spectrum calculated for $C_{34}H_{48}O_8$ m/e 584.3346 (M - 162, aglycon - H_2O) found 584.3339.

Avermectin B_{1a} Aglycon (8) and Monosaccharide (7). A mixture of 46.2 mL of H_2O, 46.2 mL of concentrated H_2SO_4, and 170 mL of THF was added over 30 min to a solution of **3** (22.2 g, 0.025 mol) in 200 mL of THF stirred in an ice bath. After the addition was completed, the reaction mixture was left at 18 °C for 24 h under a nitrogen atmosphere. Analysis by TLC and HPLC showed after 2 h about 60% of **3** and 40% of **7** and after 16 h about 60% of **7** and 40% of **8**. It also showed that the product mixture was essentially unchanged after 22 h. The dark brown reaction mixture was cooled in an ice bath followed by addition of 300 mL of ice–water. The usual workup with CH_2Cl_2 (4 × 200 mL) and washing with aqueous $NaHCO_3$ and water gave, after drying and concentration in vacuo, 17.7 g of dark brown foam. This was dissolved in 15 mL of EtOAc, filtered through silica gel (50 g) using 500 mL of EtOAc, and concentrated to give 17.2 g of light foam. Further purification was achieved on a Waters Prep LC/System 500 on two Prep PAK-500/silica cartridges (CH_2Cl_2–EtOAc, 7:3; total volume 8 L), giving 7.5 g (50%) of **8** as pale yellow foam. A 100-mg sample of this was purified for analysis by PLC (CH_2Cl_2–THF–EtOH, 89.7:10:0.3) and gave **8** as a white glass (quantitative recovery): $[\alpha]_D$ +65.5° (c 0.595, $CHCl_3$); NMR and mass spectral data (supplementary material); high-resolution mass spectrum calcd m/e 584.3346, found 584.3281; UV (MeOH) 245 nm (ϵ 28 200).

The second reaction product **7** was obtained pure as 4.67 g (25%) white foam; NMR and MS (supplementary material); UV (MeOH) 245 nm (ϵ 27 200); high resolution mass spectrum calculated for $C_{34}H_{46}O_7$ (M-162:aglycon-H_2O) 566.3240. Found: 566.3249.

23-*O*-Methylavermectin B_{2a} Aglycon (9) and 23-*epi*-*O*-Methylavermectin B_{2a} Aglycon (10). A solution of 1.26 g (1.45 mmol) of **3** and 10 g (53 mmol) of *p*-toluenesulfonic acid monohydrate in 200 mL of MeOH was kept at 18 °C for 22 h. Then it was poured into 1000 mL of ether, washed twice with ice-cold aqueous $NaHCO_3$ and water, dried, and concentrated in vacuo to 1.1 g of light foam. The crude product (1.0 g) was subjected to a preliminary purification by column chromatography (30 g of silica gel; CH_2Cl_2–EtOAc, 7:3) to give 700 mg of crude aglycon mixture as white foam, which shows one spot on TLC (CH_2Cl_2–THF–EtOH, 90:9.5:0.5). Analysis by HPLC (Corasil, 37–50 μm; column i.d. 0.2 cm, length 61 cm; CH_2Cl_2–EtOAc, 9:1) shows three components at retention times of 4.0 (**8**), 7.0 (**9**), and 9.5 (**10**) min. A 200-mg aliquot of this mixture was separated by preparative HPLC (Whatman Partisil M9, 10/50 column; CH_2Cl_2–EtOAc, 9:1) to give 15 mg of **8**, 80 mg of **9**, and 63 mg of **10** as crystalline residues.

8: mp 144–155 °C dec; HPLC (Corasil A, CH_2Cl_2–EtOAc) single peak, retention time 4.0 min; UV (MeOH) 243 nm (ϵ 26 400); H NMR and mass spectra were identical with those of authentic **8**.

9: mp 140–144 °C dec; HPLC, single peak, retention time 7.0 min; UV (MeOH) 245 nm (ϵ 29 100); ^1H and ^{13}C NMR, and mass spectral data (supplementary material); high-resolution mass spectrum calcd m/e 616.3610, found 616.3603.

10: mp 153–156 °C dec; HPLC single peak, retention time 9.5 min; UV (MeOH) 243 nm (ϵ 28 950); ^1H and ^{13}C-NMR and mass spectral data (supplementary material) high-resolution mass spectrum calcd m/e 616.3607, found 616.3661.

Acknowledgment. We are grateful to Drs. B. M. Trost and A. W. Douglas for stimulating discussions. We thank H. Flynn and J. L. Smith for obtaining spectral data. The generous supply of the avermectins by I. Putter and his staff is appreciated.

Registry No. **1**, 65195-53-1; **2**, 65195-57-5; **3**, 65195-55-3; **4**, 71828-13-2; **5**, 71828-15-4; **6**, 71837-28-0; **7**, 71831-09-9; **8**, 71828-14-3; **9**, 80010-05-5; **10**, 80041-02-7; **11**, 71861-20-6.

Supplementary Material Available: Tables of ^1H NMR (compounds **4–11**), ^{13}C NMR (compounds **4**, **5**, **8–10**), and mass spectral (compounds **1–11**) and analytical (compounds **5–11**) data (8 pages). Ordering information is given on any current masthead page.

Pyridinium Ylides Derived from Pyryliums and Amines and a Novel Rearrangement of 1-Vinyl-1,2-dihydropyridines

Alan R. Katritzky,* Amornsri Chermprapai, Ranjan C. Patel, and Alberto Tarraga-Tomas

School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, England, and the Department of Chemistry, University of Florida, Gainesville, Florida 32611

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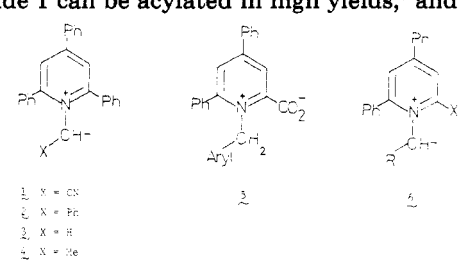
1-Benzyl-2,4-diphenylpyridiniums with benzaldehydes give oxazolopyridines which are dehydrated to 1-styryl derivatives. On pyrolysis the 1-styryl-1,2-dihydropyridine **21a** gave 2,4,6-triphenylpyridine and *m*-chlorostyrene by a ring-enlargement–ring-contraction mechanism: this is a general reaction of 1-vinyl-1,2-dihydropyridines.

Nitrogen ylides are well-known:[1] pyridinium ylides have been considerably utilized in synthesis by Kroehnke[2] and others.[3] The present paper records work which is part of our attempt to utilize synthetically pyridinium ylides derived from amines and pyrylium salts. We have found that ylide **1** can be acylated in high yields,[4] and that betaines of type **5** undergo Kroehnke reaction with *p*-nitroso *N*,*N*-dimethylaniline to afford benzaldehyde nitrones.[5] However, attempts to utilize the ylides derived from 1-benzyl-, 1-methyl-, and 1-ethyl-2,4,6-triphenylpyridinium salts (**2–4**) failed: although the corresponding pyridinium tetrafluoroborates and more soluble trifluoromethane sulfonates on treatment with lithium diisopropylamide in THF at −80 °C gave deep colors, only starting materials were obtained after the addition of various electrophiles.[6]



* To whom correspondence should be addressed at the University of Florida.

