ELECTROPHILIC SUBSTITUTION IN N-ARYL-2-PYRAZOLINES.
3.* INTRODUCTION OF NITRO-, SULFO-, AND ACYL GROUPS.
REACTION WITH MICHLER'S KETONE

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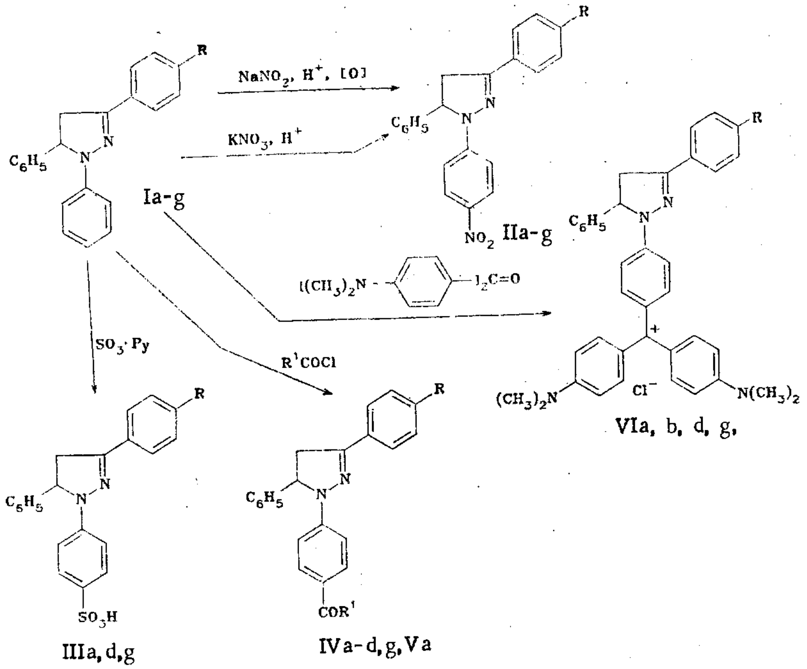
1-Phenyl-3,5-diaryl-2-pyrazolines are nitrated, sulfurated, and acylated in the para-position of the 1-phenyl ring. In the presence of $POCl_3$, pyrazolines form triphenylmethane dyes with a Michler's ketone.

In connection with the prospects for the use of aromatic derivatives of 2-pyrazolines in electrochemiluminescent [2] and electrophotoactive [3] materials, methods of their chemical modification are being used. It has been noted [1, 4] that the phenyl ring in the 1-position of 2-pyrazolines is similar to the aromatic ring of anilines. And yet, the presence of a more extended conjugated system in pyrazolines, as well as their ability to be oxidized to pyrazoles, predetermine the specificity of the conditions of electrophilic processes.

In this work we studied the nitrosylation, nitration, sulfuration, and acylation of 1,3,5-triphenyl-2-pyrazoline (Ia) and some of its derivatives (Ib-g), as well as their interaction with aromatic ketones.



I—VI a R=H, b R=CH_3, c R=OCH_3, d R=$N(CH_3)_2$, e R=Cl, f R=Br, g R=NO_2;
IV R'=CH_3; V R'=C_6H_5

The nitrosylation of 1,5-diphenyl-3-(4-R-phenyl)-2-pyrazolines (Ia-g) was carried out according to the procedure of [5] or by the action of butyl nitrite in ethanol with additions of HCl at temperatures from +14 to −15°C; individual experiments were conducted in an atmo-

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*For Communication 2, see [1].

