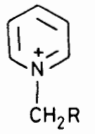
Reactions of Pyridinium Ylides with Aldehydes and with Michael Acceptors

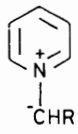
Alan R. Katritzky,* Olga Rubio, Jose M. Aurrecoechea, and Ranjan C. Patel
Department of Chemistry, University of Florida, Gainesville, Fla. 32611, U.S.A., and University of East Anglia, Norwich NR4 7TJ

1-Methyl and 1-allyl-2,4,6-triphenylpyridinium cations react with aromatic aldehydes at the α-CH_2 to give aldol products (**7**) and (**8**). The allyl adducts (**8**) were thermally converted into aldehydes and ketones, whereas thermolysis of (**7**) took a variety of courses. Zwitterions from 1-methylpyridinium cations were also added Michael-fashion to activated carbon–carbon double bonds.

The classic work of Kröhnke [1] established that the pyridinium ylides (**2**) derived from *N*-alkyl-, *N*-allyl-, and *N*-benzylpyridinium salts (**1**) react with electrophiles to give synthetically useful adducts (**3**). However, deuterium-hydrogen exchange [2] is faster at the C-2 and C-6 protons than at the α-CH_2 group of (**1a**) and (**1c**). These results indicate that an equilibrium exists between ylides of types (**2**) and (**4**).[2]



(**1**)



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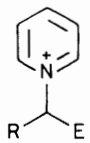

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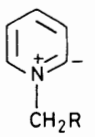

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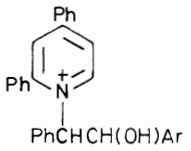

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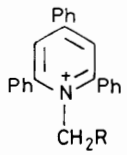


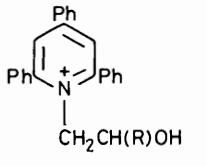
(**6**)

a; R = H, b; R = CH=CH_2, c; R = Ph

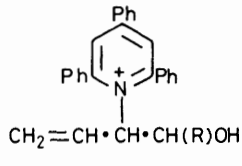
Reactions of 1-benzyl-2,4-diphenylpyridinium salts and benzaldehydes with aqueous NaOH in MeOH–EtOH at 0 °C gave the adducts (**5**),[3] and we now report the reaction of 1-methyl- and 1-allyl-2,4,6-triphenylpyridinium salts (**6a**) and (**6b**) with electrophiles.

Reactions with Aldehydes.—1-Methyl- (**6a**) and 1-allyl-2,4,6-triphenylpyridinium (**6b**) salts reacted in a mixed methanol, ethanol, and dichloromethane solvent at 0 °C over 15—48 h with aromatic and heteroaromatic aldehydes, using aqueous NaOH to give the adducts (**7**) and (**8**) respectively. A considerable excess of aldehyde was required to give good conversions and especially for the allyl salts (**8**) the yields depended drastically on the substituents in the benzaldehydes. The adducts (**7**) were also conveniently prepared by allowing the pyridinium cation (**6a**) to react with the aldehyde in the presence of KOBu^t in dimethyl sulphoxide at 20 °C for 24—30 h (Table 1), but again with the pyridinium cation (**6b**) the yields depended on the particular benzaldehyde used.

All adducts showed a medium to strong ν_{OH} absorption at *ca.* 3 400 cm^{-1} in the i.r. region. The ^1H n.m.r. spectra of the adducts (**7**) showed multiplets due to the NCH_2CH protons in the region δ 4.2—6.15. Interestingly, when the ^1H n.m.r. spectrum of (**7h**) was recorded in $CDCl_3$–TFA that obtained corresponded to the ring closed product (**9**) as deduced by comparison with the ^1H n.m.r. of (**10**):[4] δ 8.4 [(d, *J* 2 Hz, 1-H), 8.1 (m, 11-H), 7.5 (13 H, m), 7.1 (d, *J* 5 Hz, 3′-H), 6.75 (dd, *J* 5 and 4 Hz, 4′-H), 6.45 (d, *J* 4 Hz, 5′-H), and 5.0—4.4 (m, CH_2CH).

