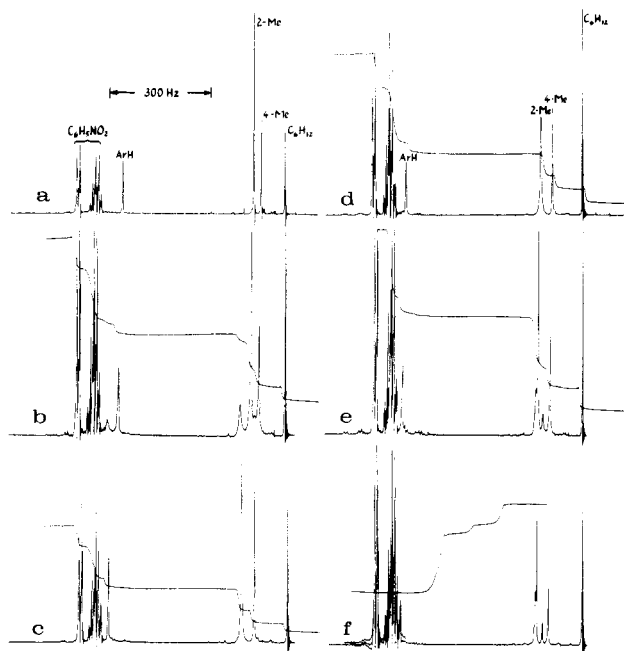


Figure 1. Proton spectra of 0.8 M solutions of 2,4,6-trimethylpyridine, **6**, and iodine or iodine monochloride in nitrobenzene- d_2 -chloroform with mole ratios of halogen to **6** of (a) 0:1, (b) 1:1 (I_2 :**6**), (c) 3:1 (I_2 :**6**), (d) 1:1 (ICl :**6**), (e) 3:1 (ICl :**6**), and (f) 6:1 (ICl :**6**).

for iodine and 2,4,6-trimethylpyridine in nitrobenzene-carbon tetrachloride from the observation of two sets of methyl resonances in proton NMR spectra. More recently,¹⁰ the presence of **2** and **3** in nitrobenzene solutions of iodine and substituted pyridines has been deduced from electrical conductivity measurements, the relative concentration of **3** increasing with increasing basicity of the pyridine and relative concentration of iodine.

It was the purpose of the present work to try to gain further insight into these systems, using proton and ^{13}C NMR spectroscopy with special attention to the behavior of pyridines in the presence of mixed halogens in relatively polar media.

Results and Discussion

Addition of 1 equiv of iodine to 0.8 M solutions of pyridine, **4**, 2,6-dimethylpyridine, **5**, or 2,4,6-trimethylpyridine, **6**, in deuteriochloroform causes medium-sized shifts of the ^{13}C resonances in the NMR spectra of the bases which resemble those which result from hydrogen bonding of the bases with 1 equiv of benzoic acid in deuteriochloroform (see Table I). These changes probably result from formation of charge-transfer complexes, **1**, the extent of which may be estimated to be 90% or greater from the association constant reported for pyridine- I_2 in benzene ($K_c = 200 \text{ L mol}^{-1}$).¹¹

When the more polar solvent nitrobenzene- d_2 -chloroform (3:2 (v/v)) is used, an additional set of peaks is observed at lower field in both the proton and ^{13}C spectra of **4**-**6** with iodine¹² (Figures 1a-c and 2). These resonances are reasonably attributed to the corresponding *N*-iododipyridinium ions, **2**, in accord with Allred's interpretation of similar proton spectra for **6** and iodine in nitrobenzene-carbon tetrachloride solutions.⁹ The extent of formation of **2** in these solutions is estimated to be 8.3,

