PROTONATED FORMS OF N-VINYLPYRROLES

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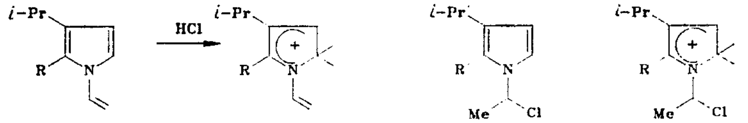
UDC 547.742:541.682'55:543.422.25

The reaction of N-vinylpyrroles with hydrogen chloride at low temperatures has been studied. At −80°C the α-position of the heterocycle is protonated while at higher temperatures products of HCl addition to the double bond and protonation of the ring are formed. The C—Cl bond of the chloroethyl radical of the product of HCl addition to the vinyl group is readily dissociated resulting in reversible interconversion of the enantiomers of the racemic mixture which is formed. By introducing a diastereotopic marker (i-Pr) this interconversion can be monitored by dynamic NMR. It has been found that the energy of this process varies with HCl concentration and with the substituents on the ring.

In the last ten years, N-vinylpyrroles, previously almost unknown, have acquired importance as promising monomers and building blocks in heterocyclic chemistry [1-3]. The impetus for this came from the recent discovery and rapid development of a new general and highly efficient synthesis of pyrroles and N-vinylpyrroles by the reaction of ketoximes with acetylene in the super-base medium KOH-DMSO [1, 2].

N-Vinylpyrroles are particularly susceptible to electrophilic attack. Under the influence of acids they form polymers or dimers in which both the pyrrole ring and the vinyl group participate [2, 3]. Similarly, their acid-catalyzed hydrolysis generally involves two of the nucleophilic centers. Although N-vinylpyrroles add certain electrophiles at the vinyl group, their acylation proceeds at the α-position of the pyrrole ring [2]. Cations formed from N-vinylpyrroles in the presence of acids can be widely used in the construction of new heterocyclic systems. Progress in this area is, however, held back by the absence of fundamental information on the structure and reactivity of protonated forms of N-vinylpyrroles. This factor also contributes to the more general problem of pyrrole polycondensation and the synthesis of conductive materials based on polypyrroles [4].

The present work is devoted to a study, by proton NMR, of the reaction of N-vinylpyrroles (I) with anhydrous HCl in CD_2Cl_2 at low temperatures and the interconversion of the protonation products:



Ia,b IIa,b IIIa,b IVa,b

I–IV a R=Me; b R=Ph

The isopropyl group in pyrroles Ia and b serves as a diastereotopic marker: its methyl groups become nonequivalent at low temperatures when HCl is added to the double bond forming a chiral center $^{*}CHClCH_3$. The substituents R (Me, Ph) were selected for the considerable difference in their induction, resonance, and steric effect on the adjacent carbocation center.

Carrying out the reaction with excess HCl at −80°C led to σ-complexes IIa and b. Subsequent increase in the temperature of the samples (in the NMR sample chamber) to −30°C was accompanied by addition of HCl to the double bond (σ-complexes IVa and b). If the reaction were carried out at −40°C, however, only the adducts IVa and b were formed; with the ratio [HCl]:[I] = 1:1 addition products to the vinyl group were observed (IIIa and b; Fig. 2).

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 24, No. 3, pp. 334-338, March, 1988. Original article submitted September 24, 1986.

