Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 22.[1] Reactions with Various Nucleophiles and a Study of the Effects of Substrate Concentration, Traces of Water, and Nature of the Gegenion on the Rates

Alan R. Katritzky,* Hanna Schultz, and Maria L. Lopez-Rodriguez
Department of Chemistry, University of Florida, Gainesville, Florida, 32611, U.S.A.
Giuseppe Musumarra and Giuseppe Cirma
Dipartimento di Scienze Chimiche, Universita di Catania, Viale A. Doria 6, 95125 Catania, Italy

First- and second-order rate components for the nucleophilic displacements of a variety of *N*-(primary alkyl), *N*-(secondary alkyl), and *N*-benzyl substituents from mono-, bi-, and tri-cyclic pyridine leaving groups by various nucleophiles are independent of substrate concentration, of the nature of the gegenion, and of traces of water in the solvent. Thus assumptions implicit in the reasoning of earlier papers of this series are confirmed, and the conclusion that these nucleophilic displacements can proceed by five independent mechanistic pathways is strengthened.

First-order rate components are invariant with the nature of the nucleophile. Second-order rate components vary with nucleophile nucleophilicity in a way that parallels Menschutkin reactions. Activation enthalpies for first-order components are less negative than those for second-order components, in agreement with previous data.

Previous papers of this series have examined the kinetics and mechanisms of the transfer of *N*-substituents from pyridinium cations to nucleophiles. In particular, the dependence of kinetic rates on the structure of the *N*-substituent,[2] on steric[3] and electronic[4] effects in the leaving group, and on solvent[5] have been described. The earlier work has been reviewed:[6,7] the conclusions are summarized in the Scheme and evidence has been provided that, depending on the structure of substrate, the nature of the nucleophile, and the reaction conditions, these nucleophilic displacements can proceed by five distinct pathways: (*a*) a radicaloid route,[8] (*b*) the classical S_N2 route, (*c*) S_N2 reaction on intimate ion–molecule pairs, (*d*) S_N1 reaction on intimate ion–molecule pairs, or (*e*) the classical S_N1 mechanism.

The purpose of the work described in the present paper was to confirm certain fundamental assumptions which were explicitly or implicitly made in the reasoning which led to the foregoing conclusions. Preliminary investigations disclosed that variation in substrate concentration caused insignificant effects on pseudo-first-order rates.[2] In the earlier studies piperidine was almost invariably the nucleophile, although we occasionally utilized anionic[9] (tetra-n-butylammonium bromide and iodide) and other neutral[2,9] nucleophiles (thiourea, morpholine, and pyridine). Recently, quinolinium and acridinium cations have been treated with a variety of neutral nucleophiles in chlorobenzene in a study[10] which allowed definition of the borderlines between reactions proceeding (e) *via* free carbocations, (d) *via* rate-determining formation of ion–molecule pairs, and (c) *via* rate-determining nucleophilic attack on ion–molecule pairs. Changing the gegenion from perchlorate to tetrafluoroborate had negligible effects on the rate constants;[11] however, no extensive investigation of the variation of rate constants with substrate concentration, or with gegenion, has been carried out previously.

We have now studied, for a series of pyridinium cations including several different leaving groups and *N*-substituents, the effect on kinetic rates of (i) substrate concentration, (ii) structure variation within a wide range of neutral nitrogen nucleophiles, (iii) traces of water in the chlorobenzene solvent, and (iv) variation of the gegenion.

Table 1. Effect of substrate concentration on pseudo-first-order rate constants ($10^5\ k_{obs}/s^{-1}$) for the reaction of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium cations with piperidine (0.16 mol l^{-1}) in chlorobenzene

