Thionyl Chloride–Pyridine Chemistry. II.[1] Synthesis and Reactions of *N*-α-Styrylpyridinium Salts

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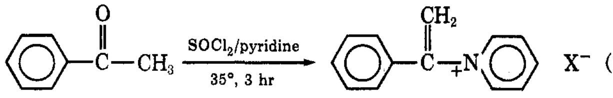
Acetophenone was readily converted to *N*-α-styrylpyridinium salts by treatment with thionyl chloride in pyridine. The synthesis, mechanism of formation, spectra, and some chemical reactions of these salts are discussed. The thermal reaction of **1b** led specifically to 1-phenylnaphthalene and pyridinium tetrafluoroborate. The mechanism of the latter transformation is also discussed.

The recent publication[2a] of the synthesis of *N*-α-styrylpyridinium iodide (**1c**) from styrene, iodonium nitrate, and pyridine prompts us to report on a new synthetic method for the production of **1** and related derivatives and on some of the chemical and spectral properties of **1**.

Results and Discussion

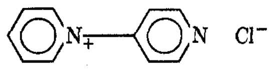
Synthesis.—When a solution of acetophenone and thionyl chloride in pyridine was prepared and maintained at room temperature or slightly above for a short time, the acetophenone was converted to *N*-α-styrylpyridinium chloride (**1a**) in very high yield (eq 1).



(1)

1a, X = Cl
b, X = BF_4
c, X = I

The integration of the ^{1}H nmr spectrum of the crude reaction product, after separation from the reaction solvent, showed that the relative integrals for phenyl: olefinic protons were 5:2; none of the original methyl protons nor those of an observed methyl-containing intermediate (*vide infra*) remained. The other observable product of this transformation was HCl; it was seen as pyridinium hydrochloride by ^{1}H nmr spectroscopy. Direct isolation of **1a** proved somewhat tedious because of its contamination by pyridinium hydrochloride and a small amount of **2**, a product known[2b] to arise from a slow side reaction between thionyl chloride and pyridine. However, it was quite easy to isolate the desired product as the tetrafluoroborate salt, **1b**. Subsequently, it was found that, if desired, **1a** could be readily regenerated using a chloride ion exchange resin.



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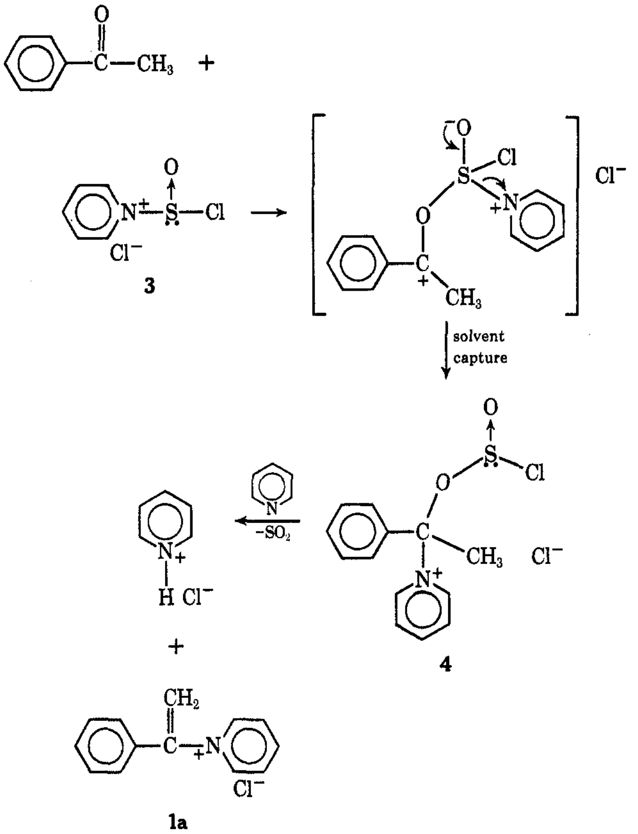
When the reaction was monitored by ^{1}H nmr spectroscopy, one could observe that as the methyl (δ 2.0) of acetophenone gradually disappeared a new methyl group at 2.4 appeared,[3] increased to some maximum value, and then also gradually disappeared, thus giving rise to the terminal olefinic carbon of **1a**. Since thionyl chloride has been reported[4,5] to lead to entirely different kinds of products with a similar ketone in the *absence* of pyridine, we suggest that **3** may be the reactive species in the present case and that one possible mechanistic description, therefore, could be that shown in Scheme I.

