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ELECTROPHILIC SUBSTITUTION IN N-ARYL-2-PYRAZOLINES.

2.* REACTIONS WITH ALDEHYDES

V. D. Orlov and M. A. Aziz

UDC 547.778

Leuco compounds of the triphenylmethane series were obtained by the reaction of 1,3-diphenyl-, 3-methyl-1,5-diphenyl-, 1,3,5-triphenyl-, and 1,5-diphenyl-3-styryl-2-pyrazolines with aromatic and heterocyclic aldehydes. The center of electrophilic attack is the para position of the aromatic ring in the 1 position of the heteroring.

It is known [1, 2] that compounds of the 2-pyrazoline group can react with benzaldehyde at high temperatures (~200°C) and in an inert atmosphere to give 4-benzylidene derivatives. It is characteristic that this phenomenon has been observed for compounds that do not contain a substituent in the 1 position of the heteroring. However, precisely pyrazoline systems of this type are devoid of a practically important property, viz., clearly expressed fluorescence [3]. It therefore seemed of interest to study the possibilities of the application of this reaction in a group of 1,3,5-triaryl-2-pyrazolines.

In the present research we selected the quite accessible 1,3,5-triphenyl-2-pyrazoline as the principal subject of our investigation. Attempts to carry out the reaction of this compound with benzaldehyde by the method in [2] (by refluxing in a medium of the pure aldehyde in an inert atmosphere) or under other conditions, viz., by heating a similar solution in sealed ampuls and by carrying out the reaction in various solvents [methanol, ethylene glycol, benzene, xylene, dioxane, and dimethylformamide (DMF)] in the absence and in the presence of catalysts with acidic (HCl, $ZnCl_2$, $AlCl_3$, and concentrated H_2SO_4) and basic (triethylamine, pyridine, and 40% NaOH) character, did not give positive results. The development of a blue-green coloration and its uniform deepening, which is complete in 1-1.5 h, are observed only when dioxane solutions are refluxed in the presence of $HClO_4$. The IR and UV spectra of the compound obtained constitute evidence for retention of the pyrazoline ring; this is also con-

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*See [9] for our previous communication.

A. M. Gor'kii Kharkov State University, Kharkov 310077, Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, p. 88-90, January, 1982. Original article submitted November 24, 1980.

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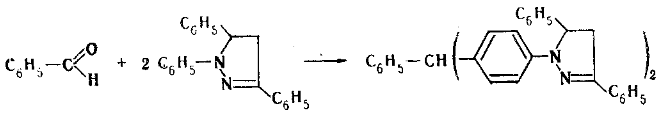
firmed by its fluorescent properties. The absorption and luminescence λ_{max} values are shifted only slightly to the long-wave region as compared with pyrazoline [4].

The described synthesis conditions are equivalent to those under which N,N-dimethylaniline reacts with benzaldehyde to give a leuco compound of the triarylmethane series [5], and the reactivity of the N-phenyl ring in the triarylpyrazolines is similar to that of the N,N-dimethylaniline ring, as demonstrated in the case of reactions with dithiols [6]. Proceeding from the information stated above and the results of elementary analysis one may assume the following pathway for the process:



Under these conditions triphenylpyrazoline reacts with various benzaldehyde derivatives to give I-VII (Table 1), as well as with 3-formyl-1,5-diphenyl- and 1-(4-formylphenyl)-3,5-diphenyl-2-pyrazolines (XI and XII). The reaction of 3-methyl-1,5-diphenyl-, 1,5-diphenyl-3-styryl-, and 1,3-diphenyl-2-pyrazolines with benzaldehydes proceeds similarly (VIII-X, respectively). The reaction is slowed down by the addition of methanol and virtually does not take place in pure methanol.

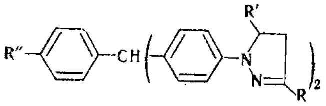
The development of a green-blue or blue coloration during the condensation is evidently due to the formation of very small amounts of cation radicals in the pyrazoline ring under the influence of concentrated $HClO_4$ rather than to the formation of salt forms of the triphenylmethane type, since identical colors develop when concentrated $HClO_4$ is added to dioxane solutions of not only I-XII but also pyrazoline itself, for which the formation of colored cation radicals and dications as oxidation intermediates has been proved [7]. The electronic absorption spectra of these ions differ fundamentally from the spectra of the ionized salt forms of the triphenylmethane type; this can be observed clearly in the case of tris[p-(3,5-diphenyl-2-pyrazolin-1-yl)phenylene]methyl chloride [8] (its leuco compound is product XII, which has two bands with λ_{max} 640 and 590 nm in the visible region). One should also note that the percentages of ionized forms in solutions of I-XII are very small, and the development of a coloration is therefore visually observed only at pyrazoline concentrations of no less than 10^{-2} to 10^{-3} mole/liter. Reduction of the methyl chloride mentioned above with $LiBH_4$ leads to XII (identified from the results of elementary analysis, the absence of a melting-point depression, and the UV and IR spectra). Under the conditions described above 1-(p-nitrophenyl)-3,5-diphenyl-2-pyrazoline does not react with benzaldehyde. The data on substitution of the N-phenyl ring are in complete agreement with the literature data on electrophilic substitution in 1-phenyl-2-pyrazolines in the case of reactions with dithiols, formylation, bromination, and diazo coupling [6, 9-12].

