Reactions of Five-membered Heteroaromatic Oxonium Cations with Amines

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The reactions of oxazolium, 1,3,4-oxadiazolium, 2-phenyloxazolo[3,2-*a*]pyridinium, oxathiolium, and thiazolium cations with primary amines are described. Ring-opening and reclosure to the corresponding azolium cations occur: in some cases open-chain or cyclic intermediates are isolated.

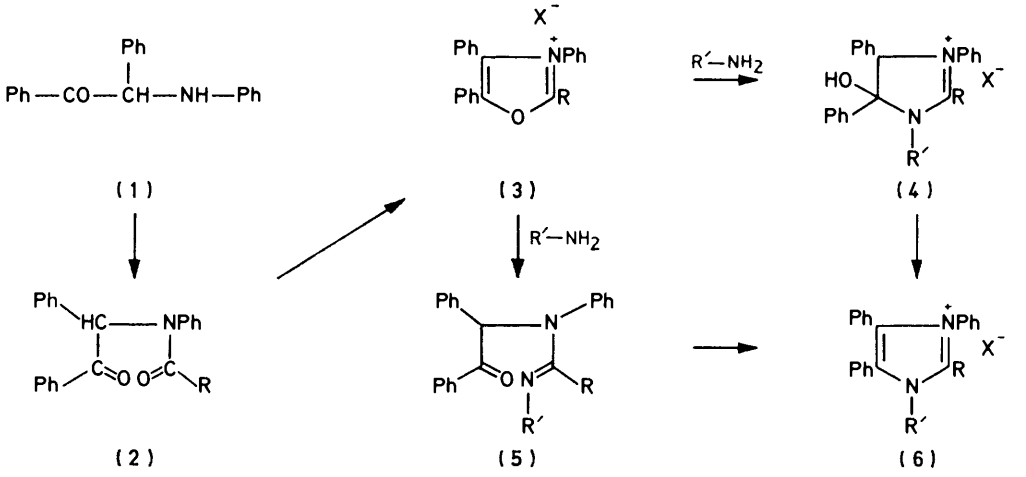
We have extensively utilised pyrylium cations to convert primary amino-groups into pyridiniums in which the pyridine ring behaves as a leaving group.[1] The present paper describes experiments in which five-membered cationic rings (mainly oxoniums) are tested for their ability to convert primary amines into azoliums. The aim was to see if the azolium ring could be used as a leaving group in place of the pyridine ring.

Oxazolium and Imidazolium Series.—Benzoin and aniline give *N*-(α-benzoylbenzyl)aniline (1) [2] which was benzoylated.[3] The *N*-benzoylaniline (2a) when digested with concentrated sulphuric acid gives, on the addition of cold water, 2,3,4,5-tetraphenyloxazolium hydrogensulphate (3a; X = HSO_4). Trifluoromethanesulphonic acid similarly yields the corresponding trifluoromethanesulphonate (3a; X = CF_3SO_3). 2,3,4,5-Tetraphenyloxazolium hydrogensulphate in water with the appropriate sodium salts gave the corresponding perchlorate and tetrafluoroborate (3a; X = ClO_4 or BF_4). 2,3,4,5-Tetraphenyloxazolium perchlorate was also obtained in good yield by treating with a cold mixture of perchloric acid and acetic anhydride either the *N*-benzoylaniline (2a) or the tetrafluoroborate from *N*-benzoylaniline (2a) and boron trifluoride–diethyl ether. The *N*-benzoylaniline (2a) upon heating with phosphorus pentoxide and the addition of potassium iodide gave 2,3,4,5-tetraphenyloxazolium iodide.

Table 1 shows the physical data of the 2,3,4,5-tetraphenyloxazolium salts prepared.

All these compounds were characterized upon the basis of spectral results. The i.r. spectra (Table 2) show characteristic bands for the 2-phenyl- and 2-α-pyridyl-3,4,5-triphenylisoxazoliums at *ca.* 1 665m and 1 600m cm^{-1} and for the 2-unsubstituted 3,4,5-triphenylisoxazoliums bands at 1 618s and 1 588s cm^{-1}. The ^1H n.m.r. spectra (Table 3) showed, as expected, only aromatic proton signals.

2,3,4,5-Tetraphenyloxazolium perchlorate was stirred in absolute ethanol with 2 mol equivalents of amine: simple primary aliphatic amines, *e.g.* ethyl- and benzylamines, needed to be stirred for only 0.25 h. For hindered amines, *e.g.* isopropyl, cyclohexyl, and α-phenylethyl, reaction was complete only after 3—4 h. Ethyl-, benzyl-, α-phenylethyl-, and n-butyl-amines gave cyclised intermediates, 3-alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazolium perchlorates (4a; X = ClO_4) which were isolated in almost quantitative yield. By contrast isopropyl- and cyclohexyl-amines gave open-chain intermediates, *N'*-alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a), in moderate yields (Scheme 1). Both types of intermediate (4a; X = ClO_4) and (5a) were reconverted into the precursor *N*-benzoyl-*N*-(α-benzoylbenzyl)aniline on attempted recrystallisation from ethanol; however both types of intermediate (4a; X = ClO_4) and (5a) were cyclised on treatment with concentrated sulphuric acid. Addition of cold water gave the required 3-alkyl-1,2,4,5-tetraphenylimidazolium perchlorates (6a; X = ClO_4) from intermediates of



