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Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 8.[1] Conductimetric and Spectrophotometric Rate Constants for the Reactions of Pyridinium and Related Cations with Piperidine in Chlorobenzene

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A conductimetric method is developed to obtain rates for the title reactions for which the spectrophotometric method fails. It gives equivalent results. *NN'*-Dimethylthiourea displaces heterocyclic leaving groups at rates similar to those for piperidine. Compared with α-hydrogen, α-methyl groups render pyridine a less effective leaving group, whereas α-ethoxycarbonyl groups show a large rate enhancement.

Previous Parts have established that the transfer of *N*-benzyl substituents from pyridinium cations to neutral nucleophiles in non-polar solvents such as chlorobenzene occurs by S_N1 and/or S_N2 mechanisms and give clean first- or second- or pseudo-first-order kinetics.[2,3] In the 2,4,6-triphenyl series, 1-(*p*-methoxybenzyl) and 1-(2-furfuryl) substituents are transferred by a combination of S_N1 and S_N2 modes and other substituted benzyl groups by the S_N2 mechanism only:[4] other pyridines acting as nucleofuges can change this pattern.[5] Electron-withdrawing groups attached to the pyridine nucleofuge,[6] and steric compression near the 1-substituent,[1,3] increase the displacement rates. Studies in diverse solvents show that the unimolecular/bimolecular dichotomy persists, and that rate variations quantitatively follow the Hughes–Ingold predictions.[7]

The demonstration that nucleophilic displacements occur in non-polar and non-nucleophilic solvents with simple kinetics allows detailed investigation of the controversial S_N1–S_N2 borderline, and a major aim of the present group of papers has been to study the solvolytic and other reactions of s-alkyl substrates. In this paper we show that a conductimetric method gives kinetic results equivalent to the u.v. method, and can be used where the u.v. method fails. The following paper (Part 9) demonstrates that the S_N1–S_N2 dichotomy exists for s-alkyl groups and explores mechanistic behaviour for a range of different *N*-substituents and pyridine nucleofuges. Part 10 establishes the potential value of *N*-s-alkylpyridinium salts as reagents and shows that they can be formed in certain cases *in situ*, spontaneously fragmenting to give capturable carbonium ions. In Part 11, we report plots of σ* *versus* log *k* for *N*-(s-alkyl) derivatives in a series of solvents, which we believe point unequivocally to firm mechanistic conclusions. Part 12 is concerned with the regio- and stereo-chemistry of the displacement reactions and the confirmation of ion–molecule return from intimate ion–molecule pairs.

In view of the preparative value of reactions of this type (quantitative comparisons in Part 9 include pyridines intermediate in nucleofugacity between chlorine and bromine) we have investigated further elaboration of the pyridine nucleofuge by αβ-polycyclic ring fusion (Part 13) and by α-heteroaryl substitution (Part 14).

We have previously reported the rate variation with steric effects in the leaving group for the reaction of *N*-benzyl-2,4,6-triphenylpyridinium and related cations with piperidine in chlorobenzene.[3] These studies showed that steric influences due to (a) substituent buttressing in the pyridinium ring, and (b) constraining α-phenyl groups to near coplanarity [in systems such as (1) or (3)] can profoundly influence the rates and mechanisms of such reactions. We have now studied compounds unsubstituted in the α-positions and also some polysubstituted derivatives.

Difficulties were encountered in following the kinetics by u.v. spectrophotometry for some of these compounds because of small differences between the u.v. absorption of the starting pyridinium salt and the final corresponding pyridine.[3] For this reason, and to provide a general check on the u.v. method, we have developed an alternative conductimetric method to obtain rate data. Data so obtained are now reported and in appropriate cases compared with those from the u.v. method, and shown to be reliable.

Substrates used were prepared by standard methods (see Experimental section).

Kinetic Determinations.—(i) *Spectrophotometric method.* Reactions were followed under pseudo-first-order conditions as previously described.[2] Observed rate constants (k_{obs}) were calculated from the slope of the plots of $\ln (\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)$ *versus* time and are recorded in Table 1.

