Synthesis of carbamoylformhydroxymoyl chlorides and study of their reactivities

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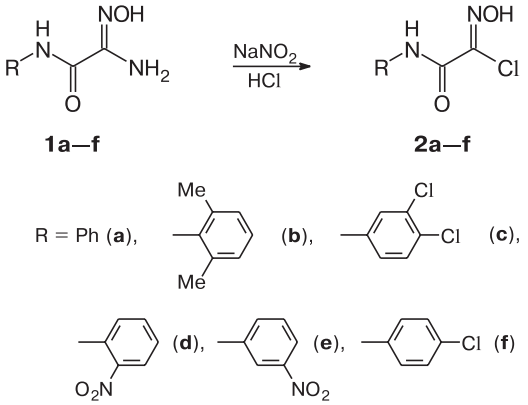
Carbamoylformhydroxymoyl chlorides were synthesized by the reactions of carbamoylformamide oximes with sodium nitrite in the presence of hydrochloric acid, and their reactivities were examined.

Key words: amide oximes, sodium nitrite, furoxanes, tetrazoles, oxathiazoles, 1,3,4-oxadiazoles, isoxazoles, isoxazolines, aldoximes.

The transformations of readily accessible carbamoylformamide oximes **1** [1] into carbamoylformhydroxymoyl chlorides **2** open up an approach to various compounds, among them bis-carbamoylfuroxanes possessing anti-hypertensive properties[2] and carbamoyl-1,3,4-oxadiazoles attracting interest as herbicides.[3] However, the replacement of the amino group in amide oximes by the chlorine atom is a poorly studied process. Only a few examples are known of the syntheses of aromatic hydroxymoyl chlorides starting from amide oximes under the action of sodium nitrite and hydrochloric acid.[4,5] Under these conditions, the reactions of aliphatic amide oximes afforded amides.[6] Nitrosation of carbamoylformamide oximes **1** has not been studied previously.

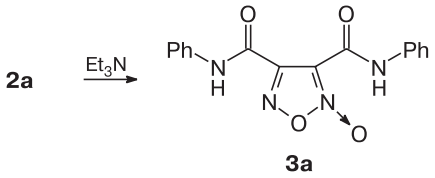
With the aim of synthesizing carbamoylhydroxymoyl chlorides **2**, we examined the reactions of amide oximes **1** with $NaNO_2$ in the presence of hydrochloric acid. It appeared that the addition of the latter to a suspension of carbamoylamide oximes **1a—f** in water gave rise to water-soluble salts. Under the action of $NaNO_2$, these compounds were rapidly transformed into hydroxymoyl chlorides **2a—f** in 42—84% yields (Scheme 1).

Scheme 1



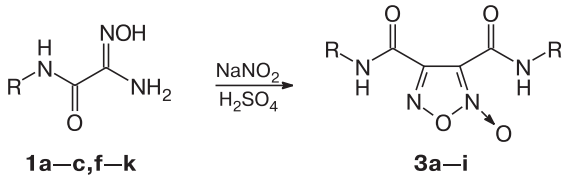
Compounds **2a—f** can be transformed into bis-carbamoylfuroxanes **3** under the action of bases. Thus, the reaction of hydroxymoyl chloride **2a** with Et_3N afforded compound **3a** (Scheme 2).

Scheme 2



Furoxanes **3** can be prepared from amide oximes **1** in one step by nitrosation of compounds **1** in the presence of H_2SO_4. In these reactions, the sulfate anions act, apparently, as a weak base thus inducing elimination of HCl from intermediate hydroxymoyl chlorides **2** (Scheme 3).

