izer temperature of 150°C, and a carrier-gas (N_2) flow rate of 40 ml/min with a flame-ionization detector (see Table 1).

Effect of Various Catalysts of the Alkaline Type on the Thermolysis of the Azine of Methyl Benzyl Ketone. A 4-g (0.015 mole) sample of the azine was subjected to thermolysis in the presence of 0.003 mole of the catalyst. The catalyst was then removed from the reaction mixture, and the latter was chromatographed under the conditions indicated above. The pyrrole/pyrazole ratios in all of the chromatographed reaction mixtures were calculated with allowance for the coefficients of sensitivity of the detector to the given compounds, which were 1 and 0.57, respectively (Table 2).

Dependence of the Thermolysis of the Azines of Benzyl Alkyl Ketones on the Length of the Carbon Chain of the Alkyl Substituent. A 0.03-mole sample of the azine was subjected to thermolysis in the presence of 0.006 mole of sodium hydride. The quantitative ratio of the principal thermolysis products was determined by GLC (Table 1). The conditions for GLC of the products of thermolysis of azines Ia-c were similar to those described above, and the products of thermolysis of azine Ie were analyzed with a G-800 chromatograph [with a catharometer, column III, a column temperature of 240°C, a vaporizer temperature of 320°C, and a carrier-gas (H_2) flow rate of 40 ml/min].

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INDOLIZINES. 6.* RELATIVE REACTIVITIES OF ISOMERIC 6-, 7-, AND 8-ETHOXYCARBONYLINDOLIZINE DERIVATIVES

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The kinetics of the alkaline hydrolysis of 2-phenyl-6-, -7-, and -8-ethoxycarbonylindolizines were studied. The rate constants for the hydrolysis of these compounds and the indexes of the dissociation constants of 2-phenylindolizine-6-, -7-, and -8-carboxylic acids were determined by spectrophotometry. The indexes of the electronic structures and reactivities of 2-methyl-6-, -7-, and -8-ethoxycarbonylindolizines were calculated from theory.

In our preceding communications of this series [1-5] we described the syntheses of isomeric 6-, 7-, and 8-ethoxycarbonyl-2-methyl(aryl)indolizines and a qualitative study of the reactivities these compounds in some electrophilic substitution processes and in reactions with nucleophilic reagents. From the point of view of a study of the mutual effect of the pyrrole and pyridine rings in condensed systems and of the reaction of the indolizine

*See [1] for Communication [5].
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TABLE 1. Quantitative Characteristics of the Reactivities of Ethoxycarbonyl- and Carboxyindolizines

Compound	K, liter·mole/min	pK_a	Compound	pK_a
I	82,8±2,4	9,00±0,05	IV	6,17±0,05
II	53,6±3,7	9,95±0,05	V	6,60±0,08
III	34,0±1,1	8,85±0,05	VI	6,60±0,07

TABLE 2. Indexes of the Electronic Structures and Reactivities of Ethoxycarbonylindolizines

Compound	Position, i	q_π^i	f_π^i	F^i	$E_\pi(\beta)$	E_{UBMO} (β)	E_{LAMO} (β)
VII	1	1,184	0,237	0,483	14,573	0,380	−0,489
	3	1,198	0,270	0,539			
	5	0,897	0,123	0,532			
	7	1,005	0,133	0,460			
	8	1,011	0,108	0,446			
VIII	1	1,039	0,023	0,670	14,640	0,492	−0,465
	3	1,047	0,102	0,482			
	5	1,022	0,062	0,460			
	6	1,029	0,040	0,416			
	8	0,843	0,003	0,464			
IX	1	1,194	0,244	0,473	14,582	0,408	−0,406
	3	1,205	0,286	0,535			
	5	0,924	0,117	0,500			
	6	1,031	0,042	0,392			
	7	0,918	0,066	0,472			

