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Registry No. 1, 56524-88-0; piperidine, 110-89-4; pyridine, 110-86-1; 2-picoline, 109-06-8; thiourea, 62-56-6; tetra-*n*-butylammonium bromide, 1643-19-2; tetra-*n*-butylammonium iodide, 311-28-4.

Supplementary Material Available: A table of pseudo-first-order rate constants for the reaction of 1-benzyl-2,4,6-triphenylpyridinium cation with piperidine at 100 °C in various solvents (1 page). Ordering information is given on any current masthead page.

Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. 2.[1] *N*-Benzylpyridinium Cations: Rate Variation with Steric Effects in the Leaving Group[2]

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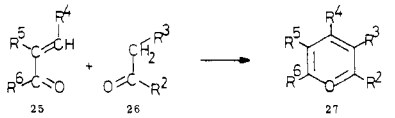
N-Benzyl groups are transferred to piperidine from pyridinium ions by unimolecular S_N1 and/or bimolecular S_N2 mechanisms. Steric acceleration by α-phenyl groups is reduced by an adjacent β-methyl group but increased by constraining the phenyl to near planarity by a CH_2CH_2 chain. Fused five-membered rings are less effective than six-membered rings in steric acceleration. Steric effects at the α and α' positions are not additive. S_N1 rates are increased by α-*tert*-butyl groups.

Investigation of the synthetic utility of nucleophilic displacement of N substituents from 2,4,6-triphenylpyridinium cations has indicated that leaving group ability can vary considerably with structure.[3] For example, aryl thiocyanates were obtained only by the use of *N*-arylnaphthopyridiniums.[4] Qualitative comparisons of various pyridiniums under preparative conditions also clearly indicated considerable rate differences.[5]

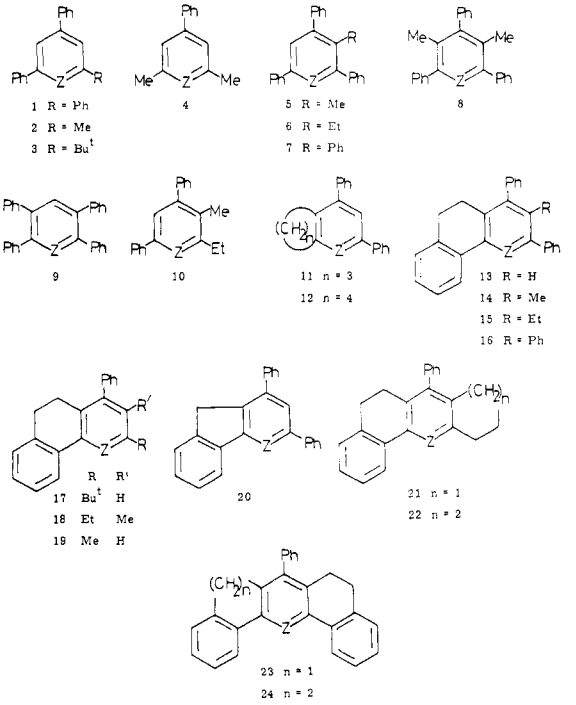
The reaction described above forms the second step of a two-stage conversion of primary amino groups into other functionalities. Cognate work[6] has shown that the pyrylium to pyridinium stage can be carried out under mild conditions at ambient temperatures. We have therefore undertaken a kinetic investigation of a wide variety of 1-benzylpyridiniums (Scheme I) with the aim of defining structure–reactivity relations within this series and of defining mild preparative conditions.

Preparation of Compounds. Kinetics have been reported for 1-benzyl-2,4,6-triphenylpyridinium.[1] Preparative details for the pyrylium salts (A), pyridines (B), and *N*-benzylpyridinium salts (C) have already been reported for the following series (see Scheme I): **3**, **13**, **24** (all ref 5), **2**,[7] **9**.[8] The remaining pyryliums (A) were prepared by one or both of two routes.

(i) They were prepared from the corresponding chalcone (1.2 mol) and ketone (1 mol) by heating with boron trifluoride etherate according to **25** + **26** → **27**. In this reaction sequence it is always preferable and sometimes essential to use the chalcone derived from the least reactive ketone, as discussed in ref 5. Details are recorded in Table I.



Scheme I. Pyrylium (A; Z = O^+), Pyridines (B; Z = N) and Pyridinium Cations (C; Z = N^+CH_2Ph)



(ii) With cycloaliphatic ketones, the preceding method did not give satisfactory results, and the enamine method

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(1) For part 1 see A. R. Katritzky, G. Musumarra, K. Sakizadeh, and M. Misic-Vukovic, *J. Org. Chem.*, preceding paper in this issue.
(2) A. R. Katritzky, G. Musumarra, and K. Sakizadeh, *Tetrahedron Lett.*, 2701 (1980).
(3) A. R. Katritzky, *Tetrahedron*, **36**, 679 (1980).
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(5) A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans.* **1**, 1895 (1980).

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Table I. Preparation of Pyryliums, Pyridines, and *N*-Benzylpyridiniums

	series A: pyrylium tetrafluoroborate salts[a]								series B: pyridines					series C: *N*-benzylpyridiniums				
	starting matl[b]		time,	temp,		recryst	cryst	yield		recryst		cryst	yield,		recryst		yield,
compd	chalcone	ketone	h	°C	mp, °C	solvent[c]	color[d]	%	compd	solvent[e]	mp, °C	form/color[f]	%	compd	solvent[g]	mp, °C	%
5A	BA	P	4	130	248	MC	Y	48	**5B**	Pi	140	ne	83	**5C**	Pi	124	70
6A	BA	B	4	130	184	MC/Pi	Y	60	**6B**	Pi	78	pr	78	**6C**	Pi	172	82
7A[h]	BA	D	1	100	188–189	A/E	Y	70	**7B**	Et/P	182–183[i]	ne		**7C**[h]	E/Cl	115–118	85
10A	BA	K	2	100	214–217	Et	Y	23	**8B**	Pi	134	mi	71	**8C**	Pi	146	80
10A[j]	BA	K	2	100	224–225[k]	Ac	Y	18	**10B**	Et (95%)	165–168	ppr	75	**10C**	Pi/E	*l*	60
11A[j,m]	BA	C	5	0	245–250	Ac	Lb	30	**11B**	Et	144–146	ypr	63	**11C**	EO	139–140	64
14A	BT	P	4	130	256	Me	Y	70	**12B**	Et (95%)	103–104	pr	80	**12C**	Et	109–110	89
15A	BT	B	4	130	236	MC/E	Y	59	**14B**	Pi	148	pr	76	**14C**	Pi	134	65
16A[j]	BT	D	3	100	292–293	Ac	Y	43	**15B**	Pi	130	mi	86	**15C**	Pi	120	73
17A[h]	BP	T	1	100	203	A/E	Y	74	**16B**	HC	235–238	pr	96	**16C**[j]	Et	185–186	94
17A	BP	T	1	100	215	Ac	Y	72	**17B**	Et/H	97	pr	95	**17C**[j]	E	134–136 dec	54
17A	BP	T	1	100	175–176	Et	Y	68	**18B**	Et	90–93	st	95	**17C**	E	140–142 dec	60
18A	BT	K	2	100	210–213	Et	Y	30	**19B**	Et/Ac	138–145 dec	pr	68	**18C**	Et	208–209	82
19A	BC	T	3	100	211–214	A/E	Y	20	**20B**	Pi	156	bmi	88	**19C**	Et	215–216	80
20A	BA	N	4	130	254	MC/E	Y	75	**22B**	Et	151–152	pr	95	**20C**	Pi	226	78
23A	BT	N	4	130	268	MC/E	G	67	**23B**	Pi	158	bmi	79	**21C**	Et	188–189	95
8A	DK				266	Ac	W	85						**22C**	Et	209–211	90
11A	DK				224–227[n]	Ac	Br	82						**23C**	Pi	120	73
12A	DK				211–214[o]	Et	Y	85									
21A	DK				152–157 dec	Pi/E	Br	76									
21A[h]	DK				141–145	E	Y	72									
22A	DK				197–198	Et/E	Y	99									

