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Abstract

Full Text

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STRUCTURE OF SCHIFF BASES OF N-ARYLPYRROLINES

In the reaction of α-(2-chloroethyl)-β-chlorocrotonaldehyde I with aqueous solutions of hydrochlorides of aromatic amines ($ArNH_2 \cdot HCl$), we obtained Schiff bases of N-arylpyrrolines (ShOP) (^{1}). The structure of ShOP may be represented by two formulas (II) and (III).

$$\begin{gathered} CH_3{-}C(Cl){=}C(CH_2CH_2Cl){-}C({=}\,O)H \\ \text{(I)} \\ \downarrow\ ArNH_2 \cdot HCl \\ \text{(II)} \quad \text{(III)} \end{gathered}$$

$$(Ar =: \text{a) } C_6H_5,\ \text{b) } n\text{-}CH_3C_6H_4,\ \text{c) } n\text{-}CH_3OC_6H_4,\ \text{d) } n\text{-}C_2H_5OC_6H_4,\ \text{e) } n\text{-}BrC_6H_4 \\ \text{f) } n\text{-}NO_2C_6H_4,\ \text{g) } m\text{-}NO_2C_6H_4,\ \text{h) } \alpha\text{-}C_{10}H_7,\ \text{i) } (C_2H_5)_2NC_6H_4)$$

A more detailed study of the reaction of I with $ArNH_2 \cdot HCl$ made it possible to note certain features. In the reaction of I with hydrochlorides of aniline or of aromatic amines containing electron-acceptor substituents in the nucleus, the formation of a single, principal reaction product was observed. In the reaction of I with $ArNH_2 \cdot HCl$ containing electron-donor substituents in the nucleus, the formation, along with the principal product, of a side reaction product was observed and proved by chromatography on aluminum oxide; the amount of this product for different amines varies from 3 to 20%. The principal and side reaction products in each individual case were separated chromatographically on aluminum oxide. The data of elemental analysis of each pair of separated substances confirm the identity of these compounds. On this basis it may be assumed that the principal and side reaction products are either cis-trans isomers with respect to the newly formed C=N bond, or the isomeric compounds II and III.

Hydrogenation of IIa in methanol over Raney Ni led to the formation of a mixture of reaction products. From this mixture, along with the normal product of complete hydrogenation of ShOP, products of ShOP cleavage at the C=N bond

Reaction scheme: compound (IIa) hydrogenates to compounds (IV), (VI), and (V).

Figure 1: Reaction scheme: compound (IIa) hydrogenates to compounds (IV), (VI), and (V).

NMR spectrum plot.

Figure 2: NMR spectrum plot.

were isolated: aniline and N-phenylalkylpyrrolidine with the formula $C_{12}N_{17}N$. The NMR spectrum of N-phenylalkylpyrrolidine, recorded in carbon tetrachloride on a JNM-C-60 NMR spectrometer (60 MHz), showed the presence in this compound of two methyl groups, i.e., established the structure of the resulting N-phenylalkylpyrrolidine as N-phenyldimethylpyrrolidine V (Fig. 1). Thus, on the basis of the NMR spectrum, and also on the basis—

On the basis of structure I it may be considered proven that the synthesized Schiff bases of pyrrolines (the main reaction products) have structure II. The structure of the by-products of the reaction of I with ArAH is subject to further investigation.

Experimental Part

All Schiff bases of pyrrolines (SBP) were obtained by a single procedure (Table 1—main reaction products; Table 2—by-products of the reaction). In most cases the SBP were isolated as hydrochlorides, from which the bases were then obtained and characterized as picrates. In those cases where the SBP hydrochlorides were noncrystallizing oils, the SBP were obtained as bases, bypassing the stage of isolation of the corresponding hydrochlorides.

Hydrochlorides of SBP. To a concentrated aqueous solution of the hydrochloride of an aromatic amine (ArAH), I was added dropwise with shaking (the molar ratio I : ArAH was 1 : 2.2). After all of I had been added, the reaction mixture was shaken for another 30–40 min and left for 24 h at room temperature. The precipitate of the SBP hydrochloride was filtered off, washed with a small amount of cold water and ether, and recrystallized several times from water or from aqueous solutions of methanol or ethanol. For analysis it was dried in vacuo over P_2O_5 with heating.

