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TRANSFORMATIONS OF PYRIDINIUMS DERIVED FROM AMINO-ALCOHOLS AND FROM DIAMINES

NOVEL RING CLOSURES

ALAN R. KATRITZKY,*† ROLAND T. LANGTHORNE, RANJAN C. PATEL and (in part) GERARD LHOMMET
School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, England

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Abstract—Pyridiniums derived from amino alcohols cyclise to ethers or rearrange to aldehydes on heating. Monopyridiniums from diamines can be acylated or converted into ureas or thioureas: these products cyclise on heating in solution to give dihydro-thiazoles, -4H-thiazines, -oxazoles, -4H-oxazines, or tetrahydro-3H-thiazepines.

We have shown that conversion of primary amines by pyryliums into pyridiniums and subsequent nucleophilic displacement affords a useful method for the conversion of amines into a variety of other functionality.[1] Previously the nucleophilic attack has been intermolecular; the present paper is concerned with intramolecular nucleophilic attack, i.e. the cyclisation of amines carrying another functional group.

Preparation of pyridiniums from amino alcohols. Ethanolamine (**3**), 2- and 3 - hydroxypropylamine (**4** and **5**) and 2 - hydroxy - 2 - methylpropylamine have previously given pyridiniums with 2,4,6 - triphenylpyrylium perchlorate (**1c**) and/or tetrafluoroborate (**1a**).[2]

We have found that a variety of amino alcohols (**3–8**) reacted readily with triphenylpyrylium (**1**) and also the pentacyclic analogue (**2**) to yield pyridiniums **9–14** (Scheme 1): the acridinium analogue was used to give a better leaving group.[3] The pyryliums were prepared following literature methods.[4,5] The pyridiniums (Table 1) are readily prepared at 20° in dichloromethane using triethylamine as catalyst by the standard procedure described elsewhere.[6]

The dibenzoacridinium system with tetrafluoroborate anion gave products that were difficult to crystallise; use of the trifluoromethanesulphonate anion overcame this.

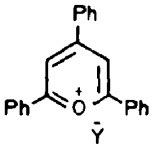
The conditions and the products of pyrolysis are summarised in Table 2. The compounds prepared with the trifluoromethanesulphonate anion were observed to decompose when a specific temperature was reached, whereas those with the tetrafluoroborate anion slowly decomposed over a wider temperature range.

The formation of ethylene oxide from pyrolysis of the N - (2 - hydroxyethyl) pyridinium (**9a**) has previously been reported.[2] Attempts to prepare other small rings, however, failed: instead aldehydes were formed via a 1,2 hydrogen migration (**9e**, **13b**) or a 1,2 methyl group migration (**10e**). Intramolecular nucleophilic attack by O occurred preferentially with the longer chain analogue; 5-aminopentanol (**6**) was cyclised to tetrahedropyran in 78% yield. The attempted preparation of morpholine from N - (2 - hydroxyethyl) ethylene diamine (**8**) yielded an unidentifiable mixture of products.

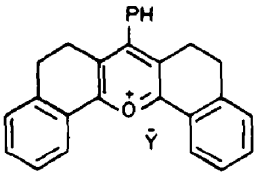
Preparation of pyridiniums from diamines. 1,6 - Diaminohexane with 2,4,6 - triphenyl- and 2,4 - dimethyl - 6 - phenylpyrylium gives the bispyridiniums.[7] We have previously studied the reactions of 2,4,6, - triphenylpyrylium tetrafluoroborate (**1a**) with 1,2 - diaminoethane (**15**), 1,3 - diaminopropane (**16**), 1,4 - diaminobutane (**17**) and 1,12 - diaminododecane: the first two gave the monopyridinium[2] and the others afforded bis - pyridiniums.[8]

It was reasoned that diamines when reacted with suitable pyryliums would give aminoalkylpyridiniums which could be acylated or thioacylated; intramolecular cyclisation should then give heterocycles, e.g. 1,2 - diamine would give dihydro - oxa- and -thia - zoles, whereas 1,3 - diamine would give perhydro oxa- and -thia - zines.

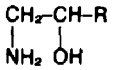
In this paper we describe the reactions of five diamines (**15–19**) with the triphenyl (**1**) and pentacyclic (**2**) pryryliums; the general procedure[6] gave the pyridiniums in good yield (Table 3). Reaction of the dibenzoxanthylium trifluoromethanesulphonate (**2b**) with 1,4 - diaminobutane (**17**) gave a product that was characterised as the bis - trifluoromethanesulphonate salt.



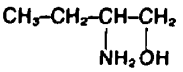
Y	
BF_4	**1a**
CF_3SO_3	**1b**
ClO_4	**1c**