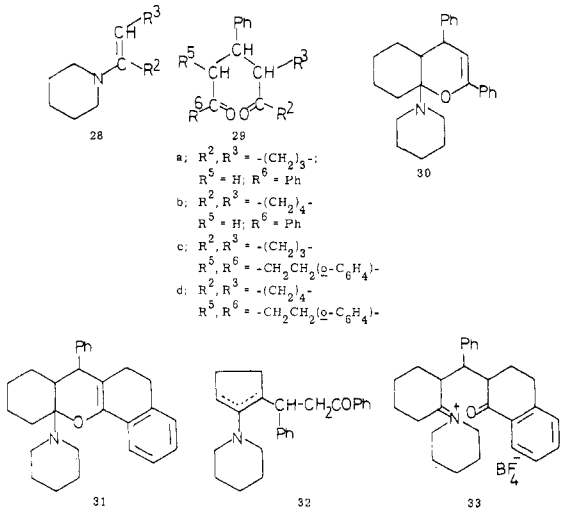
[a] All compounds crystallized as prisms except **10A**·ClO_4^- and **11A** (needles); all gave satisfactory analysis. [b] BA = benzylideneacetophenone, BT = 2-benzylidene-1-tetralone, BP = benzylidenepinacolone, BC = benzylideneacetone, DK = 1,5-diketone, P = propiophenone, B = butyrophenone, D = deoxybenzoin; K = diethyl ketone, C = cyclopentanone, T = 1-tetralone, N = 1-indanone. [c] MC = MeCN, Pi = Pr-*i*-OH, A = Me_2CO, E = Et_2O, Et = EtOH, Ac = AcOH, Me = MeOH. [d] Y = yellow, Lb = light brown, G = green, W = white, Br = brown. [e] Py = pyridine, HC = $HCONMe_2$, H = H_2O. [f] ne = needles, pr = prisms, ppr = pale yellow prisms, ypr = yellow prisms, mi = microcrystals, st = sticks, bmi = buff microcrystals. [g] All compounds formed white prisms; Cl = CH_2Cl_2, EO = EtOAc. [h] $CF_3SO_3^-$ salt (not BF_4^-). [i] W. Zecher and F. Krohnke, *Chem. Ber.*, **94**, 698 (1961), give a melting point of 180–182 °C. [j] ClO_4^- salt (not BF_4^-). [k] G. N. Dorofeenko and L. B. Olekhnovich, *Khim. Geterosikl. Soedin.*, 883 (1972), report a melting point of 223–225 °C. [l] Isolated as gum and characterized by ^1H NMR and IR. [m] Lit.[30] mp 230–232 °C. [n] Lit.[30] mp 226–228 °C. [o] Lit.[9] mp 212–214 °C.

Table II. 1,5-Diketones 29[a]

	starting matl					
compd	piperidine enamine from	chalcone	recryst solvent	mp, °C	crystal form	yield, %
29a[a]	cyclopentanone	benzylideneacetophenone	EtOH (95%)	73–76[b,c]	colorless needles	94
29b	cyclohexanone	benzylideneacetophenone	EtOH (95%)	149[d]	white needles	94
29c[a]	cyclopentanone	2-benzylidene-1-tetralone	EtOH	168–172	colorless prisms	67
29d[a]	cyclohexanone	2-benzylidene-1-tetralone	EtOH	160–165	colorless prisms	73

[a] Satisfactory analysis was obtained. [b] Reference 30; no melting point, procedure, or reference cited. [c] Mp 78–80 °C.[26] [d] Reference 9 quotes a melting point of 141 °C, and ref 27 quotes a melting point of 149 °C; also obtained by direct condensation of benzylideneacetophenone and cyclohexanone in the presence of NaOH (1 equiv) in 85% yield.

Chart I



for the preparation of 1,5-diketones was applied (**25** + **28** → **29**). In two cases the cyclic enamine adduct intermediates **30** and **31** were isolated (Chart I). The piperidinobenzoxanthene **31** was found to undergo a retro-Michael reaction readily upon crystallization in ethanol, giving back 2-benzylidene-1-tetralone quantitatively. However, small amounts of acetic acid suppressed this fragmentation. The corresponding 1,5-diketone (**29d**) also underwent a retro-Michael reaction in the presence of base (e.g., morpholine) in ethanol.

In one case a mixture of the open substituted enamines **32** was isolated (cf. ref 9). Attempted conversion of **31** into the pyrylium **22A** directly by using benzylideneacetophenone as a dehydrogenating agent and BF_3 etherate (cf. ref 10) gave instead the imminium salt **33** (Chart I) The IR of the latter showed the carbonyl stretching at 1680 cm^{-1} and the characteristic imminium C=N$^+$ bond at 1640 cm^{-1}. Attempted hydrolysis of imminium salt **33** with sodium acetate gave back the enamine adduct **31**.

The 1,5-diketones **29** obtained by acid hydrolysis of the enamine adducts are recorded in Table II. Refluxing these 1,5-diketones (**29**) with 1 equiv of benzylideneacetophenone as a hydride abstractor (cf. ref 10b) and boron trifluoride etherate in ether gave the pyrylium salts (Table II). The pyrylium trifluoromethanesulfonate (**21A**) was obtained from the diketone **29c** and CF_3SO_3H at 20 °C.

The pyrylium salts all reacted with benzylamine to give the corresponding *N*-benzylpyridinium salts (Table I) and with ammonia to give the pyridines (Table I).

Pyridiniums **17C** and **23C** were difficult to recrystallize because of their high reactivity.

