305. *Interaction at a Distance in Conjugated Systems. Part II.*[1] *The Preparation and Basicities of a Series of 4-Styryl- and 4-Phenylethynyl-pyridines.*

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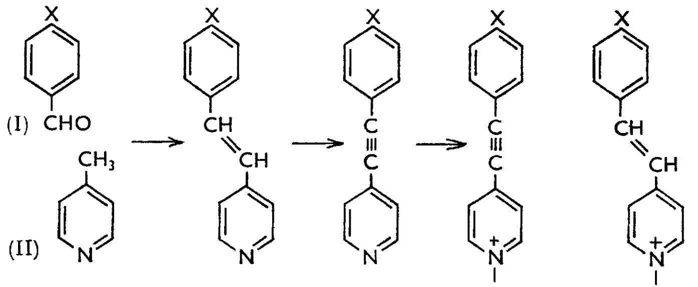
The preparation of a series of 4-styryl- and 4-phenylethynyl-pyridines and their 1-oxides is described. The basicities of the pyridines indicate that interaction between the substituents on the benzene rings and the pyridine ring is quite small, but is larger in the styryl than in the phenylethynyl compounds.

A SERIES of styryl- and phenylethynyl-pyridines and -pyridine 1-oxides has been prepared and the pK_a values have been measured to investigate interaction over distances greater than those for the substituted phenyl-pyridines and 1-oxides studied in the preceding paper.[1]



Preparation of Compounds.—Aromatic aldehydes (I) with γ-picoline (II) gave substituted γ-stilbazoles (III) which were converted by bromination and dehydrobromination into the corresponding acetylenes (IV); the acetylenes yielded the *N*-oxides (V) by oxidation with perbenzoic acid. The stilbazole *N*-oxides (VI) were obtained more efficiently by reaction of the aldehyde (I) with γ-picoline 1-oxide than by direct oxidation of the stilbazoles (cf. ref. 2). Details are recorded in Table 1. The pK_a values in Table 2 were measured by the spectrophotometric method.

Discussion.—The basicities of 3- and 4-substituted pyridines can be correlated by Hammett's equation,[3] and by using the determined ρ value of 5·7, Hammett σ constants have now been calculated for the substituted styryl and phenylethynyl groups (Table 2).

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[1] Part I, Katritzky and Simmons, preceding paper.
[2] Katritzky and Monro, *J.*, 1958, 150.
[3] Jaffé and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441.

TABLE 1.

No.	X	Yield (%)	Solvent for recrystn.*	Crystal form	M. p. (found)	M. p. (lit.)	Ref.
trans-4-(*p*-Substituted styryl)pyridines, $X{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_5H_4N$							
1	NMe_2	12	MeOH	Plates	239·5—241°	240—241°	*a*
2	OMe	70	Pet.	Plates	131·5—132·5	135	*b*
3	Me	66	$EtOH-H_2O$	Plates	150·5—151 [c]	101—102	*d*
4	H	70	$EtOH-H_2O$	Plates	131 [e]	131	*f*
5	Cl	93	$EtOH-H_2O$	Plates or needles	113 [g]	110	*h*
6	NO_2	89	EtOH	Needles	171—172	171	*i*
4-(*p*-Substituted phenylethynyl)pyridines, $X{\cdot}C_6H_4{\cdot}C{\vdots}C{\cdot}C_5H_4N$							
7	OMe	95	$EtOH-H_2O$ Pet.	Plates Needles	118—119·5 [j] 104·5—105·5 [j]	—	—
8	Me	60	Pet.	Needles	114·5—115·5	—	—
9	H	62	$EtOH-H_2O$	Plates	104·5—105·5	104	*k*
10	Cl	79	EtOH	Cubes	119·5—122	119·5—122	*h*
11	NO_2	76	$EtOH-H_2O$	Needles	115·5—116·5	—	—
trans-4-(*p*-Substituted styryl)pyridine 1-oxides, $X{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_5H_4N^+{\cdot}O^-$							
12	NMe_2	11	C_6H_6–Pet.	Plates	257—258	239·4—240	*l*
13	OMe	40	C_6H_6–Pet.	Cubes	159—160	—	—
14	Me	35	C_6H_6–Pet.	Cubes	185—187	—	—
15	H	—	—	—	—	—	*m*
16	Cl	40	EtOH		164—166	—	—
17	NO_2	43	EtOH	Yellow needles	233·5—234·5	—	—
4-(*p*-Substituted phenylethynyl)pyridine 1-oxides, $X{\cdot}C_6H_4{\cdot}C{\vdots}C{\cdot}C_5H_4N^+{\cdot}O^-$							
18	Me	52	C_6H_6–Pet.	Needles	158—159 [n]	—	—
19	H	92	EtOH	Needles	184·5—185·5	—	—
20	Cl	50	$EtOH-H_2O$	Needles	171·5—172	—	—
21	NO_2	43	EtOH	Plates	204—206 (decomp.)	—	—