(1) Johnson, A. W. "Ylid Chemistry"; Academic Press: New York, 1966.
(2) Kroehnke, F. *Ber. Dtsch. Chem. Ges.* **1935**, *68*, 1177 (and many subsequent papers). Cf.: *Angew, Chem., Int. Ed. Engl.* **1963**, *2*, 225.
(3) Ratts, K. W.; Howe, R. K.; Phillips, W. G. *J. Am. Chem. Soc.* **1969**, *91*, 6115.
(4) Katritzky, A. R.; Burgess, K.; Yeung, W. K.; Patel, R. C., unpublished work.
(5) Katritzky, A. R.; Dabbas, N.; Patel, R. C., unpublished work.

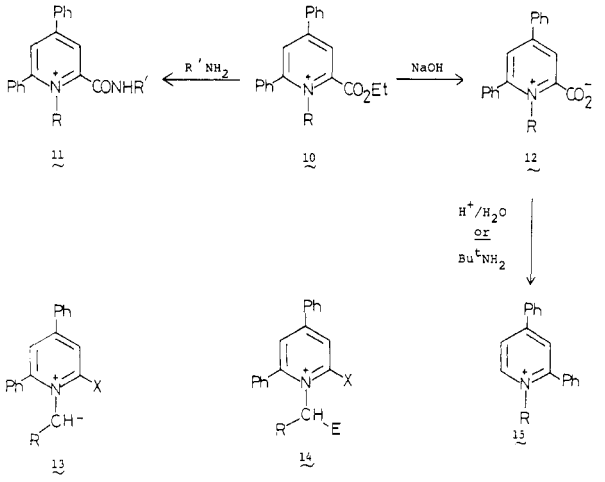
0022-3263/82/1947-0492$01.25/0

Table I. Preparation of 1-Substituted 2-(Ethoxycarbonyl)-4,6-diphenylpyridinium Tetrafluoroborate (10),[a] 1-Substituted 4,6-diphenylpyridinium-2-carboxylate Betaines (12), and 1-Substituted 2,4-Diphenylpyridinium Tetrafluoroborate (15)[b]

		2-ethoxycarbonyl (10)			2-CO_2^- betaines (12)		2-unsubstituted (15)	
series	1-substituent	reaction time, h	yield, %	mp,[c] °C (form[e])	yield, %	mp,[c] °C (form[e])	yield, %	mp,[c] °C (form[e])
a	$PhCH_2$	0.5	93	172-174 (N)	85	131-132 (N)	90	120-122 (Pr)
b	4-$ClPhCH_2$	1	80	150-152 (N)	75	114-115 dec (Pl)	92	122-124 (Pr)
c	2-$ClPhCH_2$	1	82	165-166 (Pr)	80	110-112 dec (Pl)	87	128-130 (Pr)
d	4-CH_3PhCH_2	1	72	127-129 (N)	80	121-123 (Pl)	75	156-158 (Pr)
e	$CH_3(CH_2)_2CH_2$	0.5	83	130-132 (Pr)	87	97-99 (Pr)	93	85-87 (Pl)
f	$(CH_3)_2CH$	12	46	126-128 (Pr)	87	120-122 (Pl)	88	162-164 (Pl)
g	CH_3CH_2	8	50	98-100 (Pr)	83	103-105 dec (Pl)	82	151-153 (Pl)
h	C_6H_{11}	3	63	153-155 (Pl)			95	166-168 (Pr)
i	$PhCH_2CH_2$	2	85	147-150 (N)			80	120-122 (Pl)
j	4-$ClPhCH_2CH_2$	2	81	188-190 (Pl)				

[a] Reactions carried out in CH_2Cl_2 at 20 °C. [b] Reactions in absolute EtOH. [c] For crystal form designated. [d] Recrystallized from absolute EtOH. Satisfactory analyses were reported for all new compounds. [e] Crystal form: N, needles; Pr, prisms; Pl, plates.

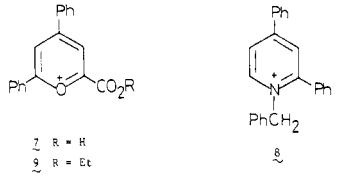
Scheme I



[a] For designations of R in **10**, **12**, and **15**, see Table I.

At the time, this failure was considered to be due to steric hindrance by the α,α'-diphenyl groups and/or to insufficient stability of the ylide. We have now studied other ylides of type **6** in which X was selected to facilitate ylide formation.

2-Carboxy-4,6-diphenylpyrylium (**7**) was prepared from benzalacetophenone with pyruvic acid and trityl tetrafluoroborate by following ref 7; we also made **9** from ethyl benzalpyruvate and acetophenone, but yields were low. Reaction of **7** with benzylamine either gave recovered starting material or decarboxylated pyridinium **8**.



Chalcone, ethyl pyruvate, and BF_3·Et_2O gave the 2-(ethoxycarbonyl)pyrylium **9** (33%) which reacted readily with a series of primary amines to give the corresponding pyridiniums **10** in good yields (Table I) and with ammonia to give 2-(ethoxycarbonyl)-4,6-diphenylpyridine. Heating

Table II. Preparation of 1-Substituted 2-Carboxamido-4,6-diphenylpyridinium Tetrafluoroborate (11)[a]

compd	1-substituent (R)	R'	reaction time, h	yield, %	mp, °C (form[b,d])
11a	$PhCH_2$	n-Bu	5	74	108-110 (Pr)
11b	n-Bu	n-Bu	4	91	90-91 (Pr)
11c	i-Pr	n-Bu	5	81	170-172 (Pr)
11d	$PhCH_2$	CH_3	6	92	135-137 (N)
11e	n-Bu	CH_3	6	92	125-127 (Pr)
11f	CH_3	CH_3	3[c]	80	161-164 (N)

[a] Reactions carried out in CH_2Cl_2 at 20 °C. [b] Recrystallized from absolute ethanol. [c] Prepared directly from 2-(ethoxycarbonyl)-4,6-diphenylpyrylium tetrafluoroborate. Satisfactory analyses were obtained for all new compounds. [d] See footnote *e* of Table I.

1-benzyl-2-(ethoxycarbonyl)-4,6-diphenylpyridinium tetrafluoroborate (**10a**) in pyridine gave 1-benzylpyridinium tetrafluoroborate (see Scheme I) and established the nucleofugicity of 2-(ethoxycarbonyl)-4,6-diphenylpyridine.

