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SYNTHESIS OF 2,5-DISUBSTITUTED 1,3,4-OXADIAZOLES CONTAINING A STERICALLY HINDERED 4-HYDROXY-3,5-DI(TERT-BUTYL)PHENYL GROUP

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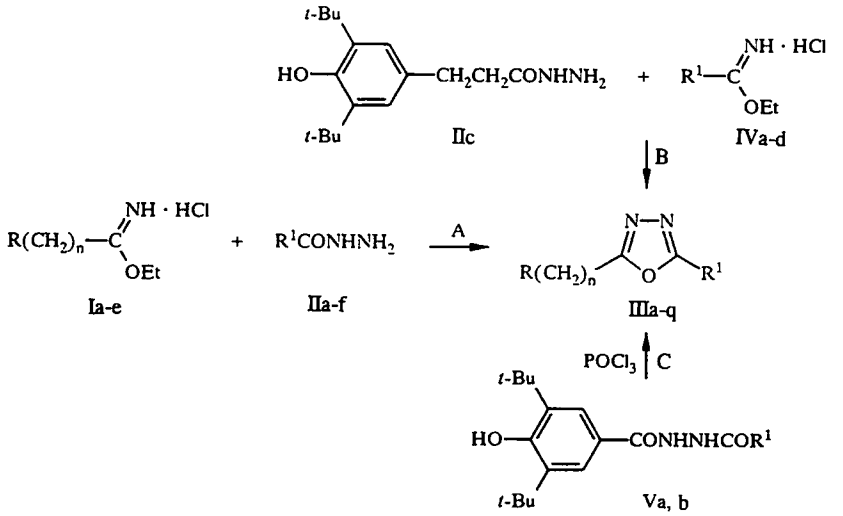
A series of 2,5-disubstituted 1,3,4-oxadiazoles containing one or two 4-hydroxydi(tert-butyl)phenyl groups has been synthesized. These sterically hindered compounds were prepared by condensation of acids containing the indicated fragment and their derivatives with hydrazine dihydrochloride, hydrazides, and hydrochlorides of iminoesters of acids, by the reaction of 4-hydroxy-3,5-di(tert-butyl)thiphenol with 2-chloromethylsubstituted 1,3,4-oxadiazoles in the presence of KOH, and by cyclodehydration of N-acyl-N'-[4-hydroxy-3,5-di(tert-butyl)benzoyl]hydrazones under action of $POCl_3$.

Continuing our studies of the synthesis of azoles containing groups of screened phenol [1-4], this paper presents data on the preparation of 2,5-disubstituted 1,3,4-oxadiazoles containing 4-hydroxy-3,5-di(tert-butyl)phenyl (HDBP) substituents.

Data presented in the literature pertain only to the preparation and properties of 1,3,4-oxadiazoles containing groups of sterically hindered phenol [3, 5-7], although compounds of this type may be of interest as potential biologically active substances, and also as stabilizers and additives to polymeric materials, hydrocarbon fuels, and lubricating oils.



Ia, b, IIIa-g, p, q R = 4-HO-3,5-$(t\text{-Bu})_2C_6H_2$; Ia, IIIa-d n = 0; Ib, IIIe-g, p, q n = 2; Ic-e, IIIh-o R = 4-HO−3,5-$(t\text{-Bu})_2C_6H_2S$; Ic, IIIh-j n = 0; Id, IIIk, *l* n = 1; Ie, IIIm-o n = 2; IIa, IIIa, e, k, IVa, Va R^1 = Ph; IIb, IIIb, h, m Vb R^1 = $4\text{-}NO_2C_6H_4$; IIc, IIIc, f R^1 = 4-HO-3,5-$(t\text{-Bu})_2C_6H_2CH_2CH_2$; IId, IIId, g, n, IVb R^1 = 5-nitrofuryl-2; IIe, IIIi R^1 = ClC_6H_4; IIf, IIIj, *l*, o R^1 = indolyl-3-methyl; IIIp, IVc R^1 = $Me_2C(NO_2)CH_2CH_2$; IIIq, IVd R^1 = $PhCH_2SCH_2CH_2$

