After removal of most of the solvent at reduced pressure, the residue was distilled to give a mixture of **9** and **10**: 6.48 g (36.2 mmol, 75%); bp 55–70 °C (1 torr). Since the ^{1}H NMR spectrum showed that this material still contained a few percent of **7**, a portion (3.50 g) was redistilled to give a purer sample of **9** and **10** (1.74 g): bp 50–55 °C (0.5–0.7 torr); ^{1}H NMR (360 MHz, $CDCl_3$) δ ~1.11 (c, H_A of **9** and **10**), 1.130 and 1.136 (s and s, CH_3s of **9**), 1.141 (s, CH_3s of **10**), 2.28 (s, OH of **9** and **10**), 2.69 (d, J_{AC} = 4.0 Hz, H_C of **10**), 2.97 (d, J_{AB} = 7.6 Hz, H_B of **9**), 3.67 and 3.75 (each a d of d, J_{AD} = 6.2 Hz, J_{AE} = 8.2 Hz, J_{DE} = 11.6 Hz, H_D and H_E of **9**), 3.55 and ~3.72 (each a d of d, J_{AD} = 8.0 Hz, J_{AE} = 13.8 Hz (?), J_{DE} = 11.4 Hz, H_D and H_E of **10**); mass spectrum, *m/z* (M^+ too weak for high-resolution mass determination) 146.9787 and 148.9803 ($M^+ - CH_2OH$), calcd for C_5H_8Br 146.9799 and 148.9779. The composition of this mixture was determined from the relative areas of the ^{1}H NMR absorptions of H_B of **9** and H_C of **10** to be 74% **9** and 26% **10** (these figures are probably accurate to ±2%).

Reaction of 8 and Zinc: Preparation of 9 and 10. Zinc powder (J.T. Baker, 40 g, 612 mmol) was added in small portions over a 2-h period to a stirred and heated (47 °C bath) solution of **7** (8.0 g, 31.0 mmol) in glacial acetic acid (250 mL) that was under an argon atmosphere. The mixture was maintained in the 47 °C bath and stirred for 42 h. Then the mixture was cooled to ambient temperature and filtered, and the solids were washed with diethyl ether. Most of the diethyl ether and some of the acetic acid were removed from the filtrate at reduced pressure. Water was added to the remainder, and aqueous sodium hydroxide solution (6 M) was added until the solution was strongly alkaline. The solution was extracted with four 50-mL portions of diethyl ether, and the combined extracts were washed with water (25 mL) and dried (Na_2SO_4). The ether was removed at reduced pressure and the residue distilled to give a mixture of **9** and **10**: 2.59 g (14.5 mmol, 47%); bp 30–60 °C (1 torr). A ^{1}H NMR spectrum ($CDCl_3$) of this material and also of material collected from the gas chromatograph (85 °C) showed the composition to be 80–85% **9** and 10–15% **10** (the determination of composition was less accurate than in the experiment above since 60-MHz ^{1}H NMR spectra were used).

Formation and Hydrolysis of a Metalated Grignard Reagent from 9 and 10. A diethyl ether solution of methylmagnesium bromide (Ventron Corp., 4.76 M, 3.52 mL, 16.8 mmol) was added dropwise over a few minutes to a stirred solution of **9** and **10** (74% **9** and 26% **10**, 1.50 g, 8.4 mmol) in diethyl ether (60 mL, dried over sodium wire) under an argon atmosphere. The solution was allowed to stir for 1 h, and then magnesium (Johnson Matthey Chemicals Limited Puratronic, 0.204 g, 8.4 mmol) and ethylene bromide (~0.1 g) were added. After the resulting mixture had been stirred for 3 h, most of the magnesium had disappeared. A portion of the solution (20 mL) was transferred to another flask and D_2O (1 mL) was added. Then the ether solution was decanted from the solid and filtered through a plug of glass wool and the filtrate was dried (Na_2SO_4). The remainder of the reaction was refluxed for 16 h. Then one-half of the solution was hydrolyzed as above with D_2O and the other one-half in the same manner but with H_2O. Most of the ether was removed from each portion under reduced pressure. GC analysis (50 °C) of each residue showed only one significant peak past that due to the solvent.

The material resulting from H_2O hydrolysis was collected and found to be **11**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.13 (d of d, 1, $J_{AC} \simeq$ 4.9 Hz, $J_{BC} \simeq$ 4.9 Hz, H_C), 0.48 (d of d, 1, J_{AB} = 8.5 Hz, J_{BC} = 4.3 Hz, H_B), 0.91 (m, 1, H_A), 1.08 and 1.12 (s and s, 3 each, CH_3s), 1.40 (s, 1, OH), 3.52 and 3.69 (each a d of d, 1 each, J_{AD} = 6.7 Hz, J_{AE} = 11.3 Hz, H_D and H_E).

