Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 14.[1] The Preparation and Reactions of Some Further α-Heteroaryl-pyridinium Salts

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Novel pyryliums containing fused dihydrocarbazole and dihydrobenzothiophene rings and α-benzothiazole substituents are described, together with their conversion to a variety of derived pyridiniums. The *N*-(2-pyridyl) group rearranges thermally at 60 °C from the pyridinium nitrogen to the nitrogen atom of a 2-(2-benzimidazolyl) group [in (19)]; similar rearrangement in the carbazole (7) is complicated by dehydrogenation. Compared with the corresponding 2,4,6-triphenylpyridinium, replacement of α-phenyl by α-2-benzothiazolyl has a large rate-enhancing effect for *N*-benzyl, but much smaller for *N*-n-alkyl. Replacement of α-phenyl by a fused dihydrobenzothiophene system shows rate enhancement for *N*-benzyl; ring fission occurs for *N*-n-alkyl. In the single cases studied carbazole is as effective as dibenzothiophene, but benzimidazole less so than benzothiazole.

Our research group has previously studied heteroarylpyrylium and derived pyridinium salts.[1-5] Two points of particular interest emerged: (a) the significant rate enhancement in displacement of an *N*-benzyl group from a pyridinium with an α-2-benzothiazolyl group [1] and (b) the photochemical rearrangement of pyridinium *N*-aryl groups to the nitrogen of an α-2-benzimidazolyl substituent.[4]

In this paper we seek to follow up both these leads. The elaboration of active leaving groups is important to enable amine transformations under mild conditions: the method previously adopted has been to restrict rotation of an α-phenyl group.[3,6,7] We have now combined this concept with acceleration obtained by the presence of certain α-heteroaryl substituents.

The development of more general selective transformations of *N*-aryl- and *N*-heteroaryl-pyridiniums could lead to synthetically important transformations of aryl- and heteroaryl-amines (previous success in this field has been limited [8,9]), and this is a further aim of our work.

Preparation of Pyrylium Salts (*Table* 1), *Pyridines* (*Table* 2), *and Pyridinium Salts* (*Table* 3).—Reaction of 2,3,4,9-tetrahydro-1*H*-carbazol-1-one (1) [10,11] and its sulphur analogue 2,3-dihydrodibenzothiophen-4(1*H*)-one (2) [12] with benzylideneacetophenone in the presence of trifluoromethanesulphonic acid [attempts with (1) using $HClO_4$ failed] gave the expected pyryliums (3) and (8) as trifluoromethanesulphonates. The condensed pyryliums (3) and (8) were converted by ammonia into the corresponding pyridines (4) and (9) and by primary amines into the pyridiniums (5)—(7) and (10—(14). The

Table 1. Preparation of pyrylium perchlorates and trifluoromethane sulphonates

Compd.	Crystallisation solvent	Crystal form	M.p. (°C)	Yield (%)	Molecular formula	Analysis: Found (%) C	H	N	Analysis: Required (%) C	H	N
(3) [a,c]	AcOH	Brown prisms	306—307 (dec.)	49	$C_{28}H_{20}F_3NO_4S$	64.4	3.9	2.6	64.2	3.9	2.7
(8) [a,c]	EtOH	Red needles	238—241	66	$C_{28}H_{19}F_3O_4S_2$ [e]	62.2	3.6		62.2	3.5	
(15) [d]	AcOH	Orange needles	303—305.5 (dec.) [f]	25	$C_{24}H_{17}ClN_2O_5$						
(20) [d]	AcOH	Yellow prisms	293—294 (dec.) [g]	73	$C_{24}H_{16}ClNO_5S$						
(25) [b,c]	EtOH	Orange prisms	266—274.5 (dec.)	64	$C_{27}H_{18}F_3NO_4S_2$	59.9	3.4	2.6	59.9	3.4	2.6

[a] Reaction temperature 95—100 °C. [b] Reaction temperature 100—105 °C. [c] Trifluoromethanesulphonate salt. [d] Perchlorate salt. [e] Found: S, 11.8. Required: S, 11.9%. [f] Lit. m.p. 298—300 °C.[5] [g] Lit. m.p. 285—287 °C.[5]

Table 2. Preparation of pyridines

Compd.	Time (h)	Crystallisation solvent	Crystal form	M.p. (°C)	Yield (%)	Molecular formula	Analysis: Found (%) C	H	N	Analysis: Required (%) C	H	N
(4)	5	EtOH	Prisms	196—199	95	$C_{27}H_{20}N_2$	86.9	5.5	7.5	87.1	5.4	7.5
(9)	3	Me_2CO	Needles	193—195	95	$C_{27}H_{19}NS$	83.2	5.0	3.6	83.2	4.9	3.6
(21)	1.5	AcOEt	Prisms	222—223.5 [a]	50	$C_{24}H_{16}N_2S$						
(26)	5	AcOEt	Needles	215—217	80	$C_{26}H_{18}N_2S$	80.0	4.7	7.1	80.0	4.7	7.2

