Oxidation of 2-cyanoprop-2-enethioamides with hydrogen peroxide

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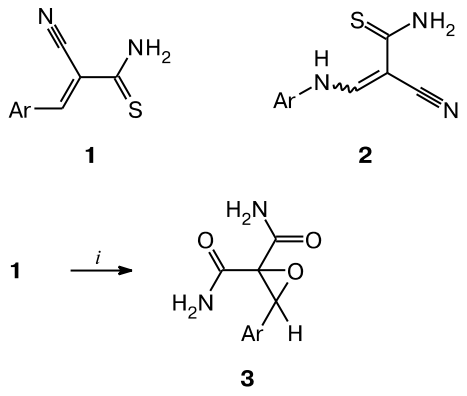
Oxidation of (*E*)-3-aryl-2-cyanoprop-2-enethioamides with 32% H_2O_2 under mild conditions gave (*E*)-3-aryl-2-cyano-1-iminioprop-2-ene-1-sulfenates in 70—88% yields. Under the conditions of the Radziszewski reaction (H_2O_2, 10% aqueous KOH) or upon prolonged treatment with H_2O_2, (*E*)-3-aryl-2-cyanoprop-2-enethioamides underwent transformations leading to complex mixtures of oxidation products. In some cases, 3-aryloxirane-2,2-dicarboxamides were isolated from those mixtures in low yields (<20%). Treatment of 3-arylamino-2-cyanoprop-2-enethioamides with the system H_2O_2/KOH in ethanol afforded (arylaminomethylidene)malononitriles.

Key words: cyanothioacetamide, thioamide *S*-oxides, thioacrylamides, hydrogen peroxide, the Radziszewski reaction, oxirane-2,2-dicarboxamide, aminomethylidenemalononitrile, dehydrosulfuration, X-ray diffraction analysis.

Oxidation of thioamides is one of the least predictable organic reactions (see reviews[1]). Its outcome largely depends on the substrate structure, the oxidant, and the reaction conditions. Most common oxidation products derived from thioamides include amides, thioamide *S*-oxides, 1,2,4-thiadiazoles, disulfides, benzothiazoles, α-oxo thioamides, 1,2-dithiolium salts, 1,2,4-dithiazoles, and 1,2,3-thiadiazolium salts. Hydrogen peroxide is one of the most accessible and efficient agents for the transformation of thioamides into amides, 1,2,4-thiadiazoles, or thioamide *S*-oxides. If a thioamide molecule contains other oxidizable functional groups, the reaction with H_2O_2 is of interest as a method for simultaneous and/or selective "one pot" modification of separate fragments of the molecule. From this point of view, the cyanothioacetamide derivatives[2] (3-aryl-2-cyanoprop-2-enethioamides **1** (see Refs 3, 4) and 3-arylamino-2-cyanoprop-2-enethioamides **2** are very attractive substrates for peroxide oxidation (Scheme 1).

Scheme 1



i. H_2O_2, 10% KOH, EtOH.

For instance, the presence of the fragment C=C—C≡N allows compound **1** to react in the Radziszewski reaction,[5] with parallel epoxidation of the double bond.[6] Earlier,[7] we have demonstrated that 3-(4-chlorophenyl)-2-cyanoprop-2-enethioamide (**1a**) treated with the system H_2O_2—KOH undergoes simultaneous oxidation at the C=C bond and the thioamide and cyano groups to form 3-(4-chlorophenyl)oxirane-2,2-dicarboxamide (**3a**, Ar = 4-ClC_6H_4) in low yield (see Scheme 1). In the present work, we tried to study in more detail the oxidation of various 2-cyanothioacrylamides with H_2O_2.

We found that brief heating of compounds **1** with excess 32% H_2O_2 in EtOH gives brightly colored (*E*)-3-aryl-2-cyano-1-iminioprop-2-ene-1-sulfenates (**4**) (Scheme 2).

