PYRAZOLINES — DERIVATIVES OF 2-NITROCHALCONE

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By the reaction of 2-nitrochalcone with hydrazine hydrate, 5-(2-nitrophenyl)-3-phenyl-1H-2-pyrazoline (I) and the hydrazone of 3-(5-(2-nitrophenyl)-3-phenyl-2-pyrazolin-1-yl)-3-(2-nitrophenyl)propiophenol (II) have been prepared. The acylation of both compounds I and II leads to N-acyl derivatives of the first. The acylating ability of formamide and N,N-dimethylformamide was observed in reactions with pyrazoline I. An x-ray structural study was carried out on compound II.

The basic method of synthesizing aromatic derivatives of 2-pyrazolines is to react hydrazines with chalcones. Hydrazones of α,β-unsaturated ketones are intermediates in this process, but the reaction, for example, with hydrazine itself, is extremely difficult to stop at the step of hydrazone formation [1]. Introduction of electron-accepting substituents into the hydrazine or ketone slows the cyclization of the hydrazones and facilitates their isolation [2].

In the present work we have studied the reaction of hydrazine hydrate with 2-nitrochalcone in boiling methanol over a 30-40 min period. Crystalline products I (red) and II (yellow) were isolated from the reaction mixture. Both compounds gradually decompose in alcoholic solutions with the evolution of nitrogen and the formation of tarry substances. Acylating agents such as acetic anhydride in pyridine or benzoyl chloride in ethanol act on substituted derivatives I and II to form the same products, III and IV, which we identified from the spectroscopic characteristics and elemental analyses (see below and Table 1) as 1-acetyl-I and 1-benzoyl-I, respectively. Boiling compounds I and II in acetic acid also forms pyrazoline III; in formic acid, formamide, and dimethylformamide, the product is V. Pyrazolines I and II do not react with benzoic acid, benzoic anhydride, or diphenylformamide (see scheme on the following page).

From elemental analyses, compounds I and II are 1:1 condensation products of hydrazine with 2-nitrochalcone. Pyrazoline I clearly shows a ν_{NH} band in the IR spectrum, and the PMR spectrum (300 MHz) contains, along with the multiplet signal from aromatic protons, three groups of signals from an AMX system, typical of the spectra of compounds containing a $CH-CH_2$ fragment. The spectrum also has a diffuse signal with δ 6.04 ppm, corresponding in integral intensity to the one proton of the NH group. These data, together with the UV spectra, identify the compound as 5-(2-nitrophenyl)-3-phenyl-1H-2-pyrazoline.

In the IR spectrum (Table 1) of compound II there are two absorption bands in the 3200-3300 cm^{-1} region that can be attributed to ν_{NH} vibrations. The PMR spectrum (300 MHz) contains signals from two AMX systems (two $CH-CH_2$ fragments), a broadened singlet from NH_2 protons, and the multiplets from aromatic protons. This is evidence of the participation of two molecules of hydrazine in the formation of compound, II, an interpretation also supported by the ^{13}C-NMR spectrum. The final solution of the molecular structure of II was obtained by x-ray diffraction, which showed compound II to be the β-amination product of the hydrazone of 2-nitrochalcone by pyrazoline I.

The reactions of α,β-unsaturated ketones with hydrazines, unlike many other addition reactions [3], is a 1,2-type process (involving the $C=O$ group), which explains why the second amino group of the hydrazine displays an α-effect. In this case, the introduction of the nitro group, strengthening the positive charge on the β-carbon of the enone, can facilitate the β-amination of the ketone. It was not possible, however, to establish the mechanism of the formation of compound II, because experiments to prepare the hydrazone of 2-nitrochalcone in the free form and to add pyrazoline I to 2-nitrochalcone (with the subsequent condensation with hydrazine as the goal) were unsuccessful.

