The Preparation of Pyridiniums from Pyryliums [1]

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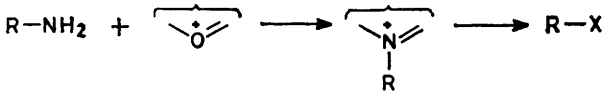
Mild preparative conditions are described for the reaction of primary alkyl-, secondary alkyl-, and aryl-primary amines (including weakly basic amines) with pyryliums (including those with bulky α-substituents). Conditions were optimised by ^{13}C n.m.r. studies.

Our transformation scheme for primary amines (1)—(4) [2] involves the reaction of pyryliums [*cf.* (2)] with amines to form intermediate pyridiniums [*cf.* (3)] which then react with nucleophilic, electrophilic, and radical initiating reagents. The wide synthetic applicability of this method has encouraged optimisation of both the reaction steps. Many pyryliums with different ring substituents have been prepared and the corresponding benzylpyridiniums used to assess kinetically structure/reactivity relationships.[3]

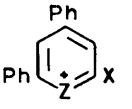


(1) (2) (3) (4)

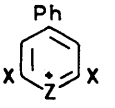
This paper describes mild preparative conditions for the reaction of (i) 2,4,6-triphenylpyrylium (5a) with hindered (secondary alkyl) and weakly basic primary amines and (ii) pyryliums having bulky α-substituents with primary alkyl-, secondary alkyl- and aryl-primary amines. The optimum conditions for these reactions were developed using ^{13}C n.m.r. spectroscopy; chemical shifts for the starting materials, products, and intermediates of this paper are listed and assigned elsewhere.[4]

Previous Preparative Conditions.—Previously, primary alkyl-primary amines have been treated with 2,4,6-triphenylpyrylium (5a) at 20 °C by stirring them in ethanol for 12 h (65—87%) [5] or stirring them in chloroform for 10—20 h (54—84%).[6] Reactions of secondary alkyl-primary amines, with pyrylium tetrafluoroborates have only been reported for cyclohexylamine; [7] it reacted with difficulty and no yield was quoted. Less generally useful iodides gave pyridiniums at 20 °C on being stirred in diethyl ether for 12—30 h (73—91%).[8] Aryl amines have previously required stronger conditions; refluxing ethanol for 2—3 h for 2,4,6-triphenylpyrylium (5a) (81—98%) [8,9] and 5,6-dihydro-2,4-diphenylbenzo-[*h*]chromenylium (11a) (74—98%).[9] Weakly basic aryl amines (2-, 3-, and 4-nitroanilines) reacted with 2,4,6-triphenylpyrylium (5a) only after a prolonged period under reflux (2- and 4- in dimethylformamide [10] and 3- in ethanol [11]) to give the corresponding pyridiniums [(5p) in 5%, (5o) in 84%, (5n) in 85%].

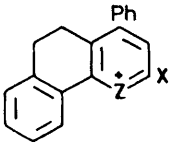
Previous Mechanistic Work.—Balaban studied the mechanism of the reactions of 2,4,6-triphenylpyrylium (5a) with methylamine and ammonia and isolated divinylogous amide intermediates (17).[12,13] The kinetics of hydrolysis of pyryliums (14) to 2-ene-1,5-diones (15) [14] and of the reverse reaction [15] have been studied. Kinetic studies of reactions of pyryliums with methoxide ion [16,17] indicated that 4-adducts are formed kinetically but pentadienones (*via* 2-adducts) are favoured thermodynamically.



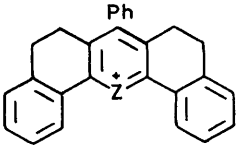
(5) X = Ph
(6) X = Me
(7) X = Bu^t
(8) X = 2-thienyl



(9) X = Bu^t
(10) X = 2-thienyl



(11) X = Ph
(12) X = Bu^t



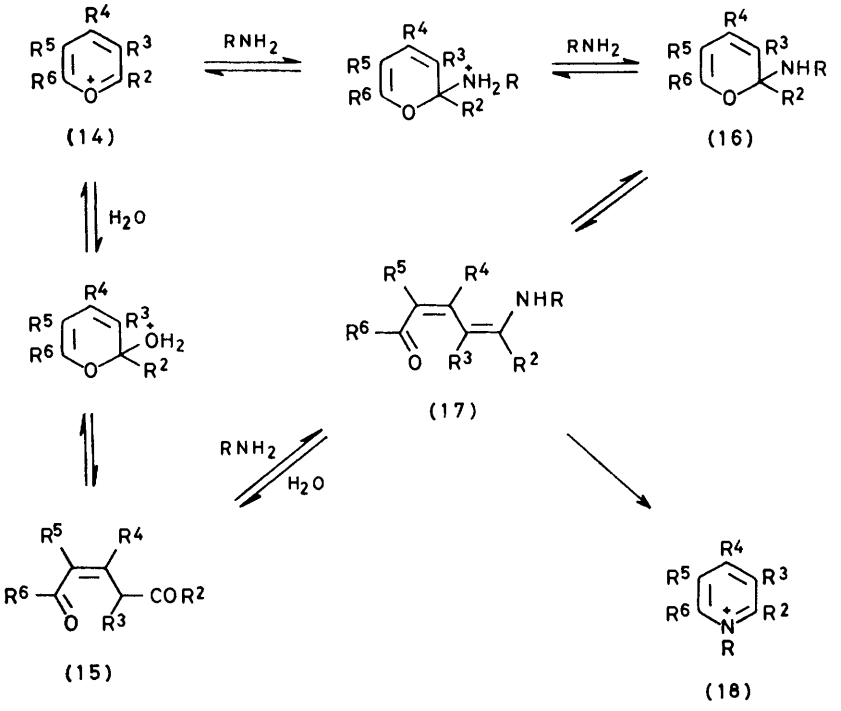
(13)