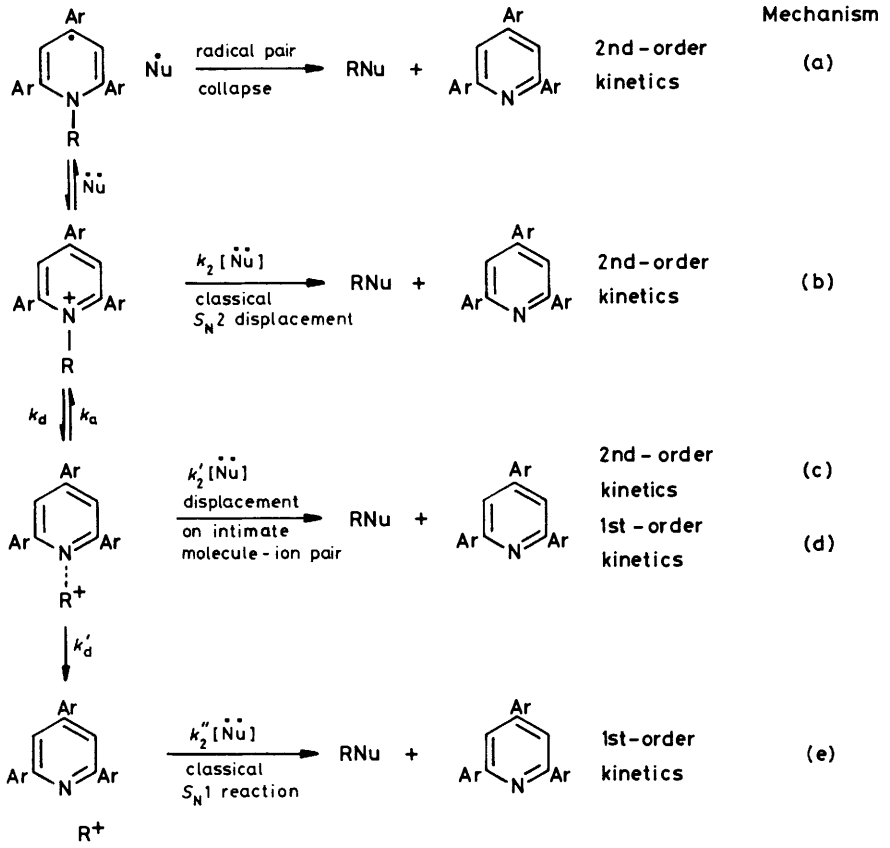
10^5 [substrate] / mol l^{-1}	R	CH_2Ph	CH_2Ph	Pr^i	Me
	X^-	BF_4^-	$CF_3SO_3^-$	BF_4^-	BF_4^-
	t/°C	40	40	60	100
3.20		73.0	100	6.57	
6.40				6.26	82.9[a]
32.0		78.0	99.0		
40.0					78.0[a]
64.0				6.42[a]	
160		74.0	105		78.5[a]

[a] From ref. 2.

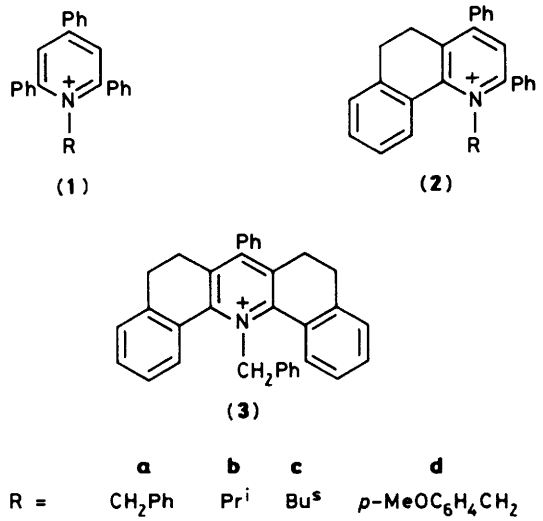
Preparation of Compounds and Kinetic Measurements.—The pyridinium salts of series (**1**)—(**3**) were prepared by standard methods from the corresponding pyrylium salts and the appropriate amines.[2,3,9] For all kinetic measurements[9] chlorobenzene was used as solvent. Observed-first-order rate constants [Table 1 and Tables I–VII (available as Supplementary Publication No. 56638; 14 pp.) †] were plotted against nucleophile concentration (see *e.g.* Figure). Except where otherwise stated, this gave straight lines which either passed through the origin or showed positive intercepts. We interpret these plots as in previous papers: the slopes are proportional to k_2, the second-order rate constants for S_N2 nucleophilic substitution; the intercepts, when present, give k_1, the first-order components.[2,3,12] Values of k_1 and k_2 are listed in Tables 2 and 4.

Effect of Substrate Concentration.—Table 1 records pseudo-first-order rate constants for the reactions of 1-substituted 5,6-

† For details of Supplementary Publications see Instructions for Authors (*J. Chem. Soc., Perkin Trans. 2*, 1986, Issue No. 1).



Scheme. Nucleophilic substitutions with pyridine leaving groups



dihydro-2,4-diphenylbenzo[*h*]quinolinium cations (**2**) with piperidine in chlorobenzene at various temperatures. Under pseudo-first-order conditions, there is no significant change in k_{obs} on varying the substrate concentration by a factor of 50 for four different *N*-alkylquinolinium cations (**2**) [including the isopropyl compound (**2f**) which exhibits a first-order component] with a variety of gegenions at different temperatures.

