(d, 1 H), 7.31–7.11 (m, 5 H), 6.83 (dd, 1 H) 2.41 (s, 3 H) 2.32 (s, 3 H). 2,4′-Dimethyl-5-iodobiphenyl: UV (CH_3CN) λ_{max} 230 nm (ϵ 28 400). ^1H NMR (chloroform-*d*) δ 7.64–6.97 (m, 7 H), 2.39 (s, 3 H), 2.19 (s, 3 H).

The structures were further confirmed by irradiation of the iodobitolyls in acetonitrile with 254-nm light. This causes the photolysis of the iodine atom, which leads to the dimethylbiphenyl. 4′,5-Dimethyl-2-iodobiphenyl produced 3,4′-dimethylbiphenyl, and 2,4′-dimethyl-5-iodobiphenyl produced 2,4′-dimethylbiphenyl, as determined by capillary GLC against authentic samples of the dimethylbiphenyls.

Photolysis Experiments. Solutions of the appropriate salt were prepared in methanol, acetone, or acetonitrile. In all cases, the concentration of the iodonium salt was 1.0×10^{-2} M. The anthracene concentration was 2.65×10^{-3} M, and the xanthone concentration was 1.07×10^{-2} M. Aliquots of the solutions were placed in quartz tubes (for 254-nm photolysis) or Pyrex tubes (for 300- and 350-nm photolysis). The tubes were sealed with rubber septa, and purged with solvent-saturated argon for 10 min prior to irradiation. The samples then were irradiated in a Rayonet photochemical reactor equipped with four bulbs emitting the desired wavelengths, in a carousel. Samples of the irradiated solutions were then diluted with water and extracted with hexanes containing *n*-tetradecane internal standard. The hexanes phase was then analyzed by capillary GLC. Quantification was accomplished by using known concentrations of authentic samples of the photoproducts, extracted in the same way as the photolysis samples. In the sensitized irradiations, the sensitizer absorbed at least 98% of the incident radiation. Measurement of the diphenyliodonium concentration was accomplished using the cobalt thiocyanate complex.[9] A 2.00-mL aliquot of the irradiated diphenyliodonium solution was diluted to 25.0 mL with chloroform. A 10.00-mL aliquot of this solution was mixed with 10.00 mL of an aqueous 0.1 M $CoCl_2$ and 0.5 M NH_4SCN solution. The two-phase mixture was shaken and allowed to stand overnight. The absorbance of the chloroform phase was measured at 624 nm, and the concentration of diphenyliodonium determined from a calibration curve determined from known concentrations of the same salt. Acid was determined by using sodium 4-nitrophenoxide. Photolysis solution (1.00 mL) was added to 5.00 mL of saturated phenoxide in acetonitrile and diluted to 25 mL. The absorbance was then measured and was converted to concentration by use of a standard absorbance curve determined from freshly prepared trifluoromethanesulfonic acid solutions in acetonitrile, whose absorbance was measured in the same way as the unknowns.

Quantum Yields. Quantum yields were determined by using a modified PTI Quantacount. Solutions were 0.01 M for direct irradiation or 0.005–0.03 M for acetone-sensitized irradiation. Three 3.00-mL aliquots were placed in Suprasil cuvettes, sealed with a rubber septum, and purged with argon for 8 min immediately prior to irradiation. The samples were then irradiated in the Quantacount, which was previously calibrated by using potassium ferrioxalate actinometry. After irradiation, the samples were transferred to tubes containing 1.00 mL of hexanes containing a small amount of *n*-tetradecane as internal standard and 10.00 mL of 0.5 M aqueous NaH_2PO_4. The tubes were stoppered and thoroughly mixed. After standing for 4 h, the hexane layer was removed and analyzed by capillary GLC. The integrator was calibrated against similar concentrations of authentic samples of the photoproducts, which were treated to a similar workup as the photolysis solutions. Benzene was quantified by irradiation of a 3.00-mL aliquot, which was transferred with an additional 1.00 mL of solvent to a tube containing 2.00 mL of *n*-pentane, 10.00 mL of 0.5 M aqueous NaH_2PO_4, and *n*-octane as an internal standard. The contents of the tube were vigorously mixed, and the tube was allowed to stand for 4 h. The pentane layer was separated and analyzed by capillary GLC. Acetanilide was analyzed in the same way, with the exception of the use of methyl *tert*-butyl ether as the extracting solvent and *n*-tetradecane as the internal standard.

Registry No. Diphenyliodonium triflate, 66003-76-7; diphenyliodonium hexafluorophosphate, 58109-40-3; bis(4-methylphenyl)iodonium hexafluorophosphate, 60565-88-0; bis(4-methylphenyl)iodonium trifluoromethanesulfonate, 123726-16-9; 3-iodobiphenyl, 20442-79-9; 2-iodobiphenyl, 2113-51-1; 4-iodobiphenyl, 1591-31-7; 4′,5-dimethyl-2-iodobiphenyl, 123726-17-0; 2,4′-dimethyl-5-iodobiphenyl, 123726-18-1.

Behavior of Pyridinium Salts Obtained from Derivatives of Pyridinedicarboxylic Acids in Basic Solutions. Addition of Hydroxide or Alkoxide To Form 1,2-Dihydropyridine Intermediates

Johanna C. Speelman and Richard M. Kellogg*

Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received March 27, 1989

The N-alkylated pyridinium salts obtained from the diethyl esters, *N*-ethyl amides, and *N,N*-diethyl amides of pyridine-3,5-dicarboxylic acid exhibit ultraviolet absorptions of moderate intensity in the region of 350 nm when dissolved in 95% ethanol. This absorption increases in intensity on addition of base and disappears on acidification of the solutions. It is not observed in rigorously dried solvents like chloroform or methylene chloride. By ^1H NMR spectroscopy it has been shown that a 1,2-dihydropyridine is formed reversibly by addition of hydroxide (or methoxide) to the 2-position of the pyridinium salts. Concurrently with the formation of these intermediates, proton–deuterium exchange (in deuterated solvents) occurs, possibly via betaines formed by base-induced deprotonation at the 2-position of the pyridinium salts. The corresponding derivatives of pyridine-2,5- and -3,5-dicarboxylic acids do not display this behavior.

Introduction

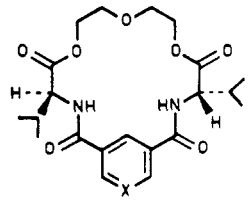
In the course of examination of the circular dichroism (CD) spectra of chiral bridged pyridines (**1**)[1] a CD effect at about 350 nm was observed for pyridinium salts (**1b**) in spectral grade 95% ethanol.[1] This Cotton effect was obviously associated with an ultraviolet absorption of modest intensity at the same wavelength. However, an absorption at such a long wavelength seems inconsistent with the electronic structure of these pyridinium salts.[2]

(1) (a) Speelman, J. C.; Talma, A. G.; Kellogg, R. M.; Meetsma, A.; de Boer, J. L.; Beurskens, P. T.; Bosman, W. P. *J. Org. Chem.* **1989**, *54*, 1055. (b) Schipper, P.; Kellogg, R. M. *J. Am. Chem. Soc.*, in press.