Z	Z	Z	Z
a; O	e; N-neoC_5H_{11}	i; N-cycloC_5H_9	m; N-2,4,6-$Me_3C_6H_2$
b; NBu^n	f; NPr^i	j; N-cycloC_7H_{13}	n; N-4-$NO_2C_6H_4$
c; NCH_2Ph	g; NBu^s	k; NCH(Ph)Me	o; N-3-$NO_2C_6H_4$
d; N-allyl	h; N-cycloC_6H_{11}	l; NPh	p; N-2-$NO_2C_6H_4$

In our laboratory, ^{13}C n.m.r. investigations showed only 2-adduct formation from 2,4,6-triphenylpyrylium (5a) and methoxide; [18] secondary amines gave stable divinylogous amides,[19] whereas the amide from n-butylamine slowly cyclised to pyridinium (5b). U.v. investigations [20] confirmed these conclusions and showed that divinylogous amide (17) formation from weakly basic amines is catalysed by triethylamine. Ring closure to pyridiniums (18) was catalysed by acetic acid (rate increase *ca.* 10^3) and enhanced in apolar solvents. Primary alkyl-primary amines reacted *ca.* 10^2 faster than secondary alkyl-primary amines.[20] Negative ρ values [21] for reactions of 2,4,6-triphenylpyrylium (5a) with substituted anilines or benzylamines indicate positive charge build up in the rate-determining step.

^{13}C N.m.r. Investigations.—Suitable preparative conditions were explored using ^{13}C n.m.r. spectroscopy to follow the ring-opening-closure sequence. As previously noted,[19] the characteristic peaks for pyrylium

(14), divinylogous amide (17), diketone (15), and pyridinium product (18) each fall in distinct regions [4] and enable all four classes of compound to be recognised quantitatively in the presence of each other. In some reactions, cyclic adducts (16) are found in place of vinylogous amide, and this can also be followed.[4]



Reaction rates and products utilising 2 mol equivalents of amine to one of pyrylium at 20 °C (procedure of 19) (Method A), were unaffected by use of 1 equivalent each of amine, pyrylium, and triethylamine (Method B). Methods C and D utilised acetic acid catalysis of ring-closure [20] with 2 equivalents of amine : 1 pyrylium or 1 amine : 1 pyrylium : 1 triethylamine.

For reactions between the tricyclic pyrylium (11a) and hindered amines, it was found advantageous to stir the reaction mixture for 30 min before addition of acetic acid (Method E). Weakly basic nitroanilines required scavenging of water before addition of the amines (Method F).

^{13}C N.m.r. study of numerous pyrylium-amine reactions [4] has demonstrated that certain pyrylium 2,6-substituents, or α- or β-branching and/or weak basicity in the amines hinders divinylogous amide cyclisation sterically or electronically. For weakly basic arylamines, the rate of amide formation becomes rate-determining.

RESULTS AND DISCUSSION

Preparations of pyridiniums in CH_2Cl_2 at 20 °C are reported in Tables 1—3. Products were precipitated with ether and washed with water to remove RNH_3^+ or Et_3NH^+ before characterisation (Tables 4 and 5).

Reactions of Alkylamines with 2,4,6-Triphenylpyrylium Tetrafluoroborate (5a) (*Table* 1).—A previous ^{13}C n.m.r. study of the reaction of n-butylamine with (5a) showed conversion into pyridinium (5b) within 20 min (Method A).[19] The same reaction with addition of acetic acid led to almost quantitative isolation of pyridinium in the same time (Method C).

The effect of acetic acid is clearly observed in experiments with neopentylamine (more steric hindrance due to β-branching). Method A showed by ^{13}C n.m.r. immediate conversion into divinylogous amide which subsequently cyclised after 5—7 days. With acetic acid (Method C) after 20 min 69% pyridinium (5e) was isolated.