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TABLE 1. Characteristics of Compounds I-V

Compound	mp, °C*3	UV spectrum, λ_{max} ($\varepsilon \times 10^{-4}$)	IR spectrum, cm^{-1}				PMR spectrum	Yield, %
			ν_{NH, NH_2}	ν_{CO}	$\nu_{NO_2}^{as}$	$\nu_{NO_2}^{s}$		
I*	119	288 (1,51)	3315		1515	1350	3,00 (1H, d.d, J = 16,6, 10,1 Hz CH$_2$); 3,79 (1H, d.d, J = 10,8, 16,6 Hz, CH$_2$); 5,41 (1H, J = 10,1, 10,8 Hz, CH); 6,04 (1H, s, NH); 7,28...8,00 (9H, m C$_6$H$_4$, C$_6$H$_5$)	70
II*	173	255 (4,04); 330 sh	3300 3230		1510	1350	2,82 (1H, d.d, J = 16,8, 14,1 Hz CH$_2$); 2,99 (1H, d.d, J = 14,4, 3,9 Hz, CH$_2$); 3,71 (1H, d.d, J = 16,8, 10,8 Hz, CH$_2$); 4,21 (1H, d.d, J = 14,4, 12,0 Hz CH$_2$); 4,49 (1H, d.d. J = 14,1, 10,8 Hz, CH); 4,60 (1H, d.d, J = 3,9, 12,0 Hz, CH); 6,36 (2H, s, NH$_2$); 7,04...8,01 (18H, m C$_6$H$_4$, C$_6$H$_5$)	15
III*2	178	287 (2,75)		1665	1515	1350	2,46 (3H, s, CH$_3$); 3,20 (1H, d d, J = 18,0, 6,0 Hz, CH$_2$); 3,96 (1H, d.d, J = 18,0, 11,5 Hz, CH$_2$); 6,20 (1H, d.d, J = 6,0, 11,5 Hz, CH); 7,25...8,15 (9H, m, C$_6$H$_4$, C$_6$H$_5$)	95
IV	212	289 (2,61)		1660	1515	1350		75
V*2	184	279 (2,88)		1670	1515	1350	3,13 (1H, d.d, J = 18,0, 6,0 Hz CH$_2$); 3,93 (1H, d.d, J = 18,0, 12,0 Hz, CH$_2$); 6,09 (1H, d.d J = 6,0; 12,0 Hz, CH); 7,07...8,00 (9H, m, C$_6$H$_4$, C$_6$H$_5$), 9,09 (1H, s, CHO)	95*4

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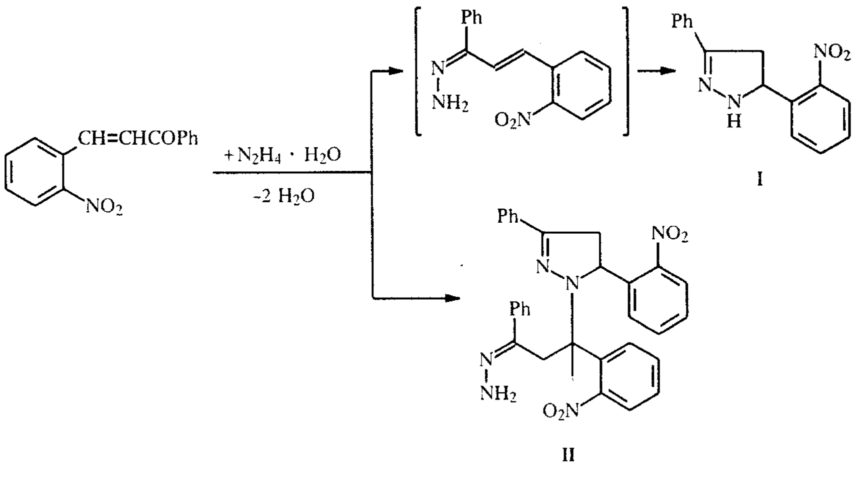
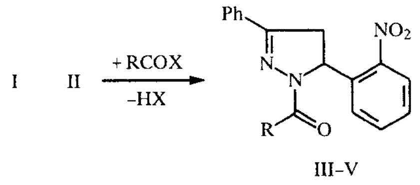
*PMR spectrum taken in CDCl$_3$.

*2PMR spectrum taken in pyridine-D$_5$.

*3Compounds I-III, V crystallized from methanol; IV, from ethanol.

*4Product obtained by boiling compound I in formic acid.