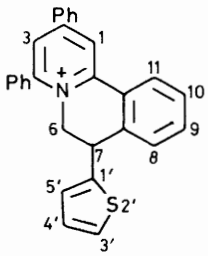


(**7**)

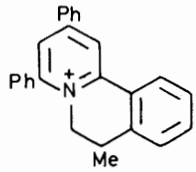


(**8**)

a; R = Ph
b; R = 2-ClC_6H_4
c; R = 2-$NO_2C_6H_4$
d; R = 3-$NO_2C_6H_4$
e; R = 2-MeC_6H_4
f; R = 2,4,6-$Me_3C_6H_2$
g; R = 2-Furfuryl
h; R = 2-Thienyl



(**9**)



(**10**)

The allylic protons in (**6b**) resonate in the ^1H n.m.r. spectrum (Table 2) in the same region as the olefinic and aliphatic protons in the adducts (**8**). The ^{13}C n.m.r. was more characteristic, and two doublets were observed in the region δ 69.2—76.3 p.p.m. The existence of diastereoisomers could also be detected by this technique [*e.g.* in (**8d**)] (Table 3).

Conjugate Addition to Acrylates.—Reaction of (**6a**) with ethyl acrylate and sodium ethoxide gave the adduct (**11a**) (72%). However, a similar procedure with methyl acrylate gave no reaction with 1 or 2 equivalents of methanolic sodium methoxide; with 3 equivalents, adduct (**11b**) was obtained but only in 25% yield. The major product was the tetrahydroindolizinium tetrafluoroborate (**13b**) (41%). The reaction between (**6a**) and acrylonitrile using potassium t-butoxide in t-butyl alcohol gave the tetrahydroindolizine (**12c**) characterised by ^1H n.m.r. spectroscopy. The tetrahydroindolizinium tetrafluoroborate (**13c**) was obtained upon addition of HBF_4 to (**12c**).

The formation of both the adducts and the cyclised products

Table 1. Preparation of pyridinium ethanols (7) and (8)

Product no.	Starting aldehyde	Method[a]	Time (h)	Yield (%)	M.p. (°C)	Recryst. solvent	Crystal form	Required (%) C	H	N	Molecular formula	Found (%) C	H	N
(7a)	Benzaldehyde	A	15	85[b]	192—194		Plates	72.2	5.1	2.7	$C_{31}H_{26}BF_4NO$	71.8	5.0	2.7
		B	30	73	195—197	EtOH	Plates				$C_{31}H_{26}BF_4NO$			
(7b)	2-Chlorobenzaldehyde	B	24	87	188—190	EtOH	Needles	67.7	4.55	2.5	$C_{31}H_{25}BClF_4NO$	68.05	4.7	2.45
(7d)	3-Nitrobenzaldehyde	A[c]	15	59[b]	145—146		Plates	66.4	4.5	5.0	$C_{31}H_{25}BF_4N_2O_3$	66.1	4.3	5.0
		B	24	86	176—178	$EtOH–Et_2O$	Microcrystals	66.4	4.5	5.0	$C_{31}H_{25}BF_4N_2O_3$	66.6	4.6	5.0
(7f)	2,4,6-Trimethylbenzaldehyde	A[c]	15	80[b]	188—189		Plates	73.3	5.8	2.5	$C_{34}H_{32}BF_4NO$	73.0	5.6	2.4
(7g)	2-Furaldehyde	A[c]	15	92[b]	178—180		Plates	68.9	4.8	2.8	$C_{29}H_{24}BF_4NO_2$	68.7	4.8	2.8
(7h)	2-Thiophenecarbaldehyde	A[c]	15	66[b]	197—199		Plates	66.8	4.6	2.7	$C_{29}H_{24}BF_4NOS$	66.6	4.5	2.7
(8a)	Benzaldehyde	A	48	46	94—96	$Me_2CO–Et_2O$	Prisms	73.2	5.2	2.6	$C_{33}H_{28}BClF_4NO$	73.5	5.3	2.7
(8b)	2-Chlorobenzaldehyde	A	16	60	132—135	$Me_2CO–Et_2O$	Microcrystals	68.8	4.7	2.4	$C_{33}H_{27}BClF_4NO$	68.7	4.7	2.4
(8c)	2-Nitrobenzaldehyde	A	26	67	114—116	$CH_2Cl_2–Et_2O$	Plates	67.6	4.6	4.8	$C_{33}H_{27}BF_4N_2O_3$	67.2	4.7	4.6
(8d)	3-Nitrobenzaldehyde	A	48	20	160—161	$Me_2CO–Et_2O$	Microcrystals	67.6	4.6	4.8	$C_{33}H_{27}BF_4N_2O_3$	67.5	4.6	4.5
		B	24	68[d]	157—159[e]	$Me_2CO–Et_2O$	Microcrystals	67.6	4.6	4.8	$C_{33}H_{27}BF_4N_2O_3$	67.4	4.6	4.6
(8e)	2-Methylbenzaldehyde	A	48	72	148—149	$CH_2Cl_2–Et_2O$	Prisms	73.5	5.4	2.5	$C_{34}H_{30}BF_4NO$	73.1	5.4	2.4

