The Synthesis and Reactions of Sterically Constrained Pyrylium and Pyridinium Salts †

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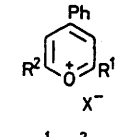
Efficient syntheses are developed for several pyrylium cations with substitution patterns more sterically demanding than 2,4,6-triphenyl and these are examined as reagents for the conversion of primary amino into a leaving group. The 2-mesityl-4,6-diphenyl derivative did not react smoothly with amines. The 2,6-di-t-butyl-4-phenyl-pyrylium cation gave the corresponding pyridinium derivatives, but they resisted nucleophilic attack. 2-t-Butyl-4,6-diphenylpyridinium cations suffer nucleophilic attack with about the same ease as the 2,4,6-triphenyl analogues. Dihydrobenzopyrylium (6) and tetrahydrodibenzoxanthylium cations (7) gave pyridinium cations which underwent much easier nucleophilic attack: thus they alkylate xanthate anion in ethanol solution and acetate anion in acetic acid.

2,4,6-TRIPHENYLPYRYLIUM SALTS (1) convert the amino-group of primary amines into a good leaving group, enabling the replacement of NH_2 by halogens,[1] and by O-,[2] S-,[3] and N-linked functionality.[4] The demonstrated[5] superiority of 2,4,6-triphenylpyridine over



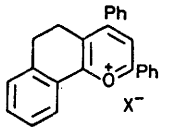
(1) $R^1 = R^2 = Ph$

(2) $R^1 = Bu^t, R^2 = Ph$

(3) $R^1 = R^2 = Bu^t$

(4) R^1 = Mesityl, $R^2 = Ph$

(5) $R^1 = R^2$ = Mesityl



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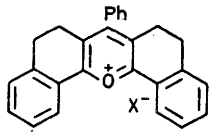

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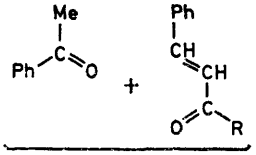
a, $X = ClO_4$; b, $X = BF_4$



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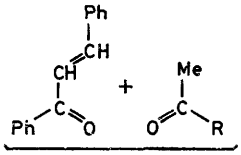

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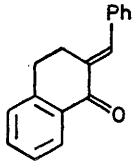
2,4,6-trimethylpyridine encouraged us to explore other substituted pyridines as leaving groups in the hope of discovering superior alternatives which would allow displacement reactions under milder conditions. This paper describes two distinct lines of exploration: first we have replaced one or both of the α-phenyl groups in (1) by other bulky functions to give the mono- (2) and di-t-butyl analogues (3) and the mono-mesityl compound (4). Secondly we made the polycyclic derivatives (6) and (7) in which the α-phenyl groups are constrained to a position more nearly in the plane of the pyrylium ring.

Preparation of Pyrylium Salts.—The pyrylium perchlorates (1a)—(4a), (6a), and (7a) were all prepared by reaction of an αβ-unsaturated ketone with the appropriate ketone containing the group $COCH_2$, in the presence of perchloric acid. The 2,4,6-triphenyl (1a)[6] and 2-t-butyl-4,6-diphenyl compounds (2a)[7] have been previously reported. For the unsymmetrical perchlorate (4a), the two possible alternative methods of preparation, (8) and (9), were both attempted. Route (8) was superior to (9) because in the latter considerable retro-aldol reaction of chalcone occurs to give benzaldehyde and acetophenone which then reacts with more chalcone to form 2,4,6-triphenylpyrylium perchlorate (1a), contaminating the product. Although retro-aldol reaction can also occur in route (8), it then gives 2-acetylmesitylene which is more sterically hindered and less reactive than acetophenone, and problems of contamination are far less. These difficulties were previously encountered in the synthesis of 2-t-butyl-4,6-diphenylpyrylium perchlorate (2a)[8] and 6-(2-nitrophenyl)-2,4-diphenylpyrylium perchlorate[9] by routes of type (9) from chalcone with pinacolone and 2-nitroacetophenone respectively, and were also overcome by utilising the alternative route (8). Attempted reaction of mesityl styryl ketone with acetylmesitylene to prepare the cation (5) failed, evidently owing to steric crowding.

The perchlorates (6a) and (7a) were obtained from α-tetralone with the corresponding chalcone; however,



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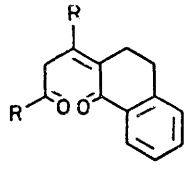

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the corresponding tetrafluoroborates (6b) and (7b) were easier to prepare and were given most attention. 5,6-Dihydro-2,4-diphenylnaphtho[1,2-*b*]pyrylium tetrafluoroborate (6b) was prepared (76%) from α-tetralone, chalcone, and boron trifluoride which acted as the condensing agent with chalcone as a hydride abstracting agent. A two-fold excess of chalcone was not needed.[10] Condensation of α-tetralone and benzaldehyde gave 2-

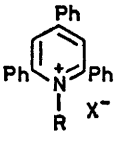
† Related work has been published in the Series ' Heterocycles in Organic Synthesis.'

