Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. 3.[1] *N*-(Substituted benzyl)-2,4,6-triphenylpyridiniums: Effects of Benzyl Substitution on First- and Second-Order Rates[2]

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1-(*p*-Methoxybenzyl)- and 1-(2-furfuryl)-2,4,6-triphenylpyridiniums react with piperidine in chlorobenzene by S_N1 and S_N2 mechanisms, the proportion of S_N1 increasing with temperature. Other 1-(substituted benzyl) derivatives show only S_N2 reaction. Activation parameters support this interpretation. Substituent effects on S_N1 and S_N2 rates are discussed.

We have shown that nucleophilic displacement reactions of 1-benzyl-2,4,6-triphenylpyridinium can be studied conveniently in nonpolar solvents and that steric[3] and electronic[4] effects in the leaving group can profoundly influence the rate and mechanism of such reactions. Preliminary experiments which indicated a very large rate enhancement for the displacement of 1-(*p*-methoxybenzyl) groups from pyridiniums led to the present investigation of the effect of benzyl substituion on rates.

Extensive previous work on the nucleophilic substitutions of benzyl halides has encompassed studies of substituent effects in substrate[5] and nucleophile[5b,6] and of solvent sensitivity.[7] The solvolysis of benzyl chlorides has been explored with regard to the effects of substituents, of added nucleophiles,[8] and of solvent.[9]

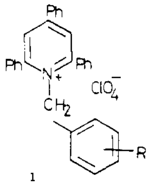
Preparation of Compounds. 2,4,6-Triphenylpyrylium perchlorate was reacted with the appropriate benzylamine to give the 2,4,6-triphenyl-1-(substituted benzyl)pyridinium perchlorates (**1c–h**, Table I, Chart I; exceptionally, compound **1b** was prepared as the tetrafluoroborate). The furyl derivative **2** was prepared similarly from furfurylamine. The *p*-methoxy derivative (**1h**) reacted preparatively with pyridine to give the expected product (**3**) in high yield.

Kinetic Determinations. Reactions in chlorobenzene solution, with piperidine, morpholine, or pyridine as nucleophile, were followed spectrophotometrically under pseudo-first-order conditions as previously described.[10] Results are given in Tables II–IV. In all cases, the observed rate was a linear function of the piperidine concentration.

We have shown previously[3,10] that k_{obsd} for the reaction of 1-benzyl-2,4,6-triphenylpyridinium with piperidine is independent of the substrate concentration. In the present work, reproducibility was good except for the *p*-methoxybenzyl compound, where difficulty was encountered at the higher temperatures. In most cases the rate was directly dependent on [piperidine] (Figure 1). However, for the *N*-*p*-methoxybenzyl and *N*-2-furfuryl derivatives a positive intercept was obtained by extrapolating the nucleophilic concentration to zero (Figures 2 and 3). For the p-methoxybenzyl compound, when morpholine and pyridine were used as nucleophiles in place of piperidine, different slopes but the same intercepts were found (Figure 2).

This behavior, with positive or zero intercepts depending on the N substituent, recalls that of *N*-benzylpyridiniums with different leaving groups.[3] The observed rate variations can therefore be interpreted in terms of the S_N2 mechanism, together with (for the *p*-methoxy and furfuryl derivatives) a contribution from the S_N1 mechanism; the S_N2 rate, but not the S_N1, rate depends on the nature of the nucleophile. Calculated S_N2 and S_N1 rate constants are given in Table V.

Chart I



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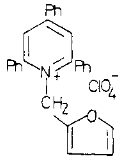

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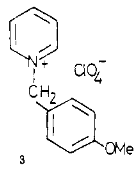
	a	b	c	d	e	f	g	h
R =	H	p-Me	m-Me	p-F	p-Cl	m-Cl	p-NO$_2$	p-OMe



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Simultaneous S_N2 and S_N1 Reaction Mechanisms. The mechanism of nucleophilic substitution has been controversial. Sneen proposed unification of the chemical duality of the S_N1 and S_N2 mechanisms in which all nucleophilic substitution involved the formation of ion pairs.[11]

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(1) Part 2: A. R. Katritzky, A. M. El-Mowafy, G. Musumarra, K. Sakizadeh, C. Sana-Ullah, S. M. El-Shafie, and S. S. Thind *J. Org. Chem.*, preceding paper in this issue.

