567. *Potentially Tautomeric Pyridines. Part V.*[1] *Phenyl 2-, 3-, and 4-Picolyl Sulphones*

By S. Golding, A. R. Katritzky, and H. Z. Kucharska

The basicities and spectra of the title compounds and the corresponding *N*-alkylated anhydro-bases show that the former exist predominantly as such: in aqueous solution the tautomeric equilibrium constants are $10^{7\cdot6}$—$10^{9\cdot6}$.

Parts II [2] and III [3] of this series considered the tautomerism of the isomeric acylamino- and sulphonylamino-pyridines. The tautomeric equilibrium constants were very different for the two classes of compound. To test the explanation then advanced for this behaviour we have now investigated some acylmethyl- and sulphonylmethyl-pyridines; the present Paper records the results for the isomeric phenyl picolyl sulphones. The tautomerism [cf. (I) $\rightleftharpoons$ (II)] of such compounds has not been studied previously.

Preparation of Compounds.—2-, 3-, and 4-Picolyl chloride gave the sulphones [cf. (I)] with sodium sulphinate. Methiodides in the 2- and 4-series yielded anhydro-bases [cf. (III)] with alkali. The red zwitterion (V) formed in solution from the 3-methiodide was not isolated.

Basicity Measurements (Table 1).—The anhydro-bases are much stronger bases than the sulphones, indicating that the latter exist predominantly as such. Quantitatively, on the reasonable assumption that the *N*-methyl group in the anhydro-bases has no large effect on the basicity, the results indicate pK_T for the 2-, 3-, and 4-series in aqueous solution of 7·9, 9·6, and 7·6, respectively.

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[1] Part IV, R. A. Jones and A. R. Katritzky, *Austral. J. Chem.*, 1964, **17**, 455.
[2] R. A. Jones and A. R. Katritzky, *J.*, 1959, 1317.
[3] R. A. Jones and A. R. Katritzky, *J.*, 1961, 378.

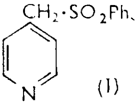
TABLE 1

pK_a Values

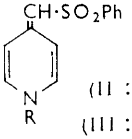
No.	Compound	Concn. (10^{-4}M)	Wavelength (mμ)	pK_a	Standard deviation
1	Phenyl 2-picolyl sulphone	0·484	265	2·54	±0·05
2	,, metho-anhydro-base	0·320	365	10·45	±0·03
3	Phenyl 3-picolyl sulphone	0·944	262	3·67	±0·04
4	,, methiodide	0·405	361	13·27	±0·03
5	Phenyl 4-picolyl sulphone	1·589	262	3·75	±0·05
6	,, metho-anhydro-base	0·244	352	11·37	±0·03

Buffers: for Nos. 1, 3, and 5, sodium acetate–hydrochloric acid and monopotassium phosphate–hydrochloric acid; for Nos. 2 and 6, sodium hydrogen carbonate–sodium hydroxide and disodium phosphate–sodium hydroxide; for No. 4, sodium hydroxide solutions.

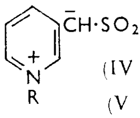
Comparison of the phenylsulphonylmethyl compounds with the pK_a of pyridine demonstrates the large base-weakening effect of the phenylsulphonyl group even when it is separated from the pyridine ring by a methylene group. The measured pK_a values are not dissimilar from those of the corresponding methoxycarbonylpyridines [4] and are much lower than the phenacylpyridines.[5]



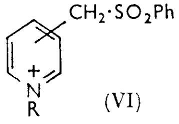
(I)



(II : R = H)
(III : R = Me)



(IV : R = H)
(V : R = Me)



(VI)

Ultraviolet Spectra (Table 2).—All the cations show essentially similar spectra, confirming that they are all of the same structural type (VI; R = H or Me). The anhydro-bases show a strong band at 353—365 mμ: at this wavelength the sulphones do not absorb to any marked extent, demonstrating the absence of appreciable amounts of tautomers of type (II).

TABLE 2

Ultraviolet spectral maxima (mμ)

	Cations				Neutral species					
Compound	λ	$10^{-3}\varepsilon$	λ	$10^{-3}\varepsilon$	λ	$10^{-3}\varepsilon$	λ	$10^{-3}\varepsilon$	λ	$10^{-3}\varepsilon$
Phenyl 2-picolyl sulphone	218 *	11·0	265	10·7	217	13·2	262	5·2	268	4·2
,, metho-anhydro-base	218	11·4	270	10·6	219	9·7	293	10·4	365	9·3
Phenyl 3-picolyl sulphone	219	13·4	262	6·7	218	14·0	262	4·0	—	—
,, method-anhydro-base	222	23·0	265	5·6	—	—	264	7·0	361	9·5
Phenyl 4-picolyl sulphone	223	14·8	260	5·9	219	13·4	264	3·4	—	—
,, metho-anhydro-base	226	15·0	264	5·5	220	12·6	—	—	353	32·5

* Shoulder.