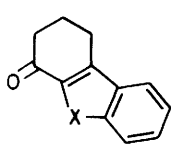
[a] Lit. m.p. 227 °C.[5]

Table 3. Preparation of pyridinium salts

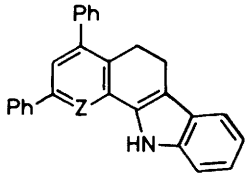
Compd.	Reaction conditions: Time (h) before addition of AcOH	Reaction conditions: Time (h) after addition of AcOH	Reaction conditions: Amount of ether [a] (ml)	Crystallisation solvent	Crystal form	M.p. (°C)
(5) [b]	0.5	5	50	EtOH	Orange needles	199—201
(6) [b]	1	6	50	*e*	Yellow needles	267—269 (dec.)
(7) [b]	0.5	5	50	CH_2Cl_2/Et_2O	Yellow prisms	221—223
(10) [b]	0.5	1	50	EtOH	Yellow prisms	166.5—168.5
(11) [b]	0.5	5	50	95% EtOH	Yellow prisms	141—143
(12) [b]	0.5	5	50	95% EtOH	Yellow prisms	203—205
(13) [b]	0.5	5	50	EtOH	Yellow prisms	217—219
(14) [b]	0.5	5	50	95% EtOH	Yellow prisms	146—148
(17) [c,d]	—	20	50	*f*	Yellow prisms	170—172.5
(18) [c]	—	20	50	*f*	Yellow needles	160—162
(19) [c]	0.5	12	75	*g*	Yellow prisms	153—155 (dec.)
(23) [c]	0.5	5	50	*h*	Yellow prisms	174.5—176.5
(24) [c]	0.5	9	25	CH_2Cl_2/Et_2O	Needles	160—162 (dec.)
(27) [b]	0.5	15	100	*i*	Yellow prisms	163—165

Compd.	Yield (%)	Molecular formula	Analysis: Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
(5) [b]	57	$C_{35}H_{27}F_3N_2O_3S$	68.7	4.4	4.5	68.6	4.4	4.6
(6) [b]	61	$C_{35}H_{27}F_3N_2O_3S$	68.7	4.5	4.5	68.6	4.4	4.6
(7) [b]	38	$C_{33}H_{24}F_3N_3O_3S$	66.3	4.1	6.9	66.1	4.0	7.0
(10) [b]	86	$C_{35}H_{26}F_3NO_3S_2$	66.7	4.2	2.2	66.8	4.2	2.2
(11) [b]	81	$C_{29}H_{22}F_3NO_3S_2$	62.7	4.1	2.5	62.9	4.0	2.5
(12) [b]	78	$C_{30}H_{24}F_3NO_3S_2$	63.3	4.3	2.4	63.5	4.3	2.5
(13) [b]	85	$C_{32}H_{28}F_3NO_3S_2$	64.5	4.8	2.3	64.5	4.7	2.4
(14) [b]	69	$C_{31}H_{26}F_3NO_3S_2$	64.0	4.5	2.4	64.0	4.5	2.4
(17) [c,d]	96	$C_{31}H_{24}ClN_3O_4$	69.1	4.6	7.8	69.2	4.5	7.8
(18) [c]	76	$C_{31}H_{24}ClN_3O_4$	69.0	4.6	7.8	69.2	4.5	7.8
(19) [c]	89	$C_{29}H_{21}ClN_4O_4$	66.4	4.0	10.6	66.4	4.0	10.7
(23) [c]	86	$C_{26}H_{21}ClN_2O_4S$	63.2	4.4	5.6	63.3	4.3	5.7
(24) [c]	96	$C_{27}H_{23}ClN_2O_4S$	63.9	4.6	5.5	64.0	4.6	5.5
(27) [b]	80	$C_{31}H_{27}F_3N_2O_3S_2$	62.5	4.6	4.6	62.4	4.6	4.7

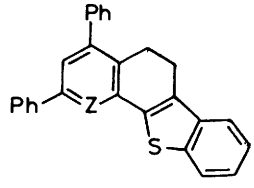
[a] Amount of ether in to which mixture after reaction was poured. [b] Trifluoromethanesulphonate salt. [c] Perchlorate salt. [d] Previously described as bisperchlorate salt.[5] [e] First cryst.: H_2O–Me_2CO 6 : 4, second cryst.: CH_2Cl_2–Et_2O. [f] First cryst.: H_2O–EtOH 7 : 3, second cryst.: CH_2Cl_2–Et_2O. [g] First cryst.: CH_2Cl_2–Et_2O, second cryst.: MeOH. [h] First cryst.: H_2L–EtOH 9 : 1, second cryst.: CH_2Cl_2–Et_2O. [i] First cryst.: CH_2Cl_2–Et_2O, second cryst.: Me_2CO–AcOEt 3 : 7.