(ii) *Conductimetric method.* The reaction was followed by monitoring the decrease in conductivity with time. The conductivity of the solution at infinite time (G_∞) was nearly equal to that of chlorobenzene (G_{PhCl}) and close to zero. The linear relationship between conductivity and concentration of pyridinium was verified for (4) in chlorobenzene at 50 °C (Figure). This linear relationship is confirmed by the linearity of the plots of the actual runs carried out as described below to follow the substitution reactions by conductivity. Moreover in these runs the conductivity became very low and constant when the reaction was complete. The conductivities of the chlorobenzene solvent, solutions of piperidine in chlorobenzene, and solutions of substituted pyridines in chlorobenzene, were found to be nearly equal and close to zero. Observed rate constants under pseudo-first-order conditions (k_{obs}) (Table 2) were calculated from equation (1). As G_∞ *ca.* 0,

$$k_{obs} = 1/t \ln (C_0/C) = 1/t \ln [(G_0 - G_\infty)/(G - G_\infty)] \qquad (1)$$

this reduces to equation (2).

$$k_{obs} = 1/t \ln (G_0/G) \qquad (2)$$

Comparison of U.v. and Conductivity Methods.—Eight compounds have now been studied by both methods. For

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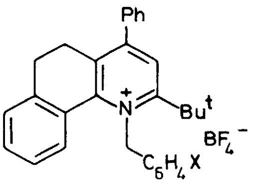
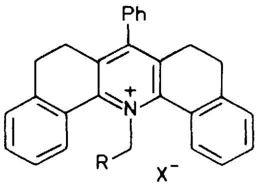


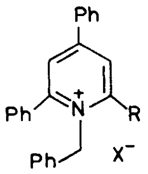
(1) X = H

(2) X = p-Cl



(3) R = Ph, X = BF_4

(4) R = p-$CH_3C_6H_4$, X = BF_4

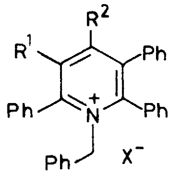


(5) R = Ph, X = BF_4

(6) R = H, X = BF_4

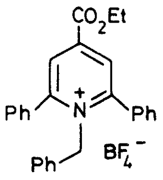
(7) R = $CONHBu^n$, X = CF_3SO_3

(8) R = CO_2Et, X = CF_3SO_3



(9) R^1 = Ph, R^2 = H, X = BF_4

(10) R^1 = H, R^2 = Ph, X = CF_3SO_3



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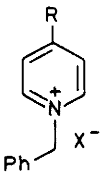
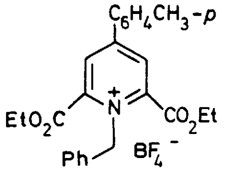


(12) R = H, X = ClO_4

(13) R = Ph, X = BF_4



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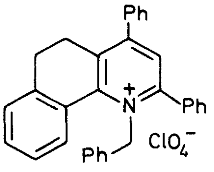

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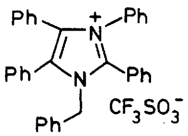

(16)

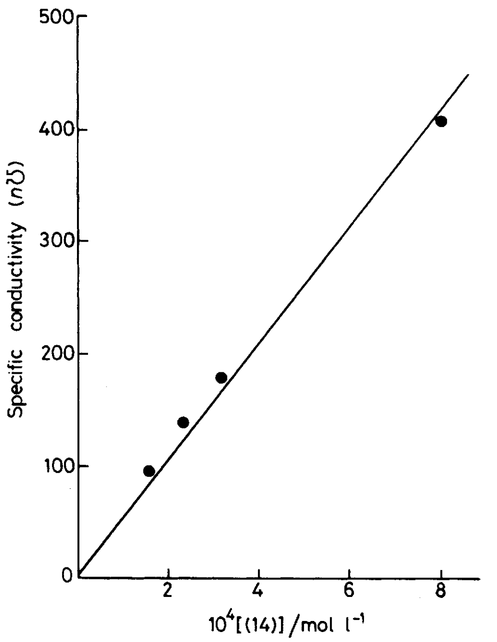

Figure. Plot of specific conductivity *versus* concentration for 14-(p-tolyl)-7-phenyl-5,6,8,9-tetrahydrobisbenzo[*c*,*h*]acridinium (4) in chlorobenzene at 50 °C