[a] For methods A and B see Experimental section. All compounds are tetrafluoroborate salts. [b] Based on recovered starting material. [c] Starting material was 1-methyl-2,4,6-triphenylpyridinium trifluoromethanesulphonate. [d] Yield of the mixture of diastereoisomers. [e] One isomer after recrystallisation.

Table 2. ^{1}H N.m.r. spectra[a] of 1-(2-aryl-2-hydroxyethyl)- (**7**) and 1-(2-aryl-2-hydroxy-1-vinylethyl)-2,4,6-triphenylpyridinium (**8**) tetrafluoroborates

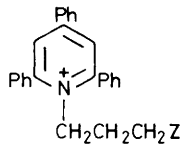
Compound no.	R	3,5-H 2 H (s) δ	R δ	H	M	Other aromatic protons (m) δ	H	$\overset{+}{N}CHR'$– δ	H	M	–CH(OH)R'' 1 H δ	M	–CH=CH$_2$ 3 H δ	M
(**7a**)	C_6H_5	8.0	7.15	3	m	7.75	15	4.70	2	b[b]	4.70	b[b]		
			6.5	2	m									
(**7b**)	2-ClC_6H_4	8.05	7.1	4	m	7.7	15	5.3—4.2	2	m[b]	5.3—4.2	m[b]		
(**7d**)	3-$NO_2C_6H_4$	8.2		[c]		8.1—6.8	19	4.85	2	b[b]	4.85	b[b]		
(**7f**)[d]	2,4,6-$Me_3C_6H_2$	8.0	6.5	2	s	7.9—7.4	15	6.15	1	dd[e]	5.5	dd[g]		
								5.0	1	dd[f]				
(**7g**)	2-Furfuryl	[c]	6.85	1	d[h]	7.8—7.0	17	4.8—4.4	2	m[b]	4.8—4.4	m[b]		
			5.85	1	dd[i]									
			5.6	1	d[j]									
(**8a**)	C_6H_5	[c]	7.2	3	m	8.3—7.4	17	6.1—4.4	1	m[b]	6.1—4.4	m[b]	6.1—4.4	m[b]
			6.75	2	m									
(**8b**)	2-ClC_6H_4	[c]	7.1	4	m	8.3—7.35	17	6.0—4.6	1	m[b]	6.0—4.6	m[b]	6.0—4.6	m[b]
(**8c**)	2-$NO_2C_6H_4$	8.15		[c]		8.1—7.1	19	6.0—4.3	1	m[b]	6.0—4.3	m[b]	6.0—4.3	m[b]
(**8d**)	3-$NO_2C_6H_4$	8.15		[c]		8.1—7.0	19	5.9—4.6	1	m[b]	5.9—4.6	m[b]	5.9—4.6	m[b]
(**8e**)[k]	2-MeC_6H_4	8.2	7.2—6.6	4	m	8.1—7.4	15	6.0—4.6	1	m[b]	6.0—4.6	m[b]	6.0—4.6	m[b]

