Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 10.[1] Reactions of s-Alkyl Primary Amines with Pyryliums

Alan R. Katritzky,* Jorge Marquet, Jeremy M. Lloyd, and James G. Keay
Department of Chemistry, University of Florida, Gainesville, Florida 32611, U.S.A.

2,4,6-Triphenylpyrylium with s-alkylamines gives isolatable pyridiniums (which undergo S_N2 substitution with nucleophiles and elimination to olefins). 2,4,6-Triphenylpyrylium with 1-phenylethylamine and α-phenylbenzylamine forms the corresponding carbonium ions which may be trapped by nucleophiles. Isolated 1-cycloalkylbenzoquinoliniums (2) solvolyse by the S_N1 mechanism (for five-, six-, and seven-membered rings) : for the cyclobutyl case an S_N2 reaction is also found.

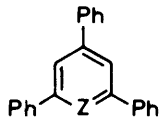
While most of our previously reported [2] extensive work on the pyrylium-mediated conversion of primary amino-groups into other functionality has involved primary alkyl primary amines, some examples involving secondary alkyl primary amines have been described.[3] Thus, isopropylamine and s-butylamine were converted into the corresponding iodides (79 and 83%, respectively) *via* 2,4,6-triphenylpyridinium iodides,[4] although 1-cyclohexyl-2,4,6-triphenylpyridinium iodide gave predominantly cyclohexene. 1-Isopropyl-2,4,6-triphenylpyridinium tetrafluoroborate with sodium *N*-phenylbenzenesulphonamide gave *N*-isopropyl-*N*-phenylbenzenesulphonamide (33%).[5] *C*-Substituted nitroalkanes were obtained [6] from 1-isopropyl-2,4,6-triphenylpyridinium tetrafluoroborate with the 2-nitropropane anion (52%) and from 1-cyclohexyl-2,4,6-triphenylpyridinium tetrafluoroborate with nitroethane and 2-nitropropane anions (33 and 48%, respectively). 1-Cyclohexyl-2,4,6-triphenylpyridinium tetrafluoroborate formed cyclohexanone (44%) [7] on refluxing with bis(tetra-n-butylammonium)dichromate and 1-(1-hydroxymethyl-1-methylpropyl)-2,4,6-triphenylpyridinium trifluoromethanesulphonate produced butyraldehyde *via* 1,2-hydrogen migration.[8] Kinetically we have shown that pyridiniums derived from secondary alkyl primary amines react in part by S_N1 mechanisms.[9]

We now report the results of a general investigation of the reaction of secondary alkyl primary amines with pyryliums, with study of further reactions of pyridiniums when isolated, and the products of spontaneous break-down when not isolated.

Preparation of Pyridiniums and Reaction of Isolated Pyridinium Salts.—Pyryliums and amines gave the pyridiniums by standard procedures [10] (see Experimental section) in good yields (Table 1).

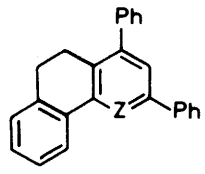
Although attempts to obtain olefins from 1-(n-alkyl)-2,4,6-pyridiniums have failed to give good results,[11] we now find that the corresponding 1-(s-alkyl) derivatives do give olefins in rather good yields. Thus, 1-cyclopentyl- (1i) and 1-cyclohexyl-2,4,6-triphenylpyridinium tetrafluoroborate (1j) when heated at 180 °C with 2,4,6-triphenylpyridine (non-nucleophilic base) gave cyclopentane (78%) and cyclohexane (79%), respectively.

Nevertheless, it was still possible to carry out substitution reactions, *e.g.* with tertiary amines as previously demonstrated [12] for the 1-(n-alkyl)analogues. Thus, on heating in pyridine, the *N*-isopropyl (1d) and *N*-s-butyl compounds (1e) gave mainly substituted products (3a and b) in 63 and 56% isolated yield, respectively. However, for the *N*-cyclopentyl (1i) and *N*-cyclohexyl derivatives (1j), similar treatment led to greater proportions of elimination (Table 2).[3]



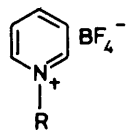
(1)

a; Z = O$^+$
b; Z = N
c; Z = N$^+$pinan-3-ylmethyl
d; Z = N$^+$Pr^i
e; Z = N$^+$Bu^s
f; Z = N$^+$s-C_7H_{15}



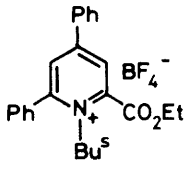
(2)

g; Z = N$^+$cyclo-C_3H_5
h; Z = N$^+$cyclo-C_4H_7
i; Z = N$^+$cyclo-C_5H_9
j; Z = N$^+$cyclo-C_6H_{11}
k; Z = N$^+$cyclo-C_7H_{13}
l; Z = N$^+$CHPhMe



(3)

a; R = Pr^i
b; R = Bu^s
c; R = cyclo-C_5H_9
d; R = cyclo-C_6H_{11}
e; R = CHMePh

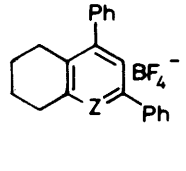


(4)

PhCH(CH$_3$)–R′ Ph$_2$CH–R′

(6) (7)

a; R′ = EtO
b; R′ = Pr^{i}O
c; R′ = EtOCH$_2$CH$_2$O
d; R′ = p-CH$_3$C$_6$H$_4$O
e; R′ = CH$_3$CO$_2$
f; R′ = p-Me$_2$NC$_6$H$_4$



(5)

a; Z = O$^+$
b; Z = N$^+$CHPhMe

Unbranched secondary halides give quite poor yields of olefin in *E*1 reactions, *e.g.* varying from 5% for isopropyl to 15% for 1-ethylpropyl bromide in 60% aqueous ethanol at 80 °C.[13] The relatively high proportions of olefin formed in the present work (≥22%) suggest considerable bimolecular character.

