Heterocycles in Organic Synthesis. Part 17.[1] Conversion of Primary Amines into Bromides and Chlorides

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Primary alkyl, benzyl, and heteroarylamines are converted both by pentaphenyl- and 2,4,6-triphenyl-pyrylium bromides into the corresponding pyridinium bromides. Pyrolysis of the triphenyl derivatives affords a convenient synthesis of alkyl and benzyl bromides. Alkyl and benzyl chlorides are prepared from the corresponding amines *via* the 2,4,6-triphenylpyridinium tetrafluoroborates by pyrolysis with a KCl–NaCl–$ZnCl_2$ eutectic.

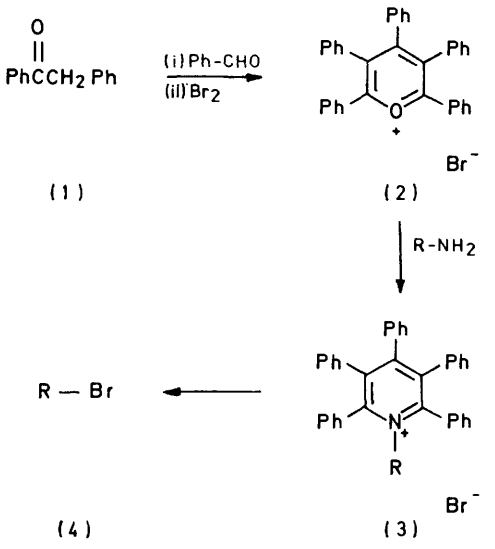
COMPARED to the ease with which aromatic amino-groups are converted into halides *via* the diazonium functions,[2] there are few comparable transformations in the aliphatic series. One extensively studied conversion of primary and secondary alkyl amines to chlorides and bromides is the von Braun method [3] of acylation of the amine to an amide which is subsequently treated with a phosphorus pentahalide [4,5] or thionyl chloride.[6] Yields are generally 50—70% for the von Braun reaction, but disadvantages include the fierce conditions and its limitation to compounds which do not have boiling points near those of either the phosphorus oxyhalide or the benzonitrile. Other conversions of tertiary amines into alkyl chlorides and bromides involve their reaction with cyanogen bromide,[7] an acid chloride,[8] or HBr.[9] The generality and synthetic utility of these methods are limited. More recently [10] primary amines have been converted by an arenediazonium salt into a triazene which on treatment with HBr gives the bromide [equation (1)]: overall yields are *ca.* 60%, but side re-

$$RNH_2 \xrightarrow{Ar\text{-}N_2^+} RNH{-}N{=}NAr \xrightarrow{HBr} R{-}Br \qquad (1)$$

actions lead to olefins and secondary amines. Alkyl amines have also been converted into arylsulphonimides [11] which on reaction with potassium bromide or iodide in dimethylformamide give alkyl halides contaminated with varying amounts of olefins.

We have previously reported [12] the transformation of primary alkyl and heteroaryl amines into various derivatives in which the NH_2 group had been replaced by a nucleophile *via* the corresponding 2,4,6-triphenylpyridinium cation, in particular the conversion of amines into iodides.[13] We now report the successful extension of this method to the synthesis of bromides and chlorides from a variety of primary amines.

Conversion of Amines into Bromides.—Our first route to bromides utilised *N*-alkyl- and *N*-heteroaryl-2,3,4,5,6-pentaphenylpyridinium bromides (3) as intermediates. Pentaphenylpyrylium bromide (2) is readily available in quantity from deoxybenzoin (1) by condensation with



benzaldehyde and subsequent bromination. Although the procedure reported for the latter step by Simalty and Carretto [14] was not in our hands satisfactory for large-scale preparations, it was successfully modified (see Experimental section). Pentaphenylpyrylium bromide (2) reacted rapidly with various primary alkyl, aralkyl, and heteroaryl amines in chloroform solution at 20 °C to give the corresponding *N*-substituted-2,3,4,5,6-pentaphenylpyridinium bromide (3). Preparative details are recorded in Table 1 and i.r. and ^1H n.m.r. spectra in Table 2.

