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Synthesis and Reactivity of Carbohydroximoyl Azides: I. Aliphatic and Aromatic Carbohydroximoyl Azides and 5-Substituted 1-Hydroxytetrazoles Based Thereon*

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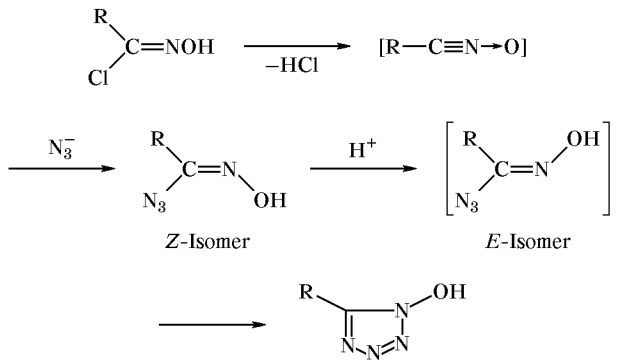
Abstract—Chlorination of 1-hydroxyiminopentane gave 1-chloro-1-nitrosopentane which reacted with sodium azide in DMF to form pentanohydroximoyl azide. The azidation of benzohydroximoyl chlorides was always accompanied by decomposition to benzonitriles. Treatment of carbohydroximoyl azides in ether with gaseous hydrogen chloride afforded 5-butyl- and 5-aryl-1-hydroxytetrazoles which reacted with acetic anhydride to form the corresponding acetates.

It was recently reported that *N*-hydroxytetrazoles are effective acylation catalysts in the synthesis of peptides [1]. However, these compounds are very few in number. Derivatives of 1-hydroxytetrazole with heterocyclic and especially aliphatic substituents have been studied very poorly. The most studied are 1-hydroxytetrazoles having an aromatic substituent in position 5. Presumably, this is the result of relatively easy preparation and stability of precursors of 5-aryl-1-hydroxytetrazoles, benzohydroximoyl oximes, as well as of accessibility of starting compounds.

Carbohydroximoyl azides are usually synthesized by reaction of alkali metal azides with nitrile oxides generated from carbohydroximoyl chlorides. The structure of the products, whether they are carbohydroximoyl azides or 1-hydroxytetrazoles, have long been the matter of discussion [2, 3]. Only in 1960s, rigorous proofs for the carbohydroximoyl structute were reported for the first time [4–6]. It was shown that carbohydroximoyl azides are fairly stable compounds which do not undergo spontaneous cyclization to 1-hydroxytetrazoles [4]. A possible reason is electron-acceptor character of the OH group which hinders π-electron density transfer from the C=N bond to the azide nitrogen atom, thus preventing the cyclization [7]. Later on, Plenkiewicz [8, 9] found that aromatic carbohydroximoyl azides can readily be converted into 1-acyloxytetrazoles by the action of acyl chlorides in an inert solvent or without a solvent. The cyclyzation was also observed on treatment of carbohydroximoyl azides with trifluoroacetic acid; however, in this case the isomerization rate was lower by a factor of 30. It was presumed that the cyclization is initiated by protonation of the azide nitrogen atom attached to carbon (which has the greatest electron density) [9]. Dignam *et al.* [10] studied the ^{1}H NMR spectra of isomeric oximes and showed that reactions of carbohydroximoyl chlorides with sodium azide are stereoselective: Only the *Z*-isomers of carbohydroximoyl azides are formed (Scheme 1).

Scheme 1.