Under second-order conditions, steric hindrance to nucleophilic attack is a factor. For example β-branching increases *E*2 with respect to S_N2, as the latter is so greatly slowed.[14]

Table 1. Preparation of *N*-substituted pyridinium salts

Compd.	Anion	Recrystallisation solvent	M.p. (°C)	Yield (%)	Preparative method	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(1d)	BF_4	Acetone–ether	187—189	88	B		*a*					
(1e)	BF_4	Acetone–ether	165—167	84	B		*a*					
	SCN	Ethanol	142—145	66	B	79.5	6.2	6.6	$C_{28}H_{26}N_2S$	79.2	6.2	6.6
	Cl	Acetone–ether	127—130	60	D		*b*		$C_{27}H_{26}ClN$			
(1f)	BF_4	Ethanol–ether	160—161	67	B	73.1	6.6	2.8	$C_{30}H_{32}BF_4N$	73.0	6.5	2.8
(1g)	BF_4	Ethanol	134—137	82	B	71.7	5.1	3.2	$C_{26}H_{22}BF_4N$	71.7	5.1	3.2
(1i)	BF_4	Acetone–ether	163—164	91	B		*a*					
(1j)	BF_4	Acetone–ether	179—180	79	B		*a*					
	SCN	Ethanol	151—153	47	B	80.2	6.3	6.2	$C_{30}H_{28}N_2S$	80.3	6.3	6.2
	Cl	Acetone–ether	127—131	60	D		*b*		$C_{29}H_{28}ClN$			
(1k)	BF_4	Ethanol–ether	168—170	81	B		*a*					
(1c)	BF_4	Ethanol–hexane	142—145	75	B	74.7	6.7	2.5	$C_{34}H_{36}NBF_4$	74.9	6.7	2.6
(2e)	ClO_4	*c*	141—143	69	C		*a*					
	BF_4	Acetone–ether	130—132	71	C	72.9	5.9	2.9	$C_{27}H_{28}NBF_4$	73.0	5.9	2.9
(2g)	BF_4	Acetone–ether	150—153	63	C	72.7	5.3	3.0	$C_{28}H_{24}NBF_4$	72.9	5.2	3.0
(2h)	BF_4	Acetone–ether	165—167	60	C	73.1	5.5	2.9	$C_{29}H_{26}NBF_4$	73.3	5.5	2.9
(2i)	BF_4	Acetone–ether	208—212	50	C	73.5	5.8	2.8	$C_{30}H_{28}NBF_4$	73.6	5.8	2.9
(2j)	BF_4	Acetone–ether	136—139	61	C	73.9	6.0	2.7	$C_{31}H_{30}NBF_4$	74.0	6.0	2.8
(2k)	BF_4	Acetone–ether	211—214	41	C	74.1	6.2	2.7	$C_{32}H_{32}NBF_4$	74.3	6.2	2.7
(4e)	BF_4	Ethanol	134—135	68	B	64.4	5.9	3.1	$C_{24}H_{26}BF_4NO_2$	64.4	5.9	3.1
(5b)	BF_4	*c*	112—114	45	A	72.8	5.9	2.9	$C_{29}H_{28}BF_4N$	73.0	5.9	2.9

[a] Previously reported in ref. 9. [b] Too hygroscopic to get a good analysis. [c] Analytically pure without recrystallisation.

Table 2. Reactions of 1-(s-alkyl)-2,4,6-triphenylpyridinium tetrafluoroborates with pyridine

	^1H N.m.r.[a] of mixtures of 1-(s alkyl)pyridinium and pyridinium salts				
	Pyridinium protons [b]			Aliphatic protons [c] Other signals	Measured corresponding
N Substituent	δ	Area (5 H)	α-CH (δ)	δ	Area	Area (5 H)
Isopropyl	7.7—9.5	21.8	5.0 (1 H, m, *J* 7 Hz)	1.6 (6 H, d, *J* 7 Hz)	20.5 (6 H)	17.1
s-Butyl	7.7—9.4	7.4	5.0 (1 H, m)	1.4—2.3 (2 H) 1.65 (3 H, d, *J* 6 Hz) 0.75 (3 H, t, *J* 7.5 Hz)	2.6 (3 H)	4.3
Cyclopentyl	7.4—9.3	27.5	5.15 (1 H, m)	1.2—2.4 (8 H)	12.5 (8 H)	7.8
Cyclohexyl	7.9—9.3	23.25	4.7 (1 H, m)	1.1—2.4 (10 H)	2.5 (10 H)	17.5

	Proportion (%)		Yield (%)	
	1-(s-alkyl)[d] pyridinium salt	Pyridinium salt	1-(s-alkyl) pyridinium salt	Pyridinium salt
Isopropyl	78	22	65	18
s-Butyl	58	42	*e*	*e*
Cyclopentyl	28	72	16	42
Cyclohexyl	8	92	4	51

[a] In $(CD_3)_2SO$. [b] Of both 1-(s-alkyl)pyridinium and pyridinium salts. [c] Of 1-(s-alkyl)pyridinium salt. [d] Calculated from the area corresponding to 5 H for 1-(s-alkyl)pyridinium salt and the total area of the signal due to the pyridinium protons. [e] Precipitation with diethyl ether led to a non-crystalline gummy solid which was not weighed.