Determination of Kinetic Rates. Throughout this paper piperidine was used as the nucleophile and chlorobenzene as the solvent, and displacements were carried out on *N*-benzyl compounds. Most reactions were carried out at 100 °C although lower temperatures were utilized for the more reactive compounds and also to obtain activation parameters. The initial concentration of pyridinium was

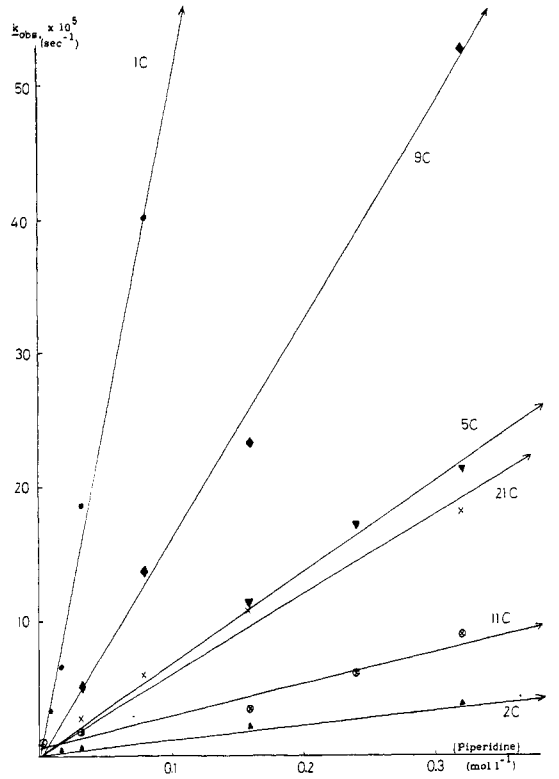


Figure 1. Plot of pseudo-first-order rate constants (k_{obsd}) vs. piperidine concentration for the reaction of *N*-benzylpyridinium and related cations with piperidine in chlorobenzene at 100 °C: **1C**, 2,4,6-triphenylpyridiniuim (●); **2C**, 2-methyl-4,6-diphenylpyridinium (▲); **5C**, 3-methyl-2,4,6-triphenylpyridiniuim (▼); **9C**, 2,3,5,6-tetraphenylpyridinium (♦); **11C**, 2,4-diphenylcyclopenteno[1,2-*b*]pyridinium (⊗); **21C**, 11-benzyl-5,6-dihydro-7-phenylcyclopenteno[1,2-*b*]benzo[*h*]quinolinium (X).

either 3.2×10^{-5} M (generally chosen for more reactive compounds) or 1.6×10^{-3} M. No significant difference was found between k_{obsd} values taken at these different concentrations. Thus for [**1C**] = 3.2×10^{-5} mol L^{-1} and [piperidine] = 0.16 mol L^{-1} we found $k_{obsd} = 77 \times 10^{-5}$; cf. $k_{obsd} = 80 \times 10^{-5}$ obtained for [**1C**] = 1.6×10^{-3} mol L^{-1} and [piperidine] = 0.16 mol L^{-1}.[1] The piperidine concentration was varied in the range 3.2×10^{-5} to 0.48 M, depending on the reaction rate.

Observed rates, k_{obsd}, under pseudo-first-order conditions for the reaction of the *N*-benzylpyridiniums at various piperidine concentrations are recorded in Table VII (supplementary material). Plots of k_{obsd} vs. [piperidine] are almost always (an exception to this generalization is mentioned later) good straight lines (Figures 1–4; Figure 4 is given as supplementary material): in many cases these plots pass within experimental uncertainty of the origin (Figures 1 and 4), indicating that the reactions are accurately first order in piperidine concentration. However, in other cases there is a significant intercept, indicating a reaction which is zeroth order in piperidine (Figures 2 and 3). Two additional kinetic runs made for reactions of **1C** with piperidine at low piperidine concentrations (see Figure 5; supplementary material) confirm the zero intercept and provide additional evidence for the constancy of k_2 with different initial pyridinium concentrations.

Together with evidence given in the following paper on the substitution reactions of 2,4,6-triphenylpyridiniums with various *N*-groups,[11] the above data show conclusively that these reactions occur by bimolecular processes, first

(6) A. R. Katritzky and R. H. Manzo, *J. Chem. Soc., Perkin Trans. 2*, 571 (1981).
(7) J. A. Durden and D. G. Crosby, *J. Org. Chem.*, **30**, 1684 (1965); A. R. Katritzky, R. C. Patel, and M. Shanta, *J. Chem. Soc., Perkin Trans. 1*, 1888 (1980).
(8) A. R. Katritzky, B. Plau, and K. Horvath, *J. Chem. Soc., Perkin Trans. 1*, 2554 (1980).
(9) F. P. Colonna, S. Fatutta, A. Risaliti, and C. Russo, *J. Chem. Soc. C*, 2377 (1970).
(10) (a) W. Schroth and G. Fischer, *Angew. Chem.*, **75**, 574 (1963); (b) J. A. Van Allen and G. A. Reynolds, *J. Org. Chem.*, **33**, 1102 (1963).

(11) Part 3: A. R. Katritzky, G. Musumarra, and K. Sakizadeh, *J. Org. Chem.*, following paper in this issue.

Table III. First- (k_1) and Second- (k_2) Order Rate Constants for the Reactions of *N*-Benzylpyridinium and Related Cations with Piperidine in Chlorobenzene

compd	temp, °C	N^a	r^b	slope		intercept		$10^3k_1/[k_2 + 10k_1]^e$	rel k_2[f]
				10^3k_2[c]	% error	10^5k_1[c,d]	% error		
1C[g]	100	6	0.9996	49.4 ± 0.13	3	<2 (0.2 ± 1.9)		<4	1
2C	100	5	0.997	0.119 ± 0.013	11	<1 (0.30 ± 0.30)		<33	0.024
3C	100	5	0.998	1.07 ± 0.08	7	8.0 ± 2.2	27	43	0.22
5C	100	4	0.991	0.82 ± 0.23	28	<5 (−2.5 ± 7.5)		<38	0.17
6C	100	4	0.994	8.0 ± 1.8	22	<30 (−10 ± 39)		<27	1.6
7C	100	5	0.999	1.62 ± 0.08	5	<3 (0.8 ± 2.4)		<17	0.33
9C	100	4	0.997	1.64 ± 0.26	16	<5 (−0.4 ± 4.9)		<−21	0.33
11C	100	6	0.988	0.220 ± 0.037	17	<2 (0.98 ± 0.98)		<47	0.045
12C	100	4	0.9999	0.431 ± 0.009	2	5.10 ± 0.28	5	54	0.087
13C	60	4	0.999	20.6 ± 2.2	10	<2 (0.4 ± 2.0)		<0.3	69[h]
15C	100	3	0.9999	25.5 ± 2.2	8	<3 (−0.8 ± 3.0)		<0.9	5.2
16C	40	3	0.9999	0.527 ± 0.036	7	<1 (0.26 ± 0.75)		<16	
16C	60	4	0.9996	1.99 ± 0.10	5	<4 (1.5 ± 2.0)		<15	3.2[i]
16C	78	4	0.999	5.16 ± 0.37	7	<8 (1.6 ± 6.9)		<14	
17C	39.7	3	0.9999	6.6 ± 0.6	9	<7 (3.5 ± 3.8)		<10	
17C	50	3	0.995	13 ± 9	66	<70 (15 ± 54)		<9	
17C	55	3	0.997	21 ± 10	48	<80 (17 ± 62)		<27	123[i]
17C	60	8	0.999	36.3 ± 1.0	3	6.2 ± 3.8	61	2	
17C	64.5	3	0.999	51 ± 17	33	<100 (1 ± 106)		<17	
18C	100	3	0.99999	8.1 ± 0.2	3	<3 (0.3 ± 2.6)		<3	1.6
19C	100	4	0.997	3.31 ± 0.55	16	<25 (−8 ± 16)		<19	0.67
20C	100	4	0.995	106 ± 14	13	11.2 ± 0.7	7	1	21
21C	100	4	0.996	0.532 ± 0.098	18	<3 (1.7 ± 1.8)		<40	0.11
22C	100	6	0.991	1.34 ± 0.19	14	<9 (4.0 ± 4.9)		<40	0.27
23C	100	4	0.991	223 ± 62	28	52 ± 11	36	1	45
24C	30	6	0.999	105 ± 4	4	<1 (0.4 ± 0.8)		<0.1	900[i]