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TABLE 1. Properties of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	R_f (solvent system)	Yield, % (method)
		C	H	N			
IIIa	$C_{22}H_{26}N_2O_2$	75,3 / 75,4	7,5 / 7,4	8,2 / 8,0	205...206 †	0,67 (a)	79 (A), 46 (B)
IIIb	$C_{22}H_{25}N_3O_4$	66,9 / 66,8	6,2 / 6,3	10,7 / 10,6	227...228 (dec.)	0,54 (a)	84 (A), 42 (C)
IIIc	$C_{32}H_{46}N_2O_3$	76,1 / 75,9	9,0 / 9,1	5,3 / 5,5	135...137	0,47 (b)	76 (A)
IIId	$C_{20}H_{23}N_3O_5$	62,2 / 62,3	5,9 / 6,0	12,6 / 12,5	174...175,5 (dec.)	0,74 (a)	83 (A)
IIIe	$C_{24}H_{30}N_2O_2$	76,1 / 76,2	8,0 / 7,9	7,6 / 7,4	112...114	0,63 (b)	77 (A), 84 (B)
IIIf	$C_{34}H_{50}N_2O_3$	76,6 / 76,4	9,3 / 9,4	5,3 / 5,2	Oil (n_D^{20} 1,5887)	0,74 (c)	88 (A), 55 (D)
IIIg	$C_{22}H_{27}N_3O_5$	64,0 / 63,9	6,6 / 6,5	10,0 / 10,2	124...125,5 (dec.)	0,41 (b)	74 (A), 80 (B)
IIIh	$C_{22}H_{25}N_3O_4S$	61,7 / 61,8	5,9 / 5,8	10,0 / 9,8	138...140	0,67 (a)	84 (A)
IIIi	$C_{22}H_{25}ClN_2O_2S$	63,5 / 63,4	5,9 / 6,0	6,9 / 6,7	Oil (n_D^{20} 1,5340)	0,57 (b)	73 (A)
IIIj	$C_{25}H_{29}N_3O_2S$	68,8 / 69,0	6,6 / 6,7	9,7 / 9,6	120...121	0,52 (a)	78 (A)
IIIk	$C_{23}H_{28}N_2O_2S$	69,9 / 69,7	7,0 / 7,1	6,8 / 7,1	151...152	0,60 (c)	86 (A), 83 (E)
IIIl	$C_{26}H_{31}N_3O_2S$	69,3 / 69,5	7,0 / 6,9	9,6 / 9,4	103...104,5	0,43 (b)	82 (A), 77 (E)
IIIm	$C_{24}H_{29}N_3O_4S$	63,1 / 63,3	6,5 / 6,4	9,0 / 9,2	188...190	0,65 (b)	77 (A)
IIIn	$C_{22}H_{27}N_3O_5S$	59,1 / 59,3	6,0 / 6,1	9,5 / 9,4	97...98,5	0,73 (c)	85 (A)
IIIo	$C_{27}H_{33}N_3O_2S$	68,9 / 70,0	7,0 / 7,1	9,3 / 9,1	190...192	0,37 (b)	72 (A)
IIIp	$C_{23}H_{35}N_3O_4$	66,9 / 66,8	8,3 / 8,4	9,9 / 10,1	Oil (n_D^{20} 1,5722)	0,76 (b)	74 (B)
IIIq	$C_{27}H_{36}N_2O_2S$	71,6 / 71,7	7,9 / 8,0	6,3 / 6,2	Oil (n_D^{20} 1,5437)	0,72 (c)	67 (B)
IIIr	$C_{30}H_{42}N_2O_3$	75,4 / 75,3	8,7 / 8,8	6,1 / 5,9	233...234,5	0,58 (a)	52 (D)

*Compounds were recrystallized: IIIa, k, r) from acetonitrile; IIIb) from aqueous DMFA; IIIc, e) from a 10:1 petroleum ether–2-propanol mixture; IIId, g, h, j, *l*, n) from aqueous ethanol; IIIm) from a 10:1 benzene–dioxane mixture; IIIo) from ethanol.

†Lit. mp 203-204°C [5].

