ELECTROPHILIC SUBSTITUTION IN N-ARYL-2-PYRAZOLINES.

4.* AZO COUPLING REACTIONS

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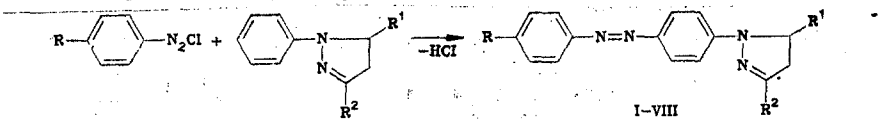
4-R-Phenyldiazonium chlorides enter into the azo coupling reaction with 2-pyrazoline derivatives at the para position of the N-aromatic nucleus. The reaction is very sensitive to steric and electronic effects of the substituting groups in the pyrazolines. The electronic spectra and acid-base properties of the synthesized azopyrazolines are discussed.

In the classification order of electrophilic agents [2], aryldiazonium salts are represented as one of the least reactive. In addition, the electrophilicity of phenyldiazonium chloride is sufficient for its reaction with 1,3-diphenyl- and 1,3,5-triphenyl-2-pyrazolines [3]. We studied the degree to which substitution in the pyrazoline nucleus affects the capacity of its N-phenyl derivatives for azo coupling reactions.

Phenyldiazonium chloride and its para derivatives with dimethylamino, methoxy, methyl, chloro, and nitro groups were studied as diazo components, and 1,3-diphenyl-, 1,5-diphenyl-3-methyl-, 3,5-diphenyl-1-(3-tolyl)-, and 1,5-diphenyl-3-(4-R-phenyl)-2-pyrazolines were studied as azo components. The azo coupling reaction was conducted by addition of an aqueous solution of the diazonium salt [4] to a chilled solution of pyrazoline in acetic acid; the excess acetic acid prevented precipitation of the starting pyrazoline.



I—VIII

I—VIII a R=OCH_3, b R=CH_3, c R=H, d R=Cl, e R=NO_2; I—VII R^1=C_6H_5, VIII R^1=H; Ia—e R^2=4-$(CH_3)_2NC_6H_4$; IIa—e R^2=4-$CH_3OC_6H_4$; IIIa—e R^2=4-$CH_3C_6H_4$; IVa—e VIIIa,c,e R^2=C_6H_5; Vc—e R^2=4-ClC_6H_4; VIe R^2=4-$O_2NC_6H_4$; VIIa—e R^2=CH_3

It is known that the phenyldiazonium ion is sensitive to steric effects in the azo component, to which the preferential attack of the para position of N,N-disubstituted anilines [5] is due. For example, the fact that 3,5-diphenyl-1-(3-methylphenyl)-2-pyrazoline does not enter into the azo coupling reaction with any of the diazo compounds used could also be attributed to steric hindrances.

The direction of azo coupling in the para position of the N-phenyl series of pyrazolines has been demonstrated experimentally: compounds Ic, IIIc, and Vc are reduced to the previously described 1-(4-aminophenyl)-3-R-5-phenyl-2-pyrazolines [6].

The azo coupling reaction takes place in a relatively acid medium (pH ∿ 2-3). It is known [4, 5] that the reactivity of the diazo component is determined by its ionized form, whose formation is favored by an increase in the acidity of the medium. Aromatic amines, on the other hand, react in the molecular form, and an increase in the concentration of the protonated form, observed in more acid media, decreases the yield of the products of azo coupling. Aromatic derivatives of pyrazoline are not protonated in weakly acid solutions [7], for this reason, bringing the pH to ∿2-3 causes the azo coupling reaction to take place by favoring the ionization of the diazo component and not decreasing the reactivity of N-phenyl-2-pyrazolines. However, not all azo coupling reactions can take place even in

*See [1] for Communication 3.

