V. G. Kul'nevich, E. Baum, and T. E. Goldovskaya

Pyrrole aldehydes interact with oxidizing agents to yield products which are oxidized to different degrees. Pyrrolecarboxylic acids are formed under the influence of silver oxides, an alkaline solution of permanganate, and 2-10% sulfuric acid [1-3]. With peroxidation of hydrogen, 5-unsubstituted pyrrole aldehydes convert to pyrrolone [4], and pyrrol-2-aldehyde converts to succinimide [5]. Chromacetate and chromium sulfuric acids oxidize pyrrole aldehydes to maleinimides [3].

Little study has been devoted to 1-(4-nitropheny1)-2-formy1pyrrole (I), and methods for its oxidation have not been previously studied. We have established that aldehyde I, like other formy1pyrroles [3], does not react with Fehling's solution even upon prolonged heating. Sulfuric acid (regardless of the concentration) in the cold does not oxidize I, and heating I with concentrated sulfuric acid leads to its resinification.

Under the influence of 2% potassium permanganate solution aldehyde I is converted to carboxylic acid II:



The optimal temperature in this case is $40-45^{\circ}$ C. Higher temperatures lead to decarboxylation of acid II, and at 25°C the reaction rate is decreased by a factor of 2.5. The structure of acid II was proved by the PMR (Table 1) and IR (Table 2) spectra. To a certain approximation the 1-H and 3-H protons proved to be magnetically equivalent and gave a common multiplet in the PMR spectrum, whereas the 2-H proton showed up in the form of a quartet. In the IR spectrum the hydroxy part of the carboxy group absorbed at 2540-2755 cm⁻¹. Physicochemical data for acid II are presented in Table 3.

N-Substituted pyrrolinone III is formed in the reaction of aldehyde I with hydrogen peroxide in the presence of mineral or organic acids. In the absence of a catalyst 1-(4-nitrophenyl)-2-formylpyrrole does not react with H_2O_2 . Pyrrolinone III is formed in only 10% yield when it is refluxed in an alcohol solution of H_2O_2 for 5 h. The synthesis of pyrrolinone III proceeds satisfactorily in solutions of organic acids and particularly rapidly in formic acid. The process is exothermic and is accompanied by resinification. Pyrrolinone III does not undergo resinification when two to three drops of triethanolamine are added at the end of the reaction. An analysis of the reaction product by thin-layer chromatography (TLC) demonstrated

Krasnodar Polytechnic Institute, Krasnodar 350006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 495-499, April, 1982. Original article submitted March 18, 1981.

TABLE 1. PMR Spectra of II-V

- p	δ, ppm (J, Hz)								
Con	1-H	2-H	3-H	4-H	5-H				
II III IV	7,18 6,22 (6) 7,06	6,37 7,50 (6) 7,06	7,18 4,68 (2)	7,65 (9) 8,12 (9) 7,67 (9)	8,31 (9) 8,20 (9) 8,28 (9)				
v	_	-	_	7,71 (9)	8,33 (9)				

TABLE 2. UV and IR Spectra of II-V

-		No. of Column 2 is not the	and the second se					
	UV spec- trum		IR spectrum, cm ⁻¹					
EE	λmax	log		NO ₂				
ଧିନ୍ଦି	nm	ε	$v_{\rm C} = 0$	v _{as}	v _s	v_{C-N}		
н	228	4,10	1688	1542	1352	866		
III	221	4,00	1705	1511	1328	853		
	328	4,19	1700					
IV	224	4,12	1732	1510	1351	855		
\mathbf{v}	224	$\frac{4,22}{4,22}$	1740	1526		864		
•	319	4,29	1787		1352			
				ι ,				

the formation of only one substance. Spectral studies confirmed the structure of III, which corresponds to Λ^3 -pyrrolin-2-one rather than to its tautomeric form — Λ^4 -pyrrolinone. The chemical shift of the corresponding methylene protons, which is 4.0-4.3 and 3.1-3.4 ppm for the Λ^3 and Λ^4 isomers, respectively, is a criterion of the difference in the Λ^3 - and Λ^4 -isomeric 3,5-unsubstituted pyrrolin-2-ones [6]. The methylene protons in pyrrolinone III are not equivalent and are split into a doublet. The spin-spin coupling constant (SSCC) of the ethylene 1-H and 2-H protons is characteristic for five-membered cyclic systems [7]. Conjugation between the carbonyl group and the double bond is responsible for deshielding of the 2-H proton, the signal of which is found at weaker field than the signal of the 1-H proton (Table 1). The presence of conjugation is confirmed by the position of the band of stretching vibrations of the carbonyl group in the IR spectrum (Table 2). The formation of the Λ^3 isomer as the only product is evidently associated with the effect of the nitrophenyl substituent attached to the heteroatom. The existence of two isomeric forms was established for pyrrolin-2-one [6] but was not observed in our case.

