Synthesis of 3-nitramino-4-(1*H*-1,2,3-triazol-1-yl)-1,2,5-oxadiazoles and their salts

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Nitration of 3-amino-4-(1*H*-1,2,3-triazol-1-yl)-1,2,5-oxadiazoles (3-amino-4-triazolylfurazans) with a mixture of $NaNO_3$ and conc. H_2SO_4 gave for the first time triazolylfurazans with a primary nitramino group attached to the furazan ring. If the starting amino(triazolyl)furazan contains an aromatic substituent, the latter also undergoes nitration under the conditions studied. Some of these nitramines were converted into salts (K, Na, and NH_4).

Key words: amino(1,2,3-triazol-1-yl)furazans, nitramino(1,2,3-triazol-1-yl)furazans, 4-amino-3-azidofurazan, 1,3-dicarbonyl compounds, 1,3-cycloaddition, nitration, hydrolysis, decarboxylation, nitramino(triazolyl)furazan salts, NMR spectroscopy.

Earlier,[1—6] a number of R-(1*H*-1,2,3-triazol-1-yl)-1,2,5-oxadiazoles (triazolylfurazans) have been obtained. However, similar structures containing a nitramino group in the oxadiazole ring have not been documented hitherto.

It is known that compounds containing nitramino groups (NNO_2) are of interest as high-energy structures or their precursors. Data on the synthesis, properties, and few reactions of primary and secondary nitraminofurazans are reviewed by Sheremetev.[7] These compounds are mainly obtained by nitration of furazans containing NH_2 or NHR groups. Furazans with an unsubstituted NH_2 group are usually nitrated with conc. HNO_3 (d = 1.5 g cm^{-3}) in CCl_4 or the system[8] $NaNO_3$—conc. H_2SO_4; nitrogen pentoxide is also used. Recently,[9] the nitration of aminofurazans with aqueous HNO_3 has been reported.

In the present work, we studied nitration of appropriate amines as a possible route to primary nitramino(triazolyl)furazans (**1**). Amino(triazolyl)furazans **2a**—**h** were employed as the starting reagents (Scheme 1). Compounds **2a**—**d** have been described earlier;[2,5,10] aminofurazans **2e**—**h** were prepared for the first time. First results of our investigation have been briefly announced.[11]

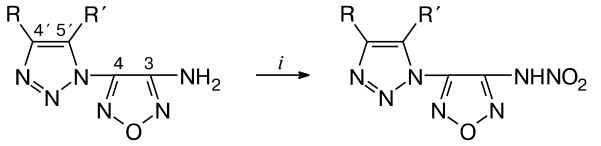
Amino(triazolyl)furazans **2e**—**g** with a 5-monosubstituted triazole ring were prepared from 4,5-disubstituted amines **2b,h,i** containing the ester group in position 4 of the triazole ring (Scheme 2).

Two of these compounds (namely, **2h** and **2i**) have not been documented hitherto. We obtained them by reactions of 4-amino-3-azidofurazan (**4**) with ethyl 4-chlorobenzoylacetate (**5a**) and methyl 4,4-dimethyl-3-oxopentanoate (**5b**), respectively, in the presence of Et_3N as described earlier[2] for the synthesis of triazolylfurazans (see Scheme 2). Hydrolysis of compounds **2b,h,i** in boiling solutions of NaOH in H_2O—EtOH (1 : 1) followed by acidification of the resulting sodium salts with 2 *M* HCl to a neutral reaction gave previously unknown carboxylic acids **3a**—**c**. Their decarboxylation[10] in boiling AcOH yielded amino(triazolyl)furazans **2e**—**g** (see Scheme 2).

Amines **2a**—**h** were nitrated with $NaNO_3$—conc. H_2SO_4 at 20 or 50 °C, depending on the starting compound. We found that amino(triazolyl)furazans **2a**—**h** under the conditions studied undergo transformations into nitramines **1a**—**h**, respectively (see Scheme 1).

For compounds **2b**,**e**,**g**,**h** containing an aromatic substituent in the triazole ring, the formation of primary nitramines is accompanied by nitration of the aromatic ring.

Scheme 1



2a—h **1a—h**

i. $NaNO_3/H_2SO_4$.