Table 1. Pseudo-first-order rate constants (k_{obs}) measured by the u.v. method for the reactions of pyridiniums with piperidine in chlorobenzene

Pyridinium (t/°C)	[Pip]/mol l^{-1}	10^5 k_{obs}/s^{-1}
(6) [a] (100)	0.160	14.9
	0.240	22.5
	0.320	29.8
(11) [b] (60)	0.0130	6.00
	0.0480	19.3
	0.0640	25.7
	0.0960	40.0
	0.130	51.4
(13) [c] (100)	0.0640	1.66
	0.0860	2.33
	0.120	3.17

[a] Concentration of substrate 1.60 × 10^{-3} mol l^{-1}. [b] Concentration of substrate 0.130 × 10^{-3} mol l^{-1}. [c] Concentration of substrate 0.380 × 10^{-3} mol l^{-1}, followed up to 40% conversion.

compound (6) only a single conductivity run was carried out. For compounds (1), (2), (4), (5), and (9)—(11) more extensive measurements were made by both methods (Tables 1 and 2). In all cases the second-order rate constants k_2 from both methods agreed within experimental error (Table 3). This means (a) that results obtained solely by the conductivity method can be used with confidence and (b) supports the results obtained previously by the u.v. method.

Kinetic Rate Determinations with NN′-*Dimethylthiourea as Nucleophile*.—The use of piperidine as nucleophile is not always desirable, due to its strong basicity and 'hard' nucleophilic character which could lead to complications, *e.g.* amide formation with ester substituents. As an alternative, we have studied the use of *NN*′-dimethylthiourea, a non-basic nucleophile, whose soft character leads to preferential attack at sp^3-carbon rather than at C=O and related sites. Under pseudo-first-order conditions, good straight line plots were found to give k_{obs} values (Table 4). Plots of k_{obs} against [nucleophile] gave straight lines from the slope and intercept of which k_2 and k_1 respectively were calculated (Table 5).

Comparisons using 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (5) as substrate (Tables 3 and 5) showed that *NN*′-dimethylthiourea reacts at rates of the same order as those observed with piperidine as nucleophile. Thus, in chlorobenzene at 100 °C, the second-order rate constant (k_2) for *NN*′-dimethylthiourea is 1.3 times that previously reported for piperidine;[3] both nucleophiles showed negligible first-order reaction. These similarities suggest that direct comparison of results obtained using either nucleophile is appropriate: similar conclusions are reached from literature work, *e.g.* from rates of reaction with methyl iodide in methanol.[8]

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Table 2. Pseudo-first-order rate constants (k_{obs}) measured by the conductivity method for the reactions of pyridiniums with piperidine in chlorobenzene

Pyridinium (t/°C)	[Pip]/mol l^{-1}	10^5k_{obs}/s^{-1}
(1) [a] (58.5)	0.006 40	19.9
	0.009 60	28.1
	0.0160	41.9
(2) [a] (60)	0.0130	42.7
	0.0160	53.6
	0.0260	86.0
(4) [b] (30)	0	0
	0.003 20	40.4
	0.006 40	85.2
(5) [c] (96)	0.0800	30.7
	0.120	46.5
	0.160	60.5
(6) [d] (97)	0.160	12.7
(9) [e] (97)	0.160	20.1
	0.240	31.1
	0.320	43.1
(10) [f] (97)	0	0
	0.320	33.0
	0.400	44.3
	0.480	54.9
(11) [e] (60)	0.0320	20.9
	0.0480	30.8
	0.0620	37.5
	0.0960	49.7

[a] Concentration of substrate 0.190 × 10^{-3} mol l^{-1}. [b] Concentration of substrate 0.230 × 10^{-3} mol l^{-1}. [c] Concentration of substrate 0.800 × 10^{-3} mol l^{-1}. [d] Concentration of substrate 1.40 × 10^{-3} mol l^{-1}. [e] Concentration of substrate 0.800 × 10^{-3} mol l^{-1}. [f] Concentration of substrate 1.20 × 10^{-3} mol l^{-1}.