TABLE 1

Reactions of pyrylium salts with amines

Pyrylium salt no.	X⁻	Pyrylium cation	Wt./g	Amine	Wt./g	Solvent	Vol./ml	T/°C	Time/h	Et_2O added (ml)	Pyridinium salt no.
(1a)	ClO_4^-	2,4,6-Triphenyl	4.0	$MeNH_2$	1.2 ml/ 30% EtOH	EtOH	50	20	2	200	(12a)
			3.5	$BuNH_2$	0.75	EtOH	35	20	2	50	(13a)
			4.0	$PhCH_2NH_2$	2.5 ml	EtOH	20	20	6	100	(14a)
(1b)	BF_4^-	2,4,6-Triphenyl	3.0	$PhCH_2NH_2$	1.0	EtOH	20	20	6	100	(14b)
			5.0	$Me[CH_2]_4NH_2$	1.13	EtOH	20	80	2	100	(15b)
			5.0	$Me[CH_2]_5NH_2$	1.45	EtOH	25	80	2	100	(16b)
			5.0	$Me[CH_2]_7NH_2$	1.16	EtOH	25	80	2	100	(17b)
			3.0	p-$ClC_6H_4CH_2NH_2$	1.2	EtOH	20	20	6	100	(18b)
			3.0	p-$MeC_6H_4CH_2NH_2$	1.0	EtOH	20	20	6	100	(19b)
(2a)	ClO_4^-	4,6-Diphenyl-2-t-butyl	2	$MeNH_2$	0.33	EtOH	20	20	2	50	(20a)
			2	Bu^nNH_2	1.0	EtOH	30	20	2	100	(21a)
			2	2-$NH_2C_6H_3N$	0.4	EtOH	30	80	3	50	(22a)
			1.5	$PhCH_2NH_2$	1.75	EtOH	15	20	6	100	(23a)
(2b)	BF_4^-	4,6-Diphenyl-2-t-butyl	1.5	$PhCH_2NH_2$	1.75	EtOH	15	20	6	100	(23b)
			1.5	p-Cl-$C_6H_4CH_2NH_2$	1.7	EtOH	20	20	6	100	(24b)
(3a)	ClO_4^-	4-Phenyl-2,6-di-t-butyl	2	$MeNH_2$	0.4	EtOH	20	20	2	50	(25)
(6a)	ClO_4^-	5,6-Dihydro-2,4-diphenylnaphtho-[*b*]	2.5	$MeNH_2$	0.4	EtOH	30	20	2	20	(27a)
			3	Bu^nNH_2	1 ml	EtOH	20	20	2	50	(28a)
			3	$PhCH_2NH_2$	1.0	EtOH	20	20	6	50	(29a)
			2.5	2-$NH_2C_6H_3N$	0.5	EtOH	20	80	6	50	(30a)
			3	$PhNH_2$	2 ml	EtOH	20	80	6	50	(31a)
(6b)	BF_4^-	5,6-Dihydro-2,4-diphenylnaphtho-[*b*]	4.2	$BuNH_2$	0.73	EtOH	20	20	12	50	(28b)
			4.2	$PhCH_2NH_2$	1.4	EtOH	20	20	12	50	(29b)
			2.5	2-$NH_2C_6H_3N$	0.56	EtOH	15	80	6	40	(30b)
			2.5	$PhNH_2$	2 ml	EtOH	15	80	6	50	(31b)
			4.2	o-$ClC_6H_4CH_2NH_2$	1.4	EtOH	20	20	12	50	(32b)
			4.2	p-$MeC_6H_4CH_2NH_2$	1.45	EtOH	20	20	12	50	(33b)
			4.2	4-$CH_2NH_2C_6H_3N$	1.5	EtOH	20	20	12	50	(34b)
			2.5	p-$MeC_6H_4NH_2$	0.75	EtOH	20	80	6	50	(35b)
			3.0	$OH[CH_2]_3NH_2$	0.52	EtOH	15	20	12	50	(36b)
(7a)	ClO_4^-	5,6,8,9-Tetrahydro-7-phenyldibenzo-[*c*,*h*]xanthylium	2	$MeNH_2$	0.35	EtOH	20	20	0.5	40	(38a)
			2	$BuNH_2$	0.5	EtOH	20	20	0.3	40	(39a)
			3	$PhCH_2NH_2$	1.0	EtOH	20	20	5	30	(40a)
			0.5	$PhNH_2$	0.25	$CHONMe_2$	10	Reflux	2	50	(41a)
			0.5	2-$NH_2C_6H_3N$	0.25	$CHONMe_2$	10	Reflux	2	50	(42a)
			0.5	Furfurylamine	0.2	EtOH	10	20	12	50	(43a)

benzylidene-1-tetralone (10) (75%) [11] which reacts with more α-tetralone in the presence of boron trifluoride–ether to give 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]-

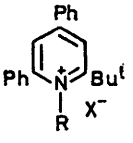


(12) R = Me
(13) R = Bu^n
(14) R = $PhCH_2$
(15) R = $Me[CH_2]_4$
(16) R = $Me[CH_2]_5$
(17) R = $Me[CH_2]_7$
(18) R = $ClC_6H_4CH_2$ (*p*)
(19) R = $MeC_6H_4CH_2$ (*p*)

xanthylium tetrafluoroborate (7b), characterised by its spectral data.

