The study of reactions of α-chlorocinnamonitriles with hydroxylamine

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The *E*-isomers of α-chlorocinnamonitriles react with hydroxylamine to give a mixture of isomeric aminoisoxazoles, while the *Z*-isomers yield 3-aryl-2-chloroacrylamide oximes.

Key words: 3-aryl-2-chloroacrylamide oximes, aminoisoxazoles, α-chlorocinnamonitriles, hydroxylamine, catalytic olefination.

α-Chlorocinnamonitriles **1**, which are easily obtained by earlier developed catalytic olefination,[1] are convenient starting materials for the synthesis of various heterocyclic compounds.[2] In the present work, we studied reactions of nitriles **1** with hydroxylamine. Since NH_2OH contains two different nucleophilic centers, the resulting isomeric adducts (in particular, aminoisoxazoles) can contain the amino group in position 3 or 5.

Isoxazoles are valuable organic compounds widely used in medicinal chemistry.[3,4] Known routes to 5-amino-3-arylisoxazoles involve reactions of hydroxylamine with α-cyano ketones.[5—7] The reactions of olefins with NOCl followed by treatment with cyanides should also be mentioned; however, this method is not regioselective for nonsymmetrical olefins.[8] Another method for the synthesis of 5-amino-3-arylisoxazoles is based on reactions of α-bromo ketoximes with sodium cyanide in aqueous methanol.[9] A mixture of isomeric aminoisoxazoles was obtained earlier[10] in reactions of 3-arylprop-2-ynenitriles and β-bromocinnamonitriles with hydroxylamine.

The dual reactivity of hydroxylamine is exhibited in its reactions with α-bromo-β-glycosyl-α,β-unsaturated nitriles and ketones to give derivatives of isoxazole or isoxazoline, respectively. The site of primary nucleophilic attack can be located from the positions of substituents in the resulting heterocycle. In addition to an activated double bond, the N atom of hydroxylamine is usually more nucleophilic and the major reaction products are the corresponding 5-aminoisoxazoles. Interestingly, the use of *N*-hydroxyurea selectively leads to isomeric 3-aminoisoxazole.[11—13]

Aminoisoxazoles containing a furan fragment were obtained by reactions of *N*-hydroxyurea with α-halo-β-(2-furyl)acrylonitrile in the presence of sodium ethoxide. The use of *N*-hydroxyurea increased the yield compared to hydroxylamine but had no effect on the regiochemistry of the reaction. The reaction can be complicated by side processes such as nucleophilic addition of the ethoxy group at the double bond followed by elimination of the halogen.[14]

In the present work, we studied reactions of hydroxylamine with some α-chlorocinnamonitriles **1a—g** prepared by catalytic olefination.

2-Chloro-3-(4-chlorophenyl)acrylonitrile (**1a**) as a mixture of two diastereomers (*E* : *Z* = 4 : 1) was chosen as a model compound. It was found that in the reaction of compound **1a** with $NH_2OH \cdot HCl$ in boiling ethanol in the presence of potassium carbonate, the diastereomeric nitriles behave differently (TLC data). It turned out that the *Z*-isomer reacts significantly more rapidly than the *E*-isomer, yielding several products.

In subsequent reactions with the individual isomers of the model nitrile (which were separated off by column chromatography), we found that the *Z*-isomer reacts with hydroxylamine even at room temperature within 20 to 30 min to give a single product, namely, earlier unknown 2-chloro-3-(4-chlorophenyl)prop-2-enamide oxime (**2a**). This compound is formed when hydroxylamine adds to the nitrile fragment of the substrate. The reaction proved to be of the general character and the corresponding amides of hydroximic acids were also obtained in high yields from other *Z*-isomeric nitriles (Scheme 1, Table 1).