1	R	R′	**2**	R	R′
a	CO_2Et	Me	**a**	CO_2Et	Me
b	CO_2Et	3-$NO_2C_6H_4$	**b**	CO_2Et	Ph
c	H	CH_2Cl	**c**	H	CH_2Cl
d	H	Me	**d**	H	Me
e	H	3-$NO_2C_6H_4$	**e**	H	Ph
f	H	Bu^t	**f**	H	Bu^t
g	H	4-Cl-3-$NO_2C_6H_3$	**g**	H	4-ClC_6H_4
h	CO_2Et	4-Cl-3-$NO_2C_6H_3$	**h**	CO_2Et	4-ClC_6H_4

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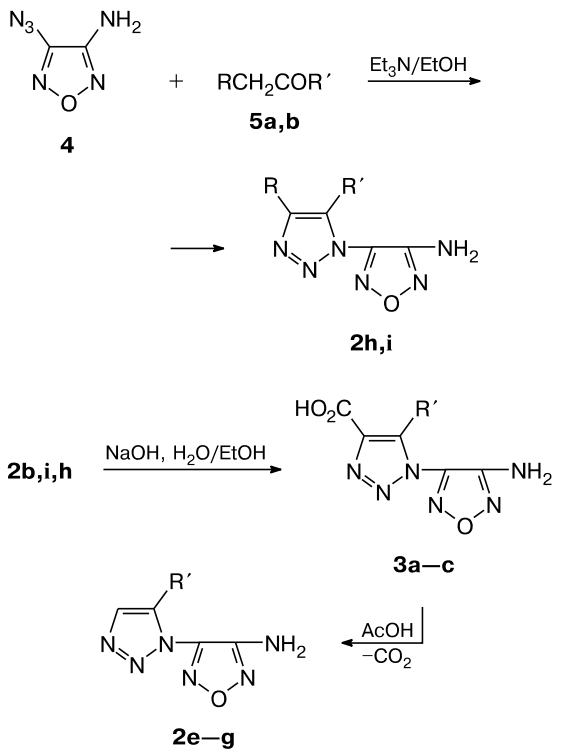
Scheme 2

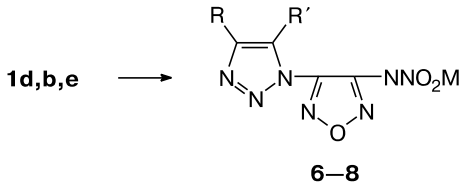


2i: R = CO_2Me, R′ = Bu^t; **3:** R′ = Ph (**a**), Bu^t (**b**), 4-ClC_6H_4 (**c**);
5: R = CO_2Et (**a**), CO_2Me (**b**), R′ = 4-ClC_6H_4 (**a**), Bu^t (**b**)

These processes occur at room temperature (20 °C) for compounds **2e**,**g**,**h** but require heating to 50 °C for compound **2b**.

Primary nitraminofurazans are known to be strong acids forming stable salts with metals and amines.[12—15] We demonstrated that nitramino(triazolyl)furazans **1d**,**b**,**e** in solutions of K_2CO_3, $NaHCO_3$, and ammonia form the corresponding potassium, sodium, and ammonium salts (**6**—**8**) (Scheme 3).

Scheme 3



Compound	R	R′	M
6	H	Me	K
7	CO_2Et	3-$NO_2C_6H_4$	Na
8	H	3-$NO_2C_6H_4$	NH_4

The structures of novel compounds **1a**—**h**, **2e**—**i**, **3a**—**c**, and **6**—**8** were determined from elemental analysis data and spectroscopic characteristics (^1H, ^{13}C, and ^{14}N NMR, IR, and MS). These and other relevant data are given in Tables 1—3.

The ^1H NMR spectra of compounds **1b**, **7**, and **8** containing the nitro group at the benzene ring show the following chemical shifts δ: a singlet (8.56 (**1b**), 8.42 (**7**), 8.41 (**8**)), two doublets (8.05, 8.50 (**1b**); 7.88, 8.36 (**7**); 7.94, 8.34 (**8**)), and a triplet (7.89 (**1b**), 7.76 (**7**), 8.34 (**8**)). These signals can be assigned to the protons at the C(2), (C(4), C(6)), and C(5) atoms of the benzene ring, respectively, which unambiguously indicates the formation of *meta*-NO_2 derivatives. For compounds **1g** and **1h** containing a chloronitrophenyl substituent, ^1H NMR data are insufficient for precise location of the NO_2 group. However, taking into account the electron-withdrawing character of the heterocycles and the directing effect of the Cl atom, which is *para* to the triazole ring, one can assume that the benzene ring in these compounds is nitrated at the *meta*-position as well.