Changing the anion of a pyrylium salt is most conveniently effected *via* the corresponding open-chain diketone (pseudobase).[1b] The tricyclic and pentacyclic pyrylium tetrafluoroborates have been thus converted into other salts.[12]

Preparation of Pyridinium Salts.—Five of the pyrylium perchlorates [(1a)—(3a), (6a), (7a)] reacted smoothly with ammonia to give the corresponding pyridines and with a variety of amines to yield the corresponding pyridinium perchlorates [(12)—(43)] (Tables 1 and 2).



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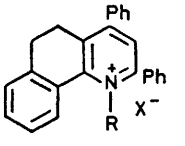

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(20) R = Me
(21) R = Bu^n
(22) R = 2-Pyridyl
(23) R = $PhCH_2$
(24) R = $ClC_6H_4CH_2$-(*p*)

a, X = ClO_4; b, X = BF_4

(27) R = Me
(28) R = Bu^n
(29) R = $PhCH_2$
(30) R = 2-Pyridyl
(31) R = Ph
(32) R = $ClC_6H_4CH_2$ (*o*)
(33) R = $MeC_6H_4CH_2$ (*p*)
(34) R = 4-Picolyl
(35) R = MeC_6H_4 (*p*)
(36) R = $HO[CH_2]_3$

All the reactions were initially attempted in ethanol as solvent and at 20 °C; however for aniline and 2-amino-

pyridine it was usually necessary to use refluxing ethanol or [in the case of the polycyclic pyrylium salt (7)] dimethylformamide. However, attempts to prepare pyridinium salts from 2-mesityl-4,6-diphenylpyrylium perchlorate (4) gave only the open-chain diketone pseudo-base. Evidently the final ring-closure is sterically hindered in this series.

as the chain length increases the salts become increasingly difficult to crystallise.

Initial nucleophilic attack by the amine is not the rate-determining step in the conversion of pyrylium into pyridinium salts. When the reaction is carried out in non-polar solvents such as carbon tetrachloride, or benzene, in which the starting material is insoluble, the