		Found (%)		Calc. (%)				Found (%)		Calc. (%)	
No.	Formula	C	H	C	H	No.	Formula	C	H	C	H
2	$C_{14}H_{13}NO$ ...	79·4	6·4	79·6	6·2	14	$C_{14}H_{13}NO$ ...	79·9	6·2	79·6	6·2
3	$C_{14}H_{13}N$	85·8	6·6	86·1	6·7	16	$C_{13}H_{10}ClNO$	67·6	4·6	67·4	4·4
7	$C_{14}H_{11}NO$ [j] ... $C_{14}H_{11}NO$ [j]	80·2 80·2	5·2 5·4	80·4 80·4	5·4 5·4	17	$C_{13}H_{10}N_2O_3$	64·4	4·1	64·5	4·1
						18	$C_{14}H_{11}NO$ [o]...	79·9	5·3	80·3	5·3
8	$C_{14}H_{11}N$	87·0	5·8	87·0	5·7	19	$C_{13}H_9NO$ ...	80·3	4·8	80·0	4·6
11	$C_{13}H_8N_2O_2$ ...	69·3	3·6	69·6	3·6	20	$C_{13}H_8ClON$...	67·6	3·5	68·0	3·5
12	$C_{15}H_{16}N_2O$ ...	75·1	6·7	75·0	6·7	21	$C_{13}H_8O_2N_2$ ...	65·1	3·5	65·0	3·4
13	$C_{14}H_{13}NO_2$ ...	74·3	6·1	74·3	5·8						

[a] Gilman and Karmas, *J. Amer. Chem. Soc.*, 1945, **67**, 342. [b] Blout and Eager, *J. Amer. Chem. Soc.*, 1945, **67**, 1319. [c] Presumably a new *polymorph*. [d] Durung, *Ber.*, 1905, **38**, 164. [e] After sublimation at 120°/0·1 mm. [f] Shaw and Wagstaff, *J.*, 1933, 7. [g] After sublimation at 100°/0·1 mm. [h] Smith, U.S.P. 2,482,521; *Chem. Abs.*, 1950, **44**, 2571. [i] Royer, *J.*, 1947, 560. [j] 4-p-*Methoxyphenylethynylpyridine* formed two polymorphs. [k] Lukes and Ernest, *Coll. Czech. Chem. Comm.*, 1949, **14**, 679. [l] Parker and Furst, *J. Org. Chem.*, 1958, **23**, 201. [m] Katritzky and Monro, *J.*, 1958, 150. [n] Sublimes at 150°/0·02 mm. [o] Found: N, 6·6. Calc.: N, 6·7%. * Pet. = light petroleum, b. p. 60—80°.

TABLE 2. pK_a *Values.*

trans 4-(*p*-Substituted styryl)pyridines, $X{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_5H_4N$.					4-(*p*-Substituted phenylethynyl)pyridines, $X{\cdot}C_6H_4{\cdot}C{\vdots}C{\cdot}C_5H_4N$.				
X	pK_a [a]	α [b]	λ (mμ)	σ_p [c]	X	pK_a [a]	α [b]	λ (mμ)	σ_p [c]
OCH_3	6·03	0·02	360	−0·13	OCH_3	4·80	0·01	355	+0·09
CH_3	5·94	0·02	350	−0·11	CH_3	4·70	0·01	337	+0·10
H	5·92	0·01	335	−0·11	H	4·62	0·01	327	+0·12
Cl	5·66	0·02	340	−0·06	Cl	4·54	0·01	330	+0·13
NO_2	5·15	0·03	340	+0·02	NO_2	4·31	0·02	326	+0·17

[a] Arithmetical mean of 6 values. [b] Standard deviation. [c] Hammett σ constant.

(Measurements were in phosphate buffers containing up to 2% of ethanol.)