^{14}N NMR data for nitraminofurazans are very scarce in the literature.[16,17] In the ^{14}N NMR spectrum of nitraminofurazan with the substituent N(O)NBu^t at the furazan ring,[16] the singlet at δ −40 corresponds to the nitro group of the nitramine fragment. The ^{14}N NMR spectra of nitramines **1a**—**h** and salts **7** and **8** we obtained in this study contain singlets at δ −14 to −17, which can be assigned to the nitro N atom of the nitramine fragment. In the spectrum of ammonium salt **8**, a very narrow singlet at δ −362 (observed together with the aforesaid singlet) is due to the N atom of the ammonium group. These data agree with the chemical shifts for the nitro N atoms in 4,4′-bis(nitramino)azofurazan and its salts.[17]

The ^{14}N NMR spectra of compounds **1b**,**e**,**g**,**h** containing the nitramino group at the furazan ring and the nitro group at the benzene ring show two singlets: one singlet mentioned above appears at δ −14 to −17 and the other, at δ −37 to −41 (narrow or broadened, see Table 1). The latter signal can be assigned to the N atom of the nitro group at the benzene ring, as with C-nitrated furazans[7] and triazolylfurazans.[6,18]

To sum up, nitration of substituted amino(1,2,3-triazol-1-yl)furazans with the system $NaNO_3$—conc. H_2SO_4 gave for the first time 3-nitramino-4-(1*H*-1,2,3-triazol-1-yl)furazans. We found that an aromatic substituent (if present in the starting compound) is also nitrated under the reaction conditions. Some of the nitramines obtained were transformed into salts. The synthesis of primary 3-nitramino-4-(1*H*-1,2,3-triazol-1-yl)furazans and their salts offers great scope for the preparation of novel compounds of this series.

Experimental

IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The ^{13}C and ^1H NMR spectra of the compounds

Table 1. Selected physicochemical characteristics of the compounds obtained

Compound	Yield (%)	M.p./°C (solvent)	R_f (eluent)	Found / Calculated (%)					Molecular formula
				C	H	N	Cl	M*	
1a	84.9	129—130 (decomp.)	0.54 (AcOEt)	33.50 33.93	3.35 3.21	34.27 34.62	— —	— —	$C_8H_9N_7O_5$
1b	53.8	133 (decomp.)	0.68 (AcOEt)	40.14 40.01	2.56 2.58	28.30 28.71	— —	— —	$C_{13}H_{10}N_8O_7$
1c	32.7	115	0.62 (AcOEt)	24.37 24.44	1.60 1.63	39.73 39.92	14.29 14.46	— —	$C_5H_4ClN_7O_3$
1d	65.8	140	0.63 (AcOEt)	28.61 28.44	2.58 2.39	46.07 46.44	— —	— —	$C_5H_5N_7O_3$
1e**	88.9	140—142 (decomp.)	0.24 (AcOEt)	37.50 37.75	1.75 1.90	34.80 35.21	— —	— —	$C_{10}H_6N_8O_5$
1f	66.7	143—144	0.60 (AcOEt)	38.21 37.95	4.20 4.38	38.94 38.72	— —	— —	$C_8H_{11}N_7O_3$
1g	63.0	117—118 (decomp.)	0.15 (AcOEt)	34.21 34.06	1.48 1.43	31.69 31.77	10.10 10.05	— —	$C_{10}H_5ClN_8O_5$
1h	79.4	160—161 (decomp.)	0.77 (AcOEt)	36.39 36.76	2.00 2.14	26.24 26.38	8.50 8.35	— —	$C_{13}H_9ClN_8O_7$
2e	88.2	121	0.53 (PhH—AcOEt, 3 : 1)	52.57 52.63	3.47 3.53	36.74 36.83	— —	— —	$C_{10}H_8N_6O$
2f	85	104—105 ($EtOH—H_2O$)	0.49 (AcOEt)	46.03 46.15	5.78 5.81	40.15 40.36	— —	— —	$C_8H_{12}N_6O$
2g	67.6	175	0.65 (PhH—AcOEt, 3 : 1)	45.65 45.73	2.61 2.69	32.15 32.00	13.43 13.50	— —	$C_{10}H_7ClN_6O$
2h	85.2	155	0.68 (PhH—AcOEt, 3 : 1)	46.57 46.65	3.34 3.31	25.27 25.11	10.49 10.59	— —	$C_{13}H_{11}ClN_6O_3$
2i	81.2	181	0.54 (PhH—AcOEt, 3 : 1)	45.50 45.11	5.16 5.30	31.70 31.56	— —	— —	$C_{10}H_{14}N_6O_3$
3a	93.4	184—185 (decomp.)	0.56 (AcOEt)	48.90 48.53	1.89 2.96	30.56 30.87	— —	— —	$C_{11}H_8N_6O_3$
3b	87.2	171 (decomp.)	0.83 (AcOEt)	42.43 42.86	4.78 4.80	33.45 33.32	— —	— —	$C_9H_{12}N_6O_3$
3c	89.5	193—194 (decomp.)	0.52 (AcOEt)	42.73 43.08	2.45 2.30	27.21 27.40	11.30 11.56	— —	$C_{11}H_7ClN_6O_3$
6	84.7	246	—	24.45 24.10	1.82 1.61	39.05 39.36	— —	15.40 15.66	$C_5H_4KN_7O_3$
7**	94	166—167	—	35.94 35.53	2.56 2.73	25.25 25.51	— —	5.29 5.24	$C_{13}H_9NaN_8O_7$
8**	82	167—168 (decomp.)	—	33.66 33.15	3.25 3.31	34.58 34.80	— —	— —	$C_{10}H_9N_9O_5$