(2) On the basis of experience with pyridinium salts of esters of pyridine-3,5-dicarboxylic acid [Van Bergen, T. J.; Kellogg, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8451] we expected the maximum at about 271 nm.

0022-3263/90/1955-0647$02.50/0

The absorption was not seen in rigorously dry solvents like methylene chloride. In 95% ethanol this long-wavelength absorption increased modestly in intensity on addition of triethylamine and disappeared on addition of sufficient trifluoroacetic acid to make the solution acidic. All attempts to isolate any new product(s) led only to recovery of **1b** in quantitative yield.

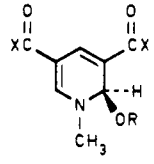


1

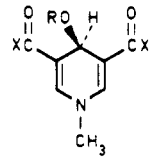
a) X = N

b) X = $\overset{\oplus}{N}CH_3, ClO_4^{\ominus}$

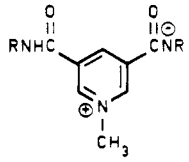
Some type of reversible interaction between **1b** and a base clearly is involved. Several explanations come to mind. First, addition of hydroxide (or alkoxide) to the pyridinium salt to generate either a 1,2- or 1,4-dihydropyridine (general structures **2** and **3**) can be considered.



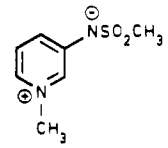
2



3



4

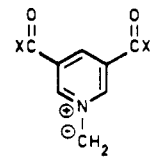


5

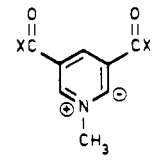
In general 1,2-dihydropyridines have two ultraviolet (UV) bands at roughly 280 and 350–380 nm whereas 1,4-dihydropyridines usually lack the 280-nm band.[3] Either might fit the long-wavelength UV absorption.

Another possibility is deprotonation of an amide hydrogen to give a betaine of general structure **4**. Compound **5** has, for example, been shown to be relatively stable.[4] A somewhat related intermediate is the ylid (**6**) derived by deprotonation at sp^3 carbon adjacent to positively charged nitrogen. Predictions of the ultraviolet spectral behavior are difficult. Such ylids are known to be formed readily if the anionic center is further stabilized by conjugation to a carbonyl or cyano group.[5]

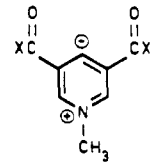
The isomeric ring betaines **7** and **8** can also be considered; these can also be represented by carbene resonance structures. Treatment of the corresponding pyridinium salt with triethylamine leads to **9a** as a presumed reaction



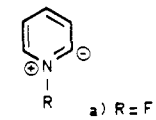
6



7



8



9

a) R = F

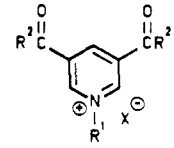
b) R = H

intermediate, and **9b** is the intermediate involved in the thermally induced decarboxylation of pyridine-2-carboxylic acid;[6a,b] similar chemistry is observed with 4-aminopyridines.[6c]

We have now identified the species responsible for the long-wavelength UV absorptions as a hydroxide (or alkoxide) addition product and in so doing have defined some previously unrecognized aspects of the chemistry of pyridinium salts.

Results

Rather than using macrocyclic (**1b**) or related compounds the synthetically more readily accessible **10a–e** and **11** were prepared by alkylation of the corresponding pyridines with CH_3I and $Mg(ClO_4)_2$ in acetonitrile at reflux[7] or $C_6H_5CH_2Br$ in ethanol at ambient temperature. Alkylation of pyridine-2,4-, pyridine-2,5-, and pyridine-2,6-dicarboxylic acid derivatives failed under these conditions apparently because of lack of nucleophilic reactivity of the pyridine nitrogen atom. Pyridinium salt **12** was finally obtained, however, from the corresponding pyridine by treatment with CH_3SO_3F for 65 h at ambient temperature.



10

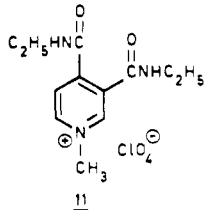
a) $R^1 = CH_3, X = ClO_4, R^2 = NHC_2H_5$

b) $R^1 = CH_3, X = ClO_4, R^2 = N(C_2H_5)_2$

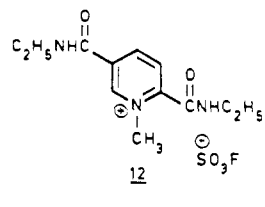
c) $R^1 = CH_2C_6H_5, X = Br, R^2 = NHC_2H_5$

d) $R^1 = CH_2C_6H_5, X = Br, R^2 = N(C_2H_5)_2$

e) $R^1 = CH_3, X = ClO_4, R^2 = OC_2H_5$



11



12

(3) (a) Palecek, J.; Ptackova, L.; Kuthan, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 427. (b) Traber, W.; Karrer, P. *Helv. Chim. Acta* **1958**, *41*, 2066. (c) Brignell, P. J.; Eisner, U.; Farrell, P. G. *J. Chem. Soc. B* **1966**, 1083.

(4) Dennis, N.; Katritzky, A. R.; Wilde, H.; Gavuzzo, E.; Vaciago, A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1304.

(5) See for representative literature: (a) Zoltewicz, J. A.; Cross, R. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1363. (b) Matsumoto, K.; Uchido, T. *J. Chem. Soc.; Perkin Trans. 1 1981*, 73. (c) Bapat, J. B.; Epsztajn, J.; Katritzky, A. R.; Pfau, B. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1692. (d) Zoltewicz, J. A.; *J. Chem. Soc., Perkin Trans, 2* **1974**, 1368.

(6) (a) Umemoto, T.; Tomizawa, G. *Tetrahedron Lett.* **1987**, *28*, 2705. (b) Oliveto, E. P. *Pyridine and Its Derivatives*; Klingsberg, E., Ed.; Interscience: New York, 1962; Part III, p 206. (c) Zoltewicz, J. A.; Meyer, J. D. *Tetrahedron Lett.* **1968**, 421.

(7) Talma, A. G.; Jouin, P.; De Vries, J. G.; Troostwijk, C. B.; Werumeus Buning, G. H.; Waninge, J. K.; Visscher, J.; Kellogg, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 3981.

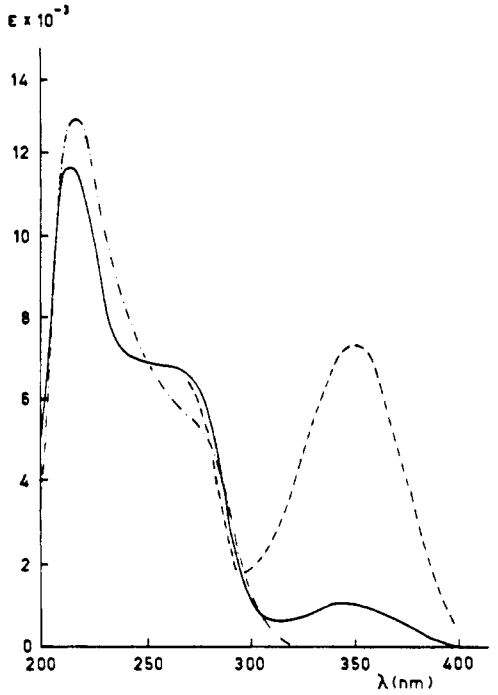


Figure 1. Ultraviolet spectrum of **10a**. (–) Solution in 95% C_2H_5OH; ((- -) after addition of $(C_2H_5)_3N$; (- · -) after addition of CF_3CO_2H.