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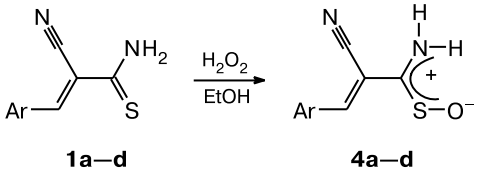
Scheme 2



1a—d **4a—d**

1, **4:** Ar = 4-ClC_6H_4 (**a**); 2-ClC_6H_4 (**b**); 3-MeO-4-HOC_6H_3 (**c**); 2-furyl (**d**)

Compounds **4** are bright red to cherry-colored crystalline solids that are insoluble in water and EtOH, moderately soluble in acetone, and well soluble in DMF. Iminiopropenesulfenates **4** are stable when stored in air at ~20 °C; however, they decompose readily when directly exposed to sunlight. Likewise, in the presence of excess H_2O_2, a heterogeneous reaction mixture containing compound **4** promptly undergoes further oxidation resulting in a pale yellow homogeneous mixture with pH 1—2. Concentrating this mixture gives colorless resinous products. According to TLC and GLC-MS data, they are complex mixtures of oxidation products, with oxirane-2,2-dicarboxamides **3** as the major components. In some cases, compounds **3** can be obtained in the individual state. For instance, treatment of thioacrylamide **1a** with H_2O_2 without isolation of intermediate **4a** affords oxiranedicarboxamide **3a** (Ar = 4-ClC_6H_4) in 11% yield. In a similar way, diamide **3b** (Ar = 2-ClC_6H_4, 20% yield) is obtained from isomeric thioamide **1b**. The probable mechanism of formation of compounds **3** can involve oxidation of the sulfenate fragment followed by hydrolysis as proposed earlier[8] and the subsequent Radziszewski tandem oxidation of the cyano group that involves intramolecular epoxidation through hydroperoxy imine intermediate **5** (Scheme 3).

The low yields of compounds **3** are probably due to inevitable transformations of the oxirane ring and the carbamoyl groups in strongly acidic medium; clearly, the oxidation of iminiopropenesulfenates **4** or 3-aryl-2-cyanoprop-2-enethioamides **1** cannot be recommended for the preparative synthesis of compounds **3**.

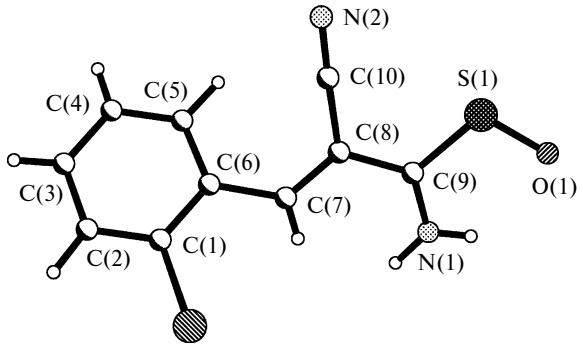
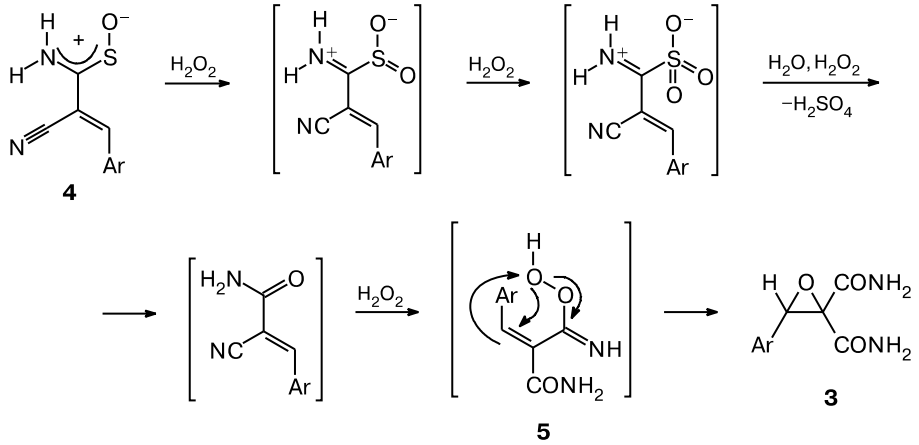


Fig. 1. Structure of (*E*)-3-(2-chlorophenyl)-2-cyano-1-iminioprop-2-ene-1-sulfenate (**4b**).