Y	
BF_4	**2a**
CF_3SO_3	**2b**



R	
H	**3**
CH_3	**4**



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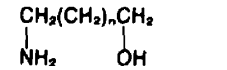
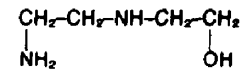


n	
1	**5**
3	**6**



8

†Present address: Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

Table 1. Pyridinium salts from amino alcohols

Product no.	Amino-alcohol Name	No.	Pyrylium system	Anion	Procedure	Yield %	M.p. °C	Recrystallisation solvent	Crystal form	Found % C	H	N	Molecular formula	Required C	H
9e	2-aminoethanol	3	Pentacyclic	CF_3SO_3	C	92	221-223	Et_2O/Me_2CO	needles	65.3	4.7	2.5	$C_{30}H_{26}F_3NO_4S$	65.1	4.7
10a	1-amino-2-propanol	4	Triphenyl	BF_4	A	80	202-204	EtOH	needles	68.6	5.2	2.9	$C_{26}H_{24}BF_4NO$	68.9	5.3
10e	1-amino-2-propanol	4	Pentacyclic	CF_3SO_3	C	86	244-246	Et_2O/Me_2CO	prisms	65.3	5.0	2.4	$C_{31}H_{28}F_3NO_4S$	65.6	4.9
11a	3-amino-1-propanol	5	Triphenyl	BF_4	A	89	191-193[a]	EtOH	prisms	-	-	3.0	$C_{28}H_{24}BF_4NO$	-	-
11d	3-amino-1-propanol	5	Pentacyclic	BF_4	B	71	122-124	Et_2O/Me_2CO	prisms	71.2	5.7	2.6	$C_{30}H_{28}BF_4NO$	71.3	5.5
11e	3-amino-1-propanol	5	Pentacyclic	CF_3SO_3	C	95	206-208	Et_2O/Me_2CO	needles	65.5	5.3	2.2	$C_{31}H_{28}F_3NO_4S$	65.6	4.9
12a	5-amino-1-pentanol	6	Triphenyl	BF_4	A	71	201-203	EtOH	needles	69.6	5.8	2.9	$C_{28}H_{28}BF_4NO$	69.8	5.8
12d	5-amino-1-pentanol	6	Pentacyclic	BF_4	B	72	161-163	Et_2O/Me_2CO	prisms	71.8	6.1	2.9	$C_{32}H_{32}BF_4NO$	72.0	6.0
12e	5-amino-1-pentanol	6	Pentacyclic	CF_3SO_3	C	91	219-221	Et_2O/Me_2CO	prisms	66.6	5.6	2.3	$C_{33}H_{32}F_3NO_4S$	66.6	5.4
13a	2-amino-1-butanol	7	Triphenyl	BF_4	A	90	132-134	EtOH	prisms	69.2	5.5	2.9	$C_{27}H_{26}BF_4NO$	69.4	5.6
13b	2-amino-1-butanol	7	Triphenyl	CF_3SO_3	A	62	56-58	Et_2O/Me_2CO	prisms	64.0	5.1	2.4	$C_{28}H_{26}F_3NO_4S$	63.5	4.8
14e	N-(2-hydroxyethyl) ethylenediamine	8	Pentacyclic	CF_3SO_3	C	83	187-189	Et_2O/Me_2CO	prisms	63.9	5.2	4.6	$C_{32}H_{31}F_3N_2O_4S$	64.4	5.2

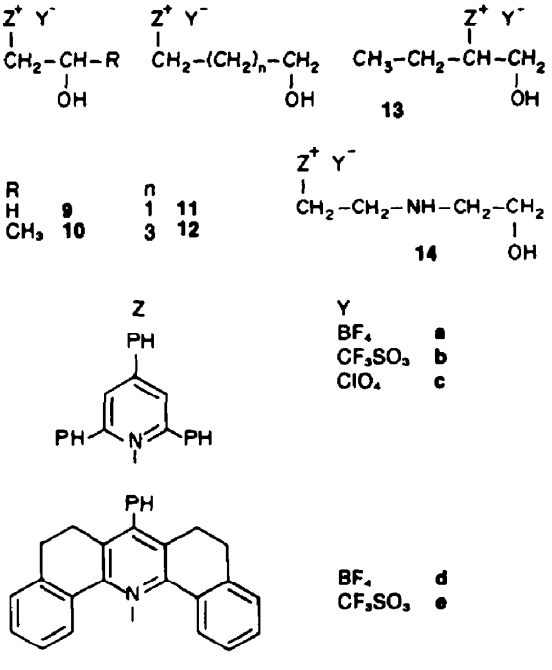
[a] Lit.[2] m.p. 188-189°.

Table 2. Thermolysis of hydroxy-alkyl pyridinium salts

Salt no.	Temp. °C	Conditions Pressure mm	Flux[a] equiv.	Product[b]	Yield %
9e	180	760	1	CH_3CHO	54
10e	190	15	0.1	CH_3CH_2CHO	85
12e	170	15	0.1	$(CH_2)_5O$	78
13b	120	15	0.1	$CH_3CH_2CH_2CHO$	29

[a] 2,4,6-Triphenylpyridine.

[b] Products identified by ^1H NMR.



Scheme 1. Pyridiniums from amino-alcohols.

Previously 4,5 - dihydro - 1,3 - oxa- and -thia - zoles have been prepared by base induced intramolecular ring closures in 2 - N - acyl-[9] or 2 - N - thioacyl - amino - bromoethanes[10] (Scheme 3i). These acyl compounds are prepared from unstable and toxic 2 - aminobromoethanes. 4,5 - Dihydro - 1,3 - oxazoles[11] and 5,6 - dihydro - (4*H*) - 1,3 - oxazines[11b,12] (Scheme 3ii) have also been prepared from the reaction of benzaldehydes with azido - alcohols and by the reaction of benzonitriles with amino - alcohols in the presence of catalysts such as $ZnCl_2$, $Cd(OAc)_2$ and $Mn(OAc)_2$.[13]

2 - Aminophenyl - 5,6 - dihydro - (4*H*) - 1,3 - oxazines and thiazines have been prepared by isomerisation of azetidine ureas[14] and thioureas,[15] (Scheme 3iii) and the latter more recently by reacting phenyl isothiocyanate with 3 - aminopropanol[15] (Scheme 3iv). Anilines with ω - bromoalkylisothiocyanates (prepared using thiophosgene and ω - bromoalkylamine hydrobromides) gave 1,3 - thiaza - heterocycles,[16] (55% overall for 2 - iminophenyl - 4,5,6,7 - tetrahydro - (3*H*) - 1,3 - triazepine) (Scheme 3v).