The *Z*-isomer is likely to be stabilized by formation of intramolecular hydrogen bond, and it can be stored for a relatively long time. Treatment of *Z*-isomer with gaseous hydrogen chloride in ether results in

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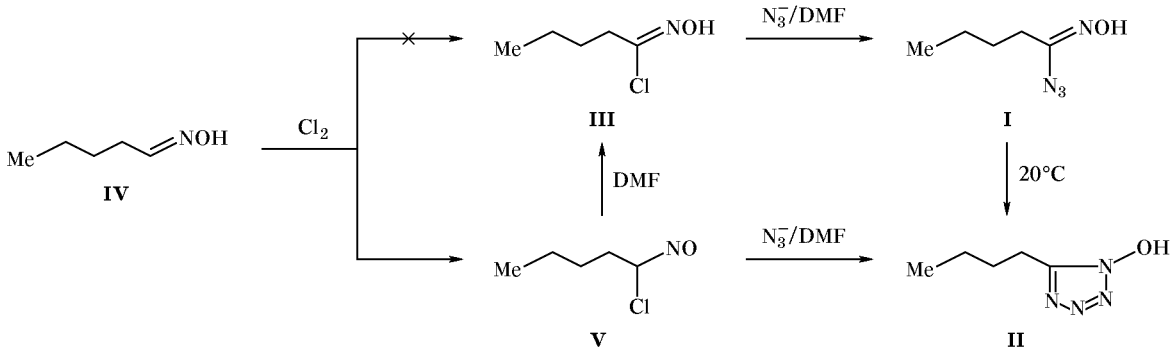
Scheme 2.



isomerization into unstable *E*-isomer which readily undergoes cyclization to 1-hydroxytetrazole.

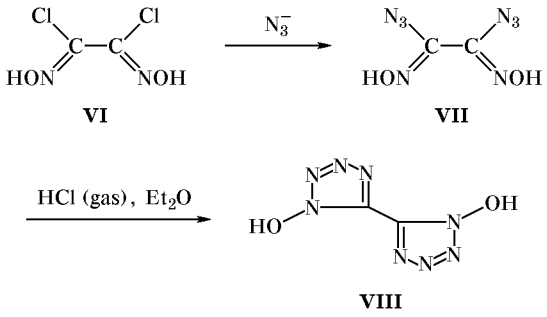
We have studied the possibility of synthesizing pentanohydroximoyl azide (**I**) and its isomerization to 5-butyl-1-hydroxytetrazole (**II**). Compound **I** was obtained by the traditional scheme including the synthesis of pentanohydroximoyl chloride (**III**) via chlorination of oxime **IV** and treatment of **III** with sodium azide (Scheme 2). The chlorination of **IV** was carried out in various solvents (diethyl ether, methylene chloride, dilute hydrochloric acid, etc.) at –8 to –10°C. It is generally assumed that halogenation of oximes involves intermediate formation of the corresponding 1-chloro-1-nitroso derivative which undergoes fast rearrangement into carbohydroximoyl chloride [11]. However, regardless of the solvent, the chlorination of oxime **IV** stopped at the stage of formation of nitroso chloride **V** which was stable for 24 h at room temperature (no spontaneous isomerization to carbohydroximoyl chloride **V** occurred). The ^{1}H NMR spectrum of the chlorination product contained signals at δ 0.9 (3H, CH_3), 1.5 (4H, CH_2), 2.4 (2H, CH_2), and 9.9 ppm (1H, CH). On prolonged storage of product **V** we observed evolution of HCl and formation of a mixture of compounds.

On the other hand, heating of a solution of **V** in ether containing a small amount of a basic solvent (DMF) resulted in rearrangement to chloride **III**, presumably through intermediate α-chloro-α-nitrosocarbanion. The signal at δ 9.9 ppm, corresponding to the CH proton, disappeared from the ^{1}H NMR spectrum, and a new signal appeared at δ 10.9 ppm, which belongs to the NOH proton. We succeeded in obtaining carbohydroximoyl azide **I** in more than 70% yield by treatment of chloronitrosopentane **V** with sodium azide directly in dimethylformamide. The use of methanol instead of DMF also favored isomerization of **V**, but in this case the main process was its decomposition.

