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REACTIONS OF PYRYLIUM SALTS WITH NUCLEOPHILES—V

REACTION OF 2,4,6-TRIMETHYLPYRYLIUM PERCHLORATE WITH PRIMARY AMINES

C. TOMA and A. T. BALABAN*
Institute of Organic Chemistry and Institute of Atomic Physics
P.O. Box 35, Bucharest, Roumania

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Abstract—N-Aryl-2,4,6-trimethylpyrydinium salts were prepared from 2,4,6-trimethylpyrylium perchlorate and $ArNH_2$, the aryl group being *p*-chloro-, bromo, iodo, methyl-, hydoxy- or amino-phenyl. The reaction of 2,4,6-trimethylpyrylium perchlorate with primary aliphatic amines (methyl, ethyl, n-propyl, n-butyl, isopentyl, benzyl, cyclohexyl, n-heptyl and n-octadecyl) was found to afford along with N-alkylpyridinium salts, N-alkyl-3,5-xylidines. Such cyclizations to an aniline derivative were known only in the reactions of pyrylium salts with secondary amines. A third kind of product is formed in very small yield with aromatic amines, in larger yield with higher aliphatic amines and as the only product with t-butyl amine; it is possibly an imino-enol. IR and NMR spectra are discussed and assignments of bands are made on the basis of deuteration of amino and methyl groups. In N-aryl-2,4,6-trimethylpyridinium salts the upfield shift of the α-methyl NMR signal implies non-coplanarity of the pyridinium and phenyl rings.

INTRODUCTION

THE reaction of pyrylium salts (I) with ammonia and primary amines RNH_2, leading to pyridines and pyridinium salts (II) respectively, discovered by Baeyer and Piccard,[1,2] affords a convenient method for the synthesis of 2,4,6-trisubstituted derivatives. While the reaction with ammonia has been extensively applied for preparative purposes (cf. reviews[3,4]), the reaction with amines has been less investigated. It was mainly applied by Dilthey[5,6] and by Wizinger *et al.*[7,8] for the synthesis of coloured pyridinium derivatives starting from triarylpyrylium salts and aliphatic or aromatic primary amines. Diels and Alder have found[9] that secondary amines react with pyrylium salts possessing an α-standing methyl group ($R''' = CH_3$) with ring closure to a benzene

* To whom correspondence should be addressed.

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3 K. Dimroth, *Angew. Chem.* **72**, 331 (1960).

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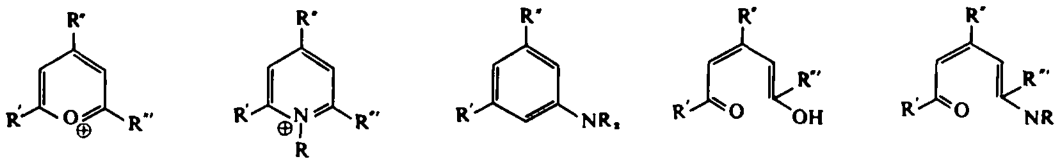
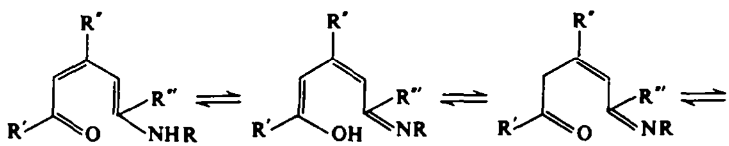
8 A. Bellefontaine, *Dissertation.* Bonn (1935).

9 O. Diels and K. Adler, *Ber. Dtsch. Chem. Ges.* **60**, 716 (1927).

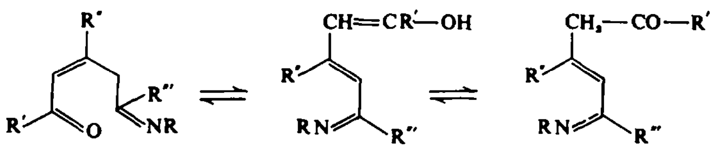
(aniline) derivative (III). Studies by Lombard *et al.*[10,11] have shown that (i) 2,4,6-triarylpyrylium salts react with an excess of tertiary amines (and also with primary or secondary amines in equimolar amounts) leading to 1,5-enediones (pseudobases) IV, that (ii) excess of secondary amines (R_2NH) leads to red N,N-dialkyl-keto-dien-amines (V) and that (iii) excess of primary amines gives pyridinium salt (II); in the case of cyclohexylamine, an N-alkyl-keto-dien-aminic intermediate (VI) could be isolated, which on standing in the reaction medium is dehydrated to the pyridinium salt (II).[11] The interesting solvatochromic 2,4,5-triphenylpyridinium betaines obtained with *p*-aminophenol[12] also deserve mention.



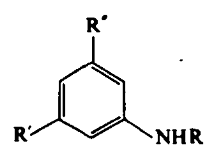
I II III IV V



VI VI' VI''



VI''' VI^{IV} VI^{V}



VII

R′ = R″ = R‴ = CH_3; R = C_6H_5 (a), p-$H_3CC_6H_4$ (b), p-ClC_6H_4 (c), p-BrC_6H_4 (d), p-IC_6H_4 (e), o-HOC_6H_4 (f), p-HOC_6H_4 (g), p-$H_2NC_6H_4$ (h), $PhCH_2$ (i), CH_3 (j), C_2H_5 (k), n-C_3H_7 (l), n-C_4H_9 (m), i-C_5H_{11} (n), cyclo-C_6H_{11} (o), n-C_7H_{15} (p), n-$C_{18}H_{37}$ (q)

[10] R. Lombard and J. P. Stephan, *Bull. Soc. chim. Fr.* 1458 (1958).

[11] R. Lombard and A. Kress, *Bull. Soc. chim. Fr.* 1528 (1960).

[12] K. Dimroth, C. Reichardt, T. Siepmann and F. B. Bohlmann, *Liebigs Ann.* **661**, 1 (1963).

TABLE 1. N-ARYL-2,4,6-TRIMETHYLPYRIDINIUM SALTS II ($R' = R'' = R''' = CH_3$) (Found/Calc.)