SCHEME 1 a, R = Ph; b, R = 2-pyridyl; c, R = H

TABLE 1

Oxazolium salts

Anion	Yield (%)	M.p. (°C)	Solvent cryst.	Crystal form	Found (%) C	H	N	Formula	Required (%) C	H	N
2,3,4,5-Tetraphenyloxazoliums											
ClO_4	100	337 [a] (decomp.)	MeCN	Needles	68.2	4.2	3.0	$C_{27}H_{20}ClNO_5$	68.4	4.2	2.9
BF_4	100	304 (decomp.)	MeCN	Needles	70.3	4.6	3.0	$C_{27}H_{20}BF_4NO$	70.3	4.3	3.0
I	60	310—315 (decomp.)	MeCN	Needles	64.6	3.9	2.7	$C_{27}H_{20}INO$	64.6	4.0	2.8
CF_3SO_3	100	210—215	EtOH	Needles	64.2	3.9	2.8	$C_{28}H_{20}F_3NO_4S$	64.2	3.8	2.7
3,4,5-Triphenyl-2-(2-pyridyl)oxazoliums											
ClO_4	75	252—255	MeCN	Plates	65.5	3.8	5.8	$C_{26}H_{19}ClN_2O_5$	65.7	4.0	5.9
BF_4	75	261—263	AcOH	Plates	67.3	3.9	5.9	$C_{29}H_{19}BF_4N_2O$	67.5	4.1	6.0
3,4,5-Triphenyloxazolium											
ClO_4	78	238—242	MeCN	Plates	63.0	3.7	3.4	$C_{21}H_{16}ClNO_5$	63.4	4.0	3.5

[a] Lit.,[10] m.p. 337 °C (decomp.).

TABLE 2

I.r. [a] spectra of 2-substituted 3,4,5-triphenyloxazolium cation (3), 3-alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazoliums (4a), and *N'*-alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a)

2-Substituted-3,4,5-triphenyloxazolium cation (3)

Anion	R	$\nu_{max.}$/cm^{-1}
b	Ph	1 666m, 1 600m, 1 552m, 1 498s, 1 490s, 1 400s, 960m, 800m, 778s, 762s, 722s, 700
b	2-Pyridyl	1 664m, 1 655sh, 1 597w, 1 585w, 1 575w, 1 552s, 1 492s, 1 479w, 1 430w, 1 370m, 1 297m, 990w 961w, 800s
ClO_4	H	1 618s, 1 588s, 1 570m, 1 485m, 1 462w, 1 445s, 1 375m, 1 308w, 1 242m, 1 182w, 945w, 933w, 778s, 765s

3-Alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazoliums (4a)

Anion	R	$\nu_{max.}$/cm^{-1}
CF_3SO_3	Me	3 300s, 1 607m, 1 530s, 1 453s, 1 415s, 1 030s, 910s, 810s, 745s, 710s
ClO_4	Et	3 330s, 1 612m, 1 530s, 1 453s, 1 362s, 923m, 795s, 780s
ClO_4	Bu^n	3 340s, broad, 1 612m, 1 540s, broad, 1 453s, 895m, 832m
ClO_4	$PhCH_2$	3 340s, 1 610m, 1 537s, 1 450s, 1 355s, 1 270m, 1 030s, 975m, 760s, 750s, 720m
CF_3SO_3	$PhCH_2$	3 260s, 1 590m, 1 527s, 1 450s, 1 027s, 982m, 910m, 892s, 815s, 755s
ClO_4	PhCH(Me)	3 325s, 1 615w, 1 530s, 1 453s, 1 380m, 1 347s, 1 297s, 1 037s, 755s, 738s, 725s, 705s
CF_3SO_3	PhCH(Me)	3 220s, 1 609w, 1 599w, 1 550s, 1 510s, 1 452s, 1 349s, 1 030s, 896s, 798s, 765s, 755s

N'-Alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a)

R	$\nu_{max.}$/cm^{-1}
Pr^i	1 691s, 1 620s, 1 595s, 1 468s, 1 455s, 1 360m, 1 292m, 1 065m, 1 035m, 988m, 768s, 720s, 700s
cy-C_6H_{11}	1 690s, 1 630m, 1 592m, 1 530s, 1 450s, 1 325m, 1 300m, 955w, 895w, 783m, 770m, 760m, 700s

[a] Recorded as $CHBr_3$ mull: s = strong, m = medium, w = weak. [b] Identical spectra with ClO_4, BF_4, CF_3SO_3 and I anions, except for bands characteristic of the anion.