Pyrolysis of the pentaphenylpyridinium bromide (3) at 250—300 °C yielded the corresponding bromide (4)

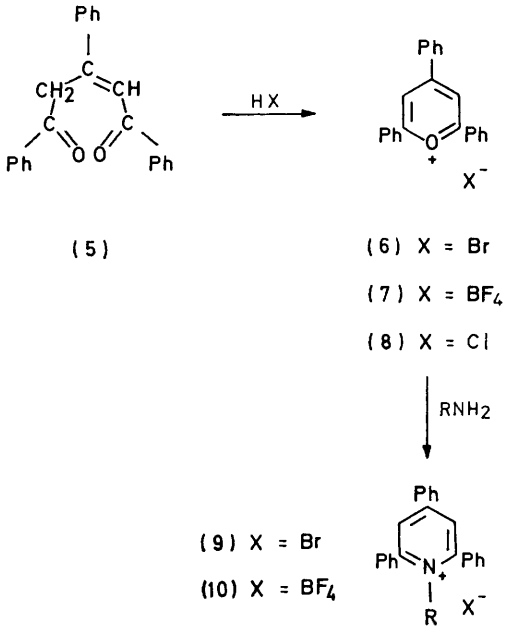
TABLE 1

N-Substituted 2,3,4,5,6-pentaphenylpyridinium bromides (3)

N-Substituent	Yield (%)	Solvent for recryst.	M.p. (θ_c/°C)	Crystal form	Found (%) C	H	N	Br	Formula	Required (%) C	H	N	Br
Ethyl	65	H_2O–HCO_2H–HBr	280	Prisms	78.6	5.4	2.6	13.9	$C_{37}H_{30}BrN,0.25H_2O$ [a]	78.2	5.3	2.5	14.1
Butyl	82	H_2O–HCO_2H–HBr	287	Prisms	78.7	5.5	2.7		$C_{39}H_{34}BrN$	78.5	5.7	2.4	
Allyl	87	H_2O–HCO_2H–HBr	268	Prisms	76.3	5.4	2.3		$C_{38}H_{30}BrN,H_2O$ [a]	76.6	5.2	2.4	
Benzyl	60	H_2O–HCO_2H–HBr	247	Plates	79.4	5.0	2.4	13.0	$C_{42}H_{32}BrN$	80.0	5.1	2.2	12.7
2-Phenylethyl	64	EtOH	300	Microcrystals	80.1	5.4	2.1		$C_{43}H_{34}BrN$	80.1	5.3	2.2	
2-Pyridyl	38	H_2O–HCO_2H–HBr	300	Prisms	77.6	5.0	4.4		$C_{40}H_{29}BrN_2$	77.8	4.7	4.5	

[a] The i.r. spectrum indicates the presence of water of crystallisation.

(Table 3). However, isolated yields of the bromides were poor: *rapid* dissociation of the pyridinium bromide



does not occur until the compound melts, and the m.p.s of the 1-substituted pentaphenylpyridinium bromides are 247—300 °C (Table 1). At the high pyrolysis temperatures needed considerable decomposition occurs and furthermore 2,3,4,5,6-pentaphenylpyridine sublimes over.[15]

Following these difficulties with the pentaphenylpyridinium bromides (3), we turned to 2,4,6-triphenylpyridinium bromides (9). 2,4,6-Triphenylpyrylium bromide (6) has previously been made from acetophenone and benzaldehyde by bromination of an intermediate diketone,[14] but for large-scale preparations we found it more convenient to treat the corresponding pseudobase (5) [16] with aqueous hydrogen bromide. The reactions of 2,4,6-triphenylpyrylium bromide (6) with primary amines were significantly slower than those of the pentaphenyl analogue: a typical reaction time was *ca.* 6 h compared with 15 min for the pentaphenyl series above. Although for the n-butyl, 3-hydroxypropyl, β-phenylethyl, and *p*-methylbenzyl derivatives satisfactory results were obtained with ethanol as solvent, this was the case for the *p*-chlorobenzyl derivative only when the amine was added gradually. For other pyridinium salts (tetramethylenebis, benzyl, 2-pyridyl, and thiazol-2-yl) reasonable yields required the use of chloroform as solvent, sometimes heating was needed. Characteristic spectral details of these *N*-substituted 2,4,6-triphenylpyridinium bromides (9) are listed in Table 4.

The *N*-substituted 2,4,6-triphenylpyridinium bromides (9) when heated to their melting points smoothly pyrolysed to yield the corresponding bromo-derivatives (RBr) (Table 3) in 44—85% yield, except for the 2-pyridyl and thiazol-2-yl compounds where only traces of the corresponding bromides were formed. The phenylethyl bromide obtained was contaminated with styrene.

