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Recyclization of 2-Aryl-4-cyano-5-hydrazinooxazoles

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Abstract — The available 2-benzoylamino-3,3-dichloroacrylonitrile and its analogs when treated with excess hydrazine hydrate convert to 2-aryl-4-cyano-5-hydrazinooxazoles. The products are fairly stable in usual conditions but undergo recyclization on heating in acetic acid to give previously unknown derivatives of 2-methyl-1,3,4-oxadiazole with a 5-acylamino(carbamoyl)methyl substituent, whose structure was established by spectroscopy and X-ray diffraction. An important role in this complex transformation is probably played by prototropic forms of 4-cyano-5-hydrazinooxazoles, viz. hydrazones of substituted 2-oxazolin-5-ones which are not aromatic and thus can be cleaved with acetic acid and then recyclize.

Reactions of 2-acylamino-3,3-dichloroacrylonitriles **I** with primary and secondary amines, which have been thoroughly studied over the last 20 years, result most commonly in substituted 5-aminooxazoles (see [1] and references therein). Cyclocondensations of the multicenter reagents **I** with hydrazine and its derivatives have only recently come into researcher's attention [2].

In the present work we found that on treatment with excess hydrazine hydrate reagents **I** undergo the same cyclization as under the action of amines. As a result, already under mild conditions, previously unknown 2-aryl-4-cyano-5-hydrazinooxazoles **II** are formed in high yields (Table 1, Scheme 1). The presence in the products of cyclization of compounds **I** of C≡N and $NHNH_2$ groups is consistent with the ^1H NMR and IR data summarized in Table 2.

Furthermore, the results of acylation of compounds

Table 1. Constants, yields, and elemental analyses of compounds **I, II**, and **VII**–**XI**

Comp. no.	Yield, %	mp, °C (solvent for crystallization)	Found, %				Formula	Calculated, %			
			C	H	Cl (F)	N		C	H	Cl (F)	N
Id	75	174–176 (benzene)	46.12	1.98	27.40	10.76	$C_{10}H_5Cl_2FN_2O$	46.36	1.95	27.37	10.81
IIa	70	200–202 (ethanol)	59.86	4.28		27.84	$C_{10}H_8N_4O$	59.99	4.03		27.99
IIb	70	166–168 (ethanol)	61.42	4.98		26.04	$C_{11}H_{10}N_4O$	61.67	4.71		26.15
IIc	74	192–194 (ethanol)	57.28	4.42		24.22	$C_{11}H_{10}N_4O_2$	57.39	4.38		24.34
IId	72	178–180 (ethanol)	55.32	3.48	(8.74)	25.42	$C_{10}H_7FN_4O$	55.05	3.23	(8.71)	25.68
VIIa	64	148–150 (acetonitrile)	55.02	4.82		21.44	$C_{12}H_{12}N_4O_3$	55.38	4.65		21.53
VIIb	62	204–206 (acetonitrile)	56.78	5.18		20.26	$C_{13}H_{14}N_4O_3$	56.93	5.15		20.43
VIIc	60	200–202 (acetonitrile)	53.42	4.90		19.24	$C_{13}H_{14}N_4O_4$	53.79	4.86		19.30
VIId	68	172–174 (acetonitrile)	51.46	4.34	(6.80)	20.04	$C_{12}H_{11}FN_4O_3$	51.80	3.99	(6.83)	20.14
VIIIa	90	224–226 (DMSO)	63.08	3.66	10.90	17.16	$C_{17}H_{11}ClN_4O$	63.26	3.44	10.98	17.36
VIIIb	90	228–230 (DMSO)	64.26	3.94	10.54	16.52	$C_{18}H_{13}ClN_4O$	64.00	3.89	10.53	16.64
IXa	85	210–212 (DMSO)	67.52	4.75		17.46	$C_{18}H_{14}N_4O_2$	67.92	4.43		17.60
IXb	85	216–218 (DMSO)	68.36	4.98		16.74	$C_{19}H_{16}N_4O_2$	68.66	4.85		16.86
Xa	62	158–160 (ethanol)	67.50	4.86		17.48	$C_{18}H_{14}N_4O_2$	67.92	4.43		17.60
Xb	60	148–150 (ethanol)	68.34	4.98		16.82	$C_{19}H_{16}N_4O_2$	68.66	4.85		16.86
XIa	72	164–166 (ethanol)	68.02	3.99	8.06	12.60	$C_{25}H_{17}ClN_4O_2$	68.11	3.89	8.04	12.71
XIb	70	140–142 (ethanol)	71.22	4.86		12.78	$C_{26}H_{20}N_4O_3$	71.55	4.62		12.84