(1) X = NH
(2) X = S



(3) Z = O^+
(4) Z = N
(5) Z = N^+CH_2Ph
(6) Z = N^+-C_6H_4Me-*p*
(7) Z = N^+-2-pyridyl



(8) Z = O^+
(9) Z = N
(10) Z = N^+CH_2Ph
(11) Z = N^+Me
(12) Z = N^+Et
(13) Z = N^+Bu^n
(14) Z = N^+Pr^i

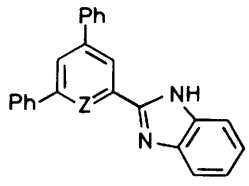
indolo-derivatives (3)—(7) are characterised by ν(NH) at 3 220—3 470 cm^{-1}. Compounds (3)—(5) also show the ^1H NH signal at low field, but in (6) and (7) this proton evidently falls in the shielding area of the 1-aryl group which now shifts the signal to higher field so it forms part of the aromatic multiplet. All the compounds show a 4 H signal for the ethylene bridge at δ 2.7—3.5: this is generally seen as a singlet in the pyridinium salts. The *N*-substituents in the pyridinium salts show the expected signals (Table 4).

2-Benzimidazolyl-4,6-diphenylpyrylium perchlorate (15) was prepared from 2-acetylbenzimidazole [13] and benzylideneacetophenone using a modification of the procedure reported

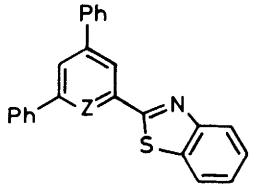
Table 4. I.r. and ^{1}H n.m.r. spectral data for indolo- and benzothiopheno-chromyliums, -quinolines, and -quinolinium salts

	I.r.[a]		N.m.r.[b]					
				Chemical shift (δ)				
	$\nu_{max.}$/cm^{-1}			NH		Ethylene bridge		
Compd.	ν(NH)	ν ring	Solvent	(1 H, s)	Aromatic	(4 H)		Other aliphatic
(3)[d]	3 220	1 620	$(CD_3)_2SO$	12.6	8.35—8.7 (2 H, m) 8.35 (1 H, s)[f] 6.95—8.0 (2 H, m)	3.15—3.4	m	
(4)	3 460	1 585	$CDCl_3$	9.3	7.95—8.3 (2 H, m) 6.95—7.7 (13 H, m)	2.7—3.1	m	
(5)[d]	3 220	1 610	$CDCl_3$	11.25	6.8—7.45 (18 H, m) 6.2—6.6 (4 H, m)[c]	3.0	s	
(6)[d]	3 470	1 620	$CDCl_3$	*j*	6.7—7.8 (20 H, m)	2.8—3.3	m	2.4 (3 H, s)[h]
(7)[d]	3 440	1 615	$CDCl_3$	*j*	8.45—8.65 (1 H, m)[g] 7.7—7.9 (2 H, m) 6.95—7.7 (17 H, m)	3.15	s	
(8)[d]		1 610	CF_3CO_2H		7.4—8.35 (15 H, m)	3.3—3.65	m	
(9)		1 570	CF_3CO_2H		7.4—8.15 (16 H, m)	3.2—3.55	m	
(10)[d]		1 615	$CDCl_3$		7.1—7.9 (18 H, m) 6.75—7.1 (2 H, m)	3.15	s	6.25 (2 H, s)[i]
(11)		1 610	$CDCl_3$		7.15—8.15 (15 H, m)	3.1	s	4.35 (3 H, s)
(12)		1 610	$CDCl_3$		7.15—8.0 (15 H, m)	3.15	s	5.0 (2 H, q, *J* 7 Hz),[i] 1.45 (3 H, t, *J* 7 Hz)
(13)[d]		1 610	CF_3CO_2H		7.35—8.2 (15 H, m)	3.3	s	5.2 (2 H, t, *J* 8 Hz),[i] 0.55—2.15 (7 H, m)
(14)		1 610	$CDCl_3$		7.15—8.0 (15 H, m)	3.15	s	5.65—6.15 (1 H, m), 1.65 (6 H, d, *J* 7 Hz)

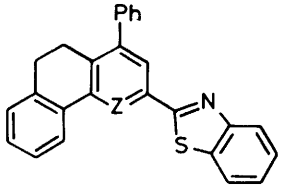
[a] In $CHBr_3$. [b] $SiMe_4$ as internal standard. [c] Together with $\equiv N^+-CH_2$ group. [d] Trifluoromethanesulphonate salt. [e] NH signal. [f] Position 3 of pyrylium nuclei. [g] Position 2 of pyridine nuclei. [h] Me group. [i] $\equiv N^+-CH_2$ group. [j] With aromatic signal.