Table 3. ^{13}C N.m.r. chemical shifts (p.p.m.) of reaction products from 1-phenylethylamine and 2,4,6-triphenylpyrylium tetrafluoroborate (1a) in $CDCl_3$

	Products						
	2,4,6-Triphenylpyridine		PhCHOHMe		$PhCH=CH_2$	$(C_5H_5NCHPhMe)^+$	
Reactants	C-α	C-γ	CH	Me	CH_2	CH	Me
1-Phenylethylamine	157.2	149.9	70.0	24.9	113.5		
(Literature values)	157.3 [a]	149.9 [a]	69.9 [b]	25.0 [b]	113.5 [c]	64.8 [d]	19.6 [d]
1-Phenylethylamine + pyridine	157.0	149.8	—	—	113.5	70.6	19.8

[a] A. R. Katritzky, J. M. Lloyd, and R. C. Patel, *Chem. Scr.*, 1981, **18**, 256. [b] L. F. Johnson and W. C. Jankowski, 'Carbon-13 N.M.R. Spectra,' Wiley, New York, 1972. [c] Ref. 17. [d] Values for 1-(1-phenylethyl)-5,6,7,8-tetrahydro-2,4-diphenylquinolinium tetrafluoroborate (6b).

Table. 4. Solvent trapping of carbonium ions formed from amines and pyrylium salts

Solvent (R'H)	Amine (RNH_2)	Pyrylium salt	Preparation Method	Time (h)	Product	Yield (%)
Ethanol	$PhCH(Me)NH_2$	$(1a)ClO_4^-$	E	72	(6a)	44
Propan-2-ol	$PhCH(Me)NH_2$	$(1a)ClO_4^-$	E	72	(6b)	51
2-Ethoxyethanol	$PhCH(Me)NH_2$	$(1a)ClO_4^-$	E	72	(6c)	47
p-Cresol	$PhCH(Me)NH_2$	$(1a)ClO_4^-$	F	72	(6d)	25
Acetic acid–NEt_3 [b]	$PhCH(Me)NH_2$	$(1a)ClO_4^-$	G	48	(6e)	89
NN-Dimethylaniline	$PhCH(Me)NH_2$	$(1a)ClO_4^-$	E	72	(6f)	38
Ethanol	Ph_2CHNH_2	$(1a)ClO_4^-$	E	72	(7a)	24
Acetic acid–NEt_3 [b]	Ph_2CHNH_2	$(1a)ClO_4^-$	G	168	(7e)	27

Solvent (R'H)	B.p. (°C)/*p* (mmHg)	Found (%) C	H	Formula	Required (%) C	H
Ethanol	95—98/24 [a]			$C_{10}H_{14}O$		
Propan-2-ol	108—112/23 [a]			$C_{11}H_{16}O$		
2-Ethoxyethanol	124—128/24	74.3	9.35	$C_{12}H_{18}O_2$	74.2	9.35
p-Cresol	*c*	85.0	7.6	$C_{15}H_{16}O$	84.9	7.6
Acetic acid–NEt_3 [b]	47—48/0.25 [d]	73.1	7.4	$C_{10}H_{12}O_2$	73.1	7.3
NN-Dimethylaniline	132—135/0.55 [e]	85.6	8.2	$C_{16}H_{19}N$	85.2	8.5
Ethanol	95—98/0.45 [f]			$C_{15}H_{16}O$		
Acetic acid–NEt_3 [b]	108—110/0.20 [g]	79.6	6.2	$C_{15}H_{14}O_2$	79.6	6.25

[a] S. Mamedov, D. N. Khydyrov, and Z. Seid-Rzaeva, *J. Gen. Chem. USSR*, 1963, **33**, 1152; (6a) b.p. 53—54 °C at 5 mmHg, (6b) 56—57 °C at 5 mmHg. [b] In 3 : 2 mol ratio. [c] H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, 1954, **76**, 519; m.p. 49—50 °C. [d] A. McKillop and M. E. Ford, *Tetrahedron*, 1974, **30**, 2467; b.p. 210—212 °C. [e] D. A. Archer, H. Booth, and R. D. Stangroom, *J. Chem. Soc. C*, 1970, 2776; b.p. 120 °C at 0.2 mmHg. [f] K. G. Rutherford, O. A. Mamer, J. M. Prokipcak, and R. A. Jobin, *Can. J. Chem.*, 1966, **44**, 2337; b.p. 160—161 °C at 19 mmHg. [g] Footnote *d*, m.p. 40 °C.

Presumably this explains the present trend of increasing elimination, isopropyl < s-butyl < cyclopentyl < cyclohexyl, although it may also be significant that isopropyl which gives the highest yield of substitution can only give a monosubstituted ethylene whereas all the others can give di-substituted ethylenes.[15]

The formation of substantial amounts of substitution products using pyridine, which is a relatively poor nucleophile, indicates that with better nucleophiles substitution should be easier. This is now confirmed in experiments with sulphur nucleophiles. Pyrolysis of 1-(s-butyl)- (1e) and 1-cyclohexyl-2,4,6-triphenylpyridinium thiocyanate (1j) each gave mixtures of the corresponding s-alkyl thiocyanate and isothiocyanate in *ca.* 70 : 30 ratio, in overall yields of 90 and 40%, respectively. However, mainly elimination occurred on pyrolysis of the 1-s-alkylpyridinium chlorides: from the 1-cyclohexyl derivative cyclohexene (90%) was isolated.

We have previously reported that s-alkyl groups could be transferred from pyridiniums to nitroalkane anions.[6,16] We now find that 1-cycloheptyl-2,4,6-triphenylpyridinium tetrafluoroborate (1k) reacts in a radicaloid reaction [16] with nitromethane anion to form nitromethylcycloheptane (41%).

Solvolysis of 1-(s-butyl)-5,6-dihydro-2,4-diphenylbenzo[*h*]-quinolinium tetrafluoroborate (2e) in *p*-cresol at 125 °C gave a mixture (1 : 2) of *p*-tolyl s-butyl ether and 2-s-butyl-*p*-cresol (50%).

Reaction involving Capture of Carbonium Ions.—The reactions of 1-phenylethylamine with various 2,4,6-triphenylpyrylium salts were studied by ^{13}C n.m.r. (Table 3). In the absence of added nucleophile the main product was the alcohol PhCH(Me)OH, presumably formed by reaction of the carbonium ion with the water released in the reaction. A trace of styrene was also detected in the reaction mixture. In the presence of pyridine, the main product was the pyridinium salt (3e); again a trace of styrene was found. In the presence of other nucleophiles such as halides or SCN^-, complex spectra indicated the formation of a variety of products.