Similar reductions in reaction time were observed for secondary alkyl-primary amines. Whereas by Method C isopropylamine gave 88% of isolated pyridinium (5f) after 20 min, using Method A cyclisation of amide required 3—10 days as shown by ^{13}C n.m.r. spectroscopy. Method C was used for the preparation of further *N*-cycloalkylpyridiniums (5h), (5i), and (5j) required for other work.[22]

As shown by ^{13}C n.m.r. spectroscopy, 1-phenylethylamine reacts readily with (5a) (Method A) giving amide which rapidly (*ca.* 20 min) formed 2,4,6-triphenylpyridine and 1-phenylethanol (shifts due to the alcohol: 70.2, 25.1 p.p.m.; lit.,[23] 69.9, 25.0). The intermediate pyridinium (5k) has considerable steric crowding in the 1-, 2-, and 6-positions; we believe that it rapidly dissociates by an S_N1 process (observed kinetically for *N*-cycloalkyl-2,4,6-triphenylpyridiniums in chlorobenzene [24]) to give the resonance-stabilised secondary carbocation (18) which is trapped by water. The application of this facile transferance of the 1-phenylethyl substrate is reported elsewhere.[25]

t-Butylamine is shown by ^{13}C n.m.r. spectroscopy to react readily with triphenylpyrylium (5a) to give an amide. Instead of cyclisation to pyridinium, the amide is slowly converted into diketone. Addition of acetic acid to this amide gives immediate reversion into pyrylium together with some conversion into diketone.

readily with benzylamine but the observed intermediate is a cyclic 2-adduct (16) which is converted with or without acetic acid solely into diketone.

5,6-Dihydro-2,4-diphenylbenzo[*h*]chromenylium (11a) and n-butylamine (with or without acetic acid) gives pyridinium (11b). For the chromenylium (11a) and

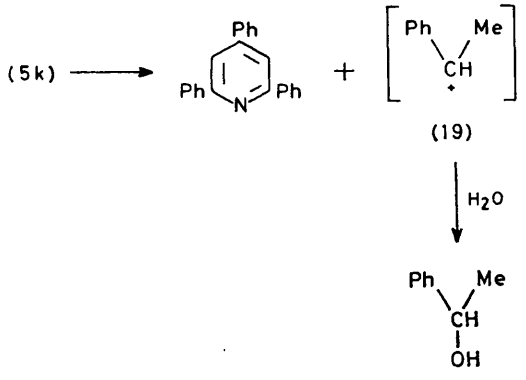
TABLE 1

Reactions of alkylamines with 2,4,6-triphenylpyrylium tetrafluoroborate

Pyridinium no.	Amine	Method	From ^{13}C n.m.r.[a] experiments: Pyrylium: time for disapp. (min.)	Amide: time for disapp. (days) [b]	% Pyridinium formed	% Diketone formed	Preparative experiments: *t*/h	Y (%) [c]
(5b)	n-Butyl	A					0.3	74
		C					0.3	96
(5e)	Neopentyl	A	<10	5—7	100	0		
		C					0.3	69
(5f)	Isopropyl	A	<10	3—10	100	0		
		C	<10	*d*	100	0	0.3	88
(5g)	s-Butyl	C					0.3	81
(5h)	Cyclohexyl	A	<10	<9	100	0	48	38
		C	<10	*d*	100	0	0.3	79
(5i)	Cyclopentyl	C					0.3	91
(5j)	Cycloheptyl	C					0.3	77
	1-Phenylethyl	A	<10	<3	0 [e]	0		
		B	<10	<9	0 [e]	0		
	t-Butyl	A	<10	<9	0	100		
		C	<10	*d*	0	100 [f]		

[a] $CDCl_3$. [b] No adduct (16) was observed by ^{13}C n.m.r. [c] I.r. and n.m.r. identical with analytical specimen (Tables 4 and 5). [d] No amide (17) was observed by ^{13}C n.m.r. [e] Pyridinium reacts further to pyridine. [f] Some pyrylium precipitates.

Reactions of Alkylamines with Other Pyrylium Tetrafluoroborates (*Table 2*).—With pyryliums 2- and/or 6-substituted by 2-thienyl groups, t-butylamine reacted to give a stable amide (see Table 2). [Note with benzylamines, 4-phenyl-2,6-di-(2-thienyl)pyrylium was converted rapidly into pyridinium (10c).[6]



2-Methyl-4,6-diphenylpyrylium gives intermediate amides (20) which can cyclise in two different ways. Rapid reaction with n-butylamine with or without acetic acid gives pyridinium, *cf.* triphenylpyrylium (5a) (see above), but reaction with cyclohexylamine leads instead to *N*-cyclohexyl-3,5-diphenylaniline (*cf.* 2,4,6-trimethylpyrylium [26]).

2-(t-Butyl)-4,6-diphenylpyrylium reacts with benzylamines at the phenyl-substituted α-carbon,[4] giving an amide which slowly cyclises to pyridinium (7e). Application of Method C leads to pyridinium formation in 20 min. 2,6-Di-(t-butyl)-4-phenylpyrylium also reacts

isopropylamine, where steric hindrance arises from both pyrylium and amines, Methods C and D led to considerable diketone formation. However, triethylamine catalysis of amide formation and after 30 min acetic acid catalysis of cyclisation (Method E) gave pyridiniums from neopentylamine (81%), isopropylamine (69%), and s-butylamine (62%) (isolated yields).

