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2-(1-Bromovinyl) pyridine, 2-ethynyl pyridine, 2-(1-alkoxyvinyl) pyridines, and 2-(2-alkoxyvinyl) pyridines (the cis and trans isomers) were detected in the reaction mixture by mass spectrometry in the reaction of 2-vinyl pyridine with bromine with subsequent dehydrobromination of the addition product with an alcohol solution of alkali. The conditions for the preparation of chromatographically pure compounds were found.

It is known that the heteroatom in 2-vinylpyridine changes the properties of the double bond conjugated with the ring appreciably as compared with styrene [1]. In particular, when styrene is treated with halogens (chlorine or bromine) it gave a stable dihalo compound, the reaction of which with an alcohol solution of potassium hydroxide leads only to an α -halostyrene. Its subsequent dehydrohalogenation to phenylacetylene proceeds with considerably greater difficulty [2]. On the other hand, the reaction of 2-vinylpyridine with halogens leads to an unstable adduct, the dehydrohalogenation of which with an alcohol solution of alkali gives, according to the data in [3], 2-(1-alkoxyvinyl)pyridines (I). According to the data in [4], only a mixture of 2-(1-halovinyl)pyridine (II) and 2-ethynylpyridine (III) is formed in this case, whereas it is known [5] that III, in contrast to phenylacetylene, reacts readily with alcohols to give cis- and trans-2-(2-alkoxyvinyl)pyridines (IV and V).

In order to select the conditions for the preparation of pure alkoxyvinylpyridines I, we used chromatographic mass-spectral analysis to study the compositions and structures of the products of the reaction of 2-vinylpyridine with bromine in methanol (a), ethanol (b), and isopropyl alcohol (c) with subsequent treatment of the reaction mixtures with an alcohol solution of potassium hydroxide.

$$Py-CH=CH_{2} \xrightarrow{Br_{2}} [Py-CH-CH_{2} \cdot Br + Py-CH-CH_{2} - Br] \xrightarrow{KOH/ROH} Br OR$$

$$\rightarrow Py-CBr=CH_{2} + Py-C(OR)=CH_{2} + Py-C=CH + Py-C=C \xrightarrow{OR} + Py-C=C \xrightarrow{H} H + Py-C=C \xrightarrow{H} H$$

It was found that the principal reaction product (60-75% yield) in the case of equivalent amounts of 2-vinylpyridine, bromine, and potassium hydroxide (molar ratio 1:1:2) is II (Fig. 1). In addition, the corresponding 2-(1-alkoxyvinyl)pyridines (Ia-c) and very small amounts (3-10%) of 2-ethylpyridine were detected in the reaction mixture.

A 1.5-fold increase in the amount of alkali leads to the disappearance of II; however, the percentage of III increases somewhat in this case (Fig. 2) and new products — IVb and Va-c — appear. Their formation is probably explained by a secondary reaction of III with excess alcohol.

The mixture of Ia-c and Va-c cannot be separated by vacuum distillation. Vinyl ethers Ia-c and bromovinyl compound II also form an azeotropic mixture. Chromatographically pure II can be obtained only in the case of isopropyl alcohol and insufficient alkali.

Chromatographically pure Ia-c can be isolated from their mixtures with bromovinyl compound II only after refluxing the mixture with excess piperidine. The process is accompanied

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Fig. 1. Chromatogram of the reaction mixture in the case of reaction in ethanol and a 2-vinylpyridine:bromine:potassium hydroxide ratio of 1:1:2.



Fig. 2. Chromatogram of the reaction mixture in the case of reaction in ethanol and a 2-vinylpyridine:bromine:potassium hydroxide ratio of 1:1:3.



Ia-c and II $P_y - c = C \cdot \frac{H}{H^2}$										
Compound	R	bp, °C (mm)	UV spec- trum, λ_{max} , nm (log ε)	$v_{C=C}$ cm ⁻¹	PMR spec- trum, δ, ppm			Mass spectrum,* m/e (intensity in percent of	d_ 7%	
					1H	2 - 11	/ _{!-2}	the maximum peak)	Yie]	
la	OCH3	9394 (13)	250 (3,8)	1630— 1640	5,63	4,27	2,0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12	
ΙÞ	OC ₂ H ₅	98–-99 (13)	258 (3.75)	1630 1640	5,60	4,23	2,0	$ \begin{array}{c} 149 \ (20), \ 134 \ (72), \ 120 \ (20), \\ 166 \ (15), \ 105 \ (78), \ 104 \\ (50), \ 93 \ (12), \ 79 \ (100), \\ 78 \ (30), \ 66 \ (26), \ 65 \ (30), \\ 51 \ (14) \end{array} $	14	
lc	OCH (CH ₃) ₂	121 - 122 (13)	265 (3.82)	1630 1640	5,60	4,24	2,0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	
II	Br	103—104 (16)	-		6,60	5,56	2,0	185 (24), 183 (25), 106 (6), 105 (14), 104 (100), 78 (64), 51 (5)	15	

*Ions with intensities greater than 5% are presented. +Based on the 2-vinylpyridine.

by the formation of piperidine hydrobromide and considerable resinification; the unstable 2-(1-piperidylvinyl)pyridine is evidently formed in this case. The physical constants, yields, and properties of the compounds obtained are presented in Table 1.