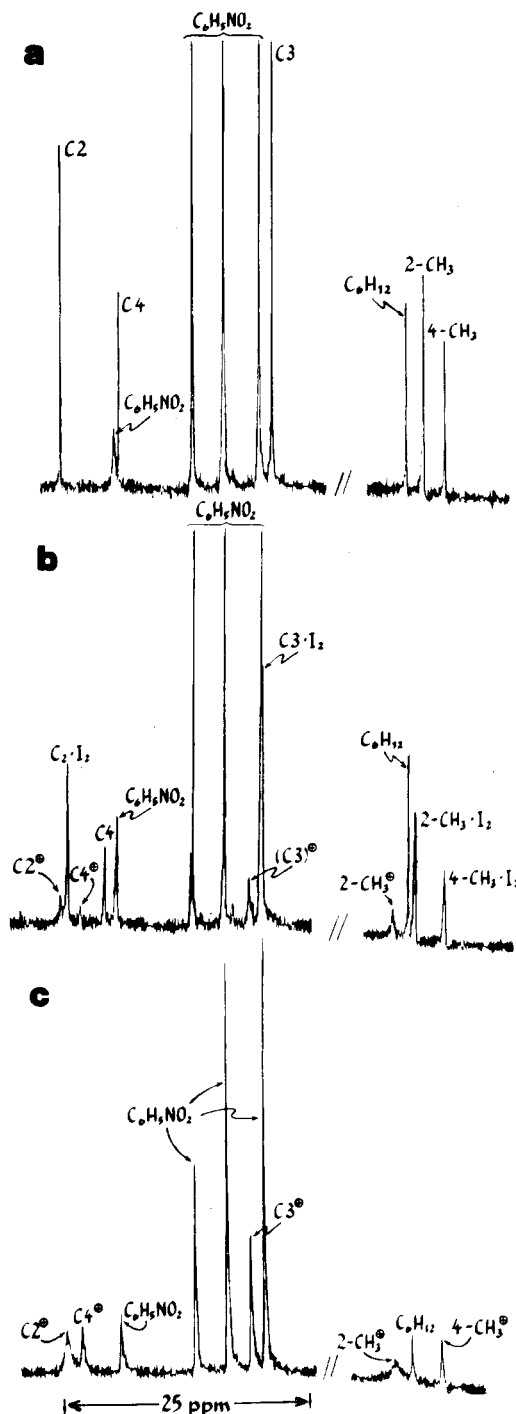


Figure 2. ^{13}C spectra of 0.8 M solutions of 2,4,6-trimethylpyridine, **6**, and iodine in nitrobenzene- d_2 -chloroform with mole ratios of iodine to **6** of (a) 0:1, (b) 1:1, and (c) 3:1. Peaks marked with C_6H_{12} , $\text{C}_6\text{H}_5\text{NO}_2$, $\text{CH}_3\cdot\text{I}_2$, and 2-CH_3^+ correspond respectively to the reference (cyclohexane), the solvent (nitrobenzene), I_2 complexes of type **1**, and ions of type **2**.

8.0, and 17.6% for **4**,¹³ **5**, and **6**, respectively, from the relative peak areas in the proton NMR spectra.¹⁴ The

(13) On heating, or after several days standing, solutions of **4** and iodine (1:1) deposit dark green needles of **2**. The counterion is I_3^- , as judged by titration of the salt in acetone with sodium thiosulfate solutions, and this agrees with the crystallographic work of O. Hassel and H. Hope, *Acta Chem. Scand.* 1961, 15, 407-16.

(14) The nature of the anion could not be determined from the NMR spectra but is probably I_3^- .^{10,13} Allred⁹ has suggested I_5^- for the counterion of **2** in dilute solution in nitrobenzene-carbon tetrachloride mixtures.

(10) Poskin, G.; Huyskens, P. *Bull. Soc. Chim. Fr.* 1976, 337-44.

(11) Plyer, E. K.; Mulliken, R. S. *J. Am. Chem. Soc.* 1959, 81, 823-6.

(12) Formation of a small amount of **2** ($X = \text{I}$) can be observed even in deuteriochloroform itself (ϵ 4.8).

Table I. ^{13}C Chemical Shifts of Complexes of Pyridine and Substituted Pyridines (B) in Nitrobenzene-Deuteriochloroform Solutions (3:2 (v/v))