The more hindered 2-(t-butyl)tricyclic pyrylium (12a) reacts with n-butylamine and benzylamine to give adducts (16) which require acetic acid for rapid con-

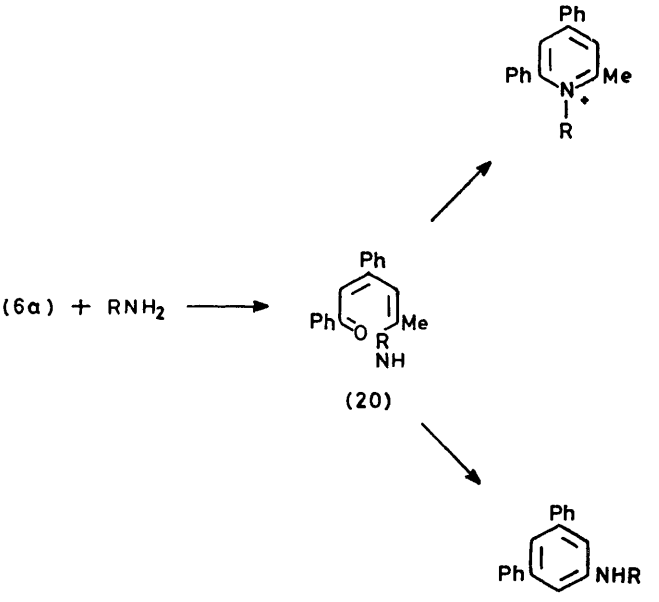


TABLE 2

Reactions of alkylamines with other pyrylium tetrafluoroborates and other salts

Pyridinium no.	Pyrylium substituents R²	R³	R⁴	R⁵	R⁶	Amine	Method	From ¹³C n.m.r.[a] experiments: Pyrylium: time for disapp. (min)	Amide: time for disapp. (days)	Adduct: time for disapp. (days)	% Pyridinium formed	% Diketone formed	Prep. experiments: t/h	Y (%)[b]
(6b)	Me	H	Ph	H	Ph	n-Butyl	A	<10	*c*	*d*	100	0	3.5	73
							C						0.3	70
						Cyclohexyl	A	<10	*c*	*d*	0[e]	0		
(7c)	Bu^t	H	Ph	H	Ph	Benzyl	A[f]	<10	3—7	*d*	100	0		
							C	<10	*c*	*d*	100	0		
	Bu^t	H	Ph	H	Bu^t	Benzyl	A[f]	<10	*c*	7—14	0	100		
							C	<10	*c*	*d*	0	100		
[g]	Th[h]	H	Ph	H	Ph	t-Butyl	A[f]	<10	>7	*d*	0	0		
(10c)[g]	Th	H	Ph	H	Th	Benzyl	A	<10	*c*	*d*	100	0		
						t-Butyl	A	<10	>7	*d*	0	0		
							A[f]	<10	>21	*d*	0	0		
(11b)	Ph	H	Ph	C_8H_8[i]		n-Butyl	A	<10	*c*	*d*	100	0		
							C	<10	*c*	*d*	100	0		
(11e)[g]						Neopentyl	E						23.5	81
(11f)						Isopropyl	C	<10	*c*	*d*	60[j]	40[j]	3	11
							D	<10	*c*	*d*	50[j]	50[j]		
[g]							E						23.5	69
(11g)[g]						s-Butyl	E						24.5	62
(12b)	Bu^t	H	Ph	C_8H_8		n-Butyl	A	<10	*c*	2—19	100	0	504	86
							C	<10	*c*	<3	100	0		
							D						0.3	43
(12c)						Benzyl	A	<10	*c*	<5	80[k]	20[k]	168	52
							D						0.3	64
						Isopropyl	A	<10	*c*	>10	0	0		
							C	>10[l,m]	*c*	*d*	0	50[m]		
(13c)[n]	C_8H_8		Ph	C_8H_8		Benzyl	A	<10	*c*	*d*	100	0		
(13d)[n]						Allyl	A[o]						0.3	93
							B						11	88
						Neopentyl	A						18	0
							B						21	0
							E						15	0

[a] In $CDCl_3$. [b] I.r. and n.m.r. identical with analytical specimen (Tables 4 and 5). [c] No amide (17) was observed by ¹³C n.m.r. [d] No adduct (16) was observed by ¹³C n.m.r. [e] Quantitative conversion of pyrylium into *N*-cyclohexyl-3,5-diphenylaniline. [f] In $(CD_3)_2SO$. [g] Perchlorate. [h] 2-Thienyl. [i] α,β-Dihydronaphtho. [j] Calculated from relative peak heights of pyridinium γ-carbon and corresponding carbon of diketone. [k] Calculated from relative peak heights of pyridinium α-carbon and carbon of diketone corresponding to pyridinium γ-carbon. [l] 50% Pyrylium, 50% diketone after 10 min. [m] Calculated from relative peak heights of pyrylium γ-carbon and corresponding carbon of diketone. [n] Trifluoromethanesulphonate. [o] 0.5 g Pyrylium used.

