Chemistry of Heterocyclic Compounds, Vol. 34, No. 8, 1998

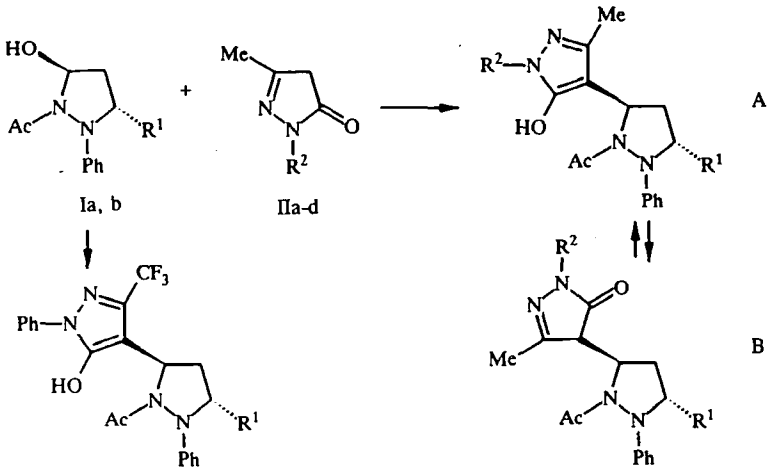
REACTIONS OF HYDROXYAZOLIDINES WITH π-DONOR HETEROCYCLES. 2.* REACTION OF 1-ACETYL-5-HYDROXYPYRAZOLIDINES WITH PYRAZOL-5-ONES ON THE SURFACE OF ADSORBENTS

L. A. Sviridova, G. A. Golubeva, I. V. Dlinnykh, I. F. Leshcheva, L. D. Ashkinadze, V. V. Nesterov, and M. Yu. Antipin

The reaction of 1-acetyl-2-phenyl-5-hydroxypyrazolidines with pyrazol-5-ones leads to the corresponding 4-(pyrazolidin-5-yl)pyrazolones, which exist mainly in the form of hydroxypyrazoles. The process proceeds on the surface of adsorbents in a nonpolar solvent. The structure and stereochemistry of the bisheterocycles obtained were studied.

Direct reaction of hydroxypyrazolidines with π-donor heterocyclic systems may serve as a convenient method for the synthesis of bisheterocycles which are combinations of saturated and aromatic heterocyclic nuclei. However, until recently, this was only managed in reactions with indoles [2].

We recently showed [1] the principal possibility of the direct attack of 5-hydroxypyrazolidines by pyrazolones on the surface of an adsorbent. Systematic investigation of this process was undertaken in the present work. We found that any, both 1-unsubstituted and 1-substituted, 3-methylpyrazol-5-ones (II) may participate in the reaction with 5-hydroxypyrazolidines (I), and the corresponding 4-(pyrazolidin-5-yl)pyrazol-5-ones (IIIa-h) and (IV) were isolated as practically the sole conversion products in all cases (Tables 1-3).



Ia, b IIa-d A B IV IIIa-h

I a R^1 = H, b R^1 = Me; II a R^2 = H, b R^2 = Ph, c R^2 = CH_2Ph, d R^2 = CH_2CH_2CN; III a R^1 = R^2 = H, b R^1 = Me, R^2 = H, c R^1 = H, R^2 = Ph, d R^1 = Me, R^2 = Ph, e R^1 = H, R^2 = CH_2Ph, f R^1 = Me, R^2 = CH_2Ph, g R^1 = H, R^2 = CH_2CH_2CN, h R^1 = Me, R^2 = CH_2CH_2CN

*For Communication 1, see [1].

M. V. Lomonosov Moscow State University, Moscow 119899, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1079-1087, August, 1998. Original article submitted May 6, 1998.