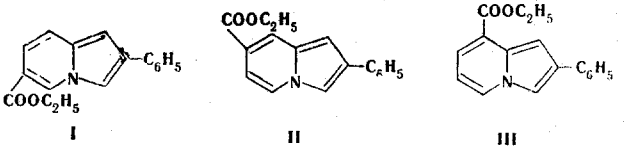
*Symbols: q_π^i are the indexes of the π-electron density, f_π^i are the electron densities of the boundary molecular orbitals, F^i are the free valence indexes, E_{UBMO} is the energy of the upper bonding molecular orbital, and E_{LAMO} is the energy of the lower antibonding molecular orbital.

system with the electron-acceptor ethoxycarbonyl group in the π-deficient fragment of the molecule, it seemed of interest to give a quantitative estimate of the relative reactivities of the investigated substances.

It was important to compare the reactivities of the ethoxycarbonyl groups as a function of their position in the indolizine and the transmission of the effect of these groups on the pyrrole portion of the two-ring system.

The reactivity of the ethoxycarbonyl groups was determined by measurement of the rate constants of their alkaline hydrolysis. The effect of the ethoxycarbonyl groups on the pyrrole portion of the indolizine molecules was estimated from the relative basicities of the compounds, since they are protonated at the C_3 position [1-5].

We used 6- (I), 7- (II), and 8-ethoxycarbonyl-2-phenylindolizines (III) as the compounds for the kinetic investigations. The kinetics of the alkaline hydrolysis of I-III were studied by means of a spectrophotometric method of analysis.



In the calculation of the hydrolysis rate constants (I) the process was regarded as a second-order reaction. We simultaneously determined the dissociation constants (pK_a) of the resulting isomeric 2-phenylindolizine-6- (IV), -7- (V), and -8-carboxylic acids (VI). The results and the previously measured [1, 5] relative basicity constants of I-III in nitromethane (ΔpK_a) are presented in Table 1.

It is apparent from Table 1 that the highest rates of hydrolysis of the ester group and the minimum pK_a values in the carboxylic acids that are formed in this case are observed for

TABLE 3. Volumes of Starting I-III and IV-VI Necessary for the Preparation of 50-ml Spectrophotometric Solutions of Model Mixtures

Model mixture No.	Volumes of the starting solutions, ml	
	I—III	IV—VI
1	8	0
2	7	1
3	5	3
4	4	4
5	3	5
6	2	6
7	0	8

the 6 isomers (I and IV). The possibility of delocalization of the effective positive charge that arises in the case of conjugation of the electron-acceptor ethoxycarbonyl and carboxyl groups in the 6 and 8 positions is lower than in the case of the 7 position. Both an examination of the possible resonance structures for these compounds and the results of a calculation of the energy and structural indexes that we carried out within the framework of the Hückel MO method (Table 2) lead to this conclusion.

The decrease in the frequency of the stretching vibration of the carbonyl group in II (ν = 1700 cm^{-1}) as compared with I and III (ν = 1710 cm^{-1}) and the bathochromic shift of 40 nm of the long-wave band in the UV spectrum (in ethanol λ = 380 nm for II and 340 nm for III) are evidence of an increase in the effect of conjugation in 7-ethoxycarbonyl-indolizines.

The electron-density deficit on the carbon atom of the carbonyl group of the substituent decreases due to the effect of conjugation in II and V. This leads to a substantial decrease in the rate of hydrolysis of ester II as compared with isomeric ester I and to a decrease in the acidity of the corresponding carboxyl derivative V as compared with IV. In addition to this, the effect of conjugation of the carbethoxy group in the 7 position leads to a considerable decrease in the π-electron density in the pyrrole fragment of the molecule (Table 2). As a consequence of this, the basicity of II decreases as compared with its isomers I and III, and its reactivity in reactions with "mild" electrophilic reagents in the Mannich and Vilsmeier reactions and in acylation decreases.