[a] All spectra recorded in $CDCl_3$–CF_3CO_2H except (**7f**) and (**7g**) (100 MHz) recorded in $CDCl_3$; δ = chemical shift (p.p.m.); *J* = coupling constant (Hz); H = number of protons, M = multiplicity, s = singlet, d = doublet, dd = double doublet, m = multiplet, b = broad singlet. [b] Obscured by signals in the same region. [c] With rest of aromatic protons. [d] C–CH_3 (s); δ 2.1 (3 H) and δ 1.4 (6 H). [e] *J* 5; 11. [f] 5; 15. [g] *J* 11; 15. [h] *J* 2. [i] *J* 4;2. [j] *J* 4. [k] C–CH_3: δ 1.7 (3 H, s).

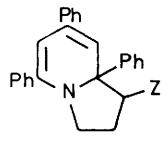
Table 3. ^{13}C N.m.r. chemical shifts[a] of the aliphatic region on pyridinium ethanols (**8**)

Compound no.	C-1′ (d)	C-2′ (d)
(**8a**)	74.0	74.4
(**8b**)	69.6	75.7
(**8c**)	68.0	76.3
(**8d**)[d]	73.5	74.4
(**8e**)[c]	69.2	75.8

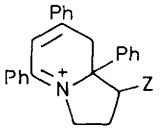
[a] Spectra recorded in $CDCl_3$–TFA with $CDCl_3$ as internal reference, chemical shift in p.p.m. [b] The mixture of diastereoisomers showed also, C-1′ at 73.1 and C-2′ at 76.0. [c] 2′-CH_3 (18.6 q).



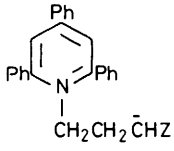
(**11**)



(**12**)



(**13**)

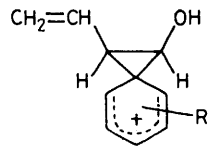


(**14**)

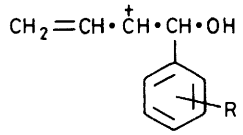
a; Z = CO_2Et; b; Z = CO_2Me, c; Z = CN

implicates the carbanionic intermediate (**14**) which is protonated or cyclised to the pyridinium ring.

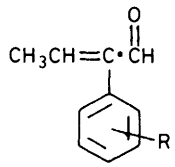
Thermolysis of the Adducts (**8**).—The adducts (**8b**) and (**8d**) when heated under reflux in chlorobenzene for 2 h, gave 2,4,6-triphenylpyridinium tetrafluoroborate together with the crotonaldehydes (**17b**) and (**17d**) and the isomeric aryl propenyl ketones (**18**). The product ratios (**17b**):(**18b**) and (**17d**):(**18d**) were as 80:20 and 46:54 respectively as judged by the ^{1}H n.m.r. ratios of the aldehyde protons to the total C–Me peak areas. The ^{13}C n.m.r. and g.c./mass spectral results confirmed the presence of the two compounds. Thermolysis of (**8b**) also gave traces of *o*-chlorobenzaldehyde, identified by g.c./mass spectroscopy. Other unidentified products were formed from (**8d**). The thermolysis of (**8e**) gave the crotonaldehyde (**17e**) with the expected ^{1}H and ^{13}C n.m.r. spectra: traces of (**18e**) were detected in the product by g.c./mass spectroscopy. The intermediacy of the phenonium ion (**15**) followed by proton loss from oxygen helps explain the formation of the aldehydes (**17b**) and (**17e**). The formation of the ketone (**18b**) and the products (**17d**) and (**18d**) from the thermolysis of the *m*-nitro derivative (**8d**) could be explained by a 1,2-H or -aryl shift on the carbenium ion (**16**).[5] The presence of the substituted benzaldehydes results from the retro-condensation reaction. This is the favoured process of thermolysis of the unsubstituted pyridinium ethanols (**3**).[6]