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Table I. Preparation of 1-Substituted 2,4,6-Triphenylpyridinium Perchlorates[a]

compd	1-substituent	% yield	cryst solvent	mp, °C	lit. mp, °C	cryst form	% found C	% found H	% found N	formula	% required C	% required H	% required N
1b[b]	*p*-$MeC_6H_4CH_2$	81	EtOH	175	174-176[c,d]	white needles	74.2	4.9	2.6	$C_{31}H_{26}BF_4N$	74.6	5.2	2.8
1c	*m*-$MeC_6H_4CH_2$	71	EtOH	127		white needles	72.3	5.0	2.7	$C_{31}H_{26}ClNO_4$	72.7	5.1	2.7
1d	*p*-$FC_6H_4CH_2$	65	EtOH	124		white needles	69.6	4.5	2.5	$C_{30}H_{23}ClFNO_4$	69.8	4.5	2.7
1e	*p*-$ClC_6H_4CH_2$	93	Me_2CO-Et_2O	143	143[c,d]	white plates	67.4	4.5	2.5	$C_{30}H_{23}Cl_2NO_4$	67.7	4.3	2.6
1f	*m*-$ClC_6H_4CH_2$	82	EtOH	177		white needles	69.2	4.3	2.6	$C_{30}H_{23}Cl_2NO_4$	67.7	4.3	2.6
1g	*p*-$O_2NC_6H_4CH_2$	69	EtOH	125		white needles	65.9	4.2	5.1	$C_{30}H_{23}ClN_2O_6$	66.3	4.2	5.2
1h	*p*-$MeOC_6H_4CH_2$	73	Me_2CO-Et_2O	144-145	148[e,f]	white plates	70.2	4.8	2.6	$C_{31}H_{26}ClNO_5$	70.5	5.0	2.7
2	2-furyl-CH_2	67	Me_2CO-Et_2O	122	122[c,g] dec	cream plates			2.9	$C_{28}H_{22}ClNO_5$			2.7

[a] Satisfactory analyses were obtained for all compounds. [b] This compound is a tetrafluoroborate. [c] Perchlorate. [d] 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*, 418 (1979). [e] Tetrafluoroborate. [f] A. R. Katritzky, U. Gruntz, A. A. Ikizler, D. H. Kenny, and B. P. Leddy, *J. Chem. Soc., Perkin Trans. 1*, 436 (1979). [g] A. R. Katritzky, M. F. Abdel-Megeed, G. Lhommet, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 426 (1979).

Table II. Pseudo-First-Order Rate Constants (k_{obsd}) for the Reaction of 1-RCH_2-Substituted 2,4,6-Triphenylpyridinium Cations with Piperidine in Chlorobenzene at 100 °C

[piperidine], mol L^{-1}	10^5k_{obsd}, s^{-1}					
	p-MeC_6H_4[a] (1b)	*m*-MeC_6H_4[b] (1c)	*p*-FC_6H_4[b] (1d)	*p*-ClC_6H_4[b] (1e)	*m*-ClC_6H_4[b] (1f)	*p*-$NO_2C_6H_4$[b] (1g)
0.032	28.8	23.3	29.2	24.3	16.0	10.8
0.08		50.0	71.4	57.9	34.6	26.1
0.16	138	97.2	127	107	69.0	47.3
0.24		149	194	152	91.8	73.2

[a] Concentration of pyridinium equal to 3.2 × 10^{-5} mol L^{-1}. [b] Concentration of pyridinium equal to 1.6 × 10^{-3} mol L^{-1}. [c] Additional values for 1b (R = *p*-MeC_6H_4) ([piperidine] in mol L^{-1}, 10^5k_{obsd} in s^{-1}): 0.0642, 50.1; 0.00321, 3.20; 0.0016, 1.68; 0.00064, 1.63.