Reactions of 2-(ethoxycarbonyl)pyridiniums with excess methylamine or *n*-butylamine in CH_2Cl_2 gave the corresponding 2-(substituted carboxamido)pyridiniums **11** (Table II): the dimethyl derivative **11** (R = R' = Me) was made directly from pyrylium **9** with $MeNH_2$. 2-(Ethoxycarbonyl)-4,6-diphenylpyridine was converted by *n*-butylamine in EtOH into 2-(*n*-butylcarbamoyl)-4,6-diphenyl-pyridine. Reaction of the 2-(ethoxycarbonyl)-pyridinium **10** with NaOH affords the 1-substituted pyridinium-2-carboxylates **12** (Table I).

The structures of all these compounds were supported by their spectra. Thus, the ν(C=O) occurred characteristically for the esters **10**, for the amides **11**, and for the betaines **12** near 1740, 1670, and 1650 cm^{-1}, respectively. Salient features of the ^1H NMR spectra are given in Table III (supplementary material). The pyridinium C-3 and C-5 protons absorbed as doublets (J = 2 Hz) above 8 ppm: the lower field doublet was assigned to the C-3 proton because of the electron-withdrawing effect of the 2-substituent. The rest of the aromatic signals were usually a multiplet in the region 6.8–7.8 ppm. The N–CH protons absorbed in the region 3.6–6.2, highest for isopropyl CH and lowest for benzyl CH_2. The CO_2Et quartet (4.2–4.7 ppm) and triplet (1.2–1.8 ppm) signals were normal.

Numerous attempts were made[6] to react the amides **11**, esters **10**, and betaines **12** with LiN-*i*-Pr_2 to afford ylides **13** and subsequently with electrophiles to give new pyridinium derivatives **14**. Although sometimes partially

(6) We do not intend to publish details of this work which can be found in: Chermprapai, A. Ph.D. Thesis, University of East Anglia, 1981.
(7) Dimroth, J.; Vogel, K.; Krafft, W. *Chem. Ber.* **1968**, *101*, 2215.
(8) Kroehnke, F.; Meyer-Delius, M. *Chem. Ber.* **1951**, *84*, 411.
(9) Katritzky, A. R.; Rubio-Teresa, O., unpublished work.

Table V. Preparation of Oxazolo[3,2-*a*]pyridine (17) and Pyridinium Ethanols 18

compd	Ar	Ar′	anion	method	yield, %	mp, °C (form[b])
17a	Ph	3-NO_2Ph		C	85	128-130 (Pl)
17b	Ph	3-ClPh		C	78	175-177 (Pl)
18a	Ph	3-NO_2Ph	ClO_4	D	70	75-77 (Pr)
18b	Ph	3-NO_2Ph	BF_4	D	68	113-115 (Pl)
18c	Ph	3-ClPh	BF_4	D	64	205-207 (Pl)
18d	Ph	2-ClPh	BF_4	D	57	210-212 (Pr)
18e	2-ClPh	3-NO_2Ph	ClO_4	D	65	185-187 (Pr)

[a] Recrystallized from absolute ethanol. [b] See footnote *e* of Table I.

Table VI. ^{1}H NMR[a] Spectral Data of Oxazolo[3,2-*a*]pyridine (17) and Pyridinium Ethanols 18

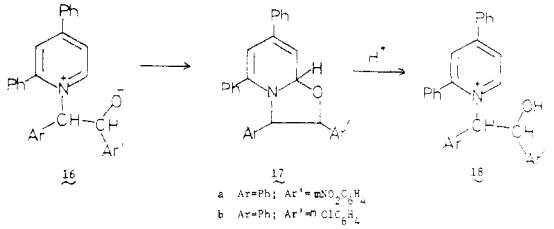
				chemical shift							
				pyridinium protons					1-substituent		
									1′-CH (1 H, d)		2′-CH (1 H, d)
compd	Ar	Ar′	anion	C(6) H (1 H, d, $J_{6,5}$ = 6 Hz), δ	C(5) H (1 H, dd, $J_{5,6}$ = 6, $J_{5,3}$ = 2 Hz), δ	C(3) H (1 H, d, $J_{3,5}$ = 2 Hz), δ	aromatic H (m) δ	aromatic H (m) no.	δ	J, Hz	δ	J, Hz
17a	Ph	3-NO_2Ph	*b*	9.56	8.24	7.98	7.05-7.92	19	5.88	8	6.06	8
17b	Ph	3-ClPh	*b*	9.25	8.25	7.95	7.06-7.93	19	5.74	8	6.03	8
18a	Ph	3-NO_2Ph	ClO_4	9.52	8.31	8.02	7.02-7.95	19	5.75	6	6.02	6
18b	Ph	3-NO_2Ph	BF_4	9.28	8.24	8.03	7.10-7.93	19	5.70	6	6.03	6
18c	Ph	3-ClPh	BF_4	9.20	8.21	7.91	7.03-7.85	19	5.71	7	6.02	7
18d	Ph	2-ClPh	BF_4	9.18	8.32	7.98	7.11-7.83	19	5.72	7	5.98	7
18e	2-ClPh	3-NO_2Ph	ClO_4	9.29	8.30	8.12	7.05-8.10	18	5.74	6	5.94	6

[a] In $CDCl_3$ with Me_4Si as an internal standard. [b] TFA was added. Spectra are similar to those of pyridinium ethanols.

successful, complex mixtures were always formed, and the approach was abandoned.

1-Substituted 2,4-Diphenylpyridiniums. The betaines **12** on being refluxed with $HClO_4$ or HBF_4 in EtOH gave the required salts **15** (method A), but they were difficult to purify. A better method was to heat the esters **10** with ethanolic *tert*-butylamine[10] (method B): this gave the products **15** in good yields (Table I). The compounds were characterized by their NMR spectra (Table IV, supplementary material), in particular the C-6 H doublet (J = 6 Hz) in the region 8.6–9.2 ppm indicative of decarboxylation. The C-5 H signal (8.1–8.4 ppm) split into a double doublet ($J_{5,6}$ = 6 Hz, $J_{5,3}$ = 2 Hz) due to coupling with the C-6 and C-3 H. The N–C**H**(H) absorption moved upfield (4.3–5.8 ppm); cf. N–C**H**(H) in the corresponding 2-CO_2Et products (**10**) at 4.6–6.2 ppm.

The 1-benzylpyridiniums **15a** and **15b** reacted with benzaldehydes in alcoholic NaOH at 0 °C to give initially oxazolo[3,2-*a*]pyridines **17** by cyclization of the zwitterionic



16 **17** **18**

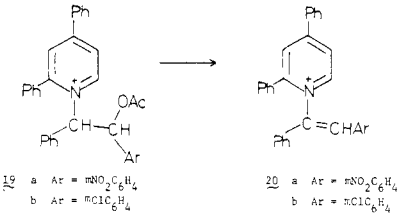
a Ar=Ph; Ar′=m$NO_2C_6H_4$
b Ar=Ph; Ar′=mClC_6H_4

intermediate **16** (method C). With acid, **17** gave the pyridinium ethanols **18** (method D). 1-Alkyl-2,4-diphenylpyridinium salts **15** e–i did not react under the above conditions with *m*-nitrobenzaldehyde.

