STRUCTURES OF THE PRODUCTS OF FORMYLATION OF 1,3,5-TRIPHENYL- AND 1,5-DIPHENYL-3-STRYL-2-PYRAZOLINES

L. A. Kutulya, A. E. Shevchenko, and Yu. N. Surov

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It was established by means of IR and PMR spectra and chemical transformations that the products of the Vilsmeier formylation of 1,3,5-triphenyl- and 1,5-diphenyl-3-styryl-2-pyrazolines are the corresponding 1-(p-formylphenyl)-2-pyrazolines. The frequencies of the stretching vibrations of the carbonyl group and the chemical shift of the aldehyde proton of these compounds indicate considerable conjugation of the p electrons of the N_1 atom of the pyrazoline ring with the aldehyde group.

Formyl derivatives of 1,3,5-triaryl-2-pyrazolines are of interest as intermediates in the synthesis of new luminescent compounds. The product of the Vilsmeier formylation of 1,3,5-triphenyl-2-pyrazoline (I) was assigned the 1,3,5-triphenyl-4-formyl-2-pyrazoline structure without proof [1]. We reproduced the method in [1], and after thorough purification we obtained II with a somewhat higher melting point of 122-123° C as compared with 116-117° according to [7], and this compelled us to make a detailed investigation of its properties and structure. The product of formylation of pyrazoline I has bright-blue luminescence in the crystalline state, violet luminescence in toluene solutions, and forms a phenylhydrazone, a bisulfite compound, and an azomethine.

Intense $\nu_{C=O}$ absorption at 1678 cm^{-1} ($\nu_{C=O}$ 1694 cm^{-1} in CCl_4) and $\nu_{C=N}$ absorption at 1600 cm^{-1}, as well as other absorption bands characteristic for aryl-2-pyrazolines [2], are observed in the IR spectrum of formyl derivative II (KBr pellet). The anomalously low $\nu_{C=O}$ value for compounds with an aldehyde group attached to a saturated carbon atom [3] and the hypsochromic shift of the luminescence spectra of the product as compared with pyrazoline I (Fig. 1), in the light of the known principles of the change in the luminescence of 2-pyrazoline derivatives as a function of their chemical structure [4, 5], do not agree with the assumption made by Baroni and Kovyrzina [1] of formylation of pyrazoline I in the 4 position.

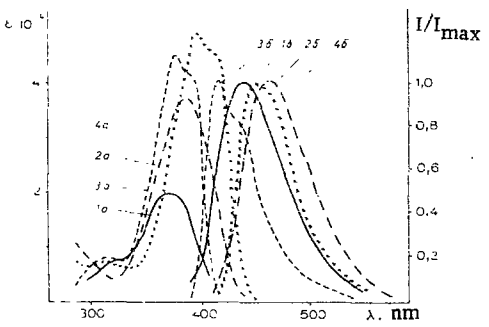

Fig. 1. Absorption (a) and luminescence (b) spectra of pyrazolines I (1), IV (2), and the products of their formylation (3 and 4, respectively).

A singlet signal with δ 9.61 ppm, which belongs to the formyl proton, is observed in the PMR spectrum of II. In addition, the character of the PMR spectrum unambiguously indicates retention in the formylation product of the methylene group of the pyrazoline ring, which is displayed as two quartets typical for 5-aryl-substituted arylpyrazolines [6-8], along with the quartet of a methylidyne proton in the 5 position (an ABX system). The following chemical shifts and spin–spin coupling constants were determined as a result of an analysis of the ABX portion of the spectrum: δ_A 3.81 (4H proton in the trans position with respect to the phenyl group [6]), δ_B 3.12 (cis 4-H proton), δ_X 5.28 ppm (5-H), J_{AB} = 17.1 Hz, J_{AX} =

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12.0 Hz, and J_{BX} = 6.2 Hz. These values are in good agreement with those obtained for other 2-pyrazoline derivatives [6, 8].