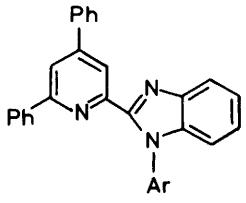
(15) Z = O^+
(16) Z = N
(17) Z = N^+CH_2Ph
(18) Z = N^+-C_6H_4Me-*p*
(19) Z = N^+-2-pyridyl



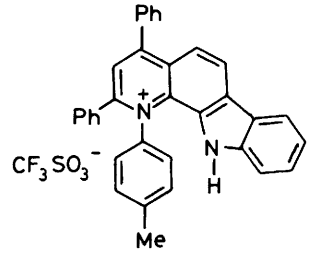
(20) Z = O^+
(21) Z = N
(22) Z = N^+CH_2Ph
(23) Z = N^+Et
(24) Z = N^+Pr^i



(25) Z = O^+
(26) Z = N
(27) Z = N^+Bu^n
(28) Z = N^+CH_2Ph



(29) Ar = Ph
(30) Ar = 2-pyridyl
(31) Ar = *p*-MeC_6H_4



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earlier.[5] Primary amines then gave the pyridiniums (17)—(19) with reasonable yields. Monoperchlorate (17) was previously prepared as the bisperchlorate.[5] 2-Benzothiazolyl-4,6-diphenylpyrylium perchlorate (20), obtained as reported,[5] was converted by ammonium acetate into pyridine (21)[5] and by ethylamine and isopropylamine into corresponding pyridiniums (23) and (24) [the *N*-benzylpyridinium (22) has been reported[5]]. The compounds were characterised spectrally (Table 5). The benzimidazolyl derivatives (15)—(19) all showed ν(NH) at 3 300—3 200 cm^{-1}. Most compounds displayed clear singlets for 3-H and 5-H, but sometimes these peaks were hidden in the aromatic multiplet. Among other signals, the aliphatic protons on the carbon attached directly to N^+ were characteristic.

2-Acetylbenzothiazole[14] and 2-benzylidene-1-tetralone[15] react in presence of trifluoromethanesulphonic acid to give the expected pyrylium (25) as trifluoromethanesulphonate. The good yield (64%) necessitated a trifluoromethanesulphonic acid–ketone ratio 2 : 1. This pyrylium reacted as expected with ammonia to give pyridine (26) and with n-butylamine to give (27). This series of compounds all showed the ^{1}H n.m.r. signal for the CH_2CH_2 group and the correct integration for the aromatic protons (Table 6). Attempts to prepare compound (28) from pyrylium (25) and benzylamine failed. The ^{1}H n.m.r. spectrum of the crude product indicates a mixture and attempted recrystallisation caused decomposition, evidently because of the great lability of the *N*-benzyl group.

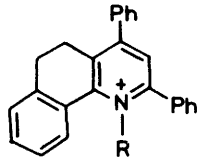
Thermal Rearrangements.—1-Aryl-2-(2-benzimidazolyl)-4,6-diphenylpyridiniums [*cf.* (18)] have been shown to undergo photochemical rearrangement of the 1-aryl group onto the

Table 5. I.r. and ^{1}H n.m.r. spectral data for α-benzimidazoyl and α-benzothiazolyl compounds (15), (17)—(21), (23), and (24)

	I.r. [a] $\nu_{max.}$/cm^{-1}		N.m.r.[b] (δ values)		
Compd.	ν(NH)	Ring	Solvent	Position 3	Position 5
(15) [c]	3 200	1 625	$(CD_3)_2SO$	*d*	*d*
(17) [c]	3 280	1 615	CF_3CO_2H	8.85 (1 H, d, *J* 2 Hz)	8.7 (1 H, d, *J* 2 Hz)
(18) [c]	3 220	1 620	$CDCl_3$	8.35 (1 H, d, *J* 2 Hz)	8.15 (1 H, d, *J* 2 Hz)
(19) [c]	3 200	1 625	$(CD_3)_2SO$	9.2 (1 H, d, *J* 2 Hz)	8.8 (1 H, d, *J* 2 Hz)
(20) [c]		1 630	CF_3CO_2H	9.1 (1 H, d, *J* 2 Hz)	8.8 (1 H, d, *J* 2 Hz)
(21)		1 595	CF_3CO_2H	8.75 (1 H, d, *J* 1 Hz)	8.55 (1 H, d, *J* 1 Hz)
(23) [c]		1 620	$CDCl_3$	*d*	*d*
(24) [c]		1 620	CF_3CO_2H	*d*	*d*