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TABLE 1. Yields of Compounds I-VIII

Compound	Yield, %	Compound	Yield, %	Compound	Yield, %	Compound	Yield, %
Ia	15	IIIa	10	Va	0	VIIa	15
Ib	20	IIIb	15	Vb	0	VIIb	20
Ic	45	IIIc	40	Vc	35	VIIc	40
Id	45	IIId	45	Vd	40	VIId	45
Ie	50	IIIe	45	Ve	40	VIIe	50
IIa	10	IVa	10	VIa	0	VIIIa	10
IIb	20	IVb	15	VIb	0	VIIIb	—
IIc	40	IVc	40	VIc	0	VIIIc	40
IIe	45	IVd	40	VId	0	VIIId	—
IId	45	IVe	45	VIe	40	VIIIe	45

TABLE 2. Characteristics of Compounds I-VIII

Compound	mp, °C (decomp.)	IR spectrum, cm^{-1}		λ_{max},* nm ($\varepsilon \cdot 10^{-3}$) (in methanol)		λ_{max}† of fluorescence, nm (in methanol)	pK_a‡	Found N, %	Empirical formula	Calculated N, %
		$\nu_{C=N}$	ν heterocycle	B	HB^+					
Ia	197	1600	1500	475 (23,5)	625	580	0,40	14,9	$C_{30}H_{29}N_5O$	14,7
Ib	192	1612	1492	470 (22,9)	595	575	—	15,3	$C_{30}H_{29}N_5$	15,2
Ic	195	1595	1510	467 (21,5)	570	570	0,86	15,8	$C_{29}H_{27}N_5$	15,7
Id	208	1589	1490	481 (21,4)	588	570	—	14,6	$C_{29}H_{26}ClN_5$	14,6
Ie	220	1600	1500	532 (24,2)	575	—	—	17,2	$C_{29}H_{25}N_6O_2$	17,1
IIa	235	1642	1480	461 (23,4)	610	555	—	12,1	$C_{29}H_{26}N_4O_2$	12,1
IIb	230	1615	1490	450 (22,7)	600	555	—	12,6	$C_{29}H_{26}N_4O$	12,5
IIc	225	1602	1497	445 (22,0)	588	545	1,0	12,9	$C_{28}H_{24}N_4O$	12,9
IId	237	1592	1515	456 (22,1)	587	545	—	12,0	$C_{28}H_{23}ClN_4O$	12,0
IIe	240	1595	1510	507 (24,0)	550	—	—	14,7	$C_{28}H_{23}N_5O_3$	14,6
IIIa	236	1600	1500	442 (23,0)	610	550	—	12,6	$C_{29}H_{26}N_4O$	12,5
IIIb	228	1595	1510	435 (22,7)	592	550	—	12,8	$C_{29}H_{26}N_4$	13,0
IIIc	221	1589	1490	431 (22,5)	588	545	0,08	13,3	$C_{28}H_{24}N_4$	13,5
IIId	230	1600	1500	446 (22,2)	588	545	—	12,2	$C_{28}H_{23}ClN_4$	12,4
IIIe	238	1592	1512	503 (24,1)	545	—	—	15,2	$C_{28}H_{23}N_5O_2$	15,1
IVa	192	1600	1500	445 (22,0)	610	550	0,45	13,0	$C_{28}H_{24}N_4O$	12,9
IVb	191	1600	1500	440 (21,5)	588	545	0,66	13,6	$C_{28}H_{24}N_4$	13,5
IVc	190	1600	1500	435 (23,0)	588	535	0,51	14,0	$C_{27}H_{22}N_4$	13,9
IVd	203	1588	1489	444 (22,9)	588	535	0,12	12,8	$C_{27}H_{21}ClN_4$	12,8
IVe	205	1596	1510	526 (20,5)	545	—	−0,04	15,8	$C_{27}H_{21}N_5O_2$	15,6
Vc	210	1595	1510	436 (23,1)	584	540	0,41	12,6	$C_{27}H_{21}ClN_4$	12,8
Vd	216	1588	1489	444 (22,6)	668	535	—	11,8	$C_{27}H_{20}Cl_2N_4$	11,9
Ve	238	1600	1500	495 (20,5)	584	—	—	14,6	$C_{27}H_{20}ClN_5O_2$	14,5
VIe	210	1595	1510	505 (22,2)	575	—	−0,45	17,1	$C_{27}H_{20}N_6O_4$	17,0
VIIa	185	1600	1500	431 (28,8)	581	550	—	15,1	$C_{23}H_{22}N_4O$	15,1
VIIb	180	1600	1500	417 (28,4)	556	550	1,1	15,6	$C_{23}H_{22}N_4$	15,8
VIIc	164	1599	1500	415 (28,0)	556	540	1,1	16,3	$C_{22}H_{20}N_4$	16,5
VIId	168	1600	1500	421 (27,7)	556	540	—	14,7	$C_{22}H_{19}ClN_4$	14,9
VIIe	190	1600	1500	433 (29,0)	548	—	0,66	18,2	$C_{22}H_{19}N_5O_2$	18,1
VIIIa	188	1610	1490	433 (22,6)	625	535	0,94	15,6	$C_{22}H_{20}N_4O$	15,7
VIIIc	186	1600	1500	441 (22,5)	581	540	0,74	17,2	$C_{21}H_{18}N_4$	17,1
VIIIe	205	1595	1510	505 (20,0)	575	—	0,83	18,8	$C_{21}H_{17}N_5O_2$	18,8