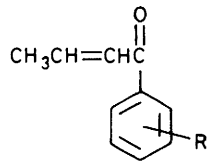
(**15**)



(**16**)



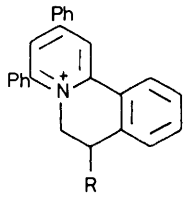
(**17**)



(**18**)

b, R = 2-Cl, d, R = 3-NO_2, e; R = 2-Me

Thermolysis of the Adducts (7).—The pyridinium ethanol (**7b**) was unaffected when heated under reflux in chlorobenzene, but at 220—230 °C gave the tetrahydroquinolizinium (**19b**) (25%). Similarly, the benzaldehyde derivative (**7a**) gave (**19a**) (54%). However, the adduct (**7d**) underwent considerable decomposition on thermolysis. In all cases, 2,4,6-triphenylpyridine was also formed, probably by loss of the aldehydes (**20**) formed by 1,2-phenyl migration.[7]



(19)

RCH_2CHO

(20)

a; R = Ph, b; R = 2-ClC_6H_4; d; R = 3-$NO_2C_6H_4$

Experimental

Melting points were determined with either a Reichert or a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer (either 257 or 283B) spectrophotometer. U.v. spectra were obtained on a Pye-Unicam PU 8800 spectrophotometer. 60 MHz ^1H N.m.r. spectra were recorded on either a Varian EM360-L or a Jeol JNM-PMX60 spectrometer. 100 MHz ^1H N.m.r. spectra were recorded using a Varian HA-100 spectrometer. The 25 MHz ^{13}C n.m.r. spectra were recorded on a Jeol JNM-FX100 spectrometer, and the g.c./mass spectroscopy results were obtained by Dr. R. W. King, on an AEI MS 30 spectrometer.

The following compounds were prepared by reported methods: 1-methyl-2,4,6-triphenylpyridinium tetrafluoroborate (**6a**) (84%), m.p. 213—214 °C (lit.,[8] m.p. 215—216 °C); 1-methyl-2,4,6-triphenylpyridinium trifluoromethanesulphonate (**6a**), m.p. 180—181 °C (lit.,[9] m.p. 184—185 °C); 1-allyl-2,4,6-triphenylpyridinium tetrafluoroborate[10] (**6b**) (70%), m.p. 164—166 °C (lit.,[11] m.p. 169—170 °C).

Reactions with Aldehydes.—Method A. For the adducts (**7**). To the pyridinium salt (**6a**) (1 mmol) and the aldehyde (5 mmol) in ethanol (15 ml), methanol (15 ml), and dichloromethane (5 ml) at 0 °C, NaOH (10M; 1 ml) was added. The resulting dark brown solution was kept at 0 °C for 15 h. The solvent was removed (25 °C/15 mmHg) and the residue extracted into ether (3 × 20 ml); aqueous HBF_4 (48%, excess) was added to the ethereal extracts, from which the adducts (**7**) crystallised and were washed with ether.