The structure of azide **I** is confirmed by the presence in its IR spectrum of a strong absorption band at 2120 cm^{-1} due to azido group. In the ^{1}H NMR spectrum we observed a signal at δ 9.4 ppm due to proton of the hydroxyimino group. Azide **I** is fairly stable in such organic solvents as diethyl ether, DMF, and acetone (the azide band in the IR spectrum of a solution of **I** in DMF is retained at least for a weak), but it decomposes in chlorinated hydrocarbons. After isolation from solution, azide **I** undergoes rearrangement into 5-butyl-1-hydroxytetrazole (**II**) in a few minutes; presumably, this process is promoted by acid impurities formed by partial decomposition of **I**. This fact provides an additional support to the acid catalysis of the rearrangement of carbohydroximoyl azides into 1-hydroxytetrazoles, for basic solvents (such as DMF) stabilize the azide structure.

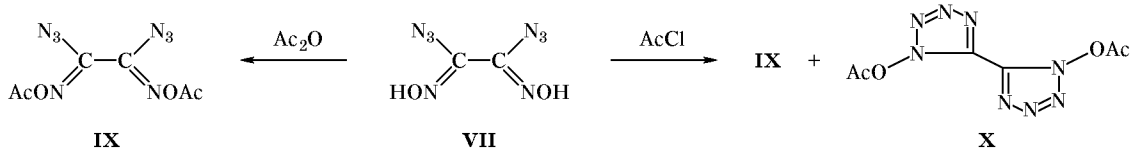
The effect of the solvent is clearly observed in the synthesis of oxalohydroximoyl diazide (**VII**) from dichloride **VI** and NaN_3 (Scheme 3).

Scheme 3.



When the reaction was carried out in acetone or acetonitrile, the yield of **VII** was 50%; in aqueous ethanol 76% of **VII** was obtained; whereas with DMF as solvent, the yield of **VII** was as high as 97%. Diazide **VII** is much more stable than azide **I**; the former can be stored for a long time without a solvent

Scheme 4.



on exposure to air (only slight evolution of nitrogen oxides was observed). However, accumulation of nitrogen oxides in a closed vessel could lead to uncontrollable decomposition of compound **VII**. Like pentanohydroximoyl azide (**I**), oxalohydroximoyl diazide (**VII**) undergoes smooth isomerization to bitetrazole **VIII** on treatment of its solution in ether with gaseous hydrogen chloride.

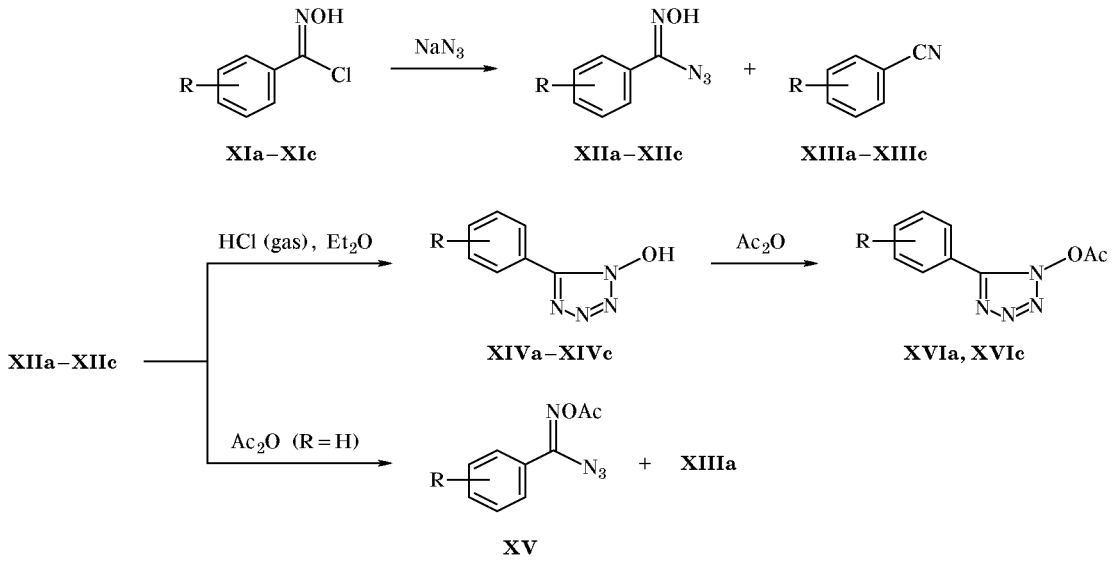
It was also interesting to examine acylation of **VII**. With acetic anhydride as acylating agent we obtained the corresponding *N*,*N*′-diacetoxy derivative **IX**. The reaction with acetyl chloride gave 1,1′-diacetoxy-5,5′-bitetrazole (**X**) and a small amount of compound **IX** (Scheme 4). In the reaction of **VII** with acetyl chloride in the presence of pyridine diacetate **IX** was formed as the sole product. Using thin-layer chromatography, we have found that the acylation with acetyl chloride initially promotes isomerization of **VII** into **VIII**, and the latter is then acylated with excess AcCl.