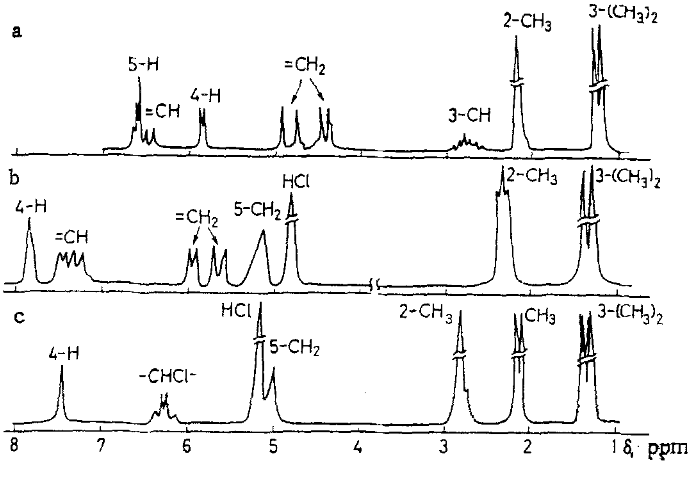


Fig. 1

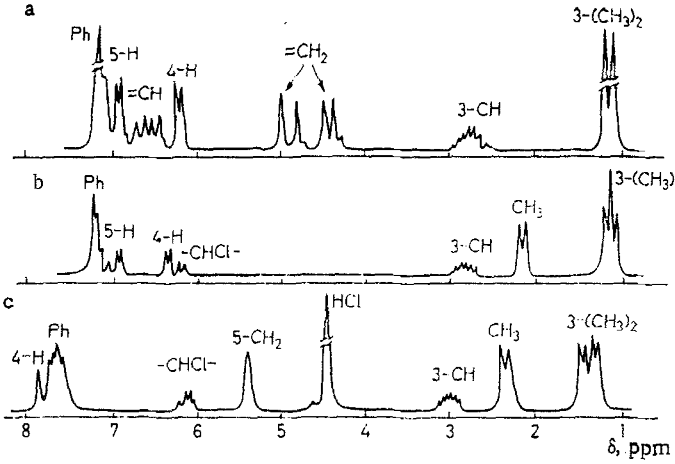
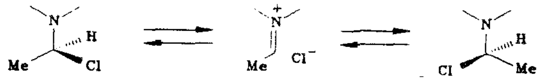


Fig. 2

Fig. 1. Proton NMR spectra. a) Compounds Ia,b; b) IIa with excess HCl at −80°C; c) IVa with excess HCl at −40°C.

Fig. 2. Proton NMR spectra. a) Compound Ib; b) IIIb, c) IVb with excess HCl at −40°C.

The methyl groups of the isopropyl radical in compounds III and IV are nonequivalent (Fig. 1c, 2b,c). On increasing the temperature of the sample these signals broaden and then blend into a single doublet which indicates the interconversion of the enantiomeric forms in the racemic mixture formed by addition of HCl to the vinyl group (degenerate dℓ ⇄ ℓd racemization) proceeding via the splitting off of a chloride ion:



The condition necessary here for the coalescence of the signals is a rapid (on the NMR scale) inversion of configuration of the asymmetric carbon which can take place either intramolecularly or intermolecularly (substitution by chloride ions from the solution). The temperature dependence of the spectra is reversible.

Since the initial species have a positive charge the stage preceding dissociation is deprotonation and the overall process can be described by the scheme:

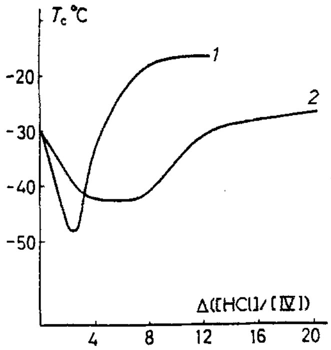


Fig. 3.

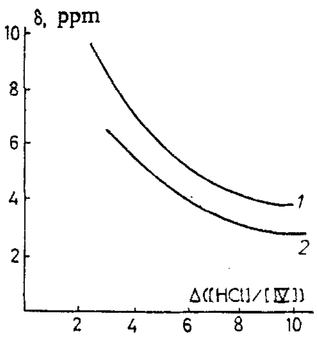


Fig. 4

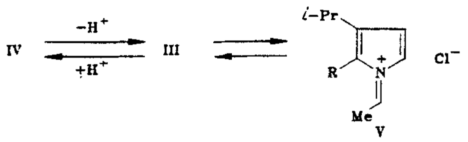
Fig. 3. Variation of the coalescence temperature of the methyl group signals in the spectra of IVa (1) and IVb (2). The points at Δ = 0 relate to IIIa and IIIb.

Fig. 4. Variation of chemical shift of the HCl signal with concentration in the spectra of IVa (1) and IVb (2).

TABLE 1. Variation of the Activation Energy of Enantiomerization with the Excess HCl Content of the Solution

Δ	$R^1=CH_3$			Δ	$R^1=C_6H_5$		
	T_c, °C	$\Delta G^{\neq}$, kJ/mole	$\rho_{HCl_2^-}$		T_c, °C	$\Delta G^{\neq}$, kJ/mole	$\rho_{HCl_2^-}$
0*	−30	53,9	—	0*	−30	53,9	—
2,6	−48	50,3	0,66	3,4	−42	49,1	0,46
3,0	−46	51,6	0,64	4,8	−42	49,1	0,40
3,6	−36	53,7	0,60	7,5	−42	49,1	0,27
4,8	−28	55,6	0,46	9,8	−35	50,7	0,25
6,9	−19	58,7	0,36	12,0	−30	51,8	0,22
8,5	−17	58,8	0,32	15,0	−28	52,2	0,20

*This value corresponds to IIIa,b not protonated on the ring.



