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NEW SYNTHESIS OF 1,2,4-OXADIAZOLES.

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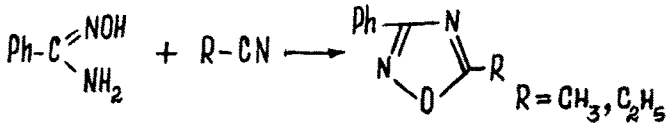
The interaction of amidoximes with nitriles in the presence of $ZnCl_2$ and HCl affords 1,2,4-oxadiazoles. The reaction of N-15-labeled amidoximes with nitriles was studied. Elimination of the amino group of the amidoxime fragment was observed in the oxadiazole formation and N-monoalkyl and N,N--dialkylamidoximes can be used in the synthesis of 1,2,4-oxadiazoles.

1,2,4-Oxadiazoles are widely applied in the synthesis of pesticides and drugs[1,2]. We have recently shown that 3,5-disubstituted derivatives of this heterocycle can be obtained by the interaction of amidoximes with organic nitriles [3].



The one-stage character of the process and the availability of nitriles and amidoxime obtained from them can be considered as advantages of the new method. Unfortunately, the reaction required drastic conditions and the yields of cyclization products did not exceed 15-20%.

The influence of various factors on the interaction of amidoximes with nitriles in order to lower the reaction time and temperature was studied in the present work and led to a greatly improved process.

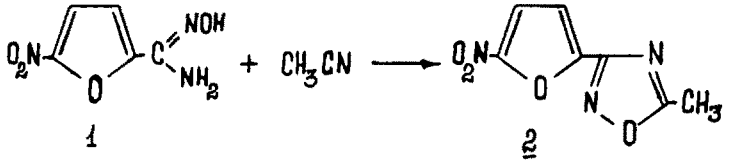
The possibility of accelerating the reaction by the use of various Lewis acids ($ZnCl_2$, $AlCl_3$, $TiCl_4$, $SbCl_5$, $CuCl_2$) and halogen hydride was studied. It was found that while boiling 5-nitro-2-furylcarboxamide oxime (1) in acetonitrile in the presence of $CuCl_2$, $TiCl_4$, or $SbCl_5$ 1,2,4-oxadiazole were not formed. The application of $ZnCl_2$ under the same conditions gave oxadiazole in insignificant yield.

The use of $AlCl_3$ and $SnCl_4$ gave 15-20% yields of 1,2,4-oxadiazole but we failed to obtain any appreciable amounts of azole using HCl as a catalyst.

Nevertheless, the application of catalysts permitted a noticeably lower reaction temperature. If originally the reaction of amidoxime with nitrile

was carried out at 180°C, in the presence of a catalyst the oxadiazole cycle is formed at acetonitrile boiling temperature.

A simultaneous effect of HCl and Lewis acid could assist in the reaction acceleration. The addition of hydrogen chloride to nitrile should lead to the formation of iminochlorides, chlorides of metals promoting the interaction of the latter with amidoximes. Indeed, in a number of cases it proved possible to increase the yield of 1,2,4-oxadiazole (Table 1).



1 2

Table 1

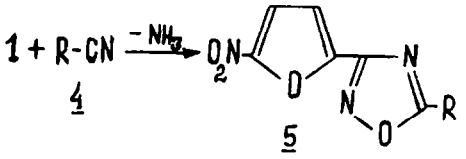
The dependence of the yield of 5-methyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (2) on Lewis acid in the presence of HCl

No	Lewis acid	Reaction time (hours)	Reaction product (yield, %)
1	$TiCl_4$	4	-
2	$SbCl_5$	2	-
3	$CuCl_2$	2	3 (24)*)
4	$SnCl_4$	8	2 (56)
5	$AlCl_3$	7	2 (79)
6	$ZnCl_2$	1,5	2 (88)

*) 2-cyano-5-nitrofuran (3) proved to be the only isolated product of the reaction.

1,2,4-Oxadiazole is not formed using $SbCl_5$, $TiCl_4$ and $CuCl_2$ obviously due to the interaction of the above metal chlorides with initial amidoxime: heating of 1 with $TiCl_4$ and $SbCl_5$ leads to its disappearance. Using $ZnCl_2$, $AlCl_3$ and $SnCl_4$ in the mixture with HCl or without it, amidoxime does not decompose. The best yield of 2 was achieved in the case of $ZnCl_2$ and HCl.