Table 3. First- (k_1) and second-order (k_2) rate constants measured by the conductimetric (C) and/or the u.v. method for the reactions of pyridiniums and related cations with piperidine in chlorobenzene

Pyridinium	t/°C	Method	N [a]	r [b]	10^3k_2 [c]/l mol^{-1} s^{-1}	% Error	10^5k_1 [d]/s^{-1}	% Error	$\dfrac{1\,000\,k_1}{k_2 + 10\,k_1}$ [e]
(1)	58.5	C	3	0.999	23 ± 6	27	(6 ± 7)		<5
	58.5	U.v.			29.6 [f]				
(2)	60	C	3	0.999	33 ± 4	14	(0.1 ± 8.8)		<3
	60	U.v. [g]	4	0.999	29.7 ± 1.9	6	(4.8 ± 1.0)	41	<2
(4)	30	C	3	0.9995	133 ± 25	18	(−1 ± 10)		<1
	30	U.v. [g]	4	0.9999	133 ± 4	4	(3.7 ± 3.1)		<1
	60	C [h]			744 ± 84	11			
(5)	96	C	3	0.9994	3.7 ± 0.8	22	(1 ± 10)		<20
	96	U.v.			4.1 [f]				
(6)	100	U.v.	3	0.9999	0.93 ± 0.07	7	(0.05 ± 1.70)		<20
(9)	97	C	3	0.9997	1.44 ± 0.23	16			<20
	100	U.v. [i]	4	0.997	1.64 ± 0.26	16	(0.4 ± 5)		<20
(10)	97	C	4	0.998	1.13 ± 0.16	14	(−0.8 ± 6)		<30
	100	U.v. [i]	5	0.999	1.62 ± 0.08	5	(0.8 ± 2.4)		<20
(11)	60	C	4	0.991	4.4 ± 1.2	27	(8.6 ± 8.0)		<30
	60	U.v.	5	0.999	3.95 ± 0.23	6	(0.8 ± 1.9)		<6
(13)	100 [j]	U.v.	3	0.9983	0.27 ± 0.10	37	(−0.02 ± 0.9)		<25

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses not significantly different from zero. [e] % Reaction by S_N1 route at [Nucleophile] 10^{-1} mol l^{-1}. [f] Interpolated value from ref. 2. [g] From ref. 5. [h] Measured under second-order reaction conditions. [i] From ref. 2. [j] Reaction followed up to 40% conversion.

Rate Data for Pyridinium Salts with Unsubstituted α-Positions.—Successive replacement of the α-phenyl groups in (5) by H [to give (6) and (13)] leads to corresponding decreases in bimolecular reaction rate at 100 °C (Table 3). The second-order rate constant (k_2) for (5) is *ca.* five times that for (6) and *ca.* 20 times greater than that estimated for (13); * k_1 is negligible for all these compounds.

These rate reductions are, however, less than those found [3] for replacing an α-phenyl by an α-methyl group: this causes a reduction in second-order rate constant (k_2) by a factor of *ca.* 40. It follows that replacement of an α-hydrogen by α-methyl makes pyridine a less effective leaving group. Evidently, steric repulsions by methyl to the approach of the nucleophile must outweigh steric acceleration caused by reduced strain in the transition state.

