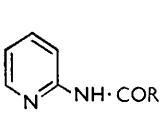
262. *Potentially Tautomeric Pyridines. Part II.*[1] 2-, 3-, *and* 4-*Acetamido- and -Benzamido-pyridine.*

By R. A. Jones and A. R. Katritzky.

The basicities and spectra of the compounds named in the title and alkylated derivatives of their alternative tautomers show that they exist predominantly in the acylamino-form; the reasons for this somewhat unexpected behaviour are discussed.

Acylamino-groups often show properties intermediate between those of free amino- and hydroxy-groups; *e.g.*, acidity and basicity and directive influence on electrophilic substitutions in benzenoid nuclei.[2] 2-, 3-, and 4-Aminopyridine exist as such,[3] but 2- and 4-hydroxypyridine exist as pyrid-2- and -4-one,[4] and 3-hydroxypyridine exists in comparable amounts as such and as anhydro-3-hydroxypyridinium hydroxide.[4] A knowledge of the tautomeric composition of 2- (I ⇌ II), 3- (III ⇌ IV), and 4-acylaminopyridines (cf. I ⇌ II) would therefore be of interest. Kenner, Reese, and Todd [5] showed



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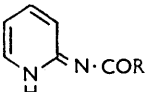

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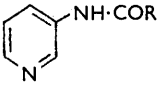

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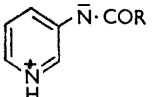

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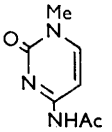

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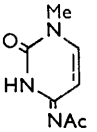


(VI)

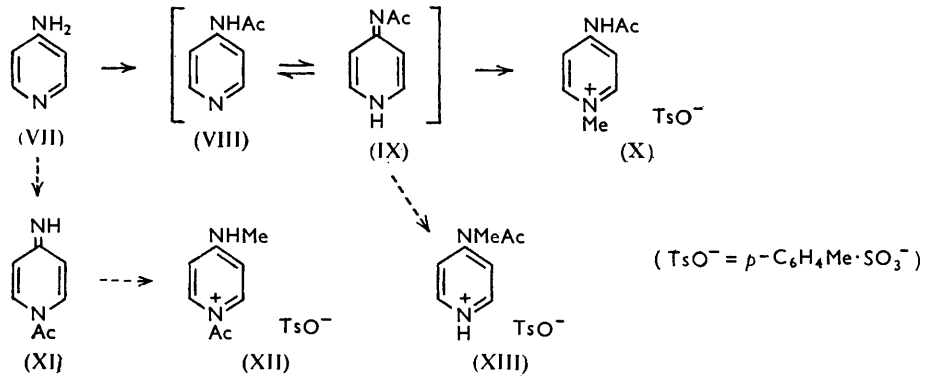
by ultraviolet-spectral comparisons that N^6-acetyl-3-methylcytosine exists predominantly as such (V) and not in the alternative form (VI); no other work has been reported. 2-, 3-, and 4-Acetamido- and -benzamido-pyridine and methylated derivatives of their alternative tautomers have now been prepared and studied by basicity and ultraviolet- and infrared-spectral techniques.[1,6]

Preparation of Compounds.—Hydrogenation of 4-methylaminopyridine 1-oxide gave

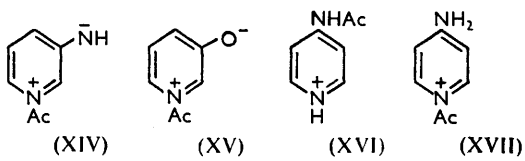
[1] Part I, Jones and Katritzky, *J.*, 1958, 3610.
[2] See, *e.g.*, Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 239.
[3] Angyal and Angyal, *J.*, 1952, 1461.
[4] Albert and Phillips, *J.*, 1956, 1294; Mason, *J.*, 1958, 674.
[5] Kenner, Reese, and Todd, *J.*, 1955, 855; cf. also Brown, Todd, and Varadarajan, *J.*, 1956, 2384.
[6] Gardner and Katritzky, *J.*, 1957, 4375.

4-methylaminopyridine (compare ref. 7). 2-[8] and 3-Methylamino-[9] and 4-amino-pyridine [7] were prepared by known methods. Monoacylation of these amines and (commercial) 2- and 3-aminopyridine (see p. 1322) yielded 2-, 3-, and 4-acetamido-, -benzamido-, -*N*-methylacetamido-, and -*N*-methylbenzamido-pyridine. The first six acylamino-compounds were heated with methyl toluene-*p*-sulphonate; 2-, 3-, and 4-acetamido- and 3- and 4-benzamido-1-methylpyridinium toluene-*p*-sulphonate were obtained, but no product could be isolated from the 2-benzamidopyridine reaction.