The developed catalytic procedure was successfully applied to the reactions of 1 with various organic nitriles. The yields of corresponding 1,2,4-oxadiazoles (5a-f) were 60-80% (Table 2). The exchange of HCl for HBr does not considerably influence the yields of the products.



4.5 a:R = C_2H_5
b:R = $ClCH_2$
c:R = Ph
d:R = $PhCH_2$
e:R = $C_2H_5CO_2CH_2$
f:R = ClC_2H_4

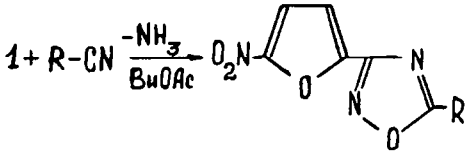
Table 2

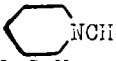
Yields and parameters of the reaction of compound (1) with nitriles

N°	Nitrile	Reaction temperature (°C)	Reaction time (h)	Reaction product (%, yield)
1	4a	100	2	5a (84)
2	4b	120	0.1	5b (67)
3	4c	110	1	5c (66)
4	4d	120	0.5	5d (63)
5	4e	110	2.5	5e (61)
6	4f	120	0.5	5f (66)

The obtained data show a possibility of use of nitriles containing such reactive fragments, as chloromethyl and chloroethyl groups, in reactions with amidoxime.

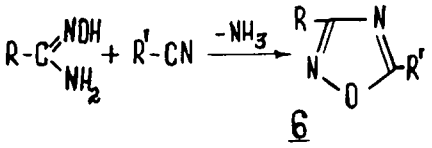
A solvent plays an important role in the reaction. The attempts to obtain 1,2,4-oxadiazole in chloroform, benzene, xylene, toluene, and dimethylsulfoxide proved unsuccessful. The oxadiazole formation occurs in ethyl acetate but at a low rate. We succeeded in decreasing reaction time using butyl acetate and isobutyl acetate. In these solvents 1 interacts with HCN forming corresponding 3-substituted-1,2,4-oxadiazole. For instance, aminonitrile in the form of its hydrogen chloride salt can be introduced into the reaction with amidoxime.



5 g:R = H
h:R = 
i:R = $NO_2C_6H_4$-
j:R = 

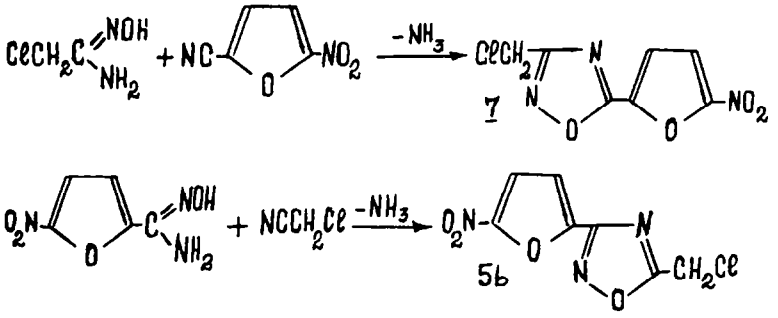
It should be noted that the reaction rate depends even on small changes in the ester solvent structure. At 80°C the ratio of reaction time of 1 with 3-chloropropiononitrile in ethyl acetate, butyl acetate, isobutyl acetate proved to be 18:7:3.5 h, respectively.

The developed method is of a general character. 1,2,4-Oxadiazoles were obtained during the interaction of nitriles with various amidoximes.