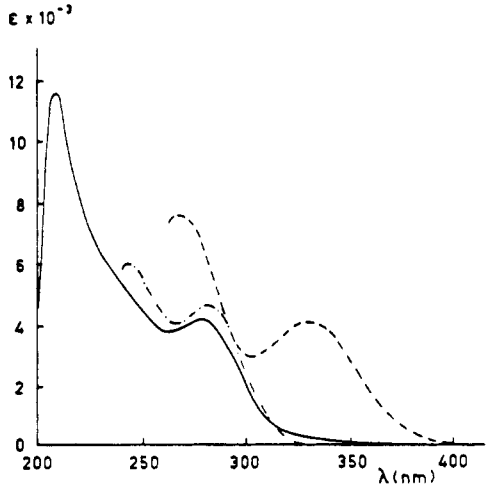


Figure 2. Ultraviolet spectrum of **10b**. (–) Solution in 95% C_2H_5OH; (- -) after addition of $(C_2H_5)_3N$; (- · -) after addition of CF_3CO_2H.

The UV spectra of **10a,b,e** under neutral conditions (95% spectrograde C_2H_5OH), basic conditions (triethylamine), and acidic conditions (sufficient CF_3CO_2H to make the solutions acidic) are given in Figures 1–3. Data for **10a–e** are collected in Table I. The *N*-ethylamide, **10a**, absorbs at 350 nm under neutral conditions (Figure 1, see captions). The absorption increases in intensity on addition of base and disappears under acidic conditions. A similar long-wavelength absorption (Figure 2) for *N,N*-diethylamide (**10b**) is seen only on addition of excess base. The ester (**10e**) (Figure 3) behaves similarly to **10a**. These observations rule out the possibility that a zwitterion (**4**) obtained by deprotonation of an amide hydrogen could be responsible for the absorption. Such deprotonation cannot take place with **10b,e**.

The *N*-benzylpyridinium salts (**10c,d**) (spectra not illustrated) behaved very similarly to their methyl counterparts **10a,b,e**. This argues against deprotonation at the

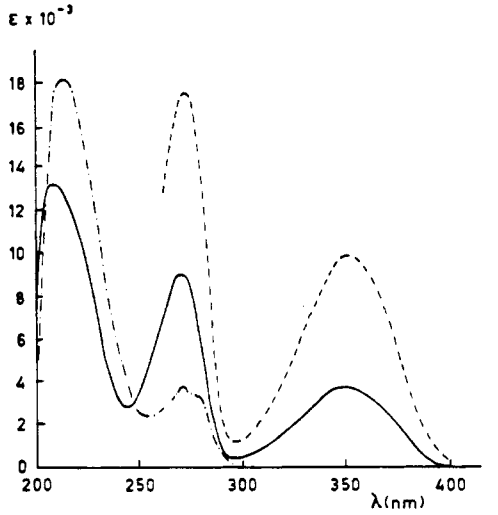


Figure 3. Ultraviolet spectrum of **10e**. (–) Solution in 95% C_2H_5OH. (- -) after addition of $(C_2H_5)_3N$; (- · -) after addition of CF_3CO_2H.

Table I. Ultraviolet Maxima for 10a–e under Neutral, Basic, and Acidic Conditions[a]

compound	addend	λ_{max}[b] (ϵ)
10a	none	351 (1080), 267 (6900), 213 (12000)
	$(C_2H_5)_3N$, 100 equiv	350 (6700), *c*
	CF_3CO_2H[d]	272 (5600), 217 (13000)
10b	none	280 (4250), 210 (12000)
	$(C_2H_5)_3N$, 200 equiv	330 (4100), *c*
	CF_3CO_2H[d]	283 (2500), *e*
10e	none	352 (3800), 271 (9000), 210 (13500)
	$(C_2H_5)_3N$, 100 equiv	352 (9900), *c*
	CF_3CO_2H[d]	271 (3550), 214 (18000)
10c	none	348 (1300), 213 (15000)
	NaOH[f]	349 (5050), 269 (9800), 215 (16000)
	CF_3CO_2H[d]	219 (16500)
10d	none	209 (22500)
	NaOH[f]	330 (7700), 266 (10000), 209 (22500)
	CF_3CO_2H[d]	232 (39100)

[a] In 95% C_2H_5OH/5% H_2O; concentration **10** ca. 10^{-4} M. [b] Wavelength of absorption maximum in nanometers. [c] Not recorded below 300 nm. [d] Excess, ca. 250 equiv. [e] Overlap with $(C_2H_5)_3N$, not observable. [f] Ca. 5 equiv.

sp^3 carbon bonded to pyridinium nitrogen, i.e. 1,2-ylide **6**. The negative charge should be better stabilized by conjugation in **10c,d** compared to **10a,b,e**. More telling, in the presence of CD_3OD under conditions under which the intermediate is observed, *no* deuterium is incorporated into this sp^3 carbon. Some deuterium is incorporated into the heterocyclic ring, however, (see further).

The pyridinium salts **11** and **12** did not exhibit a similar long-wavelength absorption even under basic conditions, and the form of the ultraviolet spectra remained essentially unchanged under neutral, basic, and acidic conditions in 95% C_2H_5OH.

Direct structural determination of the intermediate by ^1H NMR spectroscopy was next attempted. CD_3OD was used as solvent, and the concentration of pyridinium salt was raised to 10^{-2} M to facilitate observation (UV measurements were made at ca. 10^{-4} M). Large excesses of triethylamine could not be used because of spectral interference from the protons of the ethyl groups. On the basis of examination of the UV spectra it was clear that the base-induced effects also appeared if hydroxide (or deuteroxide) was added. For example, with **10a**, addition