TABLE 3

Reactions of anilines with pyrylium tetrafluoroborates

Pyridinium no.	Pyrylium substituents R²	R³	R⁴	R⁵	R⁶	Aniline substituents	Method	From ¹³C n.m.r.[a] experiments: Pyrylium: time for disapp.[b]	% Pyridinium formed	% Diketone formed	Preparative experiments: t/h	Y (%)[c]
(51)	Ph	H	Ph	H	Ph	—	D	<10 min	80[d]	20[d]		
							D[e]	<10 min	100	0	0.3	77
(5m)						2,4,6-Trimethyl	A	<9 days	100	0		
							A[f]	<5 h	100	0	0.3[g]	51
							A				3[g]	69
							B	<2 days	30[d]	70[d]		
							B[h]	<10 min	0	100		
							D	<10 min	40[d]	60[d]		
							F				0.3	36
(5n)						4-Nitro	B	<10 min	20	80		
							B[h]	<10 min	10[d]	90[d]		
							D	<10 min	30	70		
							F				0.3	59
							F				0.6[i]	64
							F				3	64
(5o)						3-Nitro	F				0.3	53
							F				0.6[i]	58
							F				3	60
(5p)						2-Nitro	B	<10 min	0	100		
							F	>2 h	0	0	55[j]	18
(6l)[k]	Me	H	Ph	H	Ph		A	<10 min	100	0	0.3	96
(6m)[k]						2,4,6-Trimethyl	A[f]	<2 days	100	0	3[g]	24

[a] In $CDCl_3$. [b] No amide (17) or adduct (16) was observed by ¹³C n.m.r. [c] I.r. and n.m.r. identical with analytical specimen (Tables 4 and 5). [d] Calculated from relative peak heights of pyridinium γ-carbon and corresponding carbon of diketone. [e] Two equivalents of Et_3N. [f] In $(CD_3)_2SO$. [g] In Me_2SO (1 ml). [h] Five equivalents of Et_3N. [i] Stirring for 20 min before HOAc addition followed by a further 15 min. [j] Refluxing. [k] Perchlorate.

TABLE 4

N-Substituted pyridinium tetrafluoroborates

Cpd. no.	Substituents R²	R³	R⁴	R⁵	R⁶	*N*-Substituent	Cryst. solvent	Crystal form	M.p. (°C)	Lit. m.p. (°C)	Ref.	Found (%) C	H	N	Formula	Required (%) C	H	N
(5b)	Ph	H	Ph	H	Ph	n-Butyl		Needles	199—201	201—202	5							
(5e)						Neopentyl	Me_2CO–Et_2O	Plates	244—245			72.1	6.0	2.9	$C_{25}H_{25}BF_4N$	72.3	6.0	3.0
(5f)						Isopropyl	Me_2CO–Et_2O	Needles	187—189	172	*a*	71.2	5.1	3.1	$C_{24}H_{24}BF_4N$	71.4	5.5	3.2
(5g)						s-Butyl	Me_2CO–Et_2O	Needles	165—167			71.4	5.9	3.1	$C_{27}H_{26}BF_4N$	71.8	5.8	3.1
(5h)						Cyclohexyl	Me_2CO–Et_2O	Needles	179—180	180	*a*	72.9	5.9	2.9	$C_{28}H_{28}BF_4N$	73.0	5.9	2.9
(5i)						Cyclopentyl	Me_2CO–Et_2O	Needles	163—164			72.3	5.4	2.9	$C_{26}H_{26}BF_4N$	72.6	5.6	3.0
(5j)						Cycloheptyl	Me_2CO–Et_2O	Needles	168—170	159—161	22	73.2	6.1	2.8	$C_{30}H_{30}BF_4N$	73.3	6.1	2.9
(5l)						Phenyl	EtOH	Plates	251—253	251	*a*							
(5m)						2,4,6-Trimethylphenyl	EtOH	Needles	214—216			75.0	5.4	2.7	$C_{32}H_{28}BF_4N$	74.9	5.5	2.7
(5n)						4-Nitrophenyl	EtOH	Plates	239—241	239	*a*	67.6	4.0	5.4	$C_{25}H_{21}BF_4N_2O_2$	67.4	4.1	5.4
(5o)						3-Nitrophenyl	EtOH	Needles	244—246			67.6	4.0	5.1	$C_{25}H_{21}BF_4N_2O_2$	67.4	4.1	5.4
(5p)						2-Nitrophenyl	EtOH	Brown plates	170—172			67.7	4.2	5.3	$C_{25}H_{21}BF_4N_2O_2$	67.4	4.1	5.4
(6b)	Me	H	Ph	H	Ph	n-Butyl	EtOH	Plates	138—140			68.3	6.2	3.5	$C_{22}H_{24}BF_4N$	67.9	6.2	3.6
(6l) *b*						Phenyl	EtOH	Plates	230—232			68.2	4.7	3.3	$C_{24}H_{20}ClNO_4$	68.3	4.8	3.3
(6m) *b*						2,4,6-Trimethylphenyl	EtOH	Green needles	159—161			70.0	5.7	3.0	$C_{27}H_{26}ClNO_4$	69.9	5.6	3.0
(11e) *b*	Ph	H	Ph		C_8H_8 *c*	Neopentyl	Me_2CO–Et_2O	Needles	229—231			71.6	6.0	2.8	$C_{30}H_{30}ClNO_4$	71.5	6.0	2.8
(11f) *b*						Isopropyl	Me_2CO–Et_2O	Yellow amorphous powder	140—142			70.5	5.6	2.9	$C_{28}H_{26}ClNO_4$	70.7	5.5	2.9
(11g) *b*						s-Butyl	Me_2CO–Et_2O	Yellow amorphous powder	137—139			71.0	5.8	2.8	$C_{29}H_{28}ClNO_4$	71.1	5.7	2.9
(12b)	But	H	Ph		C_8H_8	n-Butyl	Me_2Co–Et_2O	Needles	142—144			70.9	6.9	3.1	$C_{27}H_{32}BF_4N$	70.9	7.0	3.1
(12c)						Benzyl	Me_2CO–Et_2O	Plates	145—147			73.4	5.9	2.8	$C_{30}H_{30}BF_4N$	73.3	6.1	2.9
(13d) *d*	C_8H_8		Ph		C_8H_8	Allyl		Yellow-green needles	217—219			67.5	4.7	2.6	$C_{31}H_{24}F_3NO_3S$	67.8	4.7	2.6