	N.m.r. [b] (δ values)		
Compd.	Other aromatic and N–H	$\equiv N^+-CH_2$ and $\equiv N^+-CH=$	CH_3
(15) [c]	11.5 (1 H, s) [e]; 8.4—8.9 (4 H, m)	9.0—9.35 (2 H, m); 7.3—8.35 (10 H, m)	
(17) [c]	7.6—8.3 (16 H, m)	6.7—7.4 (6 H, m)	6.15 (2 H, s)
(18) [c]	6.7—8.0 (19 H, m)		2.1 (3 H, s)
(19) [c]	8.2—7.6 (3 H, m)	7.05—8.05 (16 H, m)	
(20) [c]	8.1—8.55 (6 H, m)	7.5—8.1 (8 H, m)	
(21)	7.5—8.45 (14 H, m)		
(23) [c]	7.3—8.35 (16 H, m)	4.85 (2 H, q, *J* 7 Hz)	1.3 (3 H, t, *J* 7 Hz)
(24) [c]	7.35—8.7 (16 H, m)	5.35 (1 H, p, *J* 7 Hz)	1.6 (6 H, d, *J* 7 Hz)

[a] In $CHBr_3$. [b] $SiMe_4$ as internal standard. [c] Perchlorate salt. [d] Hidden by other aromatic signals. [e] NH signal.



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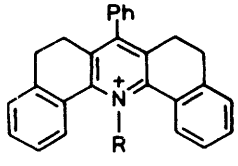

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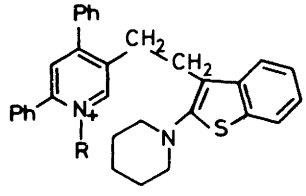

(35)

benzimidazolyl nitrogen to give products of type (29).[4] We have now attempted to effect such rearrangements thermally. However, the *p*-methylphenyl derivative (18) does not rearrange to compound (31): after 2 h at 200—210 °C over 90% of the starting material was recovered.

By contrast, the 1-(2-pyridyl) substituent in pyridinium (19) rearranges easily and in good yield onto the benzimidazolyl nitrogen giving compound (30), not only on heating at 170—180 °C, but already in refluxing methanol. The difference in the reactivity of compounds (18) and (19) is a consequence of the greater susceptibility of the pyridinium ring system to nucleophilic substitution, particularly at the 2-position. The mild conditions under which the reaction occurs are remarkable and reflect the favourable stereochemical alignment in the molecule of (19).

We felt that such stereochemical alignment might be even more favourable in the indolo-derivatives (6) and (7). However, the *p*-methylphenyl derivative (6) was recovered unchanged after heating 2 h at 240—245 °C. After 2 h at 250—260 °C, the i.r. spectrum was different from that of the starting material, but still showed ν(NH). The ^{1}H n.m.r. spectrum had lost the signal for the ethylene bridge and in the aliphatic region displayed just one signal for the methyl group. The spectrum integrated correctly for the aromatised pyridinium (32) probably formed by action of oxygen.

The rearrangement of the 2-pyridyl derivative (7) was followed by u.v. in ethanol containing NaOH: after 1 h at 80°, the intense absorption at 428 nm disappeared indicating reaction had occurred. However, attempts to isolate the product gave mixtures, following the reaction at 60° in $CDCl_3$ showed that after 8 h the peak for the bridging CH_2CH_2 disappeared. Evidently the rearrangement in this series is accompanied by dehydrogenation, and this leads to a non-homogeneous product.

Kinetic Results.—Reactions with piperidine in chlorobenzene solvent were followed spectrophotometrically under pseudo-first-order conditions, as already described.[16] Observed rate constants were calculated from the slope of the plots of $\ln[a/(a-x)]$ *versus* time (see Experimental section). Such plots showed linearity up to above 85% conversion for all compounds except (27), which exhibited curvature after 50% conversion. Observed rate constants are recorded in Table 7. Plots of $k_{obs.}$ *versus* piperidine concentration gave straight lines, the slope being considered to vary as k_2 and the intercept as k_1. First- and second-order rate constants are reported in Table 8. None of the compounds, except the *N*-isopropyl derivatives (14) and (24), showed any significant first-order component.

Discussion of Kinetic Results.—The rate enhancement in the displacement of *N*-substituents from pyridiniums by con-

Table 6. I.r. and ^1H n.m.r. spectral data for benzothiazolyl tricyclic derivatives (25)—(27)

Compd.	ν Ring [a] (cm^{-1})	N.m.r.[b] Solvent	Aromatic multiplet δ	Aromatic multiplet H	CH_2CH_2 (4 H) δ	CH_2CH_2 (4 H) Multiplicity
(25)	1 620	CF_3CO_2H	7.3—8.8 [d]	14	3.0—3.8	m
(26)	1 605	CF_3CO_2H	7.4—8.6	14	2.85—3.55	m
(27)	1 605	$CDCl_3$	7.2—8.35	14	2.9	s [e]

[a] In $CHBr_3$. [b] $SiMe_4$ as internal standard. [c] Trifluoromethanesulphonate salt. [d] Position 3 of chromylium nuclei. [e] $\equiv N^+-CH_2$ group shows at δ 5.45 (2 H, t, *J* 7 Hz); other aliphatic protons at δ 0.3—1.85 (7 H, m).