Thus it is apparent from the experiments carried out in this research that the $4-CH_2$ group of the heteroring does not participate in the reaction of aromatic aldehydes with N-phenylpyrazolines, although in azomethine systems the chemical activity of the α-methyl or methylene group can be increased sharply by quaternization of the nitrogen atom, and there are two centers of possible quaternization in the electronic system of pyrazoline. It follows from the data in [13] that for N_1H- and N_1-alkyl-2-pyrazolines quaternization is possible only at the N_1 atom (this is represented most convincingly by graphical analysis of 2-pyrazoline hydrochloride [14]). This process is not observed in triarylpyrazoline molecules, since it follows from quantum-chemical calculations [15] that significant positive charge is localized on the N_1 atom as a consequence of strong interaction of the p electrons of this atom with the adjacent π systems, which lowers the nucleophilicity of this center. As regards the nitrogen atom in the 2 position of the heteroring, its vacant electron pair is shielded by the phenyl rings in the 1 and 3 positions, and this probably explains why the N_2 atom also does not undergo quaternization. In our opinion, precisely these factors primarily determine the fundamental differences in the chemical behavior of alkyl and aryl derivatives of 2-pyrazoline.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were measured with a UR-20 spectrometer. The electronic absorption spectra of solutions of the compounds in toluene or dioxane were

TABLE 1. Characteristics of Compounds with the General Formula



Compound	R	R′	R″	mp, °C	UV spectrum λ_{max}, nm		Fluorescence spectrum, λ_{max}, nm	N found, %	Empirical formula	N calc., %	Yield, %
					in toluene	in dioxane with $HClO_4$					
I	C_6H_5	C_6H_5	H	160	363 (4,2)	746, 694, 515	455	8,1	$C_{49}H_{40}N_4$	8,2	56
II	C_6H_5	C_6H_5	CH_3	157	372 (4,2)	745, 696, 525	455	8,3	$C_{50}H_{43}N_4$	8,0	40
III	C_6H_5	C_6H_5	OCH_3	137	371 (4,4)	750, 697, 518	460	7,9	$C_{50}H_{43}N_4O$	7,8	52
IV	C_6H_5	C_6H_5	$N(CH_3)_2$	135	371 (4,7)	720, 680, 520	465	9,6	$C_{51}H_{46}N_5$	9,4	49
V	C_6H_5	C_6H_5	Cl	165	368 (4,3)	758, 705, 575	460	8,0	$C_{49}H_{39}ClN_4$	7,8	40
VI	C_6H_5	C_6H_5	Br	165	365 (4,3)	758, 704, 565	455	7,5	$C_{49}H_{39}BrN_4$	7,3	36
VII	C_6H_5	C_6H_5	NO_2	175	365 (4,3)	715, 667, 500	460	9,5	$C_{49}H_{39}N_5O_2$	9,6	50
VIII	CH_3	C_6H_5	H	130	372 (4,2)	739, 692, 502	445	9,8	$C_{39}H_{34}N_4$	10,0	30
IX	$C_6H_5CH{=}CH$	C_6H_5	H	175	392 (4,6)	741, 690, 513	490	7,9	$C_{53}H_{44}N_4$	7,6	42
X	C_6H_5	H	H	130	349 (4,2)	—	460	10,4	$C_{37}H_{30}N_4$	10,6	32
XI	C_6H_5	C_6H_5	[a]	164	375 (4,5)	740, 700, 510	475	10,0	$C_{58}H_{48}N_6$	10,1	54
XII	C_6H_5	C_6H_5	[b]	145	377 (4,7)	730, 692, 516	455	9,4	$C_{64}H_{53}N_6$	9,3	42

[a] Here, R" = 1.5-diphenyl-2-pyrazolin-3-yl. [b] Here, R" = 3,5-diphenyl-2-pyrazolin-1-yl.

recorded with a Specord UV-vis spectrophotometer. The fluorescence spectra were recorded with a Hitachi MPF-2A spectrofluorimeter.

Chemically pure-grade 1,3,5-triphenylpyrazoline was used for the investigation; the remaining starting arylpyrazolines were obtained from phenylhydrazine and α,β-unsaturated ketones by the usual method [13].

Phenylbis[N-(3,5-diphenyl-2-pyrazolin-1-yl)phenylene]methane (I). A 1-ml sample of 70% $HClO_4$ was added dropwise with stirring to a solution of 0.5 g (1.7 mmole) of triphenylpyrazoline and 0.1 g (0.9 mmole) of benzaldehyde in 10 ml of dioxane, and the mixture was heated for 1 h. It was then cooled and diluted with excess concentrated ammonium hydroxide, and the resulting precipitate was removed by filtration, washed with ammonium hydroxide, and crystallized from benzene–octane (1:10).

Compounds II-XII were similarly obtained.

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