*The values of λ_{max} of the long-wave band of molecular (B) and protonated (HB^+) forms.
†Compounds containing a nitro group do not fluoresce.
‡The pKa of compounds VIIb, c, e were obtained in a 0.1 N solution of $HClO_4$.

these conditions. For example, it has been found that the reactivity of p-$(CH_3)_2$-N-phenyldiazonium chloride was insufficient for its azo coupling with 1,3-5-triaryl-2-pyrazolines. The initial products were also recovered unchanged in a number of other experiments (Table 1).

The yield of the azo compounds (Table 1) decreased with an increase in the electron-donor properties of the substituent in the diazo component and the electron-acceptor properties of the R^2 substituent in the pyrazoline component. The first mechanism is well known [5], while the second was demonstrated unambiguously for the first time. In nitration,

TABLE 3. Values of λ_{max} of the Long-wave Absorption Band of $R_1-C_6H_4-N=N-C_6H_4-R_2$ Compounds

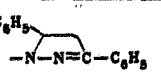
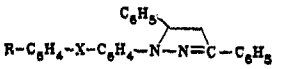
R_1	λ_{max}, nm			
	$R_2=N(CH_3)_2$ [10]		$R_2=$ 	
	in alcohol	in alcohol–HCl mixture	in alcohol	in alcohol–HCl mixture
H	412	520	441	581
4-OCH_3	410	560	443	625
4-NO_2	480	510	505	575

TABLE 4. Values of λ_{max} of the Long-wave Absorption Band of Compounds with the Following General Formula in Toluene:

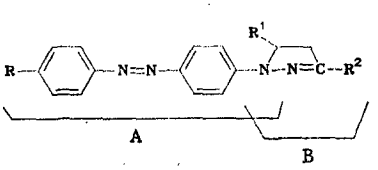


R	λ_{max}, nm			
	X=HC=N [11]	X=HC=CH [11]	X=N=CH [11]	X=N=N
H	407	393	395	435
4-NO_2	480	448	420	526

bromination, and formylation reactions [1, 7-9], the reagents are so reactive that the differences in the electron density of the N-phenyl nuclei of the aromatic derivatives of pyrazolines are totally leveled. In the azo coupling reaction, the equilibrium character of the process and the comparatively low electrophilicity of the reagent permit experimentally revealing the changes in the distribution of the electron density in the molecules of the pyrazolines caused by substitution of the aryl in position 3 of the heterocycle. It is totally obvious that the introduction of electron-acceptor substituents in the 3-phenyl substituent decreases the electron density of the N-phenyl nucleus in the pyrazoline molecule by increasing the polarization of the N–N=C–R_2 fragment. The fact that the reactive p-O_2N-phenyldiazonium chloride reacts with 1,5-diphenyl-3-(4-nitrophenyl)-pyrazoline indicates the preservation of the cross-conjugation character of the conjugated system of this pyrazoline. However, the activating effect of the $N_{(1)}$ atom on the neighboring aromatic nucleus in this compound is increasingly weakened, which is reflected in the total absence of its reaction with other aryldiazonium chlorides (Table 1). In our opinion, the reaction studied is a clear illustration of the cross-conjugated character of the p,π system of 1,3-diaryl-(and 1,3,5-triaryl) 2-pyrazolines.