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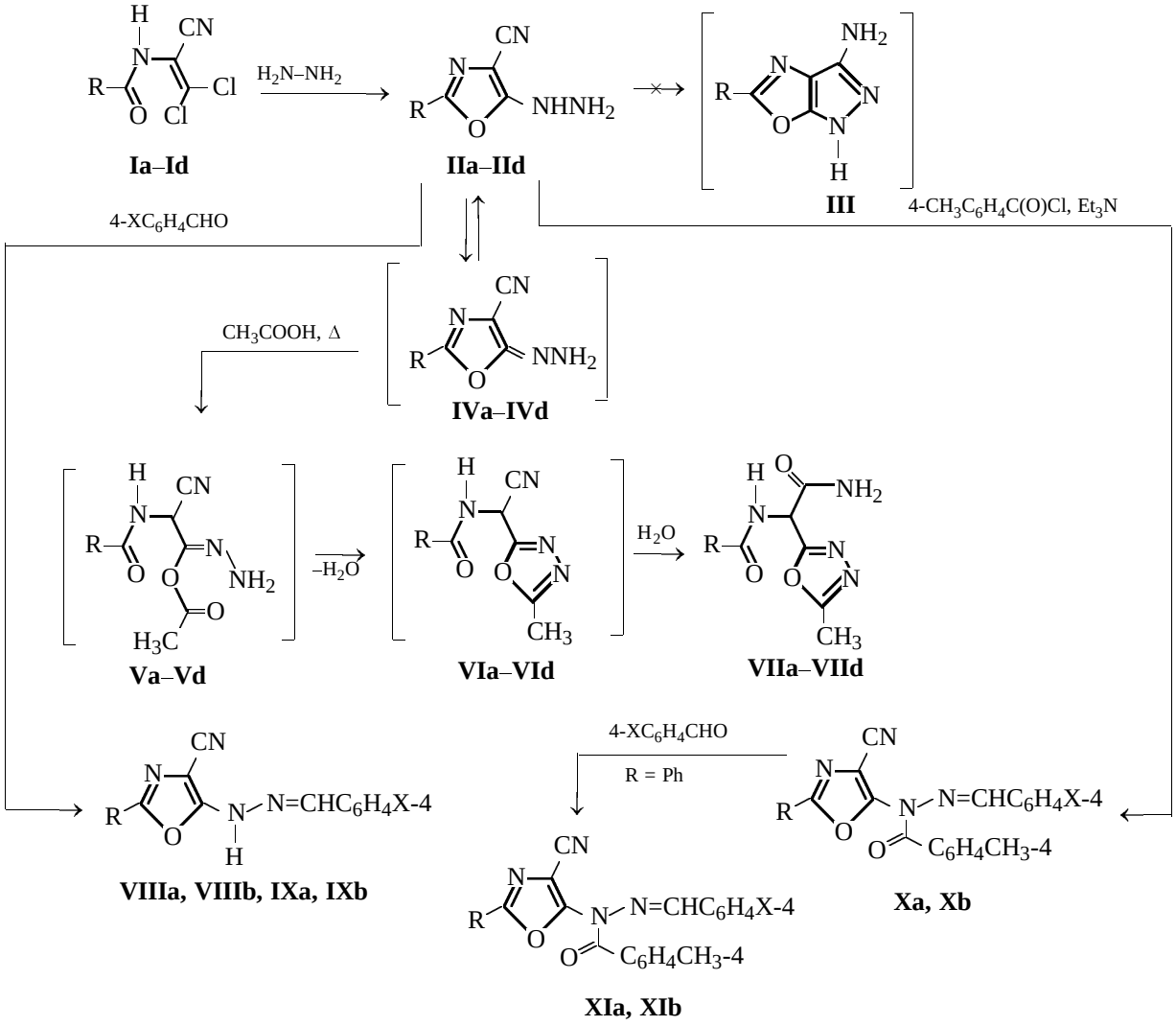
Scheme 1.