The intermediates **17** were isolated for Ar = Ph and Ar′ = *m*-NO_2Ph and *m*-ClPh as yellow low-melting solids which showed in the IR strong dihydropyridine bands at 1595 cm^{-1}. These compounds were insoluble in $CDCl_3$ and decomposed in Me_2SO-d_6. Their ^{1}H NMR were therefore recorded in $CDCl_3$/TFA in which solution the spectra were identical with those of the pyridinium alcohols **18**, see Table VI.

Details of the pyridinium ethanols are recorded in Table V. Their IR spectra all showed broad ν(OH) bands at 3400 cm^{-1} with the pyridinium ring vibration at 1630 cm^{-1}. The NMR spectra (Table VI) showed the C-6 H as a downfield-shifted doublet in the region 9.2–9.5 ppm ($J_{6,5}$ = 6 Hz). The C-5 and C-3 H resonances were typically a double doublet (8.2–8.3 ppm, $J_{5,6}$ = 6 Hz, $J_{5,3}$ = 2 Hz) and a doublet (7.9–8.1 ppm, $J_{3,5}$ = 2 Hz), respectively. The N–C**H**–C**H** substituent AB system resonated in the olefinic region (5–6 ppm) with J = 6 Hz.

Synthesis and Reactions of 1-Styrylpyridinium Salts. The bicyclic derivatives **17a** and **17b** were converted by acetic anhydride directly into the acetoxypyridiniums **19a** and **19b**, which in refluxing pyridine afforded the corresponding styryl derivatives **20a** and **20b**. Bicycle **17a** also gave a *p*-methylbenzoate corresponding to **19a** with *p*-toluoyl chloride.



19 a Ar = m$NO_2C_6H_4$
b Ar = mClC_6H_4

20 a Ar = m$NO_2C_6H_4$
b Ar = mClC_6H_4

Reduction of styrylpyridinium **20b** with $NaBH_4$ gave the expected 1,2-dihydropyridine **21a** (88%), characterized by its NMR spectrum: C-2 H at 4.08 ppm with J = 5 Hz; C-3 H at 5.61 ppm, double triplet with $J_{3,2}$ = 6 Hz and $J_{3,5}$ = 2 Hz; C-5 H at 5.9 ppm, doublet with J = 2 Hz; and N-substituent *N*-vinyl C–H singlet at 5.78; C-2 H, doublet at 4.50 ppm J = 6 Hz; C-3 H, multiplet at 3.95–4.05 ppm C-5 H, singlet at 3.9 ppm. The reaction of **21a** with acid (Scheme II) was monitored by ^{13}C NMR. The proton-decoupled ^{13}C NMR spectrum of **21a** showed clearly the three vinyl C–H resonances at δ 108.7 (C-3), 110.1 (C-5), and 116.2 (C-2′). The C-2 signal (OFR, triplet) appeared at δ 51.7. On addition of 1 equiv of CF_3SO_3H, the spectrum

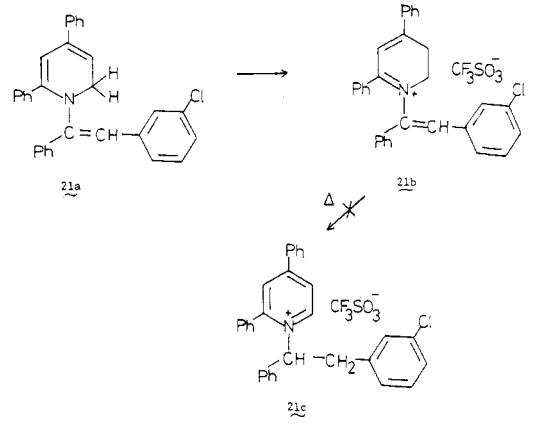
(10) Katritzky, A. R.; Awartani, R.; Patel, R. C., *J. Org. Chem.*, in press.

Table VII. ^{1}H NMR Spectral Data[a] of 1,2-Dihydropyridines

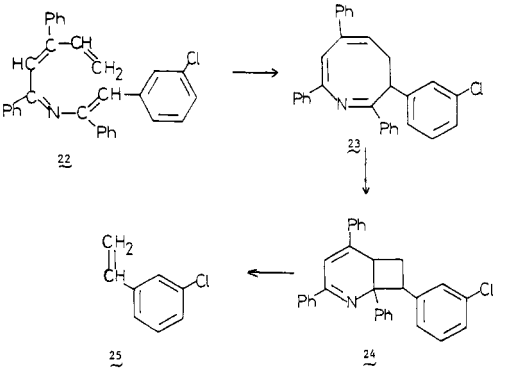
compd	C substituents	N substituents, CR=CHR′ R	R′	chemical shifts, δ: vinyl protons α	β cis	β trans	pyridine ring 2-CH_2	pyridine ring others	benzenoide
27a		p-$NO_2C_6H_4$	Ph		6.25[b]		3.85 (dd)[c]	4.4-5.8 (m)[d]	7.1-8.3 (m)[e]
27b		p-$NO_2C_6H_4$	o-ClC_6H_4		6.35[b]		3.90 (dd)[c]	4.4-5.8 (m)[d]	7.2-8.3 (m)[f]
30a	2,4,6-Ph_3	H	H	6.5 (dd)[b,g]	3.70 (dd)[b,h]	4.25 (dd)[b,i]	5.5-5.8 (m)[j]		7.1-7.6 (m)[k]
30b	2,4,6-Ph_3	H	Me	6.35 (m)[b]	[l]	4.5-5.1 (m)[b]	5.5-5.9 (m)[j]		7.2-7.6 (m)[k]

[a] In $CDCl_3$ with Me_4Si as an internal standard. Multiplicities are given in parentheses: s = singlet, d = doublet, dd = double doublet, m = multiplet. [b] 1 H. [c] J_1 = 5 Hz; J_2 = 2 Hz. [d] 4 H. [e] 9 H. [f] 8 H. [g] J_{α,β_c} = 9 Hz; J_{α,β_t} = 15 Hz. [h] $J_{\beta_c,\alpha}$ = 9 Hz; J_{β_c,β_t} = 2 Hz. [i] $J_{\beta_t,\alpha}$ = 15 Hz; J_{β_t,β_c} = 2 Hz. [j] 3 H. [k] 15 H. [l] The 3 H in the Me group appear at δ 1.5 (dd, J_{Me,H_β} = 8 Hz, J_{Me,H_α} = 1 Hz.