* M = K (**6**) and Na (**7**).

** Calculated for $C_{10}H_6N_8O_5 \cdot 1/3\ H_2O$ (**1e**), $C_{13}H_9NaN_8O_7 \cdot 1.5\ H_2O$ (**7**), and $C_{10}H_9N_9O_5 \cdot 1.5\ H_2O$ (**8**).

obtained were recorded on Bruker AC 200, Bruker AM 300, and Bruker DRx500 spectrometers using the PFG FT-NMR technique. ^{14}N NMR spectra were recorded on a Bruker AM 300 spectrometer (21.5 MHz). The ^1H and ^{13}C chemical shifts are referenced to Me_4Si as the internal standard; the ^{14}N chemical shifts are referenced to $MeNO_2$ as the external standard. In NMR experiments, samples were mostly dissolved in DMSO-d_6. The exceptions included acetone-d_6 (**1a**, ^{14}N; **1b**, **8**, ^1H, ^{13}C, ^{14}N), $CDCl_3$ (**1f**, ^{14}N), CD_3OD (**1e**, **1g**, ^{14}N), CD_3CN (**7**, ^{13}C), and THF (**1h**, ^{14}N). Mass spectra were measured on a Varian MAT CH-6 instrument. The course of the reactions was monitored by TLC on Silufol UV-254 plates.

Synthesis of nitramines 1a—h (general procedure). Amines **2a—h** were stirred with a four- to fivefold excess of $NaNO_3$ in conc. H_2SO_4 (5—10 mL) at 20 or 50 °C for 1—4 h. The reaction mixture was poured into ice water. The precipitate that formed