[a] Number of runs. [b] Correlation coefficient. [c] 90% confidence limit. [d] Values in parentheses are not significantly different from zero. [e] I.e., percent reaction by S_N1 route at [piperidine] = 10^{-1} M. [f] At 100 °C relative to k_2 for compound 1C. [g] From ref 1. [h] k_2 at 100 °C from Table VIII. [i] k_2 at 100 °C extrapolated from variable-temperature data.

order in both substrate and nucleophile. However, in some cases the bimolecular mechanism is accompanied by a unimolecular reaction, first order in substrate but independent of nucleophile concentration (and nature as we will show later[11]).

Thus the kinetic data show that these reactions occur either by an S_N2 reaction or by a combination of S_N2 and S_N1 mechanisms.

For some of these compounds, Ingold's dictum[12] ("in order that mechanism S_N1 shall operate with a practical degree of facility a solvent of suitable polarity is essential".) does not hold. Of course, the fact that the present leaving groups are neutral is of great significance, as we do not have charge creation in the transition state. The k_1 and k_2 rate constants are given in Table III.

Studies at Variable Temperatures. Compounds **13C**, **16C**, **17C**, and **24C** reacted rapidly at 100 °C, and the data in Table VIII (supplemental material) for the first three of these compounds refer to 60 °C and for the last to 30 °C. So that quantitative comparisons of the k_2 values for these compounds could be made at 100 °C with the other compounds, activation parameters were determined. Relevant variable-temperature rates are given in Table IV. For **16C** data were collected at several piperidine concentrations at each temperature, but the contribution of the S_N1 reaction is insignificant. For **13C** and **24C**, which react only by the S_N2 process (cf. Table III), experiments were confined to a single piperidine concentration. For **17C**, the activation parameters (Table V) were obtained for the S_N2 component: the S_N1 component could not be measured accurately enough for the determination of the parameters. Table IV also contains rates determined at various temperatures for **1C**, **9C**, and **15C**, compounds which also react solely by the S_N2 mechanism (Table III), from which activation parameters were calculated (Table V).

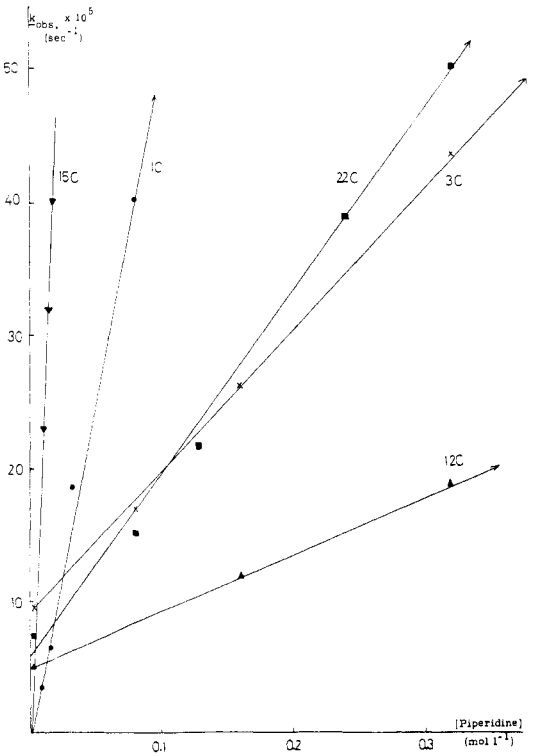


Figure 2. Plot of pseudo-first-order rate constants (k_{obsd} vs. piperidine concentration for the reaction of *N*-benzylpyridinium and related cations with piperidine in chlorobenzene at 100 °C: **1C**, 2,4,6-triphenylpyridinium (●); **3C**, 2-*tert*-butyl-4,6-diphenylquinolinium (X); **12C**, 5,6,7,8-tetrahydro-2,4-diphenylquinolinium (▲); **15C**, 3-ethyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium (▼); **22C**, 5,6,8,9,10,11-hexahydro-7-phenylbenzo[*c*]acridinium (■).

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd Ed., Cornell University Press, New York, 1969, p 425.

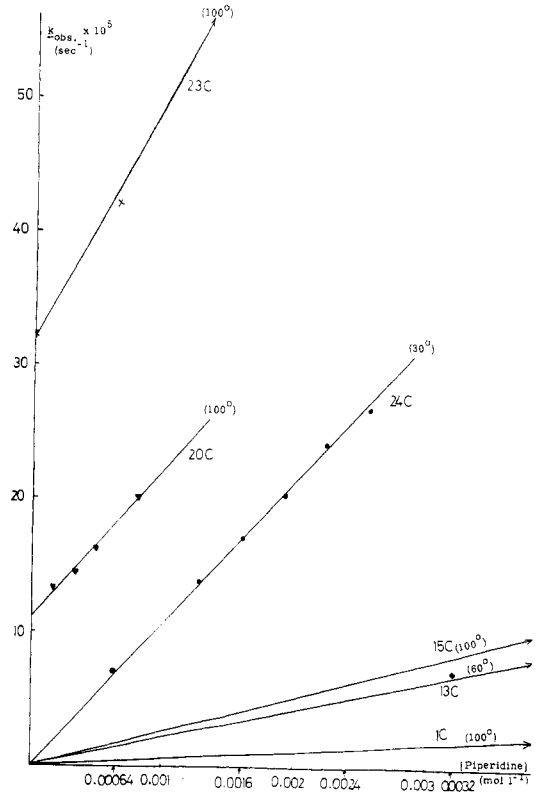


Figure 3. Plot of pseudo-first-order rate constants vs. piperidine concentration for the reaction of *N*-benzylpyridinium and related cations with piperidine in chlorobenzene: **1C**, 2,4,6-triphenylpyridinium at 100 °C; **13C**, 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium at 60 °C (♦); **20C**, 6,8-diphenylindan[1,2-*b*]pyridinium at 100 °C (X); **24C**, 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium at 30 °C (●).