base (B)	$\delta_0(^{13}\text{C})^a$	$\delta_0(^{13}\text{C}) - \delta(^{13}\text{C})^b$					
		$\text{B} \cdots \text{I}-\text{I}$ 1 ^c		$\text{B} \cdots \text{HA}$ 7 ^d	${}^+\text{B}_2\text{I}(\text{I}_{n-1}\text{Cl}_n)^-$ 2 ^e	$\text{B}^+\text{H}(\text{CF}_3\text{CO}_2^-)$ 8 ^f	$\text{B}^+\text{I}(\text{I}_{n-1}\text{Cl}_n)^-$ 3 ^g
6							
C2,6	157.3	+1.0	+1.4 ^h	+1.3	-2.2	+4.5 (+3.8) ⁱ	+2.1
C4	147.4	-2.5	-3.0 ^h	-3.1	-9.2	-10.4 (-14.9) ⁱ	-14.2
C3,5	121.1	-1.9	-2.0 ^h	-1.5	-5.0	-4.5 (-5.6) ⁱ	-5.0 ^l
2,6-CH ₃	24.1	-1.8	-1.8 ^h	+2.0	-7.5	+5.2 (+4.8) ⁱ	+4.2
4-CH ₃	20.4	-0.4	-0.3 ^h	-0.2	-0.8	-1.0 (-1.4) ⁱ	-2.1
5							
C2,6	157.7	+0.9	+1.0 ^h	+0.8	-2.9	+3.4	+3.9
C4	136.5	-2.2	-1.7 ^h	-1.9	-6.6	-8.3	-10.9
C3,5	120.1	-2.2	-1.9 ^h	-1.3	-5.3	-4.6	-5.6
2,6-CH ₃	24.3	-1.5	-1.6 ^h	+1.6	-7.5	+4.8	+4.0
4							
C2,6	149.9	+2.1	+2.6 ^h	+1.7	-0.6 ^j	+7.1	ppt ^k
C4	135.9	-2.6	-2.1 ^h	-1.7	-6.8 ^j	-8.9	
C3,5	123.8	-1.8	-2.9 ^h	-0.6	-5.1 ^j	-3.2	

^a ^{13}C shifts of ca. 0.8 M solutions of the pyridine in parts per million downfield from Me_4Si . ^b Difference between the shifts of free and complexed base. Positive signs indicate upfield shifts on complexing. ^c Equimolar in base and iodine. ^d Solutions equimolar (ca. 2 M) in base and benzoic acid in deuteriochloroform. ^e Molar ratio of ICl to base was 6:1. ^f Solutions equimolar in base and trifluoroacetic acid (ca. 2 M) in deuteriochloroform. ^g Molar ratio of ICl to base was 6:1. ^h The solvent was deuteriochloroform. ⁱ Reference 17. The solvent was dichloromethane- d_2 . ^j Molar ratio of ICl to base was 3:1. ^k A brown precipitate separated. ^l Assignment uncertain.

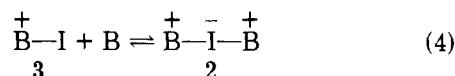
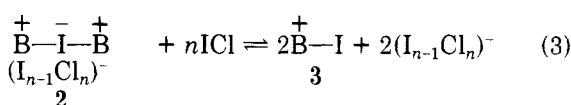
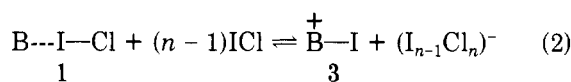
extent of formation of 2 from 5 is lower than might be expected from the relative basicities of 4 and 5.¹⁵ This suggests some steric hindrance to nitrogen-iodine covalent-bond formation by the α -methyl groups in 5, an effect which appears to be offset for the equally hindered 2,4,6-trimethylpyridine, 6, by its greater basicity. The ^{13}C shifts, relative to the free bases, of the higher field resonances are nearly those of the iodine-pyridine systems in deuteriochloroform (see Table I). These are as expected for the charge-transfer complex, 1, in rapid equilibrium with about 5% of free base.¹⁶ Interconversion of 1 and 2 is clearly slow⁹ on the NMR time scale because separate resonances are observed for each.

Addition of a threefold excess of iodine to 2,4,6-trimethylpyridine, 6, in nitrobenzene-deuteriochloroform solution causes the peaks of 1 to disappear and broadens the resonances of the α -methyl hydrogens and those of both the α and the α -methyl carbons of the N -iododipyridinium ion 2 ($\text{R}_1 = \text{R}_2 = \text{CH}_3$); see Figures 1c and 2. Such broadening may be the result of slowing of the exchange shown in eq 1⁹ because of the lower base concentration.