Thus the PMR spectrum shows that the product of formylation of pyrazoline I is the p-formylphenyl derivative rather than the 4-formyl-substituted compound. However, in view of the great complexity of the PMR spectrum in the region of resonance of phenyl protons (multiplet at 6.7-7.7 ppm), it is impossible from these data to draw a conclusion as to which of the three phenyl rings undergoes formylation. On the basis of luminescence data for the product obtained we have assumed that formylation occurs in the para position of the 1-phenyl group. In order to solve this problem we subjected formyl derivative II to Wolff–Kishner reduction [9]. The reduction product had mp 164-165° and proved to be 1-(p-tolyl)-3,5-diphenylpyrazoline (III); this was established from the identical character of the IR spectra of this product and pyrazoline III, obtained by specific synthesis from benzalacetophenone and p-tolylhydrazine [10], and from the absence of a melting-point depression for a mixture of samples of both products. Consequently, the product of Vilsmeier formylation of pyrazoline I is 1-(p-formylphenyl)-3,5-diphenylpyrazoline. This conclusion is in agreement with the established fact [11] of formylation of 1,3-diphenyl- and 1-phenyl-3-(p-tolyl)pyrazoline in the para position of the 1-phenyl group.

We formylated 1,5-diphenyl-3-styryl-2-pyrazoline (IV) under similar conditions. Wolff–Kishner reduction of reaction product V gave 1-(p-tolyl)-3-styryl-5-phenylpyrazoline, which was identical to the product obtained from dibenzalacetone and p-tolylhydrazine. Consequently, the para position of the 1-phenyl group is also formylated in this case.

The spectroscopic characteristics of 1-(p-formylphenyl)-3,5-diphenyl- and 1-(p-formylphenyl)-3-styryl-5-phenyl-2-pyrazolines that we established in the present study make it possible to form a judgment regarding the character of the electronic interactions in these systems. Thus the $\nu_{C=O}$ value in carbon tetrachloride solutions of II and IV (1694 cm^{-1}) is substantially reduced as compared with the value for benzaldehyde (1715 cm^{-1} [12]). This indicates the electron-donor effect of substituted pyrazolinyl groupings on the p-formylphenyl group and may be a consequence of the fact that there is considerable conjugation of the p electrons of the N_1 atom of the pyrazoline ring with the aldehyde group in the ground state of these molecules. The appreciably greater shielding of the aldehyde proton in 1-(p-formylphenyl)-3,5-diphenylpyrazoline (δ 9.61 ppm) as compared with benzaldehyde (δ 9.96 ppm [13]) also provides evidence in favor of this conclusion.

It should be noted that inasmuch as Vilsmeier formylation is a reaction of the electrophilic type, the established fact of the formation of 1-(p-formylphenyl) derivatives of triaryl-2-pyrazolines provides a basis for the assumption that the interaction of the p electrons of the N_1 atom with the adjoining benzene ring also occurs to a certain degree in the absence of an electron-acceptor substituent in the latter.

EXPERIMENTAL

The IR spectra of KBr pellets and carbon tetrachloride solutions of the compounds were obtained with a UR-20 spectrometer. The PMR spectrum of a carbon tetrachloride solution (1.5%) was recorded with a R-20A spectrometer (60 MHz) relative to tetramethylsilane as the internal standard. The absorption and luminescence spectra of toluene solutions (10^{-4}-10^{-5} M) were recorded, respectively, with an SF-4A spectrophotometer and an apparatus for luminescence analysis consisting of a ZMR-3 mirror monochromator, and FÉU-18 photoelectric multiplier, an M-95 microammeter, and a DRSH-500 mercury–quartz lamp (the excitation wavelength was 365 nm).

1-(p-Formylphenyl)-3,5-diphenyl-2-pyrazoline (II). Pyrazoline I was formylated with dimethylformamide (DMFA) in the presence of phosphorus oxychloride in analogy with the method in [1]. The product was purified by chromatography of a benzene solution on aluminum oxide, after which it was converted to the bisulfite compound by reaction of a saturated sodium bisulfite solution with a solution of it in alcohol. The bisulfite compound was washed thoroughly with alcohol and decomposed by refluxing with 10% sodium carbonate solution. The formylphenylpyrazoline thus obtained was recrystallized twice from ethanol to give light-yellow needles with mp 122-123° in 65% yield. Found: N 8.4, 9.0%. $C_{22}H_{18}N_2O$. Calculated: N 8.6%. The phenylhydrazone was obtained as a yellow powder with yellow-green luminescence. A toluene solution of it had turquoise luminescence. The phenylhydrazone had mp 245-247° (from butyl alcohol). Found: N 13.7, 13.8%. $C_{28}H_{24}N_4$. Calculated: N 13.4%. The azomethine was obtained by refluxing a solution of 1.6 g (0.005 mole) of pyrazoline II and I g (0.01 mole) of aniline in methanol for 40 min. The yield of bright-yellow powder with mp 173-174° (from cyclohexane) was 1.5 g (79%). Found: N 10.2, 10.6%. $C_{28}H_{23}N_3$. Calculated: N 10.5%.