Rate data for (9) and (10) have already been discussed,[3] as have those for (1),[3] (2),[5] and (4).[5]

Rate Data for Pyridinium Salts containing Ethoxycarbonyl Groups.—Results obtained at 100 °C with *NN'*-dimethylthiourea as nucleophile (Table 5) show that replacement of an α-phenyl by an ethoxycarbonyl group [(8)] causes an increase in k_2 by a factor of 38; no significant part of the reaction proceeds by the S_N1 route. Using pyridine, a weaker nucleophile, gives a much slower reaction as expected; again, comparison with previous results [2] shows an increase in k_2 by a factor of *ca.* 40. With pyridine, reaction of (8) by the S_N1 mechanism is significant with k_1 1.0 × 10^{-4} s^{-1}.

When both α-phenyl groups are replaced by ethoxy-

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* Kinetic runs were followed only to 40% conversion; after this time a competing ring-opening reaction was suspected to occur, but could not be detected by ^{13}C n.m.r. spectroscopy. Compound (12) could not be studied by u.v. due to solvent overlap, and attempts to measure the reaction rate for (12) by conductivity gave inconsistent results.

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carbonyl (14), the reaction rate at 100 °C is too fast for convenient measurement by techniques within the scope of this paper. Comparison of results obtained, with piperidine, at 30 °C, with those previously reported for the triphenylpyridinium ion (5) at 40 °C,[3] show that the increase in k_2 for (14) compared with (5) is by a factor of *ca.* 2 300.

Table 4. Pseudo-first-order rate constants (k_{obs}) measured by the u.v. method for the reaction of pyridiniums with neutral nucleophiles in chlorobenzene

Pyridinium (t/°C)	Nucleophile	10^3-[Nucleophile]/ mol l^{-1}	$10^5 k_{obs}$/s^{-1}
(5) [a] (100.0)	$(MeNH)_2CS$	0.390	0.294
		3.86	3.20
		9.58	7.41
		19.1	13.1
		37.2	24.7
(7) [b] (100.0)	$(MeNH)_2CS$	1.78	0.558 [c]
		3.55	0.803 [d]
		7.11	1.37 [e]
		17.8	3.20
(8) [f] (100.0)	$(MeNH)_2CS$	0.755	35.8
		1.89	76.5
		3.77	114
(8) [f] (79.6)	$(MeNH)_2CS$	0.776	10.5
		1.94	17.8
		3.88	31.9
(8) [f] (70.3)	$(MeNH)_2CS$	3.88	17.7
(8) [g] (60.0)	$(MeNH)_2CS$	0.0379 [h]	0.180
		0.757	1.59
		1.89	3.90
		3.79	7.85
(8) [f] (49.8)	$(MeNH)_2CS$	3.88	2.90
(8) [i] (39.4)	$(MeNH)_2CS$	0.755	0.240
		1.89	0.551
		3.77	1.07
(8) [j] (100.0)	Pyridine	1.04	10.4
		4.15	10.8
		10.4	11.9
(14) [k] (30.0)	Piperidine	1.07	14.2
		2.13	33.5
		4.26	62.1
		6.40	85.3

[a] Substrate concentration 3.96 × 10^{-5} mol l^{-1}. [b] Substrate concentration 3.54 × 10^{-5} mol l^{-1}. [c] Followed to 20% conversion. [d] Followed to 30% conversion. [e] Followed to 40% conversion. [f] Substrate concentration 3.68 × 10^{-5} mol l^{-1}. [g] Substrate concentration 3.76 × 10^{-5} mol l^{-1}. [h] Substrate concentration 3.76 × 10^{-6} mol l^{-1}. [i] Substrate concentration 4.07 × 10^{-5} mol l^{-1}. [j] Substrate concentration 3.98 × 10^{-5} mol l^{-1}. [k] Substrate concentration 6.4 × 10^{-5} mol l^{-1}.

Replacement of the γ-phenyl by an ethoxycarbonyl group in compound (11) leads to a smaller rate increase [*ca.* 12 times that for (5) at 60 °C] than for insertion of an ethoxycarbonyl group at the α-position in place of phenyl.