The two samples resulting from D_2O hydroysis were collected and found to exhibit virtually identical ^{1}H NMR spectra (360 MHz, $CDCl_3$) that showed them to be mixtures principally of **12** and **13**. Most of the absorption of H_B was a doublet (J_{AB} = 8.3 Hz) due to **12** and for H_C also principally a doublet (J_{AC} = 5.2 Hz) due to **13**. The relative areas of the H_B and H_C absorptions were 74:26 for the first sample and 70:30 for the sample taken after the reaction mixture had been refluxed (the relative areas are probably accurate to ±2 units). The H_B absorption of **12** and the H_C absorption of **13** were shifted upfield (~0.015 ppm) from those of **11**, so that the peak at lowest field both in the H_B multiplet and in the H_C multiplet of **11** was visible.[25] From the areas of these downfield peaks, it can be estimated that **11** was about 6% of both of the **11–13** mixtures obtained from D_2O hydrolysis and therefore contributed 6 units to both the H_B and H_C absorptions. If this contribution is substracted from the area ratios above, then the relative compositions of **12** and **13** are 77:23 for the first sample and 73:27 for the second sample.

In another experiment similar to that above, a sample of **9** and **10** was used that was approximately 85–90% **9** and 10–15% **10**. After the reaction mixture had been allowed to stir at ambient temperature for 4 h, most of the magnesium had disappeared. One portion of the solution was removed and hydrolyzed with D_2O; the remainder was stirred for an additional 16 h and then hydrolyzed with D_2O. GC analysis of each sample showed only one significant peak past that due to the solvent. ^{1}H NMR spectra (200 MHz, $CDCl_3$) of the collected samples were virtually identical. Determining the relative amounts of **12** and **13** was somewhat less accurate than for the reaction above since more **11** was present and the spectra were taken at 200 MHz rather than at 360 MHz. However, the relative amounts of **12** and **13** were about 85:15.

Acknowledgment. We are grateful to the National Science Foundation for the support of this research and for aiding in the purchase of the NMR spectrometers and the mass spectrometer. We thank Dr. Robert D. Minard for obtaining the mass spectra and Alan J. Freyer for obtaining the high-field NMR spectra.

Registry No. **6**, 556-82-1; **7**, 17219-12-4; **8**, 2425-45-8; **9**, 86597-75-3; **10**, 87050-58-6; **11**, 930-50-7; **12**, 87050-59-7; **13**, 87050-60-0; 3-methyl-2-butenoic acid, 541-47-9; bromoform, 75-25-2.

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A Convenient Synthesis of *N*-Vinylpyridinium Perchlorate and a Study of *N*-Vinylpyridinium Cations as Michael Reaction Acceptors

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Received June 6, 1983

The title compound is easily prepared from 1-(2-bromoethyl)pyridinium bromide and sodium hydroxide. 1-Vinylpyridinium and 1-vinyl-2,4,6-triphenylpyridinium cations add N, S, and C nucleophiles in Michael-type reactions.

Several *N*-vinyl heterocycles are of considerable commercial importance as monomers for polymerization, e.g., *N*-vinylimidazoles,[1] *N*-vinylcarbazoles, and *N*-vinylpyrrolidones[2] are in widespread use. Surprisingly, despite

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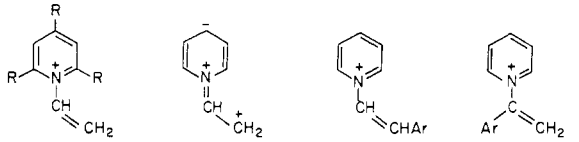
their potential practical importance and theoretical interest, little work has been done on *N*-vinylpyridinium cations.

There are two early references to the simple 1-vinylpyridinium cation (**1**): Coppola[3] first reported in 1885 the



1 R=H
2 R=Ph

3 **4** **5**

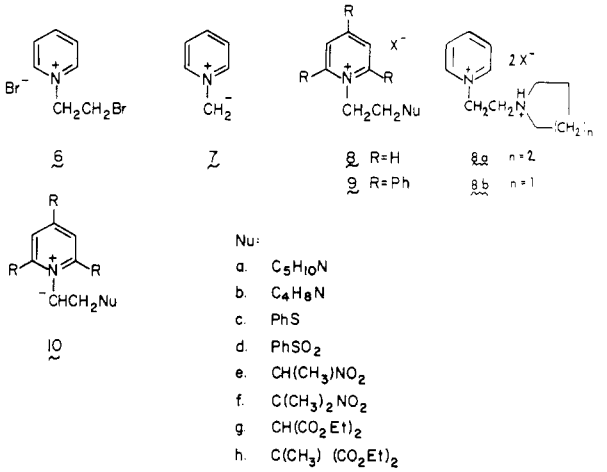
platinichloride that he obtained from 1-(2-iodoethyl)-pyridinium iodide and silver oxide. In 1913, Schmidt[4] prepared cation **1** from 1-(2-bromoethyl)pyridinium bromide and silver oxide. Then, in 1962, Duling and Price[5] improved the method (overall yield 26% from pyridine) and proved the structure by UV and IR spectroscopy and by hydrogenation to 1-ethylpiperidine and briefly examined the reactivity of **1**. It was concluded that the rate of addition of thiosulfate ion was not significantly greater than that of trimethylvinylammonium salts and hence that resonance interaction of type **3** was not very important. However tritium–hydrogen-exchange experiments on 1-allylpyridinium cations were interpreted as indicating interaction between a pyridinium ring and a *N*-vinyl group.