I, II, IV–**X**, R = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**), 4-$CH_3OC_6H_4$ (**c**), 4-FC_6H_4 (**d**); X = Cl (**VIIIa, VIIIb, XIa**), CH_3O (**IXa, IXb, XIb**).

II and of their condensations with aromatic aldehydes (Scheme 1) provide strong evidence showing that they are typical heterylhydrazines. A distinctive feature of compounds **II**, the presence of $NHNH_2$ and C≡N substituents in adjacent positions of the oxazole ring, gave us grounds to expect them to be able to intramolecular cyclization (**II** → **III**). However, all attempts to effect this reaction failed.

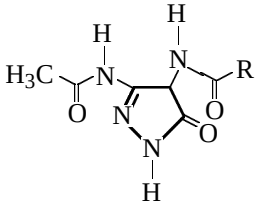
Searching for conditions for such cycloaddition, we subjected oxazoles **II** to prolonged heating in acetic acid but obtained, instead of the expected compounds **III**, novel 1,3,4-oxadiazole derivatives **VIIa**–**VIId** formed, probably, by the sequence **II** → **IV** → **V** → **VI** → **VII**. Note first of all that one should not rule out formation, by analogy with the prototropism of 5-mercaptooxazoles [3], of prototropic tautomers **IV**, while in amounts undetectable by usual spectral methods. Unlike the aromatic compounds **II**, their prototropic forms **IV** as hydrazones of substituted 2-oxazolin-5-ones are nonaromatic. Taking into account that the well-studied analogs of compounds **II**, saturated and unsaturated azlactones, are readily cleaved by various compounds with O–H, S–H, and N–H bonds, we considered it quite probable that the oxazoline ring in tautomers **IV** is cleaved by acetic acid to give intermediates **V** capable of intramolecular dehydration yielding the enegretically favorable aromatic 1,3,4-oxazolidine ring. Further the C≡N group in **VI** takes up water to give the final reaction products **VII**.