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	IR spectrum (KBr), cm^{-1}		UV spectrum (in methanol), λ_{max}, nm (log ε)	Emission spectrum (in methanol), λ_{max}, nm	Found, %		Gross formula	Calculated, %		Yield, %
		νC=N	νC=O			N	S (Cl)		N	S (Cl)	
IIIa	196—198	1600	—	359 (4,30), 310 (3,90), 236 (4,16)	465	7,5	8,6	$C_{21}H_{18}N_2O_3S$	7,4	8,5	40
IIId	240—242	1606	—	370 (4,28), 310 (4,00)	475	10,1	7,7	$C_{23}H_{23}N_3O_3S$	10,0	7,6	45
IIIg	220—222	1596	—	439 (4,38), 270 (4,37)	545	9,9	7,7	$C_{21}H_{17}N_3O_5S$	9,9	7,6	38
IVa	152	1597	1650	379 (4,37), 309 (3,83), 245 (4,15)	440	8,2	—	$C_{23}H_{20}N_2O$	8,2	—	35
IVb	155	1601	1658	379 (4,43), 305 (4,22), 250 (4,30)	485	8,0	—	$C_{24}H_{22}N_2O$	7,9	—	35
IVc	158	1602	1660	382 (4,47), 305 (3,94), 251 (4,17)	475	7,7	—	$C_{24}H_{22}N_2O_2$	7,6	—	35
IVd	184	1597	1660	394 (4,34), 305 (4,07), 250 (3,97)	485	11,1	—	$C_{25}H_{25}N_3O$	11,0	—	40
IVg	188	1596	1672	460 (3,97), 323 (4,26), 274 (4,26)	490	11,0	—	$C_{22}H_{19}N_3O_3$	10,9	—	35
Va	158	1602	1664	382 (4,44), 311 (4,18), 246 (4,46)	490	7,1	—	$C_{28}H_{22}N_2O$	7,0	—	37
VIa	>300	1590	—	613, 584 sh, 472, 361, 311, 250	—	10,2	(6,5)	$C_{36}H_{27}ClN_4$	10,2	(6,4)	75
VIc	>300	1590	—	613, 582 sh, 472, 360, 311, 251	—	9,8	(6,2)	$C_{37}H_{29}ClN_4O$	9,6	(6,1)	75
VId	>300	1588	—	630 sh, 581, 465, 371, 311, 250	—	11,9	(6,2)	$C_{38}H_{32}ClN_5$	11,8	(6,0)	80
VIg	>300	1595	—	608, 585 sh, 448, 365, 311, 270	—	11,7	(6,7)	$C_{36}H_{26}ClN_5O_2$	11,7	(6,0)	70

sphere of nitrogen. In all cases a green color was observed in the mixture (characteristic of nitroso compounds [6, p. 107]); however, crystals of 1-(4-nitrophenyl)-3-(4-R-phenyl)-5-phenyl-2-pyrazolines (IIa-g) precipitated from the solutions with quantitative yields [7].

It is known [6, p. 196] that the presence of electron donor substituents in the para-position to the nitroso group increases its ability for oxidation. N-Phenyl-2-pyrazolines (I), in contrast to N,N-dimethylaniline, are not protonated by hydrochloric acid; consequently, their $N_{(1)}$ atom retains its own electron donor character in the intermediate nitroso compounds, which is probably another factor determining the high rate of oxidative processes.

The formation of compounds II in reactions with nitrous acid is all the more interesting in that according to the data of [8], the interaction of pyrazoline Ia with nitric acid leads not to the nitroso derivative IIa, but to a bis-pyrazoline compound. In the nitrosylation of pyrazoline Ia by nitric acid, the solutions are instantaneously colored a blue-violet (a sign of formation of radical cations characteristic of pyrazolines; their recombination leads to dications of bis-pyrazolines [9]). With increasing nitric acid concentration, this is accompanied by oxidation to pyrazole. The nitration product of IIa can be obtained only under the action of potassium nitrate in acetic acid on compound Ia, but the yields in this case are lower (50%) than in the case of nitrosylation.

In a study of sulfuration it was considered that in concentrated sulfuric acid 2-pyrazolines form radical cations; this characteristic is utilized in the qualitative Knorr reaction [10]; it also explains the formation of a complex mixture of products under the action of H_2SO_4 on arylpyrazolines I. Attempts to conduct the sulfuration of a dioxane solution of compound Ia by saturation with gaseous SO_3 or by heating a dichloroethane solution of it with the complex pyridine$\bullet SO_3$ in sealed ampules proved unsuccessful. Sulfuration can be accomplished by heating pyrazolines I with the complex pyridine$\bullet SO_3$ in pyridine. The sulfuration process occurs in the 4-position of the N-phenyl ring, as evidenced by the identity of compound Ia and the product of the reaction of p-sulfophenylhydrazine with the chalcone [11].