Compounds I-VIII have very pronounced indicator properties due to the conjugation of the azo group with the pyrazoline fragment: they turn blue-violet in acid media and yellow-orange in alkaline media. The spectral characteristics of the molecular and ionic forms are reported in Table 2.

The values of λ_{max} of the long-wave band of the molecular form of azopyrazolines I-VIII were sensitive to the electronic effect of R and R^2 substituents: both the electron-donor dimethylamino group and the electron-acceptor nitro group cause a marked bathochromic shift regardless of the site of their insertion. A similar effect is also observed with the addition of two nitro groups (compound VIe). These findings illustrate the cross-conjugated character of the p,π system of azopyrazolines I-VIII.

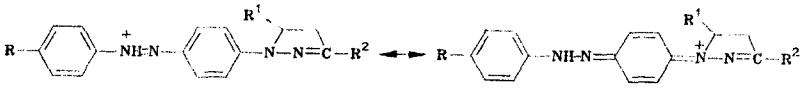


The mutual effect of chromophore subsystems A and B can be judged by the data in Table 3. The spectral characteristics of 4-R_1-4'-dimethylaminoazobenzenes can be considered the properties of fragment A in a first approximation. The bathochromic shifts of the long-wave band of azopyrazolines IVa, c, e (Table 3) should be considered the contribution of

pyrazoline chromophore B. It is evident that this effect is significant for both the molecular and for the protonated forms.

The primary responsibility of chromophore A for the long-wave absorption of azopyrazolines can also be judged by the data in Table 4, where the values of λ_{max} of the long-wave bands of π electron analogs of four types which differ with respect to bridge X are compared. Even in the absence of an R substituent the spectrum of the azopyrazoline undergoes a marked red shift which indicates significant charge transfer from the pyrazoline nucleus to the arylazo system on excitation of the molecules. The introduction of a nitro group as R, which causes such polarization, increases the difference in the absorption spectrum of the compared compounds. It also follows from the data in Table 4 that among the components of the X bridges, the azo group is characterized by the highest polarizability.

Protonation of azopyrazolines I-VIII takes place in a sufficiently acid medium (pH $\leqslant$ 1.0).



In selecting the conditions for studying their relative basicity, it was assumed that the solubility of the molecular forms in water is extremely low, and the study was thus conducted in a mixture of water and acetone. The acidity of the medium for the creation of sufficient concentrations of protonated forms in solution was attained by addition of $HClO_4$. A preliminary study was conducted to select the optimum ratio of water and acetone; it showed that the value of the pKa of the cationic acid HB^+ formed decreases with an increase in the concentration of acetone (up to an acetone–water ratio of 7:1 by weight) and then sharply increases. Since the mixture of acetone and water (9:1 by weight) has almost the same differentiating properties with respect to bases as anhydrous acetone [12, 13], this composition was selected for the measurements. With this concentration of acetone, there is no danger of a decrease in the solubility of the azopyrazolines with an increase in the pH, and the pKa are high enough to work with relatively low concentrations of $HClO_4$.

The pKa was calculated with an equation derived from the law of mass action and the Bouguer–Beer law: $pKa = pH + \log (\varepsilon - \varepsilon_B)/(\varepsilon_{HB^+} - \varepsilon)$. The values of ε_{HB^+} were usually measured in aqueous solutions of sulfuric (11 N) and perchloric (5.7 N) acids; it was first shown that the spectrum of form HB^+ changes comparatively little under the effect of the solvent. Wavelengths near the λ_{max} of the long-wave band of form HB^+ were selected as the analytic wavelengths; the ratio $\varepsilon_B \ll \varepsilon_{HB^+}$ was observed for all dyes studied. The analytic concentration of $HClO_4$: $pH = -\log c\ (HClO_4)$ was used for controlling the acidity. Electrometric measurements of the pH in such conditions are not very effective, and the significance of the value of H_0 or another acidity function in a ternary mixture still requires explanation. The dissociation of the $HClO_4$ was considered total.