Table 2. Spectral characteristics of compounds **I, II**, and **VII**–**XI**

Comp. no.	IR spectrum (KBr)[a], ν, cm^{-1}	^1H NMR spectrum [$(CD_3)_2SO$][b], δ, ppm (*J*, Hz)
Id	1660 (C=O), 2230 (C≡N), 3100–3300 (NH as.)	–
IIa	1605 [δ(NH_2)], 1690[c], 2220 (C≡N), 3100–3400 (NH, NH_2 as.)	4.89 br.s (2H, NH_2), 7.49–7.77 m (5H, C_6H_5), 9.29 br.s (1H, NH)
IIb	1615 [δ(NH_2)], 1690[c], 2230 (C≡N), 3100–3500 (NH, NH_2 as.)	2.35 s (3H, CH_3), 4.91 br.s (2H, NH_2), 7.30–7.68 m (4H, C_6H_4), 9.28 br.s (1H, NH)
IIc	1620 [δ(NH_2)], 1690[c], 2230 (C≡N), 3200–3400 (NH, NH_2 as.)	3.82 s (3H, OCH_3), 4.87 br.s (2H, NH_2), 7.07–7.71 m (4H, C_6H_4), 9.20 br.s (1H, NH)
IId	1615 [δ(NH_2)], 1680[c], 2240 (C≡N), 3200–3400 (NH, NH_2 as.)	4.89 br.s (2H, NH_2), 7.35–7.90 m (4H, C_6H_4), 9.28 br.s (1H, NH)
VIIa	1660 (C=O)[d], 1710 (C=O), 3200–3400 (NH, NH_2 as.)	2.54 s (3H, CH_3), 5.86 br.s, 7.02 br.s (2H, NH_2), 6.12 d (1H, CH, $^3J_{HH}$ 6.3), 7.48–7.90 m (5H, C_6H_5), 7.71 d (1H, NH, $^3J_{HH}$ 6.3)
VIIb[e]	1650 (C=O)[d], 1710 (C=O), 3200–3420 (NH, NH_2 as.)	2.42 s (3H, CH_3), 2.54 s (3H, CH_3), 5.82 br.s, 7.97 br.s (2H, NH_2), 6.07 d (1H, CH, $^3J_{HH}$ 6.0), 7.28–7.77 m (4H, C_6H_4), 7.63 d (1H, NH, $^3J_{HH}$ 6.0)
VIIc	1660 (C=O)[d], 1720 (C=O), 3200–3420 (NH, NH_2 as.)	2.55 s (3H, CH_3), 3.87 s (3H, OCH_3), 5.67 br.s, 6.85 br.s (2H, NH_2), 6.04 d (1H, CH, $^3J_{HH}$ 6.0), 6.98–7.85 m (4H, C_6H_4), 7.51 d (1H, NH, $^3J_{HH}$ 6.0)
VIId	1680 (C=O)[d], 1720 (C=O), 3200–3380 (NH, NH_2 as.)	2.55 s (3H, CH_3), 5.74 br.s, 6.84 br.s (2H, NH_2), 6.03 d (1H, CH, $^3J_{HH}$ 6.0), 7.17–7.92 m (4H, C_6H_4), 7.61 d (1H, NH, $^3J_{HH}$ 6.0)
VIIIa[f]	1660 (C=N), 2245 (C≡N), 3100–3300 (NH as.)	7.52–7.84 m (9H, C_6H_5, C_6H_4), 8.09 s (1H, CH)[g]
VIIIb	1660 (C=N), 2235 (C≡N), 3100–3350 (NH as.)	2.36 s (3H, CH_3), 7.03–7.84 m (8H, $2C_6H_4$), 8.07 s (1H, CH), 12.58 br.s (1H, NH)
IXa[f]	1655 (C=N), 2240 (C≡N), 3100–3350 (NH as.)	3.81 s (3H, OCH_3), 7.03–7.84 m (9H, C_6H_5, C_6H_4), 8.05 s (1H, CH)[g]
IXb[f]	1650 (C=N), 2245 (C≡N), 3050–3300 (NH as.)	2.36 s (3H, CH_3), 3.81 s (3H, OCH_3), 7.03–7.71 m (8H, $2C_6H_4$), 8.03 s (1H, CH), 12.31 br.s (1H, NH)
Xa	1645 [δ(NH_2)], 1685 (C=O), 2245 (C≡N), 3050–3500 (NH_2 as.)[h]	2.36 s (3H, CH_3), 5.88 br.s (2H, NH_2), 7.31–7.77 m (9H, C_6H_5, C_6H_4)
Xb	1620 [δ(NH_2)], 1685 (C=O)[d], 2245 (C≡N), 3050–3500 (NH_2 as.)[h]	2.37 s (6H, $2CH_3$), 5.89 br.s (2H, NH_2), 7.30–7.64 m (8H, $2C_6H_4$)
XIa[f]	1690 (C=N, C=O)[i], 2220 (C≡N)	2.42 s (3H, CH_3), 7.40–8.15 m (13H, C_6H_5, $2C_6H_4$), 8.38 s (1H, CH)
XIb[f]	1685 (C=N, C=O)[i], 2230 (C≡N)	2.42 s (3H, CH_3), 3.79 s (3H, OCH_3), 7.03–8.10 m (12H, $3C_6H_4$), 8.33 s (1H, CH)

[a] Strong bands in the ranges 1600–1750, 2100–2300, and 3000–3500 cm^{-1} are given; (as.) bands of associated groups. [b] The spectrum of compound **VIIb** was measured in $CDCl_3$. [c] The bands were not identified. [d] The band has a shoulder. [e] ^{13}C NMR spectrum of compound **VIIb** [$(CD_3)_2SO$], δ_C, ppm: 9.38 (C^2–CH_3); 19.89 ($C_6H_5CH_3$); 48.49 (CH); 126.70, 127.70 (*o*,*m*-C, Ph); 129.33 (*i*-C, Ph), 140.69 (*p*-C, Ph); 161.98, 163.11, 165.11, 165.98 (2C=O, C^2=N, C^5=N). [f] The steric stucture of the hydrazone was not established. [g] The NH proton signal was not found. [h] For 0.1 M solution in CH_2Cl_2. [i] The broad band probably comprises C=N and C=O stretching vibration bands.

The structure of compounds **VII** was confirmed by their ^1H and ^{13}C NMR and IR spectra (Table 2), but the spectral data proved insufficient for the alternative structure **A** to be ruled out.