The presently reported method for the conversion of amines into bromides represents the most satisfactory synthetic sequence currently available for primary alkyl amines although the yields and scope of the reaction are somewhat less than for the analogous reaction to give iodides.[13,*]

Conversion of Amines into Chlorides.—2,4,6-Triphenylpyrylium chloride (8) was prepared from the pseudobase (5) following Chadwick.[17] Reaction of the pyrylium chloride was attempted with several primary amines under a variety of reaction conditions.[18] Methylamine formed the known [19] *N*-methyl-2,4,6-triphenylpyridinium

* We have since shown (with Dr. R. Patel and Miss F. Al-Omran) that use of 2,4,6-triphenylpyridine as a flux enables the pyrolysis temperature to be lowered and increases significantly the yields from the pyrolysis of both the 1-substituted pentaphenyl- and 1-substituted triphenyl-pyridinium bromides.

TABLE 2

I.r. spectra [a] and proton magnetic resonance spectra of *N*-substituted 2,3,4,5,6-pentaphenylpyridinium bromides (3)

N-Substituent	$\nu_{max.}$/cm^{-1}	N.m.r. solvent	Chemical shift (δ)
Ethyl	3 060w, 1 610m, 1 575m, 1 310m, 1 180m, 1 100m, 1 080w, 1 030s, 825w, 800m, 770s, 740s, 705s	CF_3CO_2H	1.31 (3 H, t, *J* 6 Hz), 4.58 (2 H, m), 6.95 (15 H, s), 7.42 (10 H, s)
Butyl	3 080w, 3 040w, 1 670s, 1 603s, 1 585s, 1 498m, 1 265s, 1 195s, 1 100m, 1 075m, 1 030m, 980s, 760s, 700s	CF_3CO_2H	0.5 (5 H, m), 1.75 (2 H, m), 4.45 (2 H, m), 6.90 (15 H, s), 7.37 (10 H, s)
Allyl	3 080w, 1 610m, 1 580s, 1 315w, 1 295m, 1 190s, 1 160m, 1 035s, 920w, 815w, 805w, 775m, 747s, 735s, 705s	CF_3CO_2H	4.45 (m), 4.76 (m), 5.08 (m, CH_2 plus part of allyl-), 5.28 (m), 5.70 (1 H, m), 6.86 (15 H, s), 7.30 (10 H, s)
Benzyl	1 600m, 1 565m, 1 310m, 1 290m, 1 175m, 1 065m, 1 025s, 990w, 960w, 920w, 765m, 740s, 720s, 690s	CF_3CO_2H	5.65br (2 H, s), 6.90 (15 H, s), 7.15 (10 H, s)
2-Phenylethyl	1 615m, 1 570m, 1 310m, 1 180m, 1 100s, 1 025s, 925w, 800w, 755m, 737m, 725m, 698s	$CDCl_3$	3.1 (2 H, m), 4.45 (2 H, m), 7.1 (30 H, m)
2-Pyridyl	1 605w, 1 585s, 1 570s, 1 330m, 1 220m, 1 190m, 1 160m, 1 035s, 925m, 790s, 750m, 730s, 700s	CF_3CO_2H	7.0 (25 H, m), 8.25 (3 H, m), 8.65 (1 H, m)

[a] In Nujol.

chloride and 2-phenylethylamine the corresponding chloride, but conditions were not found to obtain these and other pyridinium chlorides in preparatively useful yields.*

melts at 203 °C.[21] On heating an *N*-alkyl- or *N*-benzylpyridinium tetrafluoroborate (10) with this eutectic at *ca.* 240 °C the corresponding alkyl or benzyl chloride distils out in yields of around 50% (Table 7).

TABLE 3

Pyrolysis of *N*-substituted pyridinium bromides (3) and (9)

	2,3,4,5,6-Pentaphenyl series (3)			2,4,6-Triphenyl series (9)		
N-Substituent	Pyrolysis temp. (θ_c/°C)	Yield (%)	Characterisation	Pyrolysis temp. (θ_c/°C)	Yield (%)	Characterisation
Ethyl	280	2	*a*			
Butyl	287	37	*a*	187	85	*a*, *b*
3-Hydroxypropyl				209	72	*a*, *c*
Allyl	267	6	*a*			
Tetramethylenebis [d]				170	46	*a*, *b*
Benzyl	247	32	*a*	150	61	*a*, *b*
Phenethyl	300	21	*a*	258	56 [e]	*a*, *f*
4-Chlorobenzyl				130	44	*a*, *g*
4-Methylbenzyl				116	54	*a*, *g*
2-Pyridyl	300			285	2	*a*
Thiazol-2-yl				245	2	*a*

[a] Identified by comparison with i.r. spectrum of an authentic sample. [b] Boiling points in agreement with lit. values. [c] Refractive index in agreement with lit. values. [d] 4-(*N*-2,4,6-triphenylpyridinium bromide) butyl. [e] Additional 14% of styrene. [f] N.m.r. investigation. [g] Melting points in agreement with lit. values.