Replacement of α-phenyl by a carboxamido group [compound (7)] leads to less satisfactory kinetic results (Table 4): curvature of the time plots, possibly reflects substrate decomposition over prolonged reaction times. Initial rates indicate that the α-carboxamido group has an effect opposite to that of the α-ethoxycarbonyl, and a drop in k_2 to *ca.* 1/4th the value for triphenylpyridinium is observed.

Arrhenius parameters for the α-ethoxycarbonyl derivative (8), $\Delta H_{333}^{\ddagger}$ 16.3 ± 0.1 kcal mol^{-1} and $\Delta S_{333}^{\ddagger}$ -17.90 ± 0.03 cal K^{-1} mol^{-1}, derived from temperature-variation data (Table 5), are close to values previously observed for the tricyclic compound (15).[3]

The large rate enhancement shown for α-ethoxycarbonyl is similar to that previously reported for α-2-benzo[*b*]thiazolyl.[6] It encourages synthetic work with these and similar pyryliums, and confirms that electronic as well as steric effects of substituents can influence greatly the leaving group ability of the pyridine.

Kinetic Rate for Imidazolium Cation.—The 1-benzyl-2,3,4,5-tetraphenylimidazolium salt (16) reacts very slowly with nucleophiles *e.g.* piperidine at 100 °C. With *NN'*-dimethylthiourea at 120 °C, in chlorobenzene, k_2 could only be estimated at *ca.* 0.3 × 10^{-3} l mol^{-1} s^{-1} due to competing substrate decomposition and consequent solution colouration (*cf.* ref. 9).

Rate constants obtained using the higher boiling solvent, sulpholane, are reported in Table 6. For the same nucleophile and temperature, k_2 values are smaller than those obtained in chlorobenzene: for 1-benzyl-2,4,6-triphenylpyridinium (5) at 100 °C, k_2 for reaction with piperidine by a factor of 2.2 and k_2 for reaction with *NN'*-dimethylthiourea by a factor of 44.

This shows that whereas dimethylthiourea reacts slightly faster than piperidine in chlorobenzene, it is considerably less reactive as a nucleophile in sulpholane. We have found that rates generally decrease on increasing the solvent polarity;[2,7] the present results indicate that this effect is greater than usual with *NN*-dimethylthiourea.

Comparison of second-order rate constants for *NN'*-dimethylthiourea in sulpholane at 150 °C shows that the imidazolium ion (16) reacts at *ca.* 1/50th the rate observed for

Table 5. First- (k_1) and second-order (k_2) rate constants, measured by the u.v. method, for the reactions of pyridiniums and related cations with neutral nucleophiles in chlorobenzene

Pyridinium	Nucleophile	t/°C	N [a]	r [b]	$10^3 k_2$ [c]/ l mol^{-1} s^{-1}	% Error	$10^5 k_1$ [c]/ s^{-1}	% Error	$\frac{10^3 k_1}{k_2 + 10k_1}$ [d]
(5)	$(MeNH)_2CS$	100.0	5	0.9991	6.53 ± 0.37	6	<1		<2
(7)	$(MeNH)_2CS$	100.0	4	0.9996	1.67 ± 0.09	6	0.23 ± 0.09	41	1.8
(8)	$(MeNH)_2CS$	100.0	3	0.9855	(250 ± 260)		<90		
		79.6	3	0.9993	69 ± 17	24	(4.8 ± 4.2)		1.3
		70.3	1		45.6 [e]				
		60.0	4	0.9999	20.5 ± 0.4	2	<0.2		<0.1
		49.8	1		7.46 [e]				
		39.4	3	0.9999	2.75 ± 0.03	1	0.032 ± 0.009	27	0.2
(8)	Pyridine	100.0	3	0.9974	1.63 ± 0.74	45	10.2 ± 0.5	5	40
(14)	Piperidine	30.0	4	0.9954	132 ± 26	20	<20		<1

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Percentage reaction by S_N1 route at [Nucleophile] 10^{-1} mol l^{-1}. [e] Obtained from k_{obs}/[Nu]; negligible reaction by S_N1 route.