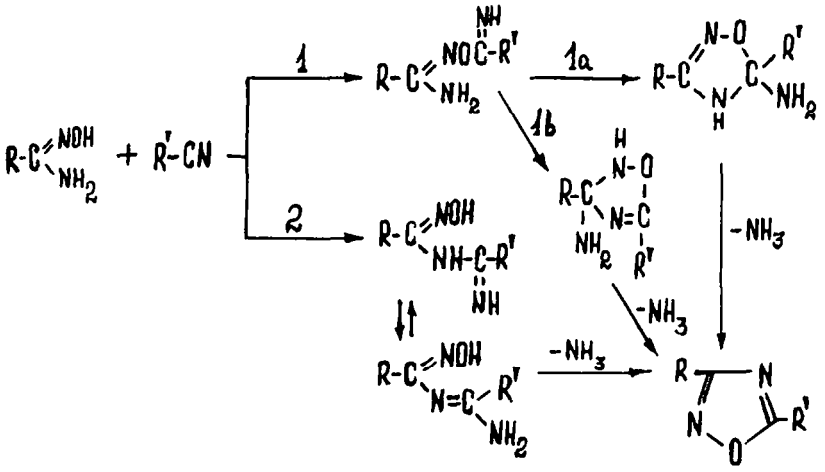


6a: R = $O_2NC_6H_4$, R' = ClC_2H_4
b: R = H_2N-(1,2,4-oxadiazol-3-yl), R' = Ph
c: R = Ph, R' = ClC_2H_4
d: R = Ph, R' = $EtCO_2CH_2$
e: R = Ph, R' = Ph

An interesting feature of the method is a possibility of synthesis of isomers of 1,2,4-oxadiazoles.

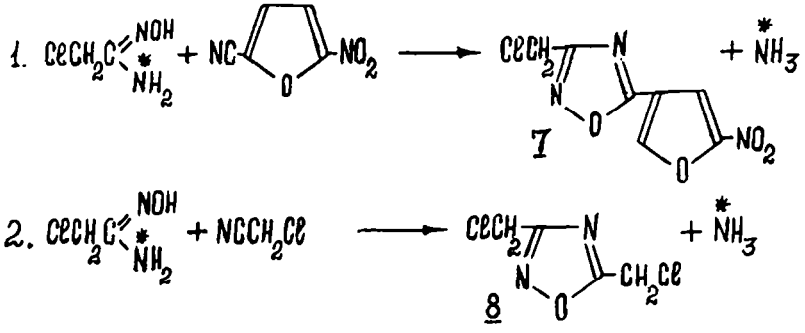


The formation of 1,2,4-oxadiazoles is accompanied by elimination of the amino group. We could have supposed that at the first stage of the reaction the nitrile addition to the amidoxime group proceeded either via the oxygen atom of the oximine fragment (1, Scheme 1), or via the amine fragment (2, Scheme 1). The cyclization stage with a further elimination of ammonium can be carried out both by the addition of the amidoxime amino group to the imine fragment (1a, Scheme 1), or at the expense of the substitution of the amidoxime amino group for the imine group obtained from nitrile (1b, Scheme 1). In the second case (2, Scheme 1) cyclization can take place only by means of the substitution of the imine fragment (or the amino group being in equilibrium with it) for the amidoxime oxime group.



Scheme 1

The direction of the reaction was studied using amidoximes enriched with ^{15}N isotope. Compounds containing ^{15}N isotope were employed in the following reactions (Scheme 2):

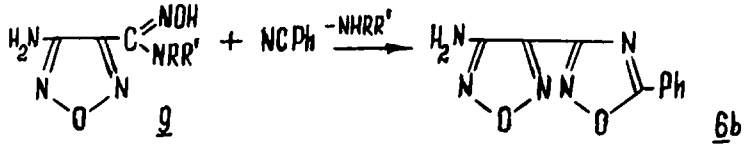


Scheme 2

The percentage of ^{15}N label in 1,2,4-oxadiazoles was determined using mass-spectroscopy. It turned out that in the interaction of labelled chloroacetamidoxime with 2-cyano-5-nitrofuran and chloroacetonitrile (reactions 1 and 2, Scheme 2) oxadiazoles without ^{15}N isotope were obtained. This indicates that both reactions proceed in the direction of 1b, but not in the direction of 1a and 2 (Scheme 1). If schemes 1a and 2 were in operation oxadiazoles containing ^{15}N atoms should be obtained.

The labelling studies have shown that the amino group is eliminated

from the amidoxime in the course of the reaction. Thus amidoxime having N-monoalkyl- and N,N-dialkylamine substituents instead of the amino group, should also interact with nitriles. Indeed, it was found that in the interaction of N-monoalkyl- and N,N-dialkylamidoximes of aminofurazan with benzonitrile 1,2,4-oxadiazole 6b was obtained in a satisfactory yield.



9a:R = H; R' = Me
b:R = R' = Me
c:R = R' = Et

It should be mentioned that the increase in the bulk of alkyl substituents in the amine fragment of amidoximes does not hamper the reaction process. Thus in the interaction of N,N-diethylamidoxime of aminofurazan (9c) with benzonitrile a corresponding 1,2,4-oxadiazole (6b) was also obtained.