Table 2. ^{1}H and ^{13}C NMR spectra of the compounds obtained

Compound	^{1}H NMR (δ, *J*/Hz)	^{13}C NMR (δ)	^{14}N NMR (δ, $\Delta\nu_{1/2}$/Hz)
1a	1.35 (t, 3 H, CH_2*Me*, *J* = 7.0); 2.58 (s, 3 H, Me); 4.38 (q, 2 H, CH_2, *J* = 7.0)	9.1 (Me); 14.1 (CH_2*Me*); 60.9 (CH_2); 135.9 (C(4′)); 141.4 (C(4)); 145.7 (C(5′)); 153.5 ($CNHNO_2$); 160.5 (CO)	−16.40 (NH*NO_2*)
1b	1.21 (t, 3 H, Me, *J* = 7.0); 4.32 (q, 2 H, CH_2, *J* = 7.0); 7.89 (t, 1H, C(5″)H, *J* = 7.8); 8.05 (d, 1 H, CH, *J* = 7.1); 8.50 (d, 1 H, C(2″)H, *J* = 8.3); 8.56 (s, 1 H, CH); 10.55 (br.s, 1 H, NH)	13.8 (Me); 61.2 (CH_2); 125.3 (Ar); 125.4 (Ar); 126.2; 130.1 (Ar); 136.4 (Ar); 136.6; 140.5; 145.9; 147.7; 155.1 ($CNHNO_2$); 160.0 (CO)	−14.00 (NH*NO_2*, $\Delta\nu_{1/2}$ = 27); −39.58 (NO_2, $\Delta\nu_{1/2}$ = 9)
1c	5.07 (s, 2 H, CH_2); 8.10 (s, 1 H, CH)	32.3 (CH_2); 134.3 (C(4′)); 136.4 (C(5′)); 145.8 (C(4)); 153.1 ($CNHNO_2$)	−16.40 (NH*NO_2*)
1d	2.40 (s, 3 H, Me); 7.80 (s, 1 H, CH)	8.6 (Me); 133.3 (C(4′)); 136.5 (C(5′)); 146.8 (C(4)); 150.4 ($CNHNO_2$)	—
1e	6.95 (m, 1 H, CH); 7.10 (d, 1 H, C(6″)H, *J* = 7.7); 7.40 (s, 1 H, C(4′)H); 7.60 (m, 2 H, 2 CH)	126.0 (C(4′)); 127.1 (Ar); 127.8 (C(5′)); 132.6 (Ar); 136.4 (Ar); 137.1 (Ar); 139.4 (*ipso*-C_{Ar}); 147.9 (C(4)); 148.0 (CNO_2); 149.7 ($CNHNO_2$)	−14.40 (NH*NO_2*, $\Delta\nu_{1/2}$ = 15); −37.26 (NO_2, $\Delta\nu_{1/2}$ = 3)
1f	1.23 (s, 3 H, Me); 7.80 (s, 1 H, C(4′)H)	29.4; 30.6; 131.3 (C(4′)); 147.7 (C(4)); 148.9 (C(5′)); 154.3 ($CNHNO_2$)	−16.87 (NH*NO_2*)
1g	7.75 (dd, 1 H, C(6″)H, *J* = 8.4, *J* = 1.8); 7.82 (d, 1 H, C(5″)H, *J* = 8.4); 8.16 (d, 1 H, C(2″)H, *J* = 1.8); 8.22 (s, 1 H, C(4′)H)	127.0 (Ar); 127.6 (Ar); 130.0 (CCl); 134.2 (Ar); 135.2 (Ar); 136.1 (Ar); 139.0 (C(4)); 148.0 (*ipso*-C_{Ar}); 148.5 (CNO_2); 150.17 ($CNHNO_2$)	−14.76 (NH*NO_2*, $\Delta\nu_{1/2}$ = 26); −37.73 (NO_2, $\Delta\nu_{1/2}$ = 10)
1h	1.17 (t, 3 H, Me, *J* = 7.0); 4.25 (q, 2 H, CH_2, *J* = 7.0); 7.55 (m, 2 H, NH, CH(Ar)); 7.91 (d, 1 H, CH, *J* = 8.4); 8.32 (d, 1 H, C(2″)H, *J* = 1.6)	14.8 (Me); 61.6 (CH_2); 125.2 (*ipso*-C_{Ar}); 127.8 (CCl); (128.0, 132.4, 135.4) (Ar); 137.3 (C(4′)); 139.6 (C(5′)); 145.9 (C(4)); 147.6 ($CNHNO_2$); 155.1 (CNO_2); 159.8 (CO)	−17.28 (NH*NO_2*, $\Delta\nu_{1/2}$ = 15); −40.95 (NO_2, $\Delta\nu_{1/2}$ = 6)
2e	6.65 (s, 2 H, NH_2); 7.43 (br.s, 5 H, Ph); 8.28 (s, 1 H, C(4′)H)	(124.8, 128.2, 129.1, 130.1) (Ph); 133.2 (C(4′)); 140.0 (C(5′)); 143.0 (C(4)); 153.2 (CNH_2)	—
2f	1.24 (s, 9 H, 3 Me); 6.67 (s, 2 H, NH_2); 7.84 (s, 1 H, C(4′)H)	29.2; 30.5; 131.5 (C(4′)); 144.5 (C(4)); 149.4 (C(5′)); 153.9 (CNH_2)	—
2g	6.65 (s, 2 H, NH_2); 7.45 (d, 2 H, 2 CH, *J* = 7.8); 7.57 (d, 2 H, 2 CH, *J* = 7.7); 8.30 (s, 1 H, C(4′)H)	123.8 (Ar); 129.3 (Ar, 2 CH); 130.3 (Ar, 2 CH); 133.6 (C(4′)H); 135.2 (Ar); 138.9 (C(5′)H); 142.9 (C(4)H); 153.0 (CNH_2)	—
2h	1.16 (t, 3 H, Me, *J* = 7.1); 4.25 (q, 2 H, CH_2, *J* = 7.1); 6.66 (s, 2 H, NH_2); 7.46 (d, 2 H, 2 CH, *J* = 8.4); 7.56 (d, 2 H, 2 CH, *J* = 8.4)	13.7 (Me); 61.0 (OCH_2); 122.7 (Ar); 128.5 (Ar, 2 CH); 131.8 (Ar, 2 CH); 135.6 (*ipso*-C_{Ar}); 136.6 (C(4′)); 142.0 (C(5′)); 142.1 (C(4)); 153.0 (CNH_2); 159.5 (CO)	—
2i	1.31 (s, 9 H, 3 Me); 3.92 (s, 3 H, OMe); 6.85 (s, 2 H, NH_2)	28.9; 32.2; 52.7 (OMe); 136.5 (C(4′)); 144.6 (C(4)); 150.7 (C(5′)); 154.0 (CNH_2); 162.3 (CO)	—
3a	6.55 (s, 2 H, NH_2); 7.45 (m, 5 H, Ph); 13.15 (br.s, 1 H, OH)	124.2 (*ipso*-C_{Ar}); 128.3 (C_{Ar}(3)); 129.9 (C_{Ar}(2)); 130.4 (C_{Ar}(4)); 137.1 (C(4′)); 142.3 (C(4)); 143.1 (C(5′)); 153.3 (CNH_2); 161.1 (CO)	—
3c	6.61 (s, 2 H, NH_2); 7.48 (m, 4 H, Ar)	—	—
6	2.32 (s, 3 H, Me); 7.75 (s, 1 H, C(4′)H)	8.0 (Me); 132.8 (C(4′)); 136.2 (C(5′)); 146.3 (C(4)); 154.9 ($CNKNO_2$)	—