It should be noted that the resulting products undergo no subsequent *in situ* transformations: their intramolecular cyclization into 3-amino-5-arylisoxazoles did not occur even when the reaction mixture was refluxed for a

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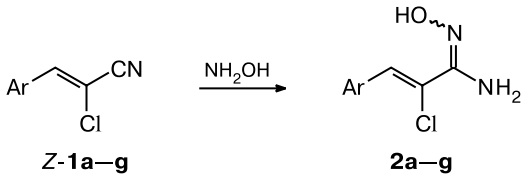
Scheme 1



Z-**1a—g** **2a—g**

Table 1. Synthesis of 3-aryl-2-chloroacrylamide oximes

Compound	Ar	Yield (%)
2a	4-Cl-C_6H_4	79
2b	2-Naphthyl	74
2c	4-Me-C_6H_4	84
2d	4-MeO-C_6H_4	82
2e	4-O_2N-C_6H	67
2f	4-Br-C_6H_4	81
2g	4-Me_2N-C_6H_4	63

long period of time. Reactions of hydroxylamine with nitriles leading to the corresponding amide oximes have been documented;[15] at the same time, reactions of hydroxylamine and its derivatives with acrylonitriles usually occur at the activated double bond rather than the cyano group.[16]

The *E*-isomers of α-chlorocinnamonitriles do not react with hydroxylamine without refluxing. The initial Michael attack of hydroxylamine on the substrate is followed by cyclization of the resulting adduct to give a mixture of the corresponding 5-amino-3-arylisoxazoles **3a—g** and 3-amino-5-arylisoxazoles **4a—g** (Scheme 2, Table 2).

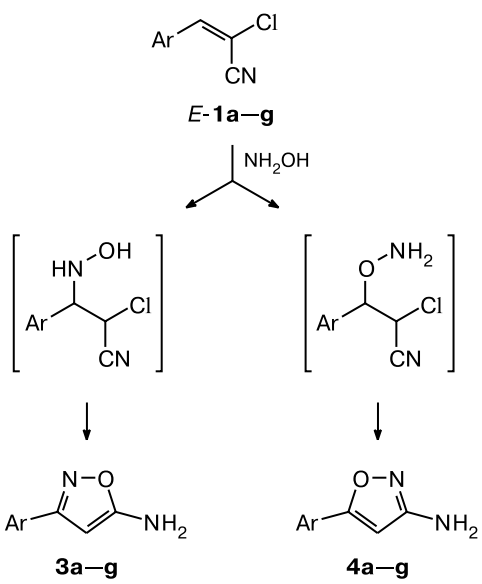
It is known that the selectivity of a chemical reaction is determined by a combination of steric and electronic factors. To compare the reactivities of the electrophilic sites in the starting nitriles and to explain the observed chemiselectivity, we performed quantum-mechanical calculations at the MP2 level for the *E*- and *Z*-isomers. The calculated LUMO coefficients and charges at the C and N atoms in the fragment of the unsaturated nitrile are given in Table 3.

Both the orbital coefficient and the charge at the C(3) atom for the *Z*-isomer are higher than those for the

Table 2. Yields and ratios of isomeric aminoarylisoxazoles

Products	Ar	Total yield of **3** and **4** (%)	Ratio of **3** : **4**
3a, **4a**	4-Cl-C_6H_4	86	2 : 1
3b, **4b**	2-Naphthyl	75	1.6 : 1
3c, **4c**	4-Me-C_6H_4	64	1 : 1.2
3d, **4d**	4-MeO-C_6H_4	73	1 : 1.1
3e, **4e**	4-O_2N-C_6H_4	52	1 : 1.5
3f, **4f**	4-Br-C_6H_4	80	1.8 : 1
3g, **4g**	4-Me_2N-C_6H_4	56	1.1 : 1

Scheme 2



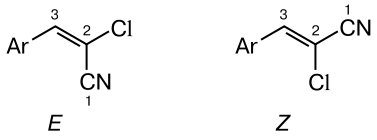
E-**1a—g** **3a—g** **4a—g**

E-isomer. At the same time, the charge at the cyano C atom is higher for the *E*-isomer; however, its orbital coefficient is somewhat lower than that for the *Z*-isomer. If the reaction were controlled by orbital interactions, a predominant attack of the nucleophile on the double bond could be expected for either isomer. The charge control would make an attack on the cyano group preferred and the *E*-isomer should be more reactive. The fact that the calculated and experimental data do not correlate can suggest that the reactions of isomeric nitriles are controlled not only by orbital or charge interactions. Apparently, the steric accessibility of a specific reactive site is

Table 3. MP2-calculated charges and LUMO coefficients

Isomer	C(3)		C(2)		C(1)		N	
	Charge	LUMO	Charge	LUMO	Charge	LUMO	Charge	LUMO
E-**1a**	0.086	0.317	−0.111	0.291	0.193	0.036	−0.277	0.107
Z-**1a**	0.087	0.338	−0.098	0.293	0.173	0.042	−0.274	0.128

substantial in this case. In the *Z*-isomer, the more reactive cyano group is not shielded by the aryl substituent and hydroxylamine attacks the site bearing the highest positive charge to give amide oximes. In the *E*-isomer, the cyano group is shielded by the aromatic substituent and hydroxylamine reacts with the less reactive but more accessible double bond to yield isomeric isoxazoles.