Duling and Price[5] showed that *N*-vinylpyridinium perchlorate polymerized readily with ionizing radiation or free-radical initiation to give polyelectrolyte polymers. Surprisingly, 1-vinylpyridinium copolymerized poorly or not at all with negative e monomers such as styrene or vinyl acetate but comparatively readily with positive ones such as methyl methacrylate or acrylonitrile.

Cationic quaternary polyelectrolytes are of considerable importance,[6] and the work of Duling and Price has been frequently cited;[7] however, the only further experimental work on these compounds has been copolymerization studies with styrene[8] and an examination of the mass spectra.[9] *N*-(Substituted-vinyl)pyridinium cations are much more common, particularly arylvinyl derivatives. *N*-(β-Arylvinyl)pyridinium salts of **4** have been extensively investigated by Kröhnke,[10] and *N*-(α-arylvinyl)pyridinium salts of **5** are available by the method of Relles.[11] We have previously studied 2,4,6-trisubstituted 1-vinylpyridinium salts which can be prepared from pyrylium salts with (β-chloroalkyl)amines[12] or advantageously from (β-hydroxyalkyl)amines followed by conversion of the 1-(2-hydroxyalkyl)pyridinium successively into the 2-chloroalkyl and vinyl derivatives.[13]

A considerable barrier to the study of the fundamental system **1** has been its inaccessibility, preparation necessitating the use of Ag_2O. By an application of our procedure previously reported for the 2,4,6-trisubstituted analogues, we now describe a convenient route to **1** in good yield together with a study of its chemistry, and in particular, concrete evidence for considerable mutual interaction between the pyridinium ring and the vinyl group in both **1** and the triphenyl analogue **2**.

1-(2-Bromoethyl)pyridinium bromide (**6**) is readily



6 **7** **8** R=H, **9** R=Ph; **8a** n=2, **8b** n=1

Nu:
a. $C_5H_{10}N$
b. C_4H_8N
c. PhS
d. $PhSO_2$
e. $CH(CH_3)NO_2$
f. $C(CH_3)_2NO_2$
g. $CH(CO_2Et)_2$
h. $C(CH_3)(CO_2Et)_2$

10

available from pyridine and 1,2-dibromoethane in 56% yield.[5] We now find that treatment of **6** with 10 M sodium hydroxide at −10 °C (reaction at 0 °C forms polymeric materials) gives the 1-vinyl cation **1**, which can be isolated as the perchlorate (65%) or as the tetrafluoroborate (53%).

Conjugation of Vinyl Group and Pyridinium Ring. It is well-known[14] that the pyridinium ring positive charge stabilizes an adjunct carbanion center in pyridinium ylides of type **7**. Whereas such ylides have previously been prepared by deprotonation,[14] it is expected that addition of a nucleophile by Michael addition to an *N*-vinylpyridinium cation (**1** → **8**) should be facilitated by stabilization of the intermediate **10**. This possibility has previously been discussed by Duling and Price[5] with no firm conclusion (see above). However, we now find that 1-vinylpyridinium cation (**1**) and its triphenyl analogue **2** *both* readily add a variety of N, S, and C nucleophiles in Michael-type reactions.

Reactions with Nucleophiles. Addition of the secondary amines piperidine and pyrrolidine to 1-vinylpyridinium salt (**1**) in methanol led to rapid polymerization. However, if acetic acid was added to the methanolic solution of **1** prior to the amine addition, the adducts **8a** and **8b** could be isolated as bis(perchlorate) salts (33–34%).

Piperidine and pyrrolidine added readily, with no complications from polymer formation, to 1-vinyl-2,4,6-triphenylpyridinium cation to give the expected products **9a** and **9b** in good yields. Primary alkyl primary amines such as *n*-propyl-, *n*-butyl-, and benzylamine behaved quite differently: ANRORC[15] reaction occurred to form the corresponding 1-*n*-alkyl- or benzylpyridinium salts. Isopropylamine gave a complex mixture, and *tert*-butylamine did not react.[16]

Aromatic amines such as aniline and *N*-methylaniline did not react with the triphenyl cation **2** at 20 °C or on