N - *Acylaminoalkylpyridiniums*. N - Aminoethyl - 2,4,6 - triphenylpyridinium (**20c**) and dibenzoacridinium (**20e**) were acylated (Table 4) smoothly (average yield 84%). When 2,4,6 - triphenylpyridine was the leaving group, internal cyclisation to the required 4,5 - dihydro - oxazole (**25c–f**) did not take place in refluxing ethanol or butanol. The corresponding dibenzoacridinium derivatives (**26e**, **27e**) with the more nucleofugic group (*ca.* 900 × faster[3]) did decompose in refluxing dioxan to give the oxazoles (**26f**) (**27f**). See Table 5 and Scheme 4. Table 6 reports ^1H NMR of the heterocycles prepared.

The analogous 2 - methyloxazole (**28f**) was not isolated from the decomposition of the acylaminoalkyldibenzoacridinium (**28e**).

N - (3 - Aminopropyl) - 5,6,8,9 - tetrahydro - 7 - phenyldibenzo[c,h]acridinium trifluoromethanesulphonate (**21e**) was smoothly benzoylated at 20°C and internal cyclisation to the 2 - substituted - 5,6 - dihydro - (4*H*) - 1,3 - oxazines (**31f**) (**32f**) was effected in high yield in refluxing dioxane (Table 5).

Acylation of the aminobutyldibenzoacridinium (**22e**)

Table 3. Pyridinium salts from diamines

No.	Diamine	Pyrylium	Anion	Procedure	Yield %	M.p. °C	Recrystallisation solvent	Crystal form	Found % C	Found % H	Found % N	Molecular formula	Required % C	Required % H	Required % N
20b	1,2-diaminoethane	Triphenyl	CF_3SO_3	A	85	63-65	Et_2O/Me_2CO	plates	50.4	3.9	3.8	$C_{27}H_{23}F_6N_2O_6S_2$ [a]	50.0	4.3	3.7
20c	1,2-diaminoethane	Triphenyl	ClO_4	C	95	150-152	$EtOH/Et_2O$	needles	66.9	5.5	5.8	$C_{25}H_{23}ClN_2O_4$	66.6	5.1	6.2
20e	1,2-diaminoethane	Pentacyclic	CF_3SO_3	B	86	219-221	Me_2CO	prisms	65.6	5.0	4.8	$C_{30}H_{27}F_3N_2O_3S$	65.2	4.9	5.0
21c	1,3-diaminopropane	Triphenyl	ClO_4	C	76	101-103	-	prisms [b]	-	-	-	$C_{26}H_{25}ClN_2O_4$	-	-	-
21e	1,3-diaminopropane	Pentacyclic	CF_3SO_3	A	92	131-133	c	prisms	65.9	5.0	4.5	$C_{31}H_{29}F_3N_2O_3S$	65.7	5.1	4.9
22e	1,4-diaminobutane	Pentacyclic	CF_3SO_3	B	66	191-194	Et_2O/Me_2CO	prisms	54.6	4.5	3.8	$C_{33}H_{32}F_6N_2O_6S_2$ [a]	54.2	4.4	3.8
23b	4-aminoethylpiperazine	Triphenyl	CF_3SO_3	A	72	107-109	Et_2O/Me_2CO	plates	63.5	5.2	6.9	$C_{30}H_{30}F_3N_3O_3S$	63.3	5.3	7.3
23e	4-aminoethylpiperazine	Pentacyclic	CF_3SO_3	B	44	121-123	Et_2O/Me_2CO	prisms	55.0	4.7	5.4	$C_{35}H_{34}F_6N_3O_6S_2$ [d]	54.5	4.4	5.5
24b	4-aminomethylpiperidine	Triphenyl	CF_3SO_3	B	74	155-157	n-hexane/Me_2CO	prisms	64.8	5.2	4.9	$C_{30}H_{29}F_3N_3O_3S$	65.0	5.2	5.0

[a] Analysed as the bis trifluoromethanesulphonate salt, 20b m.p. 122-124 °; 22e m.p. 217-219 °.

[b] Compound used without purification.

[c] Triturated with ether.

[d] Analysis indicates the bis trifluoromethanesulphonate salt was formed.

