trans-3-Chloro-6-methyl-1,3-heptadien-5-one. $(CH_3)_2CHCOCH_D{=}CClCH_C{=}CH_AH_B$, bp 47°C (1 mm), n_D^{20} 1.5086, yield 48%. PMR spectrum: 1.05 (6H, d, $2CH_3$); 2.58 (1H, septet, CH); 5.63 (1H, d. d. d, A-H, J_{AC} = 10.0, J_{AB} = J_{AD} = 1.3 Hz); 6.0 (1H, split d, B-H, J_{BC} = 15.8 Hz); 6.47 (1H, m, D-H), 7.78 m. d. (1H, d. d, C-H). IR spectrum: 1555, 1608 (C=C-C=C), 1685 cm^{-1} (C=O). Found, %: C 60.5, H 6.5. $C_8H_{11}ClO$. Calculated, %: C 60.9, H 6.9.

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STABLE N-ACYL PYRIDINIUM AND BENZPYRIDINIUM SALTS AS ALKYLATING AGENTS

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The reaction of acyl chlorides with pyridinium bases and antimony pentachloride yields stable N-acyl salts that are efficient acylating agents. The kinetics of the reaction of N-acyl-pyridinium salts with p-nitroaniline was studied, and the reactivities of acylpyridinium cations and the ion pairs were determined.

The nucleophilic mechanism of acylation catalyzed by pyridinium salts assumes the intermediate formation of N-acylpyridinium salts as the active acylating agents [1]. But until now there have been no quantitative data to characterize the acylating capability of most such salts; this is evidently due to their extreme sensitivity to traces of moisture which makes it very laborious to work with them. The exceptions are the relatively stable N-acyl salts of 4-N,N-dimethylaminopyridine, the acylating capability of which has been studied [2].

A communication has recently appeared on the synthesis of N-acetyl-, propionyl-, and benzylpyridinium hexafluoroantimonates by acylation of pyridine with solutions of carboxonium salts in SO_2 [3]. N-nitro- and N-nitrosopyridinium fluoroborates have been synthesized analogously [4]. Detailed syntheses of stable N-acyl imidazole salts have been described [5].

We have obtained stable N-acyl pyridinium (Ia-c), quinolinium (IIa-c), isoquinolinium (III), and acridinium (IVb, c) salts and have studied their acylating capability. These salts were synthesized as described in [6], by the successive addition to acyl halide solution of equivalent amounts of pyridinium base and antimony pentachloride at −50°C. The compounds thus obtained are shown in Table 1.

In the IR spectrum of the synthesized substance a strong absorption band is observed in the region 1780-1815 cm^{-1} of the vibrational valency of the carbonyl group of an acyl residue. The position of this band indicates the linkage of the acyl residue with the quarternary nitrogen atom.

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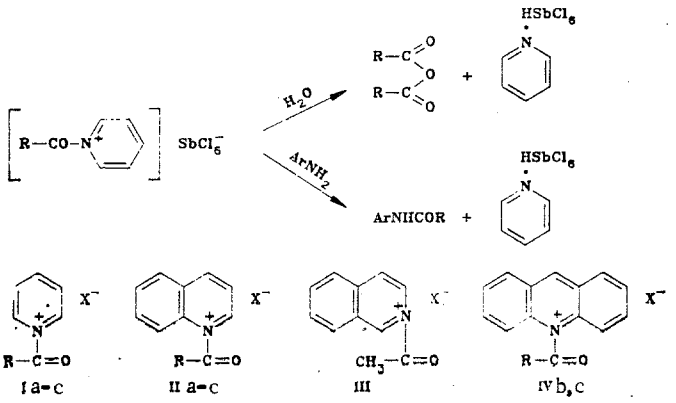
TABLE 1. N-Acyl Pyridinium and Benzypyridinium Salts I-IV