Effect of Nature of the Nucleophile.—(a) *Variation of second-order rate constants* k_2 *with nucleophilicity.* Second-order rates

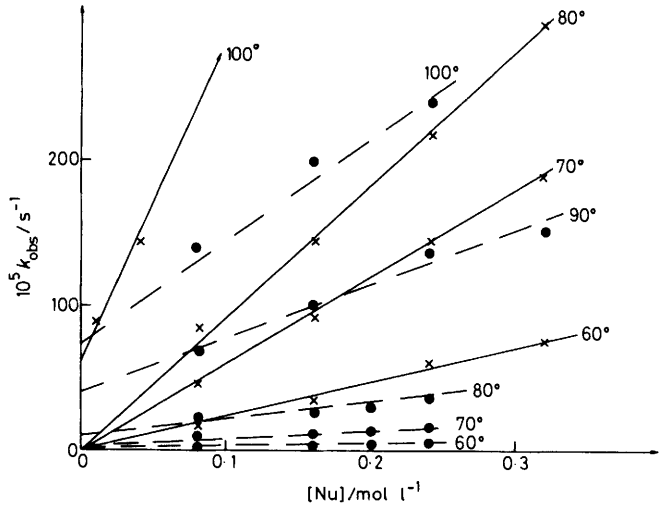


Figure. Temperature effect: plot of $k_{obs.}$ *vs.* nucleophile concentrations for the reactions of 1-isopropyl-5,6-dihydro-2,4-diphenylbenzo[*h*]-quinolinium (**2b**) tetrafluoroborate with morpholine (●, ———) and of 14-benzyl-5,6,8,9-tetrahydro-7-phenyldibenzo[*c,h*]acridinium (**3**) tetrafluoroborate with pyridine (×, ——) in chlorobenzene at various temperatures

for *N*-benzylpyridinium salts (**1a**), (**2a**), and (**3**) with various nucleophiles (Table 2) decrease in the order piperidine > morpholine > pyridine > 2-methylpyridine > 2,6-dimethylpyridine, in line with nucleophilicity as expected. The second-order rate constants relative to those for pyridine are, for these

Table 2. First-order (k_1) and second-order (k_2) rate constants for the reaction of *N*-alkyl- and *N*-benzyl-pyridinium salts with piperidine, morpholine, pyridine, 2-methylpyridine, and 2,6-dimethylpyridine in chlorobenzene

Compd.	*N*-Subst.	Gegenion	*t*/°C	Nu[a]	*N*[b]	*r*[c]	Slope 10^3k_2[d] / l mol^{-1} s^{-1}	Error (%)	Intercept 10^5k_1[d,e]/s^{-1}	Error (%)	10^3k_1[f] / $k_2 + 10k_1$
(**1a**)	$PhCH_2$	BF_4^-	100	Pip	4	0.999	5.1 ± 1.1	23	(2 ± 21)		<31
		ClO_4^-	100	Py	6	0.949	0.032 ± 0.003[g]	35	(0.3 ± 0.4)[g]		<71
			100	Pic	4	0.999	0.0056 ± 0.0005[g]	10	(0.2 ± 0.2)[g]		<28
			100	L	4	0.985	0.0026 ± 0.0009	36	0.61 ± 0.03	5	96
		BF_4^-	96	Pip	3	0.999	3.7 ± 0.9[h]	22	(1 ± 10)[h]		<23
(**1b**)	Pr^i	BF_4^-	100	M	4	0.999	0.064 ± 0.0006[i]	10	0.89 ± 0.1[i]	11	58
			100	Py	3	0.985	0.006 ± 0.004[i]	62	0.94 ± 0.3[i]	29	99
			100	Pic	4	0.998	0.061 ± 0.09	15	2.10 ± 0.19	9	77
			100	L	4	0.998	0.051 ± 0.006	12	0.94 ± 0.13	14	65
(**1c**)	Bu^s	BF_4^-	100	M	4	0.999	0.052 ± 0.004[i]	7	2.93 ± 0.07[i]	2	85
			100	Py	3	0.988	0.0034 ± 0.0034[i]	99	3.0 ± 0.12[i]	39	99
			100	Pic	4	0.945	0.11 ± 0.08	71	(1.3 ± 2)		<75
			100	L	3	0.996	0.032 ± 0.02	56	1.5 ± 04	29	82
(**2a**)	$PhCH_2$	BF_4^-	100	Py	10	0.995	2.18 ± 0.14	6	(−1 ± 2)		<4
			100	Pic	5	0.994	0.48 ± 0.07	14	(0.8 ± 1.4)		<31
			100	L	4	0.999	0.24 ± 0.02	8	0.65 ± 0.42	64	22
			80	Py	4	0.999	0.42 ± 0.04	10	(0.02 ± 0.92)		<18
(**2a**)	$PhCH_2$	BF_4^-	70	Py	4	0.997	0.20 ± 0.03	16	(0.2 ± 0.7)		<31
			60	Pip	5	0.999	15.2 ± 0.9	6	(1 ± 7)		<5
			60	M	4	0.996	6.67 ± 1.26	19	(9 ± 27)		<35
			60	Py	5	0.993	0.082 ± 0.013	16	(−0.1 ± 0.3)		<33
(**2b**)	Pr^i	BF_4^-	100	Pip	4	0.999	2.8 ± 0.2[i]	6	111 ± 3[i]	3	80
			100	M	3	0.998	6.38 ± 2.7	43	91 ± 47	52	<68
			90	M	4	0.988	3.59 ± 0.12	33	43 ± 26	61	<66
			83	Pip	4	0.996	1.66 ± 0.29[i]	18	22 ± 6[i]	29	<63
			80	M	7	0.998	1.22 ± 0.07	6	9.2 ± 1.0	11	<46
			80	Py	11	0.998	0.151 ± 0.0006	4	11.8 ± 0.34	3	89
			80	Pic	4	0.999	0.058 ± 0.006	10	12.0 ± 0.1	1	95
			80	L	8	0.831	0.03 ± 0.02	53	12.0 ± 0.46	4	98
			70	M	4	0.999	1.53 ± 0.06	11	1.1 ± 1	89	<29
			60	Pip	4	0.999	0.29 ± 0.02[i]	8	1.6 ± 0.5[i]	34	<42
			60	M	4	0.998	0.16 ± 0.02	12	0.66 ± 0.35	53	<41
			50	Pip	4	0.999	0.13 ± 0.01[i]	11	0.47 ± 0.41[i]	86	<40
(**2c**)	Bu^s	BF_4^-	81	Pip	4	0.990	3.23 ± 1[i]	30	46 ± 21[i]	44	<73
			70	Pip	4	0.999	0.74 ± 0.05[i]	7	17 ± 1[i]	7	<71
			60	Pip	4	0.999	0.29 ± 0.02[i]	6	3.1 ± 0.4[i]	11	<55
			60	Py	10	0.990	0.022 ± 0.002	10	3.1 ± 0.3	9	<94
			60	Pic	4	0.975	0.0068 ± 0.003	47	3.2 ± 0.4	14	<98
			60	L	3	0.930	0.0063 ± 0.03		3.0 ± 2.0	62	<98
(**3**)	$PhCH_2$	BF_4^-	100	Py	5	0.989	31.7 ± 6.5	21	(50 ± 64)		<26
			100	Pic	4	0.997	9.2 ± 1.4	15	34 ± 13	38	<34
			100	L	4	0.997	3.3 ± 0.5	16	36.4 ± 4.8	13	<56
			70	Py	4	0.999	6.0 ± 0.3	5	(−1 ± 8)		<10
		$CF_3SO_3^-$	65	M	5	0.999	430 ± 6.0[j]	1	6.4 ± 1.4[j]	22	<0.2
			65	Py	5	0.999	4.25 ± 0.04[j]	1	7.3 ± 0.2[j]	3	<15
		BF_4^-	60	Py	4	0.997	2.5 ± 0.4	16	(−1 ± 9)		<24
		$CF_3SO_3^-$	60	L	5	0.999	0.077 ± 0.005[j]	7	4.0 ± 0.01[j]	0.3	84
			30	M	4	0.999	35.2 ± 0.9	3	(−2 ± 4)		<0.6