The analysis of the dependence of the pKa values on the concentration of $HClO_4$ showed that in the range of concentrations (ionic strengths) greater than 0.1, the pKa increase with an increase in the concentration of acid. It is obvious that for the activity coefficients, the relation $f_{H^+} \cdot f_B \cdot f_{HB^+}^{-1} = 1$ is not respected, which is natural due to the low dielectric constant of the solvent ($\sim$24), which also intensifies the elevated salt effects without it. The formation of $HB^+ \cdot ClO_4^-$ ion pairs is also possible. The values of the pKa obtained in 0.2 N $HClO_4$ (the exceptions are given in Table 2) were used for the comparative characteristics of the basicity of the dyes. The validity of this approach is determined by the following. The basic chromophore system of the azopyrazolines studied is the same. It is also known that protonation of the nitrogen atoms in the pyrazoline ring does not take place even in more acid media than those studied here; for this reason, the possibility of protropic tautomerism of the HB^+ form, which takes place for dimethylaminoazobenzene ("quinoid–azoid tautomerism" [10]), for example, is excluded for this reason. Although the values of pKa obtained are not thermodynamic characteristics, due to the equivalence of the conditions of their measurement and the uniformity of the reaction sites, they should regularly reflect the relative basicity of the azopyrazolines.

Compounds Ia-e, which contain a dimethylamino group, are an exception: with the selected method of investigation, the constant characterizing the equilibrium between particles with a protonated dimethylamino group and particles protonated two times is measured for these dyes.

The pKa obtained even in the conditions selected as standard conditions are characterized by an error of ±0.1-0.5 pKa unit.

In analyzing the pKa values (Table 2), it is possible to distinguish several tendencies caused by the role of several factors. With a decrease in the electron-donor properties of R and R^3 substituents, the pKa decrease. For this reason, it is totally normal that compound VIe is characterized by minimum basicity. This tendency is preserved in the group of compounds in which there is a methyl group instead of an aromatic substituent in position 3 of the heterocycle. However, it should be remembered that the high pKa values observed in this group of compounds were obtained with a 0.1 N concentration of $HClO_4$, which should be taken into consideration in the comparison with the other results.

It is known [14] that the phenyl substituent in position 5 of the heterocycle creates steric hindrances to the neighboring aromatic ring included in the conjugated system of azopyrazoline molecules. Its elimination causes an increase in the planarity of the basic p,π system of azopyrazolines VIIIa, c, e and in their basicity.

In conclusion, it should be noted that the molecular form of most azopyrazolines I-VIII exhibits blue fluorescence, which is easily masked by the absorption of the ionic form (Table 2); for this reason, the acid–basic interactions of these compounds can be visually controlled both by the sharp change in the color of the solutions and by the disappearance of fluorescence.

EXPERIMENTAL

The electronic absorption spectra of compounds I-VIII were made on a Specord UV-vis spectrometer in methanol with a $(1\text{-}2)\cdot10^{-5}$ N concentration of the substances, and the IR spectra were made on a Specord IR-75 spectrometer in KBr pellets.

Determination of the pKa of the Azopyrazolines. Here 7 mg of compound IVc were dissolved in 100 ml of acetone (very pure brand, distilled three times over $KMnO_4$, K_2CO_3, and with no additives), aliquot quantities of this solution were placed in 25 ml graduated flasks, the corresponding amounts of an aqueous solution of $HClO_4$ and distilled water (total volume of water of 1.97 ml) were added, and the mixture was brought to the mark with acetone while thermostatting (25°C). The spectral studies were conducted with a set of cells 0.5-5.0 cm thick. The $HClO_4$ solution was standardized with a solution of sodium hydroxide whose concentration was determined with adipic acid recrystallized two times.