Scheme 3



R = Ph (**1a**, **3a**), 4-$MeOC_6H_4$ (**1g**, **3b**), 3,4-$Cl_2C_6H_3$ (**1c**, **3c**), 4-$NO_2C_6H_4$ (**1h**, **3d**), 2,3-$Me_2C_6H_3$ (**1i**, **3e**), 3-$MeOC_6H_4$ (**1j**, **3f**), 4-ClC_6H_4 (**1f**, **3g**), 4-MeC_6H_4 (**1k**, **3h**), 2,6-$Me_2C_6H_3$ (**1b**, **3i**)

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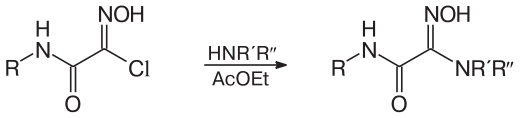
Hence, we demonstrated for the first time that furoxanes can be prepared by nitrosation of amide oximes. This procedure allows one to synthesize bis-carbamoylfuroxanes **3a—i** in good yields (60—91%) starting from available compounds.

As part of continuing studies of the synthetic potential of carbamoylhydroxymoyl chlorides, we examined the reactions of hydroxymoyl chlorides **2** with various nucleophiles.

Carbamoylhydroxymoyl chlorides **2a,f** reacted with primary (allylamine and cyclopropylamine) and secondary (diallylamine, morpholine, and thiomorpholine) amines to form carbamoylamide oximes **4a—f** in 36—80% yields (Scheme 4).

Scheme 4



2a,f **4a—f**

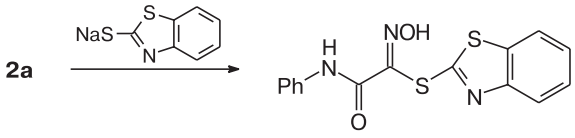
R = Ph (**2a**, **4a—e**), 4-ClC$_6$H$_4$ (**2f**, **4f**)

4: NR′R″ = —HN (**a**), —HN (**b,f**), —N (**c**),

—N O (**d**), —N S (**e**)

The reaction of compound **2a** with sodium benzothiazole-2-thiolate in EtOH gave rise to sulfide **5** (Scheme 5).

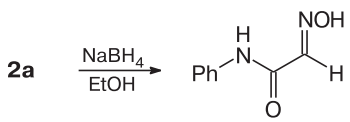
Scheme 5



5

Reduction of carbamoylhydroxymoyl chloride **2a** with $NaBH_4$ in EtOH afforded aldoxime **6** (Scheme 6).

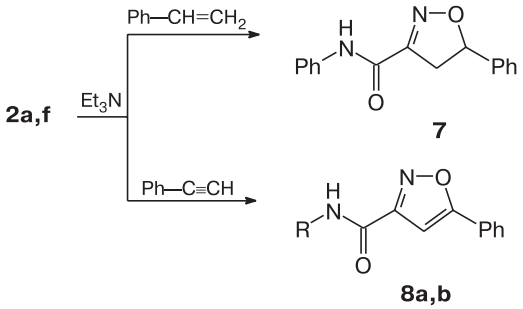
Scheme 6



6

Cycloaddition of nitrile oxides, which were generated *in situ* from hydroxymoyl chlorides **2a,f** under the action of Et_3N, to styrene and phenylacetylene produced dihydroisoxazole **7** and isoxazoles **8a,b**, respectively (Scheme 7).

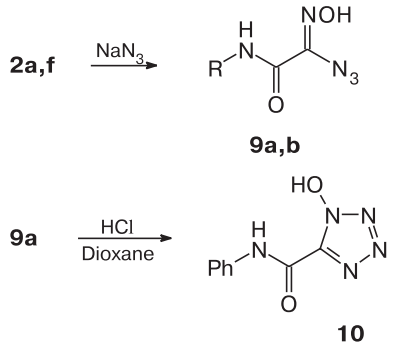
Scheme 7



8: R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**)

The reactions of carbamoylhydroxymoyl chlorides **2a,f** with NaN_3 in water yielded azides **9a,b** (Scheme 8). Compound **9a** was transformed into hydroxytetrazole **10** under the action of HCl in dioxane.