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heating in ethanol or tetrahydrofuran. However, when **2** was refluxed with *N*-methylaniline, cyclization of the vinyl group to an α-phenyl ring took place to give the pyrido[2,1-*a*]isoindolium tetrafluoroborate (**14**) (Scheme I). This type of compound (cf. **19**) has been previously synthesized[17] by photodehydrohalogenation of 1-benzyl-2-halopyridinium salts (**17**) or 1-(*o*-halobenzyl)pyridinium salts (**18**). The structure of **14** is supported by ^1H and ^{13}C NMR and MS, where the base peak at m/e 333 probably corresponds to the pyrido[2,1-*a*]isoindole radical cation **15**[17] and the peak at m/e 322 (97.5%) to the benzo[*a*]-quinolizinium cation **16**.[18] The formation of **14** from **2** probably involves an intermediate addition product **11** that is in equilibrium with **12**, ring closure to **13**, and rearomatization to form product **14**.

Sulfur nucleophiles also reacted readily. Thus, thiophenol with the 1-vinylpyridinium salts of **1** and **2** gave the expected adducts **8c** and **9c**. Benzenesulfinic acid reacted only slowly with **1** (80% of **1** recovered after 40 h). By contrast, benzenesulfinic acid reacted rapidly with **2** to give the adduct **9d**. However, relatively easy subsequent nucleophilic substitution of **9d** also formed 2,4,6-triphenylpyridine and 1,2-bis(phenylsulfonyl)ethane as deduced from the ^1H NMR spectrum of the crude product (e.g., singlet at δ 3.4 due to CH_2CH_2).

The anions derived from nitroethane, 2-nitropropane, and diethyl malonate each afforded with 1-vinylpyridinium cation (**1**) the expected adducts: **8e**, **8f**, and **8g**.

1-Vinyl-2,4,6-triphenylpyridinium tetrafluoroborate **2**·BF_4^- gave adducts with 2-nitropropane and diethyl methylmalonate anions. However, only 2,4,6-triphenyl-1*H*-pyridinium tetrafluoroborate could be isolated from the reaction of **2** with nitroethane and diethyl malonate anions; evidently further reaction had occurred on the initially formed adducts.

Spectra. Duling and Price[5] observed that although 1-vinylpyridinium salt of **1** absorbed more strongly (log ϵ = 3.92) than 1-(2-bromoethyl)pyridinium bromide (log ϵ = 3.66), there was no change in the absorption maximum (λ_{max} 258 nm). The spectra of 1-vinyl-**2** and 1-ethyl-2,4,6-triphenylpyridinium tetrafluoroborate are similar, both as regards position and intensity of the absorption maximum: λ_{max} 310 nm (log ϵ = 4.48) and λ_{max} 302 nm (log ϵ = 4.45), respectively (in MeOH). This all indicates little additional conjugation in the *N*-vinyl compound **2** consistent with twisting of the vinyl group out of the pyridinium ring plane.

The ^1H NMR spectra for the adducts (Tables I and II) display the expected patterns: the pyridinium C-3 and C-5 protons resonated as singlets in adducts **9** and as multiplets in adducts **8**. The multiplicity of the aliphatic region ranges from triplets ($\sim A_2X_2$) to multiplets (ABXY). A shielding effect due to the α-phenyl rings is observed on the Me groups of **9f** and **9h**: in **9f**, Me appeared at δ 1.1, while in **8f** at δ 1.7.

Conclusions. The Michael reactions described above do not necessarily indicate much interaction of type **3**, but they do support the importance of stabilization in the intermediate ylides of type **10**. This is consistent with the similar behavior of the unsubstituted **1** and substituted series **2**.

Experimental Section

Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Spectra were recorded with the

Table I. ^1H NMR Spectra[a] of 1-Alkylpyridinium Salts (8)

compd	solvent	2,6-H (2 H)			4-H (1 H, m), δ	3,5-H (2 H, m), δ	N^+-CH_2 (2 H)			β-CH_2 (2 H)			other H, δ (H, M)
		δ	M	J			δ	M	J	δ	M	J	
8a	D_2O[b]	8.8	dd	6, 1	8.5	8.0	4.9	t[c]		3.6	t[c]		3.4 (4 H, m), 1.6 (6 H, m)
8b	D_2O[b]	9.0	d	6	8.7	8.2	5.1	t	7.5	3.9	t	7.5	3.5 (4 H, m), 2.1 (4 H, m)
8c	$CDCl_3$-TFA	8.8	d	6	8.5	8.1	4.8	t	6	3.55	t	6	7.3 (5 H, s)
8e	TFA	9.0	d	6	8.7	8.2	4.9	t	7	2.8	t	7	4.9[d] (1 H, m), 1.7 (3 H, d, J = 7)
8f	TFA	8.9	m		8.6	8.2	4.8	t[c]		2.7	t[c]		1.7 (6 H, s)
8g	$CDCl_3$-TFA	8.8	d	6	8.5	8.1	4.8	t[c]		2.6	m		4.2 (4 H, q, J = 7), 3.65 (1 H, t, J = 7), 1.3 (6 H, t, J = 7)

[a] Chemical shift (δ) in ppm; coupling constant (J) in hertz; M = multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet). Compounds 8a and 8b are bis(perchlorate) salts. [b] Me_4Si as external standard. [c] Distorted signal. [d] Obscured by signals in the same region.

