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Abstract

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ON THE NATURE OF 1-ACYLPYRIDINIUM CHLORIDES

(Presented by Academician M. I. Kabachnik on 10 III 1964)

The opinion is widespread that pyridine and other tertiary amines serve in acylation reactions only to bind the hydrogen chloride that is formed and do not thereby enter into interaction with acid chlorides. However, a large number of kinetic studies ([1]) have proved the formation of addition products of acid halides to pyridine as active intermediate compounds. The participation of these compounds in many reactions is also confirmed by the fact that the final products in them are 1-acyl-1,4-dihydropyridines ([2–4]).

It may be expected that such intermediate compounds are acylpyridinium salts. Until recently, the existence of acylammonium salts

$$[\mathrm{RCO}-\overset{+}{\mathrm{N}}\mathrm{R^1R^2R^3}]\,\mathrm{A}^-,$$

in which a quaternary nitrogen atom is located next to the carbonyl group, was considered unlikely.

Attempts to acylate tertiary amines usually lead to amine hydrochlorides and ketenes ([5]), while protonation or alkylation of N,N-dialkylamides occurs at oxygen, as was proved with the aid of IR and NMR spectra ([6,7]). The structure of the adducts of acid chlorides and pyridine obtained in a number of works ([8–11]) was not established because of the extreme instability of these compounds under ordinary conditions. There are two points of view on the nature of such compounds. According to one of them, the adducts of acid chlorides and pyridine are built according to the type of molecular compounds of pyridine ([1]); according to the other, they are ordinary pyridinium salts ([12]) (II).

I II

pyridine ring $\quad$ pyridinium ring

$$N\cdots C(O)R-Cl \qquad N^{+}-C(O)R\ \ Cl^{-}$$

For the purpose of studying the structure of these compounds, we synthesized a series of acylpyridinium chlorides, most of which were obtained for the first time (Table 1). The synthesis was carried out in anhydrous petroleum ether or diethyl ether at −65 to −78° in an atmosphere of carefully dried nitrogen. Pyridine, being present in excess, even at such low temperatures is a dehydrochlorinating agent; therefore the reaction should be carried out in an excess of acid chloride. This was achieved by slowly adding a cooled solution of pyridine to a solution of the acid chloride; the reverse order of addition of the reagents, used by many authors, leads to the formation of pyridine hydrochlorides.

The stability of acylpyridinium compounds depends to a considerable extent both on the nature of the acyl residue and on the presence of substituents in the pyridine ring. In the case of chlorides of aliphatic acids the compounds are the less stable the longer the acyl residue. With chlorides of substituted benzoic acids, the products of addition of pyri-

stable only in the presence of electron-acceptor substituents in the benzene ring; the compounds of benzoyl chloride and *p*-methoxybenzoyl chloride with pyridine, formed at −78° as a white curdy precipitate, decomposed at room temperature. In this case the substance obtained was identified without isolating it from the solution, by means of polarography.

Table 1

No.	R	M.p., °C	Found, % Cl	Found, % N	Empirical formula	Calculated, % Cl	Calculated, % N
1	CH_3	104–107 (sealed cap.)	22.70 22.54	8.63 8.47	C_7H_8ClNO	22.54	8.88
2	C_2H_5	108–109 (sealed cap.)	19.97 20.2	8.01 7.95	$C_8H_{10}ClNO$	20.70	8.16
3	C_3H_7	110–114 (sealed cap.)	19.87 19.71	7.56 7.32	$C_9H_{12}ClNO$	19.13	7.05
4	*n*–NO_2–C_6H_4	200–202	12.98 13.05	10.02 10.25	$C_{12}H_9ClN_2O_3$	13.23	10.61

No.	R	M.p., °C	Found, % Cl	Found, % N	Empirical formula	Calculated, % Cl	Calculated, % N
5	3,5–$(NO_2)_2C_6H_3$	100–112	11.25	11.73	13.01	$C_{12}H_8ClN_3O_5$	11.47	13.57
6	*n* = Cl–C_6H_4	185–187	27.44	27.53	5.87	5.76	$C_{12}H_8Cl_2NO$	27.95	5.51