SCHEME I



The nmr observations are satisfied if one assumes that the last step in this scheme is the slowest. Attack on one of the protons of the methyl group of **4** by pyridine as SO_2 and Cl^- are eliminated might in fact be expected to be slow as a consequence of the degree of crowding around that carbon.

Interestingly, the capture of the carbonium ion center by solvent has to be very rapid compared to capture by a chloride ion, since the latter should lead to α-chlorostyrene, which was not observed.[6] Indeed, it might

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(1) Paper I: H. M. Relles, *J. Org. Chem.*, **37**, 3630 (1972).

(2) (a) U. E. Diner and J. W. Lown, *Chem. Commun.*, 333 (1970); (b) R. F. Evans, H. C. Brown, and H. C. van der Plas, *Org. Syn.*, **43**, 97 (1963).

(3) Not 1,1-dichloroethylbenzene (see Experimental Section, Table III).

(4) C. J. Ireland and J. S. Pizey, *J. Chem. Soc., Chem. Commun.*, 4 (1972).

(5) In fact, we have observed that acetophenone, in thionyl chloride, is rapidly converted to as yet unidentified products + HCl: H. M. Relles, unpublished results.

(6) However, preliminary results using quinoline as solvent indicate that *ca.* 15% of α-cholorostyrene is produced: H. M. Relles, unpublished results.

be expected that, as bonding begins between sulfur and the carbonyl oxygen, bonding between pyridine and the carbonyl carbon could simultaneously be taking place.

^{1}H Nmr Spectra.—The spectra of several α-substituted vinyltrimethylammonium salts have been reported.[7] Uniformly in D_2O, the proton cis to the positive nitrogen occurred further downfield (further from TMS) than the one trans to it, the difference (Δδ) being 22.4 ± 4.3 Hz. In the spectra of **1a** or **1b**, it seems appropriate to make the same relative assignments, especially since the Δδ is of the same order in D_2O: 20.3 ± 0.3 Hz. Of greater interest is the fact that this Δδ for the vinyl protons varies considerably with solvent (see Table I).

TABLE I

SOLVENT EFFECT ON THE DIFFERENCE IN CHEMICAL SHIFTS FOR THE OLEFINIC PROTONS OF 1

Solvent	Salt	Δδ, Hz[a]
$CDCl_3$[b]	1a	3.0
1:1 Pyridine–CH_2Cl_2[c]	1a	6.0
Pyridine[c]	1a	7.0
Pyridine	1b	11.0
CD_3COCD_3	1b	15.5
CH_3COCH_3	1b	16.0
CH_3CN	1a	16.0
CH_3COOH	1b	17.0
$(CH_3)_2NCHO$	1b	18.0
20% DCl in D_2O	1b	19.0
CH_3OH	1b	20.0
2:1 CD_3OD:D_2O	1b	20.0
D_2O	1a	20.0
D_2O	1b	20.5
H_2O	1a	20.5
H_2O	1b	21.5

[a] Measured at *ca.* 35°; accurate to ±0.5 Hz. [b] **1b** was completely insoluble in $CDCl_3$. [c] A reaction mixture, which also contained some $SOCl_2$ and pyridinium hydrochloride.

As can be seen, the Δδ for **1** is small in poorly ionizing media, such as deuteriochloroform, large, up to *ca.* 21 Hz, in ionizing media such as water and methanol, and intermediate for solvents of intermediate ionizing ability. Although the variation may result from the fluctuation of δ for only one of the olefinic protons, this cannot be stated with certainty, since all of the δ values for **1** vary somewhat with solvent. However, it is reasonable to assume that varying degrees of solvent separation of the ion pairs of **1** would lead to differences in the effective positive charge on nitrogen and that this charge would influence the δ values of the olefinic protons to different extents.

Mass Spectra.—It was not possible to obtain the mass spectra of **1a** and **1b** at low temperatures because of their lack of sufficient vapor pressure. On warming, however, it was possible, in the case of **1a**, to obtain a strong ion at *m/e* 182 corresponding to the cationic portion of the salt, although the spectrum was complicated by the presence of additional compounds. With **1b**, which presumably has even lower volatility and therefore had to be warmed even further, these additional compounds essentially dominated the spectrum and the *m/e* 182 peak was very weak. These spectra are tabulated in Table II.