For the adducts (**8**). To the pyridinium salt (**6b**) (1 mmol) and the aldehyde (5 mmol) in ethanol (6 ml), methanol (6 ml), and dichloromethane (4.8 ml) at 0 °C, NaOH (10M; 1.2 ml) was added, with occasional stirring, and the solution was kept at 0 °C for the appropriate time (Table 1). The solution was acidified with acetic acid, the solvent removed (20 °C/10 mmHg) and the residue extracted with dichloromethane (2 × 20 ml). Excess of HBF_4 (48%) was added to the organic extracts, which were washed with water and dried over $MgSO_4$. The solvent was removed (20 °C/10 mmHg) and the residue was washed and triturated with ether until crystallisation of the adducts (**8**).

Method B. Potassium t-butoxide (1.4 mmol) was added in portions to a stirred solution of the pyridinium salt (**6a**) or (**6b**) (1 mmol) and the aldehyde (2 mmol) in dry DMSO (8 ml) at 20 °C, and the reaction mixture was stirred for the appropriate time (Table 1). It was then poured into ice and extracted with dichloromethane (2 × 25 ml). The extracts were washed with water, the solvent evaporated, and the residue dissolved in ether and filtered. Addition of an excess of fluoroboric acid (48%) to the filtrate afforded the crystalline adducts.

1-[3-(*Ethoxycarbonyl*)*propyl*]-2,4,6-*triphenylpyridinium Tetrafluoroborate* (**11a**).—Ethyl acrylate (3 ml) was added at 20 °C to a stirred ethanolic suspension of (**6a**) (0.5 g, 1.2 mmol) and ethanolic sodium ethoxide [sodium (0.036 g, 1.6 mmol) in absolute ethanol (15 ml)]. The solution was refluxed for 40 h after which it was allowed to cool; a solid separated (0.21 g) and was filtered off. Solvent was removed from the filtrate under reduced pressure (20 mmHg), and the residue triturated with water, containing fluoroboric acid (48%, 0.1 mol), to afford further *adduct* (0.24 g); total yield (0.45 g, 72%). This was recrystallised from absolute ethanol to give needles, m.p. 178—182 °C (Found: C, 68.4; H, 5.5; N, 2.7. $C_{29}H_{28}BF_4NO_2$ requires C, 68.4; H, 5.5; N, 2.75%); $\nu_{max.}$($CHBr_3$) 1 730s, 1 620s, and 1 050s,br; δ($CDCl_3$) 1.1 (3 H, t, *J* 7 Hz), 1.8 (4 H, m), 3.9 (2 H, q, *J* 7 Hz), 4.5 (2 H, m), and 7.4—8.0 (17 H, m).

Reaction of (**6a**) *with Methyl Acrylate.*—This reaction was carried out following the same conditions as for (**11a**), except that sodium methoxide (3 equiv.) was used. The reaction time was 20 h. The solvent was evaporated under reduced pressure (20 mmHg), and the residue dissolved in dichloromethane and extracted with water (3 × 20 ml). Fluoroboric acid (48%) was added to the dichloromethane solution, which was washed with water (20 ml), and dried ($MgSO_4$). The solvent was removed under reduced pressure (20 mmHg) and the residue crystallised from methanol–ether to give 2,3,8,8a-tetrahydro-1-methoxycarbonyl-5,7,8a-triphenyl-1*H*-indolizinium tetrafluoroborate (**13b**) (0.28 g, 41%) as yellow plates (from methanol), m.p. 195—200 °C (Found: C, 67.8; H, 5.3; N, 2.8. $C_{28}H_{26}BF_4NO_2$ requires C, 67.9; H, 5.25; N, 2.8%); $\nu_{max.}$($CHBr_3$) 1 740s, 1 630s, and 1 050s,br; δ($CDCl_3$–TFA) 2.5 (2 H, m), 3.6 (3 H, s), 3.7—4.7 (5 H, m), 6.7 (1 H, m), and 7.1—8.0 (15 H, m); $\lambda_{max.}$(MeOH) (ε) 238 (11 700), 320sh, and 365 (13 300).