[a] Pip = piperidine, M = morpholine, Py = pyridine, Pic = 2-picoline (2-methylpyridine), L = 2,6-lutidine (2,6-dimethylpyridine). [b] Number of runs. [c] Correlation coefficient. [d] 90% Confidence limit. [e] Values in parentheses are not significantly different from zero. [f] Percent reaction by S_N1 route at [nucleophile] 10^{-1} mol l^{-1}. [g] From ref. 9. [h] From ref. 30. [i] From ref. 2. [j] From ref. 10.

N-benzyl compounds (**1a**), (**2a**), and (**3**) (Table 3), consistent with previous work.[2,9] For pyridine, 2-methylpyridine, and 2,6-dimethylpyridine, relative rates can be compared with those found for the Menschutkin reaction with methyl iodide in nitrobenzene at 25 °C (1:0.47:0.042),[13] with methyl iodide and *trans*-$[Pt(py)_2Cl_2]$ in methanol at 25 °C (1:0.29:0.02),[14] and with methyl iodide in acetonitrile at 25 °C (1:0.43:0.04)[15,16] and in Me_2SO at 23 °C (1:0.38:0.02).[17] Second-order rate constants for reactions of substrates where no first-order component is present [*i.e.* for (**1a**), (**2a**), and (**3**)] are consistent with the foregoing data, those with 2-methylpyridine being somewhat less than expected and those with 2,6-dimethylpyridine somewhat greater: possibly there is less bond formation at the transition state. For substrates where a first-order component is present [*i.e.* (**1b** and **c**) and (**2b** and **c**)], rates for piperidine and morpholine are less than the corresponding rates for the substrates (**1a**), (**2a**), and (**3**) without a first-order component. Those for 2-methylpyridine and 2,6-dimethylpyridine are greater than expected. The presence of a first-order component produces a levelling effect on second-order rates with various nucleophiles, probably due to the low percentage of reaction proceeding by S_N2 route (*cf.* last column in Table 2): moreover, in the foregoing cases, k_2 values are affected by high errors.