The activation enthalpies of 11–18 kcal mol^{-1} found for these compounds are in the same range as those found for S_N2 reactions of various N-substituted 2,4,6-triphenylpyridiniums.[11] The activation entropies are in the expected (see discussion in ref 11) range of −19 to −34 cal mol^{-1} K^{-1} with one value apparently less negative at −14 cal mol^{-1} K^{-1} for **17C**.

Effect on S_N2 Displacement Rates of Pyridinium Substitution: Monocyclic Compounds. The steric acceleration effect on an α-phenyl group is shown at once by comparison of the k_2 values for compounds **1C** and **2C**: substitution of one α-phenyl by an α-methyl reduces the rate by a factor of ca. 40. No kinetic results are reported for the 2,6-dimethyl derivative **4C** because the λ_{max} is at 291 nm, and interference from solvent absorption affects the accuracy and reproducibility: however, the rate is clearly much slower even than that of compound **2C**.[13] Replacing an α-phenyl group by α-*tert*-butyl (in **3C**) reduces the k_2 by only a factor of ca. 5; interestingly, significant S_N1 reactivity now appears.

The steric influence of an ortho substituent is generally considered to be enhanced by an additional substituent in the adjacent meta position: this is known as buttressing.[14] In previous available examples, buttressing has invariably *added* to the steric effect of a group: a good example is in biphenyl racemization rates.[15] In clear contrast, simple buttressing can have a rate-reducing effect in the present series: thus the 3-methyl group in **5C** reduces the k_2 of **1C** by a factor of ca. 6. However, the sensitivity of the system is illustrated by the ethyl analogue **6C** in which the larger ethyl group actually has a small rate-enhancing effect.

Unfortunately, λ_{max} at 291 nm for the 3,5-dimethyl-2,4,6-triphenyl compound **8C** makes accurate kinetic measurements difficult: however, approximate results indicate that, as for the monomethyl derivative, **6C**, dimethyl derivative **8C** has a rate considerably slower than that of the parent **1C**.[13] Even in **9C** where each of the α-phenyl groups is flanked by a second phenyl, k_2 is reduced by a factor of ca. 3 compared with that for **1C**. The isomeric tetraphenyl derivative **7C** shows a rate identical with that for **9C**.

The k_{obsd} values for the 2-ethyl-3-methyl derivative (**10C**, Table VII, supplementary material) plotted against [piperidine] exceptionally show significant curvature: possibly this arises from partial deprotonation of **10C** to an

(13) For full details see K. Sakizadeh, Ph.D. Thesis, University of East Anglia, Norwich, England, 1981.
(14) F. H. Westheimer in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 552.
(15) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 163.

Table IV. Temperature Dependence of Second-Order Rate Constants (k_2) for the Reactions of *N*-Benzylpyridinium and Related Cations with Piperidine in Chlorobenzene[a]

temp, °C	[Pip], M	$10^5 k_{obsd}$	$10^3 k_2$
	2,4,6-Triphenylpyridinium (1C)		
40	0.160	0.935	0.0580
60	0.162	5.20	0.321
80	0.162	20.3	1.25
90.5	0.162	40.4	2.49
100			4.94[b]
	5,6-Dihydro-2,4-diphenylbenzo[*h*]quinolinium (13C)		
40	0.00321	1.63	5.05
60			20.6[b]
80	0.00321	31.0	96.6
100	0.00321	110	343
	5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium (24C)		
25	0.000963	0.68	70.6
30			105[b]
60	0.00321	164	511
80	0.000963	189	1960
	2,3,5,6-Tetraphenylpyridinium (9C)		
90	0.162	13.5	0.833
100[b]			1.64
110	0.162	42.9	2.77
119.2	0.162	74.6	4.60
	3-Ethyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium (15C)		
60	0.16	19.7	1.23
70	0.16	36.2	2.26
80	0.16	88.8	5.55
100			25.5[b]

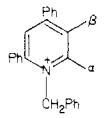
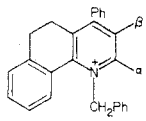
[a] Measured under pseudo-first-order conditions, in units of mol L^{-1} s^{-1}. All substrates reported in the table react exclusively by S_N2 processes (cf. Table VI). [b] From Table VII.

Table V. Thermodynamic Parameters for the S_N2 Reactions of *N*-Benzylpyridinium Cations with Piperidine in Chlorobenzene[a]

compd	$\Delta H^{\ddagger}_{373}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{373}$, cal mol^{-1} K^{-1}
1C	16.3 ± 0.6	−26.2 ± 1.8
9C	15.7 ± 1.3	−29.8 ± 3.6
13C	15.8 ± 1.5	−19.0 ± 5.0
15C	17.6 ± 2.6	−19.3 ± 7.5
16C	12.4 ± 2.6	−34.0 ± 7.8
17C	17.2 ± 3.1	−13.8 ± 9.5
24C	11.4 ± 2.2	−25.4 ± 6.7

[a] 90% confidence level.

Table VI. Effect of Constraining an α-Phenyl by a CH_2CH_2 Bridge

β-substituent / α-substituent					Et Ph		H Me	H Ph	H t-Bu
	compd	20C	11C	12C	6C	13C	2C	1C	3C
	10^3k_2 (at 100 °C)[a]	106	0.220	0.431	8.0	343[b]	0.119	4.94	1.07
	compd	23C	21C	22C	15C	24C	19C	13C	17C
	$10^3k_2^1$ (at 100 °C)[a]	223	0.532	1.30	25.5	4450[c]	3.31	343[b]	608[c]
ratio k_2^1/k_2		2.1	2.4	3.0	3.2	13	28	69	568

[a] From Table VII. [b] From Table VIII. [c] Extrapolated from variable-temperature measurements.

anhydro base; similar behavior has been observed in other systems.[16]

A more refined concept of buttressing, which takes into account only the globular size of interacting groups, has been recently provided by the so called "gear effect".[17] This effect, defined as the conformational transmission which is caused by interaction between polyhedral substituents, depends on the polyhedral shape of the groups.

Clearly no single substituent parameter[18] such as E_s' can describe the steric effect of α substituents in the present reactions.

Effects on S_N2 Displacement Rates of Pyridinium Substition: Polycyclic Compounds. The k_2 values for **11C** and **12C** afford good evidence that steric effects are dominant for the rates. The cyclohexeno analogue **12C** has a k_2 about double that of **11C**; this is explained by the higher steric hindrance due to the fused six-membered ring. A reduction of proximity effects in five-membered rings with respect to the ortho benzene position is well-known for the acid dissociation of 3-substituted thiophene-2-carboxylic acids[19] and for the alkaline hydrolysis of the corresponding carboxylates.[20]

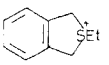
The rate for cyclopenteno derivative **11C** is itself double that for the methyl analogue **2C**: bearing in mind the rate-reducing effect of the 3-methyl group in **5C**, this shows the subtle nature of the steric effects in the series. Presumably the precise rotational orientation of the α-methyl group is significant.