TABLE II

MASS SPECTRA[a] OF **1a** AND **1b**

m/e	Relative intensities[b]: 1a (160°)[c]	Relative intensities[b]: 1b (210°)[c]
362	4	*d*
286	19	*d*
285	83	2
284	17	*d*
283	7	*d*
282	9	*d*
281	10	*d*
271	17	*d*
270	7	*d*
269	16	*d*
206	8	*d*
205	5	16
204	27	95
203	18	65
202	14	48
201	*d*	9
200	*d*	10
183	42	*d*
182	96	3
181	42	*d*
180	39	*d*
106	12	*d*
105	11	*d*
104	26	12
103	90	8
102	18	8
101	9	28
100	*d*	7
80	84	11
79	100	100
78	27	17
77	63	6
76	12	7
75	8	6

[a] Additional peaks found for **1a** were *m/e* (rel intensity) 169 (9), 168 (8), 167 (15), 154 (8), 153 (7), 152 (11), 63 (10), 53 (17), 52 (77), 51 (64), 50 (32), 39 (19), 38 (32), 37 (8), 36 (92), and 35 (15). Additional peaks for **1b** were *m/e* (rel intensity) 53 (9), 52 (69), 51 (38), 50 (24), 49 (36), and 39 (13). [b] Per cent of *m/e* 79 peak, the most intense peak in each system. [c] Probe temperature. [d] The peak was totally absent or present at less than 1% relative intensity.

Interestingly, the dominant peak in the spectrum of **1b** appeared at *m/e* 204. This corresponds to a dimer of the cationic portion of this salt minus the elements of two pyridinium ions (2 × 182 − 2 × 80) or, potentially, to a hydrocarbon having the empirical formula $C_{16}H_{12}$. Indeed, the spectrum of **1a** showed a minor peak at *m/e* 362, a major one at 285, and one at 204 which could correspond to a dimer minus two hydrogens, a dimer minus pyridine, and a dimer minus the elements of two pyridinium ions (as in **1b**), respectively. These observations are summarized schematically in Scheme II.

Cleavage of the bond between the pyridinium nitrogen and the olefinic carbon to which it is attached in the cation was also apparently significant, leading to the very strong peak for **1a** at *m/e* 103 ($C_8H_7^+$). Presumably the cluster observed around this latter *m/e* value arose from hydrogens gained or lost during this cleavage. Finally, peaks for $(C_5H_6N)^+$, $(C_5H_5N)^+$, $(C_6H_6)^+$, and $(C_6H_5)^+$ were very prominent as well.

Chemical Reactions.—A few reactions of **1** have been studied. These are described in some detail in the following sections.

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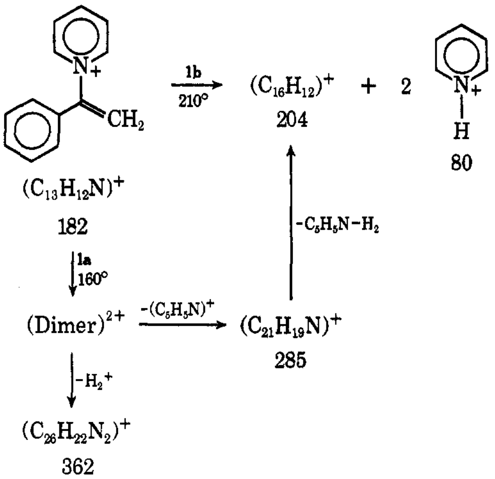
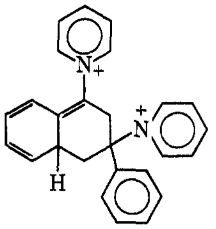
[7] M. Ohtsuru, K. Tori, J.-M. Lehn, and R. Seher, *J. Amer. Chem. Soc.*, **91**, 1187 (1969).

SCHEME II



Thermolysis.—The mass spectral results (above) suggested that it might be possible to heat the salt **1** and cause it to undergo a chemical transformation leading to a $C_{16}H_{12}$ hydrocarbon. Indeed, when **1b** was heated at 215° under reduced pressure in a sublimation apparatus or at 300° in a sealed tube there were formed just two observable products in high yield: pyridinium tetrafluoroborate and 1-phenylnaphthalene ($C_{16}H_{12}$); no 2-phenylnaphthalene or any other hydrocarbon product could be detected. The exclusive formation of 1-phenylnaphthalene places severe constraints on any mechanistic description of this reaction and one which would appear to be a likely possibility in the face of this constraint is given in Scheme III.