It is known that aromatic carbohydroximoyl azides are formed in high yields (80–90%) from *para*-substituted benzohydroximoyl chlorides in methanol [9]. We applied the same conditions to azidation of *m*-nitrobenzohydroximoyl chloride (**XIb**) and obtained about 80% of the corresponding azide **XIIb**. However, after storage of product **XIIb** for 1 h, we observed (TLC) appearance of a new compound, *m*-nitrobenzonitrile (**XIIIb**); treatment of the latter with hydroxylamine gave *m*-nitrobenzamide oxime. The decomposition of azide **XIIb** was complete in 2 days. These data led us to presume that the synthesis of carbohydroximoyl azides is always accompanied by their partial decomposition to the corresponding nitriles. In fact, when aqueous alcohol was replaced by DMF, we obtained *m*-nitrobenzonitrile (**XIIIb**) in almost quantitative yield.

We also tried to reproduce the known procedure for preparation of benzohydroximoyl azide (**XIIa**) [12]. In aqueous ethanol the yield of **XIIa** was no more than 50%, but in DMF we obtained 75–80% of the target product. In both cases benzonitrile (**XIIIa**) was formed as by-product (Scheme 5).

By azidation of *p*-isopropylbenzohydroximoyl chloride (**XIc**) in aqueous alcohol we obtained 70–72% of *p*-isopropylbenzohydroximoyl azide (**XIIc**). When DMF was used as solvent, we failed to isolate

Scheme 5.



R = H (**a**), *m*-NO_2 (**b**), *p*-*i*-Pr (**c**).

azide **XIIc**, and the major product was *p*-isopropylbenzonitrile (**XIIIc**).

Decomposition of benzohydroximoyl azides **XII** also occurred on storage in a closed vessel. The rate of decomposition depends on the substituent in the benzene ring. Unsubstituted azide **XIIa** vigorously decomposes with evolution of nitrogen oxides and formation of a mixture of products, the major of which (according to the TLC data) is benzonitrile (**XIIIa**). The latter was isolated as benzamide oxime by treatment of the decomposition product mixture with hydroxylamine. The complete decomposition of azide **XIIb** takes 2 days, and the yield of nitrile **XIIIb** is almost quantitative. The process can be accelerated by raising the temperature or dissolving in DMF or acetonitrile. The UV spectrum of a freshly prepared solution of *m*-nitrobenzohydroximoyl azide (**XIIb**) in acetonitrile contains an absorption maximum at λ 228 nm (ε 17200 l mol^{-1} cm^{-1}). On storage of the solution, the spectral pattern changes: a maximum appears at λ 255 nm (ε 11300 l mol^{-1} cm^{-1}), which is typical of *m*-nitrobenzonitrile. After 12 h, the latter maximum becomes the only present in the spectrum. Moreover, determination of the melting point of azide **XIIb** gave a value of 114–115°C which coincides with the melting point of *m*-nitrobenzonitrile [13]. For the same reason, we failed to determine the melting point and obtain satisfactory elemental analysis of *p*-isopropylbenzohydroximoyl azide (**XIIc**). Therefore, azides **XIIb** and **XIIc** were transferred into ether immediately after preparation and were treated with gaseous hydrogen chloride to obtain the corresponding 1-hydroxytetrazoles **XIVb** and **XIVc** (Scheme 5).