III-V

III R = Me (X = Cl, OH, OCOMe); IV R = Ph (X = Cl); V R = H (X = OH, NH$_2$, NMe$_2$)

TABLE 2. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) in a Molecule of Compound II

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	3119(3)	4024(2)	5870(2)	$C_{(24)}$	20(5)	3437(2)	5643(4)
$N_{(2)}$	2288(3)	4043(2)	4820(3)	$C_{(25)}$	2830(4)	5345(2)	8001(3)
$N_{(5)}$	6427(4)	2727(2)	7394(3)	$C_{(26)}$	3415(5)	5907(2)	8287(4)
$O_{(1)}$	6883(5)	2445(2)	8195(3)	$C_{(27)}$	3844(5)	6077(2)	9319(4)
$O_{(2)}$	5751(4)	2489(1)	6572(3)	$C_{(28)}$	3720(5)	5693(2)	10109(4)
$C_{(1)}$	2955(4)	3753(2)	4256(3)	$C_{(29)}$	3114(5)	5135(2)	9831(4)
$C_{(2)}$	4357(4)	3469(2)	4869(3)	$C_{(30)}$	2685(5)	4961(2)	8788(3)
$C_{(3)}$	4251(4)	3542(2)	6007(3)	$H_{(2A)}$	429(0)	305(8)	467(5)
$C_{(7)}$	2383(4)	3749(2)	3108(3)	$H_{(2B)}$	520(2)	362(2)	470(5)
$C_{(8)}$	3229(4)	3510(2)	2507(3)	$H_{(3)}$	388(4)	310(1)	622(1)
$C_{(9)}$	2732(5)	3492(3)	1430(3)	$H_{(8)}$	418(3)	337(2)	284(3)
$C_{(10)}$	1361(5)	3730(2)	955(3)	$H_{(9)}$	343(5)	333(2)	109(4)
$C_{(11)}$	506(5)	3973(2)	1537(4)	$H_{(10)}$	108(1)	370(6)	24(3)
$C_{(12)}$	1007(4)	3979(2)	2612(3)	$H_{(11)}$	-51(5)	412(7)	121(6)
$C_{(13)}$	5680(4)	3749(2)	6757(3)	$H_{(12)}$	37(6)	413(7)	303(7)
$C_{(14)}$	6695(5)	3368(2)	7401(3)	$H_{(15)}$	865(9)	324(0)	855(9)
$C_{(15)}$	8005(5)	3563(2)	8079(4)	$H_{(16)}$	922(5)	430(5)	857(7)
$C_{(16)}$	8336(5)	4158(3)	8107(4)	$H_{(17)}$	755(4)	495(0)	753(8)
$C_{(17)}$	7355(5)	4555(3)	493(4)	$H_{(18)}$	534(0)	466(5)	644(9)
$C_{(18)}$	6050(5)	4349(2)	6836(3)	$H_{(4NA)}$	223(7)	501(4)	500(6)
$N_{(3)}$	2753(4)	5515(2)	6248(3)	$H_{(4NB)}$	283(8)	564(2)	477(1)
$N_{(4)}$	2253(5)	5394(2)	5190(3)	$H_{(4)}$	304(4)	402(1)	732(2)
$N_{(6)}$	2503(5)	3037(2)	8249(3)	$H_{(5A)}$	83(2)	464(1)	587(1)
$O_{(3)}$	2194(5)	2917(3)	9031(3)	$H_{(5B)}$	72(7)	461(9)	700(9)
$O_{(4)}$	3755(4)	3119(2)	8218(3)	$H_{(21)}$	41(0)	227(9)	777(2)
$C_{(4)}$	2253(4)	4030(2)	6640(3)	$H_{(22)}$	-155(8)	226(2)	617(8)
$C_{(5)}$	1396(4)	4613(2)	6570(3)	$H_{(23)}$	-174(9)	293(3)	491(5)
$C_{(6)}$	2360(4)	5166(2)	6880(3)	$H_{(24)}$	-12(7)	370(7)	512(5)
$C_{(19)}$	1219(4)	3487(2)	6522(3)	$H_{(26)}$	359(8)	620(0)	778(1)
$C_{(20)}$	1321(5)	3040(2)	7266(3)	$H_{(27)}$	425(9)	644(1)	946(2)
$C_{(21)}$	325(5)	2575(2)	7164(4)	$H_{(28)}$	403(6)	581(0)	108(9)
$C_{(22)}$	-797(6)	2545(2)	6272(5)	$H_{(29)}$	293(0)	478(6)	1027(6)
$C_{(23)}$	-972(5)	2969(3)	5503(4)	$H_{(30)}$	211(8)	456(2)	856(9)