As the *N*-substituted 2,4,6-triphenylpyridinium chlorides are thus not readily available, we turned to the use of another anion together with added chloride as nucleophile. A series of primary amines was readily converted by 2,4,6-triphenylpyrylium tetrafluoroborate (7) [20] into the corresponding *N*-substituted 2,4,6-triphenylpyridinium tetrafluoroborates (10) (Tables 5 and 6). The mono-amines reacted readily in ethanol, but for the di-amines to get good yields it was necessary to use chloroform as a solvent and extended reaction times. For the source of chloride we considered eutectic mixtures: that of $ZnCl_2$–NaCl–KCl (60 : 20 : 20 mol %)

The pyrolysis failed for the 2-pyridyl, *p*-methoxybenzyl, and the tetramethylenebis and pentamethylenebis cases: probably in the first case because of steric hindrance, in the second because of the thermal lability of the product. For the bifunctional cases it is likely that elimination to dienes occurred to a significant extent. Overall the method presents a convenient two-step procedure for the conversion of alkyl and benzyl amines into the corresponding chlorides.

TABLE 4

I.r. spectra [a] and proton magnetic resonance spectra of *N*-substituted 2,4,6-triphenylpyridinium bromides (9)

N-Substituent	$\nu_{max.}$/cm^{-1}	N.m.r. solvent	Chemical shift [δ]
n-Butyl	3 400w (H_2O), 1 625s, 1 600m, 1 150s, 1 080m, 1 030m, 1 000m, 890m, 780s, 725s	CF_3CO_2H	0.75br (7 H, m), 4.35 (2 H, m), 7.55 (15 H, m), 8.05 (2 H, s)
3-Hydroxypropyl	1 625s, 1 605s, 1 570s, 1 350m, 1 250m, 1 170m, 1 050s, 1 025m, 885s, 790s, 775s, 705s	$CDCl_3$	1.65 (2 H, m), 3.05 (2 H, m), 3.60 (1 H, s), 4.65 (2 H, m), 7.57 (15 H, m), 7.80 (2 H, s), 8.05 (6 H, m)
NN'-Tetramethylenebis	3 400w (H_2O), 1 630s, 1 560s, 1 160m, 1 080m, 1 030m, 1 005m, 890s, 760s, 695s	CF_3CO_2H	1.10 (4 H, m), 4.05 (4 H m), 7.65 (15 H, m), 8.0 (2 H, s)
Phenethyl	1 630s, 1 610m, 1 570s, 1 250m, 1 170s, 1 080w, 1 035w, 890m, 765s, 710s	$CDCl_3$	3.05 (2 H, m), 4.75 (2 H, m), 6.30 (2 H, m), 7.15 (3 H, m), 7.55 (15 H, m), 8.10 (2 H, s)
Benzyl	3 500w (H_2O), 1 625s, 1 605m 1 570s, 1 150m, 895m, 885m, 760s, 705s	$CDCl_3$	5.90 (2 H, s), 6.45 (2 H, m), 7.05 (2 H, m), 7.50 (15 H, m), 7.94 (2 H, s)
4-Chlorobenzyl	3 300w (H_2O), 1 670s, 1 605s, 1 320m, 1 285m, 1 270s, 1 225m, 1 155m, 940s, 885s, 770s, 755s, 700s	$CDCl_3$	2.80 (2 H, s), 7.40br (21 H, m)
4-Methylbenzyl	3 400w (H_2O), 1 625s, 1 570s, 1 170m, 1 100m, 1 050w, 895s, 795s, 770s, 715s	$CDCl_3$	2.21 (3 H, s), 5.90 (2 H, s), 6.35 (2 H, d, *J* 4.5 Hz), 6.92 (2 H, d, *J* 54.5 Hz), 7.55 (15 H, m), 7.95 (8 H, m)
2-Pyridyl	3 170w (H_2O), 1 670m, 1 625m, 1 560m, 1 150m, 1 000m, 890s, 810s, 760s, 705s	$CDCl_3$	7.25 (6 H, m), 7.55 (9 H, m), 8.15 (2 H, s), 8.75 (4 H, m)
Thiazol-2-yl	3 280w (H_2O), 1 630s, 1 605m, 1 500s, 1 500m, 1 330m, 1 250s, 1 170s, 1 090m, 1 050m, 1 035m, 1 005m, 995m, 895s, 775s, 700s, 690s	$CDCl_3$	7.55 (15 H, m), 8.0 (2 H, m), 8.35 (2 H, s)

[a] In Nujol.