Decomposition of individual carbohydroximoyl azides to nitriles at 18–20°C was observed previously for benzohydroximoyl [3] and 2,4,6-trimethylbenzohydroximoyl azides [6]. Benzohydroximoyl azide (**XIIa**) showed a similar behavior on attempted acylation with acetic anhydride or acetyl chloride. With acetic anhydride as acylating agent we obtained only 10% of the corresponding acetate **XV**, whereas the major product was benzonitrile. This is consistent with the known data [13], according to which nitriles are formed on dissolution of carbohydroximoyl azides in acetic acid. The acylation with acetyl chloride gave 1-acetoxy-5-phenyltetrazole (**XVI**), presumably due to liberation of hydrogen chloride during the process. These data contradict the results reported in [9] for acylation of *para*-substituted benzohydroximoyl chlorides with benzoyl chloride, which gave the corresponding benzoates in high yield [9]. 1-Hydroxy-5-aryltetrazoles are smoothly acylated with acetic anhydride, yielding acetates **XVI** (Scheme 5).

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Perkin–Elmer R12 spectrometer (60 MHz) using HMDS as internal reference. The IR spectra were obtained on a UR-20 instrument from thin films on NaCl support. The molecular weights were determined by reverse ebullioscopy in acetonitrile.

1-Hydroxyiminopentane (IV). To a solution of 52 g (0.75 mol) of hydroxylamine hydrochloride in 70 ml of water we added with stirring below 10°C first 24 g (0.29 mol) of freshly distilled pentanal and then a solution of 30 g (0.75 mol) of NaOH in 40 ml of water. The mixture was kept for 20 h, and the precipitate was filtered off and dried in air. Yield 26 g (93%), mp 50–52°C [13] (from hexane). IR spectrum, ν, cm^{-1}: 3264, 2960, 2944, 2928, 2872, 1664, 1460, 928. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.88 t (3H, CH_3), 1.40 m (6H, CH_2), 6.60 t (1H, CH), 9.85 s (1H, NOH).

Chlorination of 1-hydroxyiminopentane. *a*. A stream of chlorine was passed through a solution of oxime **IV** in organic solvent (diethyl ether or methylene chloride) at such a rate that the temperature did not exceed –8°C. The reaction was assumed to be complete when heat no longer evolved and the solution turned bright green. The mixture was washed with water until pH 4–5 of the washings and was dried over anhydrous $MgSO_4$. Removal of the solvent gave more than 87% of product **V** as a greenish–blue liquid, n_D^{18} 1.4580. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.90 t (3H, CH_3), 1.50 m (4H, CH_2), 2.40 m (2H, CH_2), 9.90 s (1H, CH).

b. A stream of chlorine was passed through a suspension of oxime **IV** in 3% hydrochloric acid cooled to 0°C until exothermic reaction was over (the temperature was maintained at 2–5°C). The mixture was extracted with ether, and the extract was treated as described above in *a* to obtain compound **V** in ~90% yield. Compound **V** was brought into reaction with sodium azide without additional purification.

Reaction of 1-chloro-1-nitrosopentane (V) with sodium azide. To a solution of 3.5 g (0.026 mol) of compound **V** in 20 ml of DMF we added with stirring at 18–20°C 2.0 g (0.03 mol) of sodium azide. A slight exothermic effect was observed. The mixture was kept until it showed a negative test for halogen (Beilstein test) and was poured into water. The aqueous phase was treated with ether, and the ether extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated. We isolated 2.5 g (57%) of compound **I** as a light yellow liquid. After 15 min, the product

began to crystallize; the crystallization was complete in 2 h, yielding compound **II**.

Oxalohydroximoyl diazide (VII). *a*. To a solution of 1 g (6.3 mmol) of oxalohydroximoyl dichloride (**VI**) in 60 ml of acetonitrile we added with stirring at 20°C 1.06 g (16.3 mmol) of sodium azide. The mixture was heated with stirring to the boiling point and was refluxed for 30 min. It was then cooled and poured into 200 ml of water. The resulting mixture was left overnight, and the precipitate was filtered off and dried in air. Yield 0.5 g.

b. The procedure was the same as in *a*, but DMF (10 ml) was used as solvent. Yield of product **VII** 1.1 g (97%). Samples of **VII** obtained as described in *a* and *b* showed no depression of the melting point.