Table 4. Acylation of pyridinium alkylamines

Salt no.	Attached alkylamino	Pyridine leaving group	Anion	Acylating agent	Procedure	Yield %	M.p. °C	Recrystallisation solvent	Crystal form	Found % C	Found % H	Found % N	Molecular formula	Required % C	Required % H	Required % N
25c	$-(CH_2)_2NH_2$	Triphenyl	ClO_4	PhCOCl	A	84	210-212	Et_2O/Me_2CO	needles	68.9	5.0	5.0	$C_{32}H_{27}ClN_2O_5$	69.2	4.9	5.0
26e	$-(CH_2)_2NH_2$	Pentacyclic	CF_3SO_3	$4\text{-}MeC_6H_4COCl$	A	62	204-206	EtOH	prisms	67.8	4.9	4.1	$C_{38}H_{33}F_3N_2O_4S$	68.1	4.9	4.2
27e	$-(CH_2)_2NH_2$	Pentacyclic	CF_3SO_3	$4\text{-}ClC_6H_4COCl$	A	84	151-153	n-hexane/Me_2CO	prisms	64.4	4.3	4.0	$C_{37}H_{30}ClF_3N_2O_4S$	64.3	4.3	4.1
28e	$-(CH_2)_2NH_2$	Pentacyclic	CF_3SO_3	MeCOCl	A	84	160-162	n-hexane/Me_2CO	prisms	65.0	4.8	4.6	$C_{32}H_{29}F_3N_2O_4S$	64.6	4.9	4.7
30c	$-(CH_2)_2NH_2$	Triphenyl	ClO_4	PhNCS	B	97	135-137	a	prisms	65.1	4.8	7.0	$C_{32}H_{28}ClN_3O_4S$	65.6	4.8	7.2
31e	$-(CH_2)_3NH_2$	Pentacyclic	CF_3SO_3	$4\text{-}MeC_6H_4COCl$	A	91	155-157	a	prisms	68.4	5.0	3.8	$C_{39}H_{35}F_3N_2O_4S$	68.4	5.1	4.1
32e	$-(CH_2)_3NH_2$	Pentacyclic	CF_3SO_3	$4\text{-}ClC_6H_4COCl$	A	77	149-151	a	prisms	64.9	4.4	3.9	$C_{38}H_{32}ClF_3N_2O_4S$	64.7	4.5	4.0
34c	$-(CH_2)_3NH_2$	Triphenyl	ClO_4	PhNCS	B	88	105-107	a	prisms	65.7	6.7	5.1	$C_{33}H_{30}ClN_3O_4S$	66.0	7.0	5.0
36b	$-(CH_2)_2NH_2$	Triphenyl	CF_3SO_3	$4\text{-}MeC_6H_4SO_2Cl$	A	74	87-89	Et_2O/Me_2CO	plates	61.0	4.6	4.0	$C_{33}H_{29}F_3N_2O_5S_2$	60.6	4.4	4.3

[a] Triturated several times with Et_2O.

Table 5. Preparation of 1,3 - diheterocycles (f) from pyridinium alkylamides and ureas

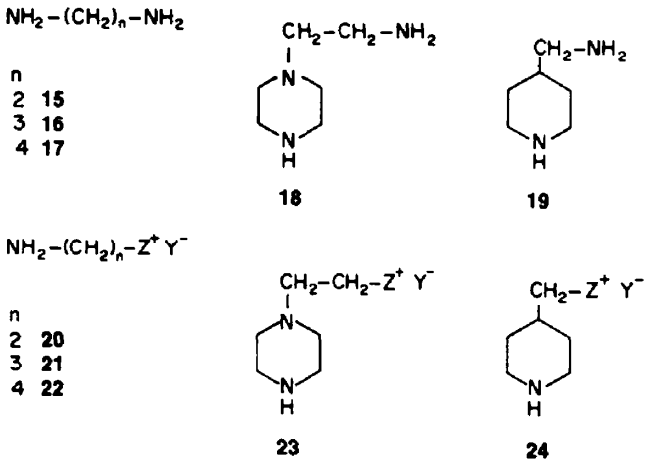
Pyridinium amide no.	Decomposition procedure Solvent/Temp./Time (°C) (hr)	Product (f)[a]	Yield %	M.p./b.p.	Lit. m.p./b.p.	Recryst. solvent	Crystal form	Found % C	H	N	Molecular formula	Required % C	H	N
26c	Dioxan/101/3	Oxazole	26	53	69-70	70-71[b]	Pet. Et_2O[c]	needles	74.2	7.0	8.6	$C_{10}H_{11}NO$	74.5	6.8	8.7
27e	Dioxan/101/4	Oxazole, H_2O	27	40	90-96	80-83[d,e]	Et_2O	prisms	53.7	5.0	6.9	$C_9H_{10}ClNO_2$	54.1	5.0	7.0
29e[f]	Dioxan/101/7	Oxazole	29	57	115-117	119-120[g]	Pet. Et_2O[c]	prisms	66.7	6.6	17.0	$C_9H_{16}N_2O$	66.7	6.2	17.3
30c	Abs. EtOH/78/3	Thiazole	30	51	160	162[h]	Me_2CO	prisms	60.6	5.6	15.7	$C_9H_{10}N_2S$	60.6	5.6	15.7
31e	Dioxan/101/4	Oxazine	31	79	$b_{1.0}$ 97-100	$b_{2.0}$ 122-124[i]	-	-	75.0	7.7	8.4	$C_{11}H_{13}NO$	75.4	7.4	8.0
32e	Dioxan/101/4	Oxazine	32	92	$b_{0.5}$ 90-93	$b_{1.5}$ 126-132[i]	-	-	61.5	5.5	7.1	$C_{10}H_{10}ClNO$	61.4	5.1	7.2
33e[f]	Dioxan/101/5	Oxazine	33	80	127-129	125-127[j]	Pet. Et_2O[c] /Me_2CO	prisms	68.1	7.1	15.8	$C_{10}H_{12}N_2O$	68.2	6.8	15.9
34c	n-BuOH/117/3	Thiazine, $HClO_4$	34	72	94	-	k	prisms	42.0	4.7	9.1	$C_{10}H_{13}ClN_2O_4S$	41.8	4.5	9.5
34e[f]	Dioxan/101/6	Thiazine	34	14	122-124	127[l]	MeOH/Et_2O	prisms	62.8	6.0	14.5	$C_{10}H_{12}N_2S$	62.5	6.2	14.6
35e[f]	Dioxan/101/6	Thiazepine	35	33	125-127	125-127[m]	MeOH/Et_2O	prisms	63.7	6.7	13.4	$C_{11}H_{14}N_2S$	64.1	6.8	13.6