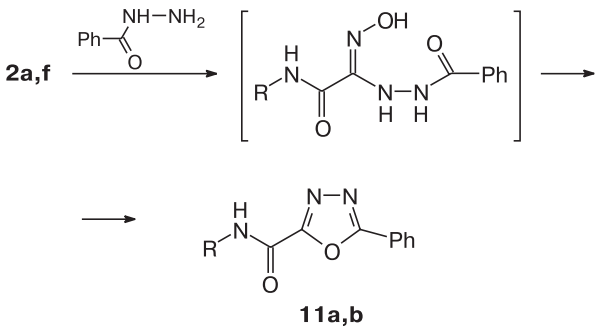
Scheme 8



9: R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**)

The IR spectrum of cyclization product **10** shows no absorption band of the azide group, which is also ob-

Scheme 9



11: R = Ph (**a**), 4-ClC$_6$H$_4$ (**b**)

served in the spectrum of azide **9a**. The mass spectrum has a molecular ion peak at *m/z* 205.

The reactions of hydroxymoyl chlorides **2a,f** with benzoic hydrazide afforded 2-carbamoyl-1,3,4-oxadiazoles **11a,b** in 44 and 65% yields, respectively (Scheme 9).

Hence, the transformations of carbamoylamide oximes **1** into carbamoylhydroxymoyl chlorides **2** enabled us to prepare a broad spectrum of carbamoyl-containing polyfunctional heterocyclic compounds.

Experimental

The IR spectra were recorded on a Specord IR-80 spectrophotometer in KBr pellets. The ^{1}H NMR spectra were measured on a Bruker WM-250 instrument (250 MHz) in DMSO-d_6. The mass spectra (EI) were obtained on Varian MAT CH-6 and Kratos MS-30 instruments with direct inlet of the sample into the ion source; the ionizing voltage was 70 eV; the emission current was 0.1 mA. The melting points were determined on a Boetius stage and were not corrected. The starting carbamoylamide oximes **1a—f** were synthesized according to a procedure reported previously.[1] The compositions of the reaction mixtures and the purities of the products were monitored by TLC on Silufol UV-254 plates (AcOEt—hexane, 1 : 1, v/v, as the eluent).

Reactions of carbamoylamide oximes 1a—f with $NaNO_2$ in the presence of hydrochloric acid (general procedure). Sodium nitrite (6 mmol) was added portionwise with stirring to a suspension of carbamoylamide oxime **1a—f** (5 mmol) in 18% hydrochloric acid (25 mL) (the temperature of the mixture

Table 1. Yields and physicochemical and spectroscopic characteristics of compounds **2—4**