Despite the difference in the relative reactivities, the results of the calculation indicate, in conformity with the experimental data, that, regardless of the position of the ethoxycarbonyl group and the six-membered fragment of the molecule, electrophilic substitution reactions should be primarily directed to the 3 and 1 positions. An examination of the effects of conjugation in a series of ethoxycarbonylindolizines made it possible to assume that the rate constant for hydrolysis of 8-ethoxycarbonylindolizine and the ionization constant of the corresponding carboxylic acid should be close to the analogous values observed for the 6 isomers. However, in this case steric interactions between the ethoxycarbonyl group in the 8 position and the proton in the 1 "peri" position begin to manifest themselves. Steric hindrance in the 8-ethoxycarbonyl isomer can be distinctly observed in the case of the construction of the molecule of the compound with Stuart—Briegleb models. The steric effects that arise hinder the hydrolysis of the ester group, and the rate of this reaction is substantially lower for III than for I and II. The acidity of VI also decreases as compared with isomer IV.

EXPERIMENTAL

The methods used for synthesis and purification and the constants of the investigated compounds are presented in [1-3]. All of the UV spectra were recorded in cuvettes with a layer thickness of 1 cm with a Perkin—Elmer-402 spectrophotometer.

1. Study of the Kinetics of the Hydrolysis of the Isomeric Derivatives of Ethoxycarbonylindolizines I-III. A) Development of a Method for the Quantitative Determination of Ethoxycarbonylindolizines I-III in the Presence of the Corresponding Indolizinecarboxylic Acids (IV-VI). In connection with the low solubility of the compounds in water, it is ex-

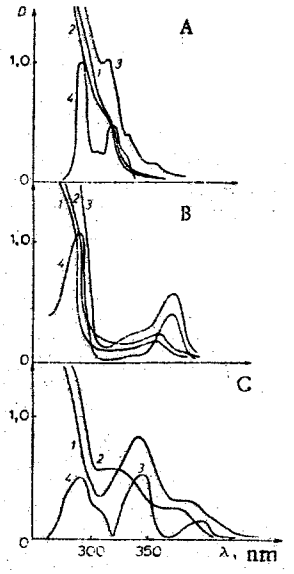


Fig. 1

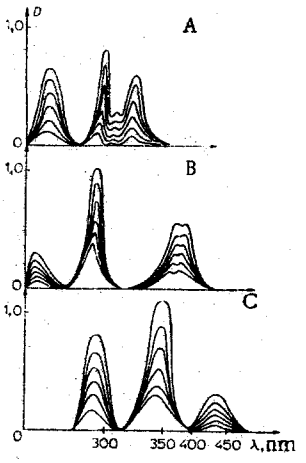


Fig. 2

Fig. 1. Spectra of 2-phenyl-6-, -7-, and -8-ethoxycarbonylindolizines (I-III) and 2-phenylindolizine-6-, -7-, and -8-carboxylic acids (IV-VI): A) 1) IV in sodium tetraborate solution; 2) IV in alkali solution; 3) I in sodium tetraborate solution; 3) IV in hydrochloric acid solution; 4) I in sodium tetraborate solution (the comparison solution was IV in sodium tetraborate solution); B) 1) V in sodium tetraborate solution; 2) V in alkali solution; 3) II in sodium tetraborate solution; 3) V in hydrochloric acid solution; 4) II in sodium tetraborate solution (the comparison solution was V in sodium tetraborate solution); C) 1) III in sodium tetraborate solution; 1) VI in hydrochloric acid solution; 2) VI in sodium tetraborate solution; 2) VI in alkali solution; 3) III in sodium tetraborate solution (the comparison solution was VI in sodium tetraborate solution); 4) VI in sodium tetraborate solution (the comparison solution was III in sodium tetraborate solution).