Table 3. Relative second-order rates for the reactions of *N*-alkyl- and *N*-benzyl-pyridinium salts with neutral nucleophiles in chlorobenzene[a]

				k_2 relative to k_2 for pyridine				
Compd.	*N*-Subst.	*t*/°C	1st-order component	Piperidine	Morpholine	Pyridine	2-Methyl-pyridine	2,6-Dimethyl-pyridine
(**1a**)	$PhCH_2$	100	no/yes[b]	153[c]	73[d]	1[c]	0.18[c]	0.08
(**1b**)	Pr^i	100	yes	23[e]	11[e]	1[e]	10	9
(**1c**)	Bu^s	100	yes	37[e]	17[e]	1[e]	32	10
(**2a**)	$PhCH_2$	100	no	162[e]		1	0.22	0.11
		60	no	185	81	1		
(**2b**)	Pr^i	100	yes	1.8[f]	1[g]			
		80	yes	6.8[h]		1	0.40	0.20
		60	yes	1.8[e]				
(**2c**)	Bu^s	60	yes	13.2		1	0.32	0.27
(**3**)	$PhCH_2$	100	no/yes[i]	140		1	0.29	0.10
		60		20[j]		1		
		30		3[j,g]	1[g]			

[a] Values of k_2 from this work (Table 2) or from refs. indicated in footnotes. [b] First-order component observed in the reaction with 2,6-dimethylpyridine. [c] From ref. 9. [d] From A. R. Katritzky, G. Musumarra, K. Sakizadeh, S. M. M. El-Shafie, and B. Jovanovic, *Tetrahedron Lett.*, 1980, 21, 2697. [e] From ref. 2. [f] From ref. 27. [g] Relative rate with respect to morpholine. [h] The second-order rate constant at 80 °C, extrapolated from variable-temperature data in ref. 2, is 0.001 03. [i] First-order component observed in the reactions with 2-methylpyridine and 2,6-dimethylpyridine. [j] From ref. 3.

Table 4. First-order rate coefficients (10^5 k_1/s^{-1}) for the reactions of 1-substituted 2,4,6-triphenylpyridinium, and 5,6-dihydro-2,4-diphenylquinolinium compounds, and 14-benzyl-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium tetrafluoroborate, with neutral nucleophiles in chlorobenzene

Compd.	*N*-Subst.	*t*/°C	Piperidine	Morpholine	Pyridine	2-Methylpyridine	2,6-Dimethylpyridine
(**1a**)	$PhCH_2$	100					0.61 ± 0.03
(**1b**)	Pr^i	100	0.72[a] ± 0.21	0.88[a] ± 0.10	0.94[a] ± 0.3	2.10 ± 0.19	0.94 ± 0.13
(**1c**)	Bu^s	100	3.2[a] ± 0.5	2.9[a] ± 0.07	3.0 ± 0.1	1.3 ± 2	1.5 ± 0.4
(**2b**)	Pr^i	80		9.2 ± 1.0	11.8 ± 0.4	12.0 ± 0.1	12.0 ± 0.5
(**2c**)	Bu^s	60	3.1 ± 0.4		3.1 ± 0.3	3.2 ± 0.4	3.0 ± 2.0
(**3**)	$PhCH_2$	100				34 ± 13	36.4 ± 4.8
		65		6.4 ± 1.4	7.3 ± 0.2		

[a] From ref. 2.

The relative second-order rate constants for the reactions of *N*-isopropyl- (**2b**) at 80 °C and *N*-s-butyl- (**2c**) quinolinium salts at 60 °C with pyridine, 2-methylpyridine, and 2,6-dimethylpyridine parallel the literature data on Menschutkin reactions (Table 3).

(b) *Invariance of the first-order rate constant* k_1. Whereas the *N*-benzyl-pyridinium (**1a**) and -quinolinium (**2a**) cations react exclusively *via* an S_N2 route, *N*-4-methoxybenzyl and *N*-(secondary alkyl) derivatives show a first-order rate component. Previous papers[10] have already provided evidence that such first-order components are independent of the nature as well as of the concentration of the nucleophile. Thus, the extrapolated first-order rates for the reaction of the *N*-isopropylquinolinium tetrafluoroborate (**2b**) with pyridine, 2-methylpyridine, and 2,6-dimethylpyridine at 80 °C are 11.8×10^{-5}, 12.0×10^{5}, and 12.0×10^{-5} s^{-1}, respectively. The reactions of the *N*-s-butylquinolinium tetrafluoroborate (**2c**) with pyridine, 2-methylpyridine, and 2,6-dimethylpyridine at 60 °C proceed to a high percentage *via* the S_N1 route. The extrapolated first-order rate constants for the reaction (see Table 4) agree with those observed for the reactions carried out in the absence of nucleophile [Table IV (deposited)].