1-(p-Tolyl)-3,5-diphenyl-2-pyrazoline (III). A 2-ml sample of hydrazine hydrate and 4 g of potassium hydroxide were added to a solution of 0.8 g (0.0025 mole) of aldehyde II in 40 ml of diethylene glycol, after which the reaction mixture was refluxed for 1 h. The temperature was then raised to 200°, and the mixture was held at this temperature for 3 h until nitrogen evolution had ceased. The mixture was then cooled and poured into 200 ml water, and the resulting precipitate was removed by filtration and washed with water to neutrality to give 0.65 g (85%) of pyrazoline III. The product was purified by chromatography of a cyclohexane solution of it on aluminum oxide and subsequent recrystallization (twice) from ethanol. The colorless needles with blue luminescence had mp 164-165° (mp 166° [10]). IR spectrum: $\nu_{C=N}$ 1608 cm^{-1} (in KBr).

1-(p-Formylphenyl)-3-styryl-5-phenyl-2-pyrazoline (V). The procedure used to formylate I was used to formylate pyrazoline IV. The reaction product was purified with a chromatographic column filled with aluminum oxide (elution by benzene) and subsequent crystallization from ethanol–benzene (6 : 1). The yield of yellow needles with yellow-green luminescence and mp 193-195° was 85%. IR spectrum: $\nu_{C=O}$ 1679 (in KBr), 1694 (in CCl_4); $\nu_{C=N}$ 1604 cm^{-1}. Found: N 7.9, 7.9%. $C_{24}H_{20}N_2O$. Calculated: N 8.0%. The phenylhydrazone was obtained as a yellow-orange powder with yellow luminescence and mp 243-244° (from butyl alcohol). Found: N 13.0, 13.0%. $C_{30}H_{26}N_4$. Calculated: N 12.7%. The azomethine was obtained by refluxing a solution of 0.8 g (0.0025 mole) of the aldehyde and 3 g (~0.03 mole) of aniline in 35 ml of butyl alcohol for 3 h. The yield of dark-yellow powder with mp 189° (from butyl alcohol) was 0.9 g (quantitative). The product had yellow luminescence in the crystalline state and turquoise luminescence in benzene solution. Found: N 10.3, 10.3%. $C_{30}H_{25}N_3$. Calculated: N 9.8%.

1-(p-Tolyl)-3-styryl-5-phenyl-2-pyrazoline. A) Pyrazoline V was reduced by the method used to reduce formyl derivative II. The yield was 95%. The product was recrystallized from methanol-benzene (5 : 1) to give bright greenish-yellow needles with green luminescence. Turquoise luminescence appeared in a toluene solution on irradiation with UV light. The product had mp 165-166° [from benzene–methanol (5:1)]. IR spectrum: $\nu_{C=N}$ 1612 cm^{-1} (in KBr).

B) A solution of 4.6 g (0.02 mole) of dibenzalacetone and 3.2 g (0.02 mole) of p-tolylhydrazine hydrochloride in 100 ml of ethanol was refluxed for 1.5 h, after which the mixture was cooled, and the resulting precipitate was removed by filtration and washed with ethanol to give 3 g (46%) of product. The product was purified with a chromatographic column filled with aluminum oxide from a solution in cyclohexane–benzene (10 : 1) and subsequent crystallization (twice) from methanol–benzene (3 : 1) to give a material with mp 167°. Found: N 8.2, 8.4%. $C_{24}H_{22}N_2$. Calculated: N 8.3%.

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