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CONDENSATION REACTIONS AT THE METHYLENE GROUP OF 1-(4-NITROPHENYL)-PYRROLIN-2-ONE AND 1-(4-NITROPHENYL)-PYRROLIN-2-ONIUM PERCHLORATE

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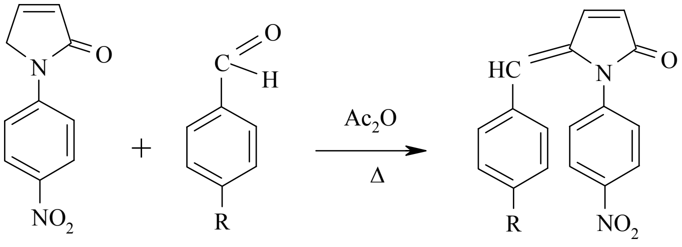
The interaction has been investigated of 1-(4-nitrophenyl)pyrrolin-2-one with aromatic aldehydes in acetic anhydride in the presence of catalytic amounts of pyridine. 1-(4-Nitrophenyl)pyrrolinium perchlorate has been synthesized and was put into a condensation reaction with aromatic aldehydes. As a result 5-arylidene-1-(4-nitrophenyl)pyrrolin-2-onium perchlorates were obtained.

Keywords: aromatic aldehydes, 1-(4-nitrophenyl)pyrrolin-2-one, 1-(4-nitrophenyl)pyrrolinonium perchlorate, condensation.

The interaction of 1-(4-nitrophenyl)pyrrolin-2-one (**1**) with aromatic aldehydes **2a-d** has been investigated.

Carrying out the reaction in ethyl alcohol in the presence of sodium ethylate, and also attempts to use acetic acid as solvent led to heavy resinification of the reaction mixture.

A positive result was obtained on carrying out the reaction in a medium of acetic anhydride at an equimolar ratio of reactants in the presence of a catalytic amount of pyridine at 80±5°C.



1 **2a–d** **3a–d**

2, 3 **a** R = H, **b** R = NO_2, **c** R = NMe_2, **d** R = Br

On increasing the temperature an increase of the resinification of the reaction mixture was observed. A change in the molar ratio of reactants to 1:2 or 1:3 did not affect the yield of the desired product.

The purity of the synthesized compounds **3a-d** was checked by TLC. The structure was demonstrated by ^{1}H NMR and IR spectra and was confirmed by data of elemental analysis (Tables 1-3).

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TABLE 1. Characteristics of Compounds **3a-d**

Compound	Empirical formula	Found, % Calculated, %			mp, °C	R_f*	Yield, %
		C	H	N			
3a	$C_{17}H_{12}N_2O_3$	68.74 69.86	3.98 4.11	11.04 9.59	110	0.63	43
3b	$C_{17}H_{11}N_3O_5$	60.92 60.53	3.76 3.26	11.99 12.46	117	0.78	45
3c	$C_{19}H_{17}N_3O_3$	69.13 68.06	4.69 5.08	13.24 12.54	166	0.83	45
3d	$C_{17}H_{11}BrN_2O_3$	55.17 54.98	2.43 2.96	6.89 7.55	187	0.86	40

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* In toluene–ethanol, 10:3.

TABLE 2. IR Spectra of Compounds **3a-d**

Compound	ν, cm^{-1}				
	C=O	C=C	NO_2		Ar
			ν_s	ν_{as}	
3a	1660	1595	1345	1530	1595, 1500
3b	1650	1590	1345	1510	1590, 1500
3c	1660	1605	1345	1520	1600, 1500
3d	1655	1590	1345	1530	1590, 1500

In the IR spectra of the condensation products of pyrrolinone **1** with aromatic aldehydes there were bands for the stretching vibrations of the carbon-carbon double bond (1590-1605 cm^{-1}), which were superimposed on the stretching vibrations of the benzene ring. A band for the stretching vibrations of the carbonyl group was detected at 1650-1660 cm^{-1}. The stretching vibrations of the nitro group were at 1510-1530 (ν_{as}), 1345 cm^{-1} (ν_s).

In the ^1H NMR spectra of pyrrolinones **3a-d** there were no proton signals in the region of 4.5 ppm and the H-3,4 proton signals were displaced towards low field in comparison with the initial pyrrolinone (H-3 6.25, H-4 7.46 ppm), which indicates the formation of condensation products at position 5 of the heterocycle.