TABLE 3

N.m.r. spectra [a] (δ) of 2-substituted-3,4,5-triphenyloxazolium cations (3), 3-alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazoliums (4a), and *N*-alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a)

2-Substituted-3,4,5-triphenyloxazolium cations [b] (3)

R	Aliphatic protons	Aromatic protons
Ph		7.5—7.7 (20 H, m)
2-Pyridyl		7.5 (15 H, m) 8.5 (3 H, m) 9.3 (1 H, m)
H		7.2—7.9 (16 H, m)

3-Alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazoliums (4a)

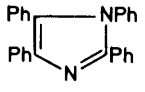
Me	3.8 (3 H, s)	7.2—7.6 (21 H, m)
Et	1.3 (3 H, t, *J* 6 Hz), 4.3 (2 H, q, *J* 8 Hz)	7.25—7.65 (21 H, m)
Bu^n	0.78—1.7 (10 H, m), 4.3 (2 H, m)	7.25—7.6 (21 H, m)
$PhCH_2$	5.5 (2 H, s)	6.9 (2 H, m), 7.25—7.5 (23 H, m)
$PhCHCH_3$	1.9 (3 H, d, *J* 7 Hz), 5.9 (1 H, q, *J* 8 Hz)	7.2—7.4 (25 H, m)
Ph		7.2—7.8 (26 H, m)

N'-Alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a)

Pr^i	1.15 (6 H, d, *J* 6 Hz), 4.05 (1 H, m) 5.82 (1 H, s)	7.0—7.7 (20 H, m)
cy-C_6H_{11}	0.75—2.0 (10 H, m), 3.2 (1 H, m), 5.95 (1 H, m)	7.18—7.8 (20 H, m)

[a] Solvent: CF_3CO_2H. [b] Identical spectra with ClO_4 and CF_3SO_3 anions.

type (4a; X = ClO_4) whereas from (5a) addition of sodium perchlorate was required to isolate the perchlorate salt (6a; X = ClO_4).



(7)

3-Alkyl-1,2,4,5-tetraphenylimidazolium perchlorates are sparingly soluble in solvents such as ethanol, acetic acid, toluene, *etc.*; to gain increased solubility 3-alkyl-1,2,4,5-tetraphenylimidazolium trifluoromethanesulphonates were prepared from the corresponding oxazolium trifluoromethanesulphonates with benzyl-, methyl-, and α-phenylethyl-amines.

Reactions of 2,3,4,5-tetraphenyloxazolium perchlorate with aniline needed to be stirred in ethanol for 48 h to yield the intermediate [*cf.* (4a)] which was then treated with sulphuric acid to give 1,2,3,4,5-pentaphenylimidazolium perchlorate [*cf.* (6a)]. The compounds (6a) and (6c) were characterized by their i.r. and ^1H n.m.r. spectra (see Supplementary publication).

Oxazolium and Imidazolium Series: 2-(2-Pyridyl) and 2-Unsubstituted Series.—(Benzoylbenzyl)aniline (1) was transformed by picolinic acid and phosphoryl chloride into *N*-(α-benzoylbenzyl)-*N*-picolinoyl-*N*-aniline (2b) which was similarly converted into the 3,4,5-triphenyl-2-(2-pyridyl)oxazolium (3b) tetrafluoroborate and perchlorate (Tables 1, 2, and 3). These salts reacted with primary amines to yield the corresponding 3-n-octyl-, 3-benzyl-, and 3-β-phenylethyl-imidazoliums (6b) (Table

TABLE 4

3-Alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazoliums (4a) and *N'*-alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a)

Anion	R	*t* (h)	Yield (%)	M.p. (°C) [a]	Found (%) C	H	N	Formula	Required (%) C	H	N
3-Alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazoliums (4a)											
ClO_4	Et	0.25	90	>300 (decomp.)	66.8	5.2	5.3	$C_{29}H_{27}ClN_2O_5$	67.1	5.2	5.4
ClO_4	Bu^n	0.25	90	>300 (decomp.)	67.8	5.7	5.0	$C_{31}H_{31}ClN_2O_5$	68.0	5.7	5.1
ClO_4	$PhCH_2$	0.25	92	>300 (decomp.)	70.5	4.9	4.8	$C_{34}H_{29}ClN_2O_5$	70.2	4.9	4.7
ClO_4	PhCH(Me)	3.0	80	>300 (decomp.)	70.7	5.0	4.6	$C_{35}H_{31}ClN_2O_5$	70.6	5.2	4.7
ClO_4	Ph	48	90	>300 (decomp.)	69.4	5.0	4.8	$C_{33}H_{27}ClN_2O_5$	69.9	4.7	4.9
CF_3SO_3	Me	0.25	95	205—207	62.7	4.5	5.0	$C_{29}H_{25}ClN_2O_5$	62.8	4.5	5.0
CF_3SO_3	$PhCH_2$	0.25	95	198—199	66.4	4.6	4.4	$C_{35}H_{29}F_3N_2O_4S$	66.6	4.6	4.4
CF_3SO_3	PhCH(Me)	0.25	90	172	67.0	4.9	4.3	$C_{36}H_{31}F_3N_2O_4S$	67.0	4.8	4.3
N'-Alkyl-*N*-(α-benzoylbenzyl)-*N*-phenylbenzamidines (5a)											
ClO_4	Pr^i	6.0	66	170	83.1	6.3	6.4	$C_{30}H_{27}N_2O$	83.3	6.4	6.4
ClO_4	cyclo-C_6H_{11}	4.0	80	155—157		*b*					

[a] As needles. [b] Insufficiently stable for analysis.