Scheme II



Scheme III

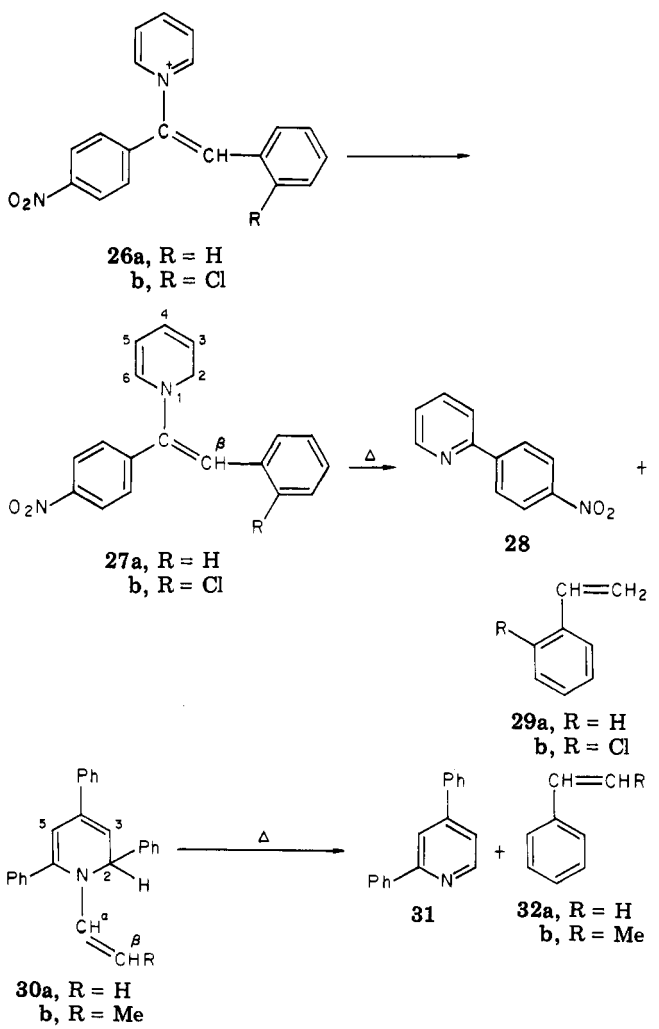


of protonated species **21b** (which was red) was observed: C-2 (t) at δ 51.5, C-3 (t) at δ 25.7, and C-5 (d) at δ 118.5 with C-2′ presumably in the aromatic signals (δ 126–135). Protonation at C-5 or C-2′ would not give a compound with a high-field methylene C signal (as observed for C-3 (t) in **21b**). Moreover, on addition of CF_3SO_3H a red compound results with λ390 nm: only **21b** has an extensive chromophore.

Compound **21b** was heated at 140 °C for 48 h in a N_2 atmosphere to effect its isomerization to compound **21c**. A mixture of pyridinium-like compounds was obtained which was insoluble in ether (TLC showed three spots). We believe that the added proton at C-3 moves to C-5 and C-2′, giving a tautomeric mixture (cf. work of Opitz and Merz[11]) with some (ca. 30% from the ^{1}H NMR appearance of a doublet at δ 9.5, J = 6 Hz, for C-2 H in **21c**) formation of the required **21c**.

Pyrolysis of **21a** gave 2,4,6-triphenylpyridine and m-chlorostyrene (**25**) probably via intermediates **22–24** (Scheme III). The scope and mechanism of this reaction were explored by further examples. The two 1,2-dihydropyridines **27a,b** (prepared by borohydride reduction of the corresponding pyridiniums **26a,b** on pyrolysis each gave 2-(p-nitrophenyl)pyridine (**28**, isolated from the pyrolysis residue in rather poor yield) together with styrene (**29a**) and o-chlorostyrene (**29b**), respectively (Scheme IV). The two 2,4,6-triphenyl-1,2-dihydropyridines (**30**), likewise made by reduction, were obtained only as oils, but they similarly afforded 2,4-diphenylpyridine (**31**) together with styrene (**32a**) or (*trans*-prop-1-enyl)benzene (**32b**), respectively. Details of the spectral characteristics of the dihydropyridiniums are given in Table VII and of the pyrolysis in Table VIII.

Scheme IV



(11) Opitz, G.; Merz, W. *Justus Liebigs Ann. Chem.* **1962**, *652*, 139, 158, 163.

Table VIII. Pyrolysis[a] of 1,2-Dihydropyridines

no.	pyrolysis temp,[a] °C	substituent	pyridine product: yield, %	pyridine product: mp, °C	pyridine product: lit. mp, °C	olefine product[b]: name	olefine product[b]: yield, %
27	180	2-*p*-$NO_2C_6H_4$	10	130-131	130-131[c]	styrene	70
27	160	2-*p*-$NO_2C_6H_4$	12	130-131	130-131[c]	*o*-chlorostyrene	66
30	200	2,4-diphenyl	78	65-67	68[d]	styrene	72
30	180	2,4-diphenyl	76	67	68[d]	*trans*-propenylbenzene	70

[a] Pyrolyses were carried out at 0.5 mmHg for 4 h. [b] Olefinic products were characterized by comparison of their IR and NMR spectrum with the ones described for authentic samples in "The Sadtler Standard Spectra": styrene, IR-241, NMR-6408; *o*-chlorostyrene, It-14032, NMR-18061; *trans*-propenylbenzene, IR-48289, NMR-20736. [c] V. S. Misra and M. P. Khare; *J. Indian Chem. Soc.*, **31**, 918 (1954). [d] C. Gastaldi, *Gazz. Chim. Ital.*, **52**, 305 (1922).

Conclusions. While it is difficult to capture zwitterions from *N*-alkylpyridiniums under strongly basic conditions, the action of alcoholic NaOH at 0 °C on *N*-benzylpyridiniums does give a useful method of condensation with aldehydes.

The novel rearrangement and fragmentation of 1-vinyl-1,2-dihydropyridines into olefins and pyridines, in addition to its mechanistic interest, offers potentially interesting routes to both types of product.

Experimental Section

IR and NMR spectra were measured with Perkin-Elmer 237 and R12 (60 MHz) and Varian HA-100 (100 MHz) instruments, respectively ($SiMe_4$ as an internal standard). Melting points (uncorrected) were determined on a Reichert hot-stage apparatus.

The following were prepared by the literature methods: **2-Carboxy-4,6-diphenylpyrylium tetrafluoroborate (7)**, mp 136–138 °C (lit.[7] mp 135 °C); **1-(*p*-nitro-α-phenylstyryl)-pyridinium bromide (26a)** mp 142–146 °C (lit.[8] mp 140–145 °C); **1-(*p*-nitro-α-[*o*-chlorophenyl)styryl]pyridinium bromide (26b)**, mp 282–285 °C (lit.[8] mp 280–283 °C); **2,4,6-triphenyl-1-vinylpyridinium tetrafluoroborate** mp 144–145 °C (lit.[9] mp 144–145 °C); **2,4,6-triphenyl-1-(prop-1-en-1-yl)pyridinium tetrafluoroborate** mp 293–294 °C (lit.[9] mp 293–294 °C).