Table III. Pseudo-First-Order Rate Constants (k_{obsd}) for the Reactions of 1-(*p*-Methoxybenzyl)-2,4,6-triphenylpyridinium Cations (1h) with Nucleophiles in Chlorobenzene

[nucleophile], mol L^{-1}	10^5k_{obsd}, s^{-1}							
	piperidine						morpholine,[c] 40 °C	pyridine,[c] 40 °C
	35 °C[a]	40 °C	45 °C[a]	50 °C[a]	55 °C[a]	60 °C[a,b]		
0.32						109.3	9.85	4.66
0.24	8.9	16.7[a]	25.8	38.3	73.7	98.2		4.78
0.16	6.8	12.4[a]	21.3	29.7	61.5	80.1	7.27	4.20
0.08	4.5	7.9[c]	15.8	23.9	49.6	68.8	5.83	4.35
0.032		5.33[c]				64.4	4.62	3.91

[a] Concentration of pyridinium equal to 3.2 × 10^{-5} mol L^{-1}. [b] Additional value: [piperidine] = 0.016 mol L^{-1}; 10^5k_{obsd} = 53.0 s^{-1}. [c] Concentration of pyridinium equal to 1.6 × 10^{-3} mol L^{-1}.

Table IV. Pseudo-First-Order Rate Constants (k_{obsd}) for the Reactions of 1-(2-Furyl)-2,4,6-triphenylpyridinium Cation (2) with Piperidine in Chlorobenzene[a]

[piperidine], mol L^{-1}	10^5k_{obsd}, s^{-1}					
	40 °C	45 °C	50 °C	55 °C	60 °C	69 °C
0.032	4.60	9.61	15.7	28.3	48.8	130
0.08	7.00	13.4	21.8	38.1	68.2	174
0.16	10.5	19.7	29.8	54.3	92.9	230

[a] Concentration of pyridinium equal to 3.2 × 10^{-5} mol L^{-1}.

This approach was criticized particularly by McLennan, who favored the traditional duality.[12] The evidence for and against each viewpoint has been reviewed.[13]

We believe that the present results show a clear duality of mechanism for the reactions of 1-(*p*-methoxybenzyl)- and 1-(2-furfuryl)-2,4,6-triphenylpyridinium with nucleophiles in chlorobenzene. The interpretation is further supported by the similar results already reported for *N*-benzylpyridiniums with different leaving groups.[3] These results do not support the Sneen unified theory of nucleophilic substitution.

In our work, the use of neutral nucleophilic and nonnucleophilic solvents exclude complications in the interpretation arising from salt effects and solvolysis reactions. Under pseudo-first-order conditions (excess of nucleophile), the unified mechanism for our reactions (eq 1) would require a kinetic dependence according to eq 2.

$$RX^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+\cdots X \xrightarrow{k_2[N]} RN^+ + X \qquad (1)$$

$$k_{obsd} = k_1k_2[N](k_{-1} + k_2[N]) \qquad (2)$$

$$k_{obsd} = k_0 + k[N] \qquad (3)$$

In place of kinetic dependence according to eq 2 we clearly find the kinetic dependence expected for the si-

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Table V. First-Order (k_1) and Second-Order (k_2) Rate Constants for the Reactions of 2,4,6-Triphenyl-1-(substituted benzyl)pyridinium Cations and Heterocyclic Analogues with Nucleophiles in Chlorobenzene