Compound	Yield (%)	M.p./°C	Found / Calculated (%)				Molecular formula	^{1}H NMR, δ (*J*/Hz)	Mass spectrum, *m/z* ([M]$^+$)
			C	H	Cl	N			
2a	84	154—155	48.56 48.36	3.45 3.55	17.57 17.88	14.05 14.11	$C_8H_7ClN_2O_2$	7.13 (t, 1 H, H arom., *J* = 7.8); 7.35 (m, 2 H, H arom.); 7.65 (d, 2 H, H arom., *J* = 8.0); 10.25 (s, 1 H, NH); 12.90 (s, 1 H, OH)	198
2b	83	155—157	52.76 52.98	4.91 4.86	15.51 15.67	12.52 12.36	$C_{10}H_{11}ClN_2O_2$	2.10 (s, 6 H, 2 Me); 7.10 (m, 3 H, H arom.); 9.75 (s, 1 H, NH); 12.95 (s, 1 H, OH)	226
2c	83	155—157	35.75 35.92	1.94 1.88	39.53 39.76	10.57 10.47	$C_8H_5Cl_3N_2O_2$	7.10 (m, 3 H, H arom.); 9.75 (s, 1 H, NH); 12.95 (s, 1 H, OH)	267, 268
2d	42	189—191	39.30 39.43	2.50 2.46	26.46 26.28	17.15 17.25	$C_8H_6ClN_3O_4$	7.80—7.90 (m, 4 H, H arom.); 10.70 (s, 1 H, NH); 13.15 (s, 1 H, OH)	243
2e	63	180—182	39.55 39.43	2.30 2.46	26.40 26.28	17.10 17.25	$C_8H_6ClN_3O_4$	7.65 (m, 1 H, H arom.); 7.95 (m, 1 H, H arom.); 8.12 (m, 1 H, H arom.); 8.70 (s, 1 H, H arom.); 10.75 (s, 1 H, NH); 13.10 (s, 1 H, OH)	243
2f	77	177—179	41.73 41.23	2.90 2.60	30.90 30.42	12.42 12.02	$C_8H_6Cl_2N_2O_2$	7.39 (d, 2 H, H arom., *J* = 8.7); 7.70 (d, 2 H, H arom., *J* = 8.7); 9.75 (s, 1 H, NH); 12.95 (s, 1 H, OH)	233
3a	60	194—196	59.07 59.26	3.75 3.70	—	17.31 17.28	$C_{16}H_{12}N_4O_4$	7.15 (m, 2 H, H arom.); 7.35 (m, 4 H, H arom.); 7.65 (m, 2 H, H arom.); 7.75 (m, 2 H, H arom.); 10.90 (m, 1 H, NH); 11.20 (m, 1 H, NH)	324
3b	85	196—198	56.20 56.25	4.15 4.19	—	14.65 14.58	$C_{18}H_{16}N_4O_6$	3.75 (s, 6 H, 2 OMe); 6.95 (m, 4 H, H arom.); 7.50 (m, 2 H, H arom.); 7.65 (m, 2 H, H arom.); 10.85 (s, 1 H, NH); 11.10 (s, 1 H, NH)	384
3c	82	243—245	41.48 41.59	1.63 1.75	30.76 30.69	12.30 12.13	$C_{16}H_8Cl_4N_4O_4$	7.45 (m, 1 H, H arom.); 7.50—7.70 (m, 3 H, H arom.); 7.90 (s, 1 H, H arom.); 8.05 (s, 1 H, H arom.); 11.15 (s, 1 H, NH); 11.40 (s, 1 H, NH)	462
3d	83	272—273	46.21 46.39	2.35 2.43	—	20.68 20.29	$C_{16}H_{10}N_6O_8$	7.80 (m, 2 H, H arom.); 8.00 (m, 2 H, H arom.); 8.30 (m, 4 H, H arom.); 11.40 (s, 1 H, NH); 11.75 (s, 1 H, NH)	414

(*to be continued*)

Table 1 (*continued*)

