AZOCOUPLING PRODUCTS. II.* SYNTHESIS AND STRUCTURAL STUDY OF AZOCOUPLING PRODUCTS OF 1-(5,6-DIMETHYL-4-X-PYRIMIDIN-2-YL)-3-METHYL-PYRAZOLIN-5-ONES WITH AROMATIC DIAZONIUM SALTS

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ABSTRACT

By the azocoupling of 1-(5,6-dimethyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones 5 with some aromatic diazonium salts 6 six new water-insoluble dyes 4 were synthesized. The ^{1}H- and ^{13}C- NMR spectra of 4 indicate the presence of only one species in the solution. The latter is compatible with the aryl-hydrazone **4d** structure of the coupling products 4. On the other hand, the absorption spectra in visible recorded in various solvents and in methanol with acid or alkali addition, respectively, suggest that **4d** is involved in tautomeric equilibria with other structures, first of all with the azo-5-hydroxy-pyrazole form **4b**.

INTRODUCTION

1-Phenyl-3-methyl-pyrazolin-5-one (PhMP) 1 represents an intermediary widely used in the manufacturing of dyes (1-6). This fact stimulated the search for 1-hetaryl- 2 analogs of 1 thought to be able to undergo the same kind of transformations leading to dyes. Indeed, a series of such analogs 2 were converted into dyes (7-16).

In our investigations pursuing similar goals we succeeded (17,18) to prepare some analogs of 1, namely 1-(5-alkyl-4-X-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones 3. By condensing 3 with aromatic, heteroaromatic and Fischer-base aldehydes and ketones, we obtained a series of methine dyes (18-21). It was demonstrated that these compounds have the structures of 4-alkylidene-1-(5-alkyl-4-X-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones, substituted at the alkylidene group, a structure which is compatible with the keto-methylenic tautomer **3a** of 3. However, the ^{1}H-NMR spectra of 3 are compatible with the iminic **3c** or hydroxy-pyrazolic **3b** tautomers of 3 (18, 21b). The tautomers **3b** and **3c** should be involved in the azocoupling reaction of the hetaryl analogs 3 of 1, reaction that made the object of a kinetic study (22).

The present paper describes the synthesis and the structure of azocoupling products 4 of 1-(5,6-dimethyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones, (3; alkyl = methyl) 5, with aromatic diazonium salts 6. The compounds for which several tautomeric forms are possible are indicated in the corresponding figure 1-5, 7-12 not accompanied by

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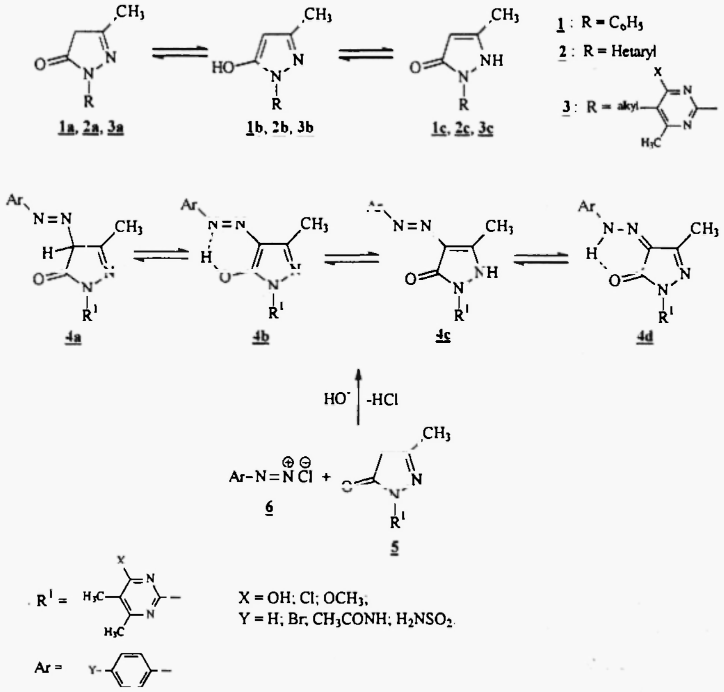
letters, except when a definite tautomer is under discussion.