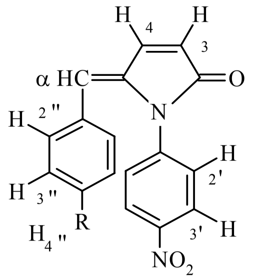
The doublets for the H-3 protons were found at 7.57-7.63 ppm with J = 6.8 Hz. The H-4 protons have a doublet-doublet splitting both with the H-3 protons (J = 6.8 Hz) and with the H_α protons with a long range coupling constant of 2.4-2.5 Hz and are at 8.21-8.45 ppm.

Since the condensation reaction of pyrrolinone **1** with aromatic aldehydes using H_2SO_4 as catalyst proceeded in low yield, the sulfuric acid was replaced by perchloric, which is distinguished by the ability to form stable salts and complexes with organic compounds [1, 2].

Probably, on adding an excess of perchloric acid to a solution of pyrrolinone, attack occurs of the proton at the oxygen atom of the carbonyl group, with the subsequent formation of a pyrrolinonium perchlorate. Ejection of the proton from position 5 is suppressed by this, since the positive charge on the carbonyl oxygen atom is stabilized by conjugation with the unshared electron pair of the nitrogen atom and the π-electrons of the double bond.

Such a structure for perchlorate **4** is confirmed by the absence from its IR spectrum of absorption bands for the stretching vibrations of the carbonyl group at 1660-1690 cm^{-1} and by the presence of an intense ν_{OH} absorption band at 3300-3500 cm^{-1}. An intense broadened absorption band for perchlorate anion was also observed at 1050-1150 cm^{-1}, superimposed on $\nu_{C–O}$.

TABLE 3. ^{1}H NMR Spectra of the Products of Condensation of 1-(4-Nitrophenyl)pyrrolin-2-one with Aromatic Aldehydes



Com-pound	Chemical shofts δ, ppm (*J*, Hz)*							
	H-3 (d)	H-4 (dd)	H$_\alpha$ (d)	H-2' (d)	H-3' (d)	H-2''	H-3''	H-4''
3a	7.57 (*J* = 6.8)	8.21 (*J* = 6.8, *J* = 2.4)	8.38 (*J* = 2.4)	7.69 (*J* = 8.9)	8.26 (*J* = 8.9)	7.73 (m)		
3b	7.63 (*J* = 6.7)	8.27 (*J* = 6.7, *J* = 2.4)	8.45 (*J* = 2.4)	7.69 (*J* = 8.9)	8.26 (*J* = 8.9)	7.63 (d, *J* = 8.7)	8.24 (d, *J* = 8.7)	—
3c	7.60 (*J* = 6.8)	8.21 (*J* = 6.8, *J* = 2.5)	8.36 (*J* = 2.5)	7.68 (*J* = 8.9)	8.26 (*J* = 8.9)	7.77 (m)		—
3d	7.61 (*J* = 6.8)	8.24 (*J* = 6.8, *J* = 2.5)	8.30 (*J* = 2.5)	7.69 (*J* = 8.9)	8.26 (*J* = 8.9)	7.73 (m)		—

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* The ^{1}H NMR spectra were taken in $(CD_3)_2CO$ (compounds **3a,c**) and in $CDCl_3$ (compounds **3b,d).**

TABLE 4. Characteristics of Compounds **5a-d**

Com-pound	Empirical formula	$\frac{\text{Found, \%}}{\text{Calculated, \%}}$			mp, °C	R_f*	IR spectrum, ν, cm^{-1}				Yield, %
		C	H	N			C=C	OH	ClO_4^-	Ar	
5a	$C_{17}H_{13}ClN_2O_7$	$\frac{52.03}{51.97}$	$\frac{3.39}{3.31}$	$\frac{7.09}{7.13}$	265*[2]	0.23	1600	3500-3300	1130-1050	1600, 1500	83
5b	$C_{17}H_{12}ClN_3O_9$	$\frac{46.71}{46.63}$	$\frac{2.79}{2.74}$	$\frac{9.63}{9.60}$	282	0.33	1600	3530-3330	1150-1035	1600, 1497	76
5c	$C_{19}H_{18}ClN_3O_7$	$\frac{52.31}{52.35}$	$\frac{4.21}{4.13}$	$\frac{9.42}{9.46}$	210*[2]	0.28	1603	3500-3300	1145-1040	1603, 1500	81
5d	$C_{17}H_{12}BrClN_2O_7$	$\frac{43.23}{43.27}$	$\frac{2.57}{2.55}$	$\frac{5.91}{5.94}$	290	0.29	1605	3510-3300	1150-1060	1605, 1500	79