Compound	Yield (%)	M.p./°C	Found / Calculated (%)				Molecular formula	^{1}H NMR, δ (*J*/Hz)	Mass spectrum, *m/z* ([M]$^+$)
			C	H	Cl	N			
3e	78	201—203	63.21 63.15	5.35 5.29	—	14.68 14.73	$C_{20}H_{20}N_4O_4$	2.10 (s, 6 H, 2 Me); 2.20 (s, 6 H, 2 Me); 7.10 (m, 3 H, H arom.); 7.20 (m, 2 H, H arom.); 7.30 (m, 1 H, H arom.); 10.40 (s, 1 H, NH); 10.75 (s, 1 H, NH)	380
3f	84	146—148	56.33 56.25	4.35 4.19	—	14.47 14.58	$C_{18}H_{16}N_4O_6$	3.75 (s, 6 H, 2 OMe); 6.75 (m, 2 H, H arom.); 7.10 (m, 1 H, H arom.); 7.20—7.40 (m, 5 H, H arom.); 10.90 (s, 1 H, NH); 11.20 (s, 1 H, NH)	384
3g	87	219—221	48.74 48.88	2.35 2.56	18.15 18.03	14.48 14.25	$C_{16}H_{10}Cl_2N_4O_4$	7.40 (m, 4 H, H arom.); 7.65 (m, 2 H, H arom.); 7.75 (m, 2 H, H arom.); 11.10 (s, 1 H, NH); 11.35 (s, 1 H, NH)	393
3h	91	201—203	61.26 61.36	4.49 4.58	—	15.83 15.90	$C_{18}H_{16}N_4O_4$	2.30 (s, 6 H, 2 Me); 7.20 (d, 4 H, H arom.); 7.50 (m, 2 H, H arom.); 7.75 (m, 2 H, H arom.); 10.90 (s, 1 H, NH); 11.10 (s, 1 H, NH)	352
3i	75	232—234	63.21 63.16	5.35 5.26	—	14.68 14.74	$C_{20}H_{20}N_4O_4$	2.20 (s, 12 H, 4 Me); 7.15 (m, 6 H, H arom.); 10.45 (s, 1 H, NH); 10.75 (s, 1 H, NH)	380
4a	73	85—87	60.18 60.26	5.83 5.98	—	19.15 19.17	$C_{11}H_{13}N_3O_2$	3.95 (m, 2 H, =CH_2); 5.05 (m, 2 H, CH_2); 5.80—5.90 (m, 1 H, NH); 5.90—6.00 (m, 1 H, CH); 7.05 (t, 1 H, H arom., *J* = 7.3); 7.30 (m, 2 H, H arom.); 7.65 (d, 2 H, H arom., *J* = 8.1); 10.10 (s, 2 H, NH + OH)	219
4b	36	82—85	60.21 60.26	5.35 5.98	—	19.26 19.17	$C_{11}H_{13}N_3O_2$	0.50 (m, 4 H, 2 CH_2); 2.80 (m, 1 H, CH); 5.90 (s, 1 H, NH); 7.05 (t, 1 H, H arom., *J* = 7.2); 7.30 (m, 2 H, H arom.); 7.65 (d, 2 H, H arom., *J* = 8.0); 9.80 (s, 1 H, NH); 10.12 (s, 1 H, OH)	219
4c	69	75—77	64.88 64.85	6.58 6.61	—	16.26 16.20	$C_{14}H_{17}N_3O_2$	3.80 (m, 4 H, 2 =CH_2); 5.20 (m, 4 H, 2 CH_2); 5.80 (m, 2 H, 2 CH); 7.05 (t, 1 H, H arom., *J* = 7.3); 7.30 (m, 2 H, H arom.); 7.60 (d, 2 H, H arom., *J* = 8.0); 10.05 (s, 1 H, NH); 10.30 (s, 1 H, OH)	259
4d	54	139—141	—	—	—	—	—	3.35 (m, 4 H, 2 CH_2); 3.65 (m, 4 H, 2 CH_2); 7.05 (t, 1 H, H arom., *J* = 7.3); 7.30 (m, 2 H, H arom.); 7.65 (d, 2 H, H arom., *J* = 8.0); 10.15 (s, 1 H, NH); 10.25 (s, 1 H, OH)	249
4e	79	155—158	54.26 54.32	5.33 5.69	—	15.96 15.84	$C_{12}H_{15}N_3O_2S$	2.65 (m, 4 H, 2 CH_2); 3.50 (m, 4 H, 2 CH_2); 7.05 (t, 1 H, H arom., *J* = 7.3); 7.30 (m, 2 H, H arom.); 7.60 (d, 2 H, H arom., *J* = 8.0); 10.05 (s, 1 H, NH); 10.30 (s, 1 H, OH)	265
4f	45	139—141	52.17 52.08	4.81 4.77	13.95 13.98	16.42 16.56	$C_{11}H_{12}ClN_3O_2$	0.51 (s, 4 H, 2 CH_2); 2.75 (s, 1 H, CH); 7.35 (d, 2 H, H arom., *J* = 8.7); 7.75 (d, 2 H, H arom., *J* = 8.7); 9.86 (s, 1 H, NH); 10.25 (s, 1 H, OH)	253

was ≤20 °C). The reaction mixture was stirred for 15 min and then diluted with water (50 mL). The precipitate that formed was filtered off and recrystallized from a 1 : 1 EtOH—H_2O mixture to obtain **2-anilino- (2a)**, **2-(2,6-dimethylanilino)- (2b)**, **2-(3,4-dichloroanilino)- (2c)**, **2-(2-nitroanilino)- (2d)**, **2-(3-nitroanilino)- (2e), and 2-(4-chloroanilino)-2-oxoethanehydroxymoyl chloride (2f)**. Their spectroscopic and physicochemical characteristics are given in Table 1.