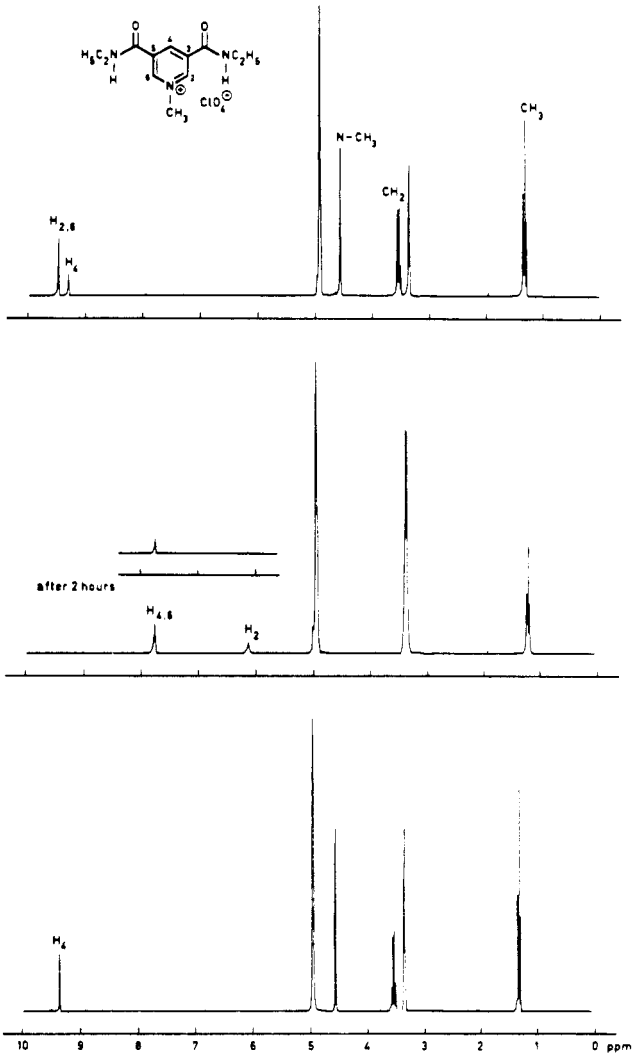


Figure 4. ^1H NMR spectra of **10a** at 300 MHz. Upper spectrum in CD_3OD, middle of the addition of 1 equiv of NaOH in CD_3OD, lower after neutralization woth DCl/D_2O. The unlabeled peaks in the upper spectrum (present also in the other two spectra) correspond to incompletely deuterated methanol.

of 1 equiv of NaOH in CD_3OD gave the same effect in the UV as addition of 15 equiv of triethylamine. Hence NaOH dissolved in CD_3OD was used as the base for the NMR experiments.

Large changes in the ^1H NMR spectra occurred on addition. Because of peak overlap that obscured some of the spectral details it was necessary to study several different pyridinium salts in order to obtain a composite picture. In Figures 4 and 5 the ^1H NMR spectra of **10a** and **10d** are illustrated (see captions) in CD_3OD solution, CD_3OD solution with 1 equiv of NaOH in D_2O, and after acidification of the basic solution with DCl/D_2O. Some selected spectra data for **10a–e** are given in Table II.

Addition of base leads to an unfield shift of the aromatic protons and the methyl group bound to the pyridinium nitrogen in **10a** (Figure 4). Unfortunately both this methyl group and CH_2 protons of the ethyl groups fall under the methanol absorptions at about δ 4.95. The absorptions at δ 7.75 and 6.12, which clearly arise from the aromatic protons of **10a**, decrease in intensity, indicative of deuterium incorporation. On acidification the spectrum of the pyridinium salt is regenerated save that the 2,6-positions of the pyridinium ring are completely deuterated. From the spectrum of **10d** it is clear that an unsymmetrical species is formed (Figure 5). The benzylic methylene group

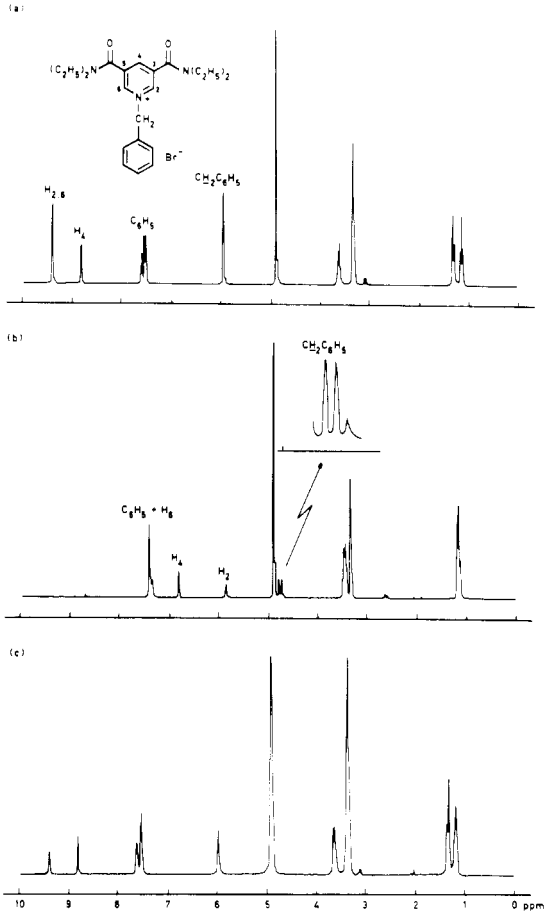


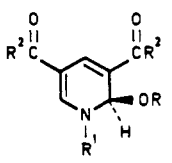
Figure 5. ^1H NMR spectra of **10d** at 300 MHz. Upper spectrum in CD_3OD, middle 5 min after addition of 1 equiv of NaOH in CD_3OD, lower after neutralization with DCl/D_2O. See caption for Figure 4 for unlabeled solvent absorptions.

Table II. Selected ^1H NMR Spectral Data for Pyridinium Salts 10a–e[a]

compound	protons	in CD_3OD (δ)	in CD_3OD with $NaOH/D_2O$ (δ)
10a	2,6-H	9.47	7.75 + 6.12[b]
	4-H	9.30	7.75
	NCH_3	4.56	*c*
10b	2,6-H	9.22	7.28 + 5.90[b]
	4-H	8.75	6.80
	NCH_3	4.52	*c*
10c	2,6-H	9.60	7.91 + 6.10[b]
	4-H	9.39	7.78
	$NCH_2C_6H_5$	6.01	4.81 (AB, J = 12 Hz)
10d	2,6-H	9.39	5.87[b,d]
	4-H	8.81	6.83
	$NCH_2C_6H_5$	5.96	4.78 (AB, J = 12 Hz)
10e	2,6-H	9.72	8.01 + 7.98
	4-H	9.40	8.01
	NCH_3	4.60	3.44

[a] Spectra measured at 300 MHz. [b] 2,6-Protons exchange with deuterium, see text. [c] Not observable because of overlap with CD_3OD absorption. [d] One peak is not visible probably because of overlap with the C_6H_5 absorption.

adjacent to pyridinium nitrogen is now shifted sufficiently downfield in the intermediate that it does not fall under a methanol peak. It is observed at δ 4.81 as an AB quartet, J = 12 Hz. This methylene group is clearly diastereotopic. This condition is met uniquely in the 1,2-dihydropyridine structure (**13d**) where the substituent R on oxygen is hydrogen or (deuterio)methyl. Similar phenomena are found for **10c** (Table II) and the ester **10e** wherein the methyl

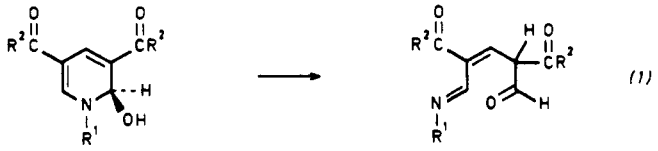


13

a) $R^1 = CH_3$, $R^2 = NHC_2H_5$
b) $R^1 = CH_3$, $R^2 = N(C_2H_5)_2$
c) $R^1 = CH_2C_6H_5$, $R^2 = NHC_2H_5$
d) $R^1 = CH_2C_6H_5$, $R^2 = N(C_2H_5)_2$
e) $R^1 = CH_3$, $R^2 = OC_2H_5$

group bound to pyridinium nitrogen can be observed free from the solvent peak. Reasoning by analogy we conclude that **10a–e** give rise in the presence of aqueous base to 1,2-dihydropyridines (**13a–e**). Competitive with the formation of **13** there is also a base-catalyzed exchange process whereby the pyridinium 2,6-protons (but not that at the 4-position) are exchanged for deuterium.