E *Z*

Thus, we studied the reactions of α-chlorocinnamonitriles with hydroxylamine and demonstrated that the *Z*-isomers react to give amides of hydroximic acids, while the *E*-isomers yield mixtures of isomeric isoxazoles. We developed the methods for the preparation of earlier unknown 3-aryl-2-chloroprop-2-enamide oximes and new 3-amino-5-arylisoxazoles, which can find wide use in organic synthesis. Based on our quantum-chemical data, we discussed possible reasons for the different reactivities of the *Z*- and *E*-isomers.

Experimental

Quantum-chemical calculations were performed with the PRIRODA program.[17,18] The cc-pVDZm basis set was used. This basis set was derived from Dunning´s well known correlation consistent basis set cc-pVDZ with retention of the number of basis functions but a different contraction scheme: {5,6/2} for H, {8,9,10/5,6/2} for C, N, and O, and {11,12,13,14/8,9,10/2} for Cl. The Mulliken population analysis was used.

IR spectra were recorded on a UR-20 spectrophotometer (Nujol). ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz for ^{1}H and ^{13}C, respectively) in $CDCl_3$ and DMSO-d_6 with Me_4Si as the internal standard. TLC analysis was carried out on Merck 60 F_{254} plates. Column chromatography was performed on Merck silica gel (63—200 mesh).

Compounds **1a—g** were prepared as described earlier.[1]

Synthesis of 3-aryl-2-chloroacrylamide oximes (2) (general procedure). A solution of the *Z*-isomer of α-chlorocinnamonitrile (1 mmol), hydroxylamine hydrochloride (0.14 g, 2 mmol), and anhydrous potassium carbonate (0.28 g, 2 mmol) in ethanol (5 mL) was stirred at room temperature for 1 h. Then water (20 mL) was added. The product was filtered off, washed with water (5 mL), and dried. When needed, the target amide can be recrystallized from ethanol.

The IR spectra of all compounds **2a—g** contain bands of NH_2 (3340—3450 cm^{-1}) and OH groups (3150—3240 cm^{-1}).

2-Chloro-3-(4-chlorophenyl)prop-2-enamide oxime (2a). The yield was 79%, colorless crystals, m.p. 120—121 °C, R_f 0.57 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 46.63; H, 3.48. $C_9H_8Cl_2N_2O$. Calculated (%): C, 46.78; H, 3.49. ^{1}H NMR (DMSO-d_6), δ: 10.12 (br.s, 1 H, OH); 7.73, 7.48 (both d, 2 H each, H arom., J = 8.6 Hz); 7.30 (s, 1 H, CH); 5.78 (br.s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 149.91 (CNH_2); 133.11, 132.91, 131.28, 128.52, 125.87, 124.88 (CCl).

2-Chloro-3-(2-naphthyl)prop-2-enamide oxime (2b). The yield was 74%, colorless crystals, m.p. 142—144 °C, R_f 0.59 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 63.35; H, 4.33. $C_{13}H_{11}ClN_2O$. Calculated (%): C, 63.29; H, 4.49. ^{1}H NMR (DMSO-d_6), δ: 10.13 (br.s, 1 H, OH); 8.26 (s, 1 H, H arom.); 7.95—7.83 (m, 4 H, H arom.); 7.55—7.51 (m, 2 H, H arom.); 7.48 (s, 1 H, CH); 5.83 (br.s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 150.02, 132.66, 132.54, 131.65, 129.17, 128.26, 127.78, 127.51, 127.00, 126.92, 126.84, 126.53, 124.44.