0009-3122/98/3408-0929$20.00

TABLE 1. Characteristics of the Compounds (III) and (IV) Obtained

Compound	Reaction time, h	Adsorbent*	Empirical formula	Found, % / Calculated, %			mp, °C	R_f	IR spectrum, cm^{-1}	Mass spectrum, M^+	M^+ calc.	Yield, %
				C	H	N						
IIIa	3	Polyamide	$C_{15}H_{18}N_4O_2$	63,00 / 62,94	6,34 / 6,29	19,49 / 19,58	165...167	0,13	1605, 1635, 1720, 2400...3200, 3460	286	286	57
IIIb	11	Polyamide	$C_{16}H_{20}N_4O_2$	64,57 / 64,00	7,20 / 6,67	18,14 / 18,60	143...145	0,15	1640, 1735, 2400...3400	300	300	65
IIIc	2	Al_2O_3	$C_{21}H_{22}N_4O_2$	69,75 / 69,60	6,03 / 6,08	15,48 / 15,50	133...135	0,75	1610, 1640, 2500... 2900			70
IIId	7	Al_2O_3	$C_{22}H_{24}N_4O_2$	70,16 / 70,21	6,45 / 6,38	14,88 / 14,89	135...137	0,85	1620, 1640 2500...3000	376	376	62
IIIe	5	Florizil	$C_{22}H_{24}N_4O_2$	70,35 / 70,21	6,68 / 6,38	14,89 / 14,89	138...139	0,45	1600, 1635, 2300...3200			55
IIIf	11	Florizil	$C_{23}H_{26}N_4O_2$	70,40 / 70,80	6,83 / 6,70		136...138	0,60	1605, 1640, 2600...3000			60
IIIg	10	AE-, DEAE-celluloses	$C_{18}H_{21}N_5O_2$				†	0,22	1605, 1625, 1705, 2260, 2500...3200	339	339	48
IIIh	15	AE-, DEAE-celluloses	$C_{19}H_{23}N_5O_2$				180 decomp.	0,27	1605, 1625, 1680, 2265, 2500...3100	353	353	25
IV	10	Al_2O_3	$C_{22}H_{21}N_4O_2F_3$	61,24 / 61,40	4,79 / 4,88	13,02 / 13,07	165...167	0,80	1605, 1635 2200...3100	430	430	60

*The adsorbents utilized can be varied in most cases. Only those on which a maximal yield is achieved are presented here.

†Oil.

TABLE 2. Chemical Shifts of the Protons of the Compounds (III) and (IV) (δ, ppm)

Compound	3'-H, m	4'-H, 4'-H', m	5'-H, m	3'-CH_3, d	CH_3CO, s	3-CH_3, s	R^2	OH
IIIa	3,41 4,00	2,29 2,61	5,17	—	2,09	1,93	9,50	9,50
IIIb	4,25	2,00 2,75	5,21	1,27	2,07	1,80	11,20	11,20
IIIc	3,36 3,96	2,28 2,68	5,14	—	2,13	1,81	6,9...7,9 (C_6H_5)	11,34
IIId	4,25	1,99 2,85	5,21	1,28	2,11	1,83	6,8...7,5 (C_6H_5)	11,40
IIIe	3,37 3,95	2,25 2,65	5,14	—	2,12	1,74	5,05, d, 5,17, d, (CH_2) 6,9...7,4 (C_6H_5)	10,81
IIIf	4,12	1,98 2,80	5,15	1,28	2,10	1,77	5,06, d, 5,17, d, (CH_2) 6,8...7,5 (C_6H_5)	10,87
IIIg	3,34 3,93	2,24 2,62	5,08	—	2,11	1,73	2,81 (CH_2CN) 4,18 (NCH_2)	11,10
IIIh	4,19	2,01 2,77	5,18	1,29	2,10	1,76	2,86 (CH_2CN) 4,24 (NCH_2)	11,05
IV	4,34	2,15 2,84	5,28	1,30	2,15	—	6,8...7,9 (C_6H_5)	12,31

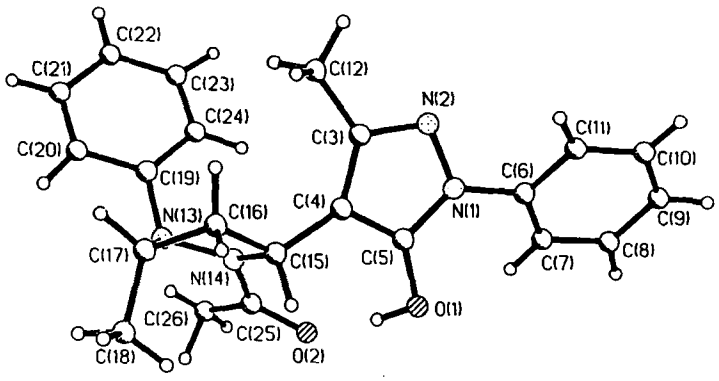


Fig. 1. General view of the molecule (IIId).