Table 7. Pseudo-first-order rate constants ($k_{obs.}$) for the reactions of heteroaryl pyridiniums with piperidine in chlorobenzene

Pyridinium (*t*/°C)	[Piperidine]/mol l^{-1}	$10^5 k_{obs.}/s^{-1}$
(5) [a] (60)	0.0192	13.9
	0.0384	28.5
	0.0576	38.5
	0.0768	46.6
(10) [a] (100)	0.001 60	23.7
	0.003 20	41.9
	0.006 40	73.9
	0.009 60	95.2
	0.0128	130.4
(11) [a] (60)	0.0320	12.1
	0.0800	28.6
	0.160	58.9
(12) [a] (60)	0.0320	14.6
	0.0400	18.4
	0.0800	35.6
(13) [c] (60)	0.0320	9.84
	0.0640	20.4
	0.0960	43.5
	0.128	58.8
(14) [a] (60)	0.0320	35.8
	0.0400	41.9
	0.0600	60.0
	0.0800	76.0
(23) [c] (100)	0.320	9.33
	0.480	15.6
	0.640	23.7
(24) [b] (100)	0.0400	21.3
	0.0800	25.7
	0.160	37.4
(27) [b,c] (100)	0.160	25.0
	0.240	35.6
	0.320	47.8
	0.400	62.2

[a] Concentration of substrate 6.40×10^{-5} mol l^{-1}. [b] Concentration of substrate 1.60×10^{-3} mol l^{-1}. [c] Kinetics followed up to 50% conversion.

Table 8. First- and second-order rate constants (k_1 and k_2) for the reactions of heteroarylpyridiniums with piperidine in chlorobenzene

Pyridinium	*t*/°C	*N* [a]	*r* [b]	$10^3 k_2$ [c]/l mol^{-1} s^{-1}	% Error	$10^5 k_1$ [c,d]/s^{-1}	% Error	$\frac{10^3 k_1}{k_2 + 10k_1}$ [e]
(5)	60	4	0.9908	5.6 ± 1.6	28	(4.9 ± 8.4)		<19
(10)	100	5	0.9971	92 ± 10	10	(11 ± 7.5)		<2
(11)	60	3	0.9997	3.7 ± 0.6	16	(−0.1 ± 6.1)		<14
(12)	60	3	0.9999	4.4 ± 0.4	9	(0.8 ± 2.1)		<6
(13)	60	4	0.9910	5.3 ± 1.5	28	(−9.4 ± 12.9)		<6
(14)	60	4	0.9996	8.5 ± 0.5	6	8.5 ± 2.8	33	9
(23)	100	3	0.9973	0.45 ± 0.21	46	(−5.4 ± 10.4)		<52
(24)	100	3	0.9978	1.4 ± 0.6	41	15.4 ± 6.0	39	77
(27) [f]	100	4	0.998	1.5 ± 0.2	14	(−0.7 ± 6.5)		<27

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses not significantly different from zero. [e] Reaction by S_N1 route at [piperidine] 10^{-1} mol l^{-1}. [f] Kinetics followed up to 50% conversion.

straining α-phenyl groups to near planarity in systems such as (33) and (34) has been reported for *N*-benzyl [3] and various *N*-alkyl [17] derivatives. In Table 9, such results are compared with the rate increases due to heteroaryl fusion and substitution, all rates being taken as relative to those for the analogously *N*-substituted 2,4,6-triphenylpyridinium compounds.

This comparison allows the following conclusions. (a) Replacement of an α-phenyl by α-2-benzothiazolyl has qualitatively a similar effect on the displacement rate in all three cases studied (22)—(24) to that found for the ' tricyclic ' analogues [system (33)]; quantitatively the effect is somewhat less. Thus, the α-2-benzothiazolyl substituent has a high rate enhancing effect for *N*-benzyl, but much less for the *N*-n-alkyl compounds. (b) In the one case investigated, the α-2-benzimidazolyl substituent had a much smaller effect than α-2-benzothiazolyl. (c) In the *N*-benzyl series the displacement rate for the fused dibenzothiophene system (10) is only *ca.* 25% of that for the tricyclic analogue (33). (d) Only one compound with a fused carbazole system was examined, the *N*-benzyl derivative (5) which reacted at a rate similar to that for the dibenzothiophene fused analogue (10). (e) The simultaneous presence of both the fused naphthalene system and the α-2-benzothiazolyl substituents in the *N*-n-butyl compound (27) had considerably less effect on the rate than that expected for additivity of the separate effects of those two structural features.