These NMR spectra provide no information whether hydroxide or (deuterio)methoxide has added to the 2-position. The lack of any absorption between δ 11 and 14 indicates that **13** bearing a *hydroxide* at position 2 has not undergone ring opening to **14** (eq 1).



(1)

13 14

Ring opening is a common fate of pyridinium salts on treatment with aqueous base.[8] The fact that this clearly does not occur in the present instance may be an argument for methoxide rather than hydroxide substitution.

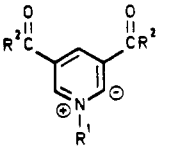
Discussion

The first comprehensive study of the chemistry of pyridinium salts derived from nicotinic acid with nucleophiles was carried out by Wallenfels[9] partially in conjunction with other work on the establishment of the 1,4-dihydropyridine structure for NADH.[10] Wallenfels and co-workers examined the interactions of these pyridinium salts with other anions such as cyanide, thiolate, enolates, and hydroxide. For the case of hydroxide, dihydropyridine formation was suspected, but the structures of the adducts were not established with certainty. A large effect of solvent polarity on the spectra of pyridinium salts with various nucleophiles, thought to reflect different degrees of association, was observed. Subsequent years have seen a surge of interest in dihydropyridine/pyridinium salt combination that can serve as models for the NADH/NAD^+ cofactor system. Much efforts has gone into the pyridine-3,5-dicarboxylic acid derivatives along with models derived from nicotinic acid.[11] A complex picture of the chemistry of the association of these types of pyridinium ions with nucleophiles has emerged. Charge transfer interactions,[12] covalent addition,[9] formation of tight ion pairs some with unusual spectral behavior,[13] and electron transfer[14] are just some of the phenomena that have been observed. The possibility for an anion to act as a base toward a pyridinium salt by abstracting a proton has been mentioned in the Introduction.

Hydroxy- or alkoxy-substituted dihydropyridines of the type identified here have been scarcely described.[15] Various charge-transfer interactions between pyridinium salts and hydroxide have been postulated.[16] Ring opening and pyridine formation have been observed as chemical consequences of the interaction of hydroxide with pyridinium salts.[13] We have definitely established that hydroxy(or alkoxy)dihydropyridines derived from pyridine-3,5-dicarboxylic acid derivatives can be generated in alcoholic solution in virtually quantitative yield and are stable in solution.

In other words, the interaction between oxide base and pyridinium salt leads to covalent bond formation. The hard alkoxide (or hydroxide) adds in a charge-controlled reaction at the 2-position of the pyridinium ring. Softer nucleophiles more subject to HOMO/LUMO control add at the 4-position.[18]

These adducts (**13**) decompose in our hands to starting material (**10**) and alcohol or water on removal of solvent. Perhaps traces of acid catalyze this reverse process. In addition to the reversible addition of alkoxide/hydroxide there is an additional process whereby the 2,6-protons of **10a–e** are exchanged for deuterium in the presence of base. A likely mechanism is via reversible formation of a betaine **15**.



15

Experimental Section

General. All compounds cited without reference are either commercially available or have been described previously in the literature. For those pyridine derivatives for which special reaction conditions were required a brief summary of the synthesis details is given. Melting points are uncorrected and were determined either on a Reichert hot stage provided with a microscope or on a Mettler automatic melting point apparatus. Ultraviolet spectra were measured with a Perkin-Elmer Lambda V apparatus in the concentration range 10^{-4} to 5×10^{-3} M. Mass spectra were determined on a MS 9 instrument and NMR spectra (10^{-2} to 2×10^{-2} M) were obtained for routine purposes on a Perkin-Elmer 21 60-MHz unit. Other spectra were measured with Nicolet

(8) See for representative literature: (a) Kosower, E. M.; *Molecular Biochemistry*; McGraw-Hill; New York, 1962; pp 166–210. (b) Burton, R. M.; Kaplan, N. O. *Arch. Biochem. Biphys.* **1963**, *101*, 139. (c) Anderson, A. G.; Berkelhammer, G. *J. Org. Chem.* **1958**, *23*, 1109. (d) Bowden, K.; Braude, E. A.; Jones, E. R. H.; Weedon, B. *J. Chem. Soc.* **1946**, *45*. (e) Dittmer, D. C.; Kolyer, J. M. *J. Org. Chem.* **1963**, *28*, 2288.

(9) Wallenfels, K.; Schüly, H. *Justus Liebig's Ann. Chem.* **1959**, *621*, 86 and following papers in the same issue.

(10) Pullman, M. E.; Colowick, S. P. *J. Biol. Chem.* **1954**, *206*, 121.

(11) See ref 7 for a compilation of references.

(12) Kosower, E. M. *J. Am. Chem. Soc.* **1956**, *78*, 3497.

(13) See for example: van Keulen, B. J.; Kellogg, R. M. *J. Am. Chem. Soc.* **1984**, *106*, 6029.

(14) Saito, G.; Colter, A. K. *Tetrahedron Lett.* **1977**, 3325.

(15) (a) One stable example of a hydroxy-substituted dihydropyridine is 2-hydroxy-1-methyl-3,4,5-tricyano-1,2-dihydropyridine: Wallenfels, K.; Hanstein, W. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 869. See also: (b) Moracci, F. M.; Casini, A.; Liberatore, F.; Carelli, V. *Tetrahedron Lett.* **1976**, *3723*. (c) Rodig, O. B. In *The Chemistry of Heterocyclic Compounds*; Interscience: New York, 1974; Vol. 14, Pyridine and Its Derivatives, Supp. Part I, p 344. (d) Evidence for hydroxide addition to the 4-position of NADH has been obtained: Bielmann, J. F.; Lapinte, C.; Haid, E.; Weimann, G. *Biochemistry* **1979**, *18*, 1212.

(16) Buron, R. M., Kaplan, N. O. *Arch. Biochem. Biophys.* **1963**, *101*, 139.

(17) Kosower, E. M. *Molecular Bichemistry*; McGraw-Hill: New York, 1962; pp 166–210.

(18) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1976; pp 66–69.

200-MHz or Varian 300-MHz spectrometer. Acid and base were added with Terumo Micro Syringe.