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Table II. ^{1}H NMR Spectra[a] of 1-Alkyl-2,4,6-triphenylpyridinium Salts (9)

compd	solvent	3,5-H (2 H, s), δ	rest of aromatic-H (15 H, m), δ	N^+-CH_2 (2 H) δ	N^+-CH_2 (2 H) M	N^+-CH_2 (2 H) J	β-CH_2 δ	β-CH_2 M	β-CH_2 J	other H, δ (H, M)
9a	$CDCl_3$	b	8.0–7.4	4.65	t	7	2.3	t	7	1.8 (4 H, m), 1.2 (6 H, m)
9b	$CDCl_3$	b	8.0–7.3[c]	4.7	t	7	2.5	t	7	1.9 (4 H, m), 1.5 (4 H, m)
9c	$CDCl_3$	b	8.0–7.3[c]	4.6	t[d]		2.9	t[d]		7.1 (3 H, m), 6.8 (2 H, m)
9d	$CDCl_3$–TFA	8.0	7.7	4.9	t[d]		3.2	t[d]		7.5 (5 H, m)
9f	$CDCl_3$–TFA	8.1	7.7	4.8–4.4	m		2.3–1.9	m		1.1 (6 H, s)
9h	$CDCl_3$–TFA	8.0	7.7	4.8–4.4	m		2.2–1.8	m		3.97 (2 H, q, J = 7), 3.95 (2 H, q, J = 7), 1.1 (6 H, t, J = 7), 0.8 (3 H, s)

[a] Chemical shift (δ) in ppm; coupling constant (J) in hertz; M = multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). [b] Obscured by the other aromatic signals. [c] See also other H. [d] Distorted signal.

following instruments: for IR a Perkin-Elmer Model 283B grating spectrophotometer (solutions in bromoform) and UV spectra with a Pye-Unicam 8-200 spectrophotometer; for ^{1}H NMR either a Varian Model A-60A, a Varian Model EM 360L, or a JEOL Model JNM-PMX 60-MHz spectrometer, Me_4Si was the internal standard; for ^{13}C NMR a JEOL Model JNM-FX 100 spectrometer operating at 25.05 MHz, and for mass spectra an AEI MS 30 spectrometer. Elemental analyses were carried out by Atlantic Microlab. Inc., Atlanta, GA. All reactions with perchlorate salts were carried out in a fumehood and with appropriate safety precautions.

The following compounds were prepared by literature methods: 1-(2-bromoethyl)pyridinium bromide (56%), mp 122–124 °C (lit.[5] mp 126–128 °C), 1-vinyl-2,4,6-triphenylpyridinium tetrafluoroborate hemihydrate (80%), mp 143–146 °C (lit.[13] mp 143–146 °C), and 1-ethyl-2,4,6-triphenylpyridinium tetrafluoroborate (85%), mp 163–164 °C (lit.[19] mp 164–165 °C).

1-Vinylpyridinium Perchlorate (1·ClO_4^-). Aqueous sodium hydroxide (10 M, 5.7 mL) and 1-(2-bromoethyl)pyridinium bromide (15 g, 56.6 mmol) in ethanol–methanol (2:1, 375 mL) were kept at −10 °C for 12 h. After addition of hydrobromic acid (48%, 1 mL), the solvent was removed at 25 °C (20 mmHg). Sodium perchlorate (7.0 g, 57.0 mmol) in water (20 mL) was added to the residue in EtOH (100 mL). On cooling, the product separated. Crystallization from acetone–ether yielded the perchlorate (7.5 g, 65%), which formed needles (from ethanol): mp 94–95 °C (lit.[5] mp 95.5–97.5 °C); ^{1}H NMR (TFA) δ 9.0–8.3 (3 H, m), 8.1 (2 H, m), 7.4 (1 H, dd, J = 8, J = 16 Hz), 5.7–6.3 (2 H, m); ^{13}C NMR (D_2O) δ 116.3 (t, $=CH_2$), 128.6 (d, β-CH), 137.4 (d, $=CH$), 142.05 (d, γ-CH), 147.5 (d, α-CH). 1-Vinylpyridinium tetrafluoroborate was obtained after addition of fluoroboric acid (48%, 15 mL) to an ethanol–methanol solution of the crude bromide. The solution was refluxed for 15 min. On cooling the tetrafluoroborate crystallized as needles (53%), mp 70–72 °C (lit.[5] mp 75.5–76.5 °C).