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.

2,3,4,5,6-*Pentaphenylpyrylium Bromide*.—Bromine (10.8

* We have since found (with Drs. B. Plau and K. Horvath) suitable conditions to convert primary amines by pyrylium chlorides into the pyridinium chlorides which thermolyse under mild conditions to give high yields of alkyl chlorides

g, 0.068 mol) in HOAc (50 ml) was added dropwise, with stirring, to 1,2,3,4,5-pentaphenylpentane-1,5-dione [22] (32.4 g, 0.068 mol) in HOAc (400 ml) at 110 °C. Heating and stirring were maintained for 10 h. The bromide separated on cooling and was crystallised from formic acid (16 g, 43.5%), m.p. 327 °C (lit.,[14] 305 °C).

Preparation of N-*Substituted* 2,3,4,5,6-*Pentaphenylpyridinium Bromides* (*Table* 1).—The amine (0.012 mol) was added, dropwise, with stirring at 20 °C to 2,3,4,5,6-pentaphenylpyrylium bromide (5.41 g, 0.01 mol) in $CHCl_3$ (50 ml). Stirring was maintained for 15 min after which the solvent was evaporated off at 80 °C/15 mmHg to leave an oil, the crystallisation of which was induced by ether. The *bromide* was then recrystallised.

TABLE 5

N-Substituted 2,4,6-triphenylpyridinium tetrafluoroborates (10)

N-Substituent	Method	Yield (%)	M.p. (θ_c/°C)	Solvent for recryst.	Crystal form	Found (%) C	H	N	Cl	Formula	Required (%) C	H	N	Cl
2-Chlorobenzyl	A	70	200	EtOH	Needles	69.2	4.3	2.5	6.8	$C_{30}H_{23}BClF_4N$	69.3	4.5	2.7	6.8
2,4-Dichlorobenzyl	A	72	239	EtOH	Needles	64.7	4.0	2.4	12.9	$C_{30}H_{22}BCl_2F_4N$	65.0	4.0	2.5	12.8
4-Methoxybenzyl	A	60	148	EtOH	Needles	72.0	4.9	2.6		$C_{31}H_{26}BF_4NO$	72.3	5.1	2.7	
Trimethylenebis	B	84	184	EtOH	Needles			3.3		$C_{49}H_{40}B_2F_8N_2$			3.4	
Tetramethylenebis	C	54	306	HOAc	Microcrystals	70.3	5.2	3.1		$C_{50}H_{42}B_2F_8N_2$, $0.5H_2O$ [b]	70.3	5.0	3.3	
Pentamethylenebis	A	56	151	EtOH	Needles			3.1		$C_{51}H_{44}B_2F_8N_2$			3.3	
Dodecamethylenebis	D	83	219	EtOH–H_2O (1 : 1)	Microcrystals	72.0	6.0	3.0		($C_{58}H_{58}B_2F_8N_2$), H_2O [b]	72.2	6.2	2.9	
2-Pyridyl	A	67	233	EtOH	Prisms	70.7	4.5	6.3		$C_{26}H_{21}BF_4N_2$	71.2	4.5	5.9	
4-Chlorobenzyl [a]	A	96	144	EtOH	Needles			2.6		$C_{30}H_{23}BClNF_4$			2.7	

[a] Compound synthesised and characterised by Dr. N. Eweiss. [b] The i.r. spectra indicate the presence of water.

TABLE 6

I.r. spectra [a] and proton magnetic resonance spectra [b] of *N*-substituted 2,4,6-triphenylpyridinium tetrafluoroborates (10)