We believe that the six-membered ring formation depicted in the dimerization of **1** is best represented as a stepwise rather than a concerted reaction. If the reaction were a (4 + 2) concerted cyclization, one would surely expect to find some 2-phenylnaphthalene which would arise *via* **9**, the intermediate which would be highly favored (relative to **6**) on steric grounds. However, no 2-phenylnaphthalene was observed. On the other hand, if the cyclization occurred stepwise to give first the bisbenzyl radical cation **5**, the observed product identity would already have been established regardless of the eventual adverse steric effects which would be encountered in closing the ring to **6**. Formation of **7** from **6** simply requires a thermal heterolysis to give pyridine and a benzyl carbonium ion followed by the removal of a proton. The conversion of **7** to **8** can occur *via* protonation–deprotonation or by a thermally allowed 1,5-sigmatropic hydrogen shift. Either path should be energetically favorable, since a simultaneous rearomatization occurs.



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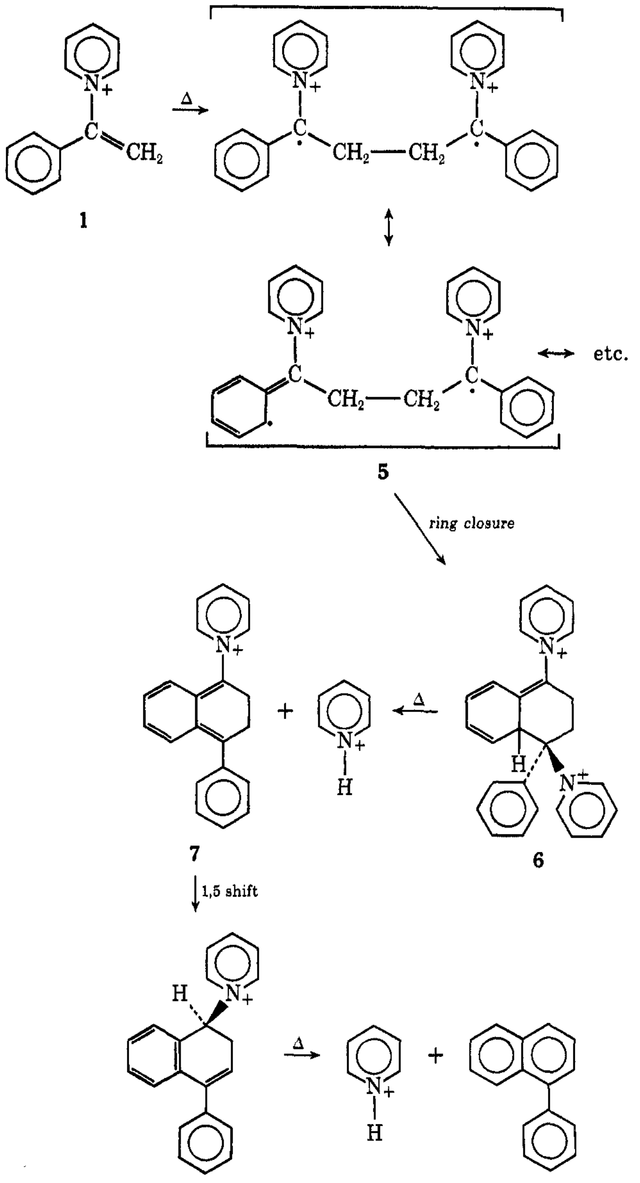
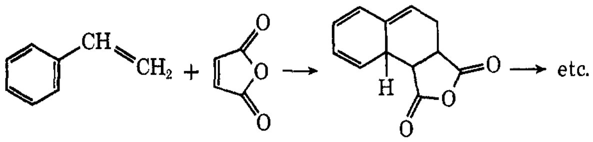
SCHEME III

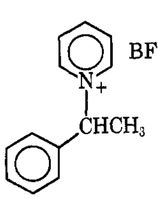


Also in favor of this mechanism is the report[8] that a cyclization reaction similar to that proposed in Scheme III occurs between styrene and maleic anhydride (eq 2).