2-Chloro-3-(4-methylphenyl)prop-2-enamide oxime (2c). The yield was 84%, colorless crystals, m.p. 124—126 °C, R_f 0.59 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 56.91; H, 5.24. $C_{10}H_{11}ClN_2O$. Calculated (%): C, 57.01; H, 5.26. ^{1}H NMR (DMSO-d_6), δ: 10.03 (br.s, 1 H, OH); 7.25 (s, 1 H, CH); 7.62, 7.22 (both d, 2 H each, H arom., J = 8.2 Hz); 5.73 (br.s, 2 H, NH_2); 2.31 (s, 3 H, Me). ^{13}C NMR (DMSO-d_6), δ: 150.01, 138.17, 131.22, 129.54, 129.02, 126.87, 123.15, 20.93 (Me).

2-Chloro-3-(4-methoxyphenyl)prop-2-enamide oxime (2d). The yield was 82%, colorless crystals, m.p. 142—144 °C, R_f 0.49 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 52.52; H, 4.76. $C_{10}H_{11}ClN_2O_2$. Calculated (%): C, 52.99; H, 4.89. ^{1}H NMR (DMSO-d_6), δ: 9.98 (s, 1 H, OH); 7.71, 6.98 (both d, 2 H each, H arom., J = 8.8 Hz); 7.22 (s, 1 H, CH); 5.70 (br.s, 2 H, NH_2); 3.78 (s, 3 H, Me). ^{13}C NMR (DMSO-d_6), δ: 159.33, 150.11, 131.19, 126.49, 121.70, 113.89, 99.51, 55.17 (Me).

2-Chloro-3-(4-nitrophenyl)prop-2-enamide oxime (2e). The yield was 67%, yellow crystals, m.p. 186—187°C, R_f 0.52 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 45.11; H, 3.46. $C_9H_8ClN_3O_3$. Calculated (%): C, 44.74; H, 3.34. ^{1}H NMR (DMSO-d_6), δ: 10.26 (s, 1 H, OH); 8.27, 7.95 (both d, 2 H each, H arom., J = 8.8 Hz); 7.45 (s, 1 H, CH); 5.85 (br.s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 149.55, 146.54, 140.69, 130.51, 127.64, 125.18, 123.48.

3-(4-Bromophenyl)-2-chloroprop-2-enamide oxime (2f). The yield was 81%, colorless crystals, m.p. 126—128 °C, R_f 0.56 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 39.19; H, 3.12. $C_9H_8BrClN_2O$. Calculated (%): C, 39.23; H, 2.93. ^{1}H NMR (DMSO-d_6), δ: 10.12 (s, 1 H, OH); 7.63 (m, 4 H, H arom.); 7.28 (s, 1 H, CH); 5.77 (br.s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 149.76, 133.22, 131.43, 131.37, 125.83, 124.87, 121.65.

2-Chloro-3-(4-dimethylaminophenyl)prop-2-enamide oxime (2g). The yield was 63%, yellow crystals, m.p. 171—172 °C, R_f 0.44 (CH_2Cl_2—EtOAc, 2 : 1). Found (%): C, 54.50; H, 5.60. $C_{11}H_{14}ClN_3O$. Calculated (%): C, 55.12; H, 5.89. ^{1}H NMR (DMSO-d_6), δ: 9.88 (s, 1 H, OH); 7.63, 6.72 (both d, 2 H each, H arom., J = 8.8 Hz); 7.12 (s, 1 H, CH); 5.63 (br.s, 2 H, NH_2); 2.94 (s, 6 H, NMe_2). ^{13}C NMR (DMSO-d_6), δ: 150.40, 150.13, 131.01, 126.95, 121.38, 118.82, 111.50, 39.65 (NMe_2).

Synthesis of aminoarylisoxazoles 3 and 4 (general procedure). A solution of the *E*-isomer of 3-aryl-2-chloroacrylonitrile (1 mmol) and hydroxylamine hydrochloride (0.14 g, 2 mmol) in ethanol (5 mL) was mixed with a solution of KOH (0.22 g, 4 mmol) in water (1 mL). The reaction mixture was refluxed for 4 h and diluted with water (20 mL). The product was extracted with methylene chloride (3×10 mL). The solvent was removed and isomeric isoxazoles were separated off by column chromatography with CH_2Cl_2—MeCN (10 : 1) as the eluent.

The IR spectra of all compounds **3a—g** contain bands of an NH_2 group (3400—3440 cm^{-1}).