The experiments just described provided strong evidence for the spontaneous formation of carbonium ions in the reaction of α-phenylethylamine and triphenylpyrylium. It was possible to trap this carbonium ion and the carbonium ion from α-phenylbenzylamine preparatively under suitable conditions (Table 4). Thus the use of primary or secondary alcohols as reaction solvent at 25 °C led to the isolation of ethers (6a—c) and (7a) in moderate yield. *p*-Cresol gave the *O*-alkylated product (6d) (25%), and any *C*-alkylated products were presumably extracted from the reaction mixture with 5M-NaOH solution. *NN*-Dimethylaniline gave a 38% yield of 1-(4-dimethylaminophenyl)-1-phenylethane (6f). Use of a 1 : 5 : 1 mol ratio of acetic acid–triethylamine as solvent resulted in the formation of 1-phenylethyl acetate (6e) and α-phenylbenzyl acetate, respectively.

All the above compounds, gave satisfactory physical and spectral data (see Tables 4 and 5).

Kinetic Studies.—Kinetic data (Table 7), obtained utilizing the u.v. method (*cf.* Table 6) as previously reported,[17] showed that the 1-s-alkyldihydrobenzoquinoliniums (2) reacted with piperidine in chlorobenzene solution by the S_N2 and/or S_N1 mechanism with the rate constants given in Table 8. Within experimental uncertainties, the cyclo-pentyl, -hexyl, and -heptyl compounds all react exclusively by the S_N1 mechanism; for the cyclobutyl analogue, the much slower S_N1 rate enables the S_N2 rate for this compound also to be measured.

Table 9 compares the S_N1 rate for the compounds investigated with literature data. The benzoquinolinium (2b) is a better S_N1 leaving group for these secondary alkyl substituents by a factor of over 100 than triphenylpyridine (1b). Comparison of the products results with those for the solvolysis in acetic acid of secondary tosylates, shows for the isopropyl, cyclopentyl, and cyclohexyl substrates a rough correspondence in rates (at 60 °C) with those for the triphenylpyridinium (at 100 °C): however, the small difference in rate between the cyclopentyl and cyclobutyl tosylates [18,19] contrasts with the much slower relative rate for cyclobutyl among the

Table 5. I.r. and ^1H n.m.r. data for solvolysis products (6) and (7)

Product	^1H n.m.r. (δ) [a] Aromatic	Methine	Methyl	Other signals	(ν$_{max.}$/cm^{-1}) [b] Principal bands
(6a)	7.27	4.23 [c]	1.37 [d]	1.13 (3 H, t), 3.32 (2 H, q)	1 275, 1 070
(6b)	7.28	4.50 [c]	1.38 [d]	1.07 and 1.13 (6 H, dd), 3.47 (1 H, m)	1 276, 1 056
(6c)	7.19	4.33 [c]	1.32 [d]	1.05 (3 H, t), 3.37 (6 H, m)	1 277, 1 050
(6d)	7.15—7.40	5.26 [c]	1.59 [d]	2.20 (3 H, s), 6.76 and 7.00 (4 H, ABq)	1 290, 1 075
(6e)	7.32	5.87 [c]	1.47 [d]	1.97 (3 H, s)	1 740 [e]
(6f)	7.18	4.08 [c]	1.56 [d]	2.81 (6 H, s), 6.62 and 7.07 (4 H, ABq)	816 [f]
(7a)	7.25—7.45	5.37		1.25 (3 H, t), 3.54 (2 H, q)	1 275, 1 072
(7c)	7.19—7.52	6.93		2.10 (3 H, s)	1 275, 1 740 [e]

[a] In $CDCl_3$. [b] Liquid film. [c] q, *J* 6.5 Hz. [d] d, *J* 6.5 Hz. [e] ν(C=O). [f] Approximate value, masked by methylene signals.

Table 6. U.v. spectral data (EtOH solution) for 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoliniums [a]

Compd.	λ$_{max.}$ nm	ε	Kinetic values nm	ε
(2k)	341	19 200	360	13 800
(2j)	347 [b]	18 500 [b]	360	11 500 [b]
(2i)	352	17 000	360	14 500
(2h)	326	18 900	360	18 800
(2g)	353	19 200	360	18 100

[a] At the kinetic wavelength (360 nm), 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoline has zero absorption (in chlorobenzene solution). [b] In chlorobenzene solution.

Table 7. Pseudo-first-order rate constants (k_{obs}) for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoliniums with piperidine in chlorobenzene

1-cyclohexyl (2j) [a] (100 °C) 10^3[Piperidine]/mol l^{-1}	10$^5k_{obs}$/s^{-1}	1-cyclopentyl (2i) [a] (100 °C) 10^3[Piperidine]/mol l^{-1}	10$^5k_{obs}$/s^{-1}
0.960	490.5	0.960	1 186
1.92	511.3	9.60	1 085
4.80	524.5	96.0	1 002
9.60	521.4	240	1 056
96.0	456.5	480	981
240	491.2		
480	460.1		

1-cycloheptyl (2k) [a] (100 °C) 10^3[Piperidine]/mol l^{-1}	10$^5k_{obs}$/s^{-1}	1-cyclobutyl (2h) [b] (100 °C) 10^3[Piperidine]/mol l^{-1}	10$^5k_{obs}$/s^{-1}
0.960	1 132	96.0	3.97
9.60	1 079	240	4.62
96.0	1 026	480	6.11
240	1 074	960	9.03

[a] Concentration 9.60×10^{-5} mol l^{-1}. [b] Concentration 0.003 00 mol l^{-1}.