1,1′-Dihydroxy-5,5′-bitetrazole (VIII). Gaseous hydrogen chloride was passed through a solution of 5 g (0.0294 mol) of diazide **VII** in 250 ml of ether, maintained at 18–20°C, until the initial compound disappeared (TLC). The solvent was removed under reduced pressure. Yield of **VIII** 4.65 g.

***O,O′*-Diacetyloxalohydroximoyl diazide (IX).** A mixture of 1.7 g (0.01 mol) of diazide **VII** and 35 ml of acetic anhydride was heated to 90°C, kept for 1 h at that temperature, cooled, and poured into 250 ml of water. The precipitate was filtered off. Yield 1.8 g.

1,1′-Diacetoxy-5,5′-bitetrazole (X). A mixture of 1 g (5.8 mmol) of diazide **VII** and 0.91 g (11.6 mol) of acetyl chloride in 100 ml of benzene and 50 ml of ether was heated to the boiling point and was refluxed for 8 h. It was then cooled, and the solvent was removed under reduced pressure to obtain 1.04 g of compound **X**. From the mother liquor we isolated (after recrystallization) 0.2 g (17%) of compound **IX** which showed no depression of the melting point on mixing with a sample of **IX** obtained as described above.

Yields, melting points, analytical data, and IR and ^{1}H NMR spectra of compounds **I**, **II**, **VII**–**X**, **XIIa**, **XIVa**–**XIVc**, **XV**, **XVIa**, and **XVIc**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %			*M*	
			C	H	N		C	H	N	found	calcd.
I	57	Liquid	42.10	6.87	38.91	$C_5H_{10}N_4O$	42.25	7.04	39.44	–	142
II	67	92–93 (CCl_4)	41.91	6.72	39.10	$C_5H_{10}N_4O$	42.25	7.04	39.44	–	142
VII	46	159 (decomp.)	13.84	0.95	66.30	$C_2H_2N_8O_2$	14.11	1.17	65.88	174	170
VIII	83	210 (decomp.)	11.70	3.00	55.00	$C_2H_2N_2O_2 \cdot 2H_20$	11.65	2.92	54.35	207	206
IX	71	122 (*i*-PrOH)	28.10	2.00	44.62	$C_6H_6N_8O_4$	28.35	2.36	44.09	257	254
X	70	147 (heptane)	28.81	2.53	44.15	$C_6H_6N_8O_4$	28.35	2.36	44.09	242	254
XIIa	72	120 (heptane)	52.00	3.58	34.41	$C_7H_6N_4O$	51.85	3.70	34.57	160	162
XIVa	60	145 (H_2O)	52.00	3.53	34.71	$C_7H_6N_4O$	51.85	5.90	34.57	163	162
XIVb	50	100 (H_2O)	36.76	2.83	30.82	$C_7H_5N_5O_3 \cdot H_2O$	37.30	4.65	31.10	–	225
XIVc	20	147–148 (benzene)	58.80	5.90	27.45	$C_{10}H_8N_4O$	58.46	3.59	27.23	–	203
XV	10	57–58 (aq. EtOH)	54.20	4.65	26.95	$C_9H_8N_4O_2$	52.94	5.58	27.45	–	204
XVIa	80	54–55 (hexane)	52.45	3.59	27.85	$C_9H_8N_4O_2$	52.94	3.45	27.45	–	204
XVIc	75	59–60 (hexane)	58.22	5.58	22.75	$C_{12}H_{14}N_4O_2$	58.54	5.70	22.76	–	246