Preparative details of cyclised (4a) and open-chain (5a) intermediates are shown in Table 4. Their i.r. spectra (summarised in Table 2) show characteristic bands as follows: (i) for the cyclic 4-hydroxy-intermediates (4a) ν(OH) at *ca.* 3 300s and ν(C=N) at *ca.* 1 610m; (ii) for the acyclic intermediates (5a) ν(C=O) at 1 690s and ν(C=N) at *ca.* 1 625 cm^{-1}. The ^1H n.m.r. spectra (Table 3) for the cyclic intermediates (4a) showed merely the expected signals for the aromatic protons and the aliphatic group attached to nitrogen; however, in the spectra of the acyclic intermediates (5a), an additional 1 H signal for the hydrogen α to the oxo-group was found at *ca.* 5.9.

Preparative data for the products (6a) are given in Table 5. I.r. and ^1H n.m.r. spectra of these compounds (6a) are recorded in a Supplementary publication [SUP No. 23155 (5 pages)]; * they are essentially as expected.

Reaction of 2,3,4,5-tetraphenyloxazolium perchlorate with 2 mol equiv. of t-butylamine in ethanol gave an intermediate which absorbed at 1 614 cm^{-1}; the n.m.r. of which showed an aromatic multiplet and a signal for a t-butyl group. Upon attempted crystallisation this intermediate decomposed into *N*-benzoyl-*N*-(α-benzoylbenzyl)aniline.

* See Notice to Authors, No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

5). Intermediates (4b) and/or (5b) were found in these reactions, but were not isolated.

N-(α-Benzoylbenzyl)aniline (1) was formylated by formic acid–acetic anhydride to give *N*-(α-benzoylbenzyl)-*N*-formylaniline (2c) which was cyclised by sulphuric acid into 3,4,5-triphenyloxazolium (3c) (Tables 1, 2, and 3). With benzylamine the corresponding 1-benzylimidazolium (6c) was formed (Table 5).

1,3,4-Oxadiazoliums and 1,2,4-Triazoliums.—In contrast to its high thermal stability, the 1,3,4-oxadiazole ring is labile to reduction and to attack by nucleophiles. Recently [4] 1,3,4-oxadiazolium salts have been treated with primary amines and ammonia to yield 1,2,4-triazolium salts and 1,2,4-triazoles respectively, *via* intermediate oxadiazolines or amidrazones resulting from the attack of amine at C-2 of the oxadiazolium ring.

Treatment of *NN'*-dibenzoylphenylhydrazine with acetic anhydride and perchloric acid gave 2,3,5-triphenyl-1,3,4-oxadiazolium perchlorate (8) in a quantitative yield.[4] Perchlorate (8) reacted with isopropyl- and α-phenylethyl-amines (2 mol equiv.) in ethanol to give intermediates assigned the open-chain structure (9) on the basis of i.r. evidence which were cyclised by triethylamine to the expected 4-alkyl-1,3,5-triphenyl-1,2,4-triazolium perchlorates (10) in moderate yields. In the

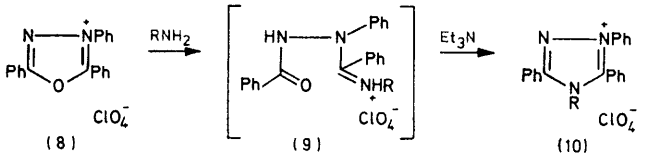
TABLE 5

2-Substituted-3-alkyl-1,4,5-triphenylimidazolium salts (6)