1-(2-Piperidinioethyl)pyridinium Bis(perchlorate) (8a). Piperidine (0.22 g, 2.6 mmol) was added dropwise to 1-vinylpyridinium perchlorate (0.3 g, 1.5 mmol) and acetic acid (0.17 g, 2.9 mmol) in methanol (5 mL). After standing at 20 °C for 14 h, the solvent was removed at 25 °C (20 mmHg). The residue was extracted with methylene chloride (3 × 10 mL), and the methylene chloride solution was evaporated at 25 °C (20 mmHg) to $^1/_3$ volume. 70% Aqueous perchloric acid (0.2 mL) was added, followed by ether (10 mL). The bis(perchlorate) separated (0.195 g, 34%) and formed needles (from acetone–ether): mp 260–263 °C; IR 1633 (m), 1490 (s), 1060 (s, b) cm^{-1}. Anal. Calcd for $C_{12}H_{20}Cl_2N_2O_8$: C, 36.82; H, 5.15; N, 7.16. Found: C, 36.86; H, 5.12; N, 7.10.

1-(2-Pyrrolidinioethyl)pyridinium bis(perchlorate) (8b) (0.18 g, 33%) was prepared similarly, microcrystals (from ethanol): mp 165–167 °C; IR 1638 (m), 1490 (s), 1060 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{18}Cl_2N_2O_8$: C, 35.01; H, 4.77; N, 7.43. Found: C, 34.94; H, 4.81; N, 7.42.

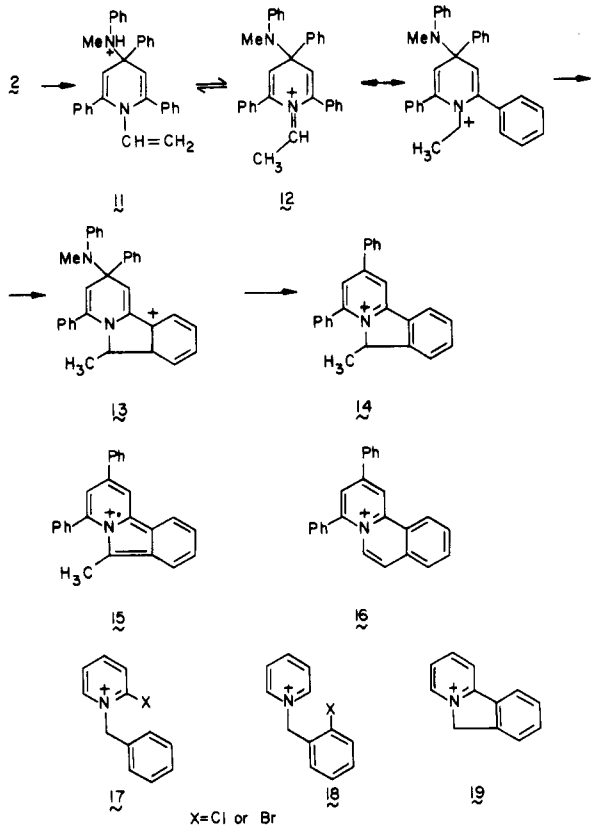
1-(2-Piperidinoethyl)-2,4,6-triphenylpyridinium Tetrafluoroborate (9a). 1-Vinyl-2,4,6-triphenylpyridinium tetrafluoroborate (0.3 g, 0.7 mmol) and piperidine (2 mL) in methylene chloride (3 mL) were stirred for 16 h at 20 °C. The solid formed was filtered and washed with water and ether to give the salt 11a (0.250 g, 72%), which formed needles (from ethanol): mp 166–167 °C; IR 1625 (s), 1600 (w), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{30}H_{31}BF_4N_2$: C, 71.17; H, 6.13; N, 5.53. Found: C, 70.96; H, 6.20; N, 5.47.

1-(2-Pyrrolidinoethyl)-2,4,6-triphenylpyridinium tetrafluoroborate (9b) (0.24 g, 70%) was prepared similarly (except that methylene chloride was not used and the excess amine was evaporated at 25 °C (20 mmHg), needles (from ethanol): mp 172–175 °C; IR 1625 (s), 1600 (m), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{29}H_{29}BF_4N_2$: C, 70.76; H, 5.90; N, 5.69. Found: C, 70.63; H, 5.96; N, 5.63.

1-(*n*-Propyl)-2,4,6-triphenylpyridinium Tetrafluoroborate. 1-Vinyl-2,4,6-triphenylpyridinium tetrafluoroborate (0.225 g, 0.5 mmol) and *n*-propylamine (1.5 mL) were stirred at 20 °C for 1 h (solid formation was observed from the first minute). The solid was filtered off and washed with water and ether to give the salt

(19) Katritzky, A. R.; Liso, G.; Lunt, E.; Patel, R. C.; Thind, S. S.; Zia, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 849.

Scheme I



(0.15 g, 66%), needles (from ethanol): mp 132–134 °C (lit.[19] mp 136 °C).