Compound	mp, °C	$\nu_{C=O}$, cm^{-1}	Found, %			Empirical formula	Calculated, %		
			C	H	N		C	H	N
Ia	177—179	1826	18,7	2,2	3,3	$C_7H_8Cl_6NOSb$	18,4	1,8	3,1
Ib	126—127	1783	27,6	2,1	2,9	$C_{12}H_{10}Cl_6NOSb$	27,8	1,9	2,7
Ic	190—192	1795	26,3	1,3	2,7	$C_{12}H_9Cl_7NOSb$	26,1	1,6	2,5
IIa	228—230	1815	26,5	2,4	2,4	$C_{11}H_{10}Cl_6NOSb$	26,1	2,0	2,8
IIb	218—220	1786	33,6	2,0	2,6	$C_{16}H_{12}Cl_6NOSb$	33,8	2,1	2,5
IIc	227—230	1790	32,1	1,8	2,5	$C_{16}H_{11}Cl_7NOSb$	31,9	1,8	2,3
III	132—135	1813	25,8	1,9	2,9	$C_{11}H_{10}Cl_6NOSb$	26,1	2,0	2,8
IVb	182—185	1780	38,3	2,6	2,0	$C_{20}H_{14}Cl_6NOSb$	38,8	2,3	2,3
IVc	202—205	1790	37,0	2,4	2,1	$C_{20}H_{13}Cl_7NOSb$	36,8	2,0	2,1

These compounds are high-melting crystalline materials that are quite stable in air and in acetonitrile or methylene chloride solution. When water is added to their solutions the respective anhydride and quaternary pyridinium salt are formed. They are active acylating agents. They react with p-nitroaniline and aniline to form the respective anilides quantitatively:

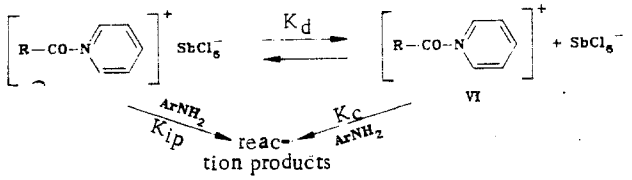


I, II, IV a R=CH_3, b R=C_6H_5, c R=p-ClC_6H_4; $X^-=SbCl_6^-$

The acylating capability of compounds Ia, b was estimated quantiatively from a spectrophotometric study of the kinetics of their reaction with p-nitroaniline (V) in acetonitrile at 25°.

Conductometric measurements were carried out using a differential transformer bridge [7]. A thermostated cell with platinum plane-parallel electrodes covered with platinum black was used for the measurements. Solvent purity was monitored conductometrically [8].

The dissociation constants were calculated from the concentration dependence of electrical conductivity by the methods of Shedlovsky [9] and Fuoss, Onsager, and Skinner [10] using an EC-1022 computer. The two methods gave similar results. The kinetic and conductometric data are shown in Table 2. It can be seen that the rate constants increase as salt concentration decreases. The evident explanation is that in polar acetonitrile (ε = 36.1) the N-acyl salts dissociate to form reactive cations:



The data are unequivocal evidence that in this case the only acylating agent is the acylpyridinium cation (VI); very probably this is related to the substantial shielding of the reactive center of the salt by the bulky anion.

EXPERIMENTAL

IR spectra were obtained with a Specord-75 IR instrument, in mineral oil between KBr plates.

TABLE 2. Reaction of N-Acylpyridinium Salts (Ia, b) with p-Nitroaniline in Acetonitrile at 25°

Compound	c, mole/liter	K_2, liter/mole·sec	K_C, liter/mole·sec	K_d, mole/liter
Ia	0,03	0,0118	0,040±0,002	0,079±0,003
	0,02	0,0160		
	0,01	0,0210		
	0,005	0,0288		
	0,0025	0,0360		
Ib	0,02	0,0117	0,012±0,001	0,097±0,003
	0,015	0,0138		
	0,0125	0,0154		
	0,0067	0,0172		

*For compounds Ia, b $K_{ip} = 0$. K_{ip} and K_C are respective rate constants of the ion pair and the acylpyridinium cation. The observed second-order rate constant K_2 is determined by the Acree equation [11]; $K_2 = K_C\alpha + K_{ip}(1 - \alpha)$, where α is degree of dissociation of salt.

Typical Procedure for Synthesis of N-acylpyridinium Hexachloroantimonates. To a solution of 0.05 mole of acyl chloride in 50 ml of absolute chloroform was added a solution of 0.05 mole of pyridine base in 20 ml of chloroform dropwise with stirring and cooling to −50°C. Then to the reaction mixture was added a solution of 0.05 mole of freshly distilled antimony pentachloride in 30 ml of chloroform and the mixture was stirred for another hour. The precipitate was filtered off and washed with chloroform and absolute petroleum ether. The yield was quantitative.