Structure		Yield	Perchlorate						Picrate				
II	R		M.p.°C	Formula	C	H	Hal	N	M.p.°C	Formula	C	H	N
a	C_6H_5	95–98%	128–129	$C_{14}H_{16}ClNO_4$	56·42 56·47	5·44 5·42	11·38 11·91	4·92 4·70	122–124	$C_{20}H_{18}N_4O_7$	56·87 56·34	4·26 4·25	13·67 13·14
b	p-$CH_3C_6H_4$	92–95%	146–147*	$C_{15}H_{18}ClNO_4$	58·09 57·79	6·08 5·82	—	4·74 4·49	108–109	$C_{21}H_{20}N_4O_7$	57·64 57·27	4·69 4·58	12·90 12·72
c	p-ClC_6H_4	90–93%	140–141	$C_{14}H_{15}Cl_2NO_4$	50·73 50·62	5·11 4·55	21·36 21·35	4·22 4·22	122–123	$C_{20}H_{17}ClNO_4O_7$	52·29 52·12	4·03 3·72	12·37 12·16
d	p-BrC_6H_4	85–90%	177–178	$C_{14}H_{15}BrClNO_4$	44·60 44·64	4·02 4·01	30·06 30·62	3·64 3·72	145–146	$C_{20}H_{17}BrN_4O_7$	47·85 47·54	3·37 3·39	11·26 11·09
e	p-IC_6H_4	90–95%	207–208	$C_{14}H_{15}ClINO_4$	39·70 39·69	3·31 3·56	36·36 38·32	3·52 3·31	161–162	$C_{20}H_{17}IN_4O_7$	43·83 43·49	3·32 3·10	10·48 10·15
f	o-HOC_6H_4	78–80%	151–152	$C_{14}H_{16}ClNO_4$	53·48 53·60	5·04 5·14	11·29 11·30	4·49 4·46	185–187	$C_{20}H_{18}N_4O_8$	54·39 54·30	4·35 4·10	12·56 12·67
g	p-HOC_6H_4	80–85%	149–150	$C_{14}H_{16}ClNO_5$	53·37 53·60	5·49 5·14	10·40 11·30	4·48 4·46	152–153	$C_{20}H_{18}N_4O_8$	54·17 54·30	4·35 4·10	12·73 12·67
h	p-$H_2NC_6H_4$	85–90%	179–180	$C_{14}H_{17}ClN_2O_4$	53·51 53·76	5·44 5·48	— —	9·05 8·95	175–176	$C_{20}H_{19}N_5O_7$	54·52 54·42	4·50 4·34	15·94 15·87

The present paper reports the reaction between 2,4,6-trimethylpyrylium perchlorate and primary amines. Only two primary amines have previously been reported to react with this cation, namely *p*-toluidine[1] and methylamine,[1,2] affording pyridinium salts. It was hoped that the reaction of the easily accessible[13] 2,4,6-trimethylpyrylium perchlorate with amines may discriminate between primary, secondary or tertiary amines and at the same time may afford crystalline derivatives of primary amines, i.e. salts II. Taking into account that the nitrogen atom in amines is an electron donor while in the pyridinium ring it has a positive charge, it can be expected that the conversion of an amine into a pyridinium salt should exert definite effects on the chemical reactivity of substituents, or on the spectra of this amine. Finally, pyridinium salts may be interesting as cationic surface active agents, or as intermediates in various syntheses.[14,15]

Reaction of 2,4,6-*trimethylpyrylium perchlorate with primary aromatic amines*

(a) *N-Arylcollidinium salts* (II, R′ = R″ = R‴ = Me, R = Ar). Primary aromatic amines react in refluxing ether, methanol or water with 2,4,6-trimethylpyrylium perchlorate giving a yield of 85–95% of pyridinium perchlorates (II, R = Ar), which may be converted into picrates, picrolonates or hexachloroplatinates. M.ps and analyses of these pyridinium salts IIa–IIh are given in Table 1. Such N-aryl pyridinium salts are obtained with difficulty by direct quaternization of pyridines.

The IR spectra of these compounds all present in the range 1650–1375 cm^{-1} three strong and medium bands at 1642–1645, 1565–1573 and 1435–1444 cm^{-1} which can be ascribed to the 8a, 8b and 19b vibration modes* of the pyridinium ring, respectively, in agreement with the discussions of vibrational spectra of pyridinium ions.[18–22] The intensity of the 1642–1645 cm^{-1} band is the highest: it is usually the second intense band in the spectrum, after the broad strongest band at 1095 cm^{-1} due to the perchloric anion, the third intense band being usually at 623 cm^{-1} also due to the $ClO_4^{\ominus}$ anion. Bands of the perchlorate anion at 458 and 930 cm^{-1} are weak. The band at 1376–1385 cm^{-1} is due to the symmetrical bending of the methyl hydrogens as shown by its disappearance in the spectrum of N-phenyl- and N-ethyl-2,4,6-tri-d_3-methylpyrydinium perchlorate prepared from 2,4,6-tri-d_3-methylpyrylium perchlorate (I, R′ = R″ = R‴ = CD_3)[21,23] and aniline or ethylamine, respectively. The asymmetrical bending vibration must be one of the two bands at 1477–1484 and 1409–1418 cm^{-1} which disappear in the deuterated compounds. We consider the band at 1477–1484 cm^{-1}, present in all compounds under investigation, as the most likely

* Notations, Refs[16,17].

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[23] A. T. Balaban, E. Gârd and C. N. Renţea, *Abh. Dtsch. Akad. d. Wiss., Klasse Chem., Geol. u. Biol.* 659 (1964).

Structure		Picrolonate					Chloroplatinate						
II	R	M.p.°C	Formula	C	H	N	M.p.°C	Formula	C	H	Hal	N	Pt
a	C_6H_5	229–230[b]	$C_{24}H_{23}N_5O_5$	62·68 62·46	5·20 5·02	15·32 15·18	>290	$C_{28}H_{32}Cl_6N_2Pt$	42·02 41·80	4·25 4·01	26·47 26·44	3·32 3·48	24·65 24·27
b	*p*-$CH_3C_6H_4$	208–209	$C_{25}H_{25}N_5O_5$	63·16 63·15	5·49 5·30	14·80 14·73	207–209	$C_{30}H_{36}Cl_6N_2Pt$	43·82 43·28	4·65 4·36	25·30 25·55	3·68 3·36	22·50 23·45
c	*p*-ClC_6H_4	250–251[b]	$C_{24}H_{22}ClN_5O_5$	58·38 58·00	4·64 4·67	14·77 14·10	244–245[b]	$C_{28}H_{30}Cl_8N_2Pt$	38·43 38·50	3·92 3·46	— —	3·97 3·21	21·00 22·35
d	*p*-BrC_6H_4	246–247[b]	$C_{24}H_{22}BrN_5O_5$	53·48 53·25	4·54 4·29	13·04 12·94	232–233[b]	$C_{28}H_{30}Br_2Cl_6N_2Pt$	35·53 34·96	3·66 3·15	— —	3·61 2·91	19·74 20·28
e	*p*-IC_6H_4	235–236	$C_{24}H_{22}IN_5O_5$	49·05 49·00	3·81 3·94	12·00 11·91	219–220[b]	$C_{28}H_{30}I_2Cl_6N_2Pt$	32·40 31·84	2·99 2·86	— —	2·95 2·65	18·25 18·48
f	*o*-HOC_6H_4	195–196	$C_{24}H_{24}N_5O_6$	60·25 60·24	5·05 5·05	14·78 14·64	284–285[b]	$C_{28}H_{32}Cl_6N_2O_2Pt$	40·28 40·20	3·91 3·86	25·44 25·43	3·22 3·35	23·02 23·34
g	*p*-HOC_6H_4	136–138	$C_{24}H_{24}N_5O_5$	60·09 60·24	5·28 5·05	14·80 14·64	214–215	$C_{28}H_{32}Cl_6N_2O_2Pt$	40·28 40·20	3·72 3·86	25·40 25·43	3·51 3·35	23·45 23·34
h	*p*-$H_2NC_6H_4$												

[a] Lit. m.p. = 141–142°
[b] Decomposition

assignment for this vibration mode, though this frequency is higher than the usual location (1460 cm^{-1})[24] of the symmetrical methyl bending vibration. This assignment calls for a revision of the previously proposed[21] assignment for the asymmetrical methyl bending vibration in 2,4,6-trimethylpyrylium perchlorate as the 1440 cm^{-1} band (which disappears on deuteration) and indicates as more likely bands for $\delta_{as}(CH_3)$ in the non-deuterated salt, the two bands at 1465 and 1502 cm^{-1} which also disappear on deuteration, being replaced by a band at 1480 cm^{-1}.[21] Table 2 contains the bands in this region with the above assignments.