EXPERIMENTAL

IR spectra were recorded on an "IR-20" spectrophotometer in thin layer or in KBr pellets. ^{1}H NMR spectra were obtained at 60 MHz on a "Tesla B 467" spectrometer in deuterioacetone solutions, δ-values are quoted relative to GMDS. Mass spectra were recorded on "Varian CH-6" instrument with a direct induction of a sample into the source with the energy of ionizing electrons-70 eV, emission current - 100 mcA, control voltage - 1.75 kV. Solvents were dried ($MgSO_4$) and distilled. Anhydrous Lewis acids were used.

The interaction of 5-nitro-2-furancarboxamide oxime (1) with acetonitrile in the presence of HCl and Lewis acids.

General procedure.

Gaseous HCl (0.003 mol) was passed through a mixture of 5-nitro-2-furancarboxamide oxime (1) (0.00292 mol) and corresponding Lewis acid (0.0088 mol) in 10 ml acetonitrile. The mixture was kept at 20° for 12h, then refluxed. It was cooled, diluted with an equal amount of water, extracted with ether (3x50) and dried ($MgSO_4$). The solvent was removed

in vacuo. The remaining residue was recrystallized from ethanol.

a) Lewis acid - zinc chloride. Boiling time 1h. 0.5 g (88%) of 5--methyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (2) was obtained. M.p. 104-105°, (lit.,[4] m.p. 104-105). ^{1}H NMR spectrum: 2.63 (3H, s); 7.38 (IH, d); 7.58 (IH, d).

b) Lewis acid - aluminium chloride. Boiling time 7h. Yield 0.45 g (79%).

c) Lewis acid - tin tetrachloride. Boiling time 8h. The product was purified on preparative silica gel TLC plate (dichloroethane: ether 2:1). Yield 0.32 g (56%).

d) When the reaction proceeds with $FeCl_3$, $SbCl_5$ and $TiCl_4$ used as Lewis acids, 5-methyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole was not formed.

e) Lewis acid - copper chloride. Boiling time 2h. The product was characterized by IR and ^{1}H NMR spectra which were identical to the corresponding spectra of 2-cyano-5-nitrofuran (3). Yield 0.09 g (24%).

5-R-3-(5-nitro-2-furyl)-1,2,4-oxadiazoles formation in liquid nitrile.

General procedure

Amidoxime (1) (0.00292 mol) and zinc chloride (0.0088 mol) were dissolved in 6 ml of corresponding nitrile, then HCl (0.00292 mol) was passed through. The mixture was heated. After cooling it was diluted with an equal amount of water, extracted with ether and dried ($MgSO_4$). After solvent evaporation the residue was recrystallized from ethanol.

a) 5-Methyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (2)
Boiling time 1.5 h. Yield 0.5 g (87%). M.p. 104-105°.

b) 5-Ethyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (5a)
Boiling time 2h. Yield 0.51 g (84%). M.p. 103-104° (lit.,[5] m.p. 98°). ^{1}H NMR spectrum: 1.31 (3H, t); 2.95 (2H, q); 7.41 (IH, d); 7.61 (IH, d).

c) 5-Chloromethyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (5b)
Heating time at 120° - 10 min. Yield 0.45 g (67%). M.p. 109-110°. (lit.,[4] m.p. 109-110°). ^{1}H NMR spectrum: 5.05 (2H, s); 7.5 (IH, d); 7.65 (IH, d).

d) 5-Phenyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (5c)
Heating time at 110-120° - 1h. Yield 0.49 g (66%). M.p. 201-202° (lit.,[4] 200-201°).

e) 5-Benzyl-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (5d)
Heating time at 110-120° - 0.5h. Yield 0.5 g (63%). M.p. 89-90° (lit.,[7] - oil).

f) Ethyl /3-(5-nitro-2-furyl)-1,2,4-oxadiazolyl-5/acetate (5e).