a M. C. Rezende, Ph.D. Thesis, University of East Anglia, 1979. *b* Perchlorate. *c* α,β-Dihydronaphtho. *d* Trifluoromethanesulphonate.

TABLE 5

I.r. [a] and ^{1}H n.m.r. [b] spectra of *N*-substituted pyridinium tetrafluoroborates

Cpd. no.	Substituents R²	R³	R⁴	R⁵	R⁶	*N*-Substituent	(ν_{max}.cm^{-1})	Chemical shift (δ) Aromatic	*N*-Substituent	R³	R⁶
(5b)	Ph	H	Ph	H	Ph	n-Butyl	3 030m, 1 623s, 1 600m, 1 580m, 1 490m, 1 411m, 1 030—1 075s	7.9—8.5 (17 H)	4.4 (2 H, t, *J* 7.5 Hz), 0.3—1.6 (7 H)		
(5e)						Neopentyl	3 065m, 1 610s, 1 595m, 1 578m, 1 495m, 1 409m, 1 030—1 095s	7.0—8.6 (17 H)	5.0 (2 H, s), 0.45 (9 H, s)		
(5f)						Isopropyl	3 050m, 1 620s, 1 600m, 1 558m, 1 495m, 1 413m, 1 025—1 085s	7.0—8.3 (17 H)	4.8—5.5 (1 H), 1.35 (6 H, d, *J* 6 Hz)		
(5g)						s-Butyl	3 060m, 1 624s, 1 600m, 1 567m, 1 495m, 1 414m, 1 030—1 080s	7.2—8.0 (17 H)	4.5—5.1 (1 H), 1.0—2.2 (2 H), 1.35 (3 H, d, *J* 6 Hz), 0.6 (3 H, t, *J* 7.5 Hz)		
(5h)						Cyclohexyl	3 060m, 1 626s, 1 600m, 1 567m, 1 493m, 1 411m, 1 040—1 080s	7.2—8.1 (17 H)	4.2—4.9 (1 H), 0.4—2.4 (10 H)		
(5i)						Cyclopentyl	3 045m, 1 620s, 1 601m, 1 567m, 1 492m, 1 413m, 1 025—1 095s	7.2—8.1 (17 H)	4.6—5.4 (1 H), 1.6—2.5 (4 H), 0.7—1.4 (4 H)		
(5j)						Cycloheptyl	3 050m, 1 620s, 1 597m, 1 570m, 1 490m, 1 409m, 1 030—1 080s	7.2—8.1 (17 H)	4.5—5.1 (1 H), 0.6—2.7 (12 H)		
(5l)						Phenyl	3 020m, 1 628s, 1 601m, 1 562m, 1 495m, 1 418m, 1 035—1 085s	6.9—8.1 (22 H)			
(5m)						2,4,6-Trimethylphenyl	3 050m, 1 620s, 1 600m, 1 580m, 1 495m, 1 413m, 1 030—1 080s	6.65—8.2 (19 H)	2.1 (3 H, s), 1.95 (6 H, s)		
(5n) *c*						4-Nitrophenyl	3 070m, 1 628s, 1 598m, 1 560m, 1 526s, 1 493m, 1 418m, 1 351s, 1 020—1 110s	7.15—8.8 (21 H)			
(5o) *c*						3-Nitrophenyl	3 070m, 1 628s, 1 600m, 1 549m, 1 539s, 1 499m, 1 419m, 1 353s, 1 030—1 080s	7.15—8.85 (21 H)			
(5p) *c*						2-Nitrophenyl	3 060m, 1 620s, 1 600m, 1 553m, 1 530s, 1 494m, 1 412m, 1 342s, 1 030—1 070s	6.9—8.7 (21 H)			