It was discovered that the coalescence temperature of the methyl group signals changes considerably depending on the concentration of the excess HCl (Δ) in the solution (Fig. 3).

The minimum observed on the curves shows that at relatively low concentrations of HCl the equilibrium III ⇄ IV, catalyzed by hydrogen chloride, predominates in the overall process. A similar electrophilic catalysis of the racemization of 1-phenylethylchloride has been described [5]. Its catalytic action arises from the formation of hydrogen bonds with the chlorine atom of the substituent. At higher HCl concentrations the equilibrium shifts towards the protonated form IV and this hinders the dissociation of the 1-chloroethyl group.

Comparison of the concentration dependencies of the coalescence temperatures, and the activation energies for the overall process calculated from these temperatures for the 2-methyl (IVa) and 2-phenyl (IVb) derivatives, reveals the following features: 1) energies of activation for the same ratio of HCl and I are 4-8 kJ/mole higher for IVa than for IVb; 2) the minimum on the curve of derivative IVb is considerably more diffuse than that for IVa; 3) the emergence of the plateau where further addition of HCl has no effect on the energy parameters of the process occurs at a very much lower HCl concentration for IVa than for IVb.

All these features are explained by the lower stability of the cation, i.e., the greater strength of the CH-acid of IVb in comparison with IVa.

In fact, the facile deprotonation of complex IVb must lower the overall activation energy of the enantiomorph exchange. At the same time, for suppression of the deprotonation of complex IVb a higher concentration of HCl is required, whence also the diffuse minimum, which is the region of concentration in which the catalyzing action of the hydrogen chloride gives place to an inhibiting effect.

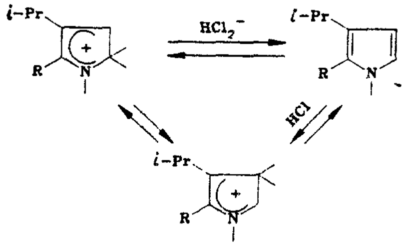
The coincidence of the coalescence temperatures for compounds IIIa and b demonstrates the very weak direct effect of the substituent at $C_{(2)}$ on the ionic dissociation of the C—Cl bond. Consequently, its effect on the overall process is realized at the stage of the III $\rightleftarrows$ IV equilibrium within the limits of the relative stability of the IVa and b cations.

The position of the signal of the excess HCl in the NMR spectra of the cations varies considerably with its concentration (Fig. 4). In a study of the reaction of triethylamine with hydrogen chloride [6] the formation of the salt $[(C_2H_5)_3NH]^+ \cdot HCl_2^-$ was demonstrated. The formation of the complex HCl_2^- anion has also been detected in the racemization of 1-phenylethyl chloride catalyzed by HCl [5]. The chemical shift of the HCl signal which we observed reflects the ratio of concentrations of HCl and HCl_2^-. Making use of the well-known formula for the chemical shift of an averaged signal [7]

$$\delta = \delta_{HCl}\rho_{HCl} + \delta_{HCl_2^-}\rho_{HCl_2^-},$$

where ρ_{HCl} and $\rho_{HCl_2^-}$ are the fractions of the corresponding particles in equilibrium, and the chemical shifts δ_{HCl} and $\delta_{HCl_2^-}$ are equal to −0.7 and 14.0 ppm [6], we calculated the HCl_2^- content of the solutions (Table 1).

In the region of $\rho_{HCl_2^-} = 0.7$ to 0.5 at temperatures of −40 to −10°C the signals, first of the 5-CH_2 group and then of the 4-H proton, in the spectrum broaden and merge with the averaged signal of HCl—HCl_2^-. This demonstrates the existence of intermolecular exchange with participation of the HCl_2^- anion and formation of β-protonated particles, although their concentration is low compared to that of the α-protonated form:



Here, the HCl_2^- procures the splitting off of a proton from a ring CH_2 group and the HCl formed protonates the more reactive 4 position [8]; the VI cation which is obtained rearranges into the thermodynamically stable cation IV.*

EXPERIMENTAL

NMR spectra were run on a BS 567A spectrometer (100 MHz). Reaction of vinylpyrroles with HCl was carried out directly in the NMR tube, cooled to −40 to −80°C by acetone + dry ice. A current of dry HCl was passed into a 0.5 M solution of vinylpyrrole in CD_2Cl_2 until the required concentration was obtained, monitored by integration of the NMR signals.