The ^1H NMR spectra of iminiopropenesulfenates **4** show signals for the protons of the fragment Ar—CH= and a very broadened peak at δ 8.73—8.98 for the signals of the acidic H_2N^+ protons. The IR spectra contain absorption bands at 3330—3310 (N—H stretching of the NH_2 group) and 2220—2215 cm^{-1} (C≡N stretching of the conjugated cyano group). Since the spectroscopic data alone are insufficient for making a definitive conclusion about the structure of compounds **4**, we additionally examined (*E*)-3-(2-chlorophenyl)-2-cyano-1-iminioprop-2-ene-1-sulfenate (**4b**) by X-ray diffraction (Fig. 1).

Analysis of the bond lengths in structure **4b** showed that this compound exists in the crystal as a zwitterion. The S(1)—O(1) bond (1.534(1) Å) is appreciably shorter than the average S=O bond[9] (1.577 Å); in addition, no hydrogen atom at the O(1) atom was revealed. This suggests that the negative charge is localized on the O(1) atom. The C(9)—N(1) bond length (1.315(2) Å) is com-

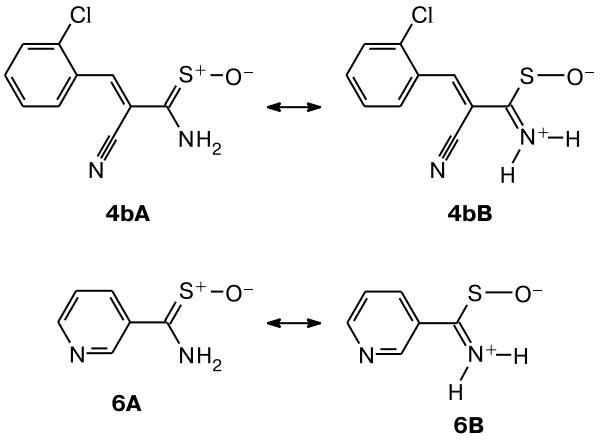
Scheme 3



4 **5** **3**

parable with the average $C_{sp2}=NH^+$ bond length (1.316 Å); the S(1)—C(9) bond (1.683(2) Å) is somewhat shorter than the average value of a single S—C bond (1.712 Å). Two H atoms were objectively located at the N(1) atom in difference electron-density maps. These atoms form the intramolecular hydrogen bond N(1)—H(1N_b)···O(1) (H···O, 2.19 Å; N—H···O, 121°). Thus, structure **4b** can be represented as a superposition of two resonance structures: thioamide *S*-oxide (**4bA**) and iminium sulfenate (**4bB**) (Scheme 4). A similar electron density distribution has been found in compound **6**.[10]

Scheme 4



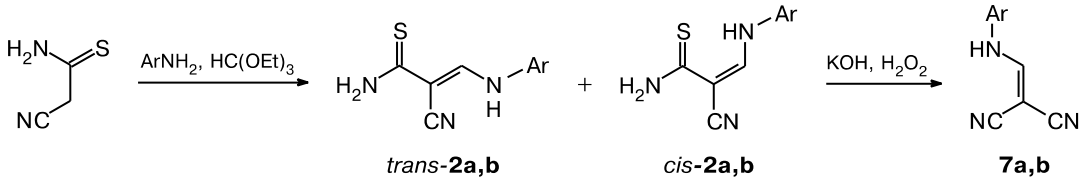
A rather strong repulsion between the aromatic ring and the substituent at the C(6) atom is evident from the shortened intramolecular contacts H(5)···C(8) (2.81 Å *vs.* 2.87 Å[11] for the sum of the van der Waals radii of the corresponding atoms), H(5)...C(10) (2.45 Å *vs.* 2.87 Å), C(5)···C(10) (3.06 Å *vs.* 3.42 Å), and H(7)···Cl(1) (2.73 Å *vs.* 3.06 Å). As a result, the π-systems of the ring and the substituent are not coplanar (the torsion angle C(5)—C(6)—C(7)—C(8) is 32.3(3)°), the double bond C(7)=C(8) is twisted (the torsion angle C(6)—C(7)—C(8)—C(10) is 7.4(3)°), and the bond angle C(8)—C(7)—C(6) is increased to 128.8(2)°. The substituent itself is also nonplanar, regardless of the presence of a conjugated π-system (the torsion angle C(7)—C(8)—C(9)—N(1) is 9.3(3)°). This can be attributed to the repulsion between the H(7) atom and the protonated imino group: the intramolecular contact H(7)···H(1N_a) (2.12 Å) is shorter than the sum of the van der Waals radii (2.34 Å).