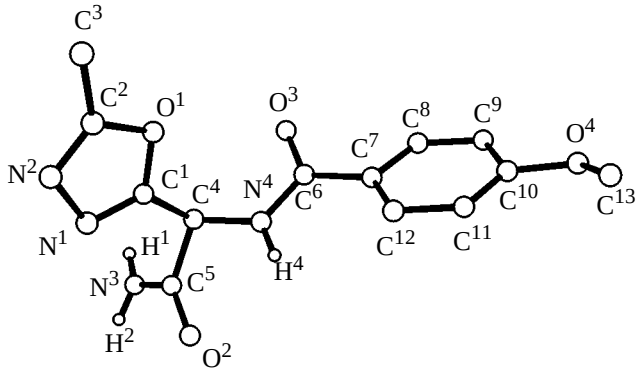
A

Therefore, we performed an X-ray diffraction analysis of the recyclization product of 4-cyano-5-

Table 3. Principle bond lengths (*d*, Å) and bond angles (ω, deg) in molecule **VIIc**

Bond	*d*	Angle	ω
O^1–C^1	1.353(2)	$C^1O^1C^2$	102.6(1)
O^1–C^2	1.365(2)	$N^2N^1C^2$	106.0(2)
O^2–C^5	1.228(2)	$N^1N^2C^2$	106.5(2)
O^3–C^6	1.233(2)	$O^1C^1N^1$	112.7(2)
O^4–C^{10}	1.365(2)	$O^1C^1C^4$	119.3(1)
N^1–N^2	1.412(2)	$N^1C^1C^4$	127.9(2)
N^1–C^1	1.274(2)	$O^1C^2N^2$	112.3(2)
N^2–C^2	1.268(3)	$O^2C^5N^3$	124.6(2)
N^3–C^5	1.313(2)	$O^2C^5C^4$	119.7(2)
N^4–C^4	1.447(2)	$N^3C^5C^4$	115.7(2)
N^4–C^6	1.341(2)	$O^3C^6N^4$	120.6(2)
C^1–C^4	1.493(3)	$O^3C^6C^7$	120.5(2)
C^2–C^3	1.531(2)	$N^4C^6C^7$	119.0(1)
C^6–C^7	1.479(2)		

hydrazino-2-(*p*-methoxyphenyl)oxazole (**IIc**), which allowed conclusive assignment of compound **VIIc** and, therefore, of its analogs **VIIa, VIIb**, and **VIId**, to 1,3,4-oxadiazole derivatives. As seen from the figure and data in Tables 3 and 4, the oxadizole ring in **VIIc** is planar within 0.001 Å, and the deviations of C^3 and C^4 from this plane do not exceed 0.026 and 0.019 Å. The N^3 and N^4 atoms has a planar-trigonal configuration (the sum of their bond angles is 359.9°). Therewith, the N^3 bond plane is turned with respect to the $C^5O^2N^3C^4$ plane by only 5.4°, while the N^4 bond plane forms with the $C^6O^3N^4C^7$ a dihedral angle of 2.4°. Such molecular conformation allows effective conjugation like $n(N^3)$–$\pi^*(C^5{=}O^2)$ and $n(N^4)$–$\pi^*(C^6{=}O^3)$. Actually, the N^3–C^5 [1.313(2) Å] and N^4–C^6 [1.341(2) Å] bonds transmittimg this interaction are much shortened compared with standard N(sp^2)–C(sp^2) bonds (1.43–1.45 Å [4, 5]). The $N^1\cdots C^5$



General view of molecule **VIIc** (hydrogen atoms are shown partly: H^1, H^2, and H^4).

Table 4. Atomic coordinates[a] and equivalent anisotropic (isotropic for H atoms) thermal parameters ($Å^2$) in structure **VIIc**