Fig. 2. Spectra obtained by recording solutions of model mixtures: A) I-IV (overall concentration $12.4 \cdot 10^{-5}$ mole/liter; B) II-V (overall concentration $7.7 \cdot 10^{-5}$ mole/liter); C) III-VI (overall concentration $25.2 \cdot 10^{-5}$ mole/liter).

pedient to monitor the hydrolysis of I-III by a spectrophotometric method in 81% (by volume) aqueous ethanol. In conformity with this, we studied the character of the UV spectra of I-VI over a broad pH range. Solutions of sodium hydroxide, sodium tetraborate, and hydrogen chloride in 81% aqueous ethanol were used as the media. The spectra are presented in Fig. 1. It is apparent from Fig. 1 that the character of the spectra make it possible to quantitatively determine esters I-III in the presence of the corresponding acids IV-VI and vice versa in solutions of sodium tetraborate and sodium hydroxide. Since special experiments showed that virtually no hydrolysis of esters I-III occurs in 0.001-0.002 M solutions of sodium tetraborate in 81% aqueous ethanol, the indicated solutions of sodium tetraborate were used in this research as diluents to slow down the hydrolysis. The virtually complete ionization of acids IV-VI in these solutions made it possible to develop a spectrophotometric method for the determination of the percentages of unsaponified esters I-III in the reaction mixtures

TABLE 4. Conditions for the Recording of the UV Spectra of Solutions of Model Mixtures

Mixtures	Wavelength intervals, nm		Wavelengths for the maxima (minima) of analytical significance
	for model mixtures 1-7 as recorded against model mixture 1	for model mixtures 1-7 recorded against model mixture 7	
I—IV	233—270	270—350	252, 317, 325
II—V	—	220—250, 270—297, 340—430	230, 385, 395, 402
III—VI	280—320	320—350	291, 346, 430

TABLE 5. Results of Statistical Treatment of the Data Obtained in the Recording of the Spectra of Solutions of Model Mixtures (a = 0, f = 5, α = 0.95 and t = 2.57 in All Cases)

Type of molecular mixture	Wavelength	Argument, mole/liter (c)	Slope, liters/mole (b)	Dispersion $\cdot 10^5$ $(s_0)^2$	Correlation coefficient (r)
I—IV	252	IV	5026±790	107,0	0,9908
	317	I	4948±310	18,0	0,9979
	325	I	2796±210	7,3	0,9979
II—V	230		4596±180	2,3	0,9994
	290		12802±1830	234,6	0,9923
	385	II	6843±330	7,7	0,9991
	395		5975±313	6,8	0,9990
	402		6316±200	2,9	0,9996
III—VI	296	VI	3202∓270	56,6	0,9972
	346	III	4441±180	13,1	0,9994
	430	III	1333∓57	2,5	0,9993

immediately after their dilution. To work out a method for the analysis of the mixtures of esters I-III with the corresponding acids IV-VI and to evaluate the reproducibility of the method, we prepared and thoroughly analyzed model mixtures. For this, accurately weighed samples of I and II (0.01 g) and III (0.02 g) and equimolar amounts of the corresponding acids IV-VI were placed in 50-ml volumetric flasks and dissolved in a 0.002 M solution of sodium tetraborate in 81% aqueous ethanol. The resulting starting solutions in the amounts indicated in Table 3 were placed in 50-ml volumetric flasks. The volumes of the resulting solutions of model mixtures were brought up to the mark with a 0.002 M solution of sodium tetraborate in 81% aqueous ethanol.

The spectra of the model mixtures were recorded at the wavelengths and under the conditions indicated in Table 4.

The spectra of solutions of model mixtures are presented in Fig. 2. The parameters of the linear dependences of the optical densities (D) on the concentrations of I-VI in solutions of model mixtures. The argument was selected in such a way that the correlation coefficient was positive. The parameters of the dependences of the form D = bc + a for the maxima that may be of analytical value are presented in Table 5.

On the basis of the results of statistical treatment of the experimental data (Table 5) we selected the analytical (working) wavelengths that are suitable for the spectrophotometric analysis of the reaction mixtures obtained in the hydrolysis of I-III with an accuracy sufficient for the calculation of the hydrolysis rate constants. The analysis of the two-component mixtures of 2-phenylethoxycarbonylindolizines with the corresponding 2-phenylindolizinecarboxylic acids can naturally be carried out in the same way under the condition of differential determination of the optical densities of two solutions of the mixture being analyzed with equal concentrations with 3 < pH < 9.