In the crystal, the molecules of **4b** form tetramers by means of the intermolecular hydrogen bond N(1)—H(1N_a)···O(1)′ (–*x*, 0.5 + *y*, –0.5 – *z*) (H···O, 1.87 Å; N—H···O, 172°) and the S...π-interactions S(1)···N(1)′ (*x*, 0.5 – *y*, 0.5 + *z*) (3.25 Å) and S(1)···C(9)′ (*x*, 0.5 – *y*, 0.5 + *z*) (3.36 Å). The crystal structure is additionally stabilized by the weak intermolecular hydrogen bond N(1)—H(1N_b)···Cl(1) (–*x*, –0.5 + *y*, –0.5 – *z*) (H···Cl, 2.98 Å; N—H···Cl, 140°).

Reactions of H_2O_2 with 3-arylamino-2-cyanoprop-2-enethioamides **2** follow an absolutely different pattern. Compounds **2** were first synthesized at our laboratory as early as the 1980s according to the Wolfbeis general procedure[12] involving three-component condensation of an amine, triethyl orthoformate, and cyanothioacetamide (Scheme 5), although the only documented[13] route to thioacrylamides **2** that has been known hitherto involving reactions of cyanothioacetamide with *N*,*N*′-diarylformamidines. Compounds **2** exist as ~2 : 9 mixtures of *cis* and *trans* isomers (^{1}H NMR data).

Oxidative cyclization of β-amino alkenethioamides in the presence of halogens or H_2O_2 is known[14,15] to be a general approach to isothiazole derivatives. Unexpectedly, the oxidation of 3-aminothioacrylamides **2** with H_2O_2 in the presence of KOH did not result in cyclization or oxidative hydrolysis of the cyano group; instead, the starting compounds undergo dehydrosulfuration leading to (arylaminomethylidene)malononitriles **7** in high yields (see Scheme 5). The structures of compounds **7** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry as well as by independent synthesis from aniline, triethyl orthoformate, and malononitrile.[12] According to the literature data, selective dehydrosulfuration of primary thioamides to nitriles can be effected under the action of diarylselenium and diaryltellurium oxides,[16] $P(NEt_2)_3$,[17] phenylpropiolamidines PhC≡CC(=NR^1)NHR,[18] the system $EtO_2CN=NCO_2Et$/PPh_3,[19] S_8/$NaNO_2$ in liquid NH_3,[20] $Ph_3SnN=C=NSnPh_3$ and $Ph_3SnNHCN$,[21] $TeCl_4$/Et_3N and $SeCl_4$/Et_3N,[22] Bu_2SnO and $(Bu_3Sn)_2O$,[23] the system benzotriazol-1-yloxytris(pyrrolidino)phosphonium hexafluorophosphate

Scheme 5



2, **7:** Ar = Ph (**a**), 4-EtC_6H_4 (**b**)

(PyBOP)—*N*,*N*-diisopropylethylamine (DIPEA),[24] arenetellurinic anhydrides,[25] 1,1′-thiocarbonyldi-2(1*H*)-pyridone,[26] the systems pyridine—phenyl chloroformate[27] and P_2I_4—Et_3N,[28] di(2-pyridyl) sulfite $(2\text{-PyO})_2S{=}O$,[29] heavy metal acetates,[30] and some other exotic systems and reagents. However, this reaction has never been observed before under the conditions of the Radziszewski oxidative hydrolysis. The surprising passivity of the cyano groups in compounds **2** and **7** toward the system H_2O_2/KOH is probably due to the specific push-pull properties of the enamino nitrile fragment.