N-Substituent	$\nu_{max.}$/cm^{-1}	Chemical shift (δ)
2-Chlorobenzyl	1 630s, 1 605w, 1 570s, 1 420w, 1 285w, 1 260w, 1 190w, 1 152m, 1 050s, 972w, 917w, 887m, 790s, 778s, 762s, 750m, 742m, 723w	5.9 (2 H, s), 7.25 (4 H, m), 7.65 (15 H, m), 8.25 (2 H, s)
2,4-Dichlorobenzyl	1 630s, 1 605m, 1 568m, 1 500m, 1 420m, 1 270w, 1 250w, 1 215w, 1 190w, 1 172s, 1 055s, 950w, 890s, 865w, 840m, 820m, 800m, 785w	5.9 (2 H, s), 6.6 (1 H, s), 7.25 (2 H, m), 7.65 (15 H, m), 8.3 (2 H, s)
4-Methoxybenzyl	1 620s, 1 590m, 1 560s, 1 510s, 1 490m, 1 410w, 1 350w, 1 340w, 1 300w, 1 280w, 1 250s, 1 175m, 1 155w, 1 145m, 1 050s, 990w, 930w, 885m, 840w, 825w, 810w, 785s, 770m, 760s, 740m, 730m, 680w, 670w	3.85 (3 H, s), 5.73 (2 H, s), 6.63 (4 H, m), 7.57 (15 H, m), 8.15 (2 H, s)
Trimethylenebis	1 630s, 1 610m, 1 570m, 1 500w, 1 420w, 1 170m, 1 055s, 835m, 770m	2.0 (2 H, s), 4.2 (4 H, s), 7.7 (30 H, m), 8.1 (4 H, s)
Tetramethylenebis	1 625s, 1 600w, 1 567w, 1 280w, 1 250w, 1 167m, 1 050s, 885s, 785m, 770s, 735w, 715m, 705m, 688w	1.05 (4 H, m), 3.95 (4 H, m), 7.6 (30 H, m), 7.9 (4 H, s)
Pentamethylenebis	1 630s, 1 610m, 1 570s, 1 500m, 1 425m, 1 360w, 1 330w, 1 290w, 1 250w, 1 190w, 1 170m, 1 060s, 1 000w, 895m, 770s	0.5 (2 H, m), 120 (4 H, m), 4.25 (4 H, m), 7.65 (30 H, m), 8.08 (4 H, s)
Dodecamethylenebis	1 625s, 1 600w, 1 585w, 1 570m, 1 285w, 1 240w, 1 180w, 1 165m, 1 050s, 890s, 850w, 760s, 737w, 695s	0.95 (6 H, m), 1.07 (4 H, m), 4.55 (4 H, m), 7.7 (30 H, m), 8.15 (4 H, m)
2-Pyridyl	1 620s, 1 590m, 1 585w, 1 570w, 1 565m, 1 550s, 1 490m, 1 430m, 1 410s, 1 305s, 1 280w, 1 260w, 1 245s, 1 220s, 1 185w, 1 160w, 1 150m, 1 050s, 990w, 920w, 880s, 790s, 770m, 760s, 745m, 735s, 715w, 675s	7.65 (15 H, m,) 8.13 (4 H, m), 8.43 (2 H, s)
4-Chlorobenzyl	1 625s, 1 603w, 1 560w, 1 495m, 1 412w, 1 379s, 1 167m, 1 050s, 895s, 790s, 769s, 760s, 747w, 705s, 692w	5.85 (2 H, s), 6.5 (2 H, d, *J* 9 Hz), 7.16 (2 H, d, *J* 9 Hz), 7.63 (15 H, m), 8.23 (2 H, s)

[a] In Nujol. [b] In CF_3CO_2H.

TABLE 7

Pyrolysis of *N*-substituted 2,4,6-triphenylpyridinium tetrafluoroborates (10) in $ZnCl_2$–NaCl–KCl (60 : 20 : 20 mol%) and their conversion into chlorides

No.	*N*-Substituent	Pyrolysis conditions Temp. (θ_c/°C)	Pressure/ (p/mmHg)	Time (t/h)	Yield (%)	Characterisation
(3a)	Butyl	240	20	2	49	*a, b*
(3b)	Benzyl	230	20	2	50	*a, b*
(3c)	2-Chlorobenzyl	245	20	2	49	*a, b*
(3d)	2,4-Dichlorobenzyl	240	20	2	52	*a, b*
(3f)	Trimethylenebis	285	15	2	40	*a, b, c*
(3k)	4-Chlorobenzyl	240	20	2	41	*a, b, d*

[a] Identified by comparison with i.r. spectrum of an authentic sample. [b] Identified by n.m.r. [c] Refractive index in agreement with lit. value. [d] Boiling point in agreement with lit. value.