TABLE 2

Properties of pyridinium salts

Compound no.	Solvent for cryst.	Cryst. form.	Yield/%	M.p./°C	Found/% C	Found/% H	Found/% N	Formula	Required/% C	Required/% H	Required/% N
(12a)	EtOH	Microcrystals	88	215 [a]							
(13a)	MeOH	Prisms	66	207—208	69.8	5.9	3.2	$C_{27}H_{26}ClNO_4$	69.9	5.7	3.0
(14a)	EtOH	Needles	84	205—207 [b]	72.0	4.9	2.6	$C_{30}H_{24}ClNO_4$	72.0	4.9	2.8
(14b)	EtOH	Prisms	94	156	74.0	4.9	2.7	$C_{30}H_{24}BF_4N$	74.2	5.0	2.9
(15b)	EtOH	Needles	51	245—246	72.4	6.1	3.1	$C_{28}H_{28}BF_4N$	72.3	6.1	3.0
(16b)	EtOH	Prisms	65	236—238	72.6	6.4	2.9	$C_{29}H_{30}BF_4N$	72.7	6.3	2.9
(17b)	EtOH	Prisms	70	155	73.2	6.8	3.8	$C_{31}H_{34}BF_4N$	73.4	6.8	2.8
(18b)	EtOH	Prisms	88	133	68.8	4.8	2.6	$C_{30}H_{23}BClF_4N$	69.3	4.5	2.8
(19b)	EtOH	Prisms	98	134	71.7	5.2	2.7 [c]	$C_{31}H_{26}BF_4N.5H_2O$	71.5	5.0	2.7
(20a)	EtOH	Prisms	64	252	65 9	6.1	3.6	$C_{22}H_{24}ClNO_4$	66.2	6.1	3.6
(21a)	EtOH	Prisms	36	154—155	67.9	6.9	3.0	$C_{25}H_{30}ClNO_4$	67 6	6.8	3.2
(22a)	EtOH–MeOH	Needles	56	199—200	66.8	5.3	5.9	$C_{26}H_{25}ClN_2O_4$	67.1	5.4	6.0
(23a)	EtOH	Needles	62	193—195 [d]	69.9	5.7	2.8	$C_{28}H_{28}ClNO_4$	70.3	5.9	2.9
(23b)	EtOH	Prisms	76	151	72.0	6.0	3.1	$C_{28}H_{28}BF_4N$	72.3	6.1	3.0
(24b)	EtOH	Prisms	68	155—157			2.8	$C_{28}H_{27}BClF_4N$			2.8
(25)	EtOH	Prisms	75	253—255	62.5	7.2	4.0	$C_{20}H_{28}ClNO_4$	62.9	7.4	3.7
(27a)	MeOH	Plates	64	160—161	69.4	4.8	3.1	$C_{26}H_{22}ClNO_4$	69.7	5.0	3.1
(28a)	EtOH–MeOH	Prisms	62	134	71.0	5.8	3.2	$C_{29}H_{28}ClNO_4$	71.1	5.8	2.9
(28b)	EtOH	Prisms	65	97—98			2.8	$C_{29}H_{28}BF_4N$			2.9
(29a)	MeOH	Needles	88	152	73.6	5.1	2.7	$C_{32}H_{26}ClNO_4$	73.3	5.0	2.7
(29b)	EtOH	Needles	94	193	75.1	5.2	2.7	$C_{32}H_{26}BF_4N$	75.2	5.1	2.7
(30a)	EtOH–MeOH	Needles	68	257—258	70.3	4.6	5.7	$C_{30}H_{23}ClN_2O_4$	70.5	4.5	5.5
(30b)	EtOH	Prisms	95	258	72.7	4.6	5.2	$C_{30}H_{28}BF_4N_2$	72.3	4.7	5.6
(31a)	MeOH	Prisms	87	304—305	72.8	4.9	2.8	$C_{31}H_{24}ClNO_4$	73.0	4.7	2.8
(31b)	EtOH	Prisms	94	274	74.8	4.7	2.8	$C_{31}H_{24}BF_4N$	74.9	4.9	2.8
(32b)	EtOH	Needles	83	189	70.2	4.4	2.4	$C_{32}H_{25}BClF_4N$	70.4	4.6	2.5
(33b)	EtOH	Needles	90	163	75.7	5.0	2.7	$C_{33}H_{28}BF_4N$	75.4	5.3	2.7
(34b)	EtOH	Prisms	69	201	72.1	4.9	5.5	$C_{31}H_{25}BF_4N_2$	73.0	4.6	5.5
(35b)	EtOH	Prisms	90	294	75.1	5.2	2.7	$C_{32}H_{26}BF_4N$	75.2	5.1	2.7
(36b)	EtOH	Prisms	88	92			3.2	$C_{28}H_{26}BF_4NO$			2.9
(38a)	Et_2O–Me_2CO	Plates	73	294	70.7	5.1	3.1	$C_{28}H_{24}ClNO_4$	71.0	5.1	3.0
(39a)	EtOH	Prisms	67	138	71.8	5.8	2.7	$C_{31}H_{30}ClNO_4$	72.2	5.8	2.7
(40a)	EtOH	Prisms	85	279	74.3	5.0	2.4	$C_{34}H_{28}ClNO_4$	74.2	5.1	2.6
(41a)	MeOH	Needles	70	>350	73.5	5.0	2.8	$C_{33}H_{26}ClNO_4$	73.9	4.9	2.6
(42a)	MeOH	Needles	85	316—318	71.4	4.7	5.4	$C_{32}H_{25}ClN_2O_4$	71.6	4.7	5.2
(43a)	MeOH	Needles	63	>350	73.2	5.0	2.4	$C_{32}H_{26}ClNO_4$	73.3	5.0	2.7

[a] Lit. m.p. 214—215.5 °C [K. Dimroth, K. Wolf, and H. Kroke, *Annalen*, 1964, **678**, 183 (*Chem. Abs.*, 1965, **62**, 512*a*)]. [b] Lit. m.p. 196—198 °C (ref. 19). [c] Lit. m.p. 174—176 °C (ref. 19). [d] Lit. m.p. 193—195 °C (ref. 8, p. 83).

The three pyrylium tetrafluoroborates [(1b), (2b), and (6b)] each gave the corresponding pyridinium tetrafluoroborates from the primary amine in ethanol (*ca.* 5 ml/g of compound) in excellent yield. The 1-alkyl and 1-benzyl-substituted tetrafluoroborates were best prepared at 20 °C, the 1-aryl analogues at higher reaction temperatures. The ease of reaction depends on the basicity of the primary amine, on the steric nature of the pyrylium ring, and on the temperature of the reaction and the solvent. Aprotic solvents such as dimethylformamide seem to enhance the rate but the purity is adversely affected. For each series of *N*-alkylpyridinium tetrafluoroborates the melting point decreases with increasing chain length of the *N*-alkyl substituent, and addition of amine quickly transforms the initial suspension into a red solution, indicative of the attack of the amine at the 2-position; the product can be formed as fast in these solvents as when polar solvents are used. Kinetic confirmation of these qualitative observations has recently been achieved.[13]