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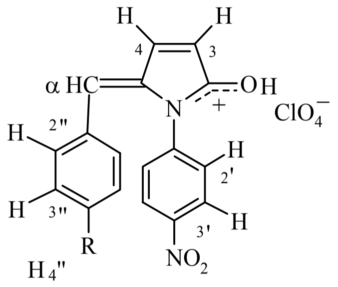
* In toluene–ethanol, 10:3.

*[2] Compound decomposes at this temperature.

TABLE 5. ^{1}H NMR Spectra of 5-(4-Arylidene)-1-(4-nitrophenyl)pyrrolin-2-one Perchlorates



Com-pound	Chemical shifts, δ, ppm (*J*, Hz)*						
	H-3 (d)	H-4 (d)	H_α (s)	H-2' (d)	H-3' (d)	H-2" (d)	H-3", H-4"
5a	8.08 (*J* = 5.0)	8.54 (*J* = 5.0)	8.70	8.08 (*J* = 7.0)	8.91 (*J* = 7.0)	8.06 (*J* = 7.1)	7.70-7.95 (m)
5b	8.08 (*J* = 5.2)	8.53 (*J* = 5.2)	8.68	8.11 (*J* = 7.1)	8.91 (*J* = 7.1)	8.11 (*J* = 7.0)	8.79 (d, *J* = 7.0)
5c	8.07 (*J* = 5.1)	8.55 (*J* = 5.1)	8.71	8.10 (*J* = 7.2)	8.90 (*J* = 7.2)	8.10 (*J* = 7.0)	8.69 (d, *J* = 7.0)
5d	8.07 (*J* = 5.1)	8.50 (*J* = 5.1)	8.68	8.09 (*J* = 7.0)	8.81 (*J* = 7.0)	8.09 (*J* = 7.1)	8.53 (d, *J* = 7.1)

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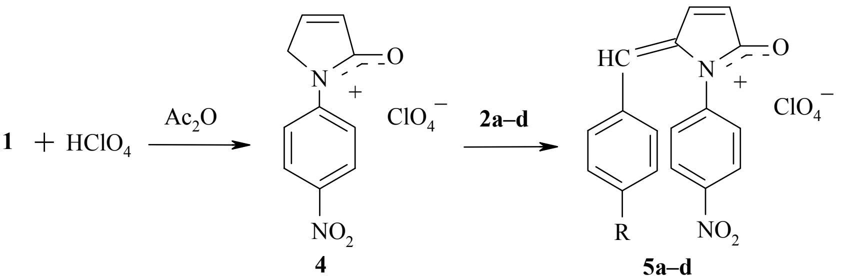
* ^{1}H NMR spectra of compounds **5a-d** were taken in trifluoroacetic acid, internal standard was *tert*-butyl alcohol (δ 1.25 ppm) or external standard was HMDS (δ 0.05 ppm).

It was established that the formation of 1-(4-nitrophenyl)pyrrolin-2-one perchlorate (**4**) is possible in acetic anhydride, or mixtures of it with acetic acid, on adding a small excess of perchloric acid.

The higher stability under the reaction conditions, compared with N-arylpyrrolin-2-ones, must assist the condensation of perchlorates with aromatic aldehydes. In reality, on carrying out the reactions of aromatic aldehydes **2a-d** with perchlorate **4** the resinification of the reaction mixture is reduced and the yield of condensation products is increased.

To optimize the process the reaction was subsequently carried out without isolating the intermediate perchlorate.

It was established that on carrying out the reaction in dilute acetic acid it was necessary to heat to 70-80°C. As a result resinification of the reaction mixture occurred and yields of products were low. On replacing the solvent by acetic anhydride, or glacial acetic acid in the presence of acetic anhydride, reaction took place in 10 min at 40-50°C with a 10% molar excess of aldehyde. Under these conditions no resinification of the mixture was observed and the yields of products were 70-80%.