As demonstrated earlier,[10,18] the *N*-benzylacridinium cation (**3**) reacts with piperidine and with morpholine almost exclusively by an S_N2 displacement on the intimate ion–molecule pair. However, reaction of (**3**) with weaker nucleophiles proceeds to a significant degree *via* a unimolecular route. Recently, we have provided further evidence[10] that first-order rates do not change appreciably on changing the nucleophile.

(c) *Variation of activation parameters with mechanism and nucleophilicity.* Values of rate constants at various temperatures (Table 2) were used to calculate activation parameters (Table 5). Data previously reported for the reactions of (**1a** and **d**), (**2a** and **b**), and (**3**) with piperidine (also included in Table 5), for the S_N1 and S_N2 components of the reactions of 1-(4-methoxybenzyl)- and 1-furfuryl-2,4,6-triphenylpyridinium with piperidine in chlorobenzene,[12] and for the corresponding S_N2 reactions of a variety of *N*-benzyl-[3] and *N*-alkyl-pyridinium[2] salts had indicated that entropies of activation for S_N1 (−10 to +2 cal mol^{-1} K^{-1})* reactions were significantly less negative than those for S_N2 (−26 to −14 cal mol^{-1} K^{-1}). The present data are in line with the previous results, supporting the separation of the reaction mechanisms.[7]

The data in Table 5 indicate that the effect of nucleophile structure on S_N2 reaction rates is probably derived mainly from variations in the activation enthalpy. Activation parameters for the S_N1 reaction are not significantly affected by the nucleophile, as expected.

Effect of Traces of Water.—Water is slightly soluble in chlorobenzene (0.033% at 23 °C).[19] Because of the possibility that small amounts of water in our chlorobenzene solvent could significantly affect measured rates, we investigated the effect of known water concentrations for the reactions of the quinolinium tetrafluoroborates (**2a**—**c**), at 100, at 80, and

* 1 cal = 4.184 J.

Table 5. Activation parameters at 373 K

Compd.	*N*-Subst.	Nu[a]	S_N2 reaction mode ΔH / kcal mol^{-1}	S_N2 reaction mode ΔS / cal mol^{-1} K^{-1}	S_N1 reaction mode ΔH / kcal mol^{-1}	S_N1 reaction mode ΔS / cal mol^{-1} K^{-1}
(**1a**)	$PhCH_2$	Pip[b]	16.3 ± 0.6	−26.2 ± 1.8		
(**1d**)	p-$MeOC_6H_4CH_2$	Pip[c]	13.6 ± 3.1	−30.4 ± 9.7	26.6 ± 3.6	7 ± 11
(**2a**)	$PhCH_2$	Pip[b]	15.8 ± 1.5	−19 ± 5		
		Py	19 ± 1	−20 ± 4		
(**2b**)	Pr^i	Pip[d]	14 ± 4	−31 ± 13	25.6 ± 0.8	−4 ± 2
		M	23 ± 2	−9 ± 5	33 ± 6	11 ± 17
(**3**)	$PhCH_2$	Pip[b]	11 ± 2	25 ± 7		
		Py	14 ± 3	−27 ± 9		

[a] See footnote [a] in Table 2. [b] From ref. 3. [c] From ref. 11. [d] From ref. 2.

Table 6. Effect of drying the solvent on first- and second-order rates for the reactions of 1-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborates with pyridine in chlorobenzene

Substrate	t/°C	Solvent	N[a]	r[b]	$10^3\ k_2$/l mol^{-1} s^{-1}[c]	$10^5\ k_1$/s^{-1}[c,d]
(**2a**)	100	A[e]	10	0.995	2.18 ± 0.14	(−1 ± 2)
		B[f]	3	0.999	2.20 ± 0.01	(1.0 ± 0.1)
(**2b**)	80	A[e]	9	0.988	1.40 ± 0.15	11.8 ± 8
		B[f]	5	0.997	1.02 ± 0.11	12.1 ± 2
(**2c**)	60	A	2[g]			2.9 ± 0.2
		B[f]	3[g]			2.8 ± 0.3

[a] Number of points. [b] Correlation coefficient. [c] 90% Confidence limits. [d] Values in parentheses are not significantly different from zero. [e] From Table 2. [f] Chlorobenzene dried by distillations over P_2O_5, stored over 4 Å molecular sieves, and eluted through an Al_2O_3 neutral column before use. [g] Number of runs.