Table 9. S_N1 and S_N2 rates at 100 °C relative to those for corresponding 1-substituted 2,4,6-triphenylpyridiniums at 100 °C as unity

	α-Heteroaryl substituent		Fused carbocyclic rings		Fused heterocyclic rings		Fused carbocyclic and α-heteroaryl
Compound	2-Benzimidazoyl (17)	2-Benzothiazolyl (22)—(24)	Tricyclic (33)	Pentacyclic (34)	Carbazole (5)	Dibenzothiophene (10)—(14)	Benzothiazolyl (27)
CH_2Ph [a]	9 [b]	64 [b]	69 [c]	900 [c]	18 [d,e]	19 [f] (0.27) [g]	*h*
Me [a]			8 [c]	42 [c]		73 [g,i] (20) [d,g]	
Et [a]		15 [f]	43 [c]	219 [c]		1 700 [g,i] (39) [d,g,j]	
Bu^n [a]				(3.5) [g]		(92) [d,g,j]	(2) [g]
Isopropyl *a*		10 [f]	20 [c]			730 [g,i] (29) [d,g]	
k		21 [f]	156 [c]			990 [g,i,l] (14) [d,g]	

[a] S_N2 ratio. [b] From 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. [c] From ref. 17. [d] Present work: figures relative to the ratio of both rates at 60 °C. [e] The ratio at 100 °C [estimating k_2 for the carbazole (5) at 100 °C as described in footnote *i*] is 14. [f] Present work. [g] Values in parentheses are ratios with respect to the tricyclic analogue (33). [h] Compound unstable. [i] Ratios at 100°; k_2 values for dibenzothiophenes (11)—(14) at 100 °C were estimated assuming an average $\Delta H^{\ddagger}_{373}$ of 16 kcal mol^{-1}, as observed for the S_N2 reactions of *N*-substituted pyridiniums, tricyclics (33), and pentacyclic (34) (see refs. 3 and 17). [j] k_2 values for the tricyclic analogues at 60 °C were estimated assuming $\Delta H^{\ddagger}_{373}$ equal to 16 kcal mol^{-1} (see footnote *i*). [k] S_N1 ratio. [l] Ratio at 100 °C. k_1 for 14 at 100 °C was estimated assuming an average $\Delta H^{\ddagger}_{373}$ of 28 kcal mol^{-1}, as observed for the S_N1 reactions of *N*-substituted tricyclics (33) (see ref. 17).

Ring Fission in the Dibenzothiophene Series.—The *N*-alkyl derivatives (11)—(13) react very quickly with piperidine. For *N*-methyl, *N*-ethyl, and *N*-n-butyl, the rates for the fused dibenzothiophene compounds (11)—(13) are respectively 20, 40, and 90 times those of the corresponding tricyclic derivatives (33). However, in these cases the reaction occurring is not simple *N*-alkyl transfer as shown clearly by the infinity u.v. spectrum which has $\lambda_{max.}$ 310 nm [contrary to expectation pyridine (9) has $\lambda_{max.}$ 352 nm]. We believe that in these cases the reaction involves attack of the piperidine on the 2-position of the benzothiophene nucleous to give products of type (35). Preparative reaction of (13) with piperidine gives a product with $\lambda_{max.}$ 233, 310, and 382 nm but shown by ^{13}C n.m.r. to be a mixture.

Conclusions and Indications for Future Work.—In an earlier paper [17] we have already commented on the variations of nucleophilic displacement rates as dependent on both the alkyl group undergoing reaction and the leaving group, in *non-additive ways*. The present results further support this conclusion, which must be taken into account in the design of more efficacious leaving groups.

Experimental

I.r. spectra were obtained for $CHBr_3$ solutions on a Perkin-Elmer 283B spectrophotometer. ^1H N.m.r. spectra were recorded on 60 MHz Varian model A-60A and EM 360L instruments; $SiMe_4$ was used as internal reference. M.p.s were uncorrected.

The following compounds were prepared by literature methods: 2,3,4,9-tetrahydro-1*H*-carbazol-1-one (1),[10,11] 55%, m.p. 166—168.5 °C (lit.,[11] 169—170 °C); 2,3-dihydrodibenzothiophen-4(1*H*)-one (2),[12] 53%, m.p. 112—114 °C (lit.,[12] 111—112 °C); 2-acetylbenzimidazole,[13] 61%, m.p. 186—188 °C (lit.,[13] 188—189 °C); 2-benzothiazolyl-4,6-diphenylpyrylium perchlorate (20) [5] (see Table 1); 2-benzothiazolyl-4,6-diphenylpyridine (21) [5] (see Table 2); 2-acetylbenzothiazole,[14] 66%, m.p. 108—110 °C (lit.,[14] 110—111 °C); 2-benzylidene-1-tetralone,[15] 85%, m.p. 103—105 °C (lit.,[15] 105 °C).