benzoquinoliniums (2). This behaviour is indicative of the S_N2 character of the tosylate solvolysis.[20]

Comparison of the present results with those for the solvolysis of the corresponding tertiary chlorides in methanol (at 25 °C) again discloses rates of the same order of magnitude as the triphenylpyridiniums (at 100 °C). Again, the comparatively high relative rate for the cyclobutyl derivative indicates considerable solvent assistance in these reactions, as previously pointed out.[20]

In all the series, the rates are similar for the cyclopentyl and cycloheptyl derivatives. The rates for the cyclohexyl analogues are lower, by small factors (2—8) for the heterocyclic leaving groups, longer for the tosylates (16) and still more for the chlorides (100). The cyclopentyl and cycloheptyl derivatives relieve *I* strain (mainly eclipsing strain) when the cation is formed,[21] being this effect larger for the tertiary (*i.e.* chlorides in Table 9) than for the secondary compounds. This effect is absent in the corresponding cyclohexyl derivative.

Experimental

M.p.s were determined with a Reichert apparatus and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer model 137 or 238B grating spectrophotometer, and ^1H n.m.r. spectra with a Varian model A-60A, a Varian model EM 360L or a JEOL model JNM-PMX60 60 MHz spectrometer (Me_4Si as internal standard). ^{13}C N.m.r. spectra were recorded with a JEOL model JNM-FX 100 spectrometer operating in the Fourier transform mode at 25.05 MHz and locked to the deuterium resonance of the solvent ($CDCl_3$). Typical spectral conditions were: 6 kHz width, 8 K data giving a digital resolution of 0.05 p.p.m.; pulse width 5 μs (30°); repetition time of 1 s. Chemical shifts in p.p.m. relative to Me_4Si were calculated by adding 76.9 p.p.m. to the shift measured relative to the centre peak of $CDCl_3$.[22]

Preparation of Pyryliums.—5,6,7,8-Tetrahydro-2,4-diphenylchromenylium (5a) tetrafluoroborate was obtained from Urögdi [23] and 5,6-dihydro-2,4-diphenylbenzo[*h*]chromenylium (2a) perchlorate from Thind.[24] The following were prepared by literature methods: 2,4,6-triphenylpyrylium (1a) tetrafluoroborate, m.p. 251—253 °C (lit.,[25] 253—255 °C); 2,4,6-triphenylpyrylium (1a) chloride, m.p. 217—221 °C (lit.,[26] 220—225 °C); 2,4,6-triphenylpyrylium (1a) thiocyanate, m.p. 190—191 °C (lit.,[27] 192 °C); and 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate, m.p. 153—156 °C (lit.,[28] 155—157 °C).

Preparation of Pyridinium Salts [10] (*Table* 1).—*Method A.* 5,6,7,8-Tetrahydro-2,4-diphenylchromenylium tetrafluoroborate (5a) (0.50 g, 0.0013 mol) and 1-phenylethylamine (0.32 g, 0.0026 mol) were stirred in CH_2Cl_2 (3.5 ml). Addition of Et_2O (50 ml) and washing with saturated aqueous sodium hydrogencarbonate gave the product.

Method B. 2,4,6-Triphenylpyrylium tetrafluoroborate (1a) (1.00 g, 0.0025 mol) and isopropylamine (0.30 g, 0.005 mol) were stirred in CH_2Cl_2 (7 ml) for 5 min. AcOH (0.30 g, 0.005 mol) was added and the mixture stirred for 1 h. Addition of Et_2O (50 ml) gave the product.

Method C. 5,6-Dihydro-2,4-diphenylbenzo[*h*]chromenylium perchlorate (2a) (1.00 g, 0.0023 mol), s-butylamine (0.17 g, 0.0023 mol), and Et_3N (0.23 g, 0.0023 mol) were stirred in CH_2Cl_2 (7 ml) for 0.5 h. AcOH (0.28 g, 0.0046 mol) was

Table 8. First- (k_1) and second- (k_2) order rate constants for the reactions of *N*-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoliniums with piperidine in chlorobenzene at 100 °C

Compd.	Slope 10^3k_2/l mol^{-1} s^{-1} [a]	% Error	Intercept 10^5k_1/s^{-1}	% Error	$\frac{10^3k_1}{[k_2 + 10k_1]}$ [b]
(2k)	<5 (−1.6 ± 7.3)		1 090 ± 100	8	>95
(2j)	<0.1 (−1.0 ± 1.0)		505 ± 21	4	>99.9
(2i)	<1 (−2.8 ± 3.5)		1 110 ± 90	8	>99
(2h)	0.0593 ± 0.0049	8	3.29 ± 0.27	8	85

[a] Values in parentheses not significantly different from zero. [b] *i.e.* % reaction by S_N1 route at [piperidine] 10^{-1} mol l^{-1}.

Table 9. Comparison of S_N1 rate constants for reactions of *N*-cycloalkylpyridiniums with those for cycloalkyl chlorides and tosylates

	Absolute rates ($s^{-1} \times 10^5$)				Relative rates (Me_2CRX = 1)			
R =	Me	H	H Triphenyl-	H Benzo-	Me	H	H Triphenyl-	H Benzo-
X =	Cl	OTs	pyridine	quinoline	Cl	OTs	pyridine	quinoline
Solvent	80% EtOH	AcOH	PhCl	PhCl	80% EtOH	AcOH	PhCl	PhCl
T (°C)	25	60	100	100	25	60	100	100
Reference	25	26	8	*a*	25	26, 27	8	*a*
Me_2CRX	0.91	0.98	0.72	112	1	1	1	1
$(CH_2)_3CRX$	0.9	13.8		3.29	1	14		0.03
$(CH_2)_4CRX$	38.3	15.8	25.4	1 110	44	16	35	10
$(CH_2)_5CRX$	0.31	0.98	3.1	505	0.35	1	4	5
$(CH_2)_6CRX$	41.7	30.5		1 090	38	31		10

[a] This paper.

added and the mixture stirred for 4 h. Addition of Et_2O (50 ml) and washing with saturated aqueous sodium hydrogencarbonate gave the product.