Scheme 1

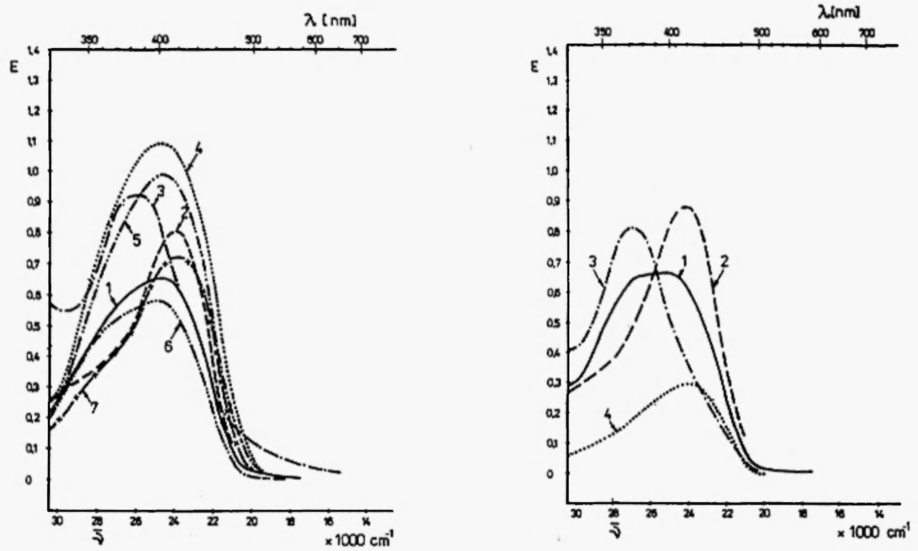
RESULTS AND DISCUSSION

Since the pyrazolin-5-one system - present in the 1-(pyrimidin-2-yl)-3-methyl- pyrazolin-5-ones 3, 5, used as coupling components - manifests itself (22) in three tautomeric forms, 3a, b, c, and the azocoupling products of the 5-hydroxy-pyrazole form, 3b, 5b, are hydroxy-azo derivatives, 4b (also able to present the azo-hydrazono tautomerism 4b ⇌ 4d), the azocoupling products 4 investigated in the present paper can appear in a total of four tautomeric forms, 4a, b, c, d. Tables I-III and Figures 1, 2 present the synthesised compounds as well as some of their characteristic properties.

Table I. Some Chemical and Physical Data of the Synthesised Compounds 4

Substituents X, Y in 4; compound no.	Yield* (%)	Melting point (°C)	Elemental analysis data, calcd./found(%)			Visible absorption spectrum data
			C	H	N	λ_{max} (nm); (ε) in methanol
X=OH; Y=H, 7	77	260-261	59.25/ 59.7	4.94/ 4.7	25.92/ 25.4	390 (26,730)
X=OCH$_3$; Y=H, 8	82.5	250-252	60.35/ 60.7	5.32/ 5.5	24.85/ 24.3	403 (24,650)
X=Cl; Y=H, 9	90	260-262	56.05/ 56.5	4.38/ 4.9	24.53/ 24.8	395 (24,850)
X=OH; Y=Br, 10	97	277-279	47.64/ 47.7	3.73/ 3.8	20.84/ 20.4	388 (19,000)
X=OH; Y=HNCOCH$_3$, 11	92	275	56.69/ 56.8	4.98/ 4.7	25.72/ 25.7	432 (24,500)
X=OH; Y=O$_2$S-NH$_2$, 12	84	290-292	47.64/ 47.2	4.21/ 4.1	24.3/ 24.0	397 (24,500)