It was necessary to confirm the gross structures assigned to the above acylated products,



because, *e.g.*, acetylation of 4-aminopyridine (VII) could have given (XI) instead of an equilibrium mixture of (VIII) and (IX). The mixture of (VIII) and (IX) and methyl toluene-*p*-sulphonate could have given (XIII) instead of (X), and 1-acetylpyrid-4-one imine (XI) could have given (XII). The following facts show that acylation did not give (XI) or its analogues. (i) 2-[10,11] and 3-Acetamido-[12] and 2-benzamido-pyridine [10] with peracetic acid gave substituted pyridine 1-oxides, of known [12] structure. (ii) In the 3-series, the alternative structures are betaines, *e.g.*, (XIV), but the products' properties did not



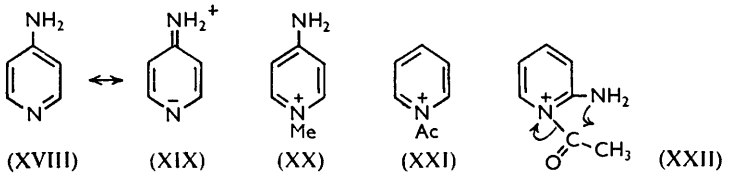
resemble those of known betaines (*e.g.*, XV).[13] (iii) The compounds were reasonably stable in dilute aqueous acid (no significant change in ultraviolet spectrum of a N-acid solution during 24 hr. for 2- and 4-acet- and -benz-amidopyridine), as would be expected for ions of type (XVI) (from VIII ⇌ IX) but not for ions of type (XVII) (from XI). (iv) Infrared spectra (see below) eliminate structures of types (XI) and (XIV).

Acylation of the nitrogen atom in the side chain rather than that in the ring is interesting, because the two principal canonical forms of 2- and 4-aminopyridine (*e.g.*, XVIII and XIX) and the net charge distribution should cause electrophilic agents to attack the ring-nitrogen atom. This generally happens; thus methylation gives compound (XX).[14] Initial acylation probably occurs on the ring-nitrogen atom, but the products

[7] Katritzky and Monro, *J.*, 1958, 1263.
[8] Anderson and Seeger, *J. Amer. Chem. Soc.*, 1949, **71**, 340.
[9] Clark-Lewis and Thompson, *J.*, 1957, 442.
[10] Katritzky, *J.*, 1957, 191.
[11] Adams and Miyano, *J. Amer. Chem. Soc.*, 1954, **76**, 2785.
[12] Jones and Katritzky, unpublished work.
[13] Williams, *J. Ind. Eng. Chem.*, 1921, **13**, 1107.
[14] Tschitschibabin and Ossetrowa, *Ber.*, 1925, **58**, 1708.

(*e.g.*, XVII) are acylating agents [cf., *e.g.*, the ion (XXI) formed during acylation in pyridine] and rearrange intermolecularly [and possibly intramolecularly, in the 2-series (*e.g.*, XXII)]. Angyal *et al.*[15] concluded that this occurred in the benzoylation and sulphonylation of 2-aminopyridine.

Methyl toluene-*p*-sulphonate did not give products of type (XIII), for the corresponding free bases were spectroscopically distinct from the (acyl-*N*-methylamino)-pyridines and had quite different basicities; the identity of the products from the



(XVIII) (XIX) (XX) (XXI) (XXII)

methylation of 2-benzamidopyridine and the benzoylation of 1-methylpyrid-2-one imine had been previously established.[16]

Basicity Measurements.—The pK_a values in Table 1 show that (*a*) the 2-, 3-, and 4-(acyl-*N*-methylamino)pyridines are weaker bases by 0·14—2·08 pK units, and (*b*) the 1-methylpyrid-2- and -4-one acylimines and the anhydro-3-acylamino-1-methylpyridinium

TABLE 1.