(6b) *d*, *e*	Me	H	Ph	H	Ph	n-Butyl	3 050m, 1 630s, 1 600m, 1 568m, 1 490m, 1 415m, 1 010—1 060s	6.95—8.5 (12 H)	4.4 (2 H, t, *J* 8 Hz), 2.1 (2 H), 1.25 (3 H, t, *J* 8 Hz), 0.65 (2 H)	2.95 (3 H, s)	
(6l) *c*, *e*						Phenyl	3 065m, 1 632s, 1 593m, 1 565m, 1 494m, 1 414m, 1 070—1 100s	7.1—8.75 (17 H)		2.55 (3 H, s)	
(6m) *c*, *e*						2,4,6-Trimethylphenyl	3 065m, 1 624s, 1 600m, 1 581m, 1 498m, 1 411m, 1 080—1 100s	6.75—8.85 (14 H)	2.3 (3 H, s), 2.0 (6 H, s)	2.55 (3 H, s)	
(11e) *c*, *e*	Ph	H	Ph		C_8H_8 *f*	Neopentyl	3 060m, 1 609s, 1 596m, 1 571m, 1 480m, 1 414m, 1 070—1 100s	7.3—8.5 (15 H)	4.75—5.6 (2 H), 0.45 (9 H, s)		2.95 (4 H, s)
(11f) *e*						Isopropyl	3 060m, 1 610s, 1 598m, 1 571m, 1 496m, 1 427m, 1 070—1 100s	7.2—8.3 (15 H)	5.0—5.7 (1 H), 1.45 (6 H, d, *J* 6 Hz)		2.85 (4 H, s)
(11g) *e*						s-Butyl	3 055m, 1 610s, 1 595m, 1 545m, 1 494m, 1 427m, 1 065—1 100s	7.2—8.5 (15 H)	4.8—5.4 (1 H), 1.1—2.3 (2 H), 1.5 (3 H, d, *J* 7.5 Hz), 0.55 (3 H, t, *J* 7.5 Hz)		2.85 (4 H, s)
(12b)	But	H	Ph		C_8H_8	n-Butyl	3 035m, 1 607s, 1 597m, 1 571m, 1 486m, 1 421m, 1 030—1 070s	7.2—8.4 (10 H)	5.1—5.5 (2 H), 0.5—1.5 (4 H), 0.65 (3 H, t, *J* 6 Hz)	1.7 (9 H, s)	2.8 (4 H, s)
(12c)						Benzyl	3 060m, 1 610s, 1 600m, 1 578m, 1 480m, 1 408m, 1 030—1 090s	6.9—8.4 (15 H)	6.45 (2 H, s)	1.8 (9 H, s)	2.5—2.9 (2 H)
(13d) *g*, *h*	C_8H_8		Ph		C_8H_8	Allyl	3 060m, 1 605s, 1 589m, 1 560m, 1 490m, 1 410m, 1 250—1 280s, 1 028s	7.2—8.7 (13 H)	4.5—6.1 (5 H)	2.85 (8 H, s)	2.0—2.5 (2 H)

a In $CHBr_3$. *b* In $CDCl_3$. *c* ^{1}H N.m.r. in $(CD_3)_2SO$. *d* I.r. in Nujol. *e* Perchlorate. *f* α,β-Dihydronaphtho. *g* Trifluoromethanesulphonate. *h* ^{1}H N.m.r. in CF_3CO_2H.

version into pyridinium; Method D gave pyridiniums in 43 and 64% isolated yields respectively.

Isopropylamine gave a mixture of addition products which was converted into diketone by acetic acid.

Pentacyclic pyrylium (13a) with benzylamine (Method A) gave rapid conversion into pyridinium (13c). Allylamine also reacted readily giving 93% isolated yield of pyridinium after 20 min but no pyridinium could be obtained from reaction with neopentylamine.