						slope		intercept			
compd	1-substituent	nucleophile	temp, °C	N^a	r^b	10^3k_2,[c] L mol^{-1} s^{-1}	error, %	10^5k_1,[c,d] s^{-1}	error, %	$10^3k_1/(k_2 + 10k_1)^e$	rel k_2^f
1a[g]	$PhCH_2$	piperidine	100	6	0.9996	4.94 ± 0.13	3	(0.25 ± 1.9)		<4	1
1b	p-$MeC_6H_4CH_2$	piperidine	40	1		0.101[h]					
			60	1		0.512[h]					
			80	1		2.23[h]					
			100	6	0.999	8.52 ± 0.40	5	(0.05 ± 2.9)		<4	1.7
1c	m-$MeC_6H_4CH_2$	piperidine	100	4	0.999	6.04 ± 0.39	6	(2.5 ± 5.9)		<12	1.2
1d	p-$FC_6H_4CH_2$	piperidine	100	4	0.999	7.81 ± 0.68	9	(5 ± 10)		<16	1.6
1e	p-$ClC_6H_4CH_2$	piperidine	100	4	0.999	6.11 ± 0.53	9	(7.0 ± 8.0)		<20	1.2
1f	m-$ClC_6H_4CH_2$	piperidine	100	4	0.996	3.70 ± 0.67	18	(5 ± 10)		<29	0.75
1g	p-$O_2NC_6H_4CH_2$	piperidine	100	4	0.999	2.96 ± 0.25	8	(1.5 ± 3.8)		<15	0.60
1h	p-$MeOC_6H_4CH_2$	piperidine	35	3	0.999	0.275 ± 0.04	14	2.33 ± 0.78	33	46	
			40	4	0.9995	0.549 ± 0.011	2	3.56 ± 0.17	5	39	
			45	3	0.998	0.625 ± 0.22	35	10.9 ± 3.9	36	64	
			50	3	0.994	0.900 ± 0.631	70	16 ± 11	69	64	
			55	3	0.999	1.51 ± 0.06	4	37.5 ± 1.2	3	71	
			60	6	0.989	1.74 ± 0.26	15	54.3 ± 4.8	9	76	
			100	*i, j*		18 ± 13	74	5290 ± 4650	88	100	3.7
		morpholine	40	4	0.997	0.177 ± 0.03	17	4.3 ± 0.5	11	71	
		pyridine	40	5	0.894	0.025 ± 0.02	84	3.9 ± 0.4	10	94	
2	2-furyl-CH_2	piperidine	40	3	0.999	0.46 ± 0.10	22	3.2 ± 1.1	33	41	
			45	3	0.999	0.79 ± 0.42	53	7.08 ± 0.04	6	47	
			50	3	0.998	1.1 ± 0.4	41	12.5 ± 4.7	37	53	
			55	3	0.999	2.0 ± 0.2	10	21.8 ± 0.03	1	52	
			60	3	0.997	3.4 ± 1.6	46	39 ± 17	42	53	
			64	3	0.998	7.8 ± 3	43	107 ± 35	33	58	
			100	*i, j*		98 ± 32	32	2400 ± 550	23	96	20

[a] Number of runs. [b] Correlation coefficient. [c] 90% confidence limits. [d] Values in parentheses are not significantly different from zero. [e] Percent reaction by S_N1 route at [nucleophile] = 10^{-1} M. [f] At 100 °C relative to k_2 for **1a**. [g] Reference 10. [h] Calculated by dividing the observed rate constants by the piperidine concentration. [i] Extrapolated value at 100 °C. [k] Calculation of errors: Lines were calculated from equations of the type $\log k = a/T + b$, with a having maximum and minimum values (90% confidence limits). These lines were constrained to pass through the average temperature of measurement (47.5 and 52 °C for **1k** and **2**, respectively) and were extrapolated to 100 °C to give extreme possible values. In the case of the *p*-methoxy compound, the errors were asymmetrical, and the average value is quoted.

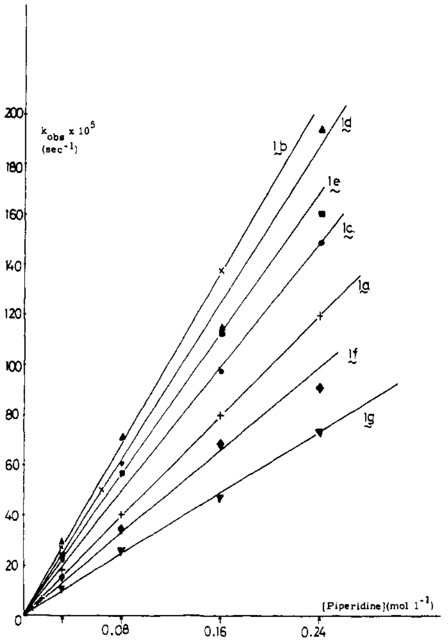

Figure 1. Plot of observed rate constants (k_{obsd}) vs. piperidine concentration for the reaction of 2,4,6-triphenyl-1-(substituted benzyl)pyridinium cations (**1a–g**) with piperidine in chlorobenzene at 100 °C.

multaneous occurrence of S_N1 and S_N2 reactions, i.e., as in eq 3.