Constraining an α-phenyl group to near planarity by a CH_2CH_2 bridge from the phenyl ortho position to the adjacent pyridiniuim β-position can have a dramatic rate-enhancing effect on k_2: relevant comparisons are given in Table VI. The rate ratios vary from 2 to 560, but within this range the β-substituted compounds show *small* values while those for derivatives containing a β-hydrogen atom are much larger. The adverse buttressing effect mentioned above in the discussion of **5C** and **8C** is apparently much more important in the fused-ring systems: cf, ratios of 2.1–3.2 for the first four entries of Table VI. With a single α substituent and the β-position free, the rate ratio now increases dramatically with the size of the α substituent: 28, 69, and 570 for Me, Ph, and *t*-Bu, respectively.

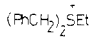
This enhanced buttressing effect is also illustrated by comparisons of **13C** with **15C** and **16C**: decreased by factors of 13 and 22 by β-Et and β-Ph, respectively. (Contrast the weak *activating* effect of β-Et in **6C**.) For the β-methyl analogue **14C** we only measured a single kinetic run (not reported) which also indicated a rate significantly lower than that of **13C**.

The rate for the fused five-membered-ring compound **20C** is less by a factor of 3 than that of the six-membered-ring analogue **13C**: this is similar to the difference found between **11C** and **12C**.

King has shown[21] by rate comparison of **34** and **35** that the inability of a benzyl group to take up its most favorable orientation in the transition state can reduce the rate of nucleophilic substitution by a factor of 10^3. This factor may well be at work in some of the compounds presently discussed.



34



35

Demethylation of *N*-methylpyridiniums by triphenylphosphine has been studied by Metzger and his collaborators,[22] who found that substitution of α-*t*-Bu for α-H increased the rate by ~50 (later work[23] suggests that iodide is the active nucleophile): similar work has been done in the azole series.[24]

Effect of Pyridinium Structure on S_N1 Displacement Rates. Quantitatively significant S_N1 rates k_1 were obtained for five compounds only (Table III): the two *tert*-butyl derivatives **3C** and **17C** (at 60° C) and three compounds containing fused five-membered rings, **12C**, **20C**, and **23C** (the kinetic data for this compound show some curvature at high [piperidine], possibly due to proton loss from the cyclic CH_2 group), for which 10^5k_1 at 100 °C was 8, 6 (at 60 °C), 5, 11, and 32, respectively. The proportion of reaction proceeding by the S_N1 mechanism at [piperidine] = 0.1 M for these compounds is 43%, 2%, 54%, 1%, and 1%, respectively.

For all but three of the other compounds the limiting value of 10^5k_1 is below 5 (and often below 2). The exceptions are **6C**, **19C**, and **22C** where the uncertainties are larger.

It is perhaps understandable that *t*-Bu groups should increase S_N1 rates: perhaps they shield nucleophile approach but cause release of steric strain in S_N1 transition states. It is less obvious why fused five-membered rings should exert the same effect, and an explanation must await further experimentation.

(16) Unpublished work with Yu Xiang Ou.
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(18) J.-E. Dubois, J. A. MacPhee, and A. Panaye, *Tetrahedron*, **36**, 919 (1980).
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(20) D. Spinelli, R. Noto, G. Consiglio, and A. Storace, *J. Chem. Soc., Perkin Trans. 2*, 1805 (1976).
(21) J. F. King and G. T. Y. Tsang, *J. Chem. Soc., Chem. Commun.*, 1131 (1979)
(22) U. Berg, R. Gallo, and J. Metzger, *J. Org. Chem.*, **41**, 2621 (1976).
(23) L. W. Deady and O. L. Korytsky, *Tetrahedron Lett.*, 451 (1979).
(24) J. Kister, U. Berg, R. Gallo, and J. Metzger, *Bull. Soc. Chim. Fr.* 484 (1979).

In 1969, Ingold wrote further[25] "The possibility of steric accelertion in unimolecular nucleophilic substitution...is highly plausible and may yet be convincingly illustrated...but the evidence adduced so far for substitution is not fully satisfactory". We believe that we have now presented satisfactory evidence.

Experimental Section

IR and NMR spectra were measured with Perkin-Elmer 237 and R12 (60 MHz) and Varian HA-100 (100 HHz) spectrometers, respectively. 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 in height and 13.5 mm in 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.

General Procedure for Preparing Pyrylium Salts from Chalcone and Ketone. The appropriate ketone (0.08 mol; for dialkyl ketones 0.3 mol was used) and then boron trifluoride etherate (0.24 mol) were added to the correct chalcone (0.1 mol), and the mixture was heated with stirring at the temperature and for the time given in Table I. The reaction mixture was cooled to 20°C and poured into Et_2O (500 mL) with vigorous stirring. The precipitate was crystallized from a suitable solvent to give the product (see Table I).

Preparation of 1,5-Diketones (29). 1,3-Diphenyl-1-(2-oxocyclopentyl)propan-3-one (29a) was obtained from the isomeric mixture of enamine adducts **32** (94%) by following procedure B mentioned below: mp 73–76 °C (lit.[26] mp 78–80 °C.

1,3-Diphenyl-1-(2-oxocyclohexyl)propan-2-one (29b). Procedure A. Benzylideneacetophenone (3 g, 0.0144 mol) and cyclohexanone (1.42 mL, 0.0144 mol) were added to a well-stirred solution of NaOH (0.63 g) in EtOH (95%, 20 mL). After the mixture was stirred at 25 °C for 12–13 min, the product was filtered off, washed with ethanol (95%, 10 mL) and then water (10 mL), and crystallized from 95% EtOH to give white needles: 3.7 g (85%): mp 148–149 °C (lit.[9] mp 141 °C, lit.[27] mp 149 °C).

Procedure B. The enamine adduct **31** (5 g, 0.13420 mol) was stirred in EtOH (50 mL), AcOH (2 mL), and water (5 mL) at 20 °C for 24 h. The product was filtered off and washed with EtOH (95%, 5 mL) and water (5 mL) to give **29b** (3.9 g, 94%).

2-[2-Oxacyclopentyl)phenylmethyl]-1-tetralone (29c). Procedure A. 1-Piperidinocyclopentenone (4.0 g, 0.26 45 mol) and 2-benzylidene-1-tetralone (7.5 g, 0.023 49 mol) were refluxed on sodium–dry toluene (75 mL) for 12 h over activated molecular sieves. Toluene was evaporated at 100 °C (20 mm), and the mixture was dissolved in hot EtOH (75 mL). AcOH (5 mL) and water (2.5 mL) were added, and the mixture was left to stand at 20 °C for 72 h. Filtration gave the 1.5-diketone **29c** in two successive crops (total 6.2 g, 74%). It crystallized from EtOH as colorless prisms: mp 168–172 °C, ν_{max} ($CHBr_3$) 1680, 1730 cm^{-1}; NMR (60 MHz, CCl_4) δ 1.14–2.30 (9 H, m), 2.34–3.12 (3 H, m), 3.32–3.60 (2 H, m), 7.00–7.74 (8 H, m), 7.78–8.00 (1 H, m).