3,4-Bis(*N*-phenylcarbamoyl)furoxane (3a). Freshly distilled Et_3N (0.69 mL, 0.50 g, 5 mmol) was added to a solution of carbamoylformhydroxymoyl chloride **2a** (1.0 g, 5 mmol) in Et_2O (5 mL). The solution was filtered off from the precipitate and concentrated on a rotary evaporator. The residue was recrystallized from EtOH. The yield was 0.81 g (50%). The spectroscopic and physicochemical characteristics of **3a** are given in Table 1.

Reactions of carbamoylformamide oximes 1a—c,f—k with $NaNO_2$ in the presence of H_2SO_4 (general procedure). The reactions were carried out according to the above-mentioned general procedure applied to the reactions of carbamoylamide oximes **1a—f** with $NaNO_2$ with the use of 20% H_2SO_4 instead of hydrochloric acid. Sodium nitrite was added upon cooling to 5—10 °C. Then the reaction mixture was diluted with H_2O (30 mL). The precipitate that formed was filtered off, dried, and recrystallized from EtOH to obtain **3,4-bis(*N*-phenylcarbamoyl)- (3a)**, **3,4-bis[*N*-(4-methoxyphenyl)carbamoyl]- (3b)**, **3,4-bis[*N*-(3,4-dichlorophenyl)carbamoyl]- (3c)**, **3,4-bis[*N*-(4-nitrophenyl)carbamoyl]- (3d)**, **3,4-bis[*N*-(2,3-dimethylphenyl)carbamoyl]- (3e)**, **3,4-bis[*N*-(3-methoxyphenyl)carbamoyl]- (3f)**, **3,4-bis[*N*-(4-chlorophenyl)carbamoyl]- (3g)**, **3,4-bis[*N*-(4-methylphenyl)carbamoyl]- (3h),** and **3,4-bis[*N*-(2,6-dimethylphenyl)carbamoyl]furoxane (3i)**. Their spectroscopic and physicochemical characteristics are given in Table 1.

2-Hydroxyimino-2-morpholino-*N*-phenylacetamide (4d). Morpholine (0.5 mL, 0.5 g, 5 mmol) was added to a solution of hydroxymoyl chloride **2a** (0.5 g, 2.5 mmol) in AcOEt (10 mL). The precipitate that formed was filtered off and the filtrate was concentrated on a rotary evaporator. The residue was recrystallized from a 1 : 1 EtOH—H_2O mixture. The yield was 0.7 g. The spectroscopic and physicochemical characteristics of **4d** are given in Table 1.

2-Allylamino-2-hydroxyimino- (4a), **2-cyclopropylamino-2-hydroxyimino- (4b)**, **2-diallylamino-2-hydroxyimino- (4c)**, **2-hydroxyimino-2-thiomorpholino-*N*-phenylacetamide (4e),** and ***N*-(4-chlorophenyl)-2-cyclopropylamino-2-hydroxyiminoacetamide (4f)** were prepared analogously. Their spectroscopic and physicochemical characteristics are given in Table 1.

***S*-Benzothiazol-2-yl 2-anilino-2-oxoethanehydroxyiminothioate (5).** Sodium benzothiazole-2-thiolate (0.1 g, 0.5 mmol) was added to a solution of carbamoylhydroxymoyl chloride **2a** (0.1 g, 0.5 mmol) in EtOH (5 mL). The reaction mixture was stirred for 24 h and filtered off from NaCl. The filtrate was concentrated on a rotary evaporator. The residue was recrystallized from EtOH. The yield was 0.13 g (80%), m.p. 205 °C. Found (%): C, 55.10; H, 3.50; N, 12.55. $C_{15}H_{11}N_3O_2S_2$. Calculated (%): C, 54.71; H, 3.34; N, 12.77. ^{1}H NMR, δ: 7.20—7.90 (m, 9 H, H arom.); 11.15 (s, 1 H, NH). MS, *m/z*: 329 $[M]^+$.