LITERATURE CITED

1. B. A. Trofimov and A. I. Mikhaleva, Khim. Geterotsikl. Soedin., No. 10, 1299 (1980).
2. B. A. Trofimov and A. I. Mikhaleva, N-Vinylpyrroles [in Russian], Nauka, Novosibirsk (1984).
3. B. A. Trofimov, L. V. Morozova, and A. I. Mikhaleva, Usp. Khim., 54, 1034 (1984).
4. A. F. Diaz and K. K. Kanazava, Extended Linear Chain Compounds, Vol. 3, Plenum Press, New York—London (1983).
5. Y. Poker, W. A. Mueller, F. Naso, and G. Tossi, J. Am. Chem. Soc., 80, 5012 (1964).
6. J. Gousseau, L. Gouin, L. U. Jones, G. Judie, and J. A. Smith, J. Chem. Soc., Faraday Trans. 2, 69, 1821 (1974).

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*This question will be considered in detail in a separate article.

7. W. A. Thomas, Annu. Rev. NMR Spectrosc., 3, 113 (1970).
8. R. A. Jones and G. P. Bean, The Chemistry of Pyrroles, Academic Press, New York (1977).

PORPHYRINS.

23.* SYNTHESIS AND PROPERTIES OF ETHANEBISPORPHYRINS

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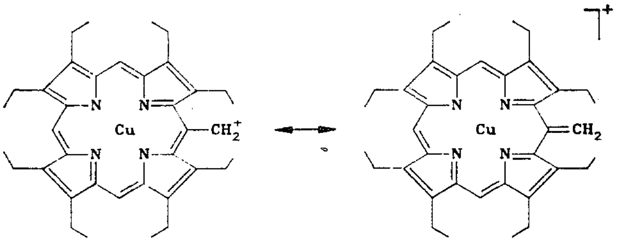
UDC 547.749'156.2.07:543.422.25

It has been shown that copper complexes of meso-hydroxy(alkoxy)methylporphyrins in trifluoroacetic acid readily dimerize to give copper complexes of ethanebisporphyrins. Selective removal of one copper atom from the dimer molecule has been achieved. The previously unknown conversion of ethanebisporphyrins to ethylenebisporphyrins has been found to take place.

It was shown previously [2] that copper complexes of meso-hydroxymethylporphyrins when protonated with trifluoroacetic acid (TFA) or gaseous HCl in solutions of dichloroethane or chloroform form a stabilized carbocation of type I, which readily reacts with nucleophiles to form the corresponding addition products. At the present time carbocations of a similar type are widely used for forming a large variety of substituents around the periphery of the porphyrin ring [3, 5].



We have found that in TFA medium in the absence of nucleophilic reagents, carbocations of copper porphyrin complexes undergo new conversions, as a result of which the main reaction products are dimeric porphyrins. Thus, when the copper complex of meso-hydroxymethyloctaethylporphyrin II is dissolved in TFA, after 5-10 min dimeric complexes III and IV are formed. The ratio of dimers varies according to the concentration of initial complex II in the reaction mixture. When changing from dilute solvents, where the ratio of dimers is 1:1, to concentrated solvents, the reaction is shifted in favor of the formation of dimer III. When the reaction mixture is treated with concentrated H_2SO_4, dimer IV decomposes and the yield of free bisporphyrin V reaches 50-55%.

The formation of bisporphyrin VII was previously detected by Johnson and coworkers [6] by prolonged heating of the nickel complex of meso-hydroxymethyloctaethylporphyrin in DMF in the presence of catalytic amounts of sulfuric acid. A determining role in dimerization is thought to be played by the central nickel atom. During reaction it changes to a trivalent state and transfers one electron to the macrocycle, thus converting it to a radical capable of dimerizing. One of the arguments in favor of such a reaction mechanism was the low yield (12%) of dimeric product III from copper complex II, since transfer of an electron from the central copper atom is questionable.

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*For Communication 22, see [1].

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