No.	Compound	pK_a [a]	σ [b]	Concn. (10^{-4}M)	Wavelength [c] (mμ)	pK_a of corresp. NH_2 cpd.[d]	pK_a of corresp. OH cpd.[d]
1	2-Acetamidopyridine	4·09	0·04	310	—	6·86	3·28 [e]
2	2-(*N*-Methylacetamido)pyridine	2·01	0·05	0·03	290	—	—
3	1-Methylpyrid-2-one acetylimine	7·12	0·06	96	—	12·2	0·32
4	2-Benzamidopyridine	3·33	0·08	310	—	6·86	3·28 [e]
5	2-(*N*-Methylbenzamido)pyridine	1·44	0·02	0·28	295	—	—
6	3-Acetamidopyridine	4·46	0·09	227	—	6·09	4·88 [e]
7	3-(*N*-Methylacetamido)pyridine	3·52	0·04	115	—	—	—
8	Anhydro-3-acetamido-1-methylpyridinium hydroxide	>11	—	—	—	—	4·96
9	3-Benzamidopyridine	3·80	0·06	1·95	280	6·09	4·88 [e]
10	3-(*N*-Methylbenzamido)pyridine	3·66	0·10	0·87	280	—	—
11	Anhydro-3-benzamido-1-methylpyridinium hydroxide	>11	—	—	—	—	4·96
12	4-Acetamidopyridine	5·87	0·03	180	—	9·17	6·62 [e]
13	4-(*N*-Methylacetamido)pyridine	4·62	0·03	130	—	—	—
14	1-Methylpyrid-4-one acetylimine	11·03	0·03	210	—	12·5	3·33
15	4-Benzamidopyridine	5·32	0·08	88	—	9·17	6·62 [e]
16	4-(*N*-Methylbenzamido)pyridine	4·68	0·01	127	—	—	—
17	1-Methylpyrid-4-one benzoylimine	9·89	0·07	135	—	12·5	3·33

[a] Arithmetical means of 6 values. Apparent values are given; thermodynamic pK_a may be calculated by using the concentration given (cf. ref. 4). [b] Standard deviation. [c] An entry in this column signifies that the determination was spectrometric (otherwise potentiometric). Measurements were made in phosphate buffers, or sulphuric acid of known H_0 and containing up to 2% of ethanol. [d] From refs. 3, 4, and Jaffe and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441. [e] These values refer to 2-, 3-, and 4-methoxypyridine. [f] Jaffe and Doak (*loc. cit.*) give 4·43.

hydroxides are stronger bases by $\geqslant$3·03 pK units than the corresponding, potentially tautomeric compounds. Observation (*b*) demonstrates that 2-, 3-, and 4-acetamido- and -benzamido-pyridine exist predominantly as such (I and III), and not as pyridine acylimines or betaines (II and IV), if the reasonable assumption is made that a methyl group has only a weak base-strengthening effect.

Observation (*a*) indicates considerable steric inhibition of resonance in the (acyl-*N*-methylamino)-compounds. The differences are least in the 3-series, where mesomeric

[15] Angyal and his co-workers, *Austral. J. Sci. Res.*, 1951, **4**, *A*, 93; 1952, **5**, *A*, 368, 375.
[16] Tschitschibabin and Bylinkin, *Ber.*, 1922, **55**, 998.

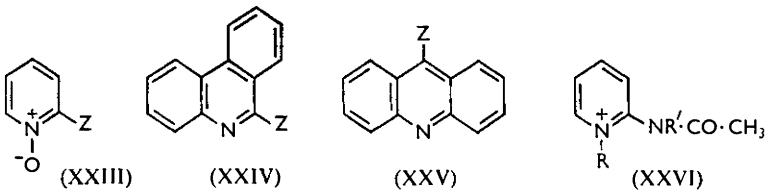
base-strengthening by the acylamino-group is of least importance, and greatest in the 2-series, where steric hindrance is most effective. The differences are smaller for the benzamido- than for the acetamido-compounds; possibly mesomerism in the former is considerably hindered before introduction of the methyl group. Similar effects are shown in alkylamino-compounds, *e.g.*, weak in the pyridine 1-oxides [6] (XXIII; Table 2, col. 1)

TABLE 2. pK_a *Values.*

Z	1	2	3
NH_2	2·67	6·30	9·45
NHMe	2·61	6·70	9·77
NMe_2	2·27	4·91	7·53

(For explanation see text.)

and strong in the phenanthridines [17] (XXIV; col. 2) and acridines [18] (XXV; col. 3). Steric inhibition of mesomerism in (*N*-methylacetamido)-compounds is also indicated by ultraviolet-spectral (see below) and kinetic evidence.[19]