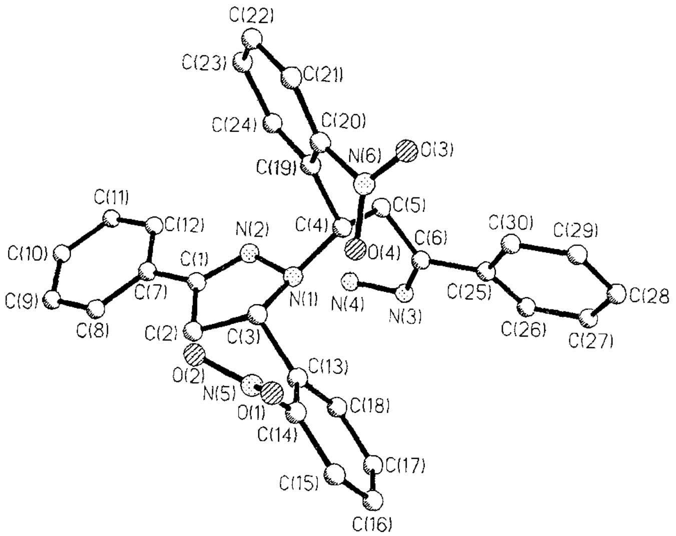


Fig. 1. Molecular structure of compound II.

TABLE 3. Bond Lengths in the Compound II Molecule

Bond	d, Å		d, Å
$N_{(1)}—N_{(2)}$	1,403(4)	$N_{(1)}—C_{(3)}$	1,494(5)
$N_{(1)}—C_{(4)}$	1,475(6)	$N_{(2)}—C_{(1)}$	1,278(6)
$C_{(1)}—C_{(2)}$	1,494(5)	$C_{(1)}—C_{(7)}$	1,474(6)
$C_{(2)}—C_{(3)}$	1,551(6)	$C_{(3)}—C_{(13)}$	1,515(5)
$N_{(4)}—H_{(4HA)}$	0,884(3)	$N_{(4)}—H_{(4NB)}$	1,044(2)
$N_{(3)}—C_{(6)}$	1,274(6)	$N_{(3)}—N_{(4)}$	1,382(5)
$N_{(5)}—O_{(1)}$	1,210(6)	$N_{(5)}—O_{(2)}$	1,226(5)
$N_{(5)}—C_{(14)}$	1,453(6)	$N_{(6)}—O_{(4)}$	1,208(6)
$N_{(6)}—O_{(3)}$	1,186(7)	$C_{(4)}—C_{(5)}$	1,524(6)
$N_{(6)}—C_{(20)}$	1,469(5)	$C_{(5)}—C_{(6)}$	1,521(6)
$C_{(6)}—C_{(25)}$	1,489(6)	$C_{(4)}—C_{(19)}$	1,538(6)

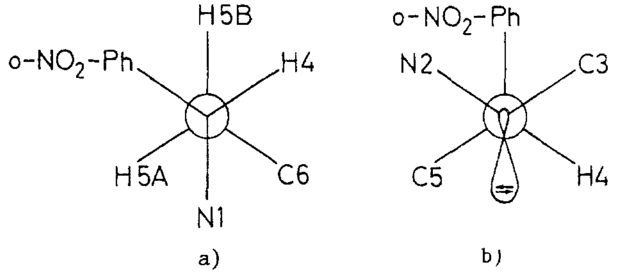


Fig. 2. Newman projections for molecule II: a) along $C_{(4)}-C_{(5)}$ bond; b) along $N_{(1)}-C_{(4)}$ bond.

The structure of compound II and the numbering of the atoms are shown in Fig. 1, and the atomic coordinates, bond lengths (except for the aromatic), and most important bond and torsional angles in Tables 2-4.