Anion	R′	Yield (%)	M.p. (°C) [a]	Solvent for cryst.	Found (%) C	H	N	Formula	Required (%) C	H	N
3-Alkyl-1,2,4,5-tetraphenylimidazolium salts (6a)											
ClO_4	Me	25 [b]	>340	EtOH	68.7	4.8	5.5	$C_{28}H_{23}ClN_2O_4$	69.0	4.7	5.7
ClO_4	Et	60	>340	EtOH	69.4	4.9	5.6	$C_{29}H_{25}ClN_2O_4$	69.5	4.9	5.6
ClO_4	Bu^n	60	>340	EtOH	70.2	5.5	5.2	$C_{31}H_{29}ClN_2O_4$	70.4	5.5	5.3
ClO_4	Pr^i	20	319	EtOH	69.9	5.0	5.3	$C_{30}H_{27}ClN_2O_4$	69.9	5.2	5.4
ClO_4	cy-C_6H_{11}	50	328 (decomp.)	EtOH			4.9	$C_{33}H_{30}ClN_2O_4$			5.0
ClO_4	$PhCH_2$	85	320—321	EtOH	72.4	4.7	4.9	$C_{34}H_{27}ClN_2O_4$	72.5	4.8	4.9
ClO_4	PhCH(Me)	50	246—247	EtOH	72.7	5.0	4.8	$C_{35}H_{29}ClN_2O_4$	72.8	5.0	4.8
ClO_4	Ph	75	340	MeCN–EtOH	71.7	4.6	5.0	$C_{33}H_{25}ClN_2O_4$	72.2	4.5	5.1
CF_3SO_3	Me	80	263—264	Pr^iOH	64.9	4.2	5.1	$C_{29}H_{23}F_3N_2O_3S$	64.9	4.3	5.2
CF_3SO_3	$PhCH_2$	85	270—272	Pr^iOH	68.3	4.7	4.5	$C_{35}H_{27}F_3N_2O_3S$	68.6	4.4	4.5
CF_3SO_3	PhCH(Me)	50	211	Pr^iOH	68.7	4.5	4.4	$C_{36}H_{29}F_3N_2O_3S$	69.0	4.6	4.5
3-Alkyl-1,4,5-triphenyl-2-(2-pyridyl)imidazolium salts (6b)											
ClO_4	$PhCH_2$	57	270—272	Pr^iOH	69.8	4.5	7.3	$C_{33}H_{26}ClN_3O_4$	70.2	4.6	7.4
BF_4	$PhCH_2CH_2$	50	268—272	AcOEt–Pr^iOH	71.8	4.9	7.3	$C_{34}H_{28}BF_4N_3$	72.2	4.9	7.4
ClO_4	n-Octyl	40	196—197	Pr^iOH–petroleum (60—80 °C)	69.7	6.1	7.1	$C_{34}H_{36}ClN_3O_4$	71.2	6.3	7.3
3-Alkyl-1,4,5-triphenylimidazolium salts (6c)											
ClO_4	$PhCH_2$	40	207—212	Pr^iOH	69.2	4.7	5.5	$C_{28}H_{23}ClN_3O_4$	69.0	4.7	5.7

[a] As needles. [b] Prepared from 2,3,4,5-tetraphenylthiazolium perchlorate, see text.

case of benzylamine, the reaction proceeded directly to product and no intermediate was isolated. Similar behaviour has previously been reported.[4] Preparative data for the 4-alkyl-1,3,5-triphenyl-1,2,4-triazolium perchlorates (10) are collected in Table 6. Compounds 10 were characterized by their i.r. and ^1H n.m.r. data (Supplementary data).



2-Phenyloxazolo[3,2-a]pyridinium Perchlorate and its Reactions with Amines.—Oxazolo[3,2-*a*]pyridinium salts (12) are intermediates when 2-bromo-1-phenacylpyridinium salts (11) are treated with aliphatic or aromatic amines:[5] the reaction of 2-bromo-1-phenacylpyridinium bromide with n-butylamine proceeds *via* an intermediate 1-butyl-2,3-dihydro-2-hydroxy-2-phenylimidazo[1,2-*a*]-pyridinium bromide (13) which is then dehydrated with polyphosphoric acid into 1-butyl-2-phenylimidazo[1,2-*a*]-pyridinium bromide (14). 1-Substituted imidazo[1,2-*a*]-pyridinium salts have also been obtained by the direct cyclisation of suitable precursors.[6]

Phenacyl bromide and 2-pyridone gave 1-phenacyl-2-pyridone (15) (80%) cyclised by concentrated sulphuric acid into 2-phenyloxazolo[3,2-*a*]pyridinium (12) which was isolated as the perchlorate (75%).[6a] 2-Phenyl-oxazolo[3,2-*a*]pyridinium perchlorate reacted with n-butylamine to give 1-n-butyl-2,3-dihydro-2-hydroxy-2-phenylimidazo[1,2-*a*]pyridinium perchlorate (13) (*cf.* ref. 5), which on refluxing with acetic anhydride for 0.5 h gave 1-n-butyl-2-phenylimidazo[1,2-*a*]pyridinium perchlorate (75%).

The same procedure for the reactions of 2-phenyl-oxazolo[3,2-*a*]pyridinium perchlorate with methyl- and benzyl-amines gave 1-methyl- and 1-benzyl-2-phenyl-imidazo[1,2-*a*]pyridinium perchlorates (75—80%). The intermediate 2,3-dihydro-2-hydroxy-1-methyl-2-phenyl-imidazo[1,2-*a*]pyridinium perchlorate [*cf.* (13)] was isolated crystalline. Corresponding reactions with iso-propyl and α-phenylethyl amines gave an identical product whose structure could not be ascertained.

Table 7 shows the yields, melting points, and elemental analyses of the products (1-alkyl-2-phenylimidazo[1,2-*a*]pyridinium perchlorates). Their spectral characterisations are part of the Supplementary publication.