(2)

Hydrogenation.—The hydrogenation of **1b** with Pd/C readily led to **10b** in very high yield. We have found no previous reports of the synthesis of this very simple molecule, presumably because those methods,



10b

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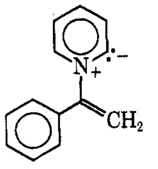
[8] R. R. DiLeone, U. S. Patent 3,410,876 (Nov 12, 1968).

which have been tried[9] involved the reaction of α-phenethyl halides with pyridine, a combination which resulted only in elimination of HX. Thus, not only does the isolation of **10b** serve as further evidence for the structure of its precursor, but it also completes a facile two-step sequence to a previously unknown type of pyridinium salt.

H–D Exchange.—When a solution of **1b** in D_2O was heated at 180°, hydrogen–deuterium exchange took place at only two carbons, the α-pyridinium carbons; no other protons in the molecule were exchanged. This we attribute to the inductive acidifying influence of the positive nitrogen on the α protons and suggest the intermediacy of a structure such as **11**, in accord with



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similar structures which have been invoked[10] under similar H–D exchange conditions for other pyridinium salts.

The extension of this thionyl chloride–pyridine reaction to other ketones and other carbonyl compounds is underway.

Experimental Section

All ^1H nmr spectra were recorded with a Varian Associates T-60 nmr spectrometer using tetramethylsilane as internal standard unless noted otherwise. All infrared spectra were taken as KBr pellets. Mass spectra were determined on a C. E. C. 21-104 analytical mass spectrometer at 70 eV.

Reagent grade acetophenone and thionyl chloride were redistilled before use.

***N*-α-Styrylpyridinium Tetrafluoroborate (1b).**—To a solution of 2.40 g (0.0200 mol) of acetophenone in 40 ml of pyridine was added 11.9 g (0.100 mol) of thionyl chloride all at once and this solution was stirred at 35° for 2.5 hr. The reaction mixture was then stirred vigorously with four separate 100-ml portions of hexane (to remove most of the excess pyridine and thionyl chloride), the hexane layers being carefully decanted each time. The viscous residue which remained was dissolved in 20 ml of water and filtered free of a trace amount of brown, amorphous material. This clear solution was then mixed with a solution prepared from 5.0 g (0.045 mol) of $NaBF_4$ and 10 ml of water. This resulted rapidly in the precipitation of a tan, crystalline material. Filtration and drying *in vacuo* (60°, 2 days) gave 4.71 g (88%) of **1b**: ^1H nmr (CD_3OD–D_2O, external TMS) δ 5.67 (d, J = 3 Hz, 1, olefinic proton cis to phenyl), 6.00 (d, J = 3 Hz, 1, olefinic proton cis to pyridinium ring), 6.90–7.40 (m, 5, phenyl), 7.63–8.23 (m, 2, β-pyridinium), 8.23–8.83 (m, 3, α- and γ-pyridinium).

A 4.30-g portion of this product was recrystallized from 20 ml of water (including a charcoal treatment). After filtering and drying *in vacuo* (60°), there was obtained 2.23 g of **1b** as colorless crystals: mp 118.5–119.5°; ^1H nmr (CD_3COCD_3) δ 6.10 (d, J = 3 Hz, 1, olefinic), 6.37 (d, J = 3 Hz, 1, olefinic), 7.10–7.67 (m, 5, phenyl), 8.15–8.62 (m, 2, β-pyridinium), 8.62–9.32 (m, 3, α- and γ-pyridinium); ir 1627 (s),[11] 1493 (m), 1488 (m), 1474 (s),[11] 1446 (m), 927 (m), 788 (m), 773 (s),[11] 723 (m), 697 (m), 681 (s), and a very strong, broad band at 1050 cm^{-1} for BF_4^-[12] dominated this spectrum; mass spectrum m/e (rel intensity) 182 (3), *N*-α-styrylpyridinium cationic part of salt **1b** (see complete mass spectrum and interpretation in Results and Discussion).

Anal. Calcd for $C_{13}H_{12}BF_4N$: C, 58.0; H, 4.5; N, 5.2. Found: C, 58.7; H, 4.5; N, 5.3.

***N*-α-Styrylpyridinium Chloride (1a).**—A column of 20 g of anion exchange resin Amberlite IRA-400-chloride form was prepared in water (interstitial volume 18 ml) and eluted with 100 ml of water; the silver nitrate test for chloride ion was negative throughout this elution.