According to the x-ray diffraction analysis, the five-membered ring in crystals of II exists in a semichair configuration. Atoms $C_{(3)}$ and $N_{(1)}$ deviate from the $N_{(2)}-C_{(1)}-C_{(2)}$ plane by $-0.30(1)$ and 0.05(1) Å, respectively. The folding parameters, calculated in accord with [4], are $s = 0.27$ and $\psi = 1.67°$.

The nitrophenyl substituent on $C_{(3)}$ occupies the equatorial position (the $C_{(1)}-C_{(2)}-C_{(3)}-C_{(13)}$ and $C_{(1)}-C_{(2)}-C_{(3)}-H_{(3)}$ torsional angles are $-136.0(4)°$ and $100.4(9)°$, respectively). Nonbonding interactions between the oxygen atoms of the nitro group and the $H_{(3)}$ and $H_{(15)}$ hydrogens ($O_{(2)}-H_{(3)}$ and $O_{(1)}-H_{(15)}$ separations of 2.18(1) and 2.40(1) Å, respectively, are less that the sums of the van der Waals radii [5]) leads to the rotation of the phenyl ring about the $C_{(3)}-C_{(13)}$ bond [$H_{(3)}-C_{(3)}-C_{(13)}-C_{(14)}$ torsional angle 21(1)°] and of the nitro group about the $C_{(14)}-N_{(5)}$ bond [($C_{(13)}-C_{(14)}-N_{(5)}-O_{(2)}$ torsional angle 33.1(7)°].

The phenyl radical on $C_{(1)}$ is conjugated with the adjacent C=N bond, as shown by the $C_{(1)}-C_{(7)}$ bond length (1.474(6) Å) and the insignificant $N_{(2)}-C_{(1)}-C_{(7)}-C_{(12)}$ torsional angle ($-9.9(6)°$).

Atoms $N_{(1)}$ and $N_{(4)}$ have a pyramidal–trigonal configuration (the sums of their torsional angles come to 340.3° and 336.7°, respectively). However, their conjugation with the π-systems of the adjacent C=N bonds is preserved which follows from the $N_{(2)}-N_{(1)}$ (1.403(4) Å) and $N_{(4)}-N_{(3)}$ (1.382 Å) bond lengths.

A Newman projection along the $C_{(4)}-C_{(5)}$ bond (Fig. 2a) shows that the nitrophenyl group and the substituent on $C_{(6)}$ are in an antiperiplanar conformation. The drive to reduce the unfavorable interaction between the hydrazone residue and the pyrazoline ring is obviously the reason that substituents on $C_{(6)}$ are virtually perpendicular to the $C_{(4)}-C_{(5)}$ bond [the $C_{(4)}-C_{(5)}-C_{(6)}-N_{(3)}$ torsional angle equals 96.3(5)°]. Despite this, however, the shortened contacts are preserved between the $H_{(4NA)}-N_{(2)}$ and $H_{(4NA)}-N_{(1)}$ atoms (2.18(1) and 2.52(1) Å, respectively; sum of van der Waals radii, 2.66 Å [5]). Nonbonding interactions between $H_{(4NA)}$ and $H_{(5A)}$ (2.15(1) Å), $N_{(4)}$ and $H_{(5A)}$ (2.47(1) Å), and $H_{(4NA)}$ and $C_{(5)}$ (2.58(1) Å) are apparently why the hydrazone group is displaced towards the phenyl group on $C_{(6)}$, as shown by the deformation of the $C_{(5)}-C_{(6)}-N_{(3)}$ (125.3(4)°) and $C_{(25)}-C_{(6)}-N_{(3)}$ (115.8(4)°) bond angles. Obviously, these same interactions are also the reason that the $C_{(5)}-C_{(6)}$ bond (1.521(6) Å) is longer than average (1.495 Å) [6].