Table 7. First- (10^5k_1/s^{-1}) and second-order rate constants ($10^3\ k_2$/l mol^{-1} s^{-1}) for the reaction of 1-benzyl-2,4,6-triphenylpyridinium (**1a**), 1-benzyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium (**2a**), and 14-benzyl-5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium (**3**) tetrafluoroborates with neutral nucleophiles in chlorobenzene

Substr.	Nucleophile (t/°C)	Gegenion	N[a]	r[b]	10^3k_2[c]	Error (%)	$k_2/k_2(BF_4^-)$	10^5k_1[c,d]	Error (%)
(**1a**)	Piperidine	BF_4^-	4	0.994	5.1 ± 1.1[e]	23	1	(2 ± 21)[e]	
	(100)	ClO_4^-	6	0.999	4.94 ± 0.17[f]	3	0.97	(1 ± 2)[f]	
		$CF_3SO_3^-$	4	0.999	5.2 ± 0.47	9	1.02	(4 ± 10)	
(**2a**)	Piperidine	BF_4^-	5	0.999	15.2 ± 0.9[e]	6	1	(1 ± 7)[e]	
	(60)	ClO_4^-	7	0.992	19.2 ± 2.2	12	1.14	(−1 ± 16)	
		$CF_3SO_3^-$	10	0.985	23.3 ± 2.7	12	1.54	(−1 ± 17)	
(**2a**)	Morpholine	BF_4^-	4	0.996	6.67 ± 1.26[e]	19	1	(9 ± 27)[e]	
	(60)	ClO_4^-	5	0.998	6.81 ± 0.54	8	1.02	(−1 ± 9)	
		$CF_3SO_3^-$	5	0.998	9.57 ± 0.82	9	1.43	(−6 ± 16)	

chlorate, m.p. 198—199 °C (lit.,[23] 196—198 °C); trifluoromethanesulphonate, m.p. 213—215 °C (lit.,[24] 216—217 °C); 1-isopropyl (**1b**), m.p. 201—204 °C (lit.,[2] 204 °C); 1-s-butyl (**1c**) tetrafluoroborate, m.p. 165—167 °C (lit.,[25] 165—167 °C); 1-benzyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium (**2a**) tetrafluoroborate, m.p. 139—141 °C (lit.,[26] 193 °C); perchlorate, m.p. 148—150 °C (lit.,[26] 152 °C); trifluoromethanesulphonate, m.p. 150—152 °C (lit.,[23] 133 °C); 1-isopropyl (**2b**) tetrafluoroborate, m.p. 143—145 °C (lit.,[27] 145—147 °C); perchlorate, m.p. 143—145 °C (lit.,[25] 140—142 °C); 1-s-butyl (**2c**) tetrafluoroborate, m.p. 142—144 °C (lit.,[2] 130—132 °C); 14-benzyl-5,6,8,9-tetrahydrodibenzo[*c,h*]acridinium tetrafluoroborate (**3**), m.p. 179—182 °C (lit.,[28] 159—160 °C).

1-*Isopropyl-5,6-dihydro-2,4-diphenylbenzo*[h]*quinolinium trifluoromethanesulphonate* (**2b**). Isopropylamine (0.001 mol) and Et_3N (0.001 mol) were added to the appropriate pyrylium salt (0.001 mol). The mixture was suspended in CH_2Cl_2 (3 ml) and stirred at 20 °C for 15 min. Acetic acid (0.06 ml) was then added and the mixture stirred for a further 6 h. Dilution with Et_2O caused deposition of the *triflate* (**2b**) (0.35 g, 67%) (colourless prisms from Me_2CO–Et_2O), m.p. 150—152 °C (Found: C, 66.2; H, 5.0; N, 2.6. $C_{29}H_{26}F_3O_3NS$ requires C, 66.3; H, 5.0; N, 2.7%).

All common laboratory chemicals, unless otherwise stated, were reagent grade and from various suppliers. The chlorobenzene solvent was purified[29] by washing with sulphuric acid, then aqueous sodium hydrogen carbonate or sodium carbonate, and water. Before distillation from phosphorus pentaoxide, it was dried over calcium chloride. Piperidine, morpholine, pyridine, and 2-methylpyridine were distilled[29] from calcium hydride, calcium oxide, or phosphorus pentaoxide. The 2,6-dimethylpyridine was purified[29] by distillation from aluminium chloride.

Kinetic Measurements.—The kinetics were followed by u.v. spectrophotometry under pseudo-first-order conditions by the procedure already described.[9] In typical runs under pseudo-first-order conditions the concentration of the pyridinium substrate was in the range 1.6×10^{-3}—3.2×10^{-5} mol l^{-1}; that of the nucleophile ranged from 0.0004 to 2.5 mol l^{-1}. Pseudo-first-order rate constants were calculated from the plot of $\ln[a/(a - x)]$ *versus* time. Such plots were linear to above 70—80% conversion. Second-order rate constants, unless otherwise stated, were calculated from the slope of the plot of k_{obs} *versus* nucleophile concentration. Extinction coefficients at the kinetic wavelength are reported in Table VII (deposited).