***N,N'*-Diethyl-3,5-pyridinedicarboxamide.** A mixture of ethylamine (3.1 g, 70% solution in H_2O, 48 mmol) in 40 mL of CH_2Cl_2 was cooled to 0 °C. A solution of pyridine-3,5-bis(carbonyl chloride) (prepared from 3.0 g (16.4 mmol) of pyridine-3,5-dicarboxylic acid and $SOCl_2$ and used immediately[7]) in 15 mL of CH_2Cl_2 was added slowly. The temperature was kept below 5 °C. After the addition was complete, the mixture was stirred at room temperature for 30 min. After addition of 30 mL of 1 N NaOH solution, the layers were separated. The water layer was saturated with NaCl and extracted with 50 mL of CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a white solid, which was recrystallized from $CHCl_3$–diethyl ether to give 13.5 mmol (82% yield) of white crystals: mp 160–164 °C (lit.[19] mp 161–162.5 °C); ^1H NMR ($CDCl_3$) δ 1.20 (t, 6 H, CH_2CH_3), 3.42 (m, 4 H, CH_2CH_3), 8.30 (t, broad, 2 H, NH), 8.58 (s, 1 H, pyr-H_4), 9.18 (s, 2 H, pyr-$H_{2,6}$); ^{13}C NMR ($CDCl_3$) δ 14.7 (q), 34.6 (t), 129.7 (s), 134.0 (d), 149.7 (d), 163.2 (s).

***N,N,N',N'*-Tetraethyl-3,5-pyridinedicarboxamide** was prepared from pyridine-3,5-dicarboxylic acid (1.7 g, 10 mmol) via the acid chloride, which was used immediately, and diethylamine (1.46 g, 20 mmol). Recrystallization from diethyl ether gave 2.03 g (7.3 mmol, 73% yield) of white crystals: mp 81–81.5 °C (lit.[20] mp 73–75 °C); IR (KBr) 2980, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (t, 12 H, CH_2CH_3), 3.35 (m, 8 H, CH_2CH_3), 7.76 (t, 1 H, pyr-H_4, J = 2 Hz), 8.71 (d, 2 H, pyr-$H_{2,6}$, J = 2 Hz); ^{13}C NMR ($CDCl_3$) (30 °C) δ 12.4 (q), 13.8 (q), 39.1 (t), 42.9 (t) 132.0 (d), 132.4 (s), 147.1 (d), 167.3 (s). On increase of the probe temperature to 60 °C coalescence set in; signals were observed at δ 13.1 (q) and 41.2 (broad, t).

***N,N'*-Diethyl-2,5-pyridinedicarboxamide** was prepared from the acid chloride (obtained from pyridine-2,5-dicarboxylic acid (3.09 g, 17.9 mmol) by treatment with $SOCl_2$ and used immediately) and ethylamine (2.5 g, 70% solution in water, 39.5 mmol). Recrystallization from $CHCl_3$–diethyl ether gave 2.7 g (12.5 mmol, 70% yield) of white crystals: mp 188–189 °C; IR (KBr) 3300, 2970, 1640, 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (t, 6 H, CH_2CH_3), 3.49 (m, 4 H, CH_2CH_3), 7.61 (t, br, 2 H, NH), 8.17 (m, 2 H, pyr-$H_{3,4}$), 8.95 (s, 1 H, pyr-H_6); ^{13}C NMR ($CDCl_3$) δ 14.6 (q), 34.3 (t), 35.1 (t), 121.6 (d), 132.3 (q), 135.7 (d), 147.0 (d), 153.4 (s), 163.3 (s), 164.9 (s).

***N,N'*-Diethyl-2,6-pryidinedicarboxamide** was prepared from pyridine-2,6-dicarboxylic acid (2.0 g, 12.0 mmol), via the acid chloride and used immediately, and ethylamine (1.6 g, 70% solution in water, 24.8 mmol). Recrystallization from $CHCl_3$–diethyl ether gave 2.2 g (9.9 mmol, 83% yield) of white crystals: mp 184.2–184.6 °C; IR (KBr) 3320, 3280, 2975, 1680, 1645, 1525 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (t, 6 H, CH_2CH_3), 3.40 (m, 4 H, CH_2CH_3), 7.81–8.48 (m, 3 H, pyr-$H_{3,4,5}$), 8.69 (t, broad, 2 H, NH); ^{13}C NMR ($CDCl_3$) δ 14.6 (q), 34.2 (t), 124.5 (d), 138.7 (d), 148.8 (s), 163.5 (s).

***N,N'*-Diethyl-2,4-pyridinedicarboxamide** was prepared from pyridine-2,4-dicarboxylic acid monohydrate (2.0 g, 10.8 mmol), via the acid chloride and used immediately, and ethylamine (1.4 g, 70% solution in water, 21.6 mmol). Recrystallization from $CHCl_3$–diethyl ether gave 1.43 g (6.5 mmol, 62% yield) of white crystals: mp 117–119 °C; IR (KBr) 3320, 2980, 1660, 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (t, 6 H, CH_2CH_3), 3.44 (m, 4 H, CH_2CH_3), 7.94 (m + d, 3 H, NH + pyr-H_5), 8.61 (s + d, 2 H, pyr-$H_{3,6}$); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 14.6 (q), 34.2 (t), 35.0 (t), 118.4 (d), 124.5 (d), 143.3 (s), 148.8 (d), 150.3 (s), 163.5 (s), 164.6 (s).

Dimethyl 3,4-pyridinedicarboxylate was prepared from pyridine-3,4-dicarboxylic acid (2.0 g, 12.0 mmol), which was suspended in a mixture of 100 mL of methanol and 50 mL of benzene. Dowex 50W × 8 (0.5 g, H^+ form) was added as an acid catalyst, and the mixture was refluxed in a round-bottomed flask equipped with a Soxhlet extraction device and filled with molecular sieves (3 Å, 10 g). The solution was allowed to reflux for 24 h, and the Soxhlet device was charged with another 10-g portion of sieves, and the mixture was allowed to reflux for an additional 48 h. Although not all the pyridine-3,4-dicarboxylic acid was consumed, the reaction was stopped at this point. The acid catalyst and the pyridine-3,4-dicarboxylic acid were removed by filtration, and the solvents were removed under reduced pressure. The yellowish oil was purified by bulb-to-bulb distillation (oven temperature 140 °C, 0.01 mmHg) to give 0.80 g (4.8 mmol, 40% yield) of the dimethyl ester: ^1H NMR ($CDCl_3$) δ 3.91 (s, 6 H, OCH_3), 7.46 (d, 1 H, pyr-H_6, J = 5 Hz), 8.79 (d, 1 H, pyr-H_5, J = 5 Hz) 9.02 (s, 1 H, pyr-H_2).