Activation Parameters. For the variable-temperature results in Table V, activation parameters were calculated for the S_N2 reaction of the *p*-methylbenzyl, *p*-methoxybenzyl, and furfuryl derivatives and also for the S_N1 reaction of the last two derivatives.

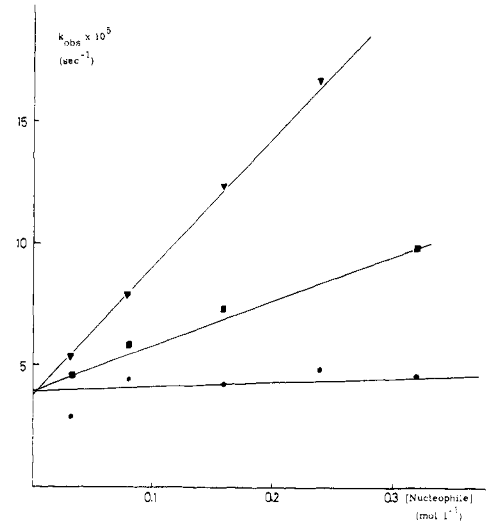

Figure 2. Plot of pseudo-first-order rate constants (k_{obsd}) vs. nucleophile concentration for reactions of 1-(*p*-methoxybenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate in chlorobenzene solution with piperidine (▼), morpholine (■), and pyridine (●) at 40 °C.

The activation enthalpies for the S_N2 reactions of these pyridinium cations of 13–20 kcal mol^{-1} (Table VI) are similar to those previously found for the bimolecular reactions of benzyl halides with anilines in ethanol which range from 10 to 15 kcal mol^{-1}[15b,6e] and with that for the parent 1-benzylpyridinium (**1a**) reported earlier.[3]

The higher activation enthalpies (24–27 kcal mol^{-1}) found for the unimolecular reaction of the 2-furfuryl and

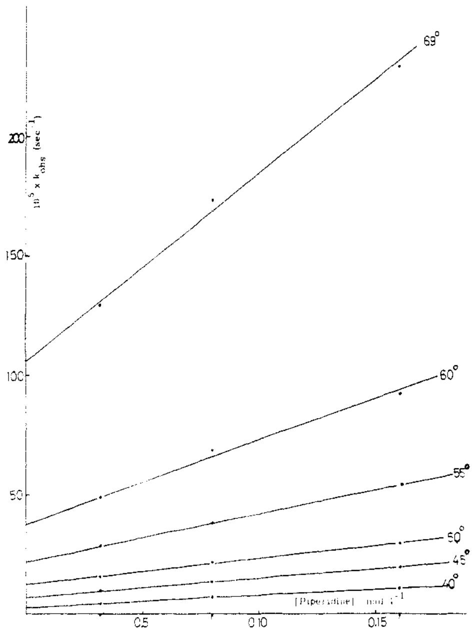

Figure 3. Plot of observed rate constants vs. piperidine concentration for the reaction of 1-(2-furfuryl)-2,4,6-triphenylpyridinium perchlorate (2) with piperidine in chlorobenzene at various temperatures.

Table VI. Activation Parameters[a]

compd	N-substituent	reaction	$\Delta H^{\ddagger}_{373}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{373}$, cal mol^{-1} K^{-1}
1a	$PhCH_2$[b]	S_N2	16.3 ± 0.6	−26.2 ± 1.8
1b	p-$MeC_6H_4CH_2$	S_N2	16.4 ± 0.4	−24.6 ± 1.0
1h	p-$MeOC_6H_4CH_2$	S_N2	13.6 ± 3.1	−30.4 ± 9.7
		S_N1	26.6 ± 3.6	+6.7 ± 11.2
2	2-furyl-CH_2	S_N2	20.0 ± 1.5	−9.7 ± 4.6
		S_N1	24.5 ± 1.1	−0.7 ± 3.4

[a] 90% confidence limits. [b] Data taken from ref 3.

of the p-methoxy derivatives are to be compared with the activation energies reported for the solvolysis of benzyl chlorides in Me_2SO/water[9a] (18–21 kcal mol^{-1}) and for the solvolysis of α-methyl-p-methoxybenzyl chloride (17.6 kcal mol^{-1}).[14]

A consequence of the higher ΔH^{*} values for S_N1 as compared to S_N2 components is that the proportion of unimolecular reaction rises as the temperature increases: this is clearly shown by the values of $10^3k_1/(k_2 + 10k_1)$ given in Table V.