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Table 6. Pseudo-first-order (k_{obs}) and second-order (k_2) rate constants measured by the u.v. method for the reactions of (5) and (16) with piperidine and with dimethylthiourea in sulpholane

Nucleophile	Cation	t/°C	[Nucleophile]/ mol l^{-1}	10^5k_{obs}/ s^{-1}	10^3k_2/ l mol^{-1} s^{-1}	10^3k_2/ l mol^{-1} s^{-1}
Piperidine	(5)	100	0.180 [a]	34.1	1.90	1.87
		100	0.450 [a]	82.6	1.84	
Dimethylthiourea	(5)	100	0.0800 [a]	1.23	0.154	0.147
		100	0.160 [b]	2.20	0.139	
		133	0.0800 [b]	12.3		1.54
		150	0.0200 [b]	21.8		
		150	0.0400 [a]	36.0		6.91 ± 0.46 [c]
		150	0.0800 [a]	60.8		
		150	0.160 [a]	119		
Dimethylthiourea	(16)	150	0.160 [a]	2.18		0.14
		180	0.160 [a]	12.1		0.76

[a] Concentration of substrate 1.60 × 10^{-3} mol l^{-1}. [b] Concentration of substrate 0.800 × 10^{-3} mol l^{-1}. [c] Calculated from the plot of k_{obs} against [dimethylthiourea]; intercept (k_1) (7.5 ± 4.3) × 10^{-5} s^{-1}, 90% confidence limit.

(5). Reasons for the poor leaving group ability of imidazole have been discussed.[9]

Experimental

Compounds.—The following were prepared by others and their preparation has been, or will be, reported elsewhere: (i) 1-benzylpyridiniums: 2,4,6-triphenyl (5), as BF_4^-, m.p. 196—197 °C;[10] 2,4-diphenyl (6), as BF_4^-, m.p. 120—122 °C;[11] 2-(*N*-n-butylcarboxamido)-4,6-diphenyl (7), as $CF_3SO_3^-$, m.p. 135—137 °C;[12] 2,4,-diphenyl-6-ethoxycarbonyl (8), as $CF_3SO_3^-$, m.p. 150—152 °C;[12] 2,3,5,6-tetraphenyl (9), as BF_4^-, m.p. 155—160 °C;[13] 2,3,4,6-tetraphenyl (10), as $CF_3SO_3^-$, m.p. 115—118 °C;[2] 2,6-diphenyl-4-ethoxycarbonyl (11), as BF_4^-, m.p. 130—134 °C;[14] 4-phenyl (13), as BF_4^-, m.p. 148—149 °C;[15] 2,6-bisethoxycarbonyl-4-(*p*-tolyl) (14), as BF_4^-, m.p. 160—162 °C;[15] (ii) 4-phenyl-5,6-dihydrobenzo[*h*]quinoliniums: 1-benzyl-2-t-butyl (1), as BF_4^-, m.p. 136—137 °C;[5] 1-(*p*-chlorobenzyl)-2-t-butyl (2), as BF_4^-, m.p. 137—138 °C;[5] (iii) 7-phenyl-5,6,8,9-tetrahydrobisbenzo[*c*,*h*]acridiniums: 14-benzyl (3), as BF_4^-, m.p. 159—160 °C;[5] 14-(*p*-tolyl) (4), as BF_4^-; m.p. 161—162 °C;[5] (iv) 3-benzyl-1,2,4,5-tetraphenylimidazolium (16), as $CF_3SO_3^-$, m.p. 270—272 °C.[9]