Attempts to prepare N-*p*-hydroxyphenyl-2,4,6-trimethylpyridinium perchlorate by hydrolysis of N-*p*-halophenyl-2,4,6-trimethylpyridinium perchlorates were unsuccessful. Heating in sealed tube with water at 200° left the N-chlorophenyl-collidinium salt unchanged; with aqueous sodium hydroxide in the same conditions, the pyridinium ring is cleaved with formation of *p*-chloroaniline and 3,5-xylenol.

Potentiometric titrations showed that pK_a values of *ortho*- and *para*-hydroxyphenyl-2,4,6-trimethylpyrydinium perchlorates are 6·77 and 9·22, respectively. The much higher acidity of the *ortho*-hydroxyphenyl derivative is due to the inductive effect of the positive nitrogen heteroatom.

(b) *Tautomeric* N-*aryl-keto-dien-amines.* As a by-product formed in less than 0·5% yield in the reaction of I(R′ = R″ = R‴ = CH_3) with 2 moles aniline, an ether-soluble red oil could be extracted from the alkaline aqueous solution. If the reaction of I(R′ = R″ = R‴ = CH_3) with aniline is effected at 0° in ethanol, followed by the addition of excess sodium hydroxide, and heating under reflux, then the yield of pyridinium salt is depressed and a sizeable yield (ca. 6%) of the red oil is formed. The IR spectrum of this product presents in CCl_4 solution OH stretching bands at 3620 (free OH) and at 3480 and 3400 cm^{-1} (hydrogen-bonded OH), and strong bands at 1153, 1288 and 1320 cm^{-1} (OH bending and C—O stretching vibrations). The CH stretching vibrations appear at 3033 (unsaturated and aromatic hydrogens), 2860, 2928 and 2980 cm^{-1} (methyl hydrogens). Weak or medium bands are present at 2740, 1705 and 1645 cm^{-1} and strong or very strong bands at 1625, 1600 and 1500 cm^{-1} (skeletal phenyl vibrations). This product could possibly be a mixture of *cis* (VI–VI^{III}) and *trans* (VI^{IV}–VI^{V}) tautomers (R = Ph). The NMR spectrum of this product (in CCl_4 solution) is complex with two weak doublets at τ 8·86, 8·67 and τ 6·75, 6·60, a strong peak at τ 7·89 (methyl groups) and weaker peaks at τ 7·66 and 3·75.

Reaction of 2,4,6-*trimethylpyrylium perchlorate with aliphatic amines*

These reagents give three kinds of products: one is the expected pyridinium salt (II, R = Alk) in agreement with literature data,[1,2] the second is an N-alkyl-3,5-xylidine (VII) and the third product is a tautomeric ketodienamine (VI $\rightleftharpoons$ VI^{V}) formed in low yields in most cases, but as the only reaction product with t-butylamine. The first two products may be separated by steam distillation or ether extraction of the alkaline solution.

(a) N-*Alkylcollidinium salts.* (II, R′ = R″ = R‴ = Me, R = Alk). Table 3 contains physical constants and analytical data of N-alkylcollidinium salts (IIi–IIq). The m.ps of the N-n-alkylcollidinium perchlorates show an interesting oscillation with increasing chain length (Fig. 1), the biggest difference being between the methyl and

[24] L. J. Bellamy, *Infra-red Spectra of Complex Molecules* (2nd Edition) Methuen, London (1958).

TABLE 2. IR BANDS OF PYRIDINIUM SALTS II IN THE 1750–1380 cm^{-1} RANGE[a] (KBr PELLET)

Structure		Band												
II	R	ν8a-Py$^{\oplus}$	ν8a-Ph	ν8b-Ph	ν8b-Py$^{\oplus}$			ν19-Ph	δCH_3(as)	ν19aPy$^{\oplus}$	ν19b-Py$^{\oplus}$			δCH_3(s)
a	C_6H_5	1645 s		1597 mw	1573 m			1495 m	1477 m	1467 m	1439 mw	1417 mw		1383 mw
a(d_3-Me)$_3$	C_6H_5	1632 s		1591 m	1563 ms			1492 ms		1461 m	1428 mw			
b	p-MeC_6H_4	1643 s		1588 w	1565 m		1513 ms	1491 m	1483 m	1463 mw	1443 m	1415 mw		1382 mw
c	p-ClC_6H_4	1643 s		1588 w	1565 m			1495 s	1483 s		1444 m	1412 m	1390 w	1376 mw
d	p-BrC_6H_4	1644 s			1565 m			1491 s	1480 ms		1436 m	1404 m	1392 w	1377 mw
e	p-IC_6H_4	1643 s			1567 m				1484 s		1443 mw	1409 mw	1395 m	1378 w
f	o-HOC_6H_4	1643 s	1611 mw	1601 m	1568 m		1511 m		1480 m	1466 s	1440 mw	1418 mw		1385 mw
g	p-HOC_6H_4	1643 s	1613 mw	1598 m	1568 m		1514 s		1482 m	1451 m	1437 mw	1416 mw		1385 mw
h	p-$H_2NC_6H_4$	1642 s	1611 m		1566 m		1520 ms		1481 m	1448 mw	1435 m	1413 w		1383 mw
i	CH_2–C_6H_5	1643 s		1601 w	1582 m	1527 vw		1495 ms	1483 m	1463 m		1421 mw		1384 mw
j	CH_3	1648 s			1582 m	1541 w			1485 ms	1455 m	1439 m	1425 w		1380 m
k	C_2H_5	1645 s			1581 m	1537 vw	1511 w		1480 m	1462 mw	1448 mw	1424 mw		1380 mw
k(d_3-Me)$_3$	C_2H_5	1633 s			1571 m		1505 w			1451 mw	1427 mw		1395 w	
l	n-C_3H_7	1645 s			1582 ms	1535 w	1503 m		1482 ms	1465 m	1449 m	1425 m		1387 m
m	n-C_4H_9	1642 s			1581 m	1533 w	1505 m		1479 ms	1455 m		1425 mw		1385 m
n	i-C_5H_{11}	1643 s			1581 ms	1543 mw	1506 m		1485 ms	1457 m	1446 mw	1423 mw		1391 m
o	cyclo-C_6H_{11}	1641 s			1576 m	1528 vw			1484 m	1456 ms		1407 m		1385 m
q	n-C_7H_{15}	1644 s			1581 m		1506 mw		1480 m	1445 mw		1425 mw		1385 mw
p	n-$C_{18}H_{37}$	1646 s			1582 m		1505 w		1475 m	1445 mw		1425 mw		1385 w

[a] Band notation after refs. 16, 17 and 21.

ethyl derivative. The IR spectra of these salts are closely related to those of N-aryl-collidinium perchlorates and are included in the lower half of Table 2 with the assignments discussed previously. The deuterated N-ethyl-2,4,6-trimethylpyridinium perchlorate (II, R′ = R″ = R‴ = CD_3, R = C_2H_5) has the strongest C–D stretching band at 2295 cm^{-1}; the asym. CH_3 deformation vibrations, which are absent in the deuterated derivative, are at 1485 and 1468 cm^{-1}, and the sym. CH_3 deformation is at 1385 cm^{-1}.