The obtaining of coloured products, which present intense absorption bands (Table I, Figure 1), shows that the coupling between diazonium salts <u>6</u> and 1-(5,6-dimethyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones <u>5</u> really occurs, because the starting compounds are not coloured.



a) b)

Figure 1. a) The UV-VIS absorption spectrum of the coupling product <u>8</u> between benzenediazonium salt and 1-(4-methoxy-5, 6-dimethyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one in: 1: methanol; 2: methanolic 0.1 M HCl; 3: methanolic 0.1M KOH; 4: benzene; 5: chloroform; 6: dimethylsulfoxide; 7: glacial acetic acid.
b) The UV-VIS absorption spectrum of the coupling product <u>7</u> between the benzenediazonium salt and 1-(4-hydroxy-5, 6-dimethyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one in: 1: methanol; 2: methanolic 0.1 M HCl; 3: methanolic 0.1M KOH; 4: glacial acetic acid.

Elemental analysis data and ^{1}H-NMR spectra confirm the formation of the azoic coupling products. Thus, for example, the ^{1}H-NMR spectrum of the coupling product between the diazonium salt of N-acetyl-*p*-phenylene-diamine and 1-(4-hydroxy-5, 6-dimethyl -pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (<u>5</u>, X=OH) presents four signals (singlets) of equal intensities in the area of the aliphatic hydrogens (Figure 2); these signals correspond to the three unequivalent methyl groups of the coupling component and to the methyl from the N-acetyl group of diazonium salt, respectively.

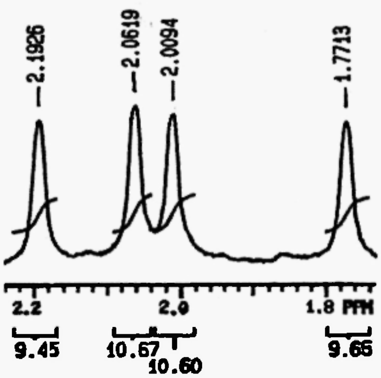
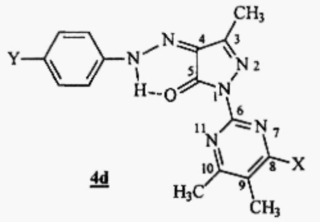


Figure 2. The ^{1}H-NMR spectrum of the coupling product <u>11</u> between *p*-(acetyl-amino)-benzenediazonium salt and 1-(4-hydroxy-5,6-dimethyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one recorded in CD_3SOCD_3 (1.7-2.4 ppm zone, corresponding to aliphatic hydrogens area)

Because of the possibility of tautomerism in the case of the prepared coupling products (4a, 4b, 4c, 4d) the assignment of the structure (or of the structures in which the coupling products appear, in different conditions) is quite difficult. It is worth mentioning that the pyrazolin-5-one azoic dyes tautomerism, including here the commercial analogues of the products 4 obtained by coupling of the aromatic diazonium salts with PhMP 1 (*e.g.* 13), is a controversial question (5,23-35).

However, most of the papers on this subject published in the last 25 years (23-26, 28-30, 32-35) report that the only tautomeric form detected in the solid state and in chloroformic solution, respectively, of the azoic coupling products of PhMP 1 is the 4-arylhydrazono-1-phenyl-3-methyl-pyrazolin-5-one form (*e.g.* 13), as the Z stereoisomer, in which exists an intramolecular hydrogen bond. The decisive proof for this tautomeric form is supposed to be (23) the appearance in the ^{1}H-NMR spectra of the azoic coupling products of the PhMP 1 of a signal at 13-14 ppm assigned to the hydrazonic hydrogen. This assignment was confirmed by ^{1}H- and ^{15}N-NMR spectra of some ^{15}N-labelled azoic coupling products of PhMP 1 (23, 30, 32, 35). The same signal, assigned to the hydrazonic hydrogen, appears in the ^{1}H-NMR spectra (Table II) of the azoic coupling products 4 described in this paper. On the other hand, the ^{1}H-NMR spectra of these products show the formal existence of a single chemical species in $CDCl_3$ or CD_3SOCD_3 solutions. These experimental observations let us estimate that in mentioned solvents only the hydrazonic tautomeric form is detectable in NMR, or that this one is involved in a rapid equilibrium whose rate is too high to distinguish the individual species in the ^{1}H-NMR spectra.