All acylpyridinium compounds in pyridine solution show a characteristic polarographic reduction curve with two waves; the potential of the first half-wave is $\sigma^{1/2} = 0.7 \div 0.9$ V, and of the second $\sigma^{1/2} = 1.3 \div 1.7$ V, which apparently corresponds to their initial reduction to 1-acyl-1,4-dihydropyridines and further to 1-acylpiperidines. The course of the polarographic curve is analogous to the reduction curves of 1-alkylpyridinium salts (13)*.

The same data were also obtained in the polarography of mixtures of benzoyl chloride or *p*-methoxybenzoyl chloride with pyridine, which indicates the formation of acylpyridinium salts in these cases as well.

The considerable stability of benzoylpyridinium chlorides with electron-acceptor substituents, and the instability of those with electron-donor substituents, contradicts the concept of the molecular nature of these compounds, since it is known that such pyridine compounds are the less stable the more electron-accepting the substituent at the nitrogen is. Data on the high electrical conductivity of 1-acetylpyridinium chloride in liquid SO_2 argue in favor of assigning the compounds under consideration to salts (14).

This is also indicated by their complete insolubility in nonpolar solvents (ether, petroleum ether) and good solubility in polar solvents (pyridine, liquid SO_2, dimethyl sulfoxide).

Confirmation of the salt-like structure of the acylpyridinium compounds was obtained by us in studying their IR spectra. As can be seen from Fig. 1, in the spectra of all the salts an intense absorption band is observed in the region 1790–1802 cm^{-1}, attributable to stretching vibrations of the carbonyl group, but elevated by approximately 100 cm^{-1} in comparison with the frequencies of the carbonyl group in amides and other similar compounds. This indicates the presence, next to the carbonyl, of a group possessing strong electron-acceptor properties. Such a group in the compounds studied is the ring nitrogen atom bearing a positive charge.

An anomalous increase in the frequency of the carbonyl group in similar cases has also been observed by other authors who investigated an acylammonium salt

* The polarograms were recorded in a solution of absolute pyridine under a

Fig. 1

Figure 1: Fig. 1

stream of dry nitrogen on a 7-77 instrument (Hungary), relative to a mercury pool.

$[C_6H_5CO-\overset{+}{N}(C_2H_5)_3][SbCl_6]^-$ (15) and acetyl- and propionylpyridinium chlorides (6).

The carbonyl absorption in the region of 1800 cm^{-1}, observed in the compounds studied by us, does not coincide with the characteristic absorption of the acid chlorides of the corresponding acids (1760–1780 cm^{-1}), of the acids themselves (1690–1700 cm^{-1}), or of their salts with pyridine (1518 cm^{-1}). The spectra of the compounds studied

Fig. 1

and in other frequency regions also differ strongly from the spectra of the compounds listed above. It follows from this that the molecules of the substances under study do not contain acid chlorides bound by any coordination bonds to pyridine (1).

Thus, the totality of all the data, including the spectral data, permits the conclusion that the compounds under study are acylpyridinium salts.

Experimental Part

1-Acylpyridinium chlorides were obtained by the gradual addition of a solution of 0.1 mole of dry pyridine in 20 ml of thoroughly dried petroleum ether to a solution, cooled to $-65 \div -78^\circ$, of 0.1 mole of acid chloride in 40 ml of petroleum ether. The precipitated white solid was filtered off, washed several times with ether, and dried. The yield of the salt was almost quantitative. All operations were carried out in a glove box in an atmosphere of dry nitrogen. Compounds 4 and 5 (Table 1) were recrystallized from absolute chloroform; the others were purified by repeated washing with ether,

with benzene or petroleum ether. IR spectra were recorded on an H-800 instrument; samples were prepared in a glove box under a stream of dry nitrogen in the form of a paste with vaseline oil.

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Note: Figure translations are in progress. See original paper for figures.