Reaction of the Pyridinium Salts with Nucleophiles.—Representative examples of the salts (12)—(43) reacted with various nucleophiles (Table 3) to give the corresponding pyridine together with the alkylated nucleophile. The pyridines were made independently by reaction of the pyrylium salts with ammonia. Attempted reactions of 1-methyl-4-phenyl-2,6-di-t-butylpyridinium perchlorate (25) with pyridine and with

piperidine failed under conditions where all the other salts tested reacted easily. This result agrees with the surprising stability reported for the methiodide of 2,6-di-t-butylpyridine; this methiodide can only be prepared under very high pressure, but once attached, the methyl group is evidently locked in place.[14]

Pyrolysis of *N*-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate with anhydrous sodium acetate at 210 °C gives benzyl acetate in 70% yield.[2] We now show that whereas this reaction does not proceed in acetic acid, the *N*-benzyl derivatives of both the dihydronaphtho (29a) and the tetrahydroacridinium

TABLE 3

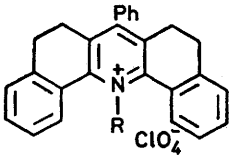
Reactions of pyridinium salts

		Triphenyl		4,6-Diphenyl-2-t-butyl		2,4-Diphenyl-dihydronaphtho[*b*]		5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]-acridinium			
N-Substituent	Reagent	Yield/%	M.p./°C	Yield/%	M.p./°C	Yield/%	M.p./°C	Yield/%	M.p./°C	Lit. M.p./°C	Ref.
Me	Pyridine	84	135	75	134—135	92	134.5	84	135	135	*b*
Bu^n	Pyridine	90 [a]				96		98			*b*
CH_2Ph	Pyridine	88	89—91	74	85—86	84	88	96	85—87	85	*c*
Me	Piperidine					96	*d*				
CH_2Ph	Piperidine	85	178.5—179 [e,f]	62	178 [f]	80	178.6 [f]			178—179	*e*
Bu^n	Morpholine					66	126—127 [f]	71	125	126—127	*g*
CH_2Ph	Morpholine	92	195 [e]			88	195.5	91	195	196	*h*
Me	$MeOCS_2^-K^+$	0		15		85 [i]		90 [i]			
Bu^n	$MeOCS^-K^+$					98 [i]		95 [i]			
CH_2Ph	$MeOCS_2^-K^+$	95 [i]				80 [i]		82 [i]			
CH_2Ph	$MeCO_2^-Na^+$	0				90 [i]		92 [i]			

[a] *N*-n-Butylpyridinium perchlorate does not crystallise (S. Ukai and K. Hirose, *Chem. Pharm. Bull. Japan*, 1968, **16**, 195). [b] See ref. in footnote *a*. [c] J. de Pascual Teresa and H. Sanchez Bellido, *Anales real soc. espan fisi y quim. Madrid*, 1954, **50B**, 71 (*Chem. Abs.*, 1955, **49**, 3054*a*). [d] Yield based on amount of substituted pyridine isolated. [e] Ref. 19. [f] Characterised as the picrate. [g] T. Ishiguro, E. Kitamura, and M. Matsumura, *J. Pharm. Soc. Japan*, 1954, **74**, 1162. [h] J. P. Mason and M. Zief, *J. Amer. Chem. Soc.*, 1940, **62**, 1450. [i] Characterised by comparison of i.r. and ^1H n.m.r. spectra with authentic samples.

The results in Table 3 indicate that for the alkylation and benzylation of pyridine, piperidine, and morpholine with *N*-substituted pyridinium salts, the use of the more complex pyridinium cations offers little significant advantage over the 2,4,6-triphenyl series. However such advantages do arise in other cases.

N-Methyl-2,4,6-triphenylpyridinium perchlorate (12a) failed to react with methyl xanthate anion ($MeOCS_2^-Na^+$) in refluxing ethanol; we previously reported that *N*-benzyl but not *N*-alkyl analogues reacted under these conditions.[3,15] By contrast, *N*-benzyl and *N*-alkyl derivatives of both the dihydronaphtho [(27a), (28a),



(37)

(38) R = Me (41) R = Ph

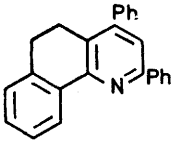
(39) R = Bu^n (42) R = 2-Pyridyl

(40) R = $PhCH_2$ (43) R = 

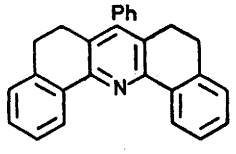
(29a)] and tetrahydroacridinium series [(38a), (39a), (40a)] reacted with xanthate anion in refluxing ethanol in high yield. *N*-Methyl-4,6-diphenyl-2-t-butyl-pyridinium perchlorate (20a) reacted with xanthate to give only a poor yield under these conditions.

series (40a) react with sodium acetate in acetic acid to give benzyl acetate in yields of 90 and 92%, respectively.