2-Hydroxyimino-*N*(1)-phenylacetamide (6). Sodium borohydride (0.3 g, 7.9 mmol) was added portionwise (0.1 g) with stirring to a solution of hydroxymoyl chloride **2a** (0.3 g, 1.5 mmol) in EtOH (5 mL) (upon the addition of the first portion, the solution was clarified and gas evolution was observed). Within 10 min after the addition of the last portion (TLC control), the solution was filtered off and concentrated on a rotary evaporator. The residue was recrystallized from EtOH. The yield was 0.15 g (56%), m.p. 193—195 °C. Found (%): C, 58.47; H, 4.59; N, 17.18. $C_8H_8N_2O_2$. Calculated (%): C, 58.54; H, 4.88; N, 17.07. ^{1}H NMR, δ: 7.05 (t, 1 H, H arom., J = 7.3 Hz); 7.30 (m, 2 H, H arom.); 7.65 (d, 2 H, H arom., J = 8.0 Hz); 7.50 (s, 1 H, CH); 10.00 (s, 1 H, NH); 12.05 (s, 1 H, OH). MS, *m/z*: 164 $[M]^+$.

***N*(3),5-Diphenyl-4,5-dihydroisoxazole-3-carboxamide (7).** Triethylamine (~10 drops) was added dropwise to a mixture of carbamoylhydroxymoyl chloride **2a** (0.20 g, 1 mmol) and styrene (6.0 mL, 5.4 g, 52 mmol) until hydroxymoyl chloride was completely dissolved. Then the liquid phase was distilled off on a rotary evaporator. The residue was washed with water, dried, and recrystallized from EtOH. The yield was 0.14 g (52%), m.p. 123—126 °C. Found (%): C, 72.10; H, 5.20; N, 10.58. $C_{16}H_{14}N_2O_2$. Calculated (%): C, 72.18; H, 5.26; N, 10.53. ^{1}H NMR, δ: 3.25 (m, 1 H, CH_2); 3.80 (m, 1 H, CH_2); 5.80 (m, 1 H, CH); 7.10 (m, 1 H, H arom.); 7.35 (m, 7 H, H arom.); 7.75 (m, 2 H, H arom.); 10.50 (s, 1 H, NH). MS, *m/z*: 266 $[M]^+$, 249 $[M - OH]^+$.

***N*(3),5-Diphenylisoxazole-3-carboxamide (8a).** Triethylamine (0.2 mL, 0.15 g, 46 mmol) was added dropwise to a suspension of carbamoylhydroxymoyl chloride **2a** (0.10 g, 0.5 mmol) in freshly distilled phenylacetylene (5.0 mL, 4.65 g, 46 mmol). After 15 min, the solution was filtered off and concentrated *in vacuo* on a rotary evaporator. The residue was recrystallized from EtOH. The yield was 0.06 g (46%), m.p. 200—202.5 °C. Found (%): C, 72.60; H, 4.70; N, 10.75. $C_{16}H_{12}N_2O_2$. Calculated (%): C, 72.72; H, 4.58; N, 10.60. ^{1}H NMR, δ: 7.15 (t, 1 H, H arom., J = 7.3 Hz); 7.35 (m, 2 H, H arom.); 7.45 (s, 1 H, CH); 7.65 (m, 3 H, H arom.); 7.80 (m, 2 H, H arom.); 7.95 (m, 2 H, H arom.); 10.65 (s, 1 H, NH). MS, *m/z*: 264 $[M]^+$.

***N*(3)-(4-Chlorophenyl)-5-phenylisoxazole-3-carboxamide 8b** was prepared analogously to compound **8a** from carbamoylhydroxymoyl chloride **2f**. The yield was 0.04 g (33%), m.p. 217—219 °C. Found (%): C, 64.18; H, 3.67; Cl, 11.76; N, 9.45. $C_{16}H_{11}ClN_2O_2$. Calculated (%): C, 64.33; H, 3.71; Cl, 11.87; N, 9.38. ^{1}H NMR, δ: 7.40 (m, 3 H, H arom. + CH); 7.55 (m, 3 H, H arom.); 7.70 (m, 2 H, H arom.); 7.95 (m, 2 H, H arom.); 10.80 (s, 1 H, NH). MS, *m/z*: 298 $[M]^+$.