When the stronger electrophile iodine chloride is substituted for iodine in nitrobenzene-deuteriochloroform solutions equimolar in base and acceptor, a single set of resonances is observed in both the proton and ^{13}C spectra of 4-6, with shifts between those of the N -iododipyridinium ions, 2, and the charge-transfer complexes, 1, of the corresponding pyridine- I_2 systems in the same solvent. This suggests the onset of rapid interconversion of 1 ($\text{X} = \text{Cl}$), 2 ($\text{X} = \text{Cl}$), and the free bases. Further addition of iodine chloride results in downfield shifts of the averaged resonances because of increasing proportions of 2 (see Table I for characteristic ^{13}C shifts of 2 and the charge-

transfer complexes 1 for 4-6). For the α -methyl-substituted pyridines 5 and 6, additional peaks appear in the proton and ^{13}C spectra of solutions containing a threefold excess of iodine chloride to base, and these increase in intensity with further increase in relative iodine chloride concentration. The reversibility of the processes giving rise to the new peaks can be demonstrated from the proton spectrum by adding sufficient base (5 or 6) and then following this with addition of excess ICl. This behavior is compatible with the formation of the 1:1 inner complex, 3, at higher acceptor concentrations through equilibria such as shown in eq 2 and 3. An increase in acceptor con-



centration should shift the equilibria (2) and (3) to the right, while an increase in base concentration should favor (4) and reduce the amount of iodine chloride through formation of species 1 and 2.

The behavior of the ^{13}C and proton resonances of the methyl groups of the 2,4,6-trimethylpyridine (6)-ICl system in nitrobenzene-deuteriochloroform as a function of relative donor-acceptor concentration is shown by Figures 3 and 1a,d-f. Similar spectra were observed for 2,6-dimethylpyridine (5)-ICl under the same conditions. The resonances of the α carbons and α -methyl carbons of complexes 2 ($\text{X} = \text{Cl}$) from 5 and 6 exhibit broadening and noticeable downfield shifts with small increases in acceptor concentration. With a threefold, or greater, excess of iodine chloride, however, the peaks sharpen again. Similar line-shape effects are observed for the α -methyl hydrogens in the corresponding proton spectra and may be attributed to a slowing of the exchange process of eq 1 with reduced

(15) The $\text{p}K_a$ values of 5.17, 6.17, and 7.59 have been reported for 4, 5, and 6, respectively.

(16) Calculated for pyridine- I_2 from the association constant in nitrobenzene, $K = 410$.¹⁰

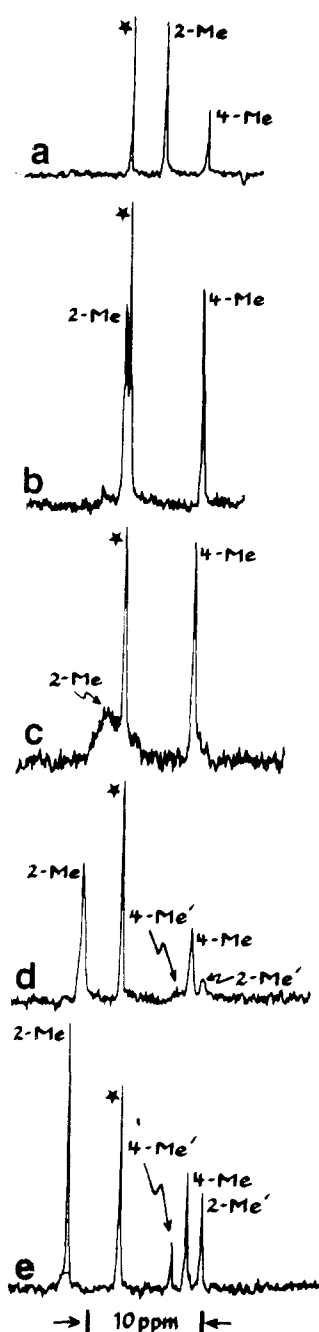
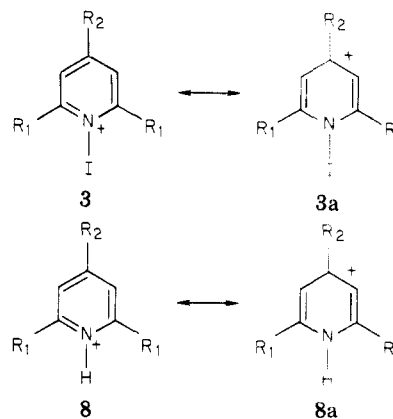


Figure 3. ^{13}C spectra of 0.8 M solutions of 2,4,6-trimethylpyridine, 6, and iodine chloride in nitrobenzene-*d*-chloroform, with mole ratios of iodine chloride to 6 of (a) 0:1, (b) 1:1, (c) 2:1, (d) 3:1, and (e) 6:1. The peaks marked with stars are of the reference, C_6H_{12} . The primed labeled resonances are those of ion 3, while the unprimed arise from 2.