5-Amino-3-(4-chlorophenyl)isoxazole (3a). The yield was 57%, light yellow crystals, m.p. 165—166 °C (*cf.* Ref. 7: 165—167 °C), R_f 0.55 (CH_2Cl_2—MeCN, 10 : 1). ^{1}H NMR ($CDCl_3$—DMSO-d_6), δ: 7.57, 7.29 (both d, 2 H each, H arom., J = 8.8 Hz); 5.58 (s, 2 H, NH_2); 5.25 (s, 1 H, CH).

3-Amino-5-(4-chlorophenyl)isoxazole (4a). The yield was 29%, colorless crystals, m.p. 137—138 °C (*cf.* Ref. 19: 141—142 °C), R_f 0.39 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 54.71; H, 3.81. $C_9H_7ClN_2O$. Calculated (%): C, 55.54; H, 3.63. ^{1}H NMR ($CDCl_3$), δ: 7.63, 7.40 (both d, 2 H each, H arom., J = 8.6 Hz); 6.06 (s, 1 H, CH); 4.01 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 166.00, 164.64, 134.43, 129.10, 127.02, 126.40, 93.36.

5-Amino-3-(2-naphthyl)isoxazole (3b). The yield was 46%, light yellow crystals, m.p. 153—154 °C (*cf.* Ref. 9: 126—128 °C), R_f 0.55 (CH_2Cl_2—MeCN, 10 : 1). ^{1}H NMR ($CDCl_3$), δ: 8.16 (s, 1 H, H arom.); 7.83—7.92 (m, 4 H, H arom.); 7.48—7.53 (m, 2 H, H arom.); 5.56 (s, 1 H, CH); 4.59 (s, 2 H, NH_2).

3-Amino-5-(2-naphthyl)isoxazole (4b). The yield was 29%, colorless crystals, m.p. 177—178 °C, R_f 0.40 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 73.48; H, 5.07. $C_{13}H_{10}N_2O$. Calculated (%): C, 74.27; H, 4.79. ^{1}H NMR ($CDCl_3$), δ: 8.23 (s, 1 H, H arom.); 7.91—7.83 (m, 3 H, H arom.); 7.76—7.73 (m, 1 H, H arom.); 7.55—7.50 (m, 2 H, H arom.); 6.20 (s, 1 H, CH); 4.07 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 167.11, 164.65, 133.22, 132.70, 128.67, 128.50, 127.70, 127.15, 126.88, 124.91, 124.47, 122.81, 93.26.

5-Amino-3-(4-methylphenyl)isoxazole (3c). The yield was 29%, colorless crystals, m.p. 149—150 °C (*cf.* Ref. 9: 149—151 °C), R_f 0.55 (CH_2Cl_2—MeCN, 10 : 1). ^{1}H NMR ($CDCl_3$), δ: 7.62, 7.24 (both d, 2 H each, H arom., J = 8.3 Hz); 5.42 (s, 1 H, CH); 4.56 (s, 2 H, NH_2); 2.39 (s, 3 H, Me).

3-Amino-5-(4-methylphenyl)isoxazole (4c). The yield was 35%, colorless crystals, m.p. 152—153 °C, R_f 0.40 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 66.00; H, 5.84. $C_{10}H_{10}N_2O \cdot 0.5H_2O$. Calculated (%): C, 65.56; H, 6.05. ^{1}H NMR ($CDCl_3$), δ: 7.61, 7.25 (both d, 2 H each, H arom., J = 8.2 Hz); 6.04 (s, 1 H, CH); 3.99 (s, 2 H, NH_2); 2.40 (s, 3 H, Me). ^{13}C NMR (DMSO-d_6), δ: 167.25, 164.51, 139.54, 129.52, 125.16, 124.93, 92.10, 20.92.

5-Amino-3-(4-methoxyphenyl)isoxazole (3d). The yield was 35%, colorless crystals, m.p. 136—137 °C (*cf.* Ref. 9: 136—138 °C), R_f 0.44 (CH_2Cl_2—MeCN, 10 : 1). ^{1}H NMR ($CDCl_3$—DMSO-d_6), δ: 7.57, 6.85 (both d, 2 H each, H arom., J = 8.8 Hz); 5.26 (s, 1 H, CH); 5.14 (s, 2 H, NH_2); 3.75 (s, 3 H, MeO).