Table II. The ^{1}H-NMR data [chemical shift δ(ppm), multiplicity,* number of hydrogens and coupling constant J(Hz)] of azocoupling products 4 in $CDCl_3$ (7-11) and CD_3SOCD_3 (12) solution, respectively.



4d

X, Y and the compound no.	Hydrogens of the group					
	C_3-CH_3 s, 3H	C_9-CH_3 s, 3H	C_{10}-CH_3 s, 3H	Aromatic ring	hydrazonic NH s, 1H	Other
X=OH Y=H; 7	2.39	2.00	2.33	7.26 ; t ; 1H ; 6.7 7.42 ; t ; 2H ; 8.0 7.46 ; d ; 2H ; 8.5	13.15	pyrimidinic NH or OH 11.2 ; bs; 1H
X=OCH_3 Y=H; 8	2.50	2.12	2.40	7.20 ; t ; 2H ; 6.5 7.37-7.50 ; m ; 4H	13.62	-OCH_3 4.09 ; s ; 3H
X=Cl Y=H; 9	2.42	2.05	2.35	7.29 ; t ; 1H ; 6.5 7.41-7.52 ; m ; 4H	13.22 b	-
X=OH Y=Br; 10	2.41	2.05	2.36	7.35 ; d ; 2H ; 8.7 7.57 ; d ; 2H	13.16	pyrimidinic NH or OH 11.09 ; bs; 1H
X=OH Y=$NHCOCH_3$; 11	2.42	2.07	2.38	7.45 ; d ; 2H ; 8.7 7.65 ; d ; 2H	13.25	acetyl's CH_3 2.21 ; s ; 3H
X=OH Y=O_2S-NH_2; 12	2.29	1.9	2.21	7.72 ; d ; 2H ; 8.5 7.84 ; d ; 2H	-	-

*: s: singlet ; d: doublet ; t: triplet ; m: complex multiplet ; b: broad.

The last assumption seems to be supported by the shape of the visible absorption band of the azoic coupling products 4, recorded in different solvents and by the effect of the addition of hydrochloric acid or potassium hydroxide on the visible spectrum of these compounds recorded in absolute methanol. Thus, the visible absorption band of compounds 4 in methanol or in other solvents (benzene, chloroform, dimethylsulfoxide) is wide, sometimes shoulders appeared (inflexion points) (Figure 1).

The addition of hydrochloric acid or potassium hydroxide, to the methanolic solution of azoic coupling products 4, until the acid or base concentration reached 0.1M, caused a shift of the visible absorption band of the methanolic solution of each products 4 (Figure 1) to a higher or to a lower, respectively, wavelength, together with an increase of about 25% of the intensity of the absorption band. Practically, the visible absorption band of each coupling product 4 in absolute methanol, as well as in the other neutral solvents, has the appearance of a superposition of its own absorption bands after the addition of hydrochloric acid (or glacial acetic acid) and potassium hydroxide, respectively (Figure 1).

It is well known that in the case of hydroxy-azo dyes the acidic conditions favour the hydrazonic tautomer (36,37) and the basic conditions favour the hydroxyazoic one (37,38). Usually the hydrazonic tautomer, with an "*o*-quinonoid" structure, has the visible absorbtion at a higher wavelength than the hydroxyazoic one, displaying an aromatic pyrazole moiety.