The method of performing the process on the surface of an adsorbent proved to be the most effective in the given conversion. This method, which has been widely used in organic chemistry and the chemistry of azolidines, was hitherto utilized as a "dry" reaction [1, 3] on the surface of a solid carrier without a solvent. We established that the optimal conditions for the investigated process are those on the surface of the adsorbent in the presence of a nonpolar solvent, in which the initial pyrazol-5-one (II) has low solubility, to increase the rate of exchange in the surface layer. In contrast to the method for the synthesis of the compounds (IIIb, d) which we described in the short communication [1], the given method allowed a threefold reduction of the required amount of the adsorbent, a reduction in the reaction time from 2 days to several hours, as well as an increase in the yield of the compounds (III) and (IV). We did not detect other substitution products. However, decomposition traces of the initial 5-hydroxypyrazolidines (I) were present in the reaction mixture.

According to spectral data, the compounds (III) and (IV) have the preferred hydroxypyrazole structure (the Form A) in solution. Although signals of the Form B are not observed in the ^1H and ^{13}C NMR spectra in $CDCl_3$, the absorption band of the cyclic amide group of the pyrazolone portion in the IR spectra of the derivatives (IIIa, b, g, h) indicates the presence of this tautomer in very small quantities in the solution of methylene chloride. The hydrogen bond between protons of the hydroxyl group of the Form A and the carbonyl oxygen atom of the 1-acetyl substituent of the pyrazolidine ring was found by the method of IR spectroscopy in solutions of the compounds (III) and (IV) which we synthesized. Its intramolecular character was established using the example of the derivative (IIId).

TABLE 3. ^{13}C Chemical Shifts for the Compounds (III) and (IV) (δ, ppm)

Carbon atoms	IIIa	IIIb	IIIc	IIId	IIIe	IIIf	IIIg	IIIh	IV
$C_{(3)}$	138,49	139,00	145,40	145,20	144,00	143,84	145,00	144,71	137,58*
$C_{(4)}$	98,87	98,37	97,20	96,71	95,57	95,09	95,88	95,31	97,56
$C_{(5)}$	161,00	160,87	152,97	152,77	152,79	152,60	152,98	152,74	154,04
3-CH_3	12,29	12,49	15,71	15,55	15,70	15,59	15,51	15,32	121,28†
$C_{(3')}$	55,04	62,37	55,35	62,50	55,45	62,74	55,32	62,87	62,16
$C_{(4')}$	28,66	33,91	27,87	33,06	27,93	33,20	27,93	32,96	34,70
$C_{(5')}$	52,32	51,37	53,22	52,07	53,39	52,24	53,08	51,90	52,39
3'-CH_3	–	19,15	–	18,75	–	18,89	–	18,72	19,54
$\underline{C}H_3CO$	21,27	21,11	21,13	21,03	21,25	21,19	21,11	20,98	21,62
$CH_3\underline{C}O$	175,23	176,02	175,82	176,39	175,70	176,31	175,75	176,23	178,33
Ph C_o	116,03	115,74	116,14	115,90	116,24	116,04	116,11	115,84	115,48
C_m	129,39	129,23	128,84	129,25	129,48	128,44	129,20	129,43	129,12
C_p	122,42	122,34	122,86	122,65	122,82	122,64	122,84	122,56	122,40
C_i	149,61	149,47	149,14	149,43	149,29	149,32	149,10	149,10	148,76
R^2			121,28	121,06	50,27	50,08	18,12	17,89	119,95
			125,72	125,48	127,49	127,29	41,77	41,49	122,53
			129,51	129,25	127,75	127,54	117,34	117,04	129,51
			138,79	138,59	128,65	129,25			138,00
					137,51	137,31			

*J_{CF} = 37 Hz.

†CF_3, J_{CF} = 270 Hz.

TABLE 4. Values of the NOE (η, %) for the Compound (IIId)

Saturated protons	Observed protons				
	5'-H	3'-H	4'-H *	4'-H' *	OH
5'-H		—	—	7,60	9,7
3'-H	—		5,40	—	—
4'-H	—	9,5		20,5	—
4'-H'	8,8	1,0	22,0		—

*4'-H is the low-field proton, and 4'-H' is the high-field proton.