2-Carboxy-4,6-diphenylpyrylium tetrafluoroborate (7) was prepared from chalcone and pyruvic acid by following the literature procedure; mp 136–138 °C (lit.[7] mp 135 °C).

Reaction of 2-Carboxy-4,6-diphenylpyrylium Tetrafluoroborate (7) with Benzylamine. A mixture of pyrylium **7** (0.4 g, 1 mmol) and benzylamine (0.1 g, 1 mmol) was refluxed in AcOH (5 mL) for 6 h. Dilution with ether gave a white solid, recrystallized from absolute ethanol as needles of **1-benzyl-2,4-diphenylpyridinium tetrafluoroborate**: 0.26 g (65%); mp 120–122 °C. Anal. Calcd for $C_{24}H_{20}NBF_4$: C, 70.42; H, 4.89; N, 3.42. Found: C, 70.25; H, 4.73; N, 3.20.

2-(Ethoxycarbonyl)-4,6-diphenylpyrylium Tetrafluoroborate (9). A mixture of chalcone (10.4 g, 50 mmol), ethyl pyruvate (5.8 g, 50 mmol), and $BF_3{\cdot}OEt_2$ (45%, 20 mL) was heated at 100 °C for 15 min. After cooling to 25 °C, ether was added to precipitate yellow crystals of **9** which were recrystallized from absolute ethanol as yellow needles: 6.5 g (33%); mp 155–157 °C; ^1H NMR ($CDCl_3$) δ 1.70 (t, 3 H), 4.82 (q, 2 H), 7.35–7.89 (m, 10 H), 8.20 (d, 1 H, J = 2 Hz), 8.51 (d, 1 H, J = 2 Hz); IR ($CHBr_3$) 1745 (s), 1630 (s), 1525 (s), 1050 cm^{-1} (br s). Anal. Calcd for $C_{20}H_{17}BF_4O_3$: C, 61.22; H, 4.36. Found: C, 61.70; H, 4.20.

2-(Ethoxycarbonyl)-4,6-diphenylpyridine. A mixture of pyrylium **9** (0.4 g, 1 mmol) and NH_4OAc (0.2 g, 3 mmol) was refluxed in AcOH (5 mL) for 4 h. Addition of H_2O gave a white solid which recrystallized from 50% EtOH as needles of **2-(ethoxycarbonyl)-4,6-diphenylpyridine**: 0.25 g (82%); mp 95–96 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 1.48 (t, 3 H), 4.50 (q, 2 H), 7.65–7.93 (m, 10 H), 8.11 (d, 1 H), 8.39 (d, 1 H); IR ($CHBr_3$) 1710 (s), 1595 cm^{-1} (s). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.21; H, 5.61; N, 4.62. Found: C, 78.76; H, 5.61; N, 4.58.

General Method for the Preparation of 1-Substituted 2-(Ethoxycarbonyl)-4,6-diphenylpyridinium Tetrafluoroborates (10). To a suspension of 2-(ethoxycarbonyl)-4,6-diphenylpyrylium tetrafluoroborate (1.2 g, 3 mmol) in CH_2Cl_2 (15 mL) was added the appropriate amine (3 mmol) dropwise. The resulting red solution was stirred for ca. 2 h at 25 °C. Dilution with ether and filtration of the resulting white solid gave the pyridinium tetrafluoroborate which was recrystallized from absolute ethanol as needles. Table I reports the physical data and Table III (supplementary material) the spectral data.

Reaction of 1-Benzyl-2-(ethoxycarbonyl)-4,6-diphenylpyridinium Tetrafluoroborate (10a) with Pyridine. The pyridinium **10a** (0.5 g, 1 mmol) was heated in refluxing pyridine for 2 days (monitored by TLC). After the reaction was completed, ether was added to give a white solid which was recrystallized from absolute ethanol as needles: 0.17 g (65%); ^1H NMR (60 MHz, $CDCl_3$) δ 5.3 (s, 2 H); 6.9–7.8 (m, 10 H); IR ($CHBr_3$) 1630 (s), 1050 cm^{-1} (s).

General Method for the Preparation of 1-Substituted 2-(Substituted carbamido)-4,6-diphenylpyridinium Tetrafluoroborates (11). The 1-substituted 2-(ethoxycarbonyl)-4,6-diphenyl pyridinium tetrafluoroborate (1 mmol) was stirred with excess amine (3 mmol) in CH_2Cl_2 for ca. 6 h at 25 °C. Dilution with ether gave the pyridinium tetrafluoroborate which was recrystallized from absolute ethanol. See Table II for physical data and Table III for the ^1H NMR data.

2-(*n*-Butylcarbamido)-4,6-diphenylpyridine. To a solution of 2-(ethoxycarbonyl)-4,6-diphenylpyridine (0.3 g, 1 mmol) in CH_2Cl_2 (5 mL) was added *n*-$BuNH_2$ (0.2 g, 3 mmol). The mixture was stirred for 6 h at 25 °C. Evaporation of the solvent gave a white solid which was crystallized from a mixture of EtOH, *i*-PrOH, and H_2O (30:30:40) as white needles: 0.3 g (91%); mp 74–76 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 0.92 (d, 3 H), 1.21 (m, 2 H), 1.73 (m, 2 H), 3.50 (q, 2 H), 7.63–7.92 (m, 10 H), 8.05 (d, 1 H), 8.30 (d, 1 H), IR ($CHBr_3$) 1675 (s), 1600 cm^{-1} (s). Anal. Calcd for $C_{22}H_{22}N_2O$: C, 80.00; H, 6.67; N, 8.48. Found: C, 79.73, H, 6.52; N, 8.51.

General Method for the Preparation of 2-Carboxy-4,6-diphenylpyridinium Betaine (12). To a suspension of the 1-substituted 2-(ethoxycarbonyl)-4,6-diphenylpyridinium tetrafluoroborate (1 mmol) in H_2O was added 0.5 N NaOH (1 mmol). The reaction mixture was allowed to stir for ca. 12 h, and the reaction course was checked by TLC (silica, EtOAc). After the reaction was complete, water was removed by filtration to give the pyridinium betaine. See Table I for physical data and Table III for ^1H NMR data.

1-Substituted 2,4-Diphenylpyridinium Tetrafluoroborates (15). Method A. 1-Substituted 2-carboxy-4,6-diphenylpyridinium betaine **12** (1 mmol) and aqueous HBF_4 (40%, 1.1 mmol) were heated under reflux in EtOH for ca. 6 h. Ether was added to precipitate the pyridinium tetrafluoroborate as a white solid. However, the product was contaminated with 1-substituted 2-carboxy-4,6-diphenylpyridinium tetrafluoroborate in some cases.