2-Azido-2-hydroxyimino-*N*(1)-phenylacetamide (9a). Sodium azide (0.10 g, 1.5 mmol) was added with stirring to a suspension of carbamoylhydroxymoyl chloride **2a** (0.10 g, 0.5 mmol) in H_2O (2 mL). The mixture was stirred for 30 min (TLC control). The precipitate was filtered off and dried. The yield was 0.92 g (90%), m.p. 138—140 °C (decomp.). IR, ν/cm^{-1}: 3300 (OH); 2920 (NH); 2860 (NH); 2150 (N_3); 1670 (C=O). MS, *m/z*: 253 $[M^+]$. The compound was used for further transformations without recrystallization.

2-Azido-*N*(1)-(4-chlorophenyl)-2-hydroxyiminoacetamide (9b) was prepared analogously to compound **9a** from carbamoylhydroxymoyl chloride **2f**. The yield was 0.90 g (85%), m.p. 129—133 °C (decomp.). MS, *m/z*: 239 $[M]^+$.

1-Hydroxy-*N*(5)-phenyl-1*H*-1,2,3,4-tetrazole-5-carboxamide (10). Gaseous HCl was passed through a solution of azide **9a** (0.1 g, 0.5 mmol) in dioxane (5 mL) for 10 min. The solution was kept at 0—5 °C for 24 h and then diluted with

H_2O (30 mL). The flocculent precipitate that formed was filtered off, dried, and recrystallized from EtOH. The yield was 0.095 g (95%), m.p. 123—125 °C. Found (%): C, 46.74; H, 3.65; N, 34.30. $C_8H_7N_5O_2$. Calculated (%): C, 46.83; H, 3.41; N, 34.15. IR, ν/cm^{-1}: 1675 (C=O), the absorption band of the azide group is absent. ^{1}H NMR, δ: 7.15 (t, 1 H, H arom., J = 7.3 Hz); 7.35 (m, 2 H, H arom.); 7.80 (d, 2 H, H arom., J = 8.1 Hz); 10.75 (s, 1 H, NH). MS, m/z: 205 $[M]^+$.

***N*(2),5-Diphenyl-1,3,4-oxadiazole-2-carboxamide (11a).** Benzoic hydrazide (0.27 g, 2 mmol) was added to a solution of carbamoylhydroxymoyl chloride **2a** (0.2 g, 1 mmol) in AcOEt (10 mL). The mixture was kept for 20 h, the solvent was distilled off on a rotary evaporator, and the residue was recrystallized from EtOH. The yield was 0.12 g (44%), m.p. 191—193 °C. Found (%): C, 68.10; H, 4.20; N, 15.35. $C_{15}H_{11}N_3O_2$. Calculated (%): C, 67.92; H, 4.15; N, 15.85. ^{1}H NMR, δ: 7.15 (t, 1 H, H arom., J = 7.3 Hz); 7.35 (m, 2 H, H arom.); 7.65 (m, 3 H, H arom.); 7.82 (m, 2 H, H arom.); 8.10 (m, 2 H, H arom.); 11.10 (s, 1 H, NH). MS, m/z: 265 $[M]^+$.

***N*(2)-(4-Chlorophenyl)-5-phenyl-1,3,4-oxadiazole-2-carboxamide (11b)** was prepared analogously to compound **11a** from carbamoylhydroxymoyl chloride **2f**. The yield was 0.11 g (65%), m.p. 173—175 °C. Found (%): C, 60.18; H, 3.45; Cl, 11.89; N, 14.15. $C_{15}H_{10}ClN_3O_2$. Calculated (%): C, 60.11; H, 3.36; Cl, 11.83; N, 14.02. ^{1}H NMR, δ: 7.30—7.60 (m, 5 H, H arom.); 7.70—7.90 (m, 4 H, H arom.); 10.50 (s, 1 H, NH). MS, m/z: 299 $[M]^+$.

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