Table. (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm
I	3200, 2960, 2120, 1464, 1288, 1096, 980	9.4 s (1H, NOH), 2.1 M (2H, CH_2), 1.4 m (4H, CH_2), 0.9 t (3H, CH_3)
II	2960, 1456, 1344, 1336, 1304, 1272	9.7 s (1H, NOH), 2.85 m (2H, CH_2), 1.55 m (4H, CH_2), 0.90 t (3H, CH_3)
VII	3180, 2200, 2170, 2155, 1630, 1365, 1065, 1020, 920	12.3 d (2H, NOH)
VIII	3500–3000, 1415, 1380, 1280, 1200, 1125, 1015, 800	7.9 s (2H, OH)
IX	2170, 2150, 1790, 1365, 1290, 1070, 1045, 1005, 955, 905	2.27 s (6H, CH_3)
X	1860, 1435, 1370, 1270, 1190, 1155, 1110, 1045, 1010, 985	2.75 s (6H, CH_3)
XIIa	3184, 2136, 2088, 1632, 1456, 1328, 1016, 948	7.65 m (2H, H_{arom}), 7.25 m (3H, H_{arom}) 10.55 s (1H, NOH)
XIVa	–	11.1 s (1H, OH), 8.85 s (1H, OH), 8.1 m (3H, H_{arom}), 8.05 m (3H, H_{arom}), 7.62 m (2H, H_{arom}), 7.55 m (2H, H_{arom})
XIVb	3296, 1856, 1520, 1372, 1352, 976	8.9 s (1H, H_{arom}), 8.45 t (2H, H_{arom}), 7.9 t (1H, H_{arom}), 6.6 br (3H, NOH, H_2O)
XIVc	2960, 1616, 1476, 1320, 1252, 840	10.2 s (1H, OH), 8.15 d (2H, H_{arom}), 7.45 d (2H, H_{arom})
XV	2184, 2120, 1776, 1592, 1556	7.90 m (2H, H_{arom}), 7.55 m (3H, H_{arom}), 2.2 s (3H, CH_3)
XVIa	3426, 1956, 1828, 1552, 1472, 1208, 1132, 932	7.9 m (2H, H_{arom}), 7.55 m (3H, H_{arom}), 2.5 s (3H, CH_3)
XVIc	–	7.95 m (2H, H_{arom}), 7.45 m (2H, H_{arom}), 2.6 s (3H, CH_3)

The chlorination of benzaldehyde oximes was performed by the procedure described above for pentanal oxime.

Benzohydroximoyl chloride (XIa). mp 45–47°C. ^1H NMR spectrum (acetone-d_6), δ, ppm: 7.80 m (3H, H_{arom}), 7.31 m (2H, H_{arom}), 11.30 s (1H, NOH).

***m*-Nitrobenzohydroximoyl chloride (XIb).** mp 101°C (from hexane). ^1H NMR spectrum (acetone-d_6), δ, ppm: 8.50 d (1H, H_{arom}), 8.15 m (2H, H_{arom}), 7.60 q (1H, H_{arom}), 11.70 s (1H, NOH).

***p*-Isopropylbenzohydroximoyl chloride (XIc)**. Colorless liquid. ^1H NMR spectrum (acetone-d_6), δ, ppm: 7.75 d (2H, H_{arom}), 7.20 d (2H, H_{arom}), 2.9 s (1H, CH), 1.25 d (6H, CH_3).

Compounds **XIa**–**XIc** are unstable, and they were brought into reaction with sodium azide immediately after preparation.

Benzohydroximoyl azide (XIIa). To a solution of 12 g (7.7 mmol) of benzohydroximoyl chloride (**XIa**) in 30 ml of DMF (or aqueous ethanol) at 18–20°C we added 6 g (9.2 mmol) of sodium azide, and the mixture was stirred until negative Beilstein test for halogen. The mixture was poured into 100 ml of water, and the precipitate was filtered off and dried in air. Yield 9 g.