N-*Butyl*-2,4,6-*triphenylpyridinium Bromide*.—2,4,6-Triphenylpyrylium bromide (5.0 g, 0.013 mol), n-butylamine (0.95 g, 0.013 mol), and EtOH (100 ml) were stirred at 20 °C for 12 h. The solvent was evaporated off at 80 °C/15 mmHg and the residue crystallised from Et_2O–EtOH (1 : 1) (or aqueous EtOH), to yield the *bromide* (1.5 g, 25%) as pale yellow needles, m.p. 187 °C (Found: C, 70.6; H, 6.1; N, 3.0. $C_{27}H_{26}BrN,H_2O$ requires C, 70.1; H, 6.1; N, 3.6%).

N-*Phenethyl*-2,4,6-*triphenylpyridinium Bromide*. This compound was prepared similarly as plates (81%) (from EtOH), m.p. 258 °C (decomp.) (Found: C, 75.4; H, 5.5; Br, 16.5; N, 2.9. $C_{31}H_{26}BrN$ requires C, 75.6; H, 5.3; Br, 16.3; N, 2.9%).

N-(3-*Hydroxypropyl*)-2,4,6-*triphenylpyridinium Bromide*.—3-Hydroxypropylamine was treated as above. Removal of solvent gave a red oil which was stirred with Et_2O (200 ml). The *bromide* separated: it crystallised from Et_2O–EtOH (4 : 1) as needles, m.p. 209 °C (3.2 g, 92%) (Found: C, 69.7; H, 5.4; Br, 17.9; N, 3.1. $C_{26}H_{24}BrNO$ requires C, 70.0; H, 5.4; Br, 17.9; N, 3.1%).

N-(4-*Methylbenzyl*)-2,4,6-*triphenylpyridinium Bromide*.—This compound was prepared as above from 4-methylbenzylamine (0.95 g, 0.007 8 mol) except that 100 ml of Et_2O was used. The *bromide* crystallised from Et_2O–EtOH (2 : 1) to yield as pale yellow needles (2.60 g, 63%), m.p. 116 °C (Found: C, 70.7; H, 5.4; Br, 15.5; N, 2.8. $C_{31}H_{26}BrN,2H_2O$ requires C, 70.5; H, 5.7; Br, 15.2; N, 2.7%).

N-(4-*Chlorobenzyl*)-2,4,6-*triphenylpyridinium Bromide*.—This compound was prepared as above except that the addition of the 4-chlorobenzylamine (1.1 g, 0.007 8 mol) was dropwise, with stirring. The *bromide* crystallised from EtOH–Et_2O (1 : 1) as yellow prisms (2.7 g, 65%), m.p. 130 °C (Found: C, 67.8; H, 4.9; Cl, 6.4; N, 2.5. $C_{30}H_{23}BrClN,H_2O$ requires C, 67.9; H, 4.7; Cl, 6.7; N, 2.6%).

NN′-*Tetramethylenebis*(*triphenylpyridinium*) *Bromide*.—2,4,6-Triphenylpyrylium bromide (5.0 g, 0.013 mol), 1,4-diaminobutane (0.87 g, 0.006 5 mol), and $CHCl_3$ (50 ml) were heated under reflux for 12 h. The mixture was cooled, concentrated aqueous HBr (0.5 ml) was added to it and the whole poured into Et_2O (200 ml). The *dibromide* separated and crystallised from aqueous HOAc (containing 0.1% HBr) as pale yellow needles (3.1 g, 55%), m.p. 170 °C (Found: C, 69.5; H, 5.0; N, 3.5. $C_{50}H_{42}Br_2N_2,2H_2O$ requires C, 69.3; H, 5.3; N, 3.5%).

N-*Benzyl*-2,4,6-*triphenylpyridinium Bromide*.—2,4,6-Triphenylpyrylium bromide (5.0 g, 0.013 mol), benzylamine (1.39 g, 0.013 mol), and $CHCl_3$ (100 ml) were stirred for 12 h at 20 °C. The first crop of bromide was filtered off and the filtrate evaporated at 80 °C/15 mmHg. The residue was triturated with Et_2O to give a second crop of *bromide*. The combined products crystallised from EtOH–Et_2O (1 : 1) (higher proportions of ether cause contamination with benzylammonium bromide) as pale yellow prisms (3.7 g, 57%), m.p. 150 °C (Found: C, 73.2; H, 5.0; N, 2.7. $C_{30}H_{24}BrN,H_2O$ requires C, 73.4; H, 5.2; N, 2.9%).