Heating time at 110-120° - 2.5h. Yield 0.42 g (61%). M.p. 73°. Cal. for $C_{10}H_9N_3O_6$: C 44.94; H 3.37; N 15.73%. Found: C 45.21; H 3.39; N 16.02%. IR spectrum (ν, cm^{-1}): 1320, 1530 (NO_2), 1720 (C=O). ^1H NMR spectrum: 1.2 (3H, t); 4.16 (2H, q); 4.26 (2H, s); 7.5 (1H, d); 7.63 (1H, d).

e) 5-(2-Chloroethyl)-3-(5-nitro-2-furyl)-1,2,4-oxadiazole (5f)

Heating time at 110-120° - 0.5h. Yield - 0.47 g (66%). M.p. 88-89°. Cal. for $C_8H_6N_3O_4Cl$: C 39.42; H 2.46; Cl 14.57; N 17.24%; Found: C 39.86; H 2.6; Cl 14.26; N 16.92%. IR spectrum (ν, cm^{-1}): 1330, 1530 (NO_2). ^1H NMR spectrum: 3.53 (2H, t); 4.08 (2H, t); 7.41 (1H, d); 7.62 (1H, d).

1,2,4-Oxadiazole formation by the interaction of amidoximes with nitriles in a solvent.

3-(5-Nitro-2-furyl)-1,2,4-oxadiazole (5g)

Hydrogen chloride 0.53 g (0.0146 mol) was introduced into a mixture dry potassium cyanide, 0.75 g (0.0116 mol), (1) 0.5 g (0.00292 mol) and zinc chloride 1.18 g (0.0088 mol) in 10 ml of butyl acetate with ice-cooling. The mixture was kept at 0° for 24h, then heated at 80° for 40 min. It was cooled, diluted with an equal amount of water, extracted with ether and dried ($MgSO_4$). The solvent was removed in vacuo. The residue was recrystallized from ethanol to give 0.25 g (47%) of (5g). M.p. 48-50° (lit.,[6] - oil). Cal. for $C_6H_3N_3O_4$: C 39.78; H 1.66; N 23.20%. Found: C 39.60; H 1.62; N 23.11%. IR spectrum (ν, cm^{-1}): 1350, 1500 (NO_2). ^1H NMR spectrum: 7.43 (1H, d); 7.63 (1H, d); 9.41 (1H, s).

3-(5-Nitro-2-furyl)-5-(2-piperidinoethyl)-1,2,4-oxadiazole (5h)

A mixture of hydrogen chloride 3-piperidinopropiononitrile 0.51 g (0.00292 mol); zinc chloride 1.19 g (0.0088 mol), (1) 0.5 g (0.00292 mol) in 6 ml butyl acetate was heated at 60° for 6h. The temperature was then increased to 100° for 4h. After cooling the mixture was diluted with water and extracted with ethyl acetate. The extract was dried ($MgSO_4$). After solvent removal the residue was recrystallized from benzene to yield 0.15 g (18%) of (5h). M.p. 89-91°. Cal. for $C_{13}H_{16}N_4O_4$: C 53.42; H 5.47; N 19.17%. Found: C 53.65; H 5.10; N 19.12%.

3-(5-Nitro-2-furyl)-5-(3-nitrophenyl)-1,2,4-oxadiazole (5i)

Zinc chloride 1.18 g (0.0088 mol), (1) 0.5 g (0.0029 mol) and 3-nitrobenzonitrile 0.43 g (0.0029 mol) were dissolved in 3 ml of butyl acetate. HCl 0.11 g (0.003 mol) was introduced. The mixture was refluxed for 8h, cooled, diluted with an equal amount of water, extracted with ethyl ace-

tate and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was boiled in a small amount ethanol in order to separate the amidoxime which did not participate in the reaction. The product insoluble in ethanol was filtered off and then recrystallized from DMF-methanol to give 0.3 g (34%) of (5i). M.p. 164°. Cal. for $C_{12}H_6N_4O_6$: C 47.68; H 1.99; N 18.54%; Found: C 48.01; H 1.99; N 18.44%. IR spectrum (ν, cm^{-1}): 1340, 1540 (NO_2).

3,5-Di-(5-nitro-2-furyl)-1,2,4-oxadiazole (5j)

A mixture of (1) 0.5 g (0.00292 mol), 2-cyano-5-nitrofuran 0.4 g (0.0029 mol), HCl 0.11 g (0.003 mol), zinc chloride 1.18 (0.0088 mol) in 4 ml of butyl acetate was refluxed for 6h. It was cooled, diluted with water, extracted with ethyl acetate and dried ($MgSO_4$). The solvent was removed and the residue was recrystallized from ethanol to give 0.3 g (34%) of (5j). M.p. 169-170° (Lit.,[7] 170°). ^1H NMR spectrum: 7.56-7.88 (4H, m).