These experiments prove conclusively that the tri- (44) and penta-cyclic pyridines (45) are far better leaving



(44)



(45)

groups than 2,4,6-triphenylpyridine. These results significantly extend the potential range of application of nucleophilic displacement of primary amino-groups by conversion into pyridinium salts. We have recently utilised this increased reactivity in a new synthesis of aryl thiocyanates.[16]

EXPERIMENTAL

The following compounds were made by the literature methods quoted: 2,4,6-triphenylpyrylium perchlorate (1a) (71%), m.p. 290 °C (lit.,[7] m.p. 290 °C), and 2-benzylidene-1-tetralone (85%), m.p. 106 °C (lit.,[17] m.p. 106—107 °C).

4,6-*Diphenyl-2-t-butylpyrylium Perchlorate* (2a).—Styryl t-butyl ketone (20 g, 0.11 mol) and acetophenone (6 g, 0.05 mol) were stirred at 100 °C with $HClO_4$ (8 g, 0.08 mol) for 6 h. On cooling to 40 °C Et_2O (200 ml) was added and the crystalline *perchlorate* (2a) formed filtered off and recrystallised from AcOH (10.1 g, 42%), prisms, m.p. 264—266 °C (Found: C, 64.8; H, 5.5. $C_{21}H_{21}ClO_5$ requires C, 64.9; H, 5.5%); $\nu_{max.}$ 1 627, 1 596, 1 588, 1 540, 1 244,

1 079, 720, and 670 cm^{-1}; δ (CF_3CO_2H) 8.1 (1 H, s), 7.8 (1 H, s), 7.5—7.8 (4 H, m), 7.2—7.4 (6 H, m), and 1.2 (9 H, s).

4-Phenyl-2,6-di-t-butylpyrylium Perchlorate (3a) (cf. *ref.* 18).—Styryl t-butyl ketone (9.4 g, 0.05 mol) and pinacolone (2.5 g, 0.025 mol) were heated at 130 °C with $HClO_4$ (3.5 g, 0.03 mol) for 8 h. The mixture was then refluxed for 1 h in absolute EtOH (50 ml) and charcoal (10 g). The EtOH was evaporated off and the product was dissolved in acetone (40 ml) and filtered. The *perchlorate* (3a) was obtained by precipitation with Et_2O (150 ml) (1.4 g, 15%). Recrystallisation from HCO_2H gave prisms, m.p. 252—253 °C (Found: C, 63.3; H, 6.7. $C_{19}H_{25}ClO_5$ requires C, 63.2; H, 6.8%); $\nu_{max.}$ 1 630, 1 600, 1 585, 1 240, 1 085, 962, 876, 766, and 680 cm^{-1}; δ (CF_3CO_2H) 7.7 (2 H, s), 7.5—7.2 (5 H, m), and 1.2 (18 H, s).

2-Mesityl-4,6-diphenylpyrylium Perchlorate (4a).—Mesityl styryl ketone (15 g) and acetophenone (3.6 g) were stirred on a steam-bath at 100 °C with $HClO_4$ (4.5 g) for 6 h. On cooling to 40 °C Et_2O (200 ml) was added. The brown oil formed the yellow crystalline *perchlorate* (4a) (4 g, 45%) as needles from AcOH, m.p. 256—257 °C (Found: C, 68.8; H, 5.2. $C_{26}H_{23}ClO_5$ requires C, 69.2; H, 5.2); $\nu_{max.}$ (Nujol) 1 628s, 1 595s, 1 585m, 1 548ms, 1 235m, 1 080s, 715m, and 680m cm^{-1}; δ (CF_3CO_2H) 8.4 (1 H, s), 8.05 (1 H, s), 7.95—6.85 (12 H, m), and 2.05 (9 H, s).

5,6-Dihydro-2,4-diphenylnaphtho[1,2-b]*pyrylium Perchlorate* (6a).—Chalcone (3 g, 0.014 mol) and α-tetralone (1.5 g, 0.01 mol) were heated to 90 °C in an oil-bath with stirring. $HClO_4$ (1.2 g, 0.012 mol) was added dropwise. The temperature was raised to 120 °C for 10 min. The product was refluxed in EtOH (20 ml) for 15 min; after cooling Et_2O (50 ml) was added to give the *perchlorate* (6a) (3.1 g, 68%) as yellow prisms (MeOH), m.p. 294—295 °C (Found: C, 68.8; H, 4.5. $C_{25}H_{19}ClO_5$ requires C, 69.1; H, 4.4%); $\nu_{max.}$ (Nujol) 740m, 763m, 787w, 875w, 1 080vs (ClO_4^-), 1 160w, 1 210w, 1 240w, 1 573mw, 1 600m, and 1 620s cm^{-1}; δ (CF_3CO_2H, 100 MHz) 8.50—8.20 (4 H, m, C_6H_4), 7.9—7.4 (11 H, m, Ph–pyrylium), and 3.4—3.1 (4 H, m, CH_2CH_2).