(*to be continued*)

Table 2 (*continued*)

Compound	^{1}H NMR (δ, *J*/Hz)	^{13}C NMR (δ)	^{14}N NMR (δ, $\Delta\nu_{1/2}$/Hz)
7	1.15 (t, 3 H, Me, *J* = 7.1); 4.24 (q, 2 H, CH_2, *J* = 7.1); 7.76 (t,1 H, C(5″)H, *J* = 7.9); 7.88 (d,1 H, C(6″)H, *J* = 7.8); 8.36 (d,1 H, C(4″)H, *J* = 8.2); 8.42 (s,1 H, C(2″)H)	13.73 (Me); 61.13 (CH_2); 125.22 (Ar); 125.28 (Ar); 125.96 (Ar); 130.02 (Ar); 136.33 (Ar); 140.13 (C(5′)); 145.53 (C(4)); 147,27 ($CNNaNO_2$); 155.46 (CNO_2); 159.46 (CO)	−13.23 ($NHNO_2$, $\Delta\nu_{1/2}$ = 22)
8	7.79 (t, 1 H, C(5″)H, *J* = 8.0); 7.95 (d, 1 H, C(6″)H, *J* = 8.0); 8.25 (s, 1 H, C(4′)H); 8.34 (dd, 1 H, C(4″)H, *J* = 8.2; *J* = 1.7); 8.41 (br.s, 1 H, C(2″)H)	123.83 (C(4′)); 124.90 (C_{Ar}(6)); 128.10 (*ipso*-C_{Ar}); 130.20 (C_{Ar}(5)); 131,00 (C(5′)); 133.86 (C_{Ar}(4)); 135.20 (C_{Ar}(2)); 138.20 (C(4)); 147.30 (CNO_2); 149.00 ($CNNO_2$)	−13.94 (NNO_2); −362 (NH_4)

Table 3. IR and mass spectra of the compounds obtained

Compound	IR, ν/cm^{-1}	MS, *m*/*z* (I_{rel} (%))
1a	3096 (NH); 2948, 2792 (CH); 1728 (CO); 1316, 1140,	283 $[M]^+$ (15), 238 $[MH - NO_2]^+$ (40), 67 (100)
1b	3112, 3040, 2968 (NH, CH); 1712 (CO); 1616, 1524, 1360, 1312	262 $[MH - NHNO_2]^+$ (18), 256 $[M - CC_6H_4NO_2]^+$ (2), 44 (100)
1c	3156 (C(4′)H); 3104, 3036, 2920, 2852 (NH, CH); 1624, 1600, 1308	—
1d	3152 (C(4′)H); 3068, 2980, 2848, 2740 (NH, CH); 1616, 1600, 1304	211 $[M]^+$ (10), 165 $[M - NNO_2]^+$ (40), 108 (100)
1e	3156 (C(4′)H); 3088, 3020, 2864 (CH, NH); 1624, 1596, 1528, 1308	273 $[M - NO_2]^+$ (10), 245 $[M - NO_2 - N_2]^+$ (5), 46 (100)
1f	3156 (C(4′)H); 3064, 2972, 2700 (NH, CH); 1620, 1596, 1316, 1256	207 $[M - NO_2]^+$ (40), 57 (100)
1g	3160, 3080, 2992, 2864 (CH, NH); 1608, 1592, 1524, 1304, 840	—
1h	3108, 2972 (NH, CH); 1720 (CO); 1620, 1540, 1312,	—
2e	3432, 3308 (NH_2); 3132 (C(4′)H); 1632, 1568, 1484, 980	—
2f	3448, 3328, 3184 (NH_2); 3136, 2976 (CH), 1640, 1560, 1252, 984	—
2g	3136 (C(4′)H); 1596, 1476, 1092, 984, 732	—
2h	3460, 3348 (NH_2); 2984 (CH); 1736 (CO); 1636, 1488, 1220, 984	—
2i	3408, 3312, 3200 (NH_2); 2952 (CH); 1732 (CO); 1644, 1564, 1364, 1232, 992	266 $[M]^+$ (21), 235 $[M - OMe]^+$ (62), 182 (85), 166 (100), 151 (95), 136 (90)
3a	3424, 3304 (NH_2); 2920, 2556 (CH, OH); 1720 (CO); 1640, 1220, 984	272 $[M]^+$ (32), 228 $[M - CO_2]^+$ (30), 145 (100)
3b	3408, 2960, 2584 (NH_2, CH, OH); 1720 (CO); 1640, 1232, 880	—
3c	3424, 3304 (NH_2); 2896, 2552 (CH, OH); 1716 (CO); 1640, 1220, 984	—
6	3132, 3104 (CH); 1524, 1396, 1336, 1316, 972	—
7	3084, 2984 (CH); 1716 (CO); 1528, 1348, 1304, 1232, 992, 740	—
8	3450, 3116 (C(4′)H); 1536, 1512, 1400, 1352, 1304, 736	—