The activation entropies of −24 to −30 cal mol^{-1} K^{-1} for the p-methylbenzyl (**1b**) and for the S_N2 components of the reactions of the p-methoxybenzyl (**1h**) compounds are comparable to that previously reported[3] for the benzyl derivative (**1a**) and with the large negative values previously found, e.g., for the S_N2 reaction of benzyl halides with anilines.[5b,6d,e]

The activation entropies for the S_N1 components of both the p-methoxybenzyl and 2-furfuryl reactions are close to zero and correspond to log A values of 14.8 ± 2.8 and 13.2 ± 0.7, respectively. These log A values are in good agreement with those found for the solvolysis of α-methyl-p-methoxybenzyl chloride[14] (11.7) and those for the solvolysis of substituted benzyl chlorides in Me_2SO/water mixtures which are in the range 7–11. Positive ΔS^{*} values are also found for the solvolysis in water of *tert*-butyl and neopentyl halides.[15] Long[16] predicted positive or small negative entropies for S_N1 reactions.

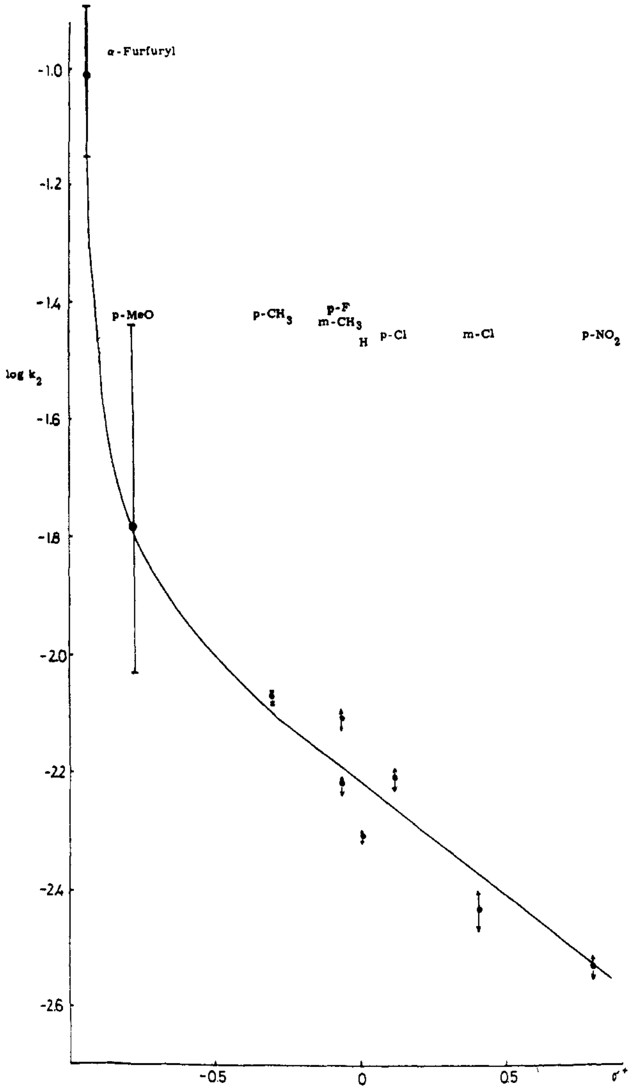

Figure 4. Hammett plot of the logarithms of the second-order rate constants (log k_2) in the reaction of 1-substituted 2,4,6-triphenylpyridinium cations (**1a–h**) and **2** with piperidine in chlorobenzene at 100 °C against σ^+ values. The σ^+ values for **1a,b,h** are from C. D. Johnson, "The Hammett Equation", Cambridge University Press, New York, 1973, p 33, and for **2** from P. Tomasik and C. D. Johnson, *Adv. Heterocycl. Chem.*, **20**, 39 (1976).