Atom	*x*	*y*	*z*	U_{eq}
O^1	0.8625(1)	–0.14795(19)	0.15542(7)	0.0500
O^2	1.05145(12)	0.25609(18)	0.01166(7)	0.0541
O^3	1.11510(12)	–0.0995(2)	0.24493(7)	0.0570
O^4	1.47227(15)	–0.7010(3)	0.1361(1)	0.0891
N^1	0.81406(14)	0.0721(2)	0.06962(9)	0.0534
N^2	0.72503(14)	–0.0614(3)	0.07651(11)	0.0610
N^3	0.97704(15)	0.4423(2)	0.1050(1)	0.0496
N^4	1.09396(12)	–0.0340(2)	0.11803(8)	0.0390
C^1	0.89116(15)	0.0146(2)	0.1167(1)	0.0392
C^2	0.75693(16)	–0.1853(3)	0.12667(13)	0.0540
C^3	0.6963(3)	–0.3572(5)	0.1541(2)	0.0839
C^4	1.00418(15)	0.1026(2)	0.1313(1)	0.0375
C^5	1.01398(15)	0.2776(2)	0.0772(1)	0.0396
C^6	1.14359(14)	–0.1294(2)	0.17737(9)	0.0368
C^7	1.23186(14)	–0.2733(3)	0.16044(9)	0.0380
C^8	1.30748(17)	–0.3236(3)	0.22049(12)	0.0524
C^9	1.38726(18)	–0.4634(3)	0.20981(13)	0.0601
C^{10}	1.39202(17)	–0.5604(3)	0.14015(12)	0.0574
C^{11}	1.31769(19)	–0.5152(4)	0.08055(13)	0.0640
C^{12}	1.23965(17)	–0.3696(3)	0.09060(11)	0.0513
C^{13A}	1.4594(16)	–0.845(3)	0.0788(11)	0.0881
C^{13B}	1.4898(14)	–0.789(3)	0.059(1)	0.0945
H^1	0.9506(17)	0.451(3)	0.1504(13)	0.052(6)
H^2	0.9744(19)	0.544(4)	0.0750(14)	0.066(7)
H^4	1.1171(17)	–0.054(3)	0.0720(12)	0.051(6)
H^8	1.3011(19)	–0.251(4)	0.2720(15)	0.077(7)
H^9	1.439(2)	–0.503(3)	0.2520(14)	0.073(7)
H^{11}	1.319(2)	–0.589(4)	0.0344(15)	0.081(8)
H^{12}	1.1882(19)	–0.337(3)	0.0494(13)	0.062(6)
H^{31}	0.694(2)	–0.346(4)	0.2100(18)	0.09(1)
H^{32}	0.622(3)	–0.361(5)	0.1356(18)	0.11(1)
H^{33}	0.735(3)	–0.488(5)	0.1341(19)	0.122(11)
H^{41}	1.0122(15)	0.148(3)	0.1863(11)	0.044(5)

[a] The C^{13} atom is disordered over two positions (A and B) with occupancies of 0.48 and 0.52.

bond length [2.771(2) Å] is appreciably smaller than the sum of the van der Waals radii of N and C atoms (3.20 Å), while the $N^1C^1C^4$ bond angle [127.9(2)°] is substantially larger than the $O^1C^1C^4$ bond angle [119.3(1)°]. Similarly, the shortened $C^{11}\cdots C^{13}$ intramolecular contact [2.838(3) Å] increases the $O^4C^{10}\cdot C^{11}$ angle to 124.3(2)°, while the $O^4C^{10}C^9$ angle is 115.6(2)°.

In the crystal of **VIIc**, there are centrosymmetrical dimers formed by the hydrogen bonds $O^3\cdots H^1N^3$ [$O^3\cdots N^3$ 2.837(2), $O^3\cdots H^1$ 2.01(2), and N^3–H^1 0.85(2) Å; $\angle O^3H^1N^3$ 165.8(1.5)°]. In turn, the dimers

pack, by the hydrogen bonds $O^2\cdots H^2N^3$ [$O^2\cdots N^3$ 2.906(2), $O^2\cdots H^2$ 2.05(2), and $N^3–H^2$ 0.87(2) Å; $\angle O^2H^2N^3$ 167.2(1.7)°], in infinite chains (the mean value for H···O hydrogen bonds like N–H···O is 2.89 Å [6]).

Thus, the structure of substituted 1,3,4-oxadiazoles **VIIa**–**VII** is beyond question, but the mechanism of their formation and the application field of the recyclization **II** → **VII** extends the range of known methods of synthesis of 1,3,4-oxadiazoles [7], deserve further investigation. Note, however, that attempts to involve in such transformation 4-cyano-5-hydroxy-2-methyloxazole obtained in [8] proved unsuccessful.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. The ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer in $(CD_3)_2SO$ or $CDCl_3$, standard TMS.