was filtered off, washed with water to a neutral reaction, and dried in air.

4-(4-Ethoxycarbonyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-3-nitramino-1,2,5-oxadiazole (1a) was obtained from amine **2a** (0.3 g, 1.26 mmol) and $NaNO_3$ (0.43 g, 5.1 mmol) at 50 °C for 4 h. The yield was 0.30 g.

4-[4-Ethoxycarbonyl-5-(3-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]-3-nitramino-1,2,5-oxadiazole (1b) was obtained from amine **2b** (0.4 g, 1.33 mmol) and $NaNO_3$ (0.45 g, 5.29 mmol) at 50 °C for 4 h. The yield was 0.28 g.

4-(5-Chloromethyl-1*H*-1,2,3-triazol-1-yl)-3-nitramino-1,2,5-oxadiazole (1c) was obtained from amine **2c** (0.2 g, 1 mmol) and $NaNO_3$ (0.34 g, 4 mmol) at 20 °C for 4 h. The yield was 0.08 g.

4-(5-Methyl-1*H*-1,2,3-triazol-1-yl)-3-nitramino-1,2,5-oxadiazole (1d) was obtained from amine **2d** (0.3 g, 1.8 mmol) and $NaNO_3$ (0.45 g, 5.29 mmol). The yield was 0.25 g.

3-Nitramino-4-[5-(3-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]-1,2,5-oxadiazole (1e) was obtained from amine **2e** (0.3 g, 1.32 mmol) and $NaNO_3$ (0.45 g, 5.29 mmol). The yield was 0.32 g.

4-(5-*tert*-Butyl-1*H*-1,2,3-triazol-1-yl)-3-nitramino-1,2,5-oxadiazole (1f) was obtained from amine **2f** (0.3 g, 1.44 mmol) and $NaNO_3$ (0.49 g, 5.76 mmol) at 20 °C for 4 h. The yield was 0.24 g.

4-[5-(4-Chloro-3-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]-3-nitramino-1,2,5-oxadiazole (1g) was obtained from amine **2g** (0.4 g, 1.53 mmol) and $NaNO_3$ (0.52 g, 6.12 mmol) in conc. H_2SO_4 (10 mL) at 20 °C for 1 h. The greasy product was filtered off, dissolved in acetone (5 mL), and reprecipitated with water (50 mL). After 24 h, compound **1g** (0.34 g) was filtered off.

4-[5-(4-Chloro-3-nitrophenyl)-4-ethoxycarbonyl-1*H*-1,2,3-triazol-1-yl]-3-nitramino-1,2,5-oxadiazole (1h) was obtained from amine **2h** (0.3 g, 0.9 mmol) and $NaNO_3$ (0.31 g, 3.6 mmol) at 20 °C. The yield was 0.27 g.

4-(5-Methyl-1*H*-1,2,3-triazol-1-yl)-3-nitramino-1,2,5-oxadiazole, potassium salt (6). A solution of nitramine **1d** (0.1 g, 0.474 mmol) in acetone (5 mL) was refluxed for 1 h in the presence of K_2CO_3 (0.04 g, 0.29 mmol). The reaction mixture was cooled, the precipitate that formed was filtered off, and the mother liquor was evaporated to dryness *in vacuo*. The yield of salt **6** was 0.1 g.