The course of the reaction was monitored spectrophotometrically at 365 nm according to the decrease in concentration of p-nitroaniline V, under pseudo first order conditions with respect to compound V, i.e., $c_{salt} >> c$. The reaction obeys second order kinetics. The observed rate constants were calculated by the equation

$$K_2 = \frac{1}{a \cdot t} \ln \frac{D_0 - D_\infty}{D_t - D_\infty},$$

where D_t, D_0, and D_∞ are the optical densities of the solution at time t, at the initial moment, and at the completion of the reaction, respectively.

The linear functions were calculated by the least squares method [12].

Solutions were prepared by the volumetric-weight method with subsequent dilution. Electrical conductivity of the solutions was measured over the $5 \cdot 10^{-2}$-$1 \cdot 10^{-4}$ mole/liter concentration range at 25°. Thermostating was carried out in a water thermostat with 0.02° precision. In view of the high hygroscopicity of the salts, solution preparation, conductivity measurements, filling of spectrophotometer cuvettes, and sampling were carried out inside a box carefully dried with phosphorus pentoxide. Measurements were carried out within 5 h after solvent purification.

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INTRAMOLECULAR CATALYTIC CYCLIZATION OF SUBSTITUTED 2-ALKENYLANILINES

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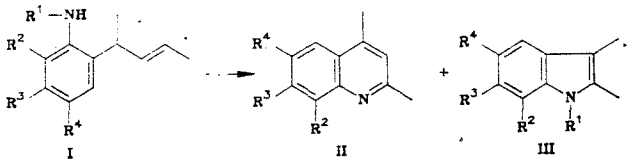
A study was carried out on the effect of the nature and structure of the substituent in the aromatic ring of 2-(1-methyl-2-butenyl)anilines on the direction and structural selectivity of the their intramolecular cyclization to derivatives of quinoline and indole by the action of catalytic amounts of $PdCl_2$ or $PdCl_2$—$(DMSO)_n$ complexes.

Transition metal complexes are rather commonly used in the synthesis of heterocyclic compounds [1, 2]. In particular, derivatives of indole and quinoline are obtained from N- and 2-alkenylarylamines by the action of palladium and nickel catalysts [3, 4]. In most cases, these reactions require stoichiometric amounts of the catalysts. We have recently developed an efficient method for the preparation of indole and quinoline derivatives by the intramolecular cyclization of N- and 2-(1-methyl-2-butenyl)anilines by the action of catalytic amounts of $PdCl_2$—$(DMSO)_n$.

In a continuation of an investigation of the intramolecular cyclization of alkenylarylamines and to expand the use of this method, we studied the effect of the substituent in the aromatic ring and at the nitrogen atom of 2-alkenylamilines on the direction of the intramolecular cyclization by the action of $PdCl_2$ complexes and $PdCl_2$—$(DMSO)_n$ in nitrobenzene. In the 2-alkenylaniline series studied (see Table 1), the nature of the substituents in the aromatic ring affects the direction and structural selectivity of the intramolecular cyclization and a mixture of the corresponding quinolines II and indoles III is formed in each experiment. The yield and composition of the reaction mixture depends significantly on the structure of the starting anilines. Thus, for example, the presence of a methyl or methoxy group at C-4 of the 2-alkenylanilines facilitates the predominant formation of quinolines II. The quinoline content in the reaction mixture is about 70% in this case. The yield of indole derivatives increases upon the introduction of substituents at C-5 and C-6 in the aromatic ring. However, we should note that the fraction of the quinolines is significantly greater in both cases. Unsubstituted and 4,6-dimethyl-substituted 2-(1-methyl-2-butenyl)anilines cyclize upon the action of catalytic amounts of $PdCl_2$ or $PdCl_2$—$(DMSO)_n$ with the formation of a mixture of equal amounts of quinolines II and indoles III.



The conversion of 2,6-di(1-methyl-2-butenyl)aniline (IV) in the presence of these catalysts at 180°C over 2 h to 2,4-dimethyl-8-(1-methyl-2-butenyl)quinoline (V) proceeds with high selectivity in 65% yield.

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