It is well known [8, 9] that convenient compounds used in the synthesis of 1,3,4-oxadiazoles are hydrochlorides of iminoesters of carboxylic acids. In the present study, the starting compounds used were hydrochlorides of ethyl iminoesters of 4-hydroxy-3,5-di(tert-butyl)benzoic (Ia), β-HDBP-propionic (Ib), s-HDBP-thiocyanic (Ic), HDBP-thioacetic (Id), and β-HDBP-propionic (Ie) acids. Condensation of compounds Ia-e with hydrazides of carboxylic acids (IIa-f) forms 2,5-disubstituted 1,3,4-oxadiazoles (IIIa-o) containing 4-hydroxy-3,5-di(tert-butyl)phenyl substituents (method A). Better yields of products IIIa-o (see Table 1) were obtained by boiling the reactants in ethanol or dioxane at a molar ratio I:II of 1.1:1. We note that the duration of the process depends on the reactivity of the initial hydrochlorides of iminoesters Ia-e. For example, formation of compounds IIIe-o is completed after the reactants are boiled in ethanol for 3 to 4 h. At the same time, in the preparation of products IIIa-d from iminoester hydrochloride Ia, which has a reduced reactivity as a result of the influence of the electron-donor hydroxyaryl substituent bound to the iminoester group [1], boiling in dioxane for 8 to 10 h is necessary.

To prepare 1,3,4-oxadiazoles IIIe, g, p, q, we also used condensation of β-HDBP-propionic acid hydrazide IIc with hydrochlorides of ethyl iminoesters of various carboxylic acids (IVa-d) (method B). The reactions were carried out by boiling the reactants (molar ratio IIc:IV of 1:1.25) in methanol for several hours; the corresponding products IIIe, g, p, q are formed in 67% to 84% yields (see Table 1).

TABLE 2. Parameters of ESR Spectra of the Synthesized Compounds*

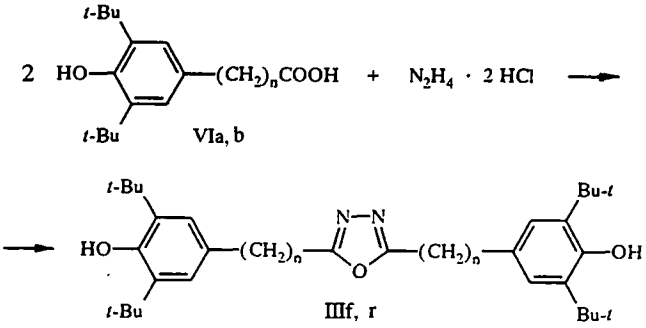
Compound	Chemical proton shifts, δ, ppm, SSCC (J), Hz			
	t-Bu, br.s,	OH, s;	2-, 6-H_{Ar}, s	other protons
IIIa	1,58 (18H)	5,05 (1H)	7,18 (2H)	6,76...6,94 (5H, m, H_{Ph})
IIIb	1,50 (18H)	5,12 (1H)	7,26 (2H)	6,90...7,10 (4H, m, H_{Ar})
IIIc	1,52 (18H), 1,68 (18H)	4,84 (1H), 5,04 (1H)	7,15 (2H), 7,33 (2H)	4,02...4,18 (4H, m, CH_2CH_2)
IIId	1,63 (18H)	4,93 (1H)	7,20 (2H)	6,50 (1H, d, J_{34} = 3,7, 3-H_{Fur}); 7,05 (1H, d, 4-H_{Fur})
IIIe	1,52 (18H)	4,88 (1H)	7,43 (2H)	3,84...4,06 (4H, m, CH_2CH_2); 6,70...6,98 (5H, m, H_{Ph})
IIIf	1,62 (36H)	5,10 (2H)	7,24 (4H)	3,90...4,15 (8H, m, CH_2CH_2)
IIIg	1,70 (18H)	4,93 (1H)	7,21 (2H)	6,68 (1H, d, J_{34} = 3,5, 3-H_{Fur}); 6,96 (1H, d, 4-H_{Fur})
IIIh	1,55 (18H)	5,21 (1H)	7,27 (2H)	6,72...6,94 (4H, m, H_{Ar})
IIIi	1,63 (18H)	4,86 (1H)	7,16 (2H)	6,85...7,06 (4H, m, H_{Ar})
IIIj	1,60 (18H)	5,15 (1H)	7,34 (2H)	3,94 (2H, s, CH_2); 7,03...7,22 (4H, m, H_{Ar}); 7,47 (1H, d, J = 2,5, 2-H_{Ind}†); 8,14 (1H, br.s, NH)
IIIk	1,67 (18H)	4,90 (1H)	7,25 (2H)	3,88 (2H, s, CH_2); 6,81...7,08 (5H, m, H_{Ph})
IIIl	1,52 (18H)	5,08 (1H)	7,17 (2H)	3,83 (2H, s, CH_2); 4,05 (2H, s, CH_2); 6,92...7,05 (4H, m, H_{Ar}); 7.54 (1H, d, J = 2,2, 2-H_{Ind}); 8,08 (1H, br.s, NH)
IIIm	1,62 (18H)	4,94 (1H)	7,37 (2H)	3,95...4,15 (4H, m, CH_2CH_2); 6,84...7,03 (4H, m, H_{Ar})
IIIn	1,54 (18H)	5,18 (1H)	7,26 (2H)	3,98...4,12 (4H, m, CH_2CH_2); 6,58 (1H, d, J_{34} = 3,6, 3-H_{Fur}); 7,10 (1H, d, 4-H_{Fur})
IIIo	1,73 (18H)	4,87 (1H)	7,22 (2H)	3,85 (2H, s, CH_2); 4,05...4,21 (4H, m, CH_2CH_2); 7,34...7,56 (4H, m, H_{Ar}); 7,73 (1H, d, J = 2,0, 2-H_{Ind}); 8,14 (1H, br.s, NH)
IIIp	1,53 (18H)	5,06 (1H)	7,32 (2H)	1,16 (6H, s, Me); 2,80...3,97 (8H, m, CH_2CH_2)
IIIq	1,67 (18H)	4,91 (1H)	7,20 (2H)	3,88 (2H, s, CH_2); 3,97...4,21 (8H, m, CH_2CH_2); 6,78...7,02 (5H, m, H_{Ph})
IIIr	1,52 (36H)	5,14 (2H)	7,28 (4H)	