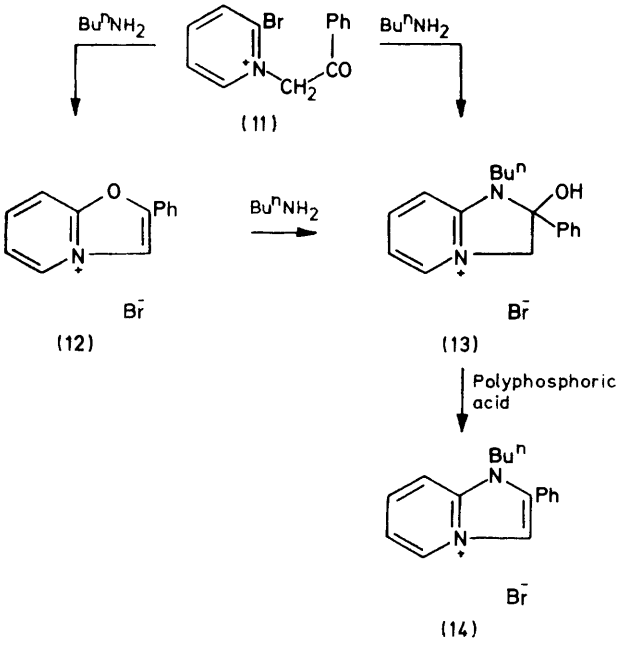
2,5-Diphenyl-1,3-oxathiolium Perchlorate and Attempted Reaction with Benzylamine.—2,5-Diphenyl-1,3-oxathio-

TABLE 6

4-Alkyl-1,3,5-triphenyl-1,2,4-triazolium perchlorates

R	Yield (%)	M.p. (°C) [a]	Solvent for cryst.	Found (%) C	H	N	Formula	Required (%) C	H	N
$PhCH_2$	60	199—200 [b]	HOAc							
Pr^i	42	249—250	HOAc	63.0	5.0	9.5	$C_{27}H_{22}ClN_3O_4$	62.8	5.0	9.5
PhCH(Me)	10	149—151	Pr^iOH	66.9	4.8	8.3	$C_{28}H_{24}ClN_3O_4$	67.0	4.8	8.4

[a] As needles. [b] Lit.,[4] m.p. 199—200 °C.



lium perchlorate (16) [7] failed to react smoothly with benzylamine in different solvents.

Although several reports describe reactions of carbon nucleophiles with 2,5-diphenyl-1,3-oxathiolium,[7,8] nothing has appeared on their reaction with amines.

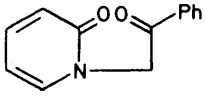
TABLE 7

1-Alkyl-2-phenylimidazo[1,2-*a*]pyridinium perchlorates [a]

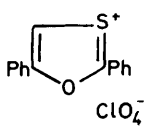
R	Yield (%)	M.p. (°C)	Lit., m.p. (°C)
Me	85	180—184	*b*
Bu^n	75	96—98	93—96 [c]
PhCH$_2$	55	133	132—134 [d]

[a] All compounds crystallised from MeOH–EtOAc as needles. [b] Found: C, 54.5; H, 4.2; N, 9.0. $C_{14}H_{13}ClN_2O_4$ requires C, 54.4; H, 4.2; N, 9.0%. [c] Ref. 5. [d] Ref. 6*b*.

2,3,4,5-*Tetraphenylthiazolium Perchlorate and its Reactions with Amines*.—*N*-(α-Benzoylbenzyl)-*N*-benzoylaniline (2) and phosphorus pentasulphide gave 2,3,4,5-tetraphenylthiazolium isolated as the perchlorate (17) (80%), which reacted with amines in ethanol to give 3-alkyl-1,2,4,5-tetraphenylimidazolium perchlorates.



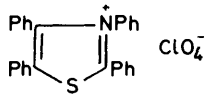
(15)



(16)

Hence, in contrast to the corresponding oxazoliums, the reaction of 2,3,4,5-tetraphenylthiazolium perchlorate with amines leads directly to the imidazolium: however, yields are low.

Attempted Nucleophilic Displacements.—Numerous attempts to carry out nucleophilic displacement reactions which would result in the transfer of an *N*-substituent from a 3-alkyl-1,2,4,5-tetraphenylimidazolium, a 4-alkyl-1,3,5-triphenyl-1,2,4-triazolium, or a 1-alkyl-2-phenylimidazo[1,2-*a*]pyridinium ring mainly failed. Although 3-benzyl-1,2,4,5-tetraphenylimidazolium triflate was debenzylated by piperidine, the reaction required a period of 6 h under reflux in an excess of piperidine to reach completion. Reactions with thiourea required high temperatures and led to decomposition.



(17)

Preliminary kinetic measurements were carried out, but the reactions were too slow to be followed satisfactorily at 100 °C, and attempts to obtain rates at higher temperatures led to considerable loss in accuracy. However, it is clear that all these five-ring heterocyclic leaving groups are far less active than triphenylpyridine. The reason for this is probably the lower degree of steric acceleration caused by the larger angles between the *N*-substituent and the adjacent phenyl groups in the five-membered as contrasted with the six-membered rings.