Reaction of Arylamines with Pyrylium Tetrafluoroborates (*see Table 3*).—Aniline reacts rapidly with (5a) in the presence of 2 equivalents of triethylamine (1 equiv. triethylamine caused some conversion into side-product diketone) to give the tetraphenylpyridinium (51) (Method D): 77% (51) was isolated after 20 min. Previously u.v. kinetics have shown that with weakly basic amines, catalysis by, *e.g.* triethylamine is required for fast amide formation.[20]

2,4,6-Trimethylaniline reacts without triethylamine catalysis (Method A) to give pyridinium (5m) (51% after 20 min, 69% after 3 h). Since the amide intermediate is not observed by ^{13}C n.m.r. spectroscopy it is likely that slow ring opening is followed by fast cyclisation to pyridinium due to unfavourable crowding in the amide. Use of increasing triethylamine catalyst favours diketone over amide formation; however, diketone formation can also be avoided by scavenging the water (Method F gave 36% isolated pyridinium after 20 min).

Method F is used for the reactions of nitroanilines with (5a); without scavenging, considerable amounts of diketone are formed. Both 3- and 4-nitroanilines react with (5a) to give isolated pyridiniums (5o) (53%) and (5n) (59%) respectively in 20 min. Longer reaction time gives slightly increased yields. However even under prolonged period of reflux, 2-nitroaniline gave only 18% of pyridinium by Method F.

In contrast to triphenylpyrylium (5a),[1] triethylamine is not required for the reaction of aniline with 2-methyl-4,6-diphenylpyrylium. Within 10 min ^{13}C n.m.r. shows quantitative formation of pyridinium (6l). Using Method A 96% of (6l) was isolated after 20 min. As observed for triphenylpyrylium (5a), 2,4,6-trimethylaniline did not require catalysis for conversion into pyridinium (6m) (24% isolated after 3 h).

EXPERIMENTAL

I.r. and n.m.r. spectra were measured with Perkin-Elmer 237 and R12 instruments respectively (Me_4Si as internal standard). Melting points (uncorrected) were determined on a Reichert hot-stage microscope.

Pyrylium Salts.—Literature methods were used as described elsewhere.[4]

^{13}C N.m.r. Investigation.—Reactions of pyryliums with amines were followed by ^{13}C n.m.r. as described elsewhere.[4] In a typical experiment, the calculated quantity of amine was added to 0.2 g of pyrylium in $CDCl_3$ or $(CD_3)_2SO$ (1.4 ml). $CDCl_3$ was replaced by CH_2Cl_2 or $CHCl_3$ for preparative experiments.

The percentages of pyridinium and diketone found given in Tables 2 and 3 were obtained by comparison of ^{13}C peak heights. It is emphasised that these results give only a rough indication of the relative proportion of the two compounds formed: the reproducibility is $\pm 10\%$ but experiments with artificial mixtures indicated that the amount of diketone is over-estimated in this way.

Preparation of Pyridinium Tetrafluoroborates (*Tables 1—5*).—*Method A.* In a typical experiment 2,4,6-triphenylpyrylium tetrafluoroborate (1 g, 2.5 mmol) and n-butylamine (0.37 g, 5 mmol) were stirred in CH_2Cl_2 (7 ml). Addition of Et_2O (50 ml) gave the product.

Method B. 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium trifluoromethanesulphonate (1 g, 2.0 mmol), allylamine (0.11 g, 2.0 mmol) and Et_3N (0.20 g, 2.0 mmol) were stirred in CH_2Cl_2 (7 ml). Addition of Et_2O (50 ml), filtration, and washing with water gave the product.

Method C. 2,4,6-Triphenylpyrylium tetrafluoroborate (1 g, 2.5 mmol) and n-butylamine (0.37 g, 5.0 mmol) were added and the mixture stirred. Addition of Et_2O (50 ml) gave the product.

Method D. 2-(t-Butyl)-5,6-dihydro-4-phenylbenzo[*h*]-chromenylium tetrafluoroborate (1 g, 2.5 mmol), n-butylamine (0.18 g, 2.5 mmol), and Et_3N (0.25 g, 2.5 mmol) were stirred in CH_2Cl_2 (7 ml) for 5 min. HOAc (0.30 g, 5 mmol) was added and the mixture stirred. Addition of Et_2O (50 ml), filtration, and washing with water gave the product.

Method E. 5,6-Dihydro-2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (1 g, 2.4 mmol), isopropylamine (0.14 g, 2.4 mmol), and Et_3N (0.25g, 2.4 mmol), were stirred in CH_2Cl_2 (7 ml) for 0.5 h. HOAc (0.28 g, 4.8 mmol) was added and the mixture stirred. Addition of Et_2O (50 ml) filtration, and washing with water gave the product.

Method F. 2,4,6-Triphenylpyrylium tetrafluoroborate (1 g, 2.5 mmol), EtOH (0.35 g, 7.5 mmol), and 4-nitroaniline (0.35 g, 2.5 mmol) were added in turn to a mixture of Et_3N (1.28 g, 12.5 mmol) and Ac_2O (0.52 g, 5.0 mmol) in CH_2Cl_2 (7 ml). The mixture was stirred for 5 min. HOAc (0.76 g, 12.5 mmol) was added and the mixture stirred. Addition of Et_2O (50 ml), filtration, and washing with water gave the product.

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