*Spectra of compounds IIIa-e, g-i, k, m, n, r recorded in DMSO-D_6; of compounds IIIf, o, p) in acetone-D_6; of compounds IIIj, *l*, q) in CD_3OD.
†Ind) indolyl.

In addition, to prepare compounds IIIa, b, we used cyclodehydration of the corresponding N-acyl-N-[4-hydroxy-3,5-di(tert-butyl)benzoyl]hydrazines (Va, b) under action of phosphorus oxychloride (method C) [8, 10]. Acylation of hydrazides IIa, b with 4-hydroxy-3,5-di(tert-butyl)benzoyl chloride in pyridine formed the corresponding N,N′-diacylhydrazines Va, b (yields, 63-67%). A brief heating of the latter with phosphorus oxychloride resulted in heavy tarring of the reaction mixtures, from which the target products IIIa, b were separated in 42-46% yields.

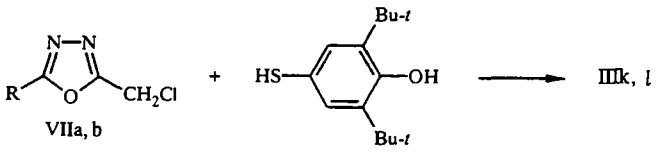
Since the reaction of carboxylic acids with hydrazines dihydrochloride in the presence of dehydrating agents ($POCl_3$, PPA, etc.) leads to symmetrically disubstituted 1,3,4-oxadiazoles [11], we decided in the present study to use this method to prepare 1,3,4-oxadiazoles containing fragments of screened phenol. It was found that heating (135-140°C) of acids (VIa, b) with hydrazine dihydrochloride for several hours formed the corresponding 1,3,4-oxadiazoles IIIf, r in 52-55% yields (method D).

To prepare 2-[4-hydroxy-3,5-di(tert-butyl)phenylthiomethyl]5-R-1,3,4-oxadiazoles (IIIk, *l*), we also used the reaction of 2-chloromethyl-5-R-1,3,4-oxadiazoles (VIIa, b) with potassium thiophenolate, produced from 4-hydroxy-3,5-di(tert-butyl)thiophenol. The reactions were carried out at 0 to 10°C (0.5 h) in the presence of equimolar amounts of KOH; under these conditions, the corresponding 1,3,4-oxadiazoles IIIk, *l* were formed in 77-83% yields (method E).