The X-ray diffraction analysis of a single crystal ($0.11 \times 0.22 \times 0.38$ mm) of compound **VIIc** was performed at room temperature on an Enraf–Nonius CAD-4 automatic four-circle diffractometer [CuK_α radiation (λ 1.54178 Å), ω/2θ 1.2, θ_{max} 65°, $0 \le h \le 13$, $0 \le k \le 8$, $-20 \le l \le 20$]. The unit cell parameters and orientation matrix were determined with 22 reflections with $24.4 < \theta < 26.5°$. A total of 2753 reflections were measured, 2394 of which were symmetrically independent (*R* 0.012). The crystals of compound **I** are monoclinic, *a* 11.898(2), *b* 6.910(1), *c* 17.183(2) Å; β 91.13(1)°, *V* 1412.4 Å^3, *M* 289.27, *Z* 4, d_{calc} 1.36 g/cm^3, μ 8.32 cm^{-1}, space group $R2_{1/C}$ (*N* 14). The structure was solved by the direct method and subjected to full-matrix least-squares anisotropic refinement using the CRYSTALS package [9]. In the refinement, 1800 reflections with $I > 3\sigma(I)$ were used (243 refined parameters, reflections/parameter 7.4). All hydrogen atoms (except for H atoms of the disordered methyl group $^{13}CH_3$) were revealed objectively by difference synthesis and refined isotropically. The $^{13}CH_3$ hydrogens were placed at computed positions and included in the refinement with fixed positional and thermal parameters. Absorption was accounted for using azimuthal scanning technique [10]. The refinement was performed by the Chebyshev weight scheme [11] with the following parameters: 1.65, 1.21, 1.63, 0.36, and 0.47. The final divergence factors were *R* 0.038 and R_W 0.042; *GOF* 1.149. The residual electron density from the Fourier difference series was 0.14 and –0.18 *e*/Å^3. The principle bond lengths and bond angles in molecule **VIIc** are listed in Table 3, and the coordinates of atoms and their thermal parameters, in Table 4.

2-Acylamino-3,3-dichloroacrylonitriles Ia–Ic were prepared as described in [12, 13]. The previously unknown 3,3-dichloro-2-*p*-fluorobenzoylaminoacrylonitrile (**Id**) was prepared like **Ia** [12].

2-Aryl-4-cyano-5-hydrazinooxazoles IIa–IId. Hydrazine hydrate, 0.035 mol, was added to a solution of 0.01 mol of compound **Ia**–**Id** in 30 ml of ethanol. The mixture was allowed to stand for 48 h at 20–25°C, the residue was filtered off, washed with water, dried at 70–80°C, and crystallized from ethanol.

5-[Acylamino(carbamoyl)methyl]-2-methyl-1,3,4-oxadiazoles VIIa–VIId. A solution of 0.005 mol of compound **IIa**–**IId** in 10 ml of glacial acetic acid was refluxed for 8 h and left to stand for 12 h at 20–25°C. The solvent was removed in a vacuum, the residue was treated with water, the precipitate was filtered off, dried at 70–80°C, and purified by crystallization.

2-Aryl-4-cyano-5-[2-*p*-chloro(methoxy)benzylydenehydrazino]oxazoles VIIIa, VIIIb, IXa, IXb. A solution of 0.005 mol of an aromatic aldehyde in 5 ml of ethanol was added to a 0.005 mol of compound **IIa** or **IIb** in 15 ml ethanol under reflux. The mixture was refluxed for 10–15 min, the precipitate that formed was filtered off, dried at 70–80°C, and purified by crystallization.

2-Aryl-4-cyano-5-(1-*p*-toluoylhydrazino)oxazoles Xa, Xb. Triethylamine and *p*-toluoyl chloride, 0.005 mol each, were added to a solution of 0.005 mol of compound **IIa** or **IIb** in 15 ml of dry acetonitrile. The mixture was left to stand for 48 h at 20–25°C, the precipitate was filtered off, the filtrate was vacuum-evaporated, the residue was dried at 70–80°C, and purified by crystallization.

5-[2-(*p*-Chloro(methoxy)benzylidene)-1-*p*-toluoylhydrazino]-4-cyano-2-phenyloxazoles XIa, XIb. An aromatic aldehyde, 0.005 mol, was added to a solution of 0.005 mol of compound **Xa** in 15 ml of ethanol, the mixture was refluxed for 2 h, and left to stand at 20–25°C for 12 h. The precipitate that formed was filtered off, and compounds **XIa, XIb** were purified by crystallization.

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