General Procedure for Preparation of Pyryliums.—Ketone (0.002 mol) and chalcone (0.004 mol) were melted and to the melt was added trifluoromethanesulphonic acid [0.002 mol; in case of pyrylium (25) 0.004 mol] dropwise. The mixture was heated for 1.5 h, acetone (2 ml) was added to the hot mixture and it was poured into ether [20 ml; in case of pyrylium (25) 40 ml]. After 2 h, the separated precipitate was filtered and washed with ether (see Table 1).

2-(2-*Benzimidazolyl*)-4,6-*diphenylpyrylium Perchlorate* (15).—Chalcone (20.82 g, 0.100 mol) was added in four portions in the course of 3 h with stirring to 2-acetylbenzimidazole [13] (8.01 g, 0.050 mol) in perchloric acid (50 ml, 70%) and acetic acid (100 ml), heated on a steam-bath. After 5 h, it was poured into ether (100 ml). The dark yellow precipitate was filtered, washed with ether, and triturated with 20 ml of ethanol four times. The product was crystallised from acetic acid (see Table 1).

General Procedure for Preparation of Pyridines.—To a stirred suspension of crude pyrylium (0.001 mol) in methanol (10 ml), acetic acid (0.002 mol) was added, and then, dropwise, an excess of ammonium hydroxide (30%, 5 ml). After 3—5 h the pyridine was filtered and washed with methanol (2 ml). Pyridines (4) and (26) were purified chromatographically on neutral alumina (activity I) with benzene as eluant (see Table 2).

General Procedure for Preparation of Pyridiniums.—To a suspension of crude pyrylium (0.001 mol) in dichloromethane (5 ml), amine (0.002 mol) (when reacting amine was aromatic, 0.001 mol of appropriate amine and 0.001 mol of triethylamine) was added. Acetic acid (0.004 mol) was added after 0.5—1 h. The mixture was left at 20 °C 1—20 h and was poured into ether. After standing 2 h [in case of pyridinium (19) 1 h], the separated precipitate was filtered and washed with ether (see Table 3).

2-[1-(2-*Pyridyl*)*benzimidazolyl*]-4,6-*diphenylpyridine* (30).—*Method A.* Pyridinium perchlorate (19) (0.19 g, 0.0005 mol) was heated at 170—180 °C for 0.5 h. The product was dissolved in dichloromethane, shaken with 5% sodium hydroxide, washed with water, and dried ($MgSO_4$). Evaporation gave the pyridine (30) which recrystallised from methanol as needles (82%), dried at 110 °C at 15 mmHg for 15 h, m.p. 207—209 °C,

Table 10. Extinction coefficients for pyridinium cations (ε_1) and for the corresponding pyridines (ε_2) at the kinetic wavelength

Compound	Kinetic λ/nm	ε_1	ε_2
(5)	446	23 500 [a]	0 [a]
(10)	396	20 500 [a]	0 [a]
(11)	396		0 [a]
(12)	396		0 [a]
(13)	396	21 000 [a]	0 [a]
(14)	396		0 [a]
(23)	318	26 500 [b]	14 000 [b]
(24)	318	33 000 [b]	14 000 [b]
(27)	380		0 [b]

[a] In chlorobenzene. [b] In 4% (v/v) chlorobenzene–ethanol.

$\nu_{max.}$ 1 590 and 1 550 cm^{-1}; δ ($CDCl_3$) 8.55—8.8 (2 H, m, ArH), 7.65—8.15 (5 H, m, ArH), and 7.05—7.65 (13 H, m, ArH) (Found: C, 82.05; H, 4.75. $C_{29}H_{20}N_4$ requires C, 82.05; H, 4.75%).

Method B. Pyridinium perchlorate (19) (0.052 g, 0.0001 mol) was refluxed in methanol (2 ml) for 2.5 h in the dark. After cooling the solution was brought to pH 8 with triethylamine. On refrigeration the pyridine separated, it was purified as in Method A (88%), m.p. 207—209 °C; spectrally identical with the above compound.

Kinetic Measurements.—Kinetics were followed by u.v. spectrophotometry, monitoring the decrease of absorbance of pyridinium cation at a fixed wavelength, using the procedure already described.[16] In typical runs under pseudo-first-order conditions the concentration of pyridinium was either 6.4×10^{-5} or 1.6×10^{-3} mol l^{-1}, while those of piperidine ranged from 0.0016 to 0.64 mol l^{-1}.

Pseudo-first-order rate constants ($k_{obs.}$) were calculated from the plot of $\ln[a/(a - x)] = \ln(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time, or from the plot of $\ln(D_0/D)$ *versus* time when the extinction coefficient of the corresponding pyridines (ε_2) was zero at the kinetic wavelength. The extinction coefficients of the pyridiniums (ε_1) and of the pyridines (ε_2) at the kinetic wavelength are recorded in Table 10. Second-order rate constants were calculated from the plot of $k_{obs.}$ *versus* piperidine concentration. For definition and calculation of errors and for estimation of precision of $k_{obs.}$ see ref. 18.

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