5-(2-Chloroethyl)-3-(3-nitrophenyl)-1,2,4-oxadiazole (6a)

3-Nitrobenzamidoxime 0.5 g (0.0028 mol), zinc chloride 1.11 g (0.0083 mol) and chloropropiononitrile 8 g (0.089 mol) were dissolved in 8 ml of butyl acetate. HCl 0.2 g (0.0055 mol) was then introdused. The mixture was refluxed for 40 min. It was cooled, diluted with 8 ml water, extracted with ether and dried ($MgSO_4$). The solvent was removed in vacuo. The residue was recrystallized from ethanol to give 0.3 g (42%) of (6a). M.p. 90°. Cal. for $C_{10}H_8N_3ClO_3$: C 47.34; H 3.15; Cl 14.00; N 16.57%. Found: C 47.21; H 3.01; Cl 13.90; N 16.35%. IR spectrum: (ν, cm^{-1}): 1330, 1500 (NO_2). ^1H NMR spectrum: 3.53 (2H, t); 4.23 (2H, t); 7.63-8.68 (4H, m).

3-(3-Amino-4-furazanyl)-5-phenyl-1,2,4-oxadiazole (6b)

a) Zinc chloride 1.19 g (0.0088 mol) and 4-amino-3-furazancarboxamide oxime 0.42 g (0.00292 mol) were dissolved in a mixture of 3 ml of butyl acetate and 3 ml of benzonitrile. HCl 0.003 mol was introdused The mixture was refluxed for 40 min, it was cooled, diluted with water, extracted with ethyl acetate and dried ($MgSO_4$). The solvent was removed in vacuo, the residue was recrystallized from ethanol to give 0.43 g (65%) of (6b). M.p. 186-187°. Cal. for $C_{10}H_7N_5O_2$: C 52.40; H 3.05; N 30.56%. Found: C 52.62; H 3.05; N 30.51%. Mass-spectrum: m/z = 229 (M^+).

b) 6b was obtained in a similar way from 3-(methylamino)oximinomethyl--4-aminofurazan (9a) 0.46 g (0.00292 mol). Yield 0.27 g (40%).

c) 6b was obtained in a similar way from 3-(dimethylamino)oximinomethyl-4-aminofurazan (9b) 0.5 g (0.00292 mol). Yield 0.3 g (44.8%).

d) 6b was obtained in a similar way from 3-(diethylamino)oximinomethyl--4-aminofurazan (9c) 0.58 g (0.00292 mol). Yield 0.31 g (47%).

5-(2-chloroethyl)-3-phenyl-1,2,4-oxadiazole (6c)

Benzamidoxime 1 g (0.0073 mol) was dissolved in 16 g of chloropropiononitrile containing $SnCl_4$ 5.69 g (0.0022 mol) and HCl 0.26 g (0.0073 mol). The mixture heated at 100° for 2h, cooled,diluted with water,extracted with ether and dried ($MgSO_4$). The solvent was removed. Preparativ TLC of the crude product (SiO_2 dichloroethane - ether 2:1) yielded 0.6 g (40%) of (6c) as an oil. Cal. for $C_{10}H_9N_2ClO$: C 57.55 H 4.31; Cl 17.02; N 13.43%. Found: C 57.66; H 4.20; Cl 16.91; N 13.57%.

Ethyl (3-phenyl-1,2,4-oxadiazolyl-5) acetate (6d)

Benzamidoxime 1 g (0.0073 mol) was dissolved in ethyl cyanoacetate 8 g (0.07 mol) containing zinc chloride 3.96 g (0.029 mol). HCl 0.26 g (0.007 mol) was introdused The mixture was then heated at 120° for 2h, cooled, diluted with water, extracted with ethyl acetate and dried ($MgSO_4$). The solvent was removed and the crude product was purified by TLC (SiO_2; dichlorochane-ether 2:1) to give 0.8 g (47%) of (6d) as an oil. Cal. for $C_{12}H_{12}N_2O_3$: C 62.07; H 5.17; N 12.07%. Found: C 62.10; H 5.11; N 12.05%. ^1H NMR-spectrum: 1.1 (3H, t); 4.1 (2H, g); 4.16 (2H, s); 7.46-7.96 (5H, m). (Lit.,[8] 150°/0.5 mm).