(XXIII) (XXIV) (XXV) (XXVI)

Ultraviolet Spectra (*Table* 3).—Each series of compounds forms similar cations, *e.g.*, Nos. 1—3 form the cation (XXVI; R and R′ = H or Me). The positions of the ultraviolet absorption maxima are similar in each series of cations, but each (acyl-*N*-methylamino)-compound shows sharply reduced intensity of absorption compared with the other two compounds, indicating partial steric inhibition of mesomerism.[20]

In each series of free bases, the positions of the absorption maxima of the (acylamino)-compounds are similar to those of the (acyl-*N*-methylamino)-compounds and not to those of the pyridone acylimines or anhydro-bases. The lower intensities of the (acyl-*N*-methylamino)- than of the (acylamino)-compounds are explained by steric inhibition of mesomerism (cf. the cations). The ultraviolet spectra therefore afford independent evidence that the acylamino-forms of the potentially tautomeric compounds predominate.

Infrared Spectra.—For monosubstituted aromatic and heteroaromatic compounds, the bands are (with few exceptions) characteristic of either the ring or the substituent, and in a series of compounds containing the same ring (or substituent), the positions and intensities of the bands are either reasonably constant or vary in a regular manner with the nature of the substituent (or ring).[21-23] The bands characteristic of the substituted nuclei are shown by pyridines with the following substituents: 2- and 4-(*N*-methylacetamido)- and 4-(*N*-methylbenzamido)- (see p. 1323); and by 2-[21], 3-[22], and 4-acetamido-[23]; 3-(*N*-methylacetamido)-[22]; 2-[21], 3-[22], and 4-benzamido-,[23] and 2-[21] and 3-(*N*-methylbenzamido-;[22] the remaining bands are characteristic of the substituent.[12] Thus, in chloroform solution, the potentially tautomeric compounds all exist predominantly in the acylamino-form.

[17] Reese, *J.*, 1958, 898.
[18] Albert and Goldacre, *J.*, 1946, 706.
[19] de la Mare and Hassan, *J.*, 1958, 1519.
[20] See, *e.g.*, Ingraham in Newman, " Steric Effects in Organic Chemistry," Chapman and Hall, London, 1956, p. 481.
[21] Katritzky and Hands, *J.*, 1958, 2202.
[22] Katritzky, Hands, and Jones, *J.*, 1958, 3168.
[23] Katritzky and Gardner, *J.*, 1958, 2198.

TABLE 3.

Free bases [a]

No.	Compounds	$\lambda_{min.}$ mμ	$\lambda_{min.}$ $10^{-3}\varepsilon$	$\lambda_{max.}$ mμ	$\lambda_{max.}$ $10^{-3}\varepsilon$	$\lambda_{min.}$ mμ	$\lambda_{min.}$ $10^{3}\varepsilon$	$\lambda_{max.}$ mμ	$\lambda_{max.}$ $10^{-3}\varepsilon$
1	2-Acetamidopyridine	213	5·0	232	10·1	252	3·2	273	7·0
2	2-(*N*-Methylacetamido)pyridine	212	4·8	224	5·3	248	3·0	262	4·1
3	1-Methylpyrid-2-one acetylimine [d]	243	5·0	265	5·4	278	4·2	311	7·4
4	2-Benzamidopyridine	219	7·2	242	11·8	260	9·9	278	12·9
5	2-(*N*-Methylbenzamido)pyridine	—		(—) [c]		253	6·2	269	7·1
6	3-Acetamidopyridine	214	4·0	236	9·8	262	3·0	271	3·1
7	3-(*N*-Methylacetamido)pyridine	—		230 *	4·7	248	3·4	260·5	3·6
8	Anhydro-3-acetamido-1-methylpyridinium hydroxide [d]	247	6·7	273	8·9	—		312 *	3·5
9	3-Benzamidopyridine	—		(—) [c]		216	10·8	258	15·8
10	3-(*N*-Methylbenzamido)pyridine	—		(—) [c]		235	13·8	262	15·7
11	Anhydro-3-benzamido-1-methylpyridinium hydroxide [d]	—		222	18·3	255	8·8	292	12·3
12	4-Acetamidopyridine	—		—		218	3·0	244	17·7
13	4-(*N*-Methylacetamido)pyridine	—		—		219	5·2	253	10·3
14	1-Methylpyrid-4-one acetylimine [d]	240	0·1	269	5·8	281	5·4	312	18·0
15	4-Benzamidopyridine	—		—		222	6·0	263	17·2
16	4-(*N*-Methylbenzamido)pyridine	—		—		234	8·4	260	13·2
17	1-Methylpyrid-4-one benzoylimine [d]	—		226	15·2	275	5·7	328	26·8