The NMR spectrum of N-methyl-2,4,6-trimethylpyridinium perchlorate[25] in liquid

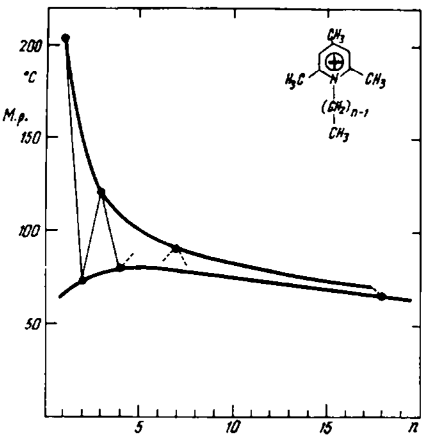


FIG. 1.

SO_2 presents methyl peaks at τ 7·25 (α-methyl groups) and 7·50 (γ-methyl group), easily differentiated by the intensity ratio. The β-protons appear at τ 2·55 (previously found[25] 2·36), and the N-methyl group gives a signal at a very low field, τ 6·00, owing to the bonding with the positively charged nitrogen heteroatom (at a value close to that of nitromethane). Similar chemical shifts are observed in the NMR spectrum of N-n-propyl-2,4,6-trimethylpyridinium perchlorate, with the α-standing methyl peak at τ 7·25, the γ-methyl at τ 7·52, and of the β-protons at τ 2·55; the n-propyl appears as a triplet centered on τ 8·90 (CH_3), a sextet centered at τ ca. 8 (medium methylene group), and a triplet centered on τ 5·60 (the N-methylene group).

One can observe a gradual deshielding of methyl and of aromatic protons in the sequence: 2,4,6-trimethylpyridine, N-alkyl-2,4,6-trimethylpyridinium, 2,4,6-trimethylpyrylium: α-methyl peaks at τ 7·62, 7·25 and 7·16 respectively; β-protons at τ 3·44, 2·55 and 2·38; γ-methyl at τ 7·91, 7·50 and 7·32 respectively.

Interestingly, the N-phenyl-2,4,6-trimethylpyridinium perchlorate shows an inversion of the α and γ methyl peaks: the γ methyl gives rise to a signal at τ 7·35, close to that in N-alkylcollidinium salts, while the α-methyl groups appear upfield at τ 7·61. This shielding of the α-standing methyl groups proves that the methyl protons are above and below the phenyl ring, in other words that the phenyl and pyridinium rings are not coplanar.

(b) N-*Alkyl*-3,5-*xylidines* (VII, R′ = R″ = Me, R = Alk). Analytical data and physical constants are given in Table 4. All xylidines (VIIj–VIIn) are liquids, only the N-cyclohexyl derivative (VIIo) is crystalline at room temperature.

[25] A. T. Balaban, G. R. Bedford and A. R. Katritzky, *J. Chem. Soc.* 1946 (1964).

TABLE 3. N-ALKYL-2,4,6-TRIMETHYLPYRIDINIUM SALTS II (R′ = R″ = R‴ = Me) (Found/Calc.)

Structure		Yield	Perchlorate					Chloroplatinate						
II	R		M.p.°C	Formula	C	H	N	M.p.°C	Formula	C	H	Cl	N	Pt
i	$CH_2C_6H_5$[a]	70–75%	138–139	$C_{15}H_{18}ClNO_4$	57·56 57·79	5·85 5·82	4·68 4·49	205–206	$C_{30}H^{3}{}_{6}Cl_6N_2Pt$	43·49 43·28	4·45 4·36	25·81 25·55	3·77 3·36	22·80 23·45
j	CH_3[b]	80–85%	202–204[c]	$C_9H_{14}ClNO_4$				232–233	$C_{18}H_{28}Cl_6N_2Pt$	31·87 31·77	4·09 4·15	31·29 31·27	4·08 4·12	28·62 28·69
k	C_2H_5	55–60%	72–74	$C_{10}H_{16}ClNO_4$	48·16 48·10	6·49 6·46	5·70 5·61	215–216[d]	$C_{20}H_{32}Cl_6N_2Pt$	33·81 33·91	4·52 4·55	29·74 30·03	4·48 3·95	27·74 27·56
l	n-C_3H_7	55–60%	120–121	$C_{11}H_{18}ClNO_4$	50·27 50·10	7·16 6·88	5·44 5·31	220–222	$C_{22}H_{36}Cl_6N_2Pt$	36·19 35·87	5·17 4·93	29·05 28·89	3·94 3·80	26·11 26·51
m	n-C_4H_9	65–70%	78–80	$C_{12}H_{20}ClNO_4$	51·75 51·90	7·33 7·26	5·23 5·04	208–210	$C_{24}H_{40}Cl_6N_2Pt$	37·61 37·70	5·25 5·27	28·34 27·82	3·70 3·67	25·61 26·54
n	i-C_5C_{11}	65–70%	88–90	$C_{13}H_{22}ClNO_4$	53·67 53·51	7·50 7·60	4·94 4·80	222–223[d]	$C_{26}H_{44}Cl_6N_2Pt$	39·02 39·40	5·65 5·60	26·75 26·84	3·66 3·53	24·95 24·63
o	Cyclo-C_6H_{11}	5–7%	176–177	$C_{14}H_{22}ClNO_4$	55·24 55·35	7·57 7·30	4·80 4·61	210–211	$C_{28}H_{44}Cl_6N_2Pt$	41·18 41·18	5·58 5·43	25·60 26·05	3·73 3·43	24·05 23·41
p	n-C_7H_{15}	90%	90–91	$C_{15}H_{26}ClNO_4$	56·06 56·33	8·42 8·19	4·53 4·38	198	$C_{30}H_{52}Cl_6N_2Pt$	42·55 42·46	6·39 6·17	25·32 25·07	3·71 3·30	23·11 23·00
q	n-$C_{18}H_{37}$	90%	65–66	$C_{26}H_{48}ClNO_4$	65·35 65·86	10·35 10·21	— —							

[a] Picrate, m.p. 112–114°. (Found: C, 57·13; H, 4·77; N, 12·94; $C_{21}H_{20}N_4O_7$ requires: C, 57·27; H, 4·58; N, 12·72%).
[b] Picrate, m.p. 128–129°. (Found: C, 49·49; H, 4·47; N, 15·50; $C_{15}H_{16}N_4O_7$ requires: C, 49·45; H, 4·42; N, 15·38%). Picrolonate, m.p. 210–211°. (Found: C, 56·74; H, 5·40; N, 17·56; $C_{19}H_{21}N_5O_5$ requires: C, 57·13; H, 5·30; N, 17·54%).
[c] Lit. m.p. = 206–207[1], 202[28], 201[29], 204[30], 204–205[31].
[d] Decomposition.
[e] Picrolonate, m.p. 115–117°. (Found: C, 62·26; H, 7·18; N, 14·32; $C_{25}H_{33}N_5O_5$ requires: C, 62·10; H, 6·88; N, 14·48%).