5,6-Dihydro-2,4-diphenylnaphtho[1,2-b]*pyrylium Tetrafluoroborate* (6b).—Chalcone (20.8 g, 0.1 mol) was heated to its melting point on a steam-bath. α-Tetralone (12 g, 0.8 mol) was added followed by boron trifluoride–ether (50 g, 0.24 mol) with mechanical stirring. The temperature was raised to 100 °C and stirring continued for 4 h. On cooling to room temperature Et_2O (200 ml) was added to give the yellow crystalline *tetrafluoroborate* (6b) (27.2 g, 78%). The product was recrystallised from AcOH, m.p. 270 °C (prisms) (Found: C, 70.7; H, 4.4. $C_{25}H_{19}BF_4O$ requires C, 71.1; H, 4.5%); $\nu_{max.}$ 708s, 745w, 765s, 783m, 822ms, 882w, 995ms, 1 050vs, 1 190ms, 1 252w, 1 380ms, 1 415s, 1 450w, 1 488vs, 1 532vs, 1 575ms, 1 588ms, 1 601s, and 1 632vs cm^{-1}; δ (CF_3CO_2H) 8.55–8.18 (4 H, m), 7.87—7.39 (11 H, m), and 3.5—3.1 (4 H, m).

5,6,8,9-Tetrahydro-7-phenyldibenzo[c,h]*xanthylium Perchlorate* (7a).—2-Benzylidene-α-tetralone (10) (12 g, 0.05 mol) and α-tetralone (5 g, 0.035 mol) were heated at 90 °C and $HClO_4$ (4 g, 0.04 mol) was added dropwise over 5 min. The mixture was stirred at 120 °C for 10 min, EtOH (50 ml) added, and the whole refluxed for 10 min. The *perchlorate* (2.4 g, 46%) crystallised from the aqueous ethanol as prisms, m.p. 318 °C (Found: C, 70.1; H, 4.9. $C_{27}H_{21}ClO_5$ requires C, 70.4; H, 4.6%); $\nu_{max.}$ 748m, 770m, 792m, 1 000—1 120vs (ClO_4^-), 1 115w, 1 170vw, 1 190m, 1 204m, 1 560ms, 1 600ms, and 1 610s cm^{-1}; δ (CF_3CO_2H) 8.0—7.77 (2 H, m), 7.40—6.80 (11 H, m), and 2.57br (8 H, s, CH_2CH_2).

5,6,8,9-Tetrahydro-7-phenyldibenzo[c,h]*xanthylium Tetrafluoroborate* (7b).—2-Benzylidene-α-tetralone (35 g, 0.15 mol) and α-tetralone (20.4 g, 0.014 mol) were heated at 100 °C with boron trifluoride–ether (32.13 g, 0.17 mol) for 4 h. The mixture was cooled to room temperature and stirred with Et_2O (200 ml). The product was filtered and washed with Et_2O (50 ml) giving *compound* (7b) (26.9 g, 42%), which was characterised without further purification, m.p. 265 °C (prisms) (Found: C, 72.5; H, 4.3. $C_{27}H_{21}BF_4O$ requires C, 72.3; H, 4.7%); $\nu_{max.}$ (Nujol) 1 612s, 1 601s, 1 590s, 1 563s, 1 530m, 1 292m, 1 263s, 1 050vs (BF_4^-), 800s, 768ms, 752s, and 735m cm^{-1}; δ (CF_3CO_2H) 8.79—8.19 (2 H, m), 8.0—7.2 (11 H, m), and 3.05 (8 H, s).

General Procedure for Preparation of Pyridinium Salts (*Table* 1).—The appropriate amounts of pyrylium salt and amine were stirred or refluxed for the time given. After cooling to 20 °C, the crystalline solid which usually separated was filtered off. The filtrate was treated with ether to give more product. If the total weight of crude product corresponded to less than 80%, solvent was removed at 50 °C and 20 mmHg. This residual material was purified by dissolving in Me_2CO and reprecipitating with ether. Properties are recorded in Table 2.

Reactions of Pyridinium Salts with Nucleophiles.—(i) *With pyridine.* The pyridinium salts (1—2 g) were refluxed in pyridine (10 ml) for 6—12 h (longer times required for alkyl derivatives). The mixture was cooled to 20 °C and ice-cooled Et_2O was added. The product if crystalline was filtered off. If a gum was obtained it was dissolved in Me_2CO and reprecipitated with Et_2O and the whole procedure repeated if necessary. The substituted pyridines were isolated by evaporating the combined filtrates at 50 °C and 20 mmHg and crystallising the residual solid from EtOH.

(ii) *With piperidine and morpholine.* The same procedure [19] as for 2,4,6-triphenylpyridinium salts was used.

(iii) *With xanthates.* The pyridinium salts were refluxed in absolute EtOH with $MeOCS_2^-Na^+$ for 2—3 h. The mixture was cooled to 0 °C in an ice-bath. On filtration the substituted pyridine was obtained. From the filtrate the solvent was removed at reduced pressure, giving the crude ester, which could be purified further by distillation at 2 mmHg.

(iv) *With acetate.* The pyridinium salts were refluxed in glacial HOAc with anhydrous NaOAc for 12 h. The solvent was removed at reduced pressure. The products extracted by dissolving in a minimum quantity of cold MeOH may be purified by distillation or column chromatography.