Method B. A mixture of the 1-substituted 2-(ethoxycarbonyl)-4,6-diphenylpyridinium tetrafluoroborate (1 mmol) and *tert*-butylamine (3 mmol) in absolute ethanol (15 mL) was refluxed for ca. 6 h [the reaction progress being monitored by TLC (EtOAc, silica)]. Removal of solvent in vacuo [40 °C (20 mmHg)] and addition of ether gave the 1-substituted 2,4-diphenylpyridinium tetrafluoroborate which was recrystallized from absolute ethanol. Table I records the physical data and Table IV (supplementary material) the ^1H NMR data.

General Method for the Reaction of Pyridinium Salts 15 with Aldehydes. Method C. To a solution of the 1-substituted 2,4-diphenylpyridinium tetrafluoroborate (10 mmol) and substituted benzaldehyde (50 mmol) in EtOH/MeOH (2:1, 20 mL)

was added dropwise at 0 °C 10 N NaOH (1 mL). The resulting red solution was left at 0 °C for 12 h: solvent removal in vacuo [20 °C (20 mmHg)] and ether addition to the residue gave the oxazolo[3,2-*a*]pyridine **17** (see Tables V and VI)

Method D. This method was as above, but after 12 h at 0 °C, excess $HClO_4$ (70%) or HBF_4 (40%) was added dropwise to give, after addition of H_2O, the pyridinium ethanol **18** as the ClO_4^- or BF_4^- salt (Tables V and VI).

Formation of Acylated Adduct 19. The oxazolo[3,2-*a*]-pyridines **17a** and **17b** (10 mmol) were stirred for 12 h in acetic anhydride (10 mL). Quenching with $NaBF_4$ (15 mmol) in water (10 mL) gave a yellow solid, which was recrystallized from absolute ethanol to give **19a** and **19b**, respectively.

1-[2-(Acetyloxy)-1-phenyl-2-(*m*-nitrophenyl)ethyl]-2,4-diphenylpyridinium tetrafluoroborate (19a): yellow needles, yield 85%; mp 113–115 °C; ^1H NMR ($CDCl_3$) δ 2.12 (s, 3 H), 6.21 (d, 1 H, J = 9 Hz), 6.89 (d, 1 H, J = 9 Hz), 7.20–7.94 (m, 19 H), 8.01 (d, 1 H, J = 2 Hz), 8.66 (dd, 1 H, J = 2 Hz, J = 7 Hz), 9.71 (d, 1 H, J = 7 Hz); IR ($CHBr_3$) 1755 (s), 1630 (s), 1530 (s), 1050 cm^{-1} (br). Anal. Calcd for $C_{33}H_{27}BF_4N_2O_2$: C, 65.78; H, 4.49; N, 4.65. Found: C, 65.41, H, 4.11; N, 4.39.

1-[2-(Acetyloxy)-1-phenyl-2-(*m*-chlorophenyl)ethyl]-2,4-diphenylpyridinium tetrafluoroborate (19b): yellow prisms; yield 82%; mp 118–120 °C; ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H), 6.23 (d, 1 H, J = 8 Hz), 6.85 (d, 1 H, J = 8 Hz), 7.25–7.93 (m, 19 H), 8.05 (d, 1 H, J = 2 Hz), 8.63 (dd, 1 H, J = 2 Hz, J = 6 Hz), 9.65 (d, 1 H, J = 6 Hz); IR ($CHBr_3$) 1750 (s), 1625 (s), 1480 (s), 1050 cm^{-1} (s). Anal. Calcd for $C_{33}H_{27}BClF_4NO_2$: C, 66.95; H, 4.56; N, 2.37; Cl, 6.00. Found: C, 66.59; H, 4.39; N, 2.53; Cl, 5.84.

1-[2-(Toluoyloxy)-1-phenyl-2-(*m*-nitrophenyl)ethyl]-2,4-diphenylpyridinium Chloride. *p*-Toluoyl chloride (2 mL) was added to a suspension of 2,3-dihydro-2-(*m*-nitrophenyl)-3,5,7-triphenyloxazolo[3,2-*a*]pyridine (2.6 g, 5 mmol) in absolute ethanol (10 mL). After the mixture was stirred at 25 °C for 12 h, ether was added to give a yellow solid which was recrystallized from absolute ethanol as the pyridinium chloride: plates; yield 75%; mp 125–127 °C; ^1H NMR ($CDCl_3$/TFA) δ 2.50 (s, 3 H), 6.60 (d, 1 H, J = 9 Hz), 6.90 (d, 1 H, J = 9 Hz), 7.7–8.1 (m, 3 H), 8.15 (d, 1 H, J = 2 Hz), 8.22 (dd, 1 H, J = 2 Hz, J = 6 Hz), 9.25 (d, 1 H, J = 6 Hz); IR ($CHBr_3$) 1730 (s), 1625 (s), 1530 (s), 1350 cm^{-1} (s). Anal. Calcd for $C_{39}H_{31}ClN_2O_4$: C, 74.70; H, 4.95; N, 4.47; Cl, 5.51. Found: C, 74.38; H, 4.83; N, 4.25, Cl, 5.39.

1-[2-(*m*-Nitrophenyl)styryl]- and 1-[2-(*m*-Chlorophenyl)styryl]-2,4-diphenylpyridinium Tetrafluoroborates (20a,b). The acetoxy derivatives **19a** and **19b** (5 mmol) were refluxed in pyridine (10 mL) for 12 h. Addition of ether afforded a yellow solid which was recrystallized from absolute ethanol as, respectively, **20a** and **20b**.

For **20a**: yellow prisms; yield 87%; mp 182–185 °C; ^1H NMR ($CDCl_3$/TFA), δ 6.95 (s, 1 H) 7.11–8.30 (m, 19 H), 8.35 (d, 1 H, J = 2 Hz), 8.42 (dd, 1 H, J = 2 Hz, J = 7 Hz), 8.72 (d, 1 H, J = 7 Hz); IR ($CHBr_3$) 1620 (s), 1530 (s), 1350 (s), 1050 cm^{-1} (s). Anal. Calcd for $C_{31}H_{23}BF_4N_2O_2$: C, 68.63; H, 4.24; N, 5.17. Found: C, 68.84; H, 4.32; N, 5.20.

For **20b**: yellow prisms; yield 75%; mp 165–167 °C; ^1H NMR ($CDCl_3$) δ 6.67 (s, 1 H), 7.05–7.45 (m, 19 H), 7.63 (d, 1 H, J = 2 Hz), 8.08 (dd, 1 H, J = 2 Hz, J = 7 Hz), 8.72 (d, 1 H, J = 7 Hz); IR ($CHBr_3$) 1620 (s), 1480 (s), 1050 cm^{-1} (s). Anal. Calcd for $C_{31}H_{23}BClF_4N$: C, 69.99; H, 4.33; N, 2.63; Cl, 6.68. Found: C, 69.63; H, 4.09; N, 2.32; Cl, 6.33.