To sum up, noncatalytic mild oxidation of (*E*)-3-aryl-2-cyanoprop-2-enethioamides with hydrogen peroxide gives primary oxidation products (the corresponding thioamide *S*-oxides (or iminium sulfenates)), the fragments C=C and C≡N of the starting compounds remaining intact. The structures of the oxidation products were proved by X-ray diffraction with (*E*)-3-(2-chlorophenyl)-2-cyano-1-iminioprop-2-ene-1-sulfenate (**4b**) as an example. When heated and treated with the system H_2O_2—KOH, 3-anilino-2-cyanoprop-2-enethioamide and 2-cyano-3-[(4-ethylphenyl)amino]prop-2-enethioamide undergo dehydrosulfuration to yield the corresponding (arylaminomethylidene)malononitriles.

Experimental

^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument (500.13 MHz) in DMSO-d_6 (for compounds **2** and **7b**) and a Varian Mercury VX-200 instrument (199.97 MHz) in DMSO-d_6 (for compounds **3**, **4**, and **7a**); Me_4Si was used as the internal standard. The ^{13}C NMR spectra of compound **6b** were recorded on a Bruker DRX-500 instrument (125.76 MHz) in DMSO-d_6 and CCl_4—DMSO-d_6 with Me_4Si as the internal standard. IR spectra were recorded on an IKS-29 spectrophotometer (in Nujol). Elemental analysis was carried out on a Perkin—Elmer C,H,N-analyzer. The mass spectrum of compound **7a** was measured on a Varian 1200L spectrometer (direct inlet probe, EI, 70 eV). The individuality of the compounds obtained was checked by TLC on Silufol UV-254 plates in acetone—heptane (1 : 1); spots were visualized with the iodine vapor or under UV light. Melting points were determined on a Kofler hot stage and are given uncorrected. The starting compounds 3-aryl-2-cyanoprop-2-enethioamides **1** were prepared by condensation of cyanothioacetamide with aldehydes according to known procedures.[3,4]

3-Anilino-2-cyanoprop-2-enethioamide (2a) was obtained according to a modified general procedure.[12] A mixture of pulverized cyanothioacetamide (3.0 g, 30 mmol), $HC(OEt)_3$ (6.5 mL, 39 mmol), and aniline (2.75 mL, 30 mmol) was refluxed with continuous stirring until the exothermic reaction subsided. Then the mixture was diluted with EtOH (10 mL), brought to boiling, and left to cool down. The dark yellow crystals that formed were filtered off and washed with hot EtOH. The yield of thioacrylamide **2a** was 5.50 g (90%), m.p. 210—211 °C (from AcOH). Found (%): C, 59.16; H, 4.46; N, 20.65. $C_{10}H_9N_3S$ (M = 203.27). Calculated (%): C, 59.09; H, 4.46; N, 20.67. IR, ν/cm^{-1}: 3420, 3270, 3180 (NH), 2195 (C≡N). ^{1}H NMR (500 MHz, DMSO-d_6), δ: 7.17* (m, 5 H, Ph); 7.40 (m, 5 H, Ph); 8.36* and 9.20* (both br.s, 1 H each, $C(S)NH_2$); 8.49* (d, 1 H, HC=, ^3J = 13.2 Hz); 8.64 and 9.09 (both br.s, 1 H each, $C(S)NH_2$); 8.73 (d, 1 H, HC=, ^3J = 14.2 Hz); 10.50 (d, 1 H, NH, ^3J = 14.2 Hz); 13.77 (d, 1 H, NH, ^3J = 13.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6), δ: 81.449* (C(3)=<u>C</u>(2)); 86.995 (C(3)=<u>C</u>(2)); 116.805 (C≡N); 117.966* (C_{Ar}); 118.451 (C_{Ar}); 119.017* (C≡N); 125.111 (C_{Ar}); 125.748* (C_{Ar}); 129.986 (C_{Ar}); 130.281* (C_{Ar}); 138.682* (C_{Ar}); 140.497 (C_{Ar}); 151.149 (<u>C</u>(3)=C(2)); 151.771* (<u>C</u>(3)=C(2)); 190.331* (C=S); 192.427 (C=S).