Method D. 2,4,6-Triphenylpyrylium chloride (1a) (2.00 g, 0.0058 mol) in super-dry EtOH was mixed with s-butylamine (1.05 g, 0.0145 mol) in sodium-dried benzene. This mixture was warmed for 5 min and AcOH (0.87 g, 0.0145 mol) was added. The mixture was refluxed for 8 h, using molecular sieves (4 Å, 20 g) in a Soxhlet extractor to remove the water. After cooling, the solvent was evaporated, and the residue in CH_2Cl_2 (20 ml) extracted with water; the dried ($MgSO_4$) organic layer was evaporated. Trituration of the residue with Et_2O gave the product.

Cyclopentene.—1-Cyclopentyl-2,4,6-triphenylpyridinium tetrafluoroborate (1j) (2.00 g, 0.0043 mol) and 2,4,6-triphenylpyridine (1b) (2.65 g, 0.0086 mol) were heated at 178 °C and 200 mmHg to give cyclopentene (0.23 g, 78%) (collected in a trap at −78 °C) with i.r. and ^{1}H n.m.r. spectra identical with the literature; [29] $\nu_{max.}$ (liquid film) 3 060, 2 935, 2 855, 1 616, 1 468, 1 352, 1 337, 1 209, 1 047, 1 029, 907, and 700 cm^{-1}; δ ($CDCl_3$) 5.8 (2 H, s), 2.1—2.6 (4 H), and 1.5—2.1 (2 H).

Cyclohexene.—1-Cyclohexyl-2,4,6-triphenylpyridinium tetrafluoroborate (1j) (2.00 g, 0.0042 mol) and 2,4,6-triphenylpyridine (1b) (2.57 g, 0.0084 mol) at 185 °C and 200 mmHg similarly gave cyclohexene (0.27 g, 79%); i.r. and ^{1}H n.m.r. spectra identical with the literature; [17] $\nu_{max.}$ (liquid film) 3 080, 2 990, 2 925, 1 659, 1 449, 1 322, 1 139, 919, 720, and 642 cm^{-1}; δ ($CDCl_3$) 5.7 (2 H, s), 1.8—2.2 (4 H), and 1.5—1.8 (4 H).

Reactions of 1-(s-Alkyl)-2,4,6-triphenylpyridinium Tetrafluoroborates with Pyridine.—1-(s-Alkyl)-2,4,6-triphenylpyridinium tetrafluoroborates (1.00 g) and pyridine (3 ml) were refluxed for 3 h. Diethyl ether (15 ml) gave a precipitate shown by ^{1}H n.m.r. to contain 1-(s-alkyl)pyridinium tetrafluoroborate and pyridinium tetrafluoroborate (Table 2).

1-Isopropylpyridinium tetrafluoroborate. 1-Isopropyl-2,4,6-triphenylpyridinium tetrafluoroborate (1d) (2.00 g, 0.0046 mol) and pyridine (2 ml) were refluxed for 3 h. Diethyl ether gave a precipitate (0.764 g). After washing with 1M-sodium methoxide in methanol (1.2 ml), the *pyridinium tetrafluoroborate* (3a) (0.604 g, 63%) crystallised on trituration with diethyl ether; it recrystallised from ethanol as plates, m.p. 83—84 °C (Found: C, 46.0; H, 5.8; N, 6.7. $C_8H_{12}BF_4N$ requires C, 45.9; H, 5.7; N, 6.7%); $\nu_{max.}$ ($CHBr_3$) 3 050, 1 630, 1 581, 1 499, 1 425, and 1 020—1 090 cm^{-1}; δ[$(CD_3)_2SO$] 7.9—9.4 (5 H), 5.0 (1 H, m, *J ca.* 7 Hz), and 1.6 (6 H, d, *J ca.* 7 Hz).

1-s-Butylpyridinium tetrafluoroborate. 1-s-Butyl-2,4,6-triphenylpyridinium tetrafluoroborate (1e) (2.00 g, 0.0044 mol) and pyridine (2 ml) were heated under reflux, for 3 h. Addition of diethyl ether gave the pyridinium tetrafluoroborate (3b) which on trituration with diethyl ether crystallised but which resisted recrystallisation. The yield estimated by n.m.r. was 0.56 g (56%), $\nu_{max.}$ (liquid film) 3 080 (w), 2 980 (w), 1 631 (m), 1 484 (s), 1 458 (m), 1 065 (s), 778 (m), and 682 (m) cm^{-1}, δ [$(CD_3)_2SO$] 8.1—9.7 (5 H), 5.0 (1 H, m), 1.4—2.3 (2 H), 1.65 (3 H, d, *J ca.* 6 Hz), and 0.75 (3 H, t, *J ca.* 7.5 Hz).

Pyrolysis of 1-(s-Butyl)-2,4,6-triphenylpyridinium (1e) *Thiocyanate.*—The pyrolysis of (1e) thiocyanate (1 g, 0.0024 mol) at 170 °C and 1 mmHg using triphenylpyridine (1 g) as a flux gave a mixture (70 : 30) (0.284 g, 90%) of s-butyl thiocyanate, δ ($CDCl_3$) 3.25 (1 H, q, *J ca.* 6 Hz), 2.0—1.5 (2 H), 1.5 (3 H, d, *J ca.* 6 Hz), 1.02 (3 H, t, *J* 6 Hz), and isothiocyanate, δ ($CDCl_3$) 3.75 (1 H, q, *J ca.* 6 Hz), 2.0—1.5 (2 H, 1.35 (3 H, d, *J* 6 Hz), and 1.00 (3 H, t, *J ca.* 6 Hz); $\nu_{max.}$ ($CHBr_3$) (mixture) 2 150 (s), 2 150—2 000 cm^{-1}. The i.r. and ^{1}H n.m.r. spectra of the mixture showed all the bands expected for s-butyl thiocyanate (compared with an authentic sample). The remaining bands in the two spectra can be assigned to the isomeric isothiocyanate. The spectra showed no other bands.