***m*-Nitrobenzohydroximoyl azide (XIIb).** To a solution of 8 g (0.04 mol) of compound **XIb** in 50 ml of aqueous ethanol we added at 18–20°C 5 g (0.07 mol) of sodium azide, and the mixture was stirred until negative Beilstein test for halogen. The mixture was poured into 150 ml of water, and the precipitate was filtered off and dried in air. Yield 0.7 g. IR spectrum, ν, cm^{-1}: 3864, 2144, 1616, 1525, 1336. ^1H NMR spectrum (acetone-d_6), δ, ppm: 8.95 s (1H, H_{arom}), 8.45 t (2H, H_{arom}), 7.8 t (1H, H_{arom}), 10.9 s (1H, NOH). UV spectrum: λ_{max} 228 nm, ε 17 200 l mol^{-1} cm^{-1}.

***m*-Nitrobenzonitrile (XIIIb).** To a solution of 1 g (0.005 mol) of chloride **XIb** in 15 ml of DMF at 18–20°C we added 0.7 g (0.01 mol) of sodium azide, and the mixture was stirred until negative Beilstein test for halogen. The mixture was poured into 100 ml of water, and the precipitate was filtered off and dried in air. Yield 0.5 g. mp 114–116°C (from hexane). IR spectrum, ν, cm^{-1}: 3840, 1528, 1368, 1352. ^1H NMR spectrum (acetone-d_6), δ, ppm: 8.55 d (1H, H_{arom}),

8.2 m (2H, H_{arom}), 7.8 m (1H, H_{arom}). UV spectrum: λ_{max} 255 nm, ε 11300 l mol^{-1} cm^{-1}. Found, %: C 56.35; H 2.67; N 19.65. $C_7H_4N_2O_2$. Calculated, %: C 56.75; H 2.70; N 19.20.

***m*-Nitrobenzamide oxime.** To a suspension of 1 g (0.015 mol) of hydroxylamine hydrochloride in 20 ml of ethanol we added a solution of 0.6 g (0.015 mol) of sodium hydroxide in a minimal amount of water, maintaining the temperature below 10°C. The precipitate was filtered off, 0.1 g (0.007 mol) of *m*-nitrobenzonitrile (see above) was added, and the mixture was kept at room temperature until the initial nitrile disappeared (TLC). The mixture was evaporated under reduced pressure, and the solid residue was treated with acetone. Removal of the solvent gave 0.07 g (58%) of a slightly colored crystalline product with mp 146–147°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 9.2 s (1H, NOH), 8.5 m (1H, $_{arom}$), 8.1 m (2H, H_{arom}), 7.6 m (1H, H_{arom}), 5.6 s (2H, NH_2). Found, %: C 46.83; H 3.19; N 22.9. $C_7H_7N_3O_3$. Calculated, %: C 46.40; H 3.86; N 23.20.

***p*-Isopropylbenzohydroximoyl azide (XIIIc).** The reaction was carried out as described above for compound **XIIIb** using 2 g (0.01 mol) of chloride **XIa** and 1 g (0.015 mol) of sodium azide in 15 ml of aqueous ethanol. Yield 1.5 g (60%). IR spectrum, ν, cm^{-1}: 2968, 2336, 2320, 2224, 2024, 1608, 1544, 1504, 1492, 1464, 1440, 1416. Product **XIIIc** was unstable, and we failed to analyze it. Immediately after preparation, it was dissolved in ether and subjected to isomerization by passing gaseous HCl.

Isomerization of benzohydroximoyl azides into 1-hydroxy-5-aryltetrazoles (*general procedure*). Gaseous hydrogen chloride was passed through a solution of azide **XII** in ether until the initial compound disappeared (TLC). The mixture was evaporated, and the solid residue was recrystallized from appropriate solvent.

***O*-Acetylbenzohydroximoyl azide (XV).** A solution of 1 g (0.006 mol) of azide **XII** in 10 ml of acetic anhydride was stirred at 18–20°C until the initial compound disappeared (TLC). Excess acetic anhydride and volatile components were removed under reduced pressure. Yield 0.12 g.

Acylation of 1-hydroxytetrazoles (*general procedure*). A solution of 0.1 mol of 1-hydroxytetrazole **XIV** in 15 ml of acetic anhydride was stirred at 18–20°C until the initial compound disappeared completely. Excess acetic anhydride was distilled off, and products **XVIa** and **XVIc** were recrystallized from hexane (see table).

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