The following were similarly prepared: **1-(*n*-butyl)-2,4,6-triphenylpyridinium tetrafluoroborate** (53%), needles (from ethanol), mp 195–197 °C (lit.[19] mp 201–202 °C) and **1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate** (12%), needles (from ethanol–ether), mp 192–194 °C (lit.[19] mp 196 °C).

6-Methyl-2,4-diphenylpyrido[2,1-*a*]isoindolium Tetrafluoroborate (14). A solution of 1-vinylpyridinium tetrafluoroborate (0.5 g, 1.2 mmol) and *N*-methylaniline (3 mL) was refluxed for 17 h. After standing at 25 °C, ether (10 mL) was added to give the salt **14** (0.42 g, 86%), microcrystals (from acetone–ether): mp 290–295 °C; IR 1630 (s), 1600 (m), 1050 (s, b) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 9.1 (1 H, d, J = 1.9 Hz), 8.1 (1 H, m), 8.0–7.7 (14 H, m), 6.2 (1 H, q, J = 6.9 Hz), 1.3 (3 H, d, J = 6.9 Hz); ^{13}C NMR (Me_2SO-d_6) δ 155.7 (s), 153.6 (s), 152.6 (s), 144.7 (s), 134.0 (s), 133.4 (d), 130.0–128.45, 123.7 (d), 123.1 (d), 116.0 (d), 68.2 (d), 17.6 (q); MS, (relative intensity) m/e 335 (3.6), 334 (25.5), 333 (100.0), 332 (97.5), 331 (19.8), 329 (33.7). Anal. Calcd for $C_{25}H_{20}BF_4N$: C, 71.29; H, 4.75; N, 3.33. Found: C, 70.98; H, 5.03; N, 3.28.

1-[2-(Phenylthio)ethyl]pyridinium Perchlorate (8c). Sodium methoxide [sodium (0.034 g, 1.5 mmol) in methanol (3 mL)] was added to a stirred suspension of 1-vinylpyridinium perchlorate (0.3 g, 1.5 mmol) and thiophenol (0.5 mL) at 50 °C. The solution was refluxed for 16 h. The solvent removed at 25 °C (20 mmHg), the residue dissolved in acetone, and perchloric acid (70%, 0.2 mL) added. The inorganic salts were filtered off. Precipitation with ether (10 mL) at 0 °C gave the adduct phenylthioethane (0.25 g, 55%) as needles (from ethanol–ether): mp 78–79 °C; IR 1632 (s), 1580 (s), 1060 (s, b) cm^{-1}. Anal. Calcd for $C_{13}H_{14}ClNO_4S$: C, 49.44; H, 4.44; N, 4.44. Found: C, 49.44; H, 4.47; N, 4.41.

1-[2-(Phenylthio)ethyl]-2,4,6-triphenylpyridinium Tetrafluoroborate (9c). To a stirred solution of **2**·BF_4^- (0.25 g, 0.58 mmol), and thiophenol (1 mL) in 2-propanol (2 mL) at 20 °C was added potassium carbonate (0.1 g, 0.75 mmol). The stirring was continued for 2 h. Methylene chloride (10 mL) was added, and the inorganic salts were extracted into H_2O (2 × 20 mL). The organic layer was acidified with HBF_4 (48%), extracted into H_2O (1 × 20 mL), and dried over $MgSO_4$. The solvent was removed at 30 °C (20 mmHg) and the residue triturated with ether, to give the salt (0.255 g, 70%), needles (from ethanol): mp 150–154 °C; IR 1622 (s), 1600 (w), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{31}H_{26}BF_4NS$: C, 70.08; H, 4.90; N, 2.64; S, 6.02. Found: C, 70.02; H, 4.94; N, 2.62; S, 5.99.

1-[2-(Phenylsulfonyl)ethyl]-2,4,6-triphenylpyridinium Tetrafluoroborate (9d). To a solution of benzenesulfinic acid (0.25 g, 1.8 mmol) in water (10 mL) at 90 °C was added 1-vinyl-2,4,6-triphenylpyridinium tetrafluoroborate (0.25 g, 0.6 mmol). The heterogeneous solution was heated and stirred for 20 h. The solution was extracted into methylene chloride (3 × 15 mL), the organic extracts were evaporated at 25 mmHg, and the residue was triturated with ether (15 mL) containing fluoroboric acid (48%, 0.2 mL). Several recrystallizations from ethanol of the solid obtained gave the adduct (80 mg, 24%) as needles: mp 147–149 °C; IR 1625 (s), 1600 (w), 1315 (s, SO_2), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{31}H_{26}BF_4NO_2S$: C, 66.09; H, 4.62; N, 2.49; S, 5.68. Found: C, 65.96; H, 4.66; N, 2.46; S, 5.73.