Fig. 1. NMR spectrum of 2,3-dimethyl-1-phenylpyrrolidine

SBP bases were obtained by treating aqueous solutions of recrystallized SBP hydrochlorides with a dilute solution of sodium hydroxide; if necessary, they were reprecipitated from acetone or methanol with water and dried in vacuo over KOH (without heating). In those cases where the SBP hydrochloride separated as a noncrystallizing oil, the aqueous layer was carefully decanted, the oily residue was dissolved in methanol or acetone, diluted with a large amount of water, and treated with dilute sodium hydroxide solution. The precipitated greenish-yellow precipitate of the SBP base was filtered off, washed with a large amount of water, and reprecipitated from acetone or methanol with water. It was dried in vacuo over KOH (without heating).

Table 1

Compound No.	Ar	Derivatives	Yield, %	m.p., °C	P_f acetic acid : petr. ether	R_f benzene : acetone	Found, % C	Found, % H	Found, % N	Found, % Cl	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % Cl
II_a	C_6H_5	Hydrochloride	96.7	217–218			72.36	[illegible]	[illegible]	11.44	$C_{18}H_{18}N_2 \cdot HCl$	72.36	6.41	9.38	11.87
II_a	C_6H_5	Base	96.7	105	0.53 (1 : 1)	0.36 (4 : 1)					$C_{18}H_{18}N_2$				
II_a	C_6H_5	Picrate	96.7	227–228			58.78	[illegible]	[illegible]	14.25	$C_{18}H_{18}N_2 \cdot C_6H_3N_3O_7$	[illegible]	4.31	14.25	
II_b	n-$CH_3C_6H_4$	Hydrochloride	quant.	203–205					8.47	[illegible]	$C_{20}H_{22}N_2 \cdot HCl$			8.57	10.85
II_b	n-$CH_3C_6H_4$	Base	quant.	114–115	0.50 (1 : 1)	0.30 (4 : 1)					$C_{20}H_{22}N_2$				
II_b	n-$CH_3C_6H_4$	Picrate	quant.	218–219			60.12	[illegible]	[illegible]	13.44	$C_{20}H_{22}N_2 \cdot C_6H_3N_3O_7$	[illegible]	4.85	13.48	
II_v	n-$CH_2OC_6H_4$	Base	81.2	149–150	0.20 (1 : 1)	0.14 (4 : 1)					$C_{20}H_{22}N_2O_2$				
II_v	n-$CH_2OC_6H_4$	Picrate	81.2	201–202			56.56	[illegible]	[illegible]	12.94	$C_{20}H_{22}N_2O_2 \cdot C_6H_3N_3O_7$	[illegible]	4.57	12.70	
II_g	n-$C_2H_5OC_6H_4$	Base	71.4	149–150	0.08 (1 : 1)	0.16 (2 : 3)					$C_{22}H_{26}N_2O_2$				
II_g	n-$C_2H_5OC_6H_4$	Picrate	71.4	199–199.5			58.19	[illegible]	[illegible]	12.01	$C_{22}H_{26}N_2O_2 \cdot C_6H_3N_3O_7$	[illegible]	5.04	12.08	
II_d	n-BrC_6H_4	Hydrochloride	96.2	200–201			47.34	[illegible]	[illegible]	16.10	$C_{18}H_{16}N_2Br_2 \cdot HCl$	[illegible]	3.65	6.24	
II_d	n-BrC_6H_4	Base	96.2	164–165	0.70 (1 : 1)	0.40 (9 : 1)					$C_{18}H_{16}N_2Br_2$				
II_d	n-BrC_6H_4	Picrate	96.2	203–204					10.60	10.47	$C_{18}H_{16}N_2Br_2 \cdot C_6H_3N_3O_7$			10.79	
II_e	n-$NO_2C_6H_4$	Hydrochloride	90.2	201–203			55.62	[illegible]	[illegible]	14.62	$C_{18}H_{16}N_4O_4 \cdot HCl$	[illegible]	4.41	14.41	