Aldehyde I is oxidized to N-substituted maleinimide IV when it is heated with chromic anhydride in acetic acid. The molecule of this compound is symmetrical, and the ethylene 1-H and 2-H protons are therefore equivalent in the PMR spectrum and show up in the form of one singlet.

Compound I is oxidized readily by bromine water to give dibromomaleinimide V, whereas the hydrogen atoms of the heteroring are only replaced by bromine in the case of other pyrrole derivatives [3]. To a certain approximation the reaction rate can be regarded as being equal to the rate of diffusion of the reagents, since as the solution of aldehyde I is added to bromine water, dibromomaleinimide V precipitates simultaneously. The tested solvents (dimethylformamide, alcohols, and acetic acid) do not affect the rate and course of the reaction. The formation of V includes two steps. The first step is oxidation of aldehyde I to maleinimide IV, and the second step is replacement of the hydrogen atoms in IV by bromine atoms. This is proved by alternative synthesis: Dibromomaleinimide V is readily formed from maleinimide IV by the action of bromine. The rates of both steps are apparently identically high, since IV is not detected in the reaction mixture.

The structure of the dibromomaleinimide was proved by spectral methods of analysis. The mass spectrum of acid II corresponds to the previously described spectrum [8]. The mechanisms

TABLE 3. Physicochemical Characteristics of II-V

, p mp,		Found, %			Empirical	Calculated, %			3.4.+			
Cor pou	°C	с	Н	Br	N	formula	С	н	Br	N		
II III IV V	191 169 162 194	59,7 58,4 49,8 32,1	3,48 4,85 2,77 1,15	 42,5	12,0 13,5 12,9 7,31	$\begin{array}{c} C_{11}H_8N_2O_4\\ C_{10}H_8N_2O_3\\ C_{10}H_6N_2O_4\\ C_{10}H_4Br_2N_2O_4\end{array}$	59,6 58,2 51,1 31,9	3,44 4,92 2,75 1,07	 42,2	12,1 13,7 12,8 7,45	232 204 218 372†	(100)* (100) (100) (36,7)

*These are the m/z values (the intensities in percent of the maximum peak are given in parentheses). *Calculated on the basis of the ⁷⁹Br isotope.

of fragmentation under electron impact for III-V, which contain a pyrroline ring, are presented in Schemes 2 and 3.



Scheme 3



A feature common to all of them is the fact that the bond between the heteroring and the nitrophenyl substituent is not cleaved in the molecular ion. Prior to cleavage of this bond either the heteroring (III) or the nitro group (IV, V) undergoes fragmentation. The lactam ring of III, which undergoes partial fragmentation up to splitting out of an NO₂ radical, proved to be the most labile under the influence of electron impact. The imide ring in IV and V is cleaved only after splitting out of NO or NO₂ radicals. The relative intensities of the $[M-NO]^+$ and $[M-NO_2]^+$ ion peaks (Table 4) indicate that "nitrite" fragmentation

TABLE 4. Peaks of the Characteristic Fragment Ions in the Mass Spectra of N-(4-Nitrophenyl)maleinimides IV and V

Fragments*	Relative intensity, %				
	IV	v			
$\begin{array}{l} [M-NO]^+ \\ [M-NO_2]^+ \\ [M-NO_3, -CO]^+ \\ C_4R_2O_2^+ \\ C_3R_2O^+ \\ C_3R_2O^+ \\ C_3R_4O^+ \\ C_6H_4N^+ \\ C_5H_4N^+ \\ C_5H_4^+ \\ C_5H_4^+ \\ C_5H_3^+ \end{array}$	$ \begin{array}{c} 36,6\\12,2\\23,2\\31,2\\2,6\\62,1\\21,9\\7,5\\5,6\\14,9\\26,8\\\end{array} $	21,7 4,3 7,9 0,5 6,5 100,0 58,7 23,9 24,4 31,8			

*Data for M⁺ are presented in Table 2.

(the successive splitting out of NO and CO particles) is more characteristic than splitting out of a nitro group in the form of a radical and subsequent cleavage of the bond between the rings with retention of the change on the phenylene ion radical (m/z 76). The chief pathway of fragmentation of IV and V is successive cleavage of the molecular ion to give $C_4R_20^+$, $C_3R_20^+$, and C_3R0^+ fragments (see Scheme 3).

Our studies showed that 1-(4-nitrophenyl)-2-formylpyrrole is readily oxidized to give various derivatives. The nitrophenyl substituent attached to the heteroatom evidently increases the tendency of aldehyde I to undergo oxidation as compared with other substituents. In addition, it is characteristic that the pyrrole ring is not opened but rather is converted to an oxidized pyrroline ring (III-V).