TABLE 5. Bond Lengths in the Molecule (IIId)

Bond	l, Å	Bond	l, Å
O(1)—C(5)	1,333(2)	C(6)—C(11)	1,380(3)
O(2)—C(25)	1,233(3)	C(7)—C(8)	1,392(4)
N(1)—C(5)	1,361(3)	C(8)—C(9)	1,378(4)
N(1)—N(2)	1,374(2)	C(9)—C(10)	1,366(5)
N(1)—C(6)	1,423(3)	C(10)—C(11)	1,376(4)
N(2)—C(3)	1,338(3)	C(15)—C(16)	1,532(3)
N(13)—N(14)	1,424(2)	C(16)—C(17)	1,521(4)
N(13)—C(19)	1,425(3)	C(17)—C(18)	1,518(5)
N(13)—C(17)	1,482(3)	C(19)—C(20)	1,382(3)
N(14)—C(25)	1,342(3)	C(19)—C(24)	1,385(3)
N(14)—C(15)	1,499(3)	C(20)—C(21)	1,364(5)
C(3)—C(4)	1,419(3)	C(21)—C(22)	1,378(5)
C(3)—C(12)	1,488(3)	C(22)—C(23)	1,364(5)
C(4)—C(5)	1,380(3)	C(23)—C(24)	1,372(4)
C(4)—C(15)	1,504(3)	C(25)—C(26)	1,496(4)
C(6)—C(7)	1,378(3)		

TABLE 6. Bond Angles in the Molecule (IIId)

Angle	ω, deg	Angle	ω, deg
C(5)—N(1)—N(2)	110,6(2)	C(9)—C(8)—C(7)	119,9(3)
C(5)—N(1)—C(6)	129,7(2)	C(10)—C(9)—C(8)	119,8(3)
N(2)—N(1)—C(6)	119,6(2)	C(9)—C(10)—C(11)	120,8(3)
C(3)—N(2)—N(1)	105,4(2)	C(10)—C(11)—C(6)	119,8(3)
N(14)—N(13)—C(19)	114,5(2)	N(14)—C(15)—C(4)	114,4(2)
N(14)—N(13)—C(17)	103,4(2)	N(14)—C(15)—C(16)	101,4(2)
C(19)—N(13)—C(17)	117,3(2)	C(4)—C(15)—C(16)	117,3(2)
C(25)—N(14)—N(13)	119,4(2)	C(17)—C(16)—C(15)	104,4(2)
C(25)—N(14)—C(15)	122,4(2)	N(13)—C(17)—C(18)	109,5(3)
N(13)—N(14)—C(15)	112,3(2)	N(13)—C(17)—C(16)	103,0(2)
N(2)—C(3)—C(4)	111,4(2)	C(18)—C(17)—C(16)	114,2(3)
N(2)—C(3)—C(12)	117,1(2)	C(20)—C(19)—C(24)	118,4(3)
C(4)—C(3)—C(12)	131,5(2)	C(20)—C(19)—N(13)	117,6(2)
C(5)—C(4)—C(3)	104,2(2)	C(24)—C(19)—N(13)	123,8(2)
C(5)—C(4)—C(15)	121,7(2)	C(21)—C(20)—C(19)	120,4(3)
C(3)—C(4)—C(15)	133,9(2)	C(20)—C(21)—C(22)	120,9(3)
O(1)—C(5)—N(1)	121,0(2)	C(23)—C(22)—C(21)	119,2(3)
O(1)—C(5)—C(4)	130,7(2)	C(22)—C(23)—C(24)	120,5(3)
N(1)—C(5)—C(4)	108,3(2)	C(23)—C(24)—C(19)	120,7(3)
C(7)—C(6)—C(11)	120,0(2)	O(2)—C(25)—N(14)	121,4(2)
C(7)—C(6)—N(1)	121,3(2)	O(2)—C(25)—C(26)	119,9(3)
C(11)—C(6)—N(1)	118,7(2)	N(14)—C(25)—C(26)	118,6(2)
C(6)—C(7)—C(8)	119,7(3)		

TABLE 7. Main Torsion Angles in the Molecule (IIId)