Variations of S_N2 Rates with Substitution in the Benzyl Group. From the variable-temperature results in Tables III and IV, we determined extrapolated rates at 100 °C for the p-methoxybenzyl and 2-furfuryl compounds (Table V). Log k_2 values at 100 °C are plotted against σ^+ in Figure 4: together with considerable scatter, distinct curvature is suggested by the extrapolated points. Plots using other σ parameters such as σ or $\sigma_R{}^0$ were still less satisfactory. Because of the experimental uncertainties increased by the temperature extrapolation, we also constructed a Hammett plot at 60 °C for the four available compounds (data for **1a** taken from ref 3). Figure 5 appears to confirm the curvature.

Variations of S_N1 Rates with Substitution in the Benzyl Group. The dependence of the S_N1 rate on electron donor substitution in the benzyl group is clearly

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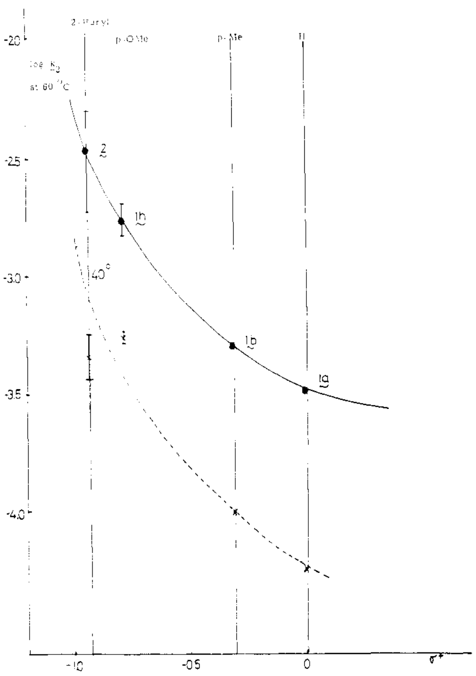

Figure 5. Hammett plot of the logarithms of the second-order rate constants (log k_2) in the reaction of 1-substituted 2,4,6-triphenylpyridinium cations **1a,b,h** and **2** with piperidine in chlorobenzene at 60 °C against σ^+ values (σ^+ values as in Figure 4).

far greater than that of the S_N2 rate. We have only limiting values for the S_N1 rates of the parent N-benzyl derivative, but comparison with N-p-OMe-$C_6H_4CH_2$ at 100 °C indicates a Hammett ρ (using σ^+) more negative than −5. As the S_N1 rates for the furfuryl compound are less than or equal to those for the p-methoxybenzyl compound, clearly there is no proper correlation with σ^+.

Previous Hammett Treatments of S_N1 and S_N2 Nucleophilic Substitutions of Benzyl Halides. Curvature in the Hammett correlations with σ and σ^+ for the reactions of benzyl halides with nucleophiles has been verified by many authors for both first-order[14,17-19] and second-order[5b,20] rate constants. This curvature has been recently discussed[21] and three possible explanations were proposed: (1) changeover of mechanism from S_N2 to S_N1 or an ion-pair mechanism; (2) change in the structure of the transition state for a single mechanism with a different balance of bond formation and bond cleavage; (3) different substituents act to stabilize the transition state with a different balance of polar and resonance effects.

The present work indicates that there can certainly be a changeover in mechanism (cf. explanation 1) but that there remains curvature in the S_N2 component which supports either explanation 2 or 3.

Experimental Section

UV spectra of reactants and products were run on a Pye Unicam SP 800A spectrophotometer. For the rate measurements at fixed wavelength, Pye Unicam SP8-200 (temperature programmable) and Pye Unicam SP6-500 UV spectrophotometers were used. Stoppered glass tubes (28-cm height, 13.5-mm diameter) were used as reaction vessels, which were placed into the hot blocks (Statim Model PROP) for convenient temperature runs. Melting points were measured on a Reichert hot-stage apparatus.