2-Cyano-3-[(4-ethylphenyl)amino]prop-2-enethioamide (2b) was obtained as described for compound **2a**. Yield 85%, m.p. 180—185 °C (decomp.). Found (%): C, 61.96; H, 5.69; N, 18.25. $C_{12}H_{13}N_3S$ (M = 231.32). Calculated (%): C, 62.31; H, 5.66; N, 18.17. IR, ν/cm^{-1}: 3420, 3290, 3180 (NH), 2195 (C≡N).

3-Aryloxirane-2,2-dicarboxamides (3). An excess of 32% H_2O_2 (6.0 mL, ~62 mmol) was added to a stirred suspension of 3-aryl-2-cyanoprop-2-enethioamide (**1a,b**) (2.0 g, 9 mmol) in EtOH (15 mL). The reaction mixture was heated until thioamide **1** began to dissolve, which was accompanied by appearance of red coloration and immediate formation of a crystalline precipitate of the corresponding iminiopropenesulfenate **4a**,**b**. The reaction mixture was stirred at 40—50 °C to complete homogenization and decoloration (*Caution! Evolution of oxygen*) and left at ~20 °C for two weeks. The crystalline precipitate of compound **3** that gradually formed was filtered off and repeatedly washed with EtOH and water.

3-(4-Chlorophenyl)oxirane-2,2-dicarboxamide (3a). Yield 11%, colorless crystals, m.p. 223—224 °C (*cf.* Ref. 7: 225—227 °C). The spectroscopic characteristics of compound **3a** agree with the literature data.[7]

3-(2-Chlorophenyl)oxirane-2,2-dicarboxamide (3b). The yield of analytically pure product **3b** was 0.44 g (20%), colorless crystals, m.p. 197—199 °C (EtOH). Found (%): C, 49.76; H, 3.80; N, 11.65. $C_{10}H_9ClN_2O_3$ (M = 240.65). Calculated (%): C, 49.91; H, 3.77; N, 11.64. IR, ν/cm^{-1}: 3425, 3200, 3150 (NH), 1675, 1660 (C=O). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 4.83 (s, 1 H, C(3)H); 7.35—7.62 (m, 4 H, Ar); 7.88 and 8.11 (both br.s, 2 H each, 2 $C(O)NH_2$).

Synthesis of (*E*)-3-aryl-2-cyano-1-iminioprop-2-ene-1-sulfenates 4 (general procedure). Pulverized thioamide **1a—d** (4.5—5.0 mmol) was suspended in EtOH (12—15 mL) in a 100-mL beaker. Then an excess of 32% H_2O_2 (4.0 mL, ~42 mmol) was added with stirring. The vigorously stirred mixture was gradually heated until an exothermic reaction began. Thioamide **1** passed into solution, the reaction mixture turned dark red, and the corresponding iminium sulfenate **4a—d** formed as a voluminous crystalline precipitate within a few seconds. The heating was immediately terminated to avoid further oxidation. The reaction mixture was rapidly cooled on an ice bath and stirred for 30 min. The precipitate of iminium sulfenate **4a—d** was filtered off and repeatedly washed with EtOH, 50% aqueous EtOH, and light petroleum. The compounds obtained are usually pure enough for analytical purposes; when necessary, the products can be recrystallized from EtOH—Me_2CO or AcOH.

(*E*)-3-(4-Chlorophenyl)-2-cyano-1-iminioprop-2-ene-1-sulfenate (4a). Yield 75%, blood-red small crystals, m.p. 172—175 °C (decomp., EtOH—Me_2CO, 1 : 3). Found (%): C, 50.48; H, 3.00;

* The signals for the minor (*cis*) isomer. The *cis* : *trans* ratio is 2 : 9 (^{1}H NMR data).

N, 11.87. $C_{10}H_7ClN_2OS$ (M = 238.70). Calculated (%): C, 50.32; H, 2.96; N, 11.74. IR, ν/cm^{-1}: 3310 (NH), 2215 (C≡N). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 7.63 and 7.85 (both d, 2 H each, 4-ClC_6H_4, ^3J = 8.2 Hz); 8.11 (s, 1 H, ArC<u>H</u>=); 8.83* (br.s, 2 H, H_2N^+=).