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $(CD_3)_2CO$ were recorded with a Tesla BS-497 spectrometer (100 MHz) with tetramethylsilane (II, III) and hexamethyldisiloxane (IV, V) as the internal standards. The UV spectra of solutions of the compounds in 96% ethanol were recorded with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions of the compounds between NaCl plates were recorded with a UR-20 spectrometer. The mass spectra were recorded with a Varian MAT-CH6 spectrometer by the electron-impact method at a source temperature of 180°C and an emission current of 100 μ A. The spectra of samples of II-V were recorded at 95, 92, 140, and 90°C, respectively.

<u>1-(4-Nitrophenyl)pyrrole-2-carboxylic Acid (II)</u>. A 2.16-g (0.01 mole) sample of aldehyde I was dissolved in 50 ml of acetone, and 64 ml of a 2% solution of KMnO₄ was added. The reaction temperature was 40°C. After the solution became colorless, it was cooled, and the precipitated manganese oxide was removed by filtration. The acetone was removed by distillation with a water aspirator, the residue was acidified with 10% HCl, and the crystals were removed by suction filtration. The yield was 1.6 g (69%).

 $1-(4-\text{Nitropheny1})-\Delta^3-\text{pyrrolin}-2-\text{one}$ (III). A 2-ml sample of 36% H₂O₂ was added to a mixture of 4.32 g (0.02 mole) of aldehyde I with 75 ml of 80% HCOOH, and the mixture was maintained at 30°C for 1 h. Two to three drops of triethanolamine were added, and, after 30 min, the solution was poured into 1 liter of water. The crystals were removed by filtration, washed with water, and air dried. The yield was 2.2 g (53%).

<u>l-(4-Nitrophenyl)pyrroline-2,5-dione (IV)</u>. A 2.16-g (0.01 mole) sample of aldehyde I was dissolved at 75°C in 60 ml of CH_3COOH , 2.6 g of CrO_3 dissolved in 10 ml of CH_3COOH and 10 ml of water was added, and the reaction was carried out at a fixed temperature for 1.5 h. The solution was then poured into 1 liter of water, and the crystals were removed by filtration, washed well with water, and air dried. The yield was 1.4 g (66%).

3,4-Dibromo-l-(4-nitrophenyl)pyrroline-2,5-dione (V). A 2.16-g (0.01 mole) sample of aldehyde I was dissolved by heating in 100 ml of CH_3COOH , and the warm solution was poured into 200 ml of water containing 2 ml of bromine. After 5 min, 1 liter of water was added, and the resulting crystals were removed by filtration, washed successively with 5% bisulfite solution and water, and air dried. The yield was 1.9 g (50%).

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REACTION OF 2-DICYANOMETHYLENEINDAN-1, 3-DIONE WITH PYRROLES

AND INDOLES

B. P. Bespalov and A. G. Abolin

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The reaction of 2-dicyanomethyleneindan-1,3-dione with pyrrole, indole, and their methyl derivatives gives products of addition at the dicyanomethylene carbon atom, viz., pyrrolyl- and indolyl(1,3-dioxo-2-indanyl)malononitriles, which upon heating or irradiation with UV light irreversibly split out HCN to give deeply colored products of replacement of the nitrile group in the acceptor by a heterocyclic group-ing. Data from the UV and PMR spectra of the compounds obtained are presented.

2-Dicyanomethyleneindan-1,3-dione is a strong organic π acid, and reactions involving nucleophilic addition at the dicyanomethylene carbon atom are characteristic for it. This acid reacts readily with nucleophiles such as aromatic and aliphatic amines to give products of addition to the double bond of the dicyanomethylene group [1]. 2-Dicyanomethyleneindan-1, 3-dione is the weakest acceptor in series of related organic π acceptors such as tetracyanoethylene and tetracyanoquinodimethane, which also readily form addition products with organic nucleophiles. Its electron affinity (E_A) is 2.45 eV, as compared with 2.75 and 2.85 eV for tetracyanoethylene and tetracyanoquinodimethane, respectively [2].

The aim of the present research was to study the effect of the electrophilicity of the dicyanomethylene carbon atom on the direction of the reaction with pyrroles and indoles.

We found that 2-dicyanomethyleneindan-1,3-dione readily forms addition products with Nheterocyclic compounds that contain one nitrogen atom in a five-membered ring. The reaction proceeds through a step involving the formation of a charge-transfer complex (CTC), which is accompanied by characteristic coloring of the solution and the appearance of the absorption of a long-wave charge-transfer band in the electronic spectra.

After a few minutes, pyrrole and its methyl derivatives in polar solvents (for example, acetonitrile, acetone, and alcohol) at 20°C react with 2-dicyanomethylene-1,3-dione to give slightly colored addition products Ia-c.

It follows from a comparison of the PMR spectra of Ia-c with the spectra of the unsubstituted heterocycles and from an analysis of the integral intensities of the signals that the

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