A solution of 0.50 g of **1b** was prepared in 15 ml of water by warming to 40° and this solution was placed on top of the resin bed. Elution with water was allowed to proceed at *ca.* 1.7 ml/min as 5 ml-fractions were collected. Fractions 3–11 showed positive chloride ion tests while fractions 1, 2, 12, and 13 were negative. Fractions 3–11 were combined and water was removed at 60° on a rotary evaporator. The residue, 0.39 g of a tan solid, was dissolved in 3 ml of $CDCl_3$ and its ^1H nmr was recorded: δ 6.14–6.33 (m, 2, olefinic), 7.14–7.70 (m, 5, phenyl), 8.43–8.80 (m, 2, β-pyridinium), 8.80–9.17 (m, 1, γ-pyridinium), 9.17–9.42 (m, 2, α-pyridinium); the latter three regions were distinct and characteristic in appearance for pyridinium compounds.[13] A small amount of water also appeared at δ 3.50 as a broadened singlet.

Solvent removal from the above nmr solution and two recrystallizations of the hygroscopic product from CH_2Cl_2–Et_2O gave 0.10 g of **1a**: mp 163–164.8°; ir very similar to that of **1b** except for absence of the large band due to BF_4^-, 1619 (s),[11] 1490 (m), 1466 (s),[11] 1447 (m), 942 (s), 800 (s), 774 (s),[11] 723 (m), 690 (s), 682 cm^{-1} (s); mass spectrum m/e (rel intensity) 182 (98), *N*-α-styrylpyridinium cationic part of salt **1a** (see complete mass spectrum and interpretation in Results and Discussion); ^1H nmr (D_2O, external TMS) δ 6.12 (d, J = 3 Hz, 1, olefinic cis to phenyl), 6.45 (d, J = 3 Hz, 1, olefinic cis to pyridinium), 7.41–7.90 (m, 5, phenyl), 8.23–8.62 (m, 2, β-pyridinium), 8.82–9.25 (m, 3, α- and γ-pyridinium).

***N*-α-Phenethylpyridinium Tetrafluoroborate (10b).**—A solution of 2.00 g (0.0074 mol) of **1b** in 50 ml of anhydrous methanol was stirred with 0.1 g of 10% Pd/C at 30.0 psi pressure of hydrogen. After 2.5 hr, the pressure had dropped to 29.3 psi and then remained constant. The catalyst was removed by filtration and the solvent was evaporated. The residue, 2.02 g, which slowly crystallized on standing and was shown to be *ca.* 85% **10b** by ^1H nmr (*vide infra*), was triturated with 4:1 hexane–chloroform at 40° to remove 0.07 g of acetophenone (identified by ^1H nmr and vpc). The residual solid was dissolved in water and this solution, after it was extracted with hexane and 2.0 g of excess $NaBF_4$ was added, was stored overnight at *ca.* 0°. The long, needle-like crystals which separated were filtered, washed with ether, and dried *in vacuo*. In this way 0.90 g of **10b** was obtained: mp 68–85° dec; ^1H nmr (CD_3OD) δ 2.17 (d, J = 7 Hz, 3, methyl), 6.25 (q, J = 7 Hz, 1, methine), 7.27–7.76 (m, 5, phenyl), 7.90–8.40 (m, 2, β-pyridinium), 8.40–8.88 (m, 1, γ-pyridinium), 8.88–9.30 (m, 2, α-pyridinium); ir 1628 (s),[14] 1495 (s),[14] 1480 (s),[14] 1450 (m),[14] 1050 (vs) (tetrafluoroborate ion),[12] 768 (m), 730 (m), 698 (m), 680 cm^{-1} (s); mass spectrum m/e (rel intensity) 79 (100), pyridine$^+$, 105 (82), α-phenethyl$^+$, complex spectrum; no M^+ for cationic portion of **10b**.

Anal. Calcd for $C_{13}H_{14}BF_4N$: C, 57.6; H, 5.2; N, 5.2. Found: C, 56.9; H, 5.2; N, 5.1.