TABLE 4. Some Valence (ω) and Torsional (τ) Angles in the Compound II Molecule

Angle	ω , degrees	Angle	ω, degrees
$N_{(2)}N_{(1)}C_{(3)}$	109,2(3)	$C_{(3)}N_{(1)}N_{(2)}C_{(1)}$	-15,7(4)
$C_{(3)}N_{(1)}C_{(4)}$	115,9(3)	$N_{(2)}N_{(1)}C_{(4)}C_{(19)}$	60,9(4)
$N_{(2)}C_{(1)}C_{(7)}$	120,7(3)	$N_{(2)}C_{(1)}C_{(7)}C_{(12)}$	-9,9(6)
$C_{(1)}C_{(2)}C_{(3)}$	101,8(4)	$C_{(1)}C_{(2)}C_{(3)}N_{(1)}$	-18,6(4)
$N_{(1)}C_{(3)}C_{(2)}$	101,1(3)	$O_{(4)}N_{(6)}C_{(20)}C_{(19)}$	-47,1(7)
$C_{(2)}C_{(3)}C_{(13)}$	113,0(3)	$C_{(4)}C_{(5)}C_{(6)}C_{(25)}$	-87,5(5)
$N_{(4)}N_{(3)}C_{(6)}$	118,2(4)	$C_{(1)}C_{(2)}C_{(3)}C_{(13)}$	-136,0(4)
$N_{(1)}C_{(4)}C_{(19)}$	112,4(3)	$C_{(5)}C_{(6)}C_{(25)}C_{(26)}$	-165,4(4)
$N_{(3)}C_{(6)}C_{(25)}$	115,8(4)	$N_{(2)}N_{(1)}C_{(3)}C_{(2)}$	21,4(4)
$N_{(2)}N_{(1)}C_{(4)}$	115,2(3)	$N_{(2)}N_{(1)}C_{(4)}C_{(5)}$	-63,5(4)
$N_{(1)}N_{(2)}C_{(1)}$	109,7(3)	$N_{(1)}N_{(2)}C_{(1)}C_{(2)}$	2,0(5)
$N_{(2)}C_{(1)}C_{(2)}$	113,6(3)	$O_{(1)}N_{(5)}C_{(14)}C_{(15)}$	32,7(7)
$C_{(2)}C_{(1)}C_{(7)}$	125,6(4)	$N_{(2)}C_{(1)}C_{(2)}C_{(3)}$	11,4(5)
$N_{(1)}C_{(4)}C_{(5)}$	110,5(3)	$N_{(4)}N_{(3)}C_{(6)}C_{(5)}$	1,1(7)
$C_{(5)}C_{(4)}C_{(19)}$	110,9(3)	$N_{(1)}C_{(4)}C_{(5)}C_{(6)}$	-65,6(4)
$C_{(4)}C_{(5)}C_{(6)}$	114,1(3)	$C_{(4)}C_{(5)}C_{(6)}N_{(3)}$	96,3(5)
$N_{(3)}C_{(6)}C_{(5)}$	125,3(4)		
$C_{(5)}C_{(6)}C_{(25)}$	118,8(4)		

The distance between $C_{(6)}$ and $C_{(25)}$ (1.489(6) Å) indicates the existence of conjugation between the phenyl ring and the hydrazone group. However, the shortened contacts between atoms $H_{(30)}$, $C_{(5)}$, and $H_{(6B)}$, $H_{(2B)}$, and $N_{(3)}$ (separations of 2.56(1), 2.13(1), and 2.80(1) Å) are probably the reason for the nonplanar structure of the conjugated system (torsional angle $N_{(3)}-C_{(6)}-C_{(25)}-C_{(26)}$ equals $-165.4(4)°$).

Nonbonding interactions between $H_{(4)}$ and $O_{(4)}$ (2.34(1) Å) apparently lead to a significant deviation of the nitro group from the plane of the phenyl ring (torsional angle $O_{(4)}-N_{(6)}-C_{(20)}-C_{(19)}$ equals $-47.1(7)°$). These interactions, and also the shortened contact between $H_{(24)}$ and $N_{(2)}$ (2.54(1) Å separation), are obviously the reason the $C_{(4)}-C_{(19)}$ bond is lengthened to 1.538(6) Å (average value 1.503 Å [6]).

A Newman projection along the $N_{(1)}-C_{(4)}$ bond shows (Fig. 2b) that the nitrophenyl substituent on $C_{(4)}$ is an antiperiplanar configuration with respect to the unshared electron pair of the $N_{(1)}$ nitrogen.