Angle	τ, deg	Angle	τ, deg
$C_{(5)}-C_{(4)}-C_{(15)}-N_{(14)}$	-87,8	$N_{(13)}-C_{(17)}-C_{(16)}-C_{(15)}$	-37,8
$N_{(13)}-N_{(14)}-C_{(15)}-C_{(4)}$	-126,6	$N_{(14)}-C_{(15)}-C_{(16)}-C_{(17)}$	22,7
$C_{(17)}-N_{(13)}-N_{(14)}-C_{(15)}$	-24,2	$N_{(13)}-N_{(14)}-C_{(15)}-C_{(16)}$	0,6
$C_{(19)}-N_{(13)}-N_{(14)}-C_{(15)}$	104,6	$O_{(2)}-C_{(25)}-N_{(14)}-C_{(15)}$	-13,9
$N_{(14)}-N_{(13)}-C_{(17)}-C_{(16)}$	37,6	$C_{(26)}-C_{(25)}-N_{(14)}-C_{(15)}$	170,2
$C_{(20)}-C_{(19)}-N_{(13)}-N_{(14)}$	175,5	$C_{(19)}-N_{(13)}-N_{(14)}-C_{(25)}$	-101,7

According to the data of PMR spectroscopy with application of the nuclear Overhauser effect, compound (IIId) has the trans disposition of substituents in the pyrazolidine ring (Table 4) by analogy with the previously described pyrazolidine derivatives, the structure of which was studied by the same method [4]. Moreover, interaction of the 5-H proton of the pyrazolidine substituent and the OH group of the pyrazolone portion was observed; this indicates their steric proximity.

The structure of compound (IIId) in the crystalline state was established by x-ray diffraction investigation. Figure 1 shows the general view of the molecule; the bond lengths, bond angles, and main torsion angles are presented in Tables 5-7 respectively.

In the molecule investigated, the dihedral angle between the plane pyrazole heterocycle and the phenyl substituent ($C_{(6)}...C_{(11)}$) is equal to 30.4°. The 87.8° torsion angle for $C_{(5)}-C_{(4)}-C_{(15)}-N_{(14)}$ indicates the torsion of the molecule around the $C_{(4)}-C_{(15)}$ bond. The pyrazolidine heterocycle occurs in the envelope conformation; the deviation of the $C_{(17)}$ atom from the plane $N_{(13)}-N_{(14)}-C_{(15)}-C_{(16)}$ (the plane is satisfied to the accuracy up to ±0.003 Å) comprises 0.580 Å, and the dihedral angle between the plane under consideration and the plane passing through the atoms $C_{(16)}-C_{(17)}-N_{(13)}$ is equal to 38.8°. The dihedral angle between the plane part of the pyrazolidine heterocycle and the phenyl ring $C_{(19)}...C_{(24)}$ comprises 107.5°. The conformation observed and the mutual orientation of the substituents of the pyrazolidine ring are probably characteristic of the overwhelming majority of known functional derivatives of pyrazolidines [5-7].

There is also observed a fairly stable intramolecular hydrogen bond $O_{(1)}-H_{(1)}...O_{(2)}$ in crystals of the compound (IIId) between the hydrogen atom of the hydroxyl group and the oxygen atom of the carbonyl group of the acetyl substituent; it has the parameters $O_{(1)}...O_{(2)}$ 2.585(3) Å, $O_{(1)}-H_{(1)}$ 0.90(3) Å, $H_{(1)}...O_{(2)}$ 1.69(3) Å, and the angle $O_{(1)}-H_{(1)}...O_{(2)}$ 169(2)°.

The remaining geometrical parameters (bond lengths and bond angles) in the molecule investigated have standard values [8], and are comparable with those established in related compounds [5-7]. Reduced intermolecular nonbonding contacts were not found in the crystal.

EXPERIMENTAL

The IR spectra were measured on the UR-20 instrument in solutions of CCl_4 and CH_2Cl_2. The PMR and ^{13}C NMR spectra were measured on the Varian VXR-400 instrument in the solution of chloroform at 28°C using TMS as the internal standard. In experiments on the NOE, the NOEDIF program was utilized [9]. The mass spectra were taken on the KRATOS MS-890 instrument with the direct input of the sample at the ion source at temperatures close to the melting temperatures; the energy of ionization was 70 eV.

The following adsorbents were utilized: aluminum oxide neutral (Brockmann), Florizil 60/100 (Merk), Polyamide (Woelm), DEAE-cellulose (Reanal) (the anion exchanger containing diethylaminoethyl groups with the capacity 0.6-0.8 meq/g) and aminoethylcellulose (Reanal) (AE with the capacity 0.3-0.5 meq/g). Monitoring of the course of reaction and the purity of the compounds obtained was accomplished by the method of TLC on plates of Silufol UV-254 in a 1:1 system of benzene–ethyl acetate; development was performed with iodine vapor and the alcoholic solution of $FeCl_3$. Purification of the compounds obtained was carried out by the method of high performance flash chromatography on silica gel type L 40/100, as well as the method of chromatography on a dry column with silica gel L 5/40.