Ions [b]

No.	$\lambda_{max.}$ mμ	$\lambda_{max.}$ $10^{-3}\varepsilon$	$\lambda_{min.}$ mμ	$\lambda_{min.}$ $10^{-3}\varepsilon$	$\lambda_{max.}$ mμ	$\lambda_{max.}$ $10^{-3}\varepsilon$	$\lambda_{min.}$ mμ	$\lambda_{min.}$ $10^{-3}\varepsilon$	$\lambda_{max.}$ mμ	$\lambda_{max.}$ $10^{-3}\varepsilon$
1	—		212	4·5	229	12·2	246	0·6	291	11·8
2	—		215	3·0	235	8·3	254	1·1	293	7·7
3	—		215	5·8	229	9·8	248	0·9	290	9·8
4	—		219	6·8	244	14·3	265	4·9	297	20·5
5	—		219	8·7	239	10·1	265	5·0	296	11·3
6	212	19·9	229	5·3	247	11·0	266	2·5	287	5·3
7	223	8·7	245	5·3	250	5·5	275	4·0	280	4·2
8	218	19·0	226	3·8	249	11·2	269	3·1	290	5·3
9	226	13·9	238	12·7	259	20·5	—		280 *	13·9
10	223	12·3	247	8·3	258	8·7	—		285 *	6·0
11	227	18·0	241	11·3	261	18·3	—		288 *	8·9
12	—		—		206	12·3	222	1·5	266	20·0
13	—		206	7·0	214	8·4	230	1·2	281	14·2
14	—		—		212 *	11·4	225	2·4	272	22·0
15	—		—		(—) [c]		225	3·6	279	32·0
16	—		210	12·9	218	14·5	250	5·7	291	13·9
17	—		—		215	17·4	235	5·3	285	32·8

Solutions were aqueous, and phosphate buffers were used.
* Inflection.
[a] Nos. 3, 8, 11, 14, and 17 in N-sodium hydroxide, others at pH 9·7. [b] Nos. 2 and 5 in 5N-sulphuric acid, others in N-sulphuric acid. [c] Peak hidden by increasing absorption. [d] These compounds decompose on storage in N-sodium hydroxide, but the spectra were measured before this was appreciable.

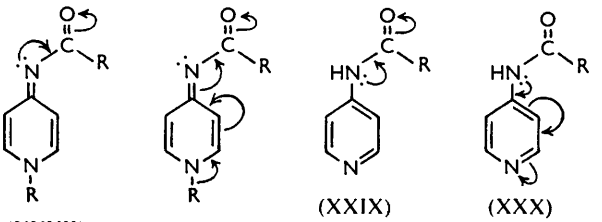
TABLE 4. *Log of parts of pyridine form present to one part of pyridone, etc., form.*

	OH [4]	NH_2 [3]	NHAc [a]	NHBz [a]	SH [b]
2-Substituted pyridine	−2·5	+5·3	+3·0	—	−4·5
3-Substituted pyridine	0	—	>6·5	>7·2	−2·5
4-Substituted pyridine	−3·3	+3·3	+5·2	+4·5	−4·0

All values refer to aqueous solutions.
[a] This work. [b] Ref. 1 and Albert, personal communication.

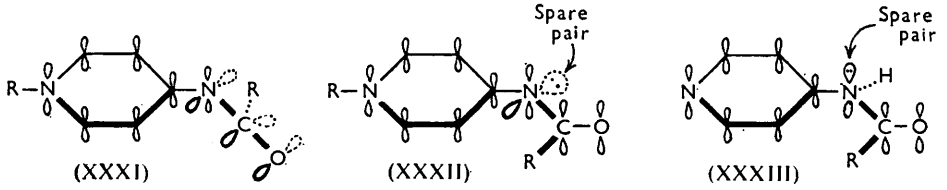
Discussion.—The equilibrium proportions of the alternative forms for the tautomeric pyridines studied are summarised in Table 4. From the discussion in the first paragraph of this paper, it would not be expected that the acylamino-, like the amino-, but unlike the hydroxy-, compounds exist overwhelmingly in the pyridine form. The basicities of the acylaminopyridines are closer to those of the methoxy- than to those of the amino-compounds (Table 1); the position of tautomeric equilibrium is determined by the base strength