4-[4-Ethoxycarbonyl-5-(3-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]-3-nitramino-1,2,5-oxadiazole, sodium salt (7). A solution of $NaHCO_3$ (0.4 g, 4.76 mmol) in water (1 mL) was added to a solution of nitramine **1b** (0.5 g, 1.28 mmol) in acetone (5 mL). The reaction mixture was stirred for 1 h and evaporated to dryness *in vacuo*. The residue was refluxed in acetone (5 mL) for 5 min, the precipitate that formed was filtered off, and the mother liquor was evaporated to dryness *in vacuo*. The yield of salt **7** was 0.5 g.

3-Nitramino-4-[5-(3-nitrophenyl)-1*H*-1,2,3-triazol-1-yl]-1,2,5-oxadiazole, ammonium salt (8). Five drops of concentrated aqueous ammonia were added to a solution of nitramine **1e** (0.05 g, 0.16 mmol) in EtOH (3 mL) to a basic reaction. The solvents were removed at room temperature. The resulting solid residue was washed with a small amount of ethanol. The yield of salt **8** was 0.07 g.

Synthesis of 3-amino-4-(1,2,3-triazol-1-yl)-1,2,5-oxadiazoles 2h and 2i. A solution of 4-amino-3-azidofurazan (**4**), 1,3-dicarbonyl compound (**5a**,**b**), and Et_3N (a twofold excess) in an alcohol was refluxed for 1 h. Then water (40—50 mL) was added at 20 °C. The precipitate that formed was filtered off and washed with water.

3-Amino-4-[5-(4-chlorophenyl)-4-ethoxycarbonyl-1*H*-1,2,3-triazol-1-yl]-1,2,5-oxadiazole (2h) was obtained from azide **4** (0.28 g, 2.23 mmol) and ethyl 4-chlorobenzoylacetate (**5a**) (0.53 g, 2.35 mmol) in EtOH (50 mL). The yield was 0.67 g.

3-Amino-4-(5-*tert*-butyl-4-methoxycarbonyl-1*H*-1,2,3-triazol-1-yl)-1,2,5-oxadiazole (2i) was obtained from azide **4** (0.38 g, 3 mmol) and methyl 4,4-dimethyl-3-oxopentanoate (**5b**) (0.5 g, 3.16 mmol) in MeOH (20 mL). Compound **2i** was recrystallized from MeOH—H_2O (1 : 1). The yield was 0.65 g.

Synthesis of carboxylic acids 3a—c (general procedure). Amino(triazolyl)furazan (**2b,i,h**) was added to a solution of NaOH (1.2 molar excess) in water (30—50 mL) or H_2O—EtOH (1 : 1). The reaction mixture was refluxed for 30 min, cooled to room temperature, and acidified by adding dropwise 2 *M* HCl to an acidic reaction. Carboxylic acid (**3a—c**) that formed was filtered off and washed with cold water.

1-(4-Amino-1,2,5-oxadiazol-3-yl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid (3a) was obtained from ester **2b** (1 g, 3.33 mmol) and NaOH (0.16 g, 4 mmol). The yield was 0.85 g.

1-(4-Amino-1,2,5-oxadiazol-3-yl)-5-*tert*-butyl-1*H*-1,2,3-triazole-4-carboxylic acid (3b) was obtained from ester **2i** (0.5 g, 1.88 mmol) and NaOH (0.1 g, 2.5 mmol). The yield was 0.41 g.

1-(4-Amino-1,2,5-oxadiazol-3-yl)-5-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylic acid (3c) was obtained from ester **2h** (0.63 g, 1.87 mmol) and NaOH (0.08 g, 2 mmol). The yield was 0.51 g.

Synthesis of 5-substituted amino(triazolyl)furazans 2e—g (general procedure). Carboxylic acid (**3a,b,c**) was dissolved in AcOH (15 mL). The resulting solution was refluxed for 30—60 min and cooled to room temperature. Water (45—60 mL) was added in small portions with stirring. The decarboxylation product (**2e,f,g**) was filtered off, washed with water, and dried in air.

3-Amino-4-(5-*tert*-butyl-1*H*-1,2,3-triazol-1-yl)-1,2,5-oxadiazole (2f) was obtained from acid **3b** (0.3 g, 1.19 mmol). The yield was 0.21 g.

3-Amino-4-(5-phenyl-1*H*-1,2,3-triazol-1-yl)-1,2,5-oxadiazole (2e) was obtained from acid **3a** (1.82 g, 6.69 mmol). The yield was 1.35 g.

3-Amino-4-[5-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl]-1,2,5-oxadiazole (2g) was obtained from acid **3c** (0.43 g, 1.41 mmol). The yield was 0.25 g. In the synthesis of compounds **2e** and **2g**, the reaction mixtures were refluxed for 5 min upon the addition of water and cooled to 20 °C. The precipitates that formed were filtered off and washed with water.

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