3-Amino-5-(4-methoxyphenyl)isoxazole (4d). The yield was 38%, colorless crystals, m.p. 176—177 °C (*cf.* Ref. 11: 171—172 °C), R_f 0.35 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 62.44; H, 5.27. $C_{10}H_{10}N_2O_2$. Calculated (%): C, 63.15; H, 5.30. ^{1}H NMR ($CDCl_3$), δ: 7.66, 6.96 (both d, 2 H each, H arom., J = 8.8 Hz); 5.97 (s, 1 H, CH); 3.99 (s, 2 H, NH_2); 3.86 (s, 3 H, MeO). ^{13}C NMR (DMSO-d_6), δ: 167.17, 164.53, 160.37, 126.87, 120.34, 114.39, 91.28, 55.26.

5-Amino-3-(4-nitrophenyl)isoxazole (3e). The yield was 21%, yellow crystals, m.p. 163—165 °C (*cf.* Ref. 9: 163—165 °C), R_f 0.40 (CH_2Cl_2—MeCN, 10 : 1). ^{1}H NMR ($CDCl_3$), δ: 8.33, 7.89 (both d, 2 H each, H arom., J = 9.0 Hz); 5.31 (s, 1 H, CH); 4.01 (s, 2 H, NH_2).

3-Amino-5-(4-nitrophenyl)isoxazole (4e). The yield was 31%, yellow crystals, m.p. 136—137 °C, R_f 0.28 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 53.08; H, 3.59. $C_9H_7N_3O_3$. Calculated (%): C, 52.69; H, 3.44. ^{1}H NMR ($CDCl_3$), δ: 8.30, 7.66 (both d, 2 H each, H arom., J = 8.8 Hz); 6.27 (s, 1 H, CH); 4.11 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 166.37, 164.59, 140.73, 129.01, 126.96, 124.30, 119.70, 92.59.

5-Amino-3-(4-bromophenyl)isoxazole (3f). The yield was 51%, colorless crystals, m.p. 164—166 °C (*cf.* Ref. 9: 164—166 °C), R_f 0.56 (CH_2Cl_2—MeCN, 10 : 1). ^{1}H NMR ($CDCl_3$—DMSO-d_6), δ: 7.51, 7.45 (both d, 2 H each, H arom., J = 8.8 Hz); 5.41 (s, 2 H, NH_2); 5.27 (s, 1 H, CH).

3-Amino-5-(4-bromophenyl)isoxazole (4f). The yield was 29%, colorless crystals, m.p. 150—151 °C (*cf.* Ref. 11: 147—149 °C), R_f 0.39 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 45.21; H, 2.75. $C_9H_7BrN_2O$. Calculated (%): C, 45.22; H, 2.95. ^{1}H NMR ($CDCl_3$), δ: 7.71, 7.68 (both d, 2 H each, H arom., J = 8.8 Hz); 6.37 (s, 1 H, CH); 5.68 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 166.03, 164.61, 131.97, 127.18, 126.69, 123.11, 93.37.

5-Amino-3-(4-dimethylaminophenyl)isoxazole (3g). The yield was 29%, light yellow crystals, m.p. 185—187 °C, R_f 0.40 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 64.84; H, 6.48. $C_{11}H_{13}N_3O$. Calculated (%): C, 65.01; H, 6.45. ^{1}H NMR ($CDCl_3$), δ: 7.61, 6.74 (both d, 2 H each, H arom., J = 9.0 Hz); 5.39 (s, 1 H, CH); 4.43 (s, 2 H, NH_2); 3.01 (s, 6 H, NMe_2). ^{13}C NMR (DMSO-d_6), δ: 170.40, 162.50, 150.99, 127.06, 117.30, 111.83, 74.61, 39.83.

3-Amino-5-(4-dimethylaminophenyl)isoxazole (4g). The yield was 27%, light yellow crystals, m.p. 174—176 °C, R_f 0.29 (CH_2Cl_2—MeCN, 10 : 1). Found (%): C, 63.19; H, 6.68. $C_{11}H_{13}N_3O \cdot 1/3H_2O$. Calculated (%): C, 63.14; H, 6.58. ^{1}H NMR ($CDCl_3$), δ: 7.59, 6.71 (both d, 2 H each, H arom., J = 9.0 Hz); 5.89 (s, 1 H, CH); 3.93 (s, 2 H, NH_2); 3.03 (s, 6 H, NMe_2). ^{13}C NMR (DMSO-d_6), δ: 168.08, 164.47, 150.99, 126.35, 115.21, 111.78, 89.56, 39.70.

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