X-Ray Diffraction Investigation. Crystals of the compound (IIId) are monoclinic with the following parameters at −25°C: a = 11.138(3) Å, b = 13.218(4) Å, c = 14.369(5) Å, β = 107.82(2)°, V = 2014(1) Å^3, d_{calc} = 1.242 g/cm^3, Z = 4, and the space group $P2_{1/n}$. Cell parameters and intensities of the 3564 independent reflections were measured on a Siemens P3/PC four-circle automatic diffractometer with λMoKα, a graphite monochromator, and $\theta/2\theta$-scanning up to the

TABLE 8. Coordinates ($\times 10^4$) and Isotropic Equivalent Thermal Parameters of Non-hydrogen Atoms (H-Isotropic) in the Molecule (IIId)

Atom	x	y	z	$U_{(eq)}$
$O_{(1)}$	733(2)	6754(1)	7055(1)	62(1)
$O_{(2)}$	1435(2)	6316(1)	5547(1)	67(1)
$N_{(1)}$	-173(2)	5566(1)	7850(1)	52(1)
$N_{(2)}$	20(2)	4593(1)	8201(1)	60(1)
$N_{(13)}$	3261(2)	4096(1)	5942(1)	59(1)
$N_{(14)}$	2432(2)	4855(1)	6091(1)	52(1)
$C_{(3)}$	1031(2)	4261(2)	7973(2)	56(1)
$C_{(4)}$	1519(2)	5020(2)	7490(2)	51(1)
$C_{(5)}$	721(2)	5833(2)	7428(2)	49(1)
$C_{(6)}$	-1176(2)	6148(2)	7994(2)	53(1)
$C_{(7)}$	-1774(2)	6885(2)	7338(2)	63(1)
$C_{(8)}$	-2768(3)	7426(2)	7494(3)	76(1)
$C_{(9)}$	-3158(3)	7212(3)	8295(3)	88(1)
$C_{(10)}$	-2549(3)	6485(3)	8944(3)	88(1)
$C_{(11)}$	-1560(3)	5951(2)	8803(2)	73(1)
$C_{(12)}$	1437(4)	3200(2)	8243(3)	78(1)
$C_{(15)}$	2668(2)	5091(2)	7153(2)	55(1)
$C_{(16)}$	3768(3)	4378(3)	7633(2)	72(1)
$C_{(17)}$	4365(2)	4164(2)	6833(2)	72(1)
$C_{(18)}$	5249(4)	4988(4)	6701(4)	112(1)
$C_{(19)}$	2695(2)	3126(2)	5693(2)	57(1)
$C_{(20)}$	3420(3)	2370(2)	5470(2)	87(1)
$C_{(21)}$	2910(4)	1442(3)	5172(3)	115(1)
$C_{(22)}$	1663(4)	1243(3)	5074(3)	114(1)
$C_{(23)}$	935(4)	1989(2)	5280(2)	91(1)
$C_{(24)}$	1437(3)	2925(2)	5579(2)	68(1)
$C_{(25)}$	1938(2)	5534(2)	5383(2)	56(1)
$C_{(26)}$	1928(4)	5292(3)	4363(2)	85(1)
$H_{(1)}$	1064(32)	6644(26)	6563(27)	132(13)
$H_{(7)}$	-1528(21)	7045(17)	6767(18)	69(7)
$H_{(8)}$	-3104(26)	7933(22)	7021(22)	97(10)
$H_{(9)}$	-3881(29)	7646(24)	8405(22)	117(10)
$H_{(10)}$	-2836(28)	6356(24)	9472(24)	110(11)
$H_{(11)}$	-1083(23)	5453(18)	9234(19)	72(8)
$H_{(121)}$	2231(29)	3168(21)	8707(23)	96(10)
$H_{(122)}$	781(33)	2813(26)	8489(25)	129(12)
$H_{(123)}$	1480(24)	2779(21)	7703(21)	86(9)
$H_{(15)}$	2940(17)	5807(15)	7226(14)	47(5)
$H_{(161)}$	3444(23)	3704(21)	7809(18)	78(8)
$H_{(162)}$	4339(24)	4712(19)	8150(19)	78(8)
$H_{(17)}$	4811(22)	3460(19)	6972(17)	72(7)
$H_{(181)}$	6024(39)	4936(27)	7270(28)	132(13)
$H_{(182)}$	4853(38)	5663(32)	6642(29)	151(17)
$H_{(183)}$	5541(38)	4691(30)	6211(30)	148(16)
$H_{(20)}$	4223(25)	2571(19)	5466(18)	71(8)
$H_{(21)}$	3417(32)	949(28)	4990(26)	137(13)
$H_{(22)}$	1283(28)	566(25)	4887(22)	110(10)
$H_{(23)}$	-21(33)	1930(24)	5165(24)	125(12)
$H_{(24)}$	955(19)	3474(17)	5745(15)	57(6)
$H_{(261)}$	1277(49)	5672(38)	3864(39)	200(20)
$H_{(262)}$	2581(44)	5763(36)	4213(33)	175(18)
$H_{(263)}$	2242(31)	4773(27)	4292(23)	104(12)