***N*-α-Styrylpyridinium Chloride (1a). Experiment for Mechanistic Information.**—Six grams (0.05 mol) of thionyl chloride was added to a solution of 1.20 g (0.0100 mol) of acetophenone in 20 ml of pyridine. This system was then stirred at 35° for 3 hr. During this time, the progress of the reaction was monitored by frequent recording of the ^1H nmr spectrum of a sample which had been removed and stored also at 35°. These results are given in Table III.

Stirring the reaction mixture vigorously with four separate 50 ml-portions of hexane, each hexane layer being carefully decanted, led to a viscous liquid residue.

A.—A sample of this residue gave the following ^1H nmr spectrum ($CDCl_3$): δ 6.18 (d, J = 3 Hz, 1, olefinic cis to phenyl), 6.34 (d, J = 3 Hz, 1, olefinic cis to pyridinium), 7.18–7.73 (m, 5, phenyl), 8.12–9.48 (m, 16, very complex multiplet containing at least the pyridinium protons of **1a** and pyridinium hydrochlo-

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(9) S. Hanai, *J. Chem. Soc. Jap.*, **63**, 352, 356 (1942); J. W. Baker, *J. Chem. Soc.*, 2631 (1932).

(10) J. A. Zoltewicz and L. S. Helmick, *J. Amer. Chem. Soc.*, **92**, 7547 (1970), and references cited therein.

(11) Correspond to strongest peaks in ir spectrum of *N*-vinylpyridinium ion: 1632, 1480, and 758 cm^{-1}, respectively. See I. N. Duling and C. C. Price, *ibid.*, **84**, 578 (1962).

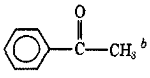
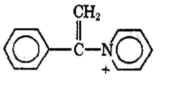
(12) Sadtler Inorganic Grating Spectral Catalog, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1967, Spectra Y 777 K and Y 955 K.

(13) See, for example, ref 1.

(14) Similar to the spectra of **1a** and **1b**.

TABLE III

^{1}H NMR OBSERVATIONS DURING THE REACTION OF ACETOPHENONE WITH THIONYL CHLORIDE AND PYRIDINE

Reaction time, min	Approximate relative molar amounts[a]			
	 [b]	Unknown[c] CH_3 compd	 Cl^- [d]	HCl[e]
0	100	0	0	0
42	12.6	31.2	56.2	*f*
49	7.1	27.3	65.6	66
63	3.4	16.6	80.0	80
72	3.1	11.9	85.0	86
87	2.1	6.6	91.3	*f*
102	0.4	3.9	95.7	*f*
120	0.0	2.0	98.0	*f*
174	0.0	0.0	100.0	102

[a] ±5%. [b] Determined from methyl integral ÷ 3. Chemical shift (*external TMS*) for methyl of acetophenone in this reaction mixture was δ 2.0. [c] Determined from integral of peak (at δ 2.4) ÷ 3. Assumed to be a new kind of methyl peak from its chemical shift and sharp singlet nature; shown not to be 1,1-dichloroethylbenzene by admixture and observing a new methyl singlet at δ 2.1. [d] Determined from olefinic integral ÷ 2; this occurred between δ 5.55 and 5.83. The rest of the spectrum of this molecule was obscured by solvent. [e] As pyridine hydrochloride. Determined from the acidic proton singlet at δ 18.0 after subtracting for the amount of water known to have been present in the pyridine. [f] The value was not determined.

ride, and probably those of some pyridine not extracted by the hexane treatment). An additional minor α-pyridinium type of multiplet (δ 9.80–10.02), probably due to some 2[3], was also present. (A control experiment indicated that 2 might be produced to the extent of about 0.0006 mol under these reaction conditions.)

B.—When the nmr solution of A was shaken with water, no solutes were left in the $CDCl_3$ phase; all had been transferred to the water phase. ^{1}H nmr (H_2O) showed integrals for phenyl: vinyl (5:2).

C.—When some of the residue was dissolved in water, potentiometrically titrated to pH 6.9, and then extracted several times with ether to remove pyridine, the residual aqueous phase displayed a ^{1}H nmr spectrum in complete accord with **1a**.