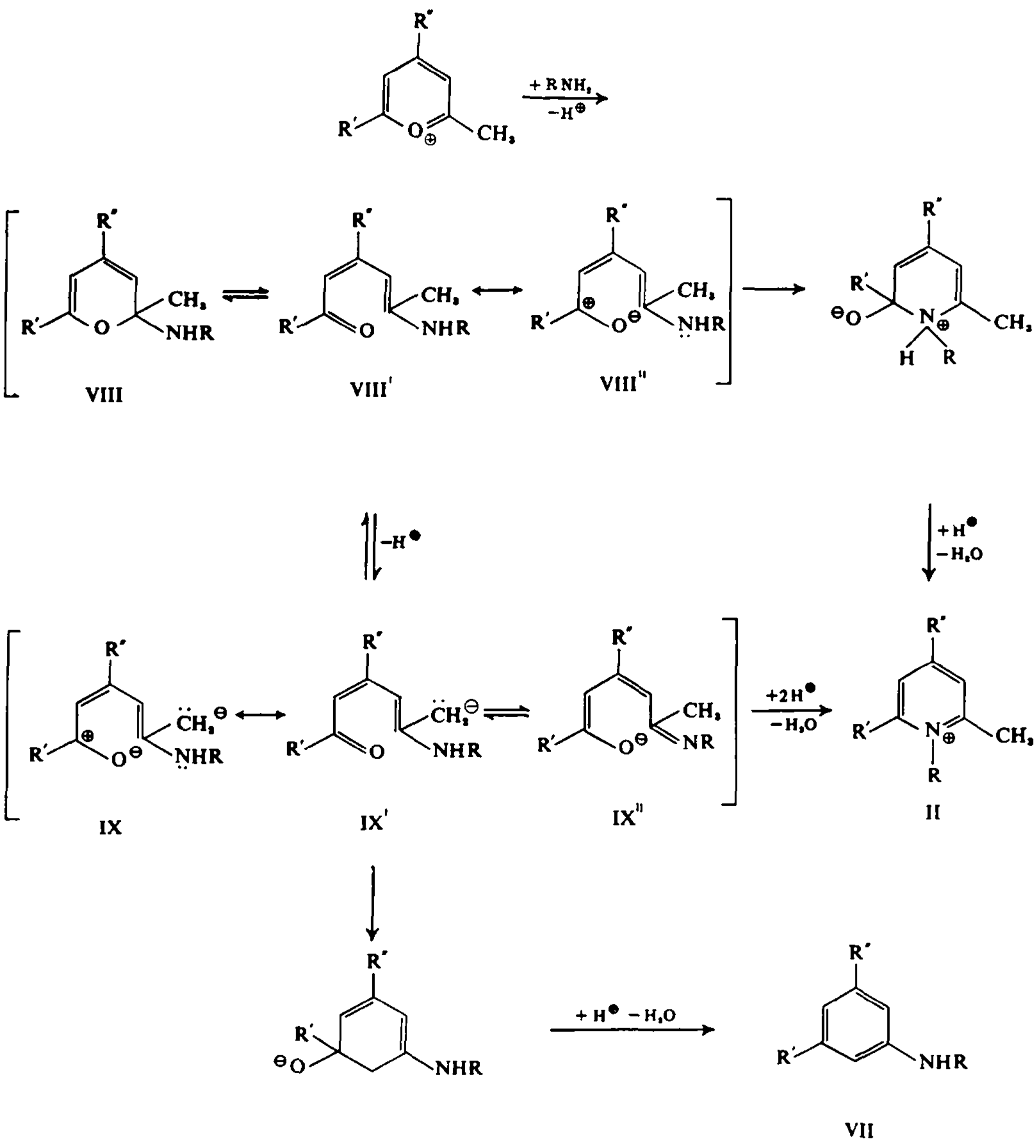
Table 4. N-alkyl-3,5-xylidines VII ($R' = R'' = Me$) and their salts (Found/Calc.)

Structure		Yield	Amine					Perchlorate				
VII	R		B.p.°C/press Torr	Formula	C	H	N	M.p.°C	Formula	C	H	N
j	CH_3	15%	110–111/15–16	$C_9H_{13}N$	80·23 79·95	9·80 9·69	10·29 10·36	130–132	$C_9H_{14}ClNO_4$	45·40 45·87	6·20 5·99	5·60 5·94
k	C_2H_5	35–40%	120–122/15–16	$C_{10}H_{15}N$	80·68 80·48	10·25 10·13	9·68 9·39	171–173	$C_{10}H_{16}ClNO_4$	48·29 48·10	6·76 6·46	5·68 5·61
l	n-C_3H_7	35–40%	130–132/15–16	$C_{11}H_{17}N$	80·73 80·92	10·64 10·50	8·48 8·58	190–192	$C_{11}H_{18}ClNO_4$	50·56 50·10	7·13 6·88	5·37 5·31
m	n-C_4H_9	30%	144–146/15–16	$C_{12}H_{19}N$	81·01 81·30	11·03 10·80	8·12 7·90	131–132	$C_{12}H_{20}ClNO_4$	51·61 51·90	7·22 7·26	5·15 5·04
n	i-C_5H_{11}	30%	150–152/15–16	$C_{13}H_{21}N^b$	79·45 81·61	11·38 11·07	7·88 7·32	147–149	$C_{13}H_{22}ClNO_4$	53·55 53·51	7·83 7·60	5·02 4·80
o	Cyclo-C_6H_{11}	70–75%	M.p. 50–52°	$C_{14}H_{21}N$	82·75 82·71	10·71 10·41	6·89 6·88	214–215	$C_{14}H_{22}ClNO_4$	55·38 55·35	7·38 7·30	4·91 4·61

Structure		Picrate					Picrolonate				
VII	R	M.p.°C	Formula	C	H	N	M.p.°C	Formula	C	H	N
j	CH_3	153–154	$C_{15}H_{16}N_4O_7$	49·52 49·45	4·75 4·43	15·53 15·38	212[a]	$C_{19}H_{21}N_5O_5$	56·99 57·13	5·49 5·30	17·95 17·54
k	C_2H_5	148–149	$C_{16}H_{18}N_4O_7$	50·78 50·79	5·05 4·80	15·03 14·81	208[a]	$C_{20}H_{23}N_5O_5$	57·85 58·10	5·80 5·61	16·76 16·94
l	n-C_3H_7	135–136	$C_{17}H_{20}N_4O_7$	51·81 52·03	5·41 5·16	14·38 14·27	183–184	$C_{21}H_{25}N_5O_5$	58·98 59·01	6·32 5·89	16·47 16·38
m	n-C_4H_9	107–109	$C_{18}H_{22}N_4O_7$	52·92 53·20	5·69 5·46	14·16 13·79	180–182	$C_{22}H_{27}N_5O_5$	59·74 59·85	6·36 6·16	16·10 15·87
n	i-C_5H_{11}						209–210[a]	$C_{23}H_{29}N_5O_5$	60·86 60·64	6·64 6·42	15·27 15·38
o	Cyclo-C_6H_{11}	128–130	$C_{20}H_{24}N_4O_7$	55·59 55·55	5·81 5·59	12·86 12·96	218–219	$C_{24}H_{29}N_5O_5$	61·30 61·65	6·44 6·25	15·17 14·98

[a] Decomposition.
[b] The IR spectrum shows the presence of a ketonic by-product.