In the series of aromtic derivatives of 2-pyrazoline, only the reaction of formylation has been studied [13]. We succeeded in carrying out acetylation by the reaction of compounds Ia, c, d with acetyl chloride in dichloroethane (catalyst $AlCl_3$). Compound Ig was also subjected to acetylation; however, the end product IVg could be isolated only by replacement of acetyl chloride by the bromide. Compound Ia also enters into a benzoylation reaction, forming the product Va. Although the yields in acylation reactions are comparatively low, nevertheless, considering the availability of the initial compounds I, the proposed method is more promising than their synthesis by condensation of 4-acetylphenylhydrazines with chalcones [14].

Compounds I readily react with Michler's ketone (with the participation of phosphorus oxychloride), forming triphenylmethane dyes (VI). Attempts to carry out the same reaction with other ketones [chalcone, its 4-$N(CH_3)_2$ derivatives, acetophenone, and benzophenone] proved unsuccessful.

EXPERIMENTAL

The electronic absorption spectra of compounds III-VI were measured in methanol at a concentration of $(1\text{-}4)\bullet 10^{-5}$ M on a Specord UV-vis spectrophotometer; the IR spectra were measured on KBr tablets on a Specord IR-75 instrument. The individuality of compounds II-VI was monitored by the method of thin-layer chromatography on Silufol UV-254 plates; the eluent was chloroform or a mixture of it with methanol (5:1).

1-(4-Nitrophenyl)-3,5-diphenyl-2-pyrazoline (IIa). A. A solution of 1 g (3.4 mmoles) 1,3,5-triphenyl-2-pyrazoline (Ia) in a mixture of 40 ml of acetic acid and 5 ml conc. HCl was cooled to -14°C, and 0.54 g sodium nitrite in 9 ml of water was added to it with simultaneous lowering of the temperature to 0°C. A precipitate of compound IIa formed with a quantitative yield (1.14 g); after crystallization from methanol its mp was 176°C (176°C [7]). Compounds IIb-g were produced analogously.

B. To a solution of 1 g 1,3,5-triphenyl-2-pyrazoline (Ia) in 40 ml of acetic acid we added 0.5 g potassium nitrite. The solution was boiled for 1 h, cooled, precipitated with water, the precipitate filtered off and crystallized from methanol. Yield 0.57 g (50%) of compound IIa.

1-(4-Sulfophenyl)-3,5-diphenyl-2-pyrazoline (IIIa). A mixture of 1 g (3.4 mmoles) 1,3,5-triphenyl-2-pyrazoline (Ia) and 3.2 g (20 mmoles) of the pyridine•SO_3 complex was boiled in 15 ml of pyridine for 20 h, poured out into 50 ml of water, the precipitate salted out by the addition of NaCl, filtered off, washed with hot hexane, and crystallized from methanol. Yield 0.5 g (40%) of compound IIIa. Compounds IIId, and g were produced analogously.

1-(4-Acetylphenyl)-3,5-diphenyl-2-pyrazoline (IVa). To a suspension of 0.5 g aluminum chloride in 10 ml dichloroethane, 0.3 g acetyl chloride was added with mixing, raising the temperature no higher than 0°C. This complex was added with mixing to a solution of 1 g 1,3,5-triphenyl-2-pyrazoline (Ia) in 10 ml of dichloroethane at the same temperatures. The mixture was mixed for another 3 h with cooling, left overnight at room temperature, and then the mixture was boiled for 6 h. After cooling the mass was poured out into a mixture of 100 g crushed ice and 5 ml conc. HCl, the organic layer was removed, washed with water, dried over $MgSO_4$, the solvent distilled off, and the residue crystallized from a benzene—hexane mixture (1:10). Yield 0.4 g (35%) of compound IVa. Compounds IVb, d, and g and Va were produced analogously.

Bis(4-dimethylaminophenyl)[4-(3,5-diphenyl-2-pyrazolinyl-1)phenyl]chloromethane (VIa). A saturated benzene solution of a mixture of 0.5 g (2 mmoles) Michler's ketone and 0.3 g (3 mmoles) $POCl_3$ was added to a solution of 0.6 g (2 mmoles) 1,3,5-triphenyl-2-pyrazoline (Ia) in 5 ml of benzene, boiled for 3 h, the precipitate removed and washed with benzene and hot hexane until traces of pyrazoline and the ketone disappeared (monitored by thin-layer chromatography). Yield 0.85 g (70%) of compound VIa. Compounds VIb, d, and g were produced analogously.

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