B) Kinetic Measurements. Accurately weighed samples of I-III were dissolved in 100 ml volumetric flasks in a solution of sodium hydroxide in 81% aqueous ethanol, the resulting solutions were poured into 5 ml ampuls, the ampuls were sealed and placed in a water-thermostat bath with forced circulation, and the temperature was maintained at 60°C until the process was complete with periodic selection of samples. Control ampuls to ensure the completeness of hydrolysis were maintained at 100°C in a boiling-water bath for 8 h. Samples for analysis were selected every 30-60 min in the course of 5-6 h. To stop the hydrolysis,

TABLE 6. Conditions for the Determination of Hydrolysis Rate Constants for I-III

Compound	Expt.	Molarity, moles · 10^4/liter: temp. °C	compound (a)	compound (b)	$\varphi = \frac{b}{a}$	Dilution, 0.02 mole/liter of sodium tetraborate, ml	Working wavelength, nm	No. of degrees of freedom	Hydrolysis rate constant (K), liter·moles/min (degree of reliability $\alpha = 0,95$)
I	1	60	8,322	94,00	11,295	3 to 25	317, 325	10	82,8±2,4
	2		7,700	87,43	11,354				
II	1	60	6,162	69,10	11,213	3 to 25	395, 402	10	53,6±3,7
	2		5,948	44,74	7,522				
III	1	60	30,87	206,0	6,673	1 to 25	291, 346	10	34,00±1,1
	2		75,34	206,0	2,734	1 to 50			

TABLE 7. Conditions and Results of Experiments for the Determination of the pK_a Values for IV-VI

Characteristics of the spectrophotometer solutions: analytical concn., mole/liter			pH			optical density at nm: 317	385	346	Calc. pK_a values		
IV	V	VI	IV	V	VI	IV	V	VI	IV	V	VI
$8,8 \cdot 10^{-5}$	$8,2 \cdot 10^{-5}$	$10,4 \cdot 10^{-5}$	2,50	2,50	2,50	0,329	0,250	0,672	—	—	—
			5,74	6,18	5,98	0,242	0,185	0,547	6,18	6,63	6,61
			5,88	6,41	6,34	0,217	0,150	0,442	6,17	6,59	6,62
			6,09	6,61	6,56	0,176	0,116	0,362	6,15	6,55	6,63
			6,35	6,84	6,73	0,130	0,095	0,289	6,16	6,63	6,61
			6,61	7,12	6,94	0,091	0,057	0,200	6,19	6,59	6,57
			6,77	7,47	7,25	0,063	0,030	0,113	6,14	6,60	6,56
			7,01	12,75	12,75	0,032	0	0	6,04	—	—
			12,75			0			—		

the ampuls (three samples) selected for analysis were cooled rapidly to 20°C, after which an aliquot of the solution from each ampul was diluted in a volumetric flask with a 0.002 M solution of sodium tetraborate in 81% aqueous ethanol.

The optical density of each of the series of solutions obtained in this way was determined by spectrophotometry. Solutions of completely hydrolyzed (at 100°C) or unhydrolyzed starting esters I-III were used as comparison solutions. The sodium hydroxide concentration in the starting solutions was determined by acidimetry (with 0.1 N HCl as the titrant). The conditions for conducting the kinetic experiments for the determination of the hydrolysis rate constants of I-III are presented in Table 6.

The rate constants were calculated from the equation

$$K = \frac{1}{\tau} \cdot \frac{1}{a-b} \cdot \ln \frac{b(a-x)}{a(b-x)}, \quad (1)$$

where K is the rate constant in liter·moles/min, τ is the hydrolysis time in minutes, a is the initial concentration of esters I-III in moles/liter, b is the initial concentration of sodium hydroxide in moles/liter, and x is the instantaneous concentration of the hydrolyzed product.