5 **a** R = H, **b** R = NO_2, **c** R = NMe_2, **d** R = Br

The structures of the synthesized compounds were demonstrated by IR and ^{1}H NMR spectroscopic methods.

In the IR spectra (Table 4) of compounds **5a-d** there were no absorption bands for the stretching vibrations of a carbonyl group at 1660-1690 cm^{-1}, but there were intense ν_{OH} absorption bands at 3300-3500 cm^{-1} and a broadened absorption band for perchlorate anion at 1050-1150 cm^{-1}, superimposed on $\nu_{C\text{-}O}$. An intense $\nu_{C=C}$ absorption band was also observed at 1600 cm^{-1}.

In the ^{1}H NMR spectra of compounds **5a-d** (Table 5), taken in trifluoroacetic acid, a complex picture was observed in the 7.7-9.0 ppm region, caused by the overlapping of the signals of all the protons of the compound. The displacement of the signals towards low field compared with the initial compounds is caused by the presence of the delocalized positive charge, which is confirmation of the formation of salt structures.

EXPERIMENTAL

The IR spectra were taken on a LOMO IKS-29 spectrophotometer in the frequency range 400-4200 cm^{-1}, with diffraction gratings of 150 lines per millimeter in the 1200-4200 cm^{-1} range and 50 lines per millimeter in the 400-1400 cm^{-1} range. The error was ±5 cm^{-1}. The ^{1}H NMR spectra were recorded on a Varian FT 80A instrument (80 MHz), resolving power $0.5\cdot10^{-9}$, precision ±0.02 ppm, and also on a Tesla BS-487 instrument (80 MHz) with a precision of 0.05 ppm. The progress of reactions and the homogeneity of the synthesized compounds was checked by TLC (Silufol UV-254 in the system toluene–ethanol, 10:3).

5-Arylidene-1-(4-nitrophenyl)pyrrolin-2-ones 3a-d. Pyrrolinone **1** (0.25 g, 1.2 mmol) and aldehyde (1.2 mmol) were loaded into a three-necked flask fitted with a reflux condenser, stirrer, and thermometer. Pyridine (2-3 drops) was added after complete solution of the reactants in acetic anhydride at 60°C. The reaction mixture was heated with vigorous stirring for 4 h until complete consumption of pyrrolinone. The progress of the process was observed with the aid of TLC (acetone–chloroform–petroleum ether, 2:1:0.5). After the end of the reaction the excess of solvent was distilled off under vacuum. The residual reaction mass was cooled, washed with water, and filtered. The filtrate was washed with diethyl ether. The precipitated crystals were recrystallized from alcohol.

1-(4-Nitrophenyl)pyrrolin-2-onium Perchlorate (4). Pyrrolinone **1** (0.1 g, 0.5 mmol) was dissolved in a mixture of glacial acetic acid (4.5 ml) and acetic anhydride (0.17 ml). Perchloric acid (70%; 0.055 ml, 0.55 mmol) was added dropwise while cooling in an ice bath. The mixture was heated to 20-25°C and precipitated with diethyl ether. The precipitated crystals were filtered off, and washed with ether. Yield 0.11 g (73%); mp 207°C. IR spectrum, cm^{-1}: ν_{OH} 3300-3500, ν_{ClO4} 1050-1150, ν_{Ar} superimposed on $\nu_{C–O}$ 1605, 1500. Found, %: C 39.43; H 3.29; N 9.23. $C_{10}H_8ClN_2O_7$. Calculated, %: C 39.28; H 3.27; N 9.17.

5-(4-Arylidene)-1-(4-nitrophenyl)pyrrolin-2-onium Perchlorates 5a-d. Pyrrolinone **1** (0.1 g, 0.5 mmol) was dissolved in a mixture of glacial acetic acid (4.5 ml) and acetic anhydride (0.17 ml). Perchloric acid (70%; 0.055 ml, 0.55 mmol) was added dropwise while cooling in an ice bath. The mixture was heated to 50±5°C, aldehyde (0.5 mmol) was added, the mixture heated for 30-35 min, cooled, and precipitated with diethyl ether. The precipitated crystals were filtered off, and washed with ether.

REFERENCES

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