[a] Products characterised by ^1H NMR (Table 6)
[b] Ref 13.
[c] B.p. 60-80°
[d] M.p. of non-hydrate.
[e] O. Exner and O. Schindler, Helv. Chim. Acta 55, 1921 (1972).
[f] The pyridinium amide was not isolated.
[g] B. Adcock, A. Lawson and D. H. Miles, J. Chem. Soc. 5120 (1961).
[h] H. Najer and R. Giudicelli, Bull. Soc. chim. Fr. 960 (1960).
[i] Ref. 12.
[j] Ref. 14.
[k] Triturated with Et_2O.
[l] Ref. 15.
[m] Ref. 16.

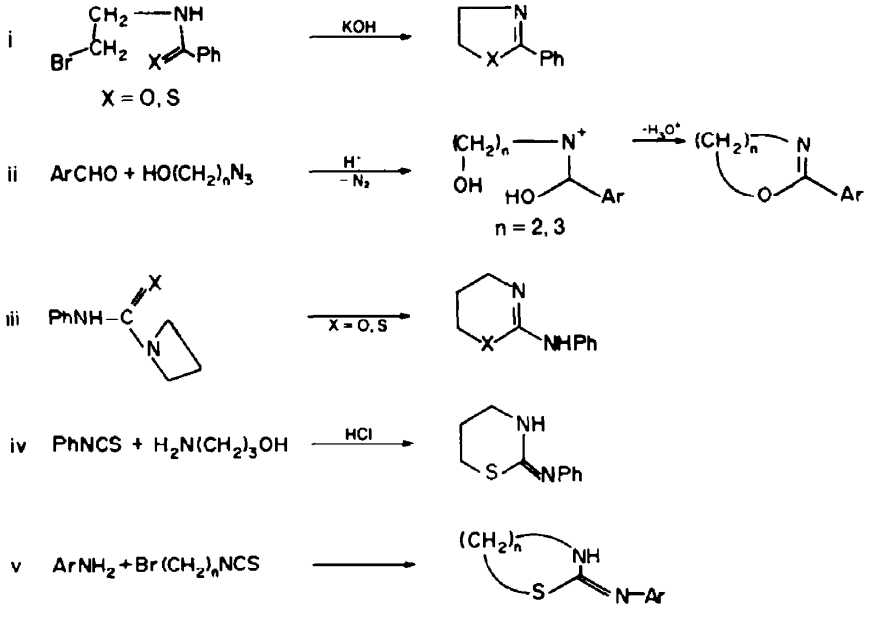
Table 6. ^1H NMR of 1,3 - diheterocycles (f) (X = O or S)

Compound (f)		^1H NMR[a] Heterocycle X-CH_2 (2 H)	N-CH_2 (2 H)	Other	2-Substituent Aromatic	Other
Oxazole	26	4.3 (m)[b]	4.1 (m)[b]		7.3, 7.9 (4 H, AA'BB' J 8)	2.4 (3 H, s)
Oxazole	27	3.7 (m)	3.1 (m)		7.3-7.9 (4 H, AA'BB' J 8)	
Oxazole	29	4.3 (t, J 8)[c]	3.8 (t, J 8)[c]	7.3 (4 H, d, J 4)	7.1 (1 H, m)	6.7 (1 H, bs)
Thiazole	30	3.8 (t, J 6)	3.3 (t, J 6)		7.0-7.5 (5 H, m)	6.5 (1 H, bs)
Oxazine	31	4.2 (t, J 6)	3.5 (t, J 6)	1.8 (2 H, q, J 6)	7.1, 7.8 (4 H, AA'BB' J 8)	2.3 (3 H, s)
Oxazine	32	4.3 (t, J 6)	3.5 (t, J 6)	1.9 (2 H, q, J 6)	7.3, 7.8 (4 H, AA'BB' J 8)	
Oxazine	33	4.2 (t, J 6)	3.4 (t, J 6)	1.9 (2 H, q, J 6)	7.2 (4 H, d, J 5) 7.0 (1 H, m)	3.7 (1 H, s)
Thiazine	34	3.4 (t, J 6)	2.9 (t, J 6)	2.0 (2 H, q, J 6)	7.0-7.4 (4 H, m)	5.8 (1 H, bs)
Thiazepine	35	3.4 (m)	2.8 (m)	1.8 (4 H, m)	6.9-7.3 (5 H, m)	5.6 (1 H, bs)

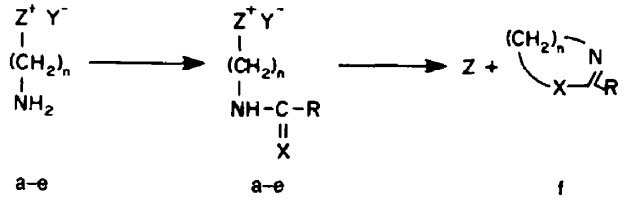
[a] In $CDCl_3$, δ ppm, J coupling constant in Hz.
[b] Second order splitting, four equivalent signals.
[c] Two triplets, complex second order coupling.