θ_{max} = 26°. The structure was interpreted by the direct method, which showed all nonhydrogen atoms, and was specified by the full-matrix MLS using the anisotropic approximation for nonhydrogen atoms. All hydrogen atoms were objectively shown by the difference Fourier syntheses, and specified isotropically. Final values of divergence factors were R = 0.047 for 2080 reflections with the $I > 2\sigma(I)$, and R_W = 0.121 for 3503 reflections. All calculations were performed using the SHELXTL PLUS program (PC version). Coordinates and isotropic equivalent (isotropic for H) thermal parameters of nonhydrogen atoms are given in Table 8.

3-Methyl-4-(1-acetyl-2-phenylpyrazolidin-5-yl)pyrazol-5-ones (IIIa-h). The solution of 4.5 mmole of the 3-methylpyrazol-5-one (II) in the minimal amount of abs. methanol is added to 5 g of the solid adsorbent. The mixture is shaken for 10 min, and the solvent is removed *in vacuo*. To the carrier, with the reagent applied to it, is added the solution of 4.55 mmole of the 5-hydroxypyrazolidine (I) in 30 ml of benzene (with 1 ml of methanol when R^2 = H). The reaction mixture is stirred with low heating at 60°C. At the end of the reaction, the solvent is filtered off, and the reaction products are extracted from the solid phase with chloroform or ethanol. The combined extracts are concentrated *in vacuo*, and the dry residue is chromatographed on a dry column with silica gel in the system benzene–ethyl acetate.

1-Phenyl-3-trifluoromethyl-4-(1-acetyl-2-phenyl-3-methylpyrazolidin-5-yl)pyrazol-5-one (IV). This compound is isolated by analogy with the compounds (IIIa-h) from 1-phenyl-3-trifluoromethylpyrazol-5-one and the 3-methyl-5-hydroxypyrazolidine (IIb).

The authors express thanks to the RFFI (Grants 96-03-32507, 96-15-97367, and 97-03-33783) for financial support of the given work.

REFERENCES

1. L. A. Sviridova, G. A. Golubeva, and I. V. Dlinnykh, Khim. Geterotsikl. Soedin., No. 11/12, 1657 (1996).
2. L. A. Sviridova, S. V. Afanas'eva, G. A. Golubeva, P. B. Terent'ev, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 9, 1204 (1990).
3. I. A. Motorina, L. A. Sviridova, G. A. Golubeva, and Yu. G. Bundel, Tetrahedron Lett., **30**, 117 (1989).
4. D. M. Musatov, L. A. Sviridova, I. A. Motorina, I. F. Leshcheva, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 4, 483 (1994).
5. L. A. Sviridova, G. A. Golubeva, A. V. Mizgunov, I. V. Dlinnykh, and V. N. Nesterov, Khim. Geterotsikl. Soedin., No. 4, 509 (1997).
6. A. V. Dovgilevich, K. N. Zelenin, A. A. Espenbetov, Yu. T. Struchkov, I. P. Bezhan, L. A. Sviridova, G. A. Golubeva, M. Yu. Malov, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 9, 1242 (1985).
7. L. A. Sviridova, G. A. Golubeva, I. V. Dlinnykh, I. F. Leshcheva, and V. N. Nesterov, Khim. Geterotsikl. Soedin., No. 3, 311 (1998).
8. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc. Perkin Trans. II, No. 12, S1 (1987).
9. M. Kinns and J. K. M. Sanders, J. Magn. Reson., **56**, 518 (1984).