Since the optical density of each of the solutions of the series is measured with respect to the starting or completely hydrolyzed (control) solutions of the same series at a constant dilution, it may be assumed that the concentrations (c) of IV-VI or I-III in these solutions are linearly related to the measured optical densities (D), i.e.,

$$c = \alpha \cdot D, \quad (2)$$

where α is a coefficient that is constant for a given experiment and component and is expressed in liters/mole. In conformity with this, Eq. (1) takes on the form

$$K = \frac{1}{\tau} \cdot \frac{1}{\alpha \cdot D_{max}(1-\varphi)} \cdot \ln \frac{\varphi(D_{max} - D_\tau)}{\varphi D_{max} - D_\tau} \quad (3)$$

or the form

$$K=\frac{1}{\tau}\cdot\frac{1}{\alpha\cdot D_{max}(1-\varphi)}\cdot\ln\frac{\varphi D_\tau}{D_{max}(\varphi-1)+D_\tau}, \quad (4)$$

where $\varphi = b/a$, D_{max} is the maximum value of the optical density for a given kinetic experiment, and D_τ is the instantaneous optical density corresponding to the hydrolysis time in the course of τ minutes. Equations (3) and (4) are directly suitable for the calculation of the rate constants. However, Eqs. (3) and (4) are transformed in order to use them for calculations by the method of least squares, assuming that $y = \ln[\varphi(D_{max} - D_\tau)/(\varphi D_{max} - D_\tau)]$ or $\ln[\varphi D_\tau/(D_{max}(\varphi - 1) + D_\tau)]$. This resulted in the linear dependence

$$y=[K\cdot D_{max}\cdot\alpha\cdot(1-\varphi)]\cdot\tau=B\tau. \quad (5)$$

The estimate of the B coefficient found by the method of least squares [6] makes it possible to calculate not only the hydrolysis rate constant but also to estimate its confidence interval using the equation

$$K=\frac{B}{\alpha\cdot D_{max}\cdot(1-\varphi)}=\frac{B}{a(1-\varphi)}. \quad (6)$$

2. Estimation of the Dissociation Constants of 2-Phenylindolizine(6,7,8)-carboxylic Acids IV-VI. A) Preparation of the Working Solutions. A weighed sample of the compound was dissolved in a 50-ml volumetric flask in 81% aqueous ethanol (the principal solution), and aliquots of the principal solution were used for the preparation of a series of seven working solutions with equal concentrations of the investigated compound and various pH values lying in the ±0.6 pK_a range. Comparison solutions with pH 2.50 and 12.70 were similarly prepared. The solutions were prepared with 25-ml volumetric flasks. Dilution in the preparation of the working solutions was accomplished with aqueous alcohol buffer solutions containing 81% ethanol and prepared on the basis of an aqueous 0.5 M acetate buffer solution with pH 4.65, for which 20 ml of this solution was diluted in a 100-ml volumetric flask with 95% ethanol.

The 0.1 M acetate alcohol—water solution containing 81% ethanol had pH 6.71. The buffer solutions required for the measurement of the pK_a values were prepared by the addition of a few drops of 1 N aqueous solutions of sodium hydroxide or hydrochloric acid to the solution with pH 6.71. Solutions with pH 2.50 and 12.70 were prepared by dilution of 20 ml of 0.05 N solutions of sodium hydroxide or hydrochloric acid with 96% ethanol in a 100-ml volumetric flask.

B) Measurements. All of the pH measurements were made at 25°C with a pHM-26 pH meter (Radiometer, Denmark) with the use of an extended scale. The pH meter was calibrated with respect to aqueous buffer solutions. The pH values of the solutions subjected to spectrophotometry were measured immediately after the determination of their optical densities. The spectra were recorded in conformity with Table 4, since the spectra of undissociated IV-VI are virtually identical to the spectra of I-III (Fig. 1).