3.5-Diphenyl-1,2,4-oxadiazole (6e)

Benzamidoxime 0.4 g (0.00292 mol) and zinc chloride 1.18 g (0.0088 mol) were dissolved in a mixture of 5 ml butyl acetate and 5 ml benzonitrile. HCl 0.11 g (0.03 mol) was introduced. The mixture was refluxed for 30 min, cooled, diluted with water, extracted with ether and dried ($MgSO_4$). The solvent was removed in vacuo. The residue was recrystallized from ethanol to give 0.45 g (70%) of (6e). M.p. 110° (Lit.,[9] 110°).

3-Chloromethyl-5-(5-nitro-2-furyl)-1,2,4-oxadiazole (7)

Chloroacetamidoxime 2 g (0.0184 mol), 2-cyano-5-nitrofuran 1.23 g (0.0092 mol) and zinc chloride 10 g (0.0736 mol) were dissolved in 15 ml of butyl acetate. HCl 0.67 g (0.0184 mol) was introduced. The mixture was refluxed for 40 min, then cooled, diluted with water, extracted with ether and dried ($MgSO_4$). The solvent was removed in vacuo. The product was purified by preparative TLC (SiO_2; dichloroethane) to give 1.4 g (66%) of (7), as an oil. Cal. for $C_7H_4N_3ClO_4$: C 36.60; H 1.74; Cl 15.47; N 18.3%. Found: C 36.78; H 1.69; Cl 15.33; N 18.4%. IR spectrum (ν, cm^{-1}): 1340, 1520 (NO_2). ^1H NMR spectrum: 4.73 (2H, s); 7.7 (2H, s).

Synthesis of compound containing ^{15}N isotope

Chloroacetamide containing ^{15}N isotope

Freshly distilled ethyl ester of chloroacetic acid 86 g (0.7 mol) were added to a solution of NH_3 12 g (0.7 mol) (containing 95% of ^{15}N) in 300 ml of methanol. The mixture was kept at +5° for 12h. Precipitated crystal were filtered off, methanol was evaporated to a one third of the initial volume. Precipitated chloroacetamide was filtered to give 62 g of chloroacetamide, m.p. 118-119° (Lit.,[10] m.p. 119°).

Chloroacetonitrile containing ^{15}N isotope

Chloroacetamide containing ^{15}N isotope(62 g) were mixed with P_2O_5 (142 g) and distilled, b.p. 122°. Phosphorous pentoxide (5 g) were added to chloroacetonitrile and repeated distillation was carred out, b.p. 123-124°. (Lit.,[11] b.p. 124°).

Chloroacetadoxime containing ^{15}N isotope

Na_2CO_3 5.3 g were added to a solution of $NH_2OH \cdot HCl$ (6.9 g) in 25 ml of water. Then ^{15}N labelled chloroacetonitrile(7.5 ml) was added during 15 min at 30°. After completion of the reaction, the mixture was extracted with ether and dried ($MgSO_4$). After the removal of the solvent the residue was recrystallized from benzene to give 7 g, of (7). M.p. 90-92° (Lit.,[11] 91-92°).

3,5-Di-(chloromethyl)-1,2,4-oxadiazole (8)

HCl 0.34 g (0.0092 mol) was passed through a solution of chloroacetamidoxime with ^{15}N 1 g (0.0092 mol), of zinc chloride 5 g (0.0368 mol) and of chloroacetonitrile 5 g (0.0368 mol) in 8 ml of butyl acetate. The mixture was refluxed for 20 min, diluted with water and extracted with ether. After drying ($MgSO_4$) the solvent was removed. The residue was distilled over to give 0.98 g (64%) of (8), b.p. - 68°/1 mm. Cal. for $C_4H_4N_2Cl_2O$: C 28.74; H 2.40; Cl 42.52; N 16.77%. Found: C 28.96; H 2.34; Cl 42.84; N 17.01%. Mass-spectrum: m/z = 166 (168) (170) (M^+). ^{15}N content - 0%.

3-Chloromethyl-5-(5-nitro-2-furyl)-1,2,4-oxadiazole (7)

The compound was obtained according to the procedure described on p.11 ^{15}N content - 0%.

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