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SYNTHESIS AND INTRAMOLECULAR ELECTRON INTERACTIONS IN TETRACHLORO-4-PYRIDYLCARBONIMIDOYL DICHLORIDE AND ITS DERIVATIVES

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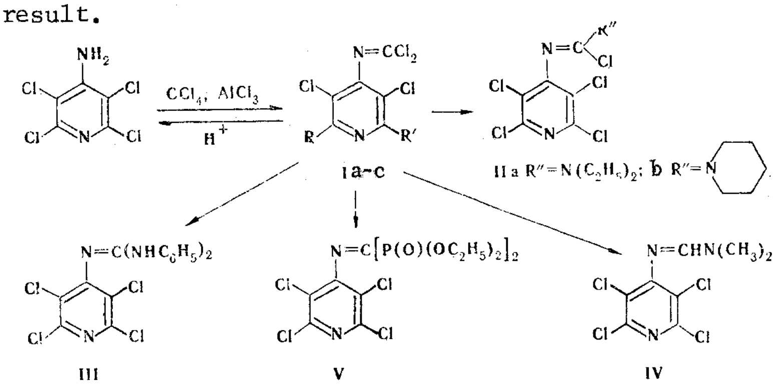
Tetrachloro-4-pyridylcarbonimidoyl dichloride was synthesized, and products of the reaction of the latter with amines, triethyl phosphite, and dimethylformamide (DMF) were obtained; acid hydrolysis was also carried out. The character of the intramolecular interactions beteen the π system of the pyridine ring and the C=N bond was investigated by IR spectroscopy.

It is known that the amino group in aminopolyhalopyridines has low nucleophilicity and in most cases is not involved in reactions. This inertness can be overcome by converting the amines to reactive iminothionyls [1] or to imidoyl dichlorides. In the present paper we describe a simple method for the preparation of polychloropyridylcarbonimidoyl dichlorides (Ia-c). We also investigated some properties of the compounds obtained.

The reaction of 4-amino-2,3,5,6-tetrachloropyridine with refluxing CCl_4 in the presence of $AlCl_3$ leads to the formation of Ia in high yield. Imidoyl dichloride Ia reacts readily with amines at room temperature to give IIa,b. It should be noted that only one chlorine atom undergoes substitution upon reaction with diethylamine and N-trimethylsilylpiperidine. We were unable to carry out the reaction at two chlorine atoms at higher temperatures and in excess amounts of these amines. However, disubstitution product III was obtained by the action of aniline on imidoyl dichloride Ia at room temperature. We were unable to obtain a monosubstitution product using aniline hydrochloride or even N-trimethylsilylaniline.

The known formamidine IV is formed when Ia is heated in dimethyl formamide (DMF); however, no reaction occurs with dimethyl sulfoxide (DMSO) under similar conditions.

The reaction of imidoyl chloride Ia with triethyl phosphite proceeds quite smoothly and leads to the formation of a product of the Arbuzov reaction (V). The acidic hydrolysis of Ia takes place readily upon heating in alcohol, and the starting 4-amino-2,3,5,6-tetrachloropyridine is formed as a result.



I a R=R¹=Cl; b R=Cl, R¹=CCl₃; c R=H, R¹=CCl₃

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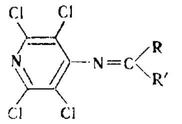
TABLE 1. Frequencies and Integral Intensities ($\nu_{C=N}$ and ν_a) of Tetrachloropyridylimidoyl Dichloride and Its Derivatives*



R	R'	$\nu_{C=N}$, cm^{-1}	A(C=N) · 10^3 liters/(mole-cm^2)	A(ν_a) · 10^3 liters/(mole-cm^2)
Cl	Cl	1662	52,1	23,2
Cl	$N(C_2H_5)_2$	1651	84,3	42,7
Cl	NC_5H_{10}	1651	152,8	70,0
H	$N(CH_3)_2$	1650	126,0	69,0
C_6H_5NH	C_6H_5NH	1648	100	—†

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*For 2,3,5,6-tetrachloro-4-methylpyridine, A(ν_a) = 11.5·10^3.
†Measurements were not made because of superimposition of other bands.