Karl-Fischer Titration.—Karl-Fischer titrations were performed in a home-built electrometric apparatus. During a titration a potential of 50 mV was applied on the platinum electrodes with a potentiostat (Princeton Applied Research 176 Current Follower). The increase in current was measured and plotted against amount of titrant added. The equivalence point was determined as the point of intersection with the line of zero current.[21]

Acknowledgements

We thank Dr. F. Saczewski for provision of some compounds, the Commission for Educational Exchange between the United States and Spain for a Fulbright M.U.I. grant (to M. L. L.-R.), and the Commission for Educational Exchange between the United States and Italy for a Fulbright travel grant (to G. M.).

References

1 Part 21, A. R. Katritzky, C. M. Marson, J. L. Chen, F. Saczewski, and R. W. King, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1331.
2 A. R. Katritzky, K. Sakizadeh, Y. X. Ou, B. Jovanovic, G. Musumarra, F. P. Ballistreri, and R. Crupi, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1427.
3 A. R. Katritzky, A. M. El-Mowafy, G. Musumarra, K. Sakizadeh, C. Sana-Ullah, S. M. M. El-Shafie, and S. S. Thind, *J. Org. Chem.*, 1981, **46**, 3823.
4 A. R. Katritzky, J. Adamson, E. M. Elisseou, G. Musumarra, R. C. Patel, K. Sakizadeh, and W. K. Yeung, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1041.
5 G. Musumarra, F. P. Ballistreri, S. Muratore, A. R. Katritzky, and S. Wold, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1049.
6 A. R. Katritzky, K. Sakizadeh, and G. Musumarra, *Heterocycles*, 1985, **23**, 1765.
7 A. R. Katritzky and G. Musumarra, *Chem. Soc. Rev.*, 1984, **13**, 47.
8 (*a*) A. R. Katritzky, M. A. Kashmiri, G. Z. de Ville, and R. C. Potel, *J. Am. Chem. Soc.*, 1983, **105**, 90; (*b*) A. R. Katritzky, J. L. Chen, S. M. Marson, A. Maia, and M. A. Kashmiri, *Tetrahedron*, 1986, **42**, 101.
9 A. R. Katritzky, G. Musumarra, K. Sakizadeh, and M. Misic-Vukovic, *J. Org. Chem.*, 1981, **46**, 3820.
10 A. R. Katritzky and B. Brycki, *Can. J. Chem.*, 1986, **64**, 1161.
11 Unpublished results from this laboratory.
12 A. R. Katritzky, G. Musumarra, and K. Sakizadeh, *J. Org. Chem.*, 1981, **46**, 3831.
13 H. C. Brown, D. Gintis, and H. Podall, *J. Am. Chem. Soc.*, 1956, **78**, 5375.
14 R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, 1968, **90**, 319.
15 J. L. Seeman, R. Galzerano, K. Curtis, J. C. Schug, and J. W. Viers, *J. Am. Chem. Soc.*, 1981, **103**, 5982.
16 J. C. Schug, J. W. Viers, and J. I. Seeman, *J. Org. Chem.*, 1983, **48**, 4892.
17 L. W. Deady and J. A. Zoltewicz, *J. Org. Chem.*, 1972, **37**, 603.
18 A. R. Katritzky, K. Sakizadeh, W. J. Le Noble, and B. Gabrielsen, *J. Am. Chem. Soc.*, 1984, **106**, 1879.
19 A. Seidell and W. F. Linke, 'Solubilities, Inorganic and Organic Compounds,' 4th edn., vol. 1, Princeton University Press, New Jersey, 1958, p. 1136.
20 B. Brycki, Z. Dega Szafran, and M. Szafran, *Adv. Molecular Relaxation Interaction Processes*, 1979, **15**, 77.
21 For details see: H. Schultz, M.S. Thesis, University of Florida, 1985.
22 A. R. Katritzky, U. Gruntz, D. H. Kenny, M. C. Rezende, and H. Sheikh, *J. Chem. Soc., Perkin Trans. 1*, 1979, 430.
23 A. R. Katritzky, J. P. 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.
24 A. R. Katritzky, A. M. El-Mowafy, L. Marzorati, R. C. Patel, and S. S. Thind, *J. Chem. Res.*, 1980, (*S*), 310; (*M*), 4001.
25 A. R. Katritzky, J. M. Lloyd, and R. C. Patel, *J. Chem. Soc., Perkin Trans. 1*, 1982, 117.
26 A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1895.
27 A. R. Katritzky, J. Marquet, and M. L. Lopez-Rodriquez, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1443.
28 A. R. Katritzky, W. H. Basinski, Y. X. Ou, G. Musumarra, and R. C. Patel, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1055.
29 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1980.
30 A. R. Katritzky, Y. X. Ou, J. Ellison, and G. Musumarra, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1421.

Received 17*th February* 1986; *Paper* 6/332