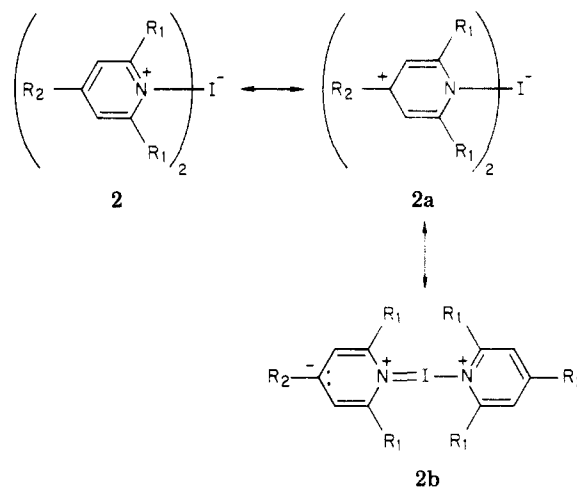
base concentration, as suggested for the pyridine- I_2 systems. The interconversion of ions 2 and 3 ($\text{X} = \text{Cl}$) must be slow on the NMR time scale because separate resonances are observed, and these remain sharp at high ICl concentration.

For less basic 4 in nitrobenzene-*d*-chloroform, a threefold excess of iodine chloride does not appear to lead to formation of the 1:1 complex 3 ($\text{R}_1 = \text{R}_2 = \text{H}$) but, instead, results only in further deshielding of the equilibrium-averaged resonances of complex 2 ($\text{R}_1 = \text{R}_2 = \text{H}$) because of the reduced concentration of base. With higher acceptor concentrations, the solution becomes unstable and deposits a brown precipitate which was not investigated further.

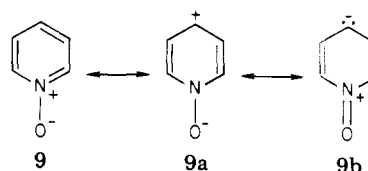
The shifts in the positions of the ^{13}C resonances of 5 and 6 resulting from formation of the 1:1 complexes 3 parallel in magnitude and direction those resulting from protonation of these bases with trifluoroacetic acid, 8 (see Table I). Thus, the β and γ carbons of 5 and 6 and the γ -methyl carbon of 6 become deshielded on formation of 3 or 8, and this reflects a decrease in electron density at these carbons.¹⁷ The effect is particularly large (8–14 ppm) for the γ carbons and suggests significant contributions from the resonance structures 3a and 8a.



Formation of the *N*-iododipyridinium ions, 2, also results in substantial deshielding of the γ carbons of 4–6 (by 7–9 ppm) and of the γ -methyl carbon of 6 (~1 ppm) and may be attributed to contributions of forms such as 2a. Unlike



pyridine *N*-oxide, 9, in which structure 9b clearly contributes significantly to the hybrid,¹⁸ resonance forms such



as 2b are not expected to be important for ions of the type 2 because of poor overlap between the diffuse orbitals of iodine and the 2p orbital of nitrogen. Thus, while both

(17) Balaban, A. T.; Wray, V. *Org. Magn. Reson.* 1977, 9, 16–22.

(18) Yavari, I.; Roberts, J. D. *Org. Magn. Reson.* 1979, 12, 87–91.

2b and **9b** should lead to increased electron density at the para position in the hybrid, the ^{13}C shift of the γ -carbon atom of pyridine *N*-oxide (in trifluoroethanol) is 10 ppm upfield from that of ion **2** ($\text{X} = \text{Cl}$) from **4**, although the shifts of the β carbons are nearly the same (128.9 and 128.3 ppm for **2** and **9**, respectively).

As expected, the influences of hydrogen bonding, **7**, and charge-transfer complex formation, **1**, on the ^{13}C shifts of the β -, γ -, and γ -methyl carbons of the pyridine bases are much smaller than those of ion formation (see Table I).

The changes in the shifts of the α carbons and α -methyl carbons of the bases on complex or ion formation seem to be useful indicators of the type of binding at the pyridine-type nitrogens because they are influenced by two mechanisms having opposite effects on the ^{13}C chemical shifts. One is reduction in electron densities which results in downfield shifts of the resonances, and the other is changes in bond order^{19,20} and/or higher excitation energies²¹ which produce upfield shifts. Thus, hydrogen bonding, protonation, and the formation of the 1:1 complex **3** cause the ^{13}C resonances of both the α and the α -methyl carbons of **5** and **6** to shift to higher fields, while formation

of ions **2** ($\text{X} = \text{Cl}$) causes downfield shifts of both carbon resonances. Interestingly, charge-transfer complexation with iodine or iodine chloride, as **1**, shifts the α -carbon resonances upfield and those of the α -methyl carbons downfield.