IIIr, VIa n = 0; IIIf, VIb n = 2

The properties of the synthesized disubstituted 1,3,4-oxadiazoles IIIa-r are shown in Table 1. The above-indicated structure of these compounds is consistent with the data of ultimate analysis and the IR and ESR spectra. Thus, the IR spectra show intense absorption maxima in the intervals 1615-1590 cm^{-1} and 1495-1460 cm^{-1}, characteristic of the stretching vibrations of the oxadiazole ring [8, 12]. The presence of the latter is also confirmed by the absorption bands at 1250-1225



cm^{-1} and 1050-1020 cm^{-1}, which pertain to the stretching vibrations of the =C−O−C= fragment in 1,3,4-oxadiazoles [13] and to the absorption peaks around 950 cm^{-1}, due to the breathing vibrations of the oxadiazole ring [12].

All the compounds under consideration also show absorption due to the residue of sterically hindered phenol: a fairly narrow band at 3655-3635 cm^{-1} characteristic of screened phenol hydroxyl [14]; two bands of medium intensity in the interval 1260-1220 cm^{-1} due to vibrations of Ar−OH bonds in screened phenols [15], and two groups of bands in the regions 885-870 cm^{-1} and 835-820 cm^{-1} (extraplanar deformation vibrations of tetrasubstituted benzene ring).

In the ESR spectra of the synthesized compounds (Table 2), the proton signals of the hydroxyl groups are represented as singlets in the interval 4.84-5.21 ppm, which is characteristic of sterically hindered phenols [14, 16]. The proton signals of the tert-butyl substituents are observed in the form of broadened singlets in the region 1.50-1.73 ppm. Singlet signals at 7.15-7.43 ppm correspond to the two magnetically equivalent protons of the hydroxyaryl fragments [3, 4, 16].

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-48 instrument in KBr pellets, in a suspension in Vaseline oil, or in a thin layer. The ESR spectra were recorded on a Bruker WP-200 spectrometer (200 MHz), with TMS as the internal standard. The course of the reaction and purity of the compounds obtained were monitored by TLC on Al_2O_3 of activity III according to Brockmann in the solvent systems, 10:1 benzene−methanol (a), 30:1 benzene−methanol (b), and 20:1 CCl_4−methanol (c); development with iodine vapor.

The initial hydrochlorides of ethyl iminoesters Ia-e [17], IVa [18], IVb [19], IVc [20], and IVd [21]; hydrazides of β-[4-hydroxy-3,5-di(tert-butyl)phenyl]propionic (IIc) [22] and indolyl-3-acetic (IIf) [23] acids; 4-hydroxy-3,5-di(tert-butyl)benzoic acid (VIa) [24] and its chloride [25], as well as 2-chloromethyl-1,3,4-oxadiazoles VIIa [26] and VIIb [27] were prepared by well-known methods, references to which are given below.

2,5-Disubstituted 1,3,4-Oxadiazoles (IIIa-o). A. A mixture of 11.0 mmole of iminoester hydrochloride Ia-e and 10 mmole of IIa-f in 30 mmole of absolute ethanol is boiled with stirring for 4 h (in the preparation of compounds IIIa-d, the mixture is boiled for 10 h in 30 ml of anhydrous dioxane). The reaction mass is evaporated to dryness under reduced pressure; in the case of compounds III-e, g, h, j-o, the residue is crystallized from a suitable solvent (see Table 1), and in the preparation of compounds IIIa-f, i, the residue is chromatographed on a column with Al_2O_3 (50 × 4.5 cm), and the elution

is done with a 15:1 benzene–methanol mixture. After the solvents are removed, the products IIIf, i are obtained in the form of viscous, dark-yellow, noncrystallizing oils.

2-{2-[4-Hydroxy-3,5-di(tert-butyl)phenyl]ethyl}-5-phenyl-1,3,4-oxadiazole (IIIe). B. A mixture of 1.75 g (6.0 mmole) of hydrazide IIc and 1.39 g (7.5 mmole) of iminoesters hydrochloride IVa in 25 ml of absolute methanol is boiled with stirring for 4 to 5 h (TLC monitoring until the disappearance of the initial hydrazide IIc from the reaction mixture). The solvent is removed at reduced pressure, the residue is crystallized from a 10:1 mixture of petroleum ether–2-propanol, and 1,3,4-oxadiazole IIIe is obtained.