Table VII. Extinction Coefficients at 312 nm for 1-Substituted 2,4,6-Triphenylpyridinium Cations[a]

compd	1-substituent	ϵ_1
1b	p-$MeC_6H_4CH_2$	28 000[b]
1c	m-$MeC_6H_4CH_2$	32 000
1d	p-$FC_6H_4CH_2$	33 000
1e	p-$ClC_6H_4CH_2$	32 000
1f	m-$ClC_6H_4CH_2$	34 000
1g	p-$O_2NC_6H_4CH_2$	32 000
1h	p-$MeOC_6H_4CH_2$	31 000, 28 000[b]
2	2-furyl-CH_2	28 000[b]

[a] In 2% (v/v) chlorobenzene/ethanol. [b] In chlorobenzene.

Preparation of 2,4,6-Triphenyl-1-(substituted benzyl)pyridinium benzyl)pyridinium Perchlorates (1b–g). 2,4,6-Triphenylpyrylium perchlorate[22] (4.09 g, 0.01 mol), substituted benzylamine (0.012 mol), and triethylamine (1.01 g, 0.01 mol) were stirred in chloroform (40 mL) at 20 °C for 24 h. The chloroform was removed under reduced pressure (15 mmHg, 50 °C): addition of diethyl ether (20 mL) to the residue gave the product (see Table I).

1-(p-Methoxybenzyl)-2,4,6-triphenylpyridinium Perchlorate (1h). 2,4,6-Triphenylpyrylium perchlorate (4.09 g, 0.01 mol) and p-methoxybenzylamine (1.37 g, 0.01 mol) were stirred in dichloromethane (40 mL) at 20 °C for 30–40 min. The solvent was removed under reduced pressure at 30 °C. Addition of diethyl ether (20 mL) gave the product (Table I). This compound decomposes very quickly on heating. Attempts to recrystallize this compound from EtOH gave 2,4,6-triphenylpyridine. The same product was obtained when the general method of the preparation of 1-substituted benzyl-2,4,6-triphenylpyridinium perchlorates was applied.

Preparation of 1-(p-Methoxybenzyl)pyridinium Perchlorate (3). 1-(p-Methoxybenzyl)-2,4,6-triphenylpyridinium perchlorate (5.28 g, 0.01 mol) was heated with pyridine (5.53 g, 0.07 mol) at 100 °C for 30 min. The mixture was washed with diethyl ether and the resulting solid (2.52 g, 84%) crystallized from acetone–ether as plates, mp 132 °C. Anal. Calcd for $C_{13}H_{14}ClNO_5$: C, 52.1; H, 4.7; N, 4.7. Found: C, 51.9; H, 4.5; N, 4.3.

Kinetic Measurements. Kinetics were followed by UV spectrophotometry, monitoring the decrease of absorbance of the pyridinium cation at 312 nm by using the procedure previously described.[10] In typical runs the initial concentration of pyridinium was 1.6×10^{-5} or 3.2×10^{-5} mol L^{-1}, while those of the nucleophile varied from 0.000 64 to 0.32 mol L^{-1}. Pseudo-first-order rate constants were calculated from the slope of conventional plots of $\ln (a/a - x) = \ln [(\epsilon_1 - \epsilon_2)/(\epsilon - \epsilon_2)]$ at 312 nm vs. time. Such plots were linear to at least 85% completion. The extinction coefficients of 2,4,6-triphenylpyridine (ϵ_2) at 312 nm in chlorobenzene and in 2% (v/v) chlorobenzene/ethanol are 9000 and 8000, respectively, while those for the pyridinium cations are reported in Table VII.

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Registry No. **1b**·BF_4^-, 72538-32-0; **1c**, 77984-67-9; **1d**, 77984-69-1; **1e**, 67066-40-4; **1f**, 77984-71-5; **1g**, 77984-73-7; **1h**, 67066-38-0; **2**, 61655-14-9; **3**, 77984-74-8; p-methylbenzylamine, 104-84-7; m-methylbenzylamine, 100-81-2; p-fluorobenzylamine, 140-75-0; p-chlorobenzylamine, 104-86-9; p-nitrobenzylamine, 7409-30-5; p-methoxybenzylamine, 2393-23-9; 2,4,6-triphenylpyrylium perchlorate, 1484-88-4; m-chlorobenzylamine, 4152-90-3; furfurylamine, 617-89-0; piperidine, 110-89-4.

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