Taking into account the influence of the addition of hydrochloric acid and potassium hydroxide, respectively, on the visible spectra (in methanol) of the products 4, the mentioned influence (36-38) of the acidic or basic conditions on the azo-hydrazono tautomeric equilibrium, and, on the other hand, the relative position of the azo tautomer absorption compared to that of the hydrazono tautomer (38,39), we suppose that the azoic coupling products 4 exist in solution (absolute methanol, benzene, chloroform, dimethylsulfoxide) as two tautomers in a rapid equilibrium (**4b** $\rightleftharpoons$ **4d**).

The formal detection of only one species compatible with such an equilibrium can be accomplished also by ^{13}C-NMR spectrum (Table III) of the coupling product (4; X=OCH_3; Y=H) 8; the phenylic and pyrazolonic carbons' chemical shifts are comparable (Table III) with those of the correspondent carbon atoms from the coupling product 13 of PhMP 1, compound reported to exist in hydrazonic form (23-25,30,32-36).

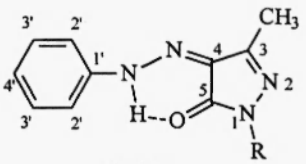
Also, we have to mention that in the infrared spectra of some coupling products 4, recorded in solid state, bands corresponding to the stretching vibrations $\nu_{C=O}$ (1630-1700 cm^{-1}) and ν_{NH} (3225 cm^{-1}) are observed, bands which are compatible with the hydrazonic **4d** or the iminocetoazoic **4c** forms.

The presence of the tautomerism in the case of the azoic coupling products 4 studied in this paper is in good agreement with our observation concerning the visible spectra of some similar dyes obtained (15,16) by coupling of the aromatic diazonium salts 6 with 1-(6-methyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones. In these spectra appear one, two or three absorbtion bands, depending on the substituent of the phenylic radical, the solvent and the acidic or basic conditions of the recording, respectively. These bands were assigned to the tautomeric forms **4b**, **4c**, **4d**, based on a spectral (NMR, UV-VIS) and quanto-chemical study (40).

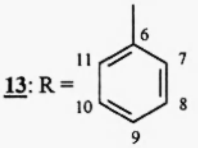
Table III. The ^{13}C-NMR chemical shifts of 3-methyl-1-phenyl-4-phenylhydrazono-pyrazolin-5-one 13 and its 1-(4-methoxy-5, 6-dimethyl-pyrimidin-2-yl)ic analogue 8d in $CDCl_3$ solution. The values of similar and therefore comparable carbon atoms are underlined.

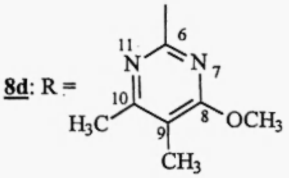
The carbon atom or the group position	^{13}C chemical shifts, ppm	
	13*	8d
3	148.4	149.8
4	128.4	127.9
5	157.7	158.3
6	138.0	165.9
7	118.4	-
8	128.8	168.5
9	125.0	112.2
10	128.8	152.4
11	118.4	-
1'	141.1	141.1
2'	115.7	116.0
3'	129.6	129.7
4'	125.7	126.0
(C_3)-CH_3	11.7	12.2
(C_9) -CH_3	-	10.6
(C_{10}) -CH_3	-	22.1
(O) -CH_3	-	54.3

*: Data from literature (24,32)