Procedure B. 2-Benzylidene-1-tetralone (10 g, 0.045 18 mol), cyclopentanone (4.93 g, 0.058 66 mol), and morpholine (5.0 g, 0.058 66 mol) were refluxed in toluene (200 mL) with azeotropic removal of water for 24 h. Solvent was evaporated in vacuo at 100 °C. The residue was dissolved in EtOH (95%, 150 mL). AcOH (10 mL) and H_2O (10 mL) were added, and the mixture was kept at 20 °C for 24 h. Water (200 mL) was added, and the resulting emulsion was kept for 12 h. Solvents were decanted, and the gummy residue was crystallized from EtOH/H_2O to give **29c** (10.5 g, 73%) in two successive crops.

2-[(2-Cyclohexanonyl)phenylmethyl]-1-tetralone (29d). The enamine adduct **31** (5 g, 0.012 51 mol) was refluxed in AcOH (15 mL) and H_2O (1 mL) for 3 h. The reaction mixture was then left to stand at room temperature for 12 h. The product, **29d**, was obtained by filtration in two successive crops (total yield 3.1 g, 75%) and was crystallized from EtOH (to which 1 drop of AcOH was added) as colorless prisms: mp 158–165 °C; ν_{max} ($CHBr_3$) 1710, 1665 cm^{-1}; NMR (60 MHz, $CDCl_3$ δ 1.00–2.30 (10 H, m), 2.36–3.00 (4 H, m), 3.05–3.44 (1 H, m), and 6.96–8.15 (9 H, m)

4a,5,6,7,8,8a-Hexahydro-2,4-diphenyl-8a-piperidino-4*H*-chromene (30). 1-Piperidinocyclohexene (4.5 g, 0.027 20 mol) and benzylideneacetophenone (5 g, 0.024 00 mol) were stirred in CH_2Cl_2 (15 mL) and petroleum ether (bp 40–60 °C, 30 mL) for 72 h. Filtration gave the product, **30** (8 g, 90%), which crystallized from petroleum ether (bp 60–80 °C) as prisms: mp 124–125 °C; ν_{max} ($CHBr_3$) 1680 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.45 (8 H, m), 2.30 (4 H, m), 2.80 (6 H, m), 3.35–3.90 (2 H, m), 5.25 (1 H, d, J = 2 Hz), 7.00–8.10 (10 H, m). Anal. Calcd for $C_{26}H_{30}NO$: C, 83.8; H, 8.1; N, 3.8. Found: C, 83.8; H, 8.4; N, 3.6.

5,6,7a,8,9,10,11,11a-Octahydro-7-phenyl-11a-piperidinobenzo[c]-7*H*-xanthene (31). 1-Piperidinocyclohexene (4.2 g, 0.0254 mol) and 2-benzylidene-1-tetralone (5 g, 0.0226 mol) were refluxed in sodium-dried toluene (60 mL) over activated molecular sieves (under a nitrogen atmosphere) for 20 h. The solvent was removed in vacuo at 100 °C. Trituration of the resulting thick oil with acetonitrile (30 mL) afforded the product (8.99 g, 99%). Crystallization from EtOH/AcOH gave **31** as prisms: mp 151–152 °C; ν_{max} ($CHBr_3$) 1660 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.12–2.18 (16 H, m), 2.88–3.62 (8 H, m), 7.10–7.90 (9 H, m). Anal. Calcd for $C_{28}H_{33}NO$: C, 84.2; H, 8.3; N, 3.4. Found: C, 84.1; H, 8.6; N, 3.4.

2-(2-Benzoyl-1-phenylethyl)-1-piperidinocyclopent-1- and -2-enes (32). 1-Piperidinocyclopentene (4 g, 0.0265 mol) and benzylideneacetophenone (5 g, 0.024 00 mol) were stirred in petroleum ether (bp 60–80 °C) at 15 °C for 3 h. The product was filtered and crystallized from petroleum ether (bp 60–80 °C) to give the product: 8.5 g (98%); mp 125–128 °C (lit.[26] mp 124–127 °C).

***N*-[2-[(1-Oxo-1,2,3,4-tetrahydro-2-naphthyl)phenylmethyl]cyclohexylidene]piperidinium Tetrafluoroborate (33).** Enamine adduct **31** (2 g, 0.0052 mol), benzylideneacetophenone (1.08 g, 0.0052 mol), and boron trifluoride etherate (2 mL) were heated at 100 °C for 30 min. EtOH (10 mL) was added, and trituration with Et_2O afforded **33** (2.1 g, 83%). Crystallization from 1,2-dichloroethane gave yellow prisms: mp 202–208 °C; ν_{max} ($CHBr_3$) 1680, 1640 cm^{-1}; NMR (60 MHz, TFA) δ 2.07 (14 H, m) 3.0 (5 H, m), 3.60–4.5 (4 H, m), 7.47 (7 H, m), 7.92 (2 H, m). Anal. Calcd for $C_{28}H_{34}BF_4NO$: C, 69.0; H, 7.0; N, 2.9. Found: C, 68.8; H, 7.1; N, 3.0.

Preparation of Pyryliums from 1,5-Diketones (29). The 1,5-diketone (0.009 60 mol) and benzylideneacetophenone were melted at 100 °C, and boron trifluoride etherate (0.019 20 mol) was added dropwise. After 1–2 h at 100 °C EtOH or AcOH as indicated (2 mL) was added and the mixture boiled for 3–5 min. Triturations with Et_2O (100–200 mL) afforded the pyrylium salt which was crystallized accordingly (Table I).

3,5-Dimethyl-2,4,6-triphenylpyrylium Tetrafluoroborate (8A). 3-Phenyl-2,4-dibenzoylpentane [prepared as in ref 28; mp 163 °C (lit[28] mp 162–163 °C); 17.65 g], benzylideneacetophenone (10.4 g), BF_3 etherate (0.24 mol, 15 mL), and glacial AcOH (200 mL) were refluxed for 10 h. On cooling the pyrylium salt separated (see Table I).

2,6-Dimethyl-4-phenylpyrylium Perchlorate. Dimethylphenylcarbinol (1.0 g, 0.0073 mol) in Ac_2O (3.0 mol) was cooled to 0 °C. $HClO_4$ (70%, 1.0 mL) was added cautiously, and the solution was stirred for 2 h. The product (0.6 g, 30%), after being washed with Et_2O, had a melting point of 215–216 °C (lit.[29] mp 215–216 °C).

Preparation of 5,6-dihydro-7-phenylcyclopenteno[1,2-*b*]benzo[*h*]chromenylium Trifluoromethanesulfonate (21A). Trifluoromethanesulfonic acid (1.5 g, 0.009 70 mol) was added to the 1,5-diketone **29c** (3.1 g, 0.009 60 mol) and benzylideneacetophenone (2 g, 0.009 60 mol) in Et_2O (50–60 mL) at 20 °C, and the mixture stirred at 20 °C for 6 h. The crystalline precipitate was filtered off and washed with ether (10 mL) to give the analytically pure pyrylium: 3.1 g (72%); mp 141–145 °C; ν_{max} ($CHBr_3$) 1030,

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1270, 1620 cm^{-1}; NMR (60 MHz, TFA) δ 2.20–2.90 (2 H, m), 2.94–3.34 (6 H, m), 3.62 (2 H, t, $J \simeq 7$ Hz), 7.30–7.90 (8 H, m), 8.10–8.40 (1 H, m).