5,6-Dihydro-2,4-diphenylbenzo[h]*quinoline* (44).—The pyrylium salt (6a) (2 g) in EtOH (20 ml) was stirred with aqueous NH_4OH (20 ml, 35%) at 20 °C for 3 h. The *quinoline* (44) separated; it crystallised from aqueous EtOH as plates, m.p. 128 °C (1.5 g, 98%) (Found : C, 90.2; H, 5.9; N, 4.0. $C_{25}H_{19}N$ requires C, 90.0; H, 5.8; N, 4.2%); $\nu_{max.}$ (Nujol) 749s, 873m, 1 030mw, 1 150mw, 1 225mw, 1 417ms, 1 498ms, 1 575s, 1 592s, and 1 608 mw cm^{-1}; δ (CCl_4) 8.7—7.0 (15 H, m, aromatic) and 2.85 (4 H, s).

5,6,8,9-Tetrahydro-7-phenyldibenzo[c,h]*acridine* (45).—The pyrylium salt (7a) (0.5 g) was stirred in EtOH (20 ml) and aqueous NH_4OH (45%, 5 ml) for 4 h at 20 °C. The *acridine* (45) separated; it crystallised from EtOH—MeOH (50 : 50) as plates, m.p. 166—167 °C (0.3 g, 87%) (Found: C, 90.3; H, 5.9; N, 4.1. $C_{27}H_{21}N$ requires C, 90.2; H, 5.9; N, 3.9%); $\nu_{max.}$ (Nujol) 659w, 709s, 730w, 742s, 762s, 773m, 781w, 818mw, 1 042mw, 1 558m, 1 595w, and 1 610w cm^{-1};

δ (CCl_4) (8.6—8.4), 8.51 (2 H, m), 7.45—6.90 (11 H, m), and 2.90—2.35 (8 H, m).

5,6,8,9-*Tetrahydro*-7-*phenyldibenzo*[c,h]*acridinium Perchlorate* [*cf.* (45)].—Compound (45) (0.25 g) was treated with $HClO_4$ (1 g) in EtOH (10 ml), and Et_2O was added. The *perchlorate* (1.1 g, 86%) separated; it crystallised from MeOH as prisms, m.p. 317 °C (Found: C, 71.0; H, 4.9; N, 3.2. $C_{27}H_{22}ClNO_4$ requires C, 70.5; H, 4.8; N, 3.1%); $\nu_{max.}$ (Nujol) 713ms, 732ms, 743s, 760s, 780ms, 800m, 1160—1030vs (ClO_4^-), 1 228m, 1 280mw, 1 570mw, and 1 620ms cm^{-1}.

4,6-*Diphenyl*-2-*t-butylpyridine*.— 4,6-Diphenyl-2-t-butylpyrylium perchlorate (2a) (3 g, 0.007 mol) was refluxed with aqueous NH_4OH (5 ml) in abs. EtOH (50 ml) for 10 min. The solvent was removed and cold water added (20 ml). The product was extracted with Et_2O (40 ml). The solvent was removed at reduced pressure (20 mmHg), and the product recrystallised from abs. EtOH as needles (1.7 g, 82%), m.p. 87—88 °C (Found: C, 87.4; H, 7.5; N, 4.9. $C_{21}H_{22}N$ requires C, 87.8; H, 7.4; N, 4.9%); $\nu_{max.}$ ($CHBr_3$) 760s, 772m, 881ms, 1 232w, 1 400ms, 1 481mw, 1 501ms, 1 552s, 1 580ms, and 1 600s cm^{-1}; δ ($CDCl_3$) 8.14 (2 H, m), 7.5 (10 H, m), and 1.4 (9 H, s).

4-*Phenyl*-2,6-*di-t-butylpyridine*.—4-Phenyl-2,6-di-t-butylpyrylium perchlorate (3a) (1.5 g, 0.004 mol) was refluxed in MeOH (10 ml) with aqueous NH_4OH (35%, 5 ml) for 5 min. The solution was cooled in ice; the crystals formed were filtered off and dried at 0.1 mmHg. The product 4-phenyl-2,6-di-t-butylpyridine (1.0 g, 95%) was obtained as prisms (from aq. MeOH), m.p. 50—51 °C (Found: C, 85.1; H, 9.6; N, 5.2. $C_{19}H_{25}N$ requires C, 85.3; H, 9.4; N, 5.2%); $\nu_{max.}$ ($CHBr_3$) 760s, 780w, 855m, 877ms, 904m, 1 030w, 1 082w, 1 201w, 1 220w, 1 240w, 1 255m, 1 360ms, 1 400ms, 1 460m, 1 478ms, 1 499ms, 1 552s, and 1 595s cm^{-1}; δ ($CDCl_3$) 7.7—7.3 (5 H, m), 7.28 (2 H, s), and 1.32 (18 H, s).

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