The relative amounts of the first two products (II and VII) differ according to the structure of the R group and to the reaction conditions. The molar ratio pyridinium salt (II) to xylidine (VII) decreases from ca. 5·5 for R = Me, to 1·5 for R = Et and n–Pr, to 2·2 for R = n-Bu and i-C_5H_{11}, and to 0·1 for R = cyclohexyl; for higher alkyl groups R (n-C_7, n-C_{18}, and benzyl), the ratio is very high, as for aromatic R groups, i.e. only pyridinium salts are isolated. A comparison between polar and non-polar solvents (water and dichloromethane, respectively) showed that in the latter less of the xylidines (VIIj and VIIm) are formed. This solvent effect may be explained by the fact that water allows an increased charge separation in VIII'', the intermediate in pyridinium salt II formation.



A different, less satisfactory, method for the separation of the first two products II and VII, which had been used initially in our experiments, consisted in treating with 70% perchloric acid the crude perchlorate (which for R = Et and n-Bu is a brown liquid, immiscible with water and ether). The precipitated perchlorates under these conditions were believed to be the expected pyridinium salts, but the IR spectra clearly revealed that they had a different structure. The intensity of the three bands of these perchlorates in the 1650–1550 cm^{-1} range was much lower than in the pyridinium salts, the 1630–1640 cm^{-1} band being the weakest (these three bands are the 8a and 8b phenyl bands and the $NH_2^{\oplus}$ deformation band of the $Me_2C_6H_3NH_2R$ group); a series of medium to strong bands appears in the 2400–2800 cm^{-1} range (NH-stretching).

These last bands led to the supposition that these compounds were perchlorates of secondary amines. When the free bases (VIIj–VIIo) were obtained by steam distillation, their IR spectra confirmed this expectation (Table 5). The secondary amine structure was revealed by the single N–H stretching band at 3428–3445 (CCl_4 solution) or 3403–3413 cm^{-1} (liquid film), by the medium or strong NH bending vibration at 1514–1518 cm^{-1} (somewhat lower than the usual range), and by the presence of strong C–N stretching bands characteristic of aliphatic (1190–1193 cm^{-1}) and aromatic (1336–1342 cm^{-1}) secondary amines.

On N-deuteration by refluxing with deuterium oxide (in the case of VIIj and VIIk), all these bands undergo characteristic shifts: the N–D stretching band to 2538–2540 cm^{-1} (CCl_4 solution) and the N–D bending band to 1110–1120 cm^{-1} (frequency ratios ν_H/ν_D 1·36); the aromatic and aliphatic C–N stretching bands are shifted to slightly higher frequencies, i.e. to 1352–1360 and 1220–1230 cm^{-1} (frequency ratios ν_H/ν_D 0·989 and 0·967 respectively. These shifts on deuteration are in agreement with literature data.[26] Another modification caused by the N-deuteration is the shift from 1095–1105 to 945–955 cm^{-1} of a medium intensity band, and the apparition of VIIj of a new band at 1173 cm^{-1} possibly also involving the C–NH–C skeleton.

The presence of a 1,3,5-trisubstituted benzene ring is revealed by strong skeletal bands at 1605–1608 and 1473–1483 cm^{-1}, and by strong out-of-plane CH bending bands at 820–822 and 690–691 cm^{-1}. The methyl and methylene groups of these bases give CH stretching bands at 2960–2980 and 2860–2875 cm^{-1}, and 2920–2930 and 2855–2858 cm^{-1}, respectively, and CH bending vibrations at 1304–1306 and 1375–1380 (sym) and 1450–1454 cm^{-1}. In the case of N-methyl-3,5-xylidine VIIj, the N-methyl group is revealed by a band at 2812 cm^{-1}.[27]

A clearer insight into the vibration modes of xylidines (VII) was possible by preparing d_3-methyl derivatives ($R' = R'' = CD_3$) from I($R' = R'' = R''' = CD_3$) and a solution of ethylamine in deuterium oxide (to avoid dedeuteration) leading to X, or aqueous methylamine leading to XI (partly deuterated). The IR spectra of the deuterated xilidines have in the C–D stretching region common bands at 2230, 2205. 2110–2115 and 2068–2070 cm^{-1}; in addition, X has a band at 2258 and XI at 2147 cm^{-1}.

From the pronounced changes in the 1300–1600 cm^{-1} range brought about by methyl-deuteration, we mention only the small shifts of the C–N stretching band from

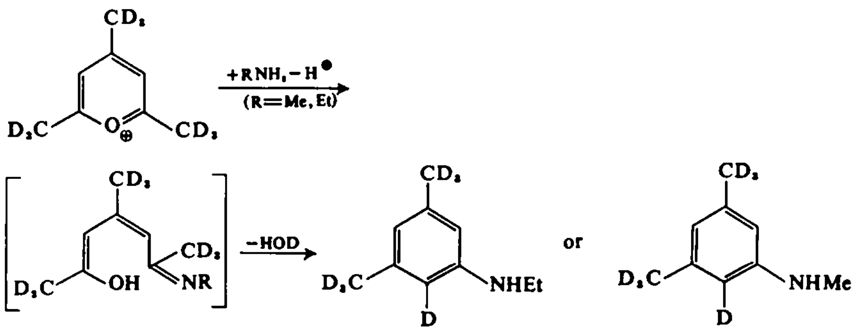
[26] D. Hadzi and M. S. Skrbljak, *J. Chem. Soc.* 843 (1957).

[27] H. B. Henbest, G. D. Meakins, B. Nicholls and A. A. Wagland, *J. Chem. Soc.* 1462 (1957); R. D. Hill and G. D. Meakins, *Ibid.* 760 (1958); F. Dalton, R. D. Hill and G. D. Meakins, *Ibid.* 2927 (1960).

TABLE 5. IR BANDS OF N-ALKYL-XYLIDINES VII ($R' = R'' = Me$)