EXPERIMENTAL

N-(α-Benzoylbenzyl)aniline (1) 65%, m.p. 97—98 °C (lit.,[2] m.p. 97—98 °C), *N*-benzoyl-*N*-(α-benzoylbenzyl)-aniline (2a) 65%, m.p. 149 °C (lit.,[3] m.p. 149 °C), *N*-(α-benzoylbenzyl)-*N*-formyl-aniline (2c) 80%, m.p. 105 °C (lit.,[3] m.p. 105 °C), 2,4,5-triphenyl-1,3,4-oxadiazolium perchlorate (8) 100%, m.p. 276 °C (lit.,[9] m.p. 278 °C), 2-phenyloxazolo[3,2-*a*]pyridinium perchlorate (12) 72%, m.p. 216—218 °C (lit.,[6a] m.p. 218—222.5 °C), and 2,5-diphenyl-1,3-oxathiolium perchlorate (16) 50%, m.p. 229—231 °C (lit.,[7] m.p. 228—230 °C) were prepared.

N-(α-*Benzoylbenzyl*)-N-*picolinoylaniline* (2b).—*N*-(α-Benzoylbenzyl)aniline (1.0 g, 3.4 mmol) was stirred in dry toluene (20 ml) and picolinic acid (0.42 g, 3.5 mmol) and Et_3N (3.0 ml) were added. After 10 min $POCl_3$ (0.54 g, 3.5 mmol) was added and the solution stirred for 4 h. N-(α-*Benzoylbenzyl*)-N-*picolinoylaniline* separated out; it crystallised from isopropyl alcohol (1.22 g, 90%) as needles, m.p. 177 °C (Found: C, 79.2; H, 5.0; N, 7.0. $C_{26}H_{20}N_2O_2$ requires C, 79.6; H, 5.1; N, 7.1%).

2-*Substituted* 3,4,5-*Triphenyloxazolium Salts* (3).—*N*-(α-Benzoylbenzyl)aniline (2) (2.5 mmol) was kept with concentrated H_2SO_4 (1.0 ml) for 15 min. Addition of water (100 ml) followed by $NaClO_4$ (0.4 g) gave 2-*substituted* 3,4,5-*triphenyloxazolium perchlorate*. The corresponding tetrafluoroborate salt was also obtained in the same way (see Table 1).

N-Benzoyl-*N*-(α-benzoylbenzyl)aniline (2a) (1.0 g, 2.5 mmol) was kept with trifluoromethanesulphonic acid (1.0 ml). Addition of water (100 ml) gave 2,3,4,5-*tetraphenyloxazolium trifluoromethanesulphonate* (see Table 1).

N-Benzoyl-*N*-(α-benzoylbenzyl)aniline (2a) (0.5 g, 1.3 mmol) and P_2O_5 (0.18 g, 1.3 mmol) were heated at 180—200 °C for 2 h. Addition of KI (0.5 g) in water (100 ml) gave 2,3,4,5-*tetraphenyloxazolium iodide* (see Table 1).

3-*Alkyl*-4,5-*dihydro*-4-*hydroxy*-1,2,4,5-*tetraphenylimidazo*-

liums (4a).—The appropriate amine (2 mmol) was added dropwise to a stirred suspension of 2,3,4,5-tetraphenyloxazolium salts (3a) (1 mmol) in absolute EtOH (25 ml) at 20 °C. The mixture was stirred from 0.25—48 h depending upon the amine. The product was filtered off (see Table 4).

N'-Alkyl-N-(α-benzoylbenzyl)-N-phenylbenzamidines (5a).—Isopropyl- or cyclohexyl-amine (2 mmol) was added dropwise to a stirred suspension of 2,3,4,5-tetraphenyloxazolium perchlorate (3a; X = ClO_4) (0.5 g, 1 mmol) in absolute EtOH (25 ml) at 20 °C. The mixture was stirred for 4—6 h and then filtered to get the title compound (see Table 4).

3-Alkyl-1,2,4,5-tetraphenylimidazolium Salts (6a).—3-Alkyl-4,5-dihydro-4-hydroxy-1,2,4,5-tetraphenylimidazolium perchlorate or trifluoromethanesulphonate (4a) (0.9 mmol) were mixed with concentrated H_2SO_4 (0.5 ml). Addition of water (50 ml) gave the product (see Table 5).

Each *N'*-alkyl-*N*-(α-benzoylbenzyl)*N*-phenylbenzamidine (5a) (1 mmol) was dissolved in concentrated H_2SO_4 (0.5 ml). Addition of $NaClO_4$ (0.15 g) in water (50 ml) gave the perchlorate (see Table 5).