Previous " normal " σ_p values for the Ph·CH:CH· and Ph·C:C· groups are respectively $-0{\cdot}05$ and $+0{\cdot}19$ as derived from ionisation constants of benzoic acids and hydrolysis rates of ethyl benzoates.[4] However, the solvolysis of benzyl toluenesulphonates, a reaction which depends strongly on electron-donor properties of substituents, would need constants much more negative (*ca.* $-1{\cdot}0$ and $0{\cdot}0$) to be correlated.[4,5] We therefore consider our values to be in reasonable agreement with the " normal " σ_p constants. The σ_p values in Table 2 show that the styryl group acts as an electron donor and the phenylethynyl group as an electron acceptor, in agreement with previous work.[6] The σ_p values within each series of substituted compounds show that the effect of a substituent in the phenyl ring is transmitted more strongly through an ethylenic than through an acetylenic group. This is in line with the known ability of ethylenic groups to interact more strongly with an adjacent unsaturated system than do ethynyl groups.[6] Comparison of these results with those for phenylpyridines[1] indicates that interaction in the series between the substituent and pyridine ring is in the order (Hammett ρ values are given in parentheses): $X\cdot C_6H_4\cdot Py$ ($0{\cdot}97 \pm 0{\cdot}03$) $\sim$ $X\cdot C_6H_4\cdot CH{:}CH\cdot Py$ ($0{\cdot}85 \pm 0{\cdot}07$) $>$ $X\cdot C_6H_4\cdot C{:}C\cdot Py$ ($0{\cdot}44 \pm 0{\cdot}04$), but the effects are small in all cases compared with the effect of substituents directly in the pyridine ring ($\rho = 5{\cdot}71 \pm 0{\cdot}30$).[3]

EXPERIMENTAL

4-*Styrylpyridines*.—The aromatic aldehyde (0·08 mole), 4-picoline (8 g.), and acetic anhydride (20 g.) were refluxed under nitrogen for 30 hr. The mixture was dissolved in chloroform or ether and extracted with aqueous hydrochloric acid (8N; 2 × 50 c.c.); basification of the extracts with ammonia precipitated the product.

4-*Phenylethynylpyridines*.—These compounds were made by a known method.[7] 4-Phenylethynylpyridine formed a *picrate*, needles, m. p. 182—183° (decomp.), from ethanol (Found: C, 55·6; H, 3·1. $C_{19}H_{12}N_4O_7$ requires C, 55·9; H, 3·0%); a *picrolonate*, needles which decomposed at *ca.* 220°, from ethanol (Found: C, 62·0; H, 4·0. $C_{23}H_{17}N_5O_5$ requires C, 62·3; H, 3·9%); and a *boron trichloride complex* (cf. ref. 9), needles, m. p. 154—158°, from ethanol (Found: C, 52·5; H, 3·4. $C_{13}H_9NBCl_3$ requires C, 52·6; H, 3·0%).

2-*Phenylethynylpyridine*, prepared (yield 68%) by the literature method,[8] had b. p. 106—108°/0·2 mm. (lit.,[8] b. p. 160—164°/3—4 mm.); it solidified and then formed prisms, m. p. 29—32°, from ether–light petroleum. The *picrate* formed needles, m. p. 152—153° (decomp.), from ethanol (Found: C, 56·4; H, 3·0%), and the *picrolonate* formed yellow needles, m. p. 165·5—166·5°, from ethanol (Found: C, 61·9; H, 4·1%).

4-*Phenylethynylpyridine* 1-*Oxides*.—The phenylethynylpyridine (0·01 mole) and perbenzoic acid in chloroform[10] (70 c.c. of 0·29M-solution) were kept at 20° for 2 days. The whole was digested at 50° with potassium carbonate (6 g.) and water (1 c.c.), and filtered, and the filtrate dried ($MgSO_4$). The oxide was recovered by evaporation.

4-*Phenylethynylpyridine* 1-*oxide picrate* crystallised in needles, m. p. 147·5—148·5°, from ethanol (Found: C, 53·9; H, 3·0. $C_{19}H_{12}N_4O_8$ requires C, 53·8; H, 2·9%).

4-*Styrylpyridine* 1-*Oxides*.—The methyl-, methoxy-, dimethylamino-, and chloro-compounds were prepared from the aldehyde, 4-picoline 1-oxide, and methanolic potassium methoxide by the method of ref. 2. The nitro-analogue was prepared by oxidation[2] of the nitrostyrylpyridine by peracetic acid.

We thank Dr. A. S. Bailey for his interest.

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[*Received, June 16th*, 1959.]

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[4] Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3452.

[5] Hammond and Reeder, *J. Amer. Chem. Soc.*, 1958, **80**, 573.

[6] Cf. discussion and references in ref. 4.

[7] Lukes and Ernest, *Coll. Czech. Chem. Comm.*, 1949, **14**, 678.

[8] Beyerman *et al.*, *Rec. Trav. chim.*, 1956, **75**, 68.

[9] Bax, Katritzky, and Sutton, *J.*, 1958, 1254.

[10] Duplessis-Kergomard and Bigou, *Bull. Soc. chim. France*, 1956, 486.