1-(3-Nitrobutyl)pyridinium perchlorate (8e) (0.19 g, 46%) was prepared as adduct **8c** (from nitroethane (1.5 mL) and a reaction time of 2 h), microcrystals (from ethanol): mp 78–79 °C; IR 1638 (m), 1550 (s, NO_2), 1060 (s, b) cm^{-1}. Anal. Calcd for $C_9H_{13}ClN_2O_6$: C, 38.50; H, 4.63; N, 9.98. Found: C, 38.39; H, 4.67; N, 9.91.

1-(3-Methyl-3-nitrobutyl)pyridinium perchlorate (8f) (0.26 g, 60%) was prepared similarly (reaction time was 16 h), needles (from ethanol–ether): mp 109–111 °C; IR 1630 (m), 1533 (s, NO_2), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{10}H_{15}ClN_2O_6$: C, 40.75; H, 5.09; N, 9.50. Found: C, 40.84; H, 5.15; N, 9.48.

1-(3-Methyl-3-nitrobutyl)-2,4,6-triphenylpyridinium Tetrafluoroborate (9f). Sodium ethoxide [sodium (0.01 g, 0.4 mmol) in ethanol (3 mL)] was added to a stirred solution of **2**·BF_4^- (0.2 g, 0.5 mmol) in 2-nitropropane (2 mL). The reaction mixture was refluxed for 16 h. The separated solid was filtered off and washed with water and ether, the solvent from the filtrate was evaporated to dryness at 40 °C (20 mmHg), and the residue was triturated with water to give further product, total yield 0.19 g (81%), yellow needles (from ethanol): mp 248–249 °C; IR 1620 (s), 1600 (m), 1540 (s, NO_2), 1350 (s, NO_2), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{28}H_{27}BF_4N_2O_2$: C, 65.91; H, 5.30; N, 5.49. Found: C, 65.97; H, 5.33; N, 5.47.

1-[3,3-Bis(ethoxycarbonyl)propyl]pyridinium perchlorate (8g) (0.16 g, 30%) was prepared similarly as **8f**, viscous oil: IR 1720 (s), 1630 (s), 1060 (s, b) cm^{-1}. Attempts to crystallise the adduct failed.

1-[3,3-Bis(ethoxycarbonyl)butyl]-2,4,6-triphenylpyridinium Tetrafluoroborate (9h). Sodium ethoxide [sodium (0.016 g, 0.7 mmol) in ethanol (5 mL)] was added to a stirred solution of 1-vinylpyridinium (**2**, 0.3 g, 0.7 mmol) and ethyl methylmalonate (1.5 mL). The reaction mixture was refluxed for 16 h. On cooling to 25 °C, fluoroboric acid (48%, 0.5 mL) was added. The solvent was concentrated at 40 °C (20 mmHg), and the residue was dissolved in methylene chloride (20 mL) and extracted with water (3 × 10 mL). The methylene chloride solution was dried ($MgSO_4$) and concentrated at 30 °C (20 mmHg). Trituration of the residue with ether gave the salt **9h** (0.17 g, 41%), needles (from ethanol): mp 141–143 °C; IR 1728 (s), 1622 (s), 1600 (m), 1050 (s, b) cm^{-1}. Anal. Calcd for $C_{33}H_{34}BF_4NO_4$: C, 66.57; H, 5.72; N, 2.35. Found: C, 66.43; H, 5.62; N, 2.41.

Acknowledgment. We thank the Departamento de Educacion, Universidades e Investigacion del Pais Vasco (Spain) for a grant to O.R.

Registry No. **1**·ClO_4^-, 49727-10-8; **2**-BF_4^-, 80561-34-8; **8a**·2ClO_4^-, 87012-87-1; **8b**·2ClO_4^-, 87012-89-3; **8c**·ClO_4^-, 87012-91-7; **8e**·ClO_4^-, 87012-93-9; **8f**·ClO_4^-, 87012-95-1; **8g**·ClO_4^-, 87012-97-3; **9a**·BF_4^-, 87012-99-5; **9b**·BF_4^-, 87013-01-2; **9c**·BF_4^-, 87013-03-4; **9d**·BF_4^-, 87013-05-6; **9f**·BF_4^-, 87013-07-8; **9h**·BF_4^-, 87013-08-9; **14**·BF_4^-, 87013-10-3; 1-(2-bromoethyl)pyridinium bromide, 10129-45-0; piperidine, 110-89-4; pyrrolidine, 123-75-1; *n*-propylamine, 107-10-8; *n*-butylamine, 109-73-9; benzylamine, 100-46-9; *N*-methylaniline, 100-61-8; thiophenol, 108-98-5; benzenesulfinic acid, 618-41-7; nitroethane, 79-24-3; 2-nitropropane, 79-46-9; ethyl methylmalonate, 6186-89-6; 1-*n*-propyl-2,4,6-triphenylpyridinium tetrafluoroborate, 74805-31-5; 1-*n*-butyl-2,4,6-triphenylpyridinium tetrafluoroborate, 66310-04-1; 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate, 66310-10-9.