In the crystal of this compound there are shortened contacts with atoms of molecules related to the initial molecule by the symmetry transformations 1-x, 1-y, 1-z [$H_{4NB)}-C'_{(18)}$ 2.63(1) Å, and $H_{(17)}-C_{(12)}'$ 2.79(1) Å].

EXPERIMENTAL

X-ray diffraction study of compound II, $C_{30}H_{26}N_6O_4$: monoclinic crystals; at 20°C, a = 9.446(2), b = 22.335(4), c = 13.295(3) Å, β = 105.87(2)°; space group P2i/C; z = 4; d_{calc} = 1.316 g/cm^3; F(000) = 1120. Cell constants and the intensities of 4438 independent reflections with $I > 2\sigma(I)$ (R_{inf} = 0.045) were measured on a Siemens P3/PC automatic, 4-circle diffractometer ($\lambda_{MoK\alpha}$, graphite monochromator, $\Theta/2\Theta$ — scanning to $2\Theta = 50°$). The structure was solved by the direct method with the SHELXTL PLUS package of programs. All of the hydrogen atoms were revealed by difference synthesis. Refinement with 2138 reflections with $F > 8\sigma(F)$ was carried out in the anisotropic (isotropic for hydrogen atoms) approximation until R = 0.062 (R_w = 0.057, $w^{-1} = \sigma^2(F)$).

The IR spectra of compounds I-V were measured in KBr pellets on a Specord IR-75 spectrophotometer; the UV spectra, in ethanol [c = (2-4)$\cdot 10^{-5}$ M] on a Specord M-40 instrument. The PMR spectra were taken in pyridine-d_5 and $CDCl_3$ on Tesla BS-497 (100 MHz), Tesla BS-457B (80 MHz), and VXR-300 Varian (300 MHz) instruments, TMS internal standard. The purity of the prepared substances was checked by TLC on Silufol UV-254 plates, chloroform/ethyl acetate eluent.

The nitrogen content of substances I-V by elemental analysis agreed with the calculated.

5-(2-Nitrophenyl)-3-phenyl-1H-2-pyrazoline (I, $C_{15}H_{13}N_3O_2$). A solution of 2.53 g (0.01 mole) of 2-nitrochalcone and 0.50 g (0.01 mole) of hydrazine hydrate in methyl, ethyl, or isopropyl alcohol (50-80 ml) is boiled for 30-40 min, cooled, and the precipitated crystals of I filtered off.

Hydrazone of 3-(5-(2-nitrophenyl)-3-phenyl-2-pyrazolin-1-yl)-3-(2-nitrophenyl)propiophenone (II, $C_{30}H_{26}N_6O_4$). Hydrazone II is a minor product of the synthesis of compound I (according to TLC). On long standing of the reaction mixture or of the mother liquor after the recrystallization of I, II precipitates as yellow crystals. Yields: trace (in methanol) to 15% (in isopropanol).

1-Acetyl-3-phenyl-5-(2-nitrophenyl-2-pyrazoline (III, $C_{17}H_{15}N_3O_3$). A solution of compound I in acetic acid is boiled for 30-40 min. After cooling and dilution with a two-fold quantity of water, crystals of III precipitate. Yield 95%. Pyrazoline III is also obtained by treating compound I with an excess of an acetyl chloride/pyridine mixture (1:5) (yield 95%) or from compound II by the action of the same mixture (yield 90%) or acetic acid (yield 85%).

1-Benzoyl-3-phenyl-5-(2-nitrophenyl)-2-pyrazoline (IV, $C_{22}H_{17}N_3O_3$). Pyrazoline I, 2.67 g (0.01 mole), is dissolved in ethyl alcohol, after which 1.41 g (0.01 mole) of benzoyl chloride is added. Crystalline product IV precipitates after cooling. Yield 75%. Pyrazoline IV is also prepared from compound II by an analogous method. Yield 70%.

1-Formyl-3-phenyl-5-(2-nitrophenyl)-2-pyrazoline (V, $C_{16}H_{13}N_3O_3$). Prepared analogously to hydrazone III by boiling compounds I or II for 30-60 min in formic acid, formamide, or dimethylformamide.

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