Compound No.	Ar	Derivatives	Yield, %	m.p., °C	P_f acetic acid : petr. ether	R_f benzene : acetone	Found, % C	Found, % H	Found, % N	Found, % Cl	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % Cl
II_e	n-$NO_2C_6H_4$	Base	90.2	167–168	0.71 (1 : 1)	0.82 (4 : 1)					$C_{18}H_{16}N_4O_4$				
II_e	n-$NO_2C_6H_4$	Picrate	90.2	198–199					16.95 16.83		$C_{17}H_{16}N_4O_4 \cdot C_6H_3N_3O_7$			16.87	—
II_{zh}	m-$NO_2C_6H_4$	Hydrochloride	90.0	208–209			55.65 55.43	[illegible]	14.30 14.51		$C_{18}H_{16}N_4O_4 \cdot HCl$	55.62	4.41	14.41	
II_{zh}	m-$NO_2C_6H_4$	Base	90.0	157–159	0.69 (1 : 1)	0.80 (4 : 1)					$C_{18}H_{16}N_4O_4$				
II_{zh}	m-$NO_2C_6H_4$	Picrate	90.0	187–188					16.93 17.02		$C_{18}H_{16}N_4O_4 \cdot C_6H_3N_3O_7$	49.57	3.29	16.87	
II_z	α-$C_{10}H_7$	Base	77.8	80–85	0.75 (1 : 1)	0.95 (4 : 1)					$C_{26}H_{22}N_2$				
II_z	α-$C_{10}H_7$	Picrate	77.8	97–100			64.60 64.23	4.38 4.21	11.86 11.75		$C_{26}H_{22}N_2 \cdot C_6H_3N_3O_7$	64.95	4.26	11.84	
II_i	n-$(C_2H_5)NC_6H_4$	Picrate		186–188*			60.40 60.32	6.28 6.15	15.51 15.33		$C_{26}H_{36}N_4 \cdot C_6H_3N_3O_7$	60.63	6.20	15.47	

* Mixture of the main and by-product.

Table 2

By-products of Schiff bases of pyrrolines

Ar	Derivatives	Yield,* %	m.p., °C	R_f, acetone : petr. ether	R_f, benzene : acetone	Found, % C	Found, % H	Found, % N	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N
n-$CH_3C_6H_4$	Base	3–5	129–130	0.80 (1 : 1)	0.93 (4 : 1)				$C_{20}H_{22}N_2$			
n-$CH_3C_6H_4$	Picrate		229.5–230			60.00	5.18		$C_{20}H_{22}N_2 \cdot C_6H_3N_3O_7$	60.12	4.85	

Ar	Derivatives	Yield,* %	m.p., °C	R_f, acetone : petr. ether	R_f, benzene : acetone	Found, % C	Found, % H	Found, % N	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N
n-$CH_3OC_6H_4$	Base	10	176–177	0.68 (1 : 1)	0.66 (4 : 1)				$C_{20}H_{22}N_2O_2$			
n-$CH_3OC_6H_4$	Picrate		162			56.79 56.72	4.48 4.57		$C_{20}H_{22}N_2O_2 \cdot C_6H_3N_3O_7$	56.62	4.57	
n-$C_2H_5OC_6H_4$	Base	18–20	148–149	0.59 (1 : 1)	0.88 (2 : 3)				$C_{22}H_{26}N_2O_2$			
n-$C_2H_5OC_6H_4$	Picrate		154–155			57.95 57.80	5.18 5.13	12.08 12.06	$C_{22}H_{26}N_2O_2 \cdot C_6H_3N_3O_7$	58.01	5.04	12.08

* Of the total amount of isolated mixture of ShOP.

Picrates of ShOP were obtained in ether, recrystallized from methanol or from aqueous methanol or ethanol solutions, and dried in vacuum over P_2O_5 with heating.

Hydrogenation of IIa. 7.8 g of IIa were dissolved in methanol, Raney Ni catalyst was added, and the mixture was hydrogenated in a duck-shaped vessel at room temperature until hydrogen absorption ceased (until the solution became decolorized). After hydrogenation was complete, the catalyst was filtered off, methanol was distilled off, the residue was diluted with water and steam-distilled. The distillate was extracted with ether, the ether extracts were dried over fused KOH, the ether was distilled off, and the residue was fractionated in vacuum. 1.05 g (38%) of aniline and 2.15 g (41.3%) of V were obtained. B.p. 130–131°/10 mm, d_4^{20} 0.971, n_D^{20} 1.5600, MR_D 58.34, calculated 55.76.

Found, %: C 82.26, 82.01; H 9.81, 9.92; N 7.96, 8.04
$C_{12}H_{17}N$. Calculated, %: C 82.22; H 9.78; N 7.99

The residue after steam distillation was extracted with ether, the ether extracts were dried over fused KOH, the ether was distilled off, and the residue was distilled in vacuum. 2.30 g (28.9%) of IV was obtained. The oil is light yellow in color. B.p. 213–215°/4 mm. In the IR spectrum there are bands of the NH group in the region 3404–3409 cm^{-1}.

Found, %: C 81.20, 81.03; H 8.59, 8.53; N 10.68
$C_{18}H_{22}N_2$. Calculated, %: C 81.16; H 8.32; N 10.52

Benzoyl derivative–m.p. 128–129° (from isooctane).

Found, %: C 81.05, 80.99; H 7.21, 7.23; N 7.35
$C_{25}H_{26}N_2O$. Calculated, %: C 81.04; H 7.07; N 7.56

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

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