of the pyridone acylimines, which are strong bases, like the pyridone imines but not the pyridones (Table 1). In other words, converting NH into N·COR decreases, relatively to the conversion of NH into O, the basicity of a pyridone form much less than that of a pyridine form. Therefore some new factor must be destabilising the pyridone acylimines relative to the acylaminopyridines. A probable explanation is that mesomerism of type (XXVII) [which requires the C=O π-orbital to be in the plane of the ring (cf. XXXI)] and mesomerism of type (XXVIII) [which requires the C=O π-orbital to be perpendicular to the ring (cf. XXXII)] cannot occur simultaneously; on the other hand, overlap of the



(XXVII) (XXVIII) (XXIX) (XXX)

nitrogen spare pair of electrons with both the ring (XXIX) and the carbonyl orbitals (XXX) at the same time is possible (cf. XXXIII).



(XXXI) (XXXII) (XXXIII)

Experimental

2-*Acetamido*-1-*methylpyridinium Toluene*-p-*sulphonate*.—2-Acetamidopyridine (m. p. 68—69°; lit.,[24] m. p. 71°) (0·25 g.) and methyl toluene-*p*-sulphonate (0·28 g.), heated for 12 hr. at 105°, gave the *toluene*-p-*sulphonate* (0·33 g., 62%) which separated from ethanol–ethyl acetate (1 : 6) in needles, m. p. 113—114° (Found: C, 55·5; H, 5·7; N, 8·5. $C_{15}H_{18}O_4N_2S$ requires C, 55·8; H, 5·6; N, 8·7%).

2-Benzamidopyridine (m. p. 79—80°; lit.,[25] m. p. 79—81°) appeared to decompose when heated with methyl toluene-*p*-sulphonate.

2-(N-*Methylacetamido*)*pyridine*.—2-(Methylamino)pyridine (1 g.), acetic acid (2 c.c.), and acetic anhydride (2 c.c.) were refluxed for 2 hr. Volatile material was removed at 100°/20 mm.; distillation of the residue gave the *pyridine* (0·75 g., 54%), b. p. 74—75°/0·2 mm., n_D^{17} 1·540 (Found: N, 18·7. $C_8H_{10}ON_2$ requires N, 18·7%). Infrared bands due to the 2-pyridine nucleus[21] were: 2990 (50), 1594 (210), 1578* (110), 1471 (180), 1434 (155), 1285* (60), 1140† (90), 1090† (90), 1045 (25), 990 (30).‡ The *picrate* formed needles (from ethanol), m. p. 189·5—190·5° (Found: N, 19·0. $C_{14}H_{13}O_8N_5$ requires N, 18·5%).

2-(*N*-Methylbenzamido)pyridine[26] had m. p. 60—63° (lit.,[26] m. p. 61—62°).

4-*Acetamido*-1-*methylpyridinium Toluene*-p-*sulphonate*.—Acetylation[24] of the amine gave 4-acetamidopyridine (92%); the hydrate, m. p. 121—123° (lit.,[24] m. p. 124°), separated from water. The anhydrous salt crystallised from chloroform in rods, m. p. 148°, (lit.,[24] m. p. 150°).

* Shoulder. † Absorption considered to be due to two peaks overlapping. ‡ Values in parentheses are apparent extinction coefficients (cf. refs. 21—23).

[24] Camps, *Arch. Pharm.*, 1902, **240**, 345.
[25] Huntress and Walter, *J. Org. Chem.*, 1948, **13**, 735.
[26] Tschitschibabin and Khunjanz, *Ber.*, 1928, **61**, 2215.

Treatment as above gave the *toluene*-p-*sulphonate* (85%), which separated from ethanol–ethyl acetate (1 : 5) in deliquescent needles, m. p. 135—137° (Found: C, 55·5; H, 5·4; N, 8·3%).

4-*Benzamido*-1-*methylpyridinium Toluene*-p-*sulphonate*.—4-Aminopyridine (0·5 g.), pyridine (3 c.c.), and benzoyl chloride (0·75 c.c.) were kept for 12 hr. at room temperature; addition of water then precipitated 4-benzamidopyridine (0·82 g., 80%), m. p. 203—204° after recrystallisation from water (lit.,[27] m. p. 202°).