1-[2-(*m*-Chlorophenyl)styryl]-4,6-diphenyl-1,2-dihydropyridine (21a). To a solution of 1-[2-(*m*-chlorophenyl)-styryl]-2,4-diphenylpyridinium tetrafluoroborate (1.06 g, 2 mmol) in CH_3CN/CH_3OH (2:1, 15 mL) was added $NaBH_4$ (0.15 g, 4 mmol) at 5 °C. The reaction mixture was allowed to warm to 20 °C; the resulting yellow crystals were filtered off and washed with CH_3CN (10 mL). Recrystallization from CH_3CN gave the 1,2-dihydropyridine: yellow prisms; yield 88% mp 104–106 °C; ^1H NMR ($CDCl_3$) δ 4.08 (d, 2 H, J = 5 Hz), 5.61 (dt, 1 H, J = 2 Hz, J = 6 Hz), 5.78 (s, 1 H), 5.90 (d, 1 H, J = 2 Hz), 6.90–7.54 (m, 19 H); ^{13}C NMR (off resonance) δ 51.7 (C-2, t), 108.7 (C-3 t), 110.1 (C-5 d), 116.2 (C-2′ d); IR ($CHBr_3$) 1610 (s), 1590 (s) 1550 (s), 1445 cm^{-1} (s). Anal. Calcd for $C_{31}H_{24}ClN$: C, 83.50; H, 5.39; N, 3.14; Cl, 7.97. Found: C, 83.18; H, 5.23; N, 3.29; Cl, 8.24.

Reaction of 1-[2-(*m*-Chlorophenyl)styryl]-4,6-diphenyl-1,2-dihydropyridine (21a) with CF_3SO_3H. Trifluoromethanesulfonic acid (1.1 mmol) was added to the 1,2-dihydropyridine (0.46 g, 1 mmol) in $CDCl_3$ under N_2. The ^1H NMR and ^{13}C NMR spectra of the compound (**21a**) changed immediately on addition of CF_3SO_3H to that of protonated 1,2-dihydropyridine (**21b**): ^1H NMR (100 MHz, $CDCl_3$) δ 3.43 (t, 2 H), 4.23 (m, 2 H), 6.95 (s, 1 H), 7.05–7.95 (m, 20 H); ^{13}C NMR (off resonance) δ C-3, 25.7 (t), C-2, 51.5 (t), C-5, 118.5 (d). On being heated neat at 140 °C for 48 h, **21b** decomposed to a mixture of three products (TLC, silica/EtOAc).

Pyrolysis of 1-[2-(*m*-Chlorophenyl)styryl]-4,6-diphenyl-1,2-dihydropyridine (21a). The 1,2-dihydropyridine (1 g, 2.2 mmol) was heated in a distillation apparatus under reduced pressure (0.3 mmHg) at 160 °C for 6 h. (The residue was 2,4,6-triphenylpyridine as shown by comparison with an authentic specimen.) The distillate was collected in a trap cooled with liquid nitrogen and was shown to be *m*-chlorostyrene (82%) by its IR and ^1H NMR spectra and elemental analysis: ^1H NMR (60 MHz, $CDCl_3$) δ 5.22 (dd, 1 H), 5.65 (dd, 1 H), 6.62 (dd, 1 H), 7.18–7.30 (m, 3 H), 7.35 (s, 1 H); IR (film) 3080 (m), 3060 (m), 3000 (w), 2980 (m), 1625 (w), 1590 (s), 1560 (s), 1475 (s), 1410 (s), 1390 (m), 1300 (w), 1270 (w), 1260 (w), 1200 (s), 1160 (w), 1075 (s), 1040 (w), 985 (s), 965 (s), 880 (s), 845 (s), 785 (s), 710 (s), 680 (s), 645 cm^{-1} (s). Anal. Calcd for C_8H_7Cl: C, 69.34; H, 5.09; Cl, 25.64. Found: C, 69.68; H, 5.35; Cl, 25.78.

General Method for the Preparation of 1-Substituted 1,2-Dihydropyridines (27a,b). The 1-substituted pyridinium bromide (**26a,b**, 1 mmol; see above) dissolved in CH_3CN (1 mL) and CH_3OH (1 mL) was stirred at 0–5 °C for 1 h with an equimolecular amount of $NaBH_4 \cdot H_2O$ (3 mL), and the resulting red solid was filtered off and washed with H_2O (20 mL).

1-(*p*-Nitro-α-phenylstyryl)-1,2-dihydropyridine (27a): yield 92%; mp 114–118 °C (prisms from ethanol); IR ($CHBr_3$) ν_{max} 1590 (s), 1680 (m), 1510 (s), 1340 (s), 1270 (m), 850 (s), 750 cm^{-1} (s); Table VII reports ^1H NMR data. Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 75.00; H, 5.26; N, 9.21. Found: C, 74.94; H, 5.35; N, 9.18.

1-[*p*-Nitro-α-(*o*-chlorophenyl)styryl] (27b): yield 94%; mp 124–216 °C (prisms from ethanol); IR ($CHBr_3$) ν_{max} 2820 (m), 1680 (m), 1600 (s), 1520 (s), 1345 (s), 1270 (m), 860 (s), 850 (s), 760 cm^{-1} (s); Table VII reports ^1H NMR data. Anal. Calcd for $C_{19}H_{15}ClN_2O_2$: C, 67.35; H, 4.43; N, 8.27, Cl, 10.48. Found: C, 67.17; H, 4.47, N, 8.23; Cl, 10.43.

General Procedure for the Formation of 1-Substituted 2,4,6-Triphenyl-1,2-dihydropyridines (30a,b). 1-Vinyl- or 1-(2-propenyl)-2,4,6-triphenylpyridinium tetrafluoroborate (1 mmol; see above) dissolved in CH_3CN (1 mL) and CH_3OH (1 mL) was stirred at 0–5 °C for 1 h with an equimolecular amount of $NaBH_4 \cdot H_2O$ (30 mL), and the solution was extracted with ether (60 mL). The ethereal layer was dried ($MgSO_4$) and evaporated at 20 °C (20 mmHg), giving the 1,2-dihydropyridine as a yellow oil which decomposed on standing at room temperature. For **30a**: yield 85%; IR ($CHBr_3$) ν_{max} 2920 (w), 1640 (m), 1620 (m), 1600 (m), 1580 (s), 1560 (s), 1490 (s), 1450 (s), 1425 (m), 1400 (m), 1320 (m), 1240 (s), 1070 (m), 910 (m), 760 (m), 750 (s), 730 cm^{-1} (m). Table VII reports ^1H NMR data. For **30b**: yield 83%; IR ($CHBr_3$) ν_{max} 2920 (w), 1640 (m), 1620 (m), 1600 (m), 1580 (s), 1560 (s), 1490 (s), 1450 (s), 1425 (m), 1400 (m), 1320 (m), 1240 (s), 1070 (m), 910 (m), 760 (m), 750 (s), 730 cm^{-1} (m); Table VII reports ^1H NMR data.

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Supplementary Material Available: Tables III and IV containing NMR and physical data for the pyridinium salts (2 pages). Ordering information is given on any current masthead page.