The pKa of the other compounds were determined similarly (Table 2).

1-(4-Phenylazophenylene)-3,5-diphenyl-2-pyrazoline (IVc). Here 1.3 g of 1,3,5-triphenyl-2-pyrazoline was dissolved in 50 ml of acetic acid while heating, the solution was cooled to 14-16°C, and a solution of phenyldiazonium chloride prepared from 0.5 ml of aniline, 2.5 ml of 5 N HCl, 0.35 g of $NaNO_2$, and 10 ml of water, was added by drops while stirring. The blue solution formed was left at room temperature overnight, then 40 g of NaOH and 250 g of ice were added to the mixture. The brown sediment precipitated was filtered off and 0.7 g (40%) of compound IVc with a mp of 190°C (from benzene) was extracted with benzene.

Compounds I-VIII were prepared in a similar manner.

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SYNTHESIS OF N-CARBOXYLALKYLBENZIMIDAZOLIN-2-ONES

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The corresponding N-mono- and N,N'-dicarboxylalkylbenzimidazolin-2-ones were prepared by the reaction of the sodium salts of benzimidazolin-2-one and its 1,5,6-substituted derivatives with chloroacetic acid, acrylonitrile, and γ-butyrolactone.

N-Alkyl-substituted benzimidazolin-2-ones are of interest as potential pesticides: they include substances which have growth-regulating [1] and fungicidal [2, 3] properties. Benzimidazolyl-N-acetic acid also exhibits some auxin activity [4]. The activity of these compounds could be explained by concepts of the mechanism of β-oxidation [5], where arylhydroxycarboxylic acids with an odd number of methylene groups can be transformed into active acetic acid homologs, while acids with an even number of methylene groups yield phenols, which have no growth-stimulating activity.

We synthesized N-carboxylalkylbenzimidazolin-2-ones (IIa-f–IVa-f) and studied the conditions of the reaction of the sodium salts of benzimidazolin-2-ones (Ia-f) with halogenated aliphatic acids (chloroacetic, α-chloro- and β-bromopropionic, and β-chlorobutryic) to determine the effect of the length of the carboxylalkyl substituent on the manifestation of pesticidal activity and the basicity of benzimidazolin-2-ones during the reaction of N-carboxylalkylation.

The products of carboxylalkylation of IIa-f (Table 1) could only be obtained with chloroacetic acid after modification of the conditions in [6]. In N-alkylation of compound Ie with bromoacetic acid ethyl ester in a solution of sodium ethylate [7], 1-carboxymethylbenzimidazolin-2-one ethyl ester was separated. However, in the alkylation of compounds Ie and f with chloroacetic acid, the isopropenyl group is preserved, and the corresponding 1-isopropenyl-3-carboxymethyl derivatives of IIe and f were obtained, which form benzimidazolin-2-ones IIg, h. Unsubstituted in position 1(3).

The negative results in the carboxylation of benzimidazolin-2-one salts Ia-f by other halogenated aliphatic acids are probably due to the higher reactivity of chloroacetic acid in comparison to the α-chloropropionic and β acids, despite the relatively higher basicity of benzimidazolin-2-one* (pKa = 10.85 [8]) in comparison to benzoazolin-2-one (pKa = 9.34 [9]) and benzoxazoline-2-thione (pKa = 6.70 [9]) (products of N-carboxyalkylation with β-bromopropionic and β-chlorobutyric acids are nevertheless obtained with the latter [10]).

N-Carboxyethylbenzimidazolin-2-ones IIIa-f (Table 1) were prepared by cyanoethylation of compounds Ia-f in the conditions in [10] with subsequent hydrolysis of N-mono- and N,N'-di-(β-cyanoethyl) derivatives with concentrated hydrochloric acid. It was previously observed [11] that cyanoethylation of benzimidazolin-2-one only takes place in the presence of trimethylphenylammonium or triethylbenzylammonium hydroxide. 1,3-Dicyanoethylbenzimi-

*We will hypothesize that the basicity of the anions of benzimidazolin-2-ones I1-f is in agreement with the basicity of the corresponding bases.

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