The identification of Ia-c and II on the chromatograms was accomplished both from their mass spectra and by the method of internal standardization. However, III, Va-c, and IVb were identified only on the basis of an analysis of their mass spectra. The mass spectra of all Ia-c are characterized by low-intensity molecular-ion peaks, intense peaks of $[M - OR]^+$ ions (104),* and intense peaks of rearranged ions (79) (Table 1). More intense molecular-ion peaks (see the experimental section) and intense peaks of $[M - R]^+$ fragment ions (120) are characteristic for the mass spectra of Va-c. The peaks of the ions at 78 are more intense than the peaks of the ions at 79. The relative intensity of the molecular-ion peak in the mass spectrum of IVb is lower than in the case of Vb (Fig. 3), and the loss of a methyl or ethoxy group (ions at 134 and 120) proceeds more efficiently in the case of the trans

*Here and subsequently, the m/e values are presented for the ions.



isomer. On the other hand, the subsequent fragmentation of these ions (to give ion peaks at 104, 105, and 106) proceeds more energetically in the mass spectrum of the cis isomer. Compounds Ib and Vb have different retention times, whereas we were unable to completely separate Vb and IVb. However, in experiments with methanol and isopropyl alcohol we were unable to identify the presence of cis isomers in the reaction mixture at all.

It should be noted that the yields of chromatographically pure vinyl esters Ia-c based on the 2-vinylpyridine used in the reaction do not exceed 12-14% and that they are even lower in the case of the sterically hindered isopropyl alcohol. The position of the alkoxy group is rigorously proved by the PMR spectra, in which the characteristic quartet of two protons of a terminal methylene group is observed at weak field. As expected, their chemical shifts are virtually independent of the size of the alkoxy group. When the latter is replaced by the more electronegative bromine atom, considerable deshielding of the methylene protons is observed: the 1-H and 2-H signals undergo shifts of 1.0 and 1.3 ppm, respectively, to weaker field, which indicates that the electron density is reduced at the end of the vinyl group.

Thus the electron-acceptor pyridine ring activates the double bond attached to it appreciably, and this leads to considerable complication in the composition of the reaction mixture in the synthesis of 2-(1-alkoxyviny1)pyridines.

EXPERIMENTAL

Chromatographic mass-spectral analysis was carried out with a Varian MAT-111 (Gnom) apparatus; chromatography was accomplished with a column (l 1.5 m, d 3.4 mm) containing 3% Carbowax 20M on Chromosorb. The carrier gas was helium, and the flow rate was 15 ml/min; programmed heating of the column from 100 to 180°C at a rate of 10 deg/min was used. The mass spectra were recorded at an ionization energy of 80 eV. The PMR spectra of CC14 solu-



Fig. 3. Mass spectra of IVb and Vb recorded at the points indicated by arrows in Fig. 2.

TABLE 2. Mass Spectra of Va,c

Com- pound	m/e values (intensities of the peaks in percent relative to the maximum peak)*								
Va	135 (12), 134 (9), 120 (36), 119 (12), 107 (20), 106 (71), 105 (17), 104 (23), 93 (43), 92 (11), 79 (100), 78 (63), 66 (14), 65 (6), 51 (12), 66 (14), 65 (
Vc	$\begin{array}{c} 66 & (14), 65 & (6), 51 & (13) \\ 163 & (8), 148 & (21), 121 & (56), 120 & (100), 104 & (5), 93 & (17), 92 & (57), \\ 78 & (9), 66 & (5), 65 & (17), 51 & (6) \end{array}$								
	·								

*Ions with intensities greater than 5% are presented.

tions of the compounds were obtained with a Varian XL 100 spectrometer with hexamethyldisiloxane as the internal standard. The UV spectra of methanol solutions were recorded with a Cary-15 spectrophotometer. The IR spectra (films) were obtained with an IKS-22 spectrometer.

<u>General Method for the Synthesis of Ia-c.</u> Bromine [16 ml (0.3 mole)] was added with stirring and cooling with ice to a solution of 0.3 mole of 2-vinylpyridine in 200 ml of the appropriate alcohol, and the mixture was stirred for 1 h. It was then treated with a solution of 34 g (0.6 mole) of potassium hydroxide in 120 ml of hot alcohol, and the mixture was refluxed for 2 h. It was filtered, and the filtrate was evaporated. The residue was extracted with ether, the ether was removed from the extract, and the residue was vacuum distilled. The fraction obtained was refluxed for 15 min with 40 ml of piperidine and filtered, and the resulting precipitate was washed with ether. The filtrate was evaporated, and the residue was vacuum distilled. The yields and constants are presented in Table 1.

<u>2-(1-Bromoviny1)pyridine (II).</u> This compound was similarly obtained in isopropyl alcohol solution with 0.3 mole of potassium hydroxide, but refluxing with piperidine was excluded in this case.

The Ia-c and II obtained were 98- to 99%-pure according to gas-liquid chromatography. Compounds Va,c were not isolated in individual form but were identified from their chromatographic mass spectra (Table 2).

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