Prepared as above, the *toluene*-p-*sulphonate* (91%) separated from ethanol–ethyl acetate (1 : 5) as deliquescent needles, m. p. 165—165·5° (Found: C, 62·5; H, 5·3; N, 6·9. $C_{20}H_{20}O_4N_2S$ requires C, 62·5; H, 5·2; N, 7·3%).

4-*Methylaminopyridine*.—4-Methylaminopyridine 1-oxide (1·9 g.) in ethanol (20 c.c.) was hydrogenated over 5% palladium–charcoal (0·5 g.) until uptake (initially *ca.* 150 c.c./hr.) ceased (*ca.* 3 hr.). Filtration, evaporation of the filtrate, and recrystallisation of the residue from benzene gave the pyridine (1·35 g., 82%), m. p. 119—120° (lit.,[14] m. p. 115—118°).

4-Methylaminopyridine (0·5 g.), acetic anhydride (1 c.c.), and acetic acid (1 c.c.) were refluxed for 2 hr. Volatile material was removed at 100°/20 mm., and the residue, in chloroform (10 c.c), digested with potassium carbonate (0·5 g.). Evaporation of the filtrate gave 4-(N-*methylacetamido*)*pyridine* (0·36 g., 52%), which separated from light petroleum in rods, m. p. 56—57° (Found: C, 63·3; H, 6·6; N, 18·7. $C_8H_{10}ON_2$ requires C, 63·9; H, 6·7; N, 18·7%). Infrared bands due to the 4-substituted pyridine nucleus[23] were: 2980 (60), 1596 (350), 1565 (65), 1495 (80), 1412 (75), 1061 (20), 997 (85), 830 (65).

4-Methylaminopyridine (0·5 g.), pyridine (0·5 c.c.), and benzoyl chloride (0·6 c.c.) were kept for 15 hr. at room temperature; 4-(N-*methylbenzamido*)*pyridine hydrochloride* (1·0 g., 86%) separated; it crystallised from ethanol–ethyl acetate (1 : 2) as plates, m. p. 189—190° (Found: C, 62·8; H, 5·3; N, 11·6. $C_{13}H_{13}ON_2Cl$ requires C, 62·7; H, 5·3; N, 11·3%). The salt (0·2 g.) was warmed with 2N-aqueous potassium hydrogen carbonate (2 c.c.) and extracted with ether; concentration of the extracts gave the *base* (0·12 g., 70%), which sublimed in needles, m. p. 85—86° (Found: C, 73·6; H, 6·0; N, 12·9. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7; N, 13·1%). Infrared bands due to the 4-substituted pyridine nucleus[23] were: 2950 (70), 1594 (320), 1563 (125), 1495 (120), 1415 (80), 1061 (15), 994 (shoulder) (25), 825 (95).

3-*Acylaminopyridine Derivatives*.—3-Acetamidopyridine had m. p. 132—133° (lit.,[28] m. p. 131°).

The following 3-substituted pyridines were prepared analogously to 4-benzamidopyridine: *benzamido* (67%), needles, m. p. 110—112°, from water (Found: C, 72·6; H, 4·9; N, 14·1. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·1; N, 14·1%); N-*methylbenzamido* (37%), cubes, m. p. 92—93°, from light petroleum (Found: C, 73·8; H, 6·0. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7%).

Prepared similarly to the 4-isomer, 3-(*N*-methylacetamido)pyridine (35%) crystallised from light petroleum as plates, m. p. 62—64° (lit.,[29] m. p. 64°).

The following were prepared as the 2-isomers: 3-*acetamido*-1-*methyl*- (61%), needles (from ethanol–ethyl acetate), m. p. 149—150° (Found: C, 55·8; H, 5·8; N, 9·0. $C_{15}H_{18}O_4N_2S$ requires C, 55·9; H, 5·6; N, 8·7%), and 3-*benzamido*-1-*methylpyridinium toluene*-p-*sulphonate* (80%), needles (from ethanol), m. p. 178—179° (Found: C, 62·7; H, 5·3; N, 7·4. $C_{20}H_{20}O_4N_2S$ requires C, 62·5; H, 5·2; N, 7·3%).

Measurement of Spectra.—See Ref. 1 for details.

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[27] Koenigs, Kinne, and Weiss, *Ber.*, 1924, **57**, 1176.
[28] Pictet and Crepieux, *Ber.*, 1895, **28**, 1908.
[29] Plazek, Marcinikow, and Stammer, *Rocznicki Chem.*, 1935, **15**, 365.