TABLE 2. Characteristics of Ib,c IIb, and III

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	Cl	N		C	H	Cl	N	
Ib	73—74	—	—	70,9	6,9	$C_7Cl_8N_2$	—	—	71,7	7,0	79
Ic	67—68	—	—	68,6	7,5	$C_7HCl_7N_2$	—	—	68,7	7,7	81
IIb	125—126	36,7	2,7	—	11,5	$C_{11}H_{10}Cl_5N_3$	36,5	2,8	—	11,6	80
III	205—207	50,7	2,8	33,5	13,1	$C_{18}H_{12}Cl_4N_4$	50,7	2,8	33,3	13,1	66

In the IR spectra of tetrachloropyridylimidoyl dichloride derivatives it is of interest to examine two characteristic absorption bands, one of which (at 1650-1680 cm^{-1}) is related to the C=N stretching vibration, while the second at 1580 cm^{-1} corresponds to the skeletal vibrations of the pyridine ring. 4-Substituted pyridines can be regarded as p,p'-disubstituted benzenes [2] if the heteroatom is assumed to be a pseudosubstituent. With respect to its form, the vibrations at 1580 cm^{-1} is similar to the ν_8 vibration of benzene, and the intensity of this band is a measure of the interaction of the ring π system with the substituent in the 4 position. According to the data in [3], the character of the intramolecular interactions in 4-substituted tetrahalopyridines differs little from that of the corresponding pyridines, and this provides a basis (for the compounds presented in Table 1) to link the degree of interaction between the pyridine ring and the imidoyl chloride fragment with the magnitude of the integral intensity (A) of the band at 1580 cm^{-1}. The introduction of an imidoyl chloride fragment increases the intensity of this band substantially as compared with 4-methyltetrachloropyridine. The integral intensity of this band as substituents R and R^1 are varied changes symbatically with A(C=N), i.e., the polarization of the C=N bond also increases as the degree of interaction of the substituent with the ring increases. However, we were unable to obtain strict correlations between the σ constants of substituents R and R^1 and the integral intensity, evidently because of the superimposition of various electronic and steric effects.

EXPERIMENTAL

The IR spectra of solutions (∿0.1 mole/liter) of the compounds in CCl_4 were recorded with a Specord IR-71 spectrometer. The accuracy in the measurement of the integral intensities was 10%.

2,3,5,6-Tetrachloro-4-pyridylcarbonimidoyl Dichloride (Ia). A 4.63-g (2 mmole) sample of 4-aminotetrachloropyridine [4] was dissolved in 50 ml of dry CCl_4, 5 g of $AlCl_3$ was added, and the mixture was refluxed for 2 h. It was then cooled, decomposed with water, and extracted with CCl_4. The extracts were dried with $CaCl_2$, the CCl_4 was evaporated in vacuo, and the residue was crystallized from aqueous alcohol to give 5.4 g (86%) of a product with mp 85-86°C. Found: Cl 67.5; N 8.9%. $C_6Cl_5N_2$. Calculated: Cl 68.2; N 9.0%.

Compounds Ib, c (see Table 2) were similarly obtained.

N^2-(2,3,5,6-Tetrachloro-4-pyridyl)-N,N'-diethylcarbonimidoyl Chloride (IIa) A) A 2-ml sample of diethylamine was added to a solution of 1.56 g (5 mmole) of Ia in 20 ml of dichloroethane, and the mixture was refluxed for 3 h. It was then cooled, treated with water, acidified with HCl, and extracted with dichloroethane. The extract was dried with $CaCl_2$, and the solvent was evaporated to give 1.3 g (75%) of a product with mp 80-81°C (from aqueous ethanol). Found: C 34.8; H 3.1; N 12.1%. $C_{10}H_{10}Cl_5N_3$. Calculated: C 34.3; H 2.9; N 12.0%.

B) This compound was similarly obtained in 82% yield from Ia and Me_3SiNEt_2.

Compounds IIb and III were similarly isolated.

N^1,N^1-Dimethyl-N^2-(2,3,5,6-tetrachloro-4-pyridyl)formamidine (IV). A 1.56-g (5 mmole) sample of Ia was dissolved in 10 ml of DMF, and the solution was refluxed for 3 h. It was then cooled and diluted with 50 ml of water, and the resulting precipitate was removed by filtration to give 1.31 g (91%) of a product with mp 125-126°C (from aqueous alcohol) (mp 98-99°C [1]). Found: C 33.6; H 2.4; Cl 49.6; N 14.6%. $C_8H_7Cl_4N_3$. Calculated: C 33.5; H 2.4; Cl 49.5; N 14.6%.

Bis(diethoxyphosphonyl)-N-(2,3,5,6-tetrachloro-4-pyridyl)methaneimine (V). A mixture of 3.13 g (10 mmole) of Ia and 5 ml of triethyl phosphite was evaporated, and the residue was distilled in vacuo at 185°C (0.09 mm) to give 4.8 g (93%) of a product with mp 141-143°C (from heptane—benzene). Found: Cl 26.7; P 12.1%. $C_{14}H_{20}Cl_4N_2O_6P_2$. Calculated: Cl 27.5; P 12.0%.

4-Amino-2,3,5,6-tetrachloropyridine. A 20-ml sample of concentrated HCl was added to a solution of 1.56 g (5 mmole) of Ia in 20 ml of propyl alcohol, and the mixture was refluxed for 8 h. The alcohol and part of the hydrochloric acid were removed by distillation to give a product with mp 212°C (from heptane). No melting-point depression was observed for a mixture of this product with a genuine sample.

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