***N,N'*-Diethyl-3,4-pyridinedicarboxamide.** A solution of 3,4-dicarbomethoxypyridine (0.2 g, 1.02 mmol) and ethylamine (0.5 g of a 70% solution in H_2O) in 3 mL of methanol was stirred at room temperature overnight. After evaporation of the solvents, the crude product was purified by flash chromatography on silica gel (6.5 g, column width 10 cm, diameter 1.5 cm) with acetone as eluent. The product was obtained as a white powder (0.18 g, 0.81 mmol, 80% yield): mp 135–136.5 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00 + 1.02 (2 t, 6 H, CH_2CH_3), 3.16 (m, 4 H, CH_2CH_3), 6.94 (d, 1 H, pyr-H_6), 7.93 + 8.01 (2 t, 2 H, NH), 8.17 (d, 1 H, pyr-H_5) 8.25 (s, 1 H, pyr-H_2); ^{13}C NMR ($CDCl_3$) δ 13.83 (q), 13.89 (q), 34.56 (t), 34.65 (t), 121.26 (d), 128.97 (s), 141.60 (s), 148.22 (d), 150.33 (d), 166.29 (s), 166.39 (s).

Diethyl 3,5-Pyridinedicarboxylate. A stirred suspension of pyridine-3,5-dicarboxylic acid (10 g, 60 mmol) in dry ethanol (100 mL) was cooled to −5 °C. $SOCl_2$ (20 mL, 32.6 g, 0.27 mol) was added slowly to the suspension. The temperature was kept below 5 °C. After the addition was complete, the mixture was heated to reflux. After 2 h a clear solution was obtained. Removal of the solvent followed by reflux for 2 h in 0.1 L of CH_2Cl_2/CCl_4 (1:1) gave the free diester. Traces of HCl were removed by dissolving the diester in CH_2Cl_2 and washing the organic layer with a 10% $NaHCO_3$ solution and water, respectively. Removal of the CH_2Cl_2 gave a yellow oil. Recrystallization from petroleum ether, 40–60 °C, gave 11.5 g (52 mmol, 85% yield) of white crystals: mp 48–50 °C (lit.[21] mp 51 °C); ^1H NMR ($CDCl_3$) δ 1.48 (t, 6 H, CH_2CH_3), 4.47 (q, 4 H, CH_2CH_3), 8.87 (t, 1 H, pyr-H_4), 9.36 (d, 2 H, pyr-$H_{2,6}$); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 61.4 (t), 125.9 (s), 137.4 (d), 153.7 (d), 164.0 (s).

1-Methyl-3,5-bis((ethylamino)carbonyl)pyridinium Perchlorate (10a). A solution of *N,N'*-diethyl-3,5-pyridinedicarboxamide (0.60 g, 2.7 mmol) and methyl iodide (0.7 mL, 1.6 g, 11.2 mmol) in 40 mL of acetonitrile was heated to reflux. After 5 min, 1.3 g (5.5 mmol) of $Mg(ClO_4)_2 \cdot H_2O$ was added carefully. The solution was refluxed overnight, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography over silica gel (220–400 mesh, 25 g, column 13 cm, diameter 2 cm) with CH_2Cl_2 as eluent to remove traces of iodine and then with CH_2Cl_2/CH_3CN (1:1) to remove traces of starting material and finally with CH_3CN to give the pyridinium salt as a white solid. Recrystallization from methanol gave 0.76 g (2.3 mmol, 85% yield) of white crystals: mp 226.0–226.6 °C; IR (KBr) 3360, 3080, 1675, 1655, 1550 cm^{-1}; ^1H NMR (CD_3CN) δ 1.20 (t, 6 H, CH_3), 3.64 (m, 4 H, CH_2CH_3), 9.45 (s, 3 H, NCH_3), 7.94 (m, 2 H, NH), 9.05 (s, 1 H, pyr-H_4), 9.18 (s, 2 H,m pyr-$H_{2,6}$); ^{13}C NMR (CD_3CN) δ 14.8 (q), 3.65 (t), 50.2 (q), 136.2 (s), 142.1 (d), 147.6 (d), 161.8 (s); UV (95% C_2H_5OH) λ_{max} 349 (ϵ 1200), 268 (ϵ 6300), 209 nm (ϵ 11 500). Anal. Calcd for $C_{12}H_{18}ClN_3O_6$: C, 42.93; H, 5.40; N, 12.52% Cl, 10.56. Found: C, 42.33; H, 5.33; N, 12.28; Cl, 10.80. An acceptable analysis for carbon could not be obtained.

1-Methyl-3,5-bis((diethylamino)carbonyl)pyridinium perchlorate (10b) was prepared from *N,N,N',N'*-tetraethyl-3,5-pyridinedicarboxamide (0.28 g, 1.01 mmol) as described for **10a**. Recrystallization from CH_3OH gave 0.35 g (0.88 mmol, 88% yield) of **10b** as white crystals: mp 158–160 °C; IR (KBr) 3080, 2980, 1630, 1460 cm^{-1}; ^1H NMR (CD_3CN) δ 1.16 (m, 12 H, CH_2CH_3), 3.51 (m, 8 H, CH_2CH_3), 4.60 (s, 3 H, NCH_3), 8.42 (s, 1 H, pyr-H_4), 8.76 (s, 2 H, pyr-$H_{2,6}$); ^{13}C NMR (CD_3CN) δ 12.9 (q), 14.3 (q), 40.6 (t), 44.4 (t), 49.8 (q), 138.5 (s), 140.9 (d), 144.4 (d), 164.0 (s); UV (95% C_2H_5OH) λ_{max} 282 (ϵ 2550), 211 nm (ϵ 7200).

1-Methyl-3,4-bis((ethylamino)carbonyl)pyridinium perchlorate (11) was obtained from the corresponding amide (0.18

(19) Kuthan, J.; Palecek, J. *Collect. Czech. Chem. Commun.* **1960**, *31*, 2618.

(20) Graf, R.; Theyer, A.; Purkert, R. *J. Prakt. Chem.* **1933**, *138*, 259.

(21) Stetter, H.; Henning, H. *Chem. Ber.* **1955**, *88*, 789.

g, 0.81 mmol) as described for **10a**. Attempts at recrystallization failed. After drying in vacuum (50 °C) there was obtained 0.24 g (0.72 mmol, 88% yield) of **11** as a white powder: mp dec; ^{1}H NMR (CD_3CN) δ 1.24 (t, 6 H, CH_2CH_3), 3.21 (m, 4 H, CH_2CH_3), 4.39 (s, 3 H, NCH_3), 8.01 (d + m, 3 H, pyr-H_6 + NH), 8.84 (d + s, 2 H, pyr H_9 + H_2); ^{13}C NMR (CD_3CN) δ 13.9 (q), 37.0 (t), 37.1 (t) 50.5 (q), 128.1 (d), 139.6 (s), 146.5 (d), 148.7 (s), 149.1 (d), 164.4 (s), 165.7 (s); UV (95% C_2H_5OH) λ_{max} 272 (ε 3000), 205 (ε 6500).

1-Methyl-3,5-bis(ethoxycarbonyl)pyridinium perchlorate (10e) was obtained analogously to other pyridinium salts. Recrystallization from methanol–diethyl ether gave, starting from 2.24 mmol pyridine, 0.60 g (1.78 mmol, 80% yield) of white crystals of **10e**: mp 138–140 °C; IR (KBr) 3080, 1725 cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.42 (t, 6 H, CH_2CH_3) 4.47 (q + s, 7 H, CH_2CH_3 + NCH_3), 9.26 (s, broad, 1 H, pyr-H_4), 9.39 (s, broad, 2 H, pyr-$H_{2,6}$); ^{13}C NMR ($CD_3CN/CDCl_3$) δ 13.0 (q), 48.6 (q), 62.8 (t), 130.3 (s), 143.9 (d), 148.6 (d), 159.7 (s); UV (95% C_2H_5OH) λ_{max} 352 (ε 3800), 271 (ε 9000), 210 nm (ε 13 500).