1-[3-(*Methoxycarbonyl*)*propyl*]-2,4,6-*triphenylpyridinium tetrafluoroborate* (**11b**). This was obtained after concentration under reduced pressure (20 mmHg) of the methanol from the above filtrate (to 5 ml), and the addition of ether. The *adduct* (0.17 g, 25%) was recrystallised from methanol to give colourless plates, m.p. 229—231 °C (Found: C, 67.8; H, 5.3; N, 2.8. $C_{28}H_{26}BF_4NO_2$ requires C, 67.9; H, 5.25; N, 2.8%); $\nu_{max.}$($CHBr_3$) 1 735s, 1 623s, and 1 050s,br; δ($CDCl_3$) 1.8 (4 H, m), 3.4 (3 H, s), 4.5 (2 H, t), 7.3—7.7 (15 H, m), and 7.9 (2 H, s).

1-*Cyano*-2,3,8,8a-*tetrahydro*-5,7,8a-*triphenyl*-1H-*indolizinium Tetrafluoroborate* (**13c**).—To stirred potassium t-butoxide (0.164 g, 1.5 mmol) in t-butyl alcohol (20 ml) was added 1-methyl-2,4,6-triphenylpyridinium tetrafluoroborate (**6a**) (0.5 g, 1.2 mmol). The mixture was stirred for 15 min and then acrylonitrile (0.064 g, 1.2 mmol) in t-butyl alcohol (5 ml) was added dropwise; the reaction mixture was then refluxed for 2 h. As it cooled, inorganic material was precipitated, and this was filtered off; HBF_4 (48%, excess) was then added to the filtrate. Addition of ether to the mixture gave a precipitate which was collected after it had been stirred for 12 h (0.3 g, 53%); it gave yellow prisms on crystallisation (from absolute ethanol), m.p. 181—183 °C (Found: C, 70.1; H, 5.0; N, 6.05. $C_{27}H_{23}BF_4N_2$ requires C, 70.2; H, 5.0; N, 6.1%); $\nu_{max.}$($CHBr_3$) 1 610s and 1 050s,br; δ($CDCl_3$–TFA) 2.7 (2 H, m), 3.8—4.9 (5 H, m), and 7.1—8.2 (16 H, m); $\lambda_{max.}$(MeOH) (ε) 242 (15 120) and 361 (8 980).

General Procedure for the Thermolysis of the Adducts (**8**).—The pyridinium ethanol (**8**) (5 mmol) was refluxed with stirring

in chlorobenzene (50 ml) for 1.5—2 h, after which the mixture was cooled and ether added to precipitate 2,4,6-triphenylpyridinium tetrafluoroborate. Solvent was removed under reduced pressure (50 °C, 20 mmHg) and ether was added to afford further 1*H*-pyridinium salt; HBF_4 (48%, excess) was added to the stirred suspension to precipitate the remaining 2,4,6-triphenylpyridine. After filtration the solution was washed with water (20 ml), the organic layer dried ($MgSO_4$), the solvent evaporated, and the remaining oil distilled under reduced pressure.

(i) Thermolysis of (**8b**) gave 2-(2-chlorophenyl)but-2-enal (**17b**), 2-chlorophenylprop-1-enyl ketone (**18b**) and 2-chlorobenzaldehyde (traces) in 56% yield; b.p. 80 °C/0.7 mmHg; $\nu_{max.}$ 1 690s and 1 640m; $\delta(CDCl_3)$ 1.85 [d, CH_3–C=, (**17b**), (**18b**)], 7.6—6.5 (aromatic-H), and 9.8 (s, CHO); $\delta_C(CDCl_3)$ 15.5 [q, (**17b**)], 18.2 [q, (**18b**)], 126.3d, 129.1d, 130.9d, 143.1s, 147.6d, 152.0d, and 191.7 (d, C*H*O). The ratio (**17b**):(**18b**) was 80:20. G.c./mass spectroscopy, *m/z* for (**17b**) 182 (1.6), 180 (4.7), 145 (100), 117 (28.8), 116 (47.1), 115 (70.9), 89 (12.7), 75 (8.7), 63 (16), and 39 (19.9); *m/z* for (**18b**) 182 (4.1), 180 (11.9), 145 (39.1), 141 (14.1), 139 (51.5), 113 (7.2), 111 (20.3), 75 (21.8), 69 (100), and 41 (41.9).