1-*Benzylpyridinium Perchlorate* (12).—Benzyl chloride (6.3 g, 0.05 mol) and pyridine (4.0 g, 0.05 mol) were heated at 100 °C for 1 h. After cooling, 70% perchloric acid (5 g, 0.05 mol) was added. The mixture was then poured into ether (100 ml) and the resulting *solid* was filtered off and washed with ethanol (9.7 g, 72%), m.p. 89—90 °C (from EtOH) (Found: C, 53.5; H, 4.3; N, 5.2. $C_{12}H_{12}ClNO_4$ requires C, 53.4; H, 4.4; N, 5.2%), $\lambda_{max.}$ (EtOH) 260 (ε 4 700) nm; $\nu_{max.}$ ($CHBr_3$) 3 130, 3 065, 1 630, 1 490, 1 455, 1 210, 765, 750, and 680 cm^{-1}; δ($CDCl_3$-CF_3CO_2H) 5.75 (2 H, s) and 7.3—9.0 (10 H, m).

Kinetic Measurements.—(a) *U.v. method.* The reactions were followed under pseudo-first-order conditions following the procedure already described.[1b,2,3] The concentrations of pyridinium ranged from 3.2 × 10^{-5} to 1.6 × 10^{-3} mol l^{-1} and those of nucleophiles from 0.0003 to 0.45 mol l^{-1}. Pseudo-first-order rate constants k_{obs} were calculated from the slope of the plot of ln $[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ against time,[1-3] reactions were followed to at least 75% conversion (unless otherwise stated), and we estimate the precision of the k_{obs} measurements as better than 5% in all cases. Unless otherwise stated, the plot of k_{obs} against nucleophile concentration was treated by a least-squares method to give, from the slope, the second-order rate constant and, from the intercept on the k_{obs} axis, the first-order rate constant. The ± error quoted for k_1 and k_2 are the 90% confidence limits in the intercept and slope calculations by multiplying the standard error found by least squares method in the intercept and slope by the appropriate $t_{student}$ value.[15] The '% error' (given *e.g.* in Table 3) is the ± error quoted as a % of the relevant k_1 or k_2. The extinction coefficients for pyridinium cations and for the corresponding pyridines are recorded in Table 7.

Table 7. Extinction coefficient for pyridinium cations (ε_1) and for the corresponding pyridines (ε_2) at the kinetic wavelength

Compound	λ/nm	ε_1	ε_2
(5)	312	34 000 [a]	8 000 [a]
(6)	305	23 000 [a]	2 000 [a]
(7)	330	15 400 [b]	700 [b]
(8)	320	19 650 [b]	2 273 [b]
(11)	360	4 000 [b]	700 [b]
(13)	300	18 500 [c]	0 [c]
(14)	362	22 000 [b]	800 [b]
(16)	310	1 000 [d]	7 500 [d]

[a] In 2% (v/v) chlorobenzene–EtOH. [b] In chlorobenzene. [c] In 8% (v/v) chlorobenzene–EtOH. [d] In 4% (v/v) sulpholane–EtOH.

(b) *Conductivity method.* The reactions were followed conductimetrically by monitoring the decrease in conductivity in a 10 ml Pyrex cell with 1.2 cm platinum disc electrodes connected in sequence to tungsten, nickel, and copper wires. The decrease in conductivity was measured by use of a Wayne Kerr B 641 bridge.

In runs under pseudo-first-order reaction conditions the concentrations of substrates varied from 2 × 10^{-4} to 14 × 10^{-4} mol l^{-1} and those of nucleophile from 3.2 × 10^{-3} to 4.8 × 10^{-1} mol l^{-1}.

A portion (10 ml) of the reaction solution was transferred into the cell, using a syringe. The electrodes were immersed in the solution and at least 1 cm below the surface of the solution. Then the cell was put in a thermostat at the required temperature. The maximum value of conductivity was taken as G_0 and the corresponding time as zero. The change of conductivity was recorded at convenient intervals of time and to at least 60% completion.

Pseudo-first-order rate constants were calculated from equation (1) or (2) (see text). First- and second-order rate constants were obtained respectively as the intercept and the slope of the plot of k_{obs} *versus* nucleophile concentration.[2,3]

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