1,2,4,5-Tetraphenylimidazole (7).—3-Benzyl-1,2,4,5-tetraphenylimidazolium trifluoromethanesulphonate (6a; R = CH_2Ph) (0.6 g, 1 mmol) was refluxed with piperidine (10 ml) for 6 h. Evaporation of the solvent gave the product which crystallised from isopropyl alcohol (60%) as square planar crystals, m.p. 217—218 °C (lit.,[10] m.p. 217—218 °C).

3-Alkyl-1,4,5-triphenyl-2-(2-pyridyl)imidazolium Salts (6b).—The appropriate amine (2 mmol) was added dropwise to a stirred suspension of 3,4,5-triphenyl-2-pyridyloxazolium salts (3b) (1 mmol) in absolute EtOH at 20 °C. The mixture was stirred for 4 h and filtered to get the intermediate [for octylamine, evaporation gave a gum which crystallised from light petroleum (b.p. 60—80 °C)]. The intermediate was treated with concentrated H_2SO_4 (0.5 ml). Addition of water (50 ml) gave the title compound (see Table 5).

3-Benzyl-1,4,5-triphenylimidazolium Perchlorate (6c).—Benzylamine (0.28 g, 2.5 mmol) was added dropwise to a stirred suspension of 3,4,5-triphenyloxazolium perchlorate (0.56 g, 1.4 mmol) in absolute EtOH at 20 °C. The solution was stirred for 2 h and then evaporated. The resulting gum was warmed with concentrated H_2SO_4 for 15 min. Addition of cold water gave the product which was recrystallised from isopropyl alcohol (see Table 5).

4-Alkyl-1,3,5-triphenyl-1,2,4-triazolium Perchlorates (10).—2,3,5-Triphenyl-1,3,4-oxadiazolium perchlorate (8) (0.5 g, 1 mmol) was suspended in EtOH (20 ml) and the appropriate amine (2 mmol) added dropwise. The mixture was stirred for 3 h, evaporated, and the residue triturated with light petroleum (b.p. 60—80 °C). The intermediate was suspended in EtOH (20 ml), Et_3N (2 ml) was added, and stirring continued for 4 h at 20 °C. Evaporation gave the product which crystallised from isopropyl alcohol (see Table 6).

1-Alkyl-2-phenylimidazo[1,2-a]*pyridinium Perchlorates* [cf. (14)].—2-Phenyloxazolo[3,2-*a*]pyridinium perchlorate (12) (0.5 g, 1.6 mmol) was refluxed with the appropriate amines (3.2 mmol) in EtOH (30 ml) for 4 h. Evaporation gave a gum which was refluxed in Ac_2O (10 ml) for 0.5 h. Evaporation of the Ac_2O and addition of CH_2Cl_2 gave the product which crystallised from MeOH–EtOAc (see Table 7).

2,3-Dihydro-2-hydroxy-1-methyl-2-phenylimidazo[1,2-a]*pyridinium Perchlorate*.—2-Phenyloxazolo[3,2-*a*]pyridinium perchlorate (12) (0.5 g, 1.6 mmol) was refluxed with $MeNH_2$ (0.1 g, 3.2 mmol) in EtOH (30 ml) for 4 h. Evaporation gave the product (0.45 g, 82%) which crystallised from MeOH–EtOAc as prisms, m.p. 157—160 °C (Found: C, 51.6; H, 4.7; N, 8.5. $C_{14}H_{15}ClN_2O_5$ requires C, 51.4; H, 4.6; N, 8.6%).

2,3,4,5-Tetraphenylthiazolium Perchlorate (17).—*N*-Benzoyl-*N*-(α-benzoylbenzyl)aniline (2a) (0.5 g, 1.3 mmol) was heated with P_2S_5 (0.3 g, 1.3 mmol) for 2 h at 100—125 °C. The product was dissolved in hot EtOAc and 70% $HClO_4$ (3 ml) added to give the *perchlorate* which crystallised from HOAc–MeCN as square planar crystals (1.0 g, 80%), m.p. 329—331 °C (Found: C, 66.2; H, 4.0; N, 2.7; S, 6.1. $C_{27}H_{20}ClNO_4S$ requires C, 66.2; H, 4.0; N, 2.8; S, 6.5%).

Reaction of 2,3,4,5-Tetraphenylthiazolium Perchlorate (17) *with Amines*.—2,3,4,5-Tetraphenylthiazolium perchlorate (0.5 g, 1 mmol) was suspended in EtOH (20 ml) and amine (2 mmol) added dropwise. The solution was refluxed for 4 h and then evaporated to get the products: 3-methyl- (see Table 5); 3-ethyl-, m.p. >340 °C (Found: C, 69.4; H, 4.8; N, 5.4. $C_{29}H_{25}ClN_2O_4$ requires C, 69.5; H, 4.9; N, 5.6%); and 3-n-butyl-1,2,4,5-tetraphenylimidazolium m.p. >340 °C (Found: C, 70.2; H, 5.5; N, 5.2. $C_{31}H_{29}ClN_2O_4$ requires C, 70.4; H, 5.5; N, 5.3%) perchlorates. The last two compounds had i.r. spectra identical with the products described in Table 5.

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