Assignment \ Compound	VIIj	VIIj (N—D)	XI	VIIk	VIIk (N—D)	X	VII l	VIIm	VIIn	VIIo
State	film	CCl_4	CCl_4	film	CCl_4	CCl_4	film	film	film	KBr
νN-H	3413 ms[a]	—	3445 m	3403 m[b]	—	3423 m	3413 m	3408 m	3408 m	3364 m[c]
	3028 s	3023 s	3028 m	3024 s	3026 m	3050 w	3023 ms	3018 s	3027 m	3028 ms
νCH	2980 ms	2977 s	2985 m	2975 ms	2975 ms	2976 s	2965 ms	2960 ms	2963 ms	2940 ms
νCH	2920 ms	2916 vs	2932 m	2924 ms	2925 m	2929 m	2928 ms	2928 ms	2930 ms	2920 m
νCH	2860 ms	2877 ms	2905 m	2875 ms	2878 m	2877 ms	2875 ms	2872 ms	2873 ms	2852 ms
νCH	2858 ms	2855 ms	2870 m	2857 ms	2858 m	2855 m	—	2858 ms	2855 m	—
νCH	2812 ms	2816 s	2810 m	—	—	—	—	—	—	—
	2732 mw	2725 mw	—	2732 w	2730 w	—	2729 mw	2725 w	2730 w	2733 w
νN-D	—	2540	—	—	2538 m	—	—	—	—	—
νC-D	—	—	—	—	—	2258 m	—	—	—	—
νC-D	—	—	2230 m	—	—	2230 m	—	—	—	—
νC-D	—	—	2205 m	—	—	2205 m	—	—	—	—
νC-D	—	—	2147 m	—	—	—	—	—	—	—
νC-D	—	—	2110 m	—	—	2115 m	—	—	—	—
νC-D	—	—	2068 m	—	—	2070 m	—	—	—	—
νCO	—	—	—	—	—	—	—	—	1665 m	—
ν8aPh	1608 vs	1603 vs	1603 vs	1605 vs	1603 vs	1587 vs	1608 vs	1608 vs	1605 vs	1605 vs
δN-H	1518 ms	—	1511 ms	1517 m	—	—	1518 ms	1514 ms	1518 s	1514 m
ν19aPh	1483 s	1478 s	1481 ms	1480 ms	1481 ms	1486 ms	1474 ms	1475 ms	1473 ms	1468 m
δas·CH_3	1450 ms	1450 mw	1454 m	1455 m	1455 m	1452 w	—	1450 w	1450 w	1449 ms
	1409 ms	1410 w	1425 m	1417 ms	1415 mw	1412 s	1421 m	1416 ms	—	1424 mw
δs·CH_4	1377 m	1385 m	—	1378 m	1385 m	1380 mw	1379 m	1380 m	1375 ms	1374 m
	—	—	—	—	1368 m	—	—	—	—	—
νAr-N	1342 s	1360 s	1344 ms	1336 s	1352 m	1334 ms	1339 s	1336 s	1342 s	1339 s
	—	1315 ms	—	—	1332 m	—	—	—	—	—
δs·CH_3	1306 ms	—	—	1304 m	—	—	1304 m	1306 m	1306 ms	1312 mw
	1268 m	1280 mw	1275 w	1265 mw	1280 w	1274 ms	1274 mw	1270 mw	1274 m	1276 mw
	—	—	1238 vw	—	—	1240 vw	—	—	—	—
νR-N	—	1230 ms	1220 vw	—	1220 m	1225 vw	—	—	—	—
νR-N	1193 s	1192 m	1198 ms	1191 s	1190 m	1209 mw	1190 s	1190 s	1191 s	1186 s
	—	1173 ms	—	—	—	—	—	—	—	—
	1155 m	1160 ms	1153 w	1145 m	1145 m	1165 mw	1143 m	1140 mw	1153 m	1145 m
δN-D	—	1120 m	1130 w	—	1110 mw	1123 w	—	—	—	—
νC-N-C	1095 mw	—	1092 w	1105 w	—	—	1095 w	1098 w	1095 mw	1108 m
	—	—	1051 w	1072 mw	1075 w	1055 w	—	—	—	—
	1036 m	1038 m	—	1035 m	1036 m	—	1037 m	1034 mw	1036 mw	1028 mw
	991 ms	995 m	995 w	992 m	994 m	998 w	991 m	990 m	993 m	990 m
	—	965 mw	—	—	—	970 w	—	—	—	—
νC-N-C	—	945 m	—	—	955 mw	960 w	—	—	—	—
	921 m	920 ms	902 mw	—	920 w	920 vw	—	—	—	—
δCH(o.o.p.)	820 vs	—	—	821 vs	—	—	820 vs	820 vs	822 vs	824 vs
δCH(o.o.p.)	690 vs	—	—	691 vs	—	—	691 s	690 s	691 s	692 ms

Notes: In carbon tetrachloride solution the N-H band appears at: [a] 3445 cm^{-1}; [b] 3428 cm^{-1}; [c] 3425 cm^{-1}



X XI

1190–1193 to 1198 (in XI) or 1200 cm^{-1} (in X), of the 8a skeletal band from 1605–1608 cm^{-1} to 1603 (in X) or 1587 cm^{-1} (in XI) and the disparition of the sym. methyl band at 1304–1306 cm^{-1}. Assignments made difficult by the presence of the N-methyl and ethyl groups.

(c) *Tautomeric* N-*alkyl-keto-dien-amines* (VI). After the steam distillation of the volatile N-alkyl-xylidines (VII) the aqueous alkaline solution containing the pyridinium perchlorate (II) still contains water-insoluble material, which can be extracted by ether. Evaporation of the ether afforded a red oil (in the reaction with n-propylamine, the yield is ca. 5%; with t-butylamine this is the only product, formed in ca. 80% yield). Non-volatile N-alkylxylidines are separated from the pyridinium salts by ether extraction from alkaline aqueous solutions. Distillation in vacuum on the xylidine leaves similar products (octadecylamine affords an orange-coloured solid in ca. 10% yield).

These products give in CCl_4 IR spectra presenting free O–H stretching bands at 3620 cm^{-1} (which are shifted to 2675 cm^{-1} on deuteration by refluxing with D_2O), and hydrogen-bonded OH stretching bands at 3428 cm^{-1}; the N-octadecyl-derivative presents in KBr pellet only a broad band centred on 3445 cm^{-1} with a shoulder at 3620 cm^{-1}. All these compounds have very strong bands at 1600–1608 cm^{-1} and intense bands at 1185–1195 cm^{-1} (1155 cm^{-1} for the t-butyl derivative), 1455–1475 cm^{-1} and 1713–1723 cm^{-1}. The NMR spectrum of the t-butyl derivative presents a t-butyl peak at τ 8·70 and peaks close to those of the phenyl derivative (VI, R = Ph) discussed under (b), p. 14, two doublets at τ 8·95, 8·84 and 6·70, 6·59, a strong methyl peak at τ 7·85 and a weaker one at τ 7·58, and a olefinic proton peak at τ 3·74. In addition, weak or medium peaks at τ 8·28, 8·05, 3·56 and 3·30 are visible. The possible structure of these products is VI(R = Alk).

In conclusion, the reaction of 2,4,6-trimethylpyrylium perchlorate with lower aliphatic primary amines affords not only 1-alkyl-2,4,6-trimethylpyridinium salts (II) as described in the literature,[1–9,15] but also N-alkyl-xylidines (VII). Such a cyclization to an aniline derivative was believed to be possible only in the reaction with secondary amines.[3,9–11] This is a convenient method for the preparation of difficultly available N-alkyl-3,5-dimethyl-(or generally dialkyl)-anilines.

EXPERIMENTAL

N-*Phenyl*-2,4,6-*trimethylpyridinium perchlorate* (IIa). 2,4,6-Trimethylpyrylium perchlorate[14] (2·2 g, 10 mmoles) was refluxed with 1·8 ml (20 mmoles) aniline in 20 ml ether for 1 hr. The resulting insoluble oil crystallized on standing and was purified from EtOH–ether.

The *picrate* and *picrolonate*, were obtained from the crude perchlorate and the respective acid in EtOH, and recrystallized from aqueous EtOH, and EtOH, respectively; the *chloroplatinate* was obtained from the aqueous solution of the perchlorate by acidification with HCl and precipitation with hexachloroplatinic acid; it was then recrystallized from dil HClaq. If the reaction was carried out with five-fold larger amounts in 25 ml water, refluxing for 10 min, followed by alkalinization, steam-distillation of unreacted aniline and extraction with ether of the alkaline solution, then the ethereal extract on evaporation left a red oil (ca. 70 mg); acidification of the alkaline solution with perchloric acid and concentration on the steam bath gave 14 g crystalline perchlorate (IIa). If the reaction was effected at 0–5° by stirring 7·7 g (1 equiv) trimethylpyrylium perchlorate in 20 ml EtOH with 63 ml (2 equiv) aniline added gradually with good cooling, for 1·5 hr, then adding 2 g NaOH in EtOH solution and refluxing for 15 min, and steam distilling the unreacted aniline, the ethereal extract of the alkaline solution after evaporation left 0·5 g red oil (VI, R = Ph). Acidification of the aqueous layer with perchloric acid, removal of traces of sym-xylenol with ether and concentration of the aqueous solution on the steam bath afforded 4 g N-phenylcollidnium perchlorate.