Infrared Spectra.—These were determined for chloroform solutions and for Nujol mulls. The spectra of the potentially tautomeric compounds showed the characteristic bands [6] for the 2-, 3-, and 4-substituted pyridine rings and for the phenylsulphonyl group, and thus demonstrated conclusively the predominance of the picolyl sulphone form. The spectra of the anhydro-compounds were quite distinct, with some resemblance to those for the corresponding pyridones.[7] Details of these spectra are given elsewhere.[8]

Nuclear Magnetic Resonance Spectra.—Further evidence for the picolyl sulphone form is

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[4] A. Albert, in " Physical Methods in Heterocyclic Chemistry," vol. I, ed. A. R. Katritzky, Academic Press, New York, 1963, p. 72.

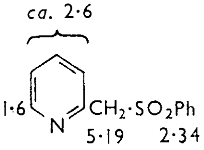
[5] A. R. Katritzky, H. Z. Kucharska, and J. D. Rowe, following Paper.

[6] A. R. Katritzky and A. P. Ambler, in " Physical Methods in Heterocyclic Chemistry," vol. II, ed. A. R. Katritzky, Academic Press, London, 1963, p. 165.

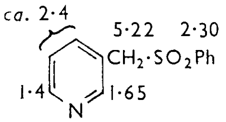
[7] A. R. Katritzky and R. A. Jones, *J.*, 1960, 2947.

[8] A. R. Katritzky, H. Z. Kucharska, J. D. Rowe, and S. Golding, *Spectrochim. Acta*, to be published.

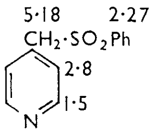
afforded by the nuclear magnetic resonance spectra (VII—IX: τ values given for solutions in dimethylsulphoxide), particularly the methylene signal which appears as a singlet at *ca.* 5·3 τ. This signal is retained in the spectra of the corresponding methiodides (in trifluoroacetic acid), but it is displaced to lower field and occurs at τ 4·79, 5·08, and 5·05 for the 2-, 3-, and 4-methiodides, respectively.



(VII)



(VIII)



(IX)

Conclusions.—The above results show that the picolyl sulphone forms predominate for solutions in polar and in non-polar solvents, and that they exist in the crystalline state. The relation of these results to those for other potentially tautomeric pyridines is discussed in the following Paper.

EXPERIMENTAL

Phenyl 2-Picolyl Sulphone.—2-Picolyl chloride hydrochloride (8 g.), sodium benzene sulphinate dihydrate (10 g.), and sodium acetate (8 g.) were refluxed in n-butanol (35 c.c.) for 5 hr. The cold suspension was added to water (700 c.c.) to yield the *sulphone* (more was obtained by extraction of the filtrate with ethyl acetate) (total yield 9·5 g., 82%), which formed needles, m. p. 111·5—112·5° (from ethanol) (Found: C, 61·5; H, 4·9. $C_{12}H_{11}NO_2S$ requires C, 61·8; H, 4·7%).

The sulphone (2 g.), methyl iodide (4 c.c.), and methanol (13 c.c.) were refluxed for 5 hr. Cooling yielded the *methiodide* (1·7 g., 80%), needles, m. p. 233—234° (decomp.) (from water) (Found: C, 41·6; H, 3·9. $C_{13}H_{14}INO_2S$ requires C, 41·6; H, 3·8%).

1,2-Dihydro-1-methyl-2-(phenylsulphonylmethylene)pyridine.—The methiodide with 0·5N-sodium hydroxide gave the *anhydro-base* (100%) which formed yellow plates, m. p. 162·5—163·5° (decomp.) (from ethanol) (Found: C, 63·0; H, 5·3. $C_{13}H_{14}NO_2S$ requires C, 63·2; H, 5·3%).

The following were prepared similarly: *phenyl 3-picolyl sulphone* (52%), plates, m. p. 134·5—135·5° (from ethanol) (Found: C, 61·8; H, 4·7%); *methiodide* (100%), needles, m. p. 178·5—179·5° (decomp.) (from methanol) (Found: C, 41·7; H, 3·7%); phenyl 4-picolyl sulphone (68%), plates, m. p. 203—204° (from ethanol) (lit.,[9] 201·5°) (Found: C, 62·0; H, 4·7%); *methoperchlorate* (prepared from the crude phenyl 4-picolyl sulphone methiodide with 60% perchloric acid), needles, m. p. 215—216° (from water) (Found: C, 44·9; H, 3·8. $C_{13}H_{14}ClNO_6S$ requires C, 44·9; H, 4·0%); *anhydro-base* (100%), brown crystals, m. p. 128—129° [from ethyl acetate–light petroleum (b. p. 60—80°)] (Found: C, 63·1; H, 5·5%).

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[9] Z. Foldi, *Chem. and Ind.*, 1958, 684.