Thermal Reaction of 1b. Experiment I.—A 1.00-g sample of **1b** was heated in a sublimation apparatus at 215° for 17.5 hr at *ca.* 0.10 mm pressure. The residue, 0.73 g, was shown by nmr to be unchanged **1b**. The sublimate, 0.23 g, was a pale yellow, oily solid which proved to be only partially soluble in water, only partially soluble in chloroform, but completely soluble in acetone. Its ^{1}H nmr spectrum (CD_3COCD_3, external TMS) showed no vinyl protons and was in accord with pyridinium tetrafluoroborate plus a $(C_8H_6)_x$ aromatic hydrocarbon: δ 6.4 [broad band, $W_{1/2}$ = 20 Hz, 0.91 (after subtracting for HDO of solvent), NH^+], 7.68–8.08 (m, 2.0, β-pyridinium), 8.26–8.83 (m, 3.0, α- and γ-pyridinium), and 6.89–7.68 (m, 5.8, aromatic).

Experiment II.—A 0.20-g sample of **1b** was heated in a sealed tube at 300° for 3.25 hr. The products were mixed with 1.5 ml of D_2O and 1.5 ml of $CDCl_3$, the layers were separated, and the ^{1}H nmr spectrum of each was recorded: D_2O phase, 86:14 mole ratio of pyridinium tetrafluoroborate: **1b**; $CDCl_3$ phase, only an aromatic multiplet essentially identical with that found for an authentic sample of 1-phenylnaphthalene ($C_{16}H_{12}$).

The contents of the $CDCl_3$ phase were examined further: vpc (6 ft 10% SE-30, 220°; retention time given in minutes) reaction product, 4.05; 1-phenylnaphthalene, 4.05; 2-phenylnaphthalene, 5.60; tlc on silica gel (1:9 benzene–hexane, R_f given) reaction product, 0.48; 1-phenylnaphthalene, 0.48; 2-phenylnaphthalene, 0.52; tlc on alumina (25:75 benzene–hexane) reaction product, 0.76; 1-phenylnaphthalene, 0.76; 2-phenylnaphthalene, 0.71. Trace components were also present (R_f 0.00–0.02) in the $CDCl_3$ phase.

Experiment III.—A 2.0-g sample of **1b** was heated at 300° for 4.5 hr in a sealed tube. The contents of the tube were stirred with 50 ml of hexane and extracted twice with 50-ml portions of water. The hexane solution was dried ($MgSO_4$), filtered, and freed of all solvent *in vacuo*, giving 0.41 g of a tan oil: ^{1}H nmr ($CDCl_3$) δ 7.33–8.13 (m, aromatic, superimposable on the spectrum of authentic 1-phenylnaphthalene), 7.08–7.33 (m, aromatic, minor portion of the spectrum, <5% of aromatic area, due to some other minor component); vpc again showed 1-phenylnaphthalene and indicated that, at the most, only 1% of the isolated material could be 2-phenylnaphthalene. The product was passed through a short alumina column in 1:3 benzene–hexane to remove some color and then analyzed further by its mass spectrum: *m/e* (rel intensity) 204 (100) M^+, 203 (66.7) $(M - 1)^+$, 202 (50.0) $(M - 2)^+$. Relative intensities found for the 204, 203, 202 sequence for authentic 1-phenylnaphthalene were 100:66.4:49.8; for authentic 2-phenylnaphthalene, these values were 100:17.0:30.2.

Deuterium Incorporation by 1b in D_2O.—A solution of 0.10 g of **1b** in 1.0 g of D_2O was heated in a sealed nmr tube at 180° for 3 days. After this time, the ^{1}H nmr spectrum indicated that H–D exchange had occurred essentially exclusively and nearly completely at the α-pyridinium carbons: δ 6.10 (d, J = 3 Hz, 0.98, olefinic), 6.43 (d, J = 3 Hz, 0.98, olefinic), 7.42–7.93 (m, 5.00, phenyl), 8.23–8.57 (d, slightly broadened, J = 7.5 Hz, 1.93, β-pyridinium protons, coupled only to γ proton), 8.75–9.20 (t, slightly distorted, $J \cong 7.5$ Hz, 1.16, γ-pyridinium protons + residual α-pyridinium protons); the HDO peak of solvent had increased, as expected, by the corresponding amount. This α-exchanged pyridinium ring gave virtually the identical ^{1}H nmr spectrum as found for the ring protons of 2,6-dimethylpyridinium hydrochloride.[15]

Registry No.—**1a**, 38434-89-8; **1b**, 579-54-4; **10b**, 38434-91-2; thionyl chloride, 7719-09-7; pyridine, 110-86-1; acetophenone, 98-86-2.

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(15) H. M. Relles, unpublished results.