Similarly, from hydrazide IIc and iminoester hydrochlorides IVb-d, 1,3-4-oxadiazoles IIIg, p, q, respectively, are synthesized. In the preparation of compounds IIIp, q, the residue remaining after the removal of the solvent is chromatographed on a column with Al_2O_3 (50 × 4.5 cm), and the elution is carried out with a 15:1 benzene–methanol mixture.

N-Benzoyl-N′-[4-hydroxy-3,5-di(tert-butyl)benzoyl]hydrazine (Va). To an agitated solution of 2.72 g (20 mmole) of hydrazide IIa in 45 ml of anhydrous pyridine is added in portions 5.37 g (20 mmole) of 4-hydroxy-3,5-di(tert-butyl)benzoyl chloride. The reaction mixture is boiled with stirring for 2 h, cooled to 20°C, and poured into 200 ml of ice water. The precipitate is filtered off, washed with water on a filter, dried, and crystallized from ethanol. Hydrazide Va is obtained in the amount of 4.48 g (63%), mp 138-139.5°C. R_f 0.48 (c). IR spectrum: 3650 (ν_{OH}), 3310-3200 (ν_{NH}), 3080, 1655, 1630 ($\nu_{C=O}$), 1555-1540 (δ_{NH}), 1260, 1245, 1140 (N–N), 880, 835, 750, 725 cm^{-1}. Found, %: C 71.8; H 7.5; N 7.8. $C_{22}H_{28}N_2O_3$. Calculated, %: C 71.7, H 7.6; N 7.6.

N-(4-Nitrobenzoyl)-N′-[4-hydroxy-3,5-di(tert-butyl)benzoyl]hydrazine (Vb) is similarly prepared from hydrazide IIb. Yield, 67%, mp 183-184°C (from 2-propanol). R_f 0.37 (b). Found, %: C 64.0; H 6.4; N 10.0. $C_{22}H_{27}N_3O_5$. Calculated, %: C 63.9; H 6.5; N 10.2.

2-[4-Hydroxy-3,5-di(tert-butyl)phenyl]-5-phenyl-1,3,4-oxadiazole (IIIa). C. A mixture of 4.4 g (12 mmole) of hydrazine Vb and 30 ml of $POCl_3$ is boiled for 0.5 h with stirring. The reaction mass is then cooled to 20°C, poured out onto 200 g of ice, and neutralized with aqueous ammonia to pH 7.5. The extract is evaporated to dryness at reduced pressure, and the residue is crystallized from acetonitrile.

Similarly, 1,3,4-oxadiazole IIIb is synthesized from N,N′-diacylhydrazine.

2,5-Bis[4-hydroxy-3,5-di(tert-butyl)phenyl]-1,3,4-oxadiazole (IIIr). D. A mixture of 5.5 g (22 mmole) of acid VIa and 1.36 g (13 mmole) of hydrazine dihydrochloride in 45 ml of PPA is stirred for 4 h at 135-140°C. The reaction mass is then cooled to 20°C, poured into 300 ml of cold water, and neutralized with 5% aqueous $NaHCO_3$. The precipitate is filtered off, washed with water on a filter, dried, and crystallized from acetonitrile.

Similarly, 1,3,4-oxadiazole IIIf is synthesized from β-[4-hydroxy-3,5-di(tert-butyl)phenyl]propionic acid (VIb).

2-[4-Hydroxy-3,5-di(tert-butyl)phenylthiomethyl]-5-phenyl-1,3,4-oxadiazole (IIIk). E. To a stirred solution of potassium thiophenolate obtained from 2.38 g (10 mmole) of 4-hydroxy-3,5-di(tert-butyl)thiophenol and 0.56 g (10 mmole) of KOH in 50 ml of absolute ethanol at 0°C is added in portions 1.94 g (10 mmole) of 2-chloromethyl-1,3,4-oxadiazole VIIa. The reaction mixture is stirred for 0.5 h at 0-10°C and poured into 150 ml of ice water. The precipitate is filtered off, washed with water on filter, dried, and crystallized from acetonitrile.

1,3,4-Oxadiazole III*l* is similarly synthesized from 2-chloromethyl-1,3,4-oxadiazole VIIb.

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