N-*p-Toyl-2,4,6-trimethylpyridinium perchlorate* (IIb)[1] was obtained similarly from *p*-toluidine; the resulting oil was twice dissolved in EtOH and precipitated with ether. The *picrate* and *picrolonate* were prepared in aqueous EtOH and recrystallized from 20% EtOH.

N-p-*Chloro-, bromo and iodo-phenyl-2,4,6-trimethylpyridinium perchlorates* (IIc, d, e) were obtained from 10 mmoles pyrylium perchlorate and 20 mmoles *p*-chloro-, bromo- or iodo-aniline in 15 ml MeOH by refluxing for 1 hr, then precipitating with 100 ml ether and recrystallizing from EtOH. The *picrates* and *picrolonates* were prepared in and recrystallized from 50% EtOH.

Attempted hydrolysis of N-p-*chlorophenyl-2,4,6-trimethyl pyridinium perchlorate* in sealed tube with excess NaOHaq at 150° or 200° for 8 or 24 hr, gave a tar. The aqueous solution on acidification gave 3,5-xylenol m.p. 59–60° identified by mixed m.p. The tar was triturated with EtOH and filtered. The filtrate was evaporated, the residue dissolved in hot water, acidified with perchloric acid, and extracted with ether. From the aqueous layer, crystals of unreacted *p*-chlorophenylcollidinium perchlorate were deposited. After filtration and standing, *p*-chloroaniline perchlorate, m.p. 183–185° (dec) was formed, which did not depress the m.p. of an authentic specimen.

N-o-*Hydroxyphenyl-2,4,6-trimethylpyridinium perchlorate* (IIf) was prepared from equal quantities of 2,4,6-trimethylpyrylium perchlorate and *o*-aminophenol by refluxing for 1 hr in 20 ml water. The crude product was recrystallized from water, then from EtOH–ether.

N-p-*Hydroxyphenyl-2,4,6-trimethylpyridinium perchlorate* (IIg) was prepared similarly in MeOH, and ether added. The resulting oil was boiled with charcoal in EtOH, and after filtration ether was added.

N-p-*Aminophenyl-2,4,6-trimethylpyridinium perchlorate* (IIh) was obtained from equimolar amounts of trimethylpyrylium perchlorate and *p*-phenylenediamine in hot MeOH; dilution with water afforded crystals which after washing with ether were recrystallized from water in the presence of charcoal.

Reaction of 2,4,6-trimethylpyrylium perchlorate with methylamine. The reaction was performed in 15 ml water with 10 mmoles trimethylpyrylium perchlorate (I) and 20 mmoles methylamine (aqueous solution, 33%) by refluxing for 5 min. The 1,2,4,6-tetramethylpyridinium perchlorate (IIj) deposited on cooling was recrystallized from water, m.p. 205–206° (lit. m.p. 206–207,[1] 202,[28] 201,[29] 204,[30] 204–205[31]).

The perchlorate (IIj) was converted into the *picrate* (purified from MeOH), the *picrolonate* (in water, purified from MeOH), and the *chloroplatinate* (recrystallized from dil HCl).

By carrying out the reaction with ten times larger amounts and refluxing for 0·5 hr, then adding 4 g NaOH and steam distillation, together with 16 g 1,2,4,6-tetramethylpyridinium perchlorate crystallizing in the distillation flask after cooling, a liquid amine (VIIj) was obtained in the distillate (2 g). This was extracted with ether and purified from any 3,5-xylenol or ketones which could have been formed, by extraction with alkali, then extraction with dil HClaq, alkalinization of the aqueous acid layer, and fractionation.

If the reaction was carried out in dichloromethane (50 ml), the yield of pyridinium salt (IIj) was

[28] E. Weitz and T. König, *Ber. Dtsch. Chem. Ges.* **55**, 2864 (1922).
[29] B. Emmert and O. Varenkamp, *Ber. Dtsch. Chem. Ges.* **56**, 491 (1923).
[30] T. Takahashi and K. Satake, *J. Pharm. Soc. Japan* **74**, 135 (1954).
[31] E. M. Kosower and J. C. Burbach, *J. Amer. Chem. Soc.* **78**, 5838 (1956).

increased and less xylidine (VIIj) was formed (1 g). The VIIj was then converted into the *picrate* and *picrolonate* (recrystallized from aqueous EtOH).

Reaction of 2,4,6-*trimethylpyrylium perchlorate with ethylamine, n-propylamine, n-butylamine, isopentylamine and cyclohexylamine.* The perchlorate (I) in water was refluxed for 5–10 min with two equiv amine (ethylamine as 30% aqueous solution). After cooling, the solution with the oily reaction products was made alkaline with NaOH and steam-distilled for lower amines or extracted with ether for the higher amines. The ethereal extract or the distillate extracted with ether were evaporated and the VIIk-o distilled *in vacuo*. The *picrates* and *picrolonates* of these amines were prepared in and recrystallized from aqueous EtOH. The *perchlorates* of these xylidines may be obtained from the amines and perchloric acid, but they were prepared initially from the crude reaction product (before alkalinization) by treatment with 70% perchloric acid. Under these conditions the pyridinium perchlorates (II) are soluble and the xylidine perchlorates (VII) crystallize; they were filtered off on a sintered glass filter, washed with a little ether, and pressed on a porous plate.

The xylidine obtained from isopentylamine has medium-intensity absorption at 1670–1710 cm^{-1} owing to traces of ketonic by-products.

The aqueous alkaline solution was acidified with perchloric acid. The pyridinium perchlorates (II) separated as oils which were dissolved in EtOH and precipitated with ether, when they crystallized. They were converted into *picrolonates* with picrolonic acid in aqueous EtOH, and into *chloroplatinates* with $PtCl_4$ in dil HCl.

Reaction of 2,4,6-*trimethylpyrylium perchlorate with benzylamine and n-heptylamine.* The reaction was carried out as before. After heating under reflux perchloric acid was added. The oily reaction product consisted mostly of IIi and IIp which were purified from EtOH by repeated precipitation with ether.

Reaction of 2,4,6-*trimethylpyrylium perchlorate with octadecylamine.* The perchlorate (10 mmoles) in 20 ml MeOH was refluxed with 10 mmoles octadecylamine for 5 min, then left overnight. An orange-coloured solid separated, which was filtered off. The methanolic solution was diluted with water and IIq filtered off and recrystallized from 30% MeOH.

Reaction of 2,4,6-*trimethylpyrylium perchlorate with t-butyl amine.* The perchlorate (20 mmoles) was refluxed in 15 ml water with 40 mmoles t-butylamine for 5 min. After cooling the solution was made alkaline with cold NaOHaq and extracted with ether. The ethereal extract was dried on $MgSO_4$ and evaporated, leaving a red-coloured amorphous product.

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