Scheme 2. Pyridiniums from diamines (see Scheme 1 for disignation of Z and Y).



Scheme 3.



n	X	R	
2	O	Ph	25
		4-MeC$_6$H$_4$	26
		4-ClC$_6$H$_4$	27
		Me	28
		PhNH	29
2	S	PhNH	30
3	O	4-MeC$_6$H$_4$	31
		4-ClC$_6$H$_4$	32
		PhNH	33
3	S	PhNH	34
4	S	PhNH	35

Scheme 4. (See Scheme 1 for designation of Z and Y).

and decomposition in refluxing dioxane led to mixed products. Presumably a competing reaction, the formation of N - acylpyrrolidine is taking place. Attempts to acylate the bis - trifluoromethanesulphonate salt in excess triethylamine failed.

N - *Phenyl*, N' - (*alkylpyridiniumyl*) *thioureas and ureas.* Reaction of N - aminoethyl - 2,4,6 - triphenylpyridinium (**20c**) with phenyl isothiocyanate proceeded readily to give the thiourea (**30c**) (97%). This decomposed readily in ethanol and, after separation of the triphenyl pyridine by column chromatography and neutralisation of the residue, 4,5 - dihydro - 2 - aminophenyl - 1,3 - thiazole (**30f**), identified by ^{13}C NMR, was obtained (51%).

This scheme was extended to 3 - aminopropyl - 2,4,6 - triphenylpyridinium (**21c**) which reacted with phenyl isothiocyanate to give the corresponding thiourea (**34c**) (88%). Intramolecular cyclisation to give 2 - aminophenyl - 5,6 - dihydro - (4*H*) - 1,3 - thiazine perchlorate (**34f**), (72%) proceeded rapidly in n - butanol. From the N - (3 - aminopropyl)dibenzoacridinium trifluoromethanesulphonate (**21e**) a one pot preparation of the thaizine (**34f**) was accomplished (44%) without isolation of the intermediate thiourea.

The bis - trifluoromethanesulphonate salt of the N - (4 - aminobutyl)dibenzoacridinium (**22e**) was stable to phenyl isothiocyanate; preparation of the N - phenyl, N' - (4 - aminobutyl) thiourea and reaction with the dibenzoxanthylium trifluoromethanesulphonate (**2b**) gave a one pot preparation of 2 - iminophenyl - 4,5,6,7 - tetrahydro - (3*H*) - 1,3 - thiazepine (**35f**) (33%) Table 5.

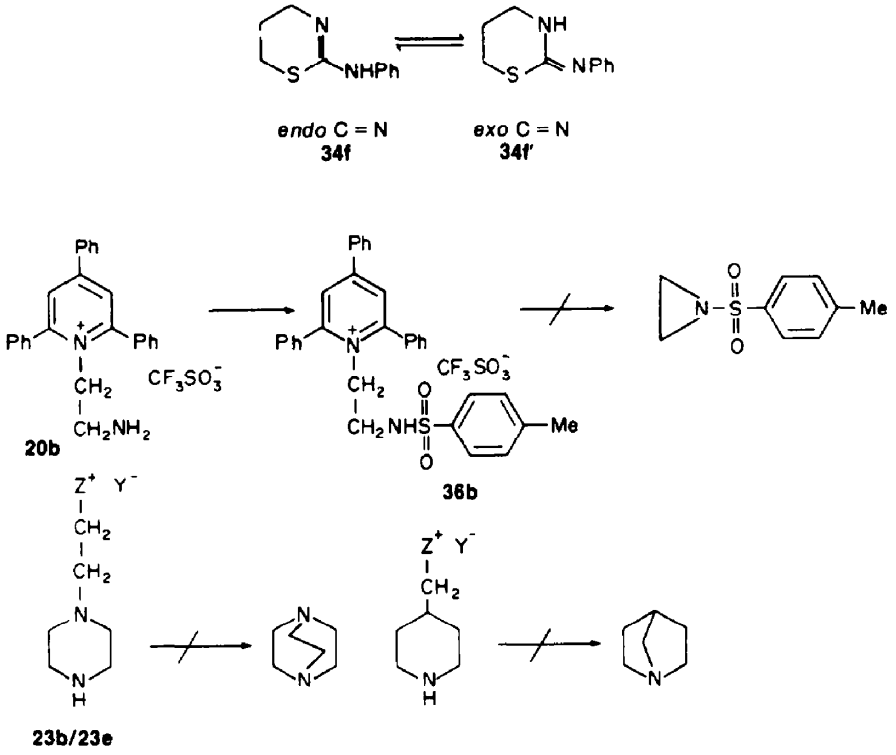
Two tautomeric forms exist for these 1,3 - thiaza - heterocycles:

For the thiazine ring system some authors favour the imino (*exo*) form and some the amino (*endo*) form[15] *cf* respectively **34f** and **34f'**. For the thiazepine ring system (*cf* **35f**) it has been shown by ^1H NMR that the imino form predominates since when the double bond is exocyclic the δ_{N-CH_2} value is lower,[16] imino $\delta_{N-CH_2} \simeq 3.32$; amino $\delta_{N-CH_2} \simeq 3.57$).