Pyrolysis of 1-Cyclohexyl-2,4,6-triphenylpyridinium (1j) *Thiocyanate.*—Under above conditions (1j) thiocyanate (1 g,

0.0023 mol) gave a mixture (70 : 30) (0.127 g, 40%) of cyclohexyl thiocyanate, δ($CDCl_3$) 3.25 (1 H) and 2.3—1.2 (10 H), and cyclohexyl isothiocyanate, δ($CDCl_3$) 3.65 (1 H) and 2.3—1.2 (10 H), $\nu_{max.}$ ($CHBr_3$) (mixture) 2 150 (m) and 2 060br cm^{-1}. The i.r. and ^1H n.m.r. spectra of the mixture showed all the bands expected for cyclohexyl isothiocyanate (comparison spectrum obtained from an authentic sample) and cyclohexyl thiocyanate (comparison with published [29] spectrum) and no other bands.

Pyrolysis of 1-*Cyclohexyl*-2,4,6-*triphenylpyridinium* (1j) *Chloride*.—Pyrolysis of (1j) chloride (1 g, 0.0023 mol) at 150 °C and 20 mmHg gave cyclohexene (0.175 g, 90%) which was identified by comparison of the i.r. and ^1H n.m.r. spectra with those of an authentic sample.

Nitromethylcycloheptane.—Ethanolic sodium ethoxide (from 0.295 g, 0.0121 mol sodium and 20 ml absolute ethanol), CH_3NO_2 (0.689 g, 0.0121 mol), and 1-cycloheptyl-2,4,6-triphenylpyridinium tetrafluoroborate (1k) (5 g, 0.0121 mol) were heated to reflux for 24 h. After cooling the mixture was filtered and CH_2Cl_2 (20 ml) added. The whole was extracted with water (3 × 20 ml). The dried ($MgSO_4$) organic layer was evaporated and the residue chromatographed on silica gel eluted with hexane to give *nitromethylcycloheptane* (0.77 g, 41%), b.p. *ca.* 140 °C at 25 mmHg (Found: C, 61.2; H, 9.6; N, 8.9. $C_8H_{15}NO_2$ requires C, 61.1; H, 9.6; N, 8.9%), $\nu_{max.}$ ($CHBr_3$) 2 925, 2 860, 1 545, 1 460, 1 445, 1 430, 1 375, and 1 295 cm^{-1}, δ($CDCl_3$) 4.20 (2 H, d, *J ca.* 7 Hz), 2.35 (1 H, m), and 2.15—1.15 (12 H, m).

Solvolysis of 1-(*s-Butyl*)-5,6-*dihydro*-2,4-*diphenylbenzo*[h]-*quinolinium* (2e) *Tetrafluoroborate*.—Tetrafluoroborate (2e) (10.0 g, 0.0210 mol) and *p*-cresol (56.70 g, 0.54 mol) were heated to 125 °C for 4 h. After cooling the mixture was distributed between CH_2Cl_2 (100 ml) and NaOH (0.1M, 250 ml). The organic layer residue was chromatographed in silica gel to give (a) *p*-tolyl s-butyl ether (0.58 g, 17%) (eluted with hexane), b.p. 90—93 °C at 20 mmHg (lit.,[30] 58—59 °C at 4 mmHg); δ($CDCl_3$) 7.05 (2 H, d, *J ca.* 8 Hz), 6.75 (2 H, d, *J ca.* 8 Hz), 4.2 (1 H), 2.25 (3 H, s), 1.90—1.30 (2 H), 1.25 (3 H, d, *J ca.* 6 Hz), and 0.92 (3 H, t, *J ca.* 6 Hz).

2-s-Butyl-4-methylphenol (1.13 g, 33%) (eluted with hexane–benzene), b.p. 118—122 °C at 20 mmHg (lit.,[30] 93—94 °C at 5 mmHg); δ($CDCl_3$) 7.0—6.4 (3 H), 2.25 (3 H, s), 1.8—1.3 (2 H), 1.20 (3 H, d, *J ca.* 6.5 Hz), and 0.85 (3 H, t, *J ca.* 6.5 Hz).

Solvent Trapping of Carbonium Ions (*see Tables* 4 *and* 5).—*Method E*. To a stirred suspension of the pyrylium salt (1a) (0.005 mol) in solvent (25 ml) was added the s-alkyl primary amine (0.0075 mol) and triethylamine (0.50 g, 0.0059 mol). After 72—84 h at 25 °C the solvent was removed *in vacuo* and the residue extracted with ether (3 × 50 ml), dried ($MgSO_4$), and HCl gas passed through until precipitation of amine hydrochlorides was complete. Filtration, evaporation *in vacuo*, distillation, and/or column chromatography (silica; 5% EtOAc–hexane) gave the products as oils (see Tables 4 and 5).

Method F. The pyrylium salt (1a) (0.005 mol) and s-alkyl primary amine (0.0075 mol) were stirred in triethylamine (8.17 g, 0.081 mol) and freshly distilled *p*-cresol (8.10 g, 0.075 mol) for 72—84 h at 25 °C, before diluting with ether (75 ml). The ether solution was then washed with 5N aqueous NaOH (3 × 25 ml), water (2 × 20 ml), and dried ($MgSO_4$) before passing in dry HCl. Filtration, evaporation *in vacuo*, and column chromatography (silica, 5% EtOAc–hexane) and/or distillation giving the products.