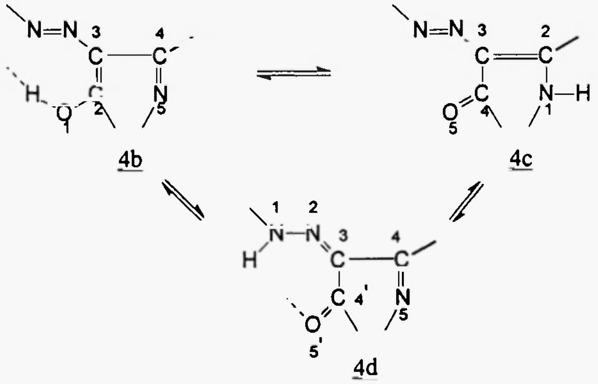


13, 8d





In fact, the tautomeric forms, 4b, c, and d, represent a set of isomers connected by [1,5] sigmatropic shifts of hydrogen atoms (Scheme 2). This implies that the respective interconversions, thermally allowed as suprafacial processes, take place with high velocity, even at room temperature. Forms 4b and 4d are components of a pair interconnected by reactions involving obvious "aromatic" transition states, and, of course, these are the main actors in the equilibria under discussion, with the 4d structure favored by thermodynamic factors, as shown by NMR and quanto-mechanical calculations (40). Transitions involving the 4c tautomer are significantly more difficult from the geometrical point of view, but still favored by the orbital criteria. In contrast, the structure 4a can be reached, starting from any other tautomer, only by [1,3] shifts, forbidden for hydrogen; such interconversions, if ever occurring (none of our experimental facts point out definitely to the existence of this form in the tautomeric mixture) could be only the result of charge-controlled, ionic, processes.



Scheme 2

CONCLUSIONS

In this paper the first synthesis of six azoic coupling products 4 of 1-(5,6-dimethyl-4-X- pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones 5 with aromatic diazonium salts 6 was described. The UV-VIS and (^{1}H, ^{13}C)-NMR spectra support the assumption that the azoic coupling products 4 exist in solution in a hydrazono-azohydroxy tautomeric equilibrium (4b $\rightleftharpoons$ 4d). The high rate of tautomerism makes impossible to distinguish the tautomers in NMR spectra; these spectra formally show the existence of only one, hydrazonic, species. The chemical shifts (^{1}H, ^{13}C) correspond to those assigned to hydrazonic tautomers of the analogous azoic coupling products obtained from 1-phenyl-3-methyl-pyrazolin-5-one 1.

EXPERIMENTAL

The procedures for the preparation of 1-(5,6-dimethyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones 5 are the same as those previously described (17,18). Aromatic amines used for the preparation of diazonium salts 6 were commercial products; their diazotation was achieved by standard methods (5,41). The coupling reaction between diazonium salts 6 and 1-(5,6-dimethyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones 5 was performed in conditions similar to those used for the azoic coupling of 1-phenyl-3-methyl pyrazolin-5-one 1 (5,6) and 1-(6-methyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones (15,16), respectively.

Elemental analyses were carried out at the Chemistry and Pharmaceutical Research Institute Cluj-Napoca. Melting points were recorded with an Electrothermal IA 6304 apparatus and are uncorrected. UV-VIS spectra were performed on a SPECORD UV-VIS spectrophotometer; the analytical grade reagents and solvents provided by Reactivul (Bucharest, Romania), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland) were used without further purification. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ and CD_3SOCD_3 at room temperature on a Varian Gemini 300 (300 MHz) apparatus. Infrared spectra were recorded in solid state (KBr pellets) with a Karl Zeiss Jena UR20 spectrophotometer.

General procedure for the azoic coupling: 0.01 Mol of each 1-(5,6-dimethyl-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one 5 was treated with a warm solution prepared from 0.01-0.02 Mol sodium hydroxide, 0.005 Mol sodium carbonate and 20 mL water (pH□10). This mixture was cooled to 0-5°C and into it was poured, under stirring and by keeping the temperature below 10°C, one of the diazonium salts 6 freshly prepared from 0.01 Mol of the corresponding aromatic amine. Usually the coupling reaction was rapid, the reaction mixture became coloured immediately; however, the mixture was stirred for 0.5-12 hours at 15°C. After that the pH of the mixture was corrected to 6-7 with acetic acid. The suspension was filtered, washed on the filter with water, dried and recrystallized from methanol. The dyes prepared in this manner, the yields and some characteristics are presented in Table I.

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