(ii) The thermolysis of (**8d**) gave 2-(3-nitrophenyl)but-2-enal (**17d**) and 3-nitrophenyl prop-1-enyl ketone (**18d**) together with unidentified products; b.p. 160 °C/3.5 mmHg, $\nu_{max.}$ 1 690s, 1 675s, 1 620s, 1 530s, and 1 350s; $\delta(CDCl_3)$ 2.05 [CH_3–C= (**17d**), (**18d**)], 8.9—6.8 (aromatic-H), and 9.8 (s, CHO). The ratio (**17d**):(**18d**) was 46:54. The mixture could not be separated by g.c./mass spectroscopy.

(iii) From the thermolysis of (**8e**), 2-(2-methylphenyl)but-2-enal (**17e**) was obtained in 61% yield; b.p. 176—178 °C/2.2 mmHg; $\nu_{max.}(CHBr_3)$ 1 690s and 1 630m; $\delta(CDCl_3)$ 1.8 (d, 3 H, *J* 7 Hz), 2.1 (s, 3 H), 6.7—7.4 (m, 5 H), and 9.7 (s, 1 H); $\delta_C(CDCl_3)$ 15.6 (q, CH_3C=), 19.3 (q, CH_3–Ar), 125.4d, 127.9d, 129.3d, 129.8d, 132.3s, 136.2s, 145.6s, 151.3d, and 192.9 (d, CHO) (Found: M^+, 160.0879. Calc. for $C_{11}H_{12}O$: M^+, 160.0888).

General Procedure for the Thermolysis of the Adducts (**7**).—The pyridinium ethanol (**7**) (1 mmol) was heated at 230 °C for 20—60 min. On cooling the residue was triturated with ether, until crystallisation occurred.

(i) 6,7-*Dihydro*-2,4,7-*triphenylbenzo*[a]*quinolizinium tetrafluoroborate* (**19a**). This was obtained from (**7a**) in 54% yield (time 60 min), m.p. 141—144 °C, needles (from acetone–ether) (Found: C, 74.9; H, 4.9; N, 2.8. $C_{31}H_{24}BF_4N$ requires C, 74.9; H, 4.8; N, 2.8%); $\nu_{max.}(CHBr_3)$ 1 625s and 1 050s,br; $\delta(CDCl_3$–TFA) 4.3—5.1 (3 H, m), 6.7—8.4 (20 H, m), and 8.5 (1 H, m); $\delta_C(CDCl_3$–TFA) 40.8 (C-7), 55.6 (C-6), and 120.5—155.2 (aromatic-C).

(ii) 7-(2-*Chlorophenyl*)-6,7-*dihydro*-2,4-*diphenylbenzo*[a]*quinolizinium tetrafluoroborate* (**19b**). This was prepared from (**7b**) in 25% yield (time 20 min), m.p. 268—270 °C, needles (from ethanol) (Found: C, 69.7; H, 4.3; N, 2.4. $C_{31}H_{23}BClF_4N$ requires C, 70.0; H, 4.3; N, 2.6%); $\nu_{max.}$ 1 625s and 1 050s,br; $\delta[(CD_3)_2SO]$ 4.4—5.4 (3 H, m), 6.7—7.10 (1 H, m), 7.1—8.1 (14 H, m), 8.4 (3 H, m), 8.85 (1 H, m), and 9.15 (1 H, br); $\delta_C[(CD_3)_2SO]$ 38.4 (C-7), 53.6 (C-6), and 120.7—155.2 (aromatic-C).

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