Preparation of 2,4-Diphenylcyclopenteno[1,2-*b*]pyrylium Perchlorate (11A). To a well-stirred cooled solution (ice–salt bath) of benzylideneacetophenone (5 g, 0.024 00 mol) in Et_2O (20 mL) was added dropwise a cooled mixture of $HClO_4$ (70%, 1.72 mL) and Ac_2O (5 mL). Cyclopentanone (2.12 mL) was added dropwise, and a further cooled mixture of $HClO_4$ (70%, 1.72 mL) and Ac_2O (5 mL) was added. The reaction mixture was stirred at 0 °C for 5 h. The crystals which separated were filtered off and washed with Et_2O (10 mL) to give **11A** (2.7 g, 30%), which crystallized from AcOH as dark purple prisms, mp 245–250 °C (lit.[30] mp 230–232 °C).

Preparation of Pyridines. The pyrylium salt was suspended in EtOH or MeOH and treated either with aqueous ammonia and stirred or with gaseous ammonia. In some instances the whole was heated. After standing, the pyridine was filtered off and crystallized (see Table I).

Preparation of Pyridinium Salts. The pyrylium salt (0.01 mol) suspended in absolute EtOH (20 mL) was treated with benzylamine (ca. 20% excess) dropwise at 20 °C over 10 min. After the mixture was stirred for 10 h at 20 °C, Et_2O (100 mL) was added. After the mixture was stirred an additional 1 h, the pyridinium salt was filtered off and crystallized from 2-propanol (see Table I).

Variations on this general procedure were needed for the following cases: (i) superdry EtOH (Mg) was used as solvent for **10C**, **11C**, **12C**, and **21C**; (ii) sodium-dried Et_2O (with 5 days of stirring) was used as the solvent for **19C**; (iii) $CHCl_3$ was used as the solvent with 2 days of stirring followed by crystallization below 25 °C for **17C**.

Kinetic Measurements. Kinetics were followed by UV spectrophotometry by monitoring the decrease of absorbance of the pyridinium cation at a fixed wavelength and using the procedure already described.[1]. In typical runs under pseudo-first-order conditions the concentration of pyridinium was 1.6×10^{-3} and/or 3.2×10^{-5} mol L^{-1}, while those of the nucleophile varied from 0.000 032 to 0.48 mol L^{-1}. Pseudo-first-order rate constants were calculated from the slope of conventional plots of $\ln (a/a - x) = \ln [(\epsilon_C - \epsilon_B)/(\epsilon - \epsilon_B)]$ (at the kinetic wavelength) vs. time. Such plots were linear to at least 80% completion. The kinetic λ and the extinction coefficients at that λ in 2% (v/v) chlorobenzene/EtOH and/or in pure chlorobenzene for all the compounds studied are reported in the supplementary material (Table VIII).

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Registry No. 1B, 580-35-8; **1C**, 56524-87-9; **2B**, 1912-16-9; **2C**, 47484-87-7; **3B**, 75865-15-5; **3C**, 75505-88-3; **4A**·ClO_4^-, 3044-70-0; **4C**, 78018-60-7; **5A**·BF_4^-, 70336-71-9; **5B**, 3558-62-1; **5C**·BF_4^-, 78018-61-8; **6A**·BF_4^-, 78018-62-9; **6B**, 64292-70-2; **6C**·BF_4^-, 78018-64-1; **7A**·$CF_3SO_3^-$, 76017-14-6; **7B**, 3558-63-2; **7C**·$CF_3SO_3^-$, 76017-21-5; **8A**·BF_4^-, 78018-65-2; **8B**, 78018-66-3; **8c**·BF_4^-, 78018-68-5; **9B**, 24301-97-1; **9C**, 71670-94-5; **10A**·BF_4^-, 78018-69-6; **10A**·ClO_4^-, 38120-82-0; **10B**, 78018-70-9; **10C**·BF_4^-, 78018-72-1; **11A**·ClO_4^-, 21016-30-8; **11B**, 78018-73-2; **11C**·BF_4^-, 78018-74-3; **12B**, 15997-45-2; **12C**·BF_4^-, 78018-76-5; **13B**, 67913-78-4; **13C**, 75505-91-8; **14A**·BF_4^-, 78018-78-7; **14B**, 78018-79-8; **14C**·BF_4^-, 78018-81-2; **15A**·BF_4^-, 78018-83-4; **15B**, 78018-84-5; **15C**·BF_4^-, 78018-86-7; **16A**·ClO_4^-, 78018-88-9; **16B**, 78018-89-0; **16C**·ClO_4^-, 78018-91-4; **17A**·BF_4^-, 73286-95-0; **17A**·$CF_3SO_3^-$, 78018-92-5; **17B**, 78018-93-6; **17C**·BF_4^-, 78018-94-7; **17C**·ClO_4^-, 78018-95-8; **18A**·BF_4^-, 78018-97-0; **18B**, 78039-67-5; **18C**·BF_4^-, 78039-69-7; **19A**·BF_4^-, 78018-99-2; **19B**, 78019-00-8; **19C**·BF_4^-, 78019-02-0; 20A·BF_4^-, 33913-79-0; **20B**, 57162-72-8; **20C**·BF_4^-, 78019-04-2; **21A**·$CF_3SO_3^-$, 78019-06-4; **21C**·BF_4^-, 78019-08-6; **22B**, 65646-35-7; **22C**, 78019-09-7; **23A**, 78019-10-0; **23B**, 78019-11-1; **23C**, 75505-93-0; **24B**, 57366-68-4; **24C**, 75505-94-1; **29a**, 39745-17-0; **29b**, 2682-98-6; **29c**, 65419-98-9; **29d**, 65419-99-0; **30**, 78019-12-2; **31**, 32631-50-8; **32** (isomer 1), 73045-82-6; **32** (isomer 2), 78019-13-3; **33**·BF_4^-, 78019-15-5.

Supplementary Material Available: Table VII, pseudo-first-order rate constants (k_{obsd}) for the reactions of *N*-benzylpyridinium and related cations with piperidine in chlorobenzene; Table VIII, UV spectral data for the pyridinium and related cations 1C–24C and for the corresponding pyridines 1B–24B and extinction coefficients at the kinetic wavelength; Figure 4, plot of pseudo-first-order constants vs. piperidine concentration for the reaction of *N*-benzylpyridinium and related cations with piperidine in chlorobenzene; Figure 5, plot of k_{obsd} vs. piperidine concentration for the reaction of 1C with piperidine at 100 °C in chlorobenzene at low piperidine concentrations (7 pages). Ordering information is given on any current masthead page.