Phenyl isocyanate was reacted with the N - (2 - aminoethyl)- and the N - (3 - aminopropyl) - dibenzoacridiniums (**20e**) and (**21e**), respectively. The intermediate ureas **29e** and **33e** respectively, were decomposed without isolation to yield 2 - aminophenyl - 4,5 - dihydro - 1,3 - oxazole (**29f**) (57%) and 2 - aminophenyl - 5,6 - dihydro - (4*H*) - 1,3 - oxazine (**33f**) (80%). Although nitrogen is more nucleophilic than oxygen we have found that nucleophilic attack occurred by the latter to form for example the aminophenyloxazine rather than a tetrahydro - (1*H*) - 3 - phenylpyrimidin - 2 - one.[17] The oxygen is presumably activated by the presence of the two adjacent electron donating nitrogens (Scheme 4).

N - 2 - (*Toluene* - p - *sulphonamido*) *ethyl pyridiniums.* Toluene - *p* - sulphonyl chloride was reacted with the N - (2 - aminoethyl)dibenzoacridinium trifluoromethanesulphonate (**20e**) to prepare a precursor for toluene - *p* - sulphonylaziridine (Scheme 5). However the intermediate tended to decompose to dibenzoacridine in the reaction media at 10°. Reaction of toluene - *p* - sulphonyl chloride with N - (2 - aminoethyl) - 2,4,6 - triphenylpyridinium trifluoromethanesulphonate (**20b**) gave the sulphonamide (**36b**) but the intermediate was stable to pyrolysis, ethoxide and triethylamine. The pyridine N-CH_2 bond could not be cleaved.

N - (4 - *Ethylpiperazino*) - *and* N - (4 - *methylpiperidino*) - *pyridiniums.* Attempts to prepare 1,4 - diazabicyclo[2.2.2]octane and 1 - azabicyclo[2.2.1]heptane (Scheme 5) by reaction of dibenzoxanthylium trifluoromethanesulphonate (**2b**) with 4 - (amino-



Scheme 5. (See Scheme 1 for disignation of Z and Y).

ethyl)piperazine and 4 - (aminomethyl)piperidine respectively failed. The pentacyclic system with the piperidino amine was unstable—the intermediate could not be characterised. Use of the 2,4,6 - triphenylpyrylium trifluoromethanesulphonate (**1b**) gave stable intermediates (**24b**) but decomposition of the pyridiniums yielded polymeric material. It has been established recently[18] that pyridiniums with N - aminoethyl (or other 1,3 - aminoalkylpyridiniums) are unstable due to the facile formation of a three membered ring (which polymerises) and the leaving pyridine.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Perkin–Elmer R-12 spectrometer using internal Me_4Si as a standard. IR spectra were obtained on a Perkin–Elmer 297 spectrophotometer. M.ps were recorded on a hot stage apparatus and are uncorrected.

The following compounds were prepared using standard literature procedures: 2,4,6 - triphenylpyrylium BF_4^- m.p. 249–251° (lit.[4] m.p. 253–255°), $CF_3SO_3^-$ m.p. 252–254° (lit.[5] 257–259°) and ClO_4^- m.p. 286–288° (lit.[19] m.p. 290°); 5,6,8,9 - tetrahydro - 7 - phenyldibenzo[c,h]xanthylium BF_4^- m.p. 258–260° (lit.[20] m.p. 265°), $CF_3SO_3^-$ m.p. 301–303° (lit.[5] m.p. 304°).

Preparation of N - *substituted* - 2,4,6 - *triphenylpyridinium and* N - *substituted* 5,6,8,9 - *tetrahydro* - 7 - *phenyldibenzo[c,h]acridinium* BF_4^- *and* $CF_3SO_3^-$ *salts from amino - alcohols* (The pyridiniums were prepared following the previously determined general procedures.)[6]

Procedure A. To a suspension of the pyrylium (0.01 mol) in CH_2Cl_2 (75 ml) was added dropwise a mixture of the amino–alcohol (0.01 mol) and Et_3N (0.01 mol). The resulting soln was stirred for 1 hr at 20°. AcOH (10 drops) was added and the red soln stirred overnight. Dilution with ether (150 ml) yielded crystals which were filtered off, washed with water (5 ml), ether (10 ml) and dried.

Procedure B. As A above except that a gum was obtained on dilution with ether which was crystallised by stirring in ice.

Procedure C. As A above except that the product was precipitated with ether after 3 hr at 20°.

Thermolysis of hydroxy - alkyl pyridinium salts. The pyridinium salt, intimately mixed with 2,4,6 - triphenyl pyridine,[4] was heated in an oil bath *in vacuo* (15 mmHg). The distillate was collected in a trap immersed in a solid CO_2/acetone cooled Dewar flask.

Preparationof N - *substituted pyridinium and acridinium tetrafluoroborate and trifluoromethanesulphonate salts from diamines*

Procedure A. To a suspension of the pyrylium (0.01 mol) in CH_2Cl_2 (50 ml) was added dropwise a mixture of the diamine (0.01 mol) and Et_3N (0.01 mol). After stirring for 1 hr at 20° AcOH (10 drops) was added and the soln stirred for 3 hr. Dilution with ether (100 ml) yielded crystals which were filtered off, washed with water (5 ml), ether (10 ml) and dried.