N-(2-*Pyridyl*)-2,4,6-*triphenylpyridinium Bromide*.—2,4,6-Triphenylpyrylium bromide (5.0 g, 0.013 mol), 2-aminopyridine (1.22 g, 0.013 mol), and $CHCl_3$ (30 ml) were heated under reflux for 0.5 h. The solvent was evaporated off at 80 °C/15 mmHg and the residue triturated with Et_2O (50 ml). The *bromide* crystallised from aqueous EtOH as pale yellow plates (5.55 g, 90%), m.p. 285 °C (Found: C, 71.3; H, 4.4; Br, 17.2; N, 6.2. $C_{28}H_{21}BrN_2S,0.5H_2O$ requires C, 70.9; H, 4.6; Br, 16.9; N, 5.9%).

N-*Thiazol*-2-*yl*-2,4,6-*triphenylpyridinium Bromide*.—This compound was similarly prepared except that a 6 h reflux period was used; the product crystallised from EtOH–Et_2O (1 : 1) as pale yellow cubes (3.75 g, 64%), m.p. 245 °C (Found: C, 65.4; H, 4.1; Br, 16.6; N, 5.6; S, 6.8. $C_{26}H_{19}BrN_2S,0.5H_2O$ requires C, 65.0; H, 4.2; Br, 17.0; N, 5.8; S, 6.8%).

Pyrolysis of Pentaphenylpyridinium Bromides.—The *N*-substituted pentaphenylpyridinium bromide (*ca.* 4 g, *ca.* 7 mmol) was dried at 30 °C/0.5 mmHg for 3 h and immediately transferred to a distillation apparatus (designed with a small hold-up) and heated to its melting point. After complete melting had occurred, the apparatus was connected to a vacuum pump (0.2—0.5 mmHg), and the distillate collected at liquid nitrogen temperature. The product was dissolved in light petroleum (b.p. 30—40 °C, *ca.* 50 ml), dried ($MgSO_4$), filtered, and the solvent removed at 20 °C/15 mmHg to yield the bromide.

Pyrolysis of Triphenylpyridinium Bromides.—The same procedure was used as for the pentaphenylpyridinium bromides except that the whole operation was carried out at 1.0—2.0 mmHg.

Preparation of the N-*Substituted* 2,4,6-*Triphenylpyridinium Fluoroborates* (3) (*Table* 5).—*Method A*. In a typical experiment, 2,4,6-triphenylpyrylium tetrafluoroborate (3.96 g, 0.01 mol) and 2-chlorobenzylamine (1.69 g, 0.012 mol) were stirred in absolute EtOH (40 ml) at 20 °C for 24 h. The EtOH was removed under reduced pressure (15 mmHg, 50 °C) and addition of Et_2O (15 ml) to the residue gave the product.

Method B. 2,4,6-Triphenylpyrylium tetrafluoroborate (3.96 g, 0.01 mol) was added to 1,3-diaminopropane (0.37 g, 0.005 mol) in $CHCl_3$ (50 ml). After the mixture had been stirred at 20 °C for 20 h, HBF_4 (2.5 ml of a 40% w/v solution) was added to it, and stirring was continued for 4 h. The product separated.

Method C. 1,4-Diaminobutane (0.44 g, 0.005 mol) was added with stirring to 2,4,6-triphenylpyrylium tetrafluoroborate (3.96 g, 0.01 mol) in $CHCl_3$–Me_2CO (1 : 1). The mixture was stirred at 20 °C for 10 h. The product precipitated on addition of Et_2O.

Method D. 2,4,6-Triphenylpyrylium tetrafluoroborate (3.96 g, 0.01 mol) was added to 1,12-diaminododecane (1.0 g, 0.005 mol) in $CHCl_3$ (50 ml). After the mixture had been stirred at 20 °C for 16 h, HBF_4 (5 ml of a 40% w/v solution) was added to it, and the stirring continued for 1 h. The volume of the mixture was reduced (to 10 ml) at 50 °C/18 mmHg. The product precipitated on addition of Et_2O (200 ml).

Pyrolysis of Triphenylpyridinium Tetrafluoroborates.—The *N*-substituted triphenylpyridinium tetrafluoroborate (*ca.* 1.4 g, *ca.* 3 mmol) was mixed with the eutectic mixture of $ZnCl_2$–NaCl–KCl (60 : 20 : 20 mol %) (3 g), dried at 110 °C/0.5 mmHg for 4 h, and immediately transferred to a distillation apparatus. The temperature was raised to *ca.* 240 °C (the precise temperature is given in Table 7) and at a pressure of 15—20 mmHg the chloride distilled out of the reaction mixture and was collected in a receiver cooled with liquid nitrogen.

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