Method G. To a stirred suspension of the pyrylium salt (1a) (0.005 mol) in acetic acid (9.00 g, 15 mol) and triethylamine (10.10 g, 0.10 mol) at 25 °C was added the amine (0.0075 mol). After 16—168 h water (50 ml) was added followed by ether extraction (3 × 25 ml), and washing of the extracts with water (2 × 20 ml) before drying ($MgSO_4$) and passing in dry HCl. Filtration, evaporation *in vacuo*, and distillation and/or column chromatography (silica; 5% EtOAc–hexane) gave the products as oils.

Kinetics Measurements.—U.v. spectra of reactants and products were run on a Pye–Unicam SP8 200 spectrophotometer. For the rate measurements at fixed wavelength, u.v. spectrophotometer of type SP6-550 was used. Stoppered glass tubes (28 cm high and 13.5 cm in diameter) were used as reaction vessels which were placed into the hot-blocks (Statim Model Prop.) for convenient temperature runs.

Kinetics were followed by u.v. spectrophotometry monitoring the decrease of absorbance of the pyridinium cation at fixed wavelength using the procedure already described.[23] In typical runs under pseudo-first-order conditions the concentration of pyridinium was 9.6×10^{-5} or 3.2×10^{-3} mol l^{-1}, while those of the nucleophile varied from 9.6×10^{-4} to 0.96 mol l^{-1}. Pseudo-first-order rate constants were calculated from the slope of conventional plots of $\ln(a/a - x) = \ln[(\varepsilon_c - \varepsilon_b)/(\varepsilon - \varepsilon_b)]$ (at the kinetic wavelength) *versus* time. Such plots were linear to at least 80% completion. The kinetic λ and the extinction coefficients at that λ for all compounds studied are reported in Table 6. The analysis of kinetic data was done following ref. 31.

Acknowledgements

We thank the S.E.R.C. for studentships (to J. M. L. and J. G. K.).

References

1 Part 9, A. R. Katritzky, K. Sakizadeh, Y. X. Ou, B. Jovanovic, G. Musumarra, F. P. Ballistreri, and R. Crupi, preceding paper.
2 For a review see A. R. Katritzky, *Tetrahedron*, 1980, **36**, 679.
3 For more details see J. M. Lloyd, Ph.D. Thesis, University of East Anglia, 1981.
4 A. R. Katritzky, N. F. Eweiss, and P.-L. Nie, *J. Chem. Soc., Perkin Trans. 1*, 1979, 433.
5 A. R. Katritzky, G. Liso, E. Lunt, R. C. Patel, S. S. Thind, and A. Zia, *J. Chem. Soc., Perkin Trans. 1*, 1980, 849.
6 A. R. Katritzky, G. de Ville, and R. C. Patel, *Tetrahedron*, 1981, **37**, Suppl. 1, 25.
7 A. R. Katritzky and S. S. Thind, *J. Chem. Soc. Pak.*, 1980, **2**, 51.
8 A. R. Katritzky, R. T. Langthorne, R. C. Patel, and G. Lhommet, *Tetrahedron*, 1981, **37**, 2383.
9 A. R. Katritzky, G. Musumarra, K. Sakizadeh, S. M. M. El-Shafie, and B. Jovanovic, *Tetrahedron Lett.*, 1980, **21**, 2697.
10 A. R. Katritzky, J. M. Lloyd, and R. C. Patel, *J. Chem. Soc., Perkin Trans. 1*, 1982, 117.
11 A. R. Katritzky and A. M. El-Mowafy, *J. Org. Chem.*, 1982, **47**, 3506.
12 A. R. Katritzky, J. B. Bapat, R. J. Blade, B. P. Leddy, P.-L. Nie, C. A. Ramsden, and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, 1979, 418.
13 M. L. Dhar, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1948, 2058.
14 M. L. Dhar, E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1948, 2055.
15 M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, *J. Chem. Soc.*, 1948, 2093.
16 A. R. Katritzky, G. Z. de Ville, and R. C. Patel, *Tetrahedron Lett.*, 1980, **21**, 1723.
17 A. R. Katritzky, G. Musumarra, K. Sakizadeh, and M. M. Vukovic, *J. Org. Chem.*, 1981, **46**, 3820.

18 J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 1951, **73**, 5034.
19 C. A. Bunton, ' Nucleophilic Substitution at a Saturated Carbon Atom,' Elsevier, London, 1963.
20 T. W. Bentley and P. von R. Schleyer, ' Medium Effects on the Rates and Mechanisms of Solvolytic Reactions ' in ' Advances in Physical Organic Chemistry,' ed. V. Gold, Academic Press, London, 1977, and references therein.
21 (*a*) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, 1951, **73**, 212; (*b*) H. C. Brown and M. Borkovski, *ibid.*, 1952, **74**, 1894.
22 G. C. Levy and J. D. Cargioli, *J. Magn. Reson.*, 1972, **6**, 143.
23 A. R. Katritzky, R. C. Patel, and L. Urögdi, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1349.
24 A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1895.
25 R. Lombard and J.-P. Stephan, *Bull. Soc. Chim. Fr.*, 1958, 1458.
26 A. R. Katritzky, K. Horvath, and B. Plau, *Synthesis*, 1979, 437.
27 A. R. Katritzky, U. Gruntz, H. Mongelli, and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1953.
28 A. R. Katritzky, A. Chermprapai, R. C. Patel, and A. Tárraga-Tomás, *J. Org. Chem.*, 1982, **47**, 492.
29 ' The Sadtler Standard Spectra,' Sadtler, U.S.A., 1976.
30 L. S. Kharchenko and S. V. Zavgorodnii, *Ukr. Khim. Zh.*, 1964, **30**, 261 (*Chem. Abstr.*, 1964, **60**, 14 414).
31 E. S. Swinbourne, ' Analysis of Kinetic Data,' Nelson, London, 1971.

Received 21*st June* 1982; *Paper* 2/1036