Procedure B. As A above except that the reaction was carried out at 0°.

Procedure C. As A above except that absolute EtOH was used as solvent and the reaction stirred overnight.

Functionalisation of N - *substituted pyridinium alkylamines*

Procedure A. The pyridinium alkylamine (0.01 mol) in CH_2Cl_2 (100 ml) was treated dropwise with Et_3N (0.01 mol) followed by the acylating agent (0.01 mol). After stirring for 3 hrs at 20° the soln was shaken with water (2 × 20 ml), dried over Na_2SO_4 and the solvent removed *in vacuo* (15 mmHg). The resulting crystalline product was washed with ether (20 ml).

Procedure B. To a soln of the pyridinium alkylamine (0.01 mol) in $CHCl_3$ (40 ml) was added a soln of phenyl isothiocyanate (0.012 mol) in $CHCl_3$ (10 ml). After stirring for 2 hr at 20° the solvent was removed *in vacuo* (15 mmHg) and the resulting crystals triturated with ether (20 ml).

The pentacyclic pyridinium alkylbenzamide trifluoromethanesulphonates **26e**, **27e**, **31e**, **32e**, were decomposed according to the following general procedure: The benzamide (0.008 mol) in dioxan (75 ml) was refluxed for the appropriate length of time (Table 5). Any insoluble material was filtered off and the solvent removed *in vacuo* (15 mmHg). The residue was extracted with hot water (3 × 25 ml) and the combined extracts basified with solid K_2CO_3 (2.0 g). The free amine was extracted with CH_2Cl_2 (2 × 25 ml), dried over Na_2SO_4 and the solvent removed *in vacuo* (15 mmHg).

2 - *Aminophenyl* - 4,5 - *dihydro* - 1,3 - *oxazole* (**29f**). Compound **20e** (3.26 g, 0.006 mol) in dioxan (50 ml) was treated with phenyl isocyanate (0.71 g, 0.006 mol) and warmed on a water bath. After 1 hr the soln was refluxed for 7 hr, cooled, and the solvent removed *in vacuo* (15 mmHg). The residue was extracted with hot water (3 × 30 ml) and the combined aqueous extracts basified with solid K_2CO_3 (2.0 g). The free amine was extracted with CH_2Cl_2 (2 × 30 ml), dried over Na_2SO_4, and the solvent removed *in vacuo* (15 mmHg) to yield the oxazole (0.42 g, 57%).

2 - *Aminophenyl* - 4,5 - *dihydro* - 1,3 - *thiazole* (**30f**). Compound **30c** (5.9 g, 0.01 mol) was refluxed for 3 hr in abs EtOH (50 ml). After cooling to 0°, the resulting 2,4,6 - triphenypyridine was filtered off and the solvent removed *in vacuo* (15 mmHg). The thiazoline perchlorate was purified by column chromatography (silica) using EtOAc/light petroleum b.p. 60–80° (75:25) as eluant and treated with KOH (1.0 g) in CH_2Cl_2 (25 ml) to yield the 2 - aminophenylthiazole (0.9 g, 51%).

2 - *Aminophenyl* - 5,6 - *dihydro* - (4H) - 1,3 - *oxazine* (**33f**). Compound **21e** (3 g, 0.0053 mol) in dioxan (50 ml) was treated with phenyl isocyanate (0.63 g, 0.0053 mol). The procedure as for **29f** gave 2 - aminophenyl oxazine (0.75 g, 80%).

2 - *Aminophenyl* - 5,6 - *dihydro* - (4H) - 1,3 - *thiazine* $HClO_4$ (**34f**). Compound **34c** (6 g, 0.01 mol) in n - BuOH (50 ml) was refluxed for 3 hr. After cooling to 0° the ppt was filtered off and the solvent removed *in vacuo* (15 mmHg). The resultant oil was triturated with ether (3 × 10 ml) to yield the perchlorate (2.1 g, 72%).

2 - *Aminophenyl* - 5,6 - *dihydro* - (4H) - 1,3 - *thiazine* (**34f**). Compound **21e** (2.15 g, 0.004 mol) in dioxan (35 ml) was treated with phenyl isothiocyanate (0.54 g, 0.004 mol). The procedure as for **29f** gave the dihydro - 1,3 - thiazine (0.34 g, 44%).

2 - *Iminophenyl* - 4,5,6,7 - *tetrahydro* - (3H) - 1,3 - *thiazepine* (**35f**). Compound **2b** (1.04 g, 0.002 mol) in CH_2Cl_2 (35 ml) was treated with a mixture of N' - (4 - aminobutyl) - N - phenyl thiourea (0.46 g, 0.002 mol) [prepared by treating 1,4 - diaminobutane (0.005 mol) in Et_2O (25 ml) with phenyl isothiocyanate (0.005 mol) and used as crude] and Et_3N (0.002 mol). After stirring for 1 hr at 20° AcOH (5 drops) was added and stirring was continued for 1 hr. Dioxan (50 ml) was added and the CH_2Cl_2 distilled off. The soln was refluxed for 6 hr, evaporated to dryness *in vacuo* (15 mmHg) and the residue extracted with hot water (2 × 30 ml). Basification with solid K_2CO_3 (1.0 g), extraction with CH_2Cl_2 (2 × 30 ml), drying over Na_2SO_4 and removal of the solvent *in vacuo* (15 mmHg) gave the 1,3 - thiazepine (0.135 g, 33%).

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