C) Calculations. The calculations of the pK_a values were made from the equation [7]

$$pK_a=pH\pm\lg\frac{D_I-D}{D-D_M}, \quad (7)$$

where pK_a is the index of the dissociation constant; pH, the hydrogen index of the solution undergoing spectrophotometry; D, the optical density of the solution undergoing spectrophotometry; D_I, the optical density of a solution of the investigated compound in the completely ionized form; and D_M, the optical density of a solution of the investigated compound in the molecular form.

The molar concentrations of the solutions with optical densities D, D_I, and D_M are equal. When $D_I > D_M$, the right-hand portion of the equation is a sum, whereas when $D_M > D_I$, the right-hand portion is a difference. The results of the calculations are presented in Table 7.

Since the optical densities in all cases were determined with the use of the solution with pH 12.75 as the comparison solution, in the calculation of the pK_a values from Eq. (7) it was assumed that $D_I - D = D_X$ and $D - D_M = D_{X\,max} - D_X$. This is an agreement with the case $D_I > D_M$.

The pK_a values found are presented in Table 1. The theoretical calculation of the indexes of the electronic structures and reactivities of 2-methyl-6-, -7-, and 8-ethoxycar-

bonylindolizines (VII-IX) was accomplished by the Hückel MO method with the use of the standard Pullman parameters.

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SYNTHESIS OF 6-ALKYLTHIOIMIDAZO[1,2-a]PYRIDINES

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UDC 547.785.5'825

A number of 6-alkylthio(and sulfonyl)-substituted imidazo[1,2-a]pyridines were synthesized by the reaction of 5-alkylthio- and 5-alkylsulfonyl-2-aminopyridines with ω-bromoacetophenone and α-chlorocyclohexanone in order to search for new compounds that have fungicidal activity. 5-Alkylthio-2-aminopyridines were obtained from the double salt of 5-mercapto-2-aminopyridine with $SnCl_2$ and HCl by reaction with alkyl halides or tert-C_4H_9OH and 75% H_2SO_4. 5-tert-Butylthio-2-aminopyridine was oxidized by means of $KMnO_4$ to 5-tert-butylsulfonyl-2-aminopyridine. A double salt was synthesized from 2-aminopyridine-5-sulfonic acid.

It has been shown [1] that 3-alkylthio-substituted imidazo[1,2-a]pyridines have significant fungicidal activity. In our search for more effective compounds of this series we decided to synthesize 6-alkylthioimidazo[1,2-a]pyridines with an alkylthio group in the pyridine ring rather than in the imidazole ring.

Our attempts to replace the bromine atom in 6-bromo-2-phenylimidazo[1,2-a]pyridine by an alkylthio group through the Grignard reaction (by the action of Mg or EtMgBr) or by exchange with Li and by the action of BuLi under various conditions were unsuccessful. In most cases the starting bromo compound was recovered. We were able to solve this problem by a different method, viz., by starting from 2-amino-5-alkylthiopyridines. The key compound — 2-amino-5-mercaptopyridine (I) was obtained in the form of a double salt with $SnCl_2$ and HCl from 2-aminopyridine-5-sulfonic acid. We were unable to obtain 2-amino-5-mercaptopyridine in the base form from salt I. 5,5'-Bis(2-aminopyridyl) disulfide (VIII) was obtained by the action of iodine in an alkaline medium on salt I.

5-Alkylthio-2-aminopyridines (II-IV, Table 1) were obtained by alkylation of salt I with alkyl halides in the presence of alkali. Very small amounts of dialkylated products were formed along with sulfides II-IV; the former were detected by thin-layer chromatography (TLC). In one case this product was isolated and characterized by conversion to the picrate. Its structure can be tentatively expressed by formula V. The indicated impurities are difficult to separate, but their presence does not prevent the use of sulfides II-IV for the preparation of 6-alkylthioimidazo[1,2-a]pyridines.

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