Experimental Section

The pyridine bases used in this study were commercial materials and were dried for several days over molecular sieves and then used without further purification. Iodine (resublimed, Mallinckrodt) was sublimed again and then stored in a desiccator. All solvents were reagent grade and were dried several days over molecular sieves.

Natural-abundance ^{13}C NMR spectra of 0.8 M solutions of the bases were obtained at about 26 °C, with proton-noise decoupling at 15.1, 25.1, and 45.3 MHz, using a Bruker DFS, a Varian XL-100, and a Bruker WH-180 spectrometer, respectively. Chemical shifts were measured relative to internal 3% cyclohexane and then converted to parts per million from Me_4Si utilizing $\delta_{(\text{CH}_2)_6}(\text{Me}_4\text{Si}) = 27.0$. Proton spectra were obtained before and after the recording of the ^{13}C spectra, using a Varian EM-390 spectrometer operating at 90 MHz.

Registry No. **4**, 110-86-1; **4-I**₂, 2078-94-6; **4-PhCO**₂**H**, 3427-97-2; **4-CF**₃**CO**₂**H**, 464-05-1; **5**, 108-48-5; **5-I**₂, 17210-91-2; **5-PhCO**₂**H**, 3372-55-2; **5-CF**₃**CO**₂**H**, 70320-26-2; **6**, 108-75-8; **6-I**₂, 696-90-2; **6-PhCO**₂**H**, 57313-86-7; **6-CF**₃**CO**₂**H**, 57313-93-6; bis(pyridine)iodine(1+), 33571-24-3; bis(2,6-dimethylpyridine)iodine(1+), 69417-62-5; bis-(2,4,6-trimethylpyridine)iodine(1+), 69417-65-8; 1-iodo-2,6-dimethylpyridinium, 70320-27-3; 1-iodo-2,4,6-trimethylpyridinium, 70320-28-4; **I**₂, 7553-56-2; **ICl**, 7790-99-0.

(19) Pugmire, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 697-706.

(20) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 261.

(21) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 654-667.

Reactions of Halobenzenes with Cyanomethyl Anion in Liquid Ammonia by the $\text{S}_{\text{RN}}1$ Mechanism¹

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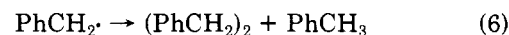
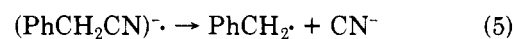
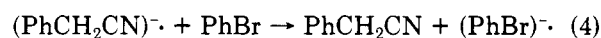
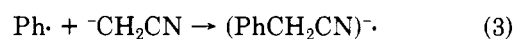
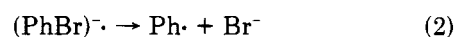
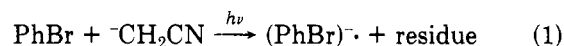
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The reactions of fluoro-, chloro-, bromo-, and iodobenzenes with cyanomethyl anion in liquid ammonia have been studied with regard to the product distribution (1,2-diphenylethane/phenylacetonitrile ratio). All the substrates gave about the same ratio. The addition of good electron acceptors such as naphthalene, anthracene, or pyridine inhibited the photostimulated reactions and gave a slight increase in the yield of 1,2-diphenylethane. In reactions stimulated by electrons the presence of naphthalene or benzoate ion as electron acceptors makes the yield of phenylacetonitrile drop almost to zero, whereas yields of the other products increase. Alternative reaction pathways are suggested.

Bromobenzene and cyanomethyl anion in liquid ammonia react under photostimulation giving 1,2-diphenylethane (DPE) (18% yield) and phenylacetonitrile (PAN) (8% yield) as major products, together with 62% of unreacted starting materials.²

This result was explained by the mechanism of Scheme I.

Scheme I



A special feature of this reaction, as compared with other

(1) Research supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina. Presented in part at the Primera Reunión Argentina de Físico-Química, La Plata, Argentina, September 1978, p 39.

(2) J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **38**, 4156 (1973).