1-Benzyl-3,5-bis((ethylamino)carbonyl)pyridinium Bromide (10c). To a stirred solution of 0.5 g (2.26 mol) of the corresponding amide in 8 mL of ethanol was added 1.4 mL (2.0 g, 11.8 mmol) of benzyl bromide. The solution was stirred for 24 h, after which time a precipitate had formed. After slow addition of diethyl ether, this precipitate was filtered with suction and washed with cold ether. Recrystallization from ethanol–diethyl ether gave 0.57 g (1.5 mmol, 66% yield) of white crystals: mp 209–210.5 °C; IR (KBr) 3250, 2980, 1660 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.16 (t, 6 H, CH_2CH_3), 3.35 (m, 4 H, CH_2CH_3), 6.03 (s, 2 H, CH_2Ar), 7.5 (m, 5 H, C_6H_5), 9.34 (t, 2 H, NH), 9.52 (t, 1 H, pyr-H_4), 9.81 (d, 2 H, pyr-$H_{2,6}$); ^{13}C NMR (DMSO-d_6) δ 14.5 (q), 34.7 (t), 63.8 (t), 129.3 (d), 129.4 (d), 129.6 (d), 133.8 (s), 141.6 (d), 146.0 (d), 160.6 (s).

1-Benzyl-3,5-bis((diethylamino)carbonyl)pyridinium bromide (10d) was prepared form *N,N,N',N'*-tetraethyl-3,5-pyridinedicarboxamide (0.5 g, 1.8 mmol). Recrystallization from acetonitrile–diethyl ether gave 0.55 g (1.23 mmol, 68% yield) of **10d** as white crystals: mp 165–167 °C; IR (KBr) 2970, 1630, 1445 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 0.99 + 1.13 (2 t, 12 H, CH_2CH_3), 3.19 + 3.41 (2 q, 8 H, CH_2CH_3), 5.94 (s, 2 H, CH_2Ar), 7.57 (m, 5 H, C_6H_5), 8.73 (s, 1 H, pyr-H_4), and 9.56 (s, 2 H, pyr-$H_{2,6}$); ^{13}C NMR (DMSO-d_6) δ 12.7 (s), 39.3 (t), 43.2 (t), 63.6 (t), 29.3 (d), 129.9 (d), 133.9 (s), 137.3 (s), 140.4 (d), 142.9 (d), 163.1 (s).

1-Methyl-2,5-bis((ethylamino)carbonyl)pyridinium Fluorosulfonate (12). Methyl fluorosulfonate (1 mL) was added to a solution of *N,N'*-diethyl-2,5-pyridinedicarboxamide (0.25 g, 1.13 mmol) in 50 mL of dry CH_2Cl_2. The solution was stirred for 65 h with exclusion of moisture. After evaporation of the solvent, there was obtained an oil, which became solid after drying in vacuum at 50 °C. The yield of **12** was 0.38 g (11.3 mmol, 100% yield) as a white powder: mp 163–165.5 °C; ^{1}H NMR (CD_3CN) δ 1.25 (t, 6 H, CH_2CH_3), 3.42 (m, 4 H, CH_2CH_3), 4.35 (s, 3 H, NCH_3), 7.98 (d, 1 H, pyr-H_3), 8.32 (m, 2 H, NH), 8.75 (d, 1 H, pyr-H_4), 9.06 (s, 1 H, pyr-H_6); ^{13}C NMR (CD_3CN) δ 14.8 (q), 36.4 (t), 36.5 (t), 48.2 (q), 128.4 (d), 136.0 (s), 145.9 (d), 148.1 (d), 151.3 (s), 161.1 (s), 162.3 (s); UV (95% C_2H_5OH) λ_{max} 275 (ε 11 000), 206 nm (ε 10 000).

Attempts to alkylate the pyridine using other methods failed to give significant amounts of the desired pyridinium salt.

γ-Silicon Stabilization of Carbonium Ions in Solvolysis. 4. Solvolysis of *cis*- and *trans*-3-(Trimethylsilyl)cyclohexyl and -3-*tert*-Butylcyclohexyl *p*-Bromobenzenesulfonates[1]

V. J. Shiner, Jr.,* and Mark W. Ensinger

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

George S. Kriz and Karen A. Halley

Department of Chemistry, Western Washington University, Bellingham, Washington 98225

Received May 24, 1989

The solvolyses of *cis*- and *trans*-3-(trimethylsilyl)cyclohexyl and -3-*tert*-butylcyclohexyl *p*-bromobenzenesulfonates (1–4) have been examined in several ethanol- and trifluoroethanol–water solvent mixtures. The α- and β-deuterium kinetic isotope effects have been determined, and the products have been identified. The *cis*-silyl compound (1) solvolyzes with participation by bridging across the ring between the γ-carbon and the reaction center, promoted by the γ-trimethylsilyl group. Products of the solvolysis are mainly those of substitution with retention of configuration, but a significant fraction of bicyclo[3.1.0]hexane is also formed. The *trans*-silyl compound (2) undergoes rate-determining ionization without significant acceleration by the trimethylsilyl group but with substantial participation by the β-hydrogens. The solvolysis products are 3- and 4-(trimethylsilyl)cyclohexenes formed by 1,2-elimination and cyclohexene formed by Wagner–Meerwein rearrangement and subsequent loss of the trimethylsilyl group. The solvolyses of the carbon analogue compounds (**3** and **4**) involve rate-determining ionization to form an intimate ion pair, followed by elimination of β-hydrogens or reaction with nucleophile. 1,2-Elimination is the principal product-forming process.

The effects of silicon substituents on carbonium ion formation have been investigated previously by several authors.[2-6] Apeloig and Stanger examined the solvolyses of 2-(trimethylsilyl)-2-adamantyl and 2-methyl-2-adamantyl *p*-nitrobenzoates in 80% acetone and 97% 2,2,2-trifluoroethanol solvents at 25 °C.[2d] They found that the solvolysis rates for the two compounds were very similar. On the basis of the results of ab initio calculations, they concluded that, relative to a methyl substituent, an α-trimethylsilyl substituent destabilizes the 2-adamantyl cation by several kcal/mol and retards the rate of solvolysis.

(1) Part of this research has already appeared as a communication to the editor: Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842.

(2) (a) Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 481. (b) Sommer, L. H.; Goldberg, G. M.; Dorfman, E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 1083. (c) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, A.; Schiavelli, M. D.; Hughey, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6852. (d) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

(3) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

(4) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(5) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153.

(6) Fessenden, R. J.; Seeler, K.; Dagani, M. *J. Org. Chem.* **1966**, *31*, 2483.

0022-3263/90/1955-0653$02.50/0