(*E*)-3-(2-Chlorophenyl)-2-cyano-1-iminioprop-2-ene-1-sulfenate (4b). Yield 70%, bright red crystals, m.p. 165—168 °C (decomp., EtOH—Me_2CO (1 : 2) or AcOH). Found (%): C, 50.44; H, 2.99; N, 11.83. $C_{10}H_7ClN_2OS$ (M = 238.70). Calculated (%): C, 50.32; H, 2.96; N, 11.74. IR, ν/cm^{-1}: 3310 (NH), 2215 (C≡N). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 7.49—7.66 (m, 3 H, Ar); 7.91 (m, 1 H, Ar); 8.28 (s, 1 H, ArC<u>H</u>=); 8.98* (br.s, 2 H, H_2N^+=).

(*E*)-2-Cyano-3-(4-hydroxy-3-methoxyphenyl)-1-iminioprop-2-ene-1-sulfenate (4c). Yield 73%, bright red fine crystalline powder, m.p. 188—190 °C (decomp., Me_2CO). Found (%): C, 52.62; H, 4.07; N, 11.33. $C_{11}H_{10}N_2O_3S$ (M = 250.28). Calculated (%): C, 52.79; H, 4.03; N, 11.19. IR, ν/cm^{-1}: 3330, 3185 (NH), 2220 (C≡N). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 3.79 (s, 3 H, MeO); 6.93 (d, 1 H, Ar, ^3J = 8.2 Hz); 7.36 (d, 1 H, Ar, ^3J = 8.2 Hz), 7.56 (s, 1 H, Ar); 7.98 (s, 1 H, ArC<u>H</u>=); 8.74** (br.s, 2 H, H_2N^+=); 10.32 (s, 1 H, OH).

(*E*)-2-Cyano-3-(2-furyl)-1-iminioprop-2-ene-1-sulfenate (4d). Yield 88%, cherry-red bright needles, decomp. >140 °C. Found (%): C, 49.20; H, 3.07; N, 14.53. $C_8H_6N_2O_2S$ (M = 194.21). Calculated (%): C, 49.48; H, 3.11; N, 14.42. IR, ν/cm^{-1}: 3310 (NH), 2220 (C≡N). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 6.81, 7.27, and 8.12 (all m, 1 H each, 2-furyl); 7.95 (s, 1 H, ArC<u>H</u>=); 8.73* (br.s, 2 H, H_2N^+=).

Synthesis of (arylaminomethylidene)malononitriles 7a,b (general procedure). A 10% aqueous solution of KOH (3.0 mL, 5.4 mmol) was added to a suspension of an appropriate 3-aminothioacrylamide **2a,b** (5 mmol) in EtOH (10 mL). The reaction mixture was heated with stirring to homogenization. The resulting red solution was filtered through a paper filter. The mother liquor was cooled and an excess of 32% H_2O_2 (5.0 mL, ~51.7 mmol) was added dropwise. This initiated a vigorous exothermic reaction accompanied by oxygen evolution and rapid formation of a light yellow precipitate. The mixture was stirred at 20 °C for 2 h and the precipitate was filtered off. To remove inorganic impurities, it was washed with water and dissolved in acetone—EtOH (1 : 1). The resulting solution was filtered through a paper filter. After 3—4 days, product **7a**,**b** was isolated from the mother liquor.

(Anilinomethylidene)malononitrile (7a). Yield 80%, light yellow crystals, m.p. 250—252 °C (EtOH—acetone) (subl., transformed into large colorless needles; *cf.* Refs: m.p. 240—242 °C,[12] 253—255 °C,[31,32] 254—256 °C,[33] and 245—247 °C[34]). Found (%): C, 70.80; H, 4.16; N, 24.80. $C_{10}H_7N_3$ (M = 169.19). Calculated (%): C, 70.99; H, 4.17; N, 24.84. IR, ν/cm^{-1}: 3200—3180 (NH), 2210 and 2224 (2 C≡N), 1650 (C=C). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 7.11 (t, 1 H, C(4)H_{Ph}, ^3J = 7.2 Hz); 7.42—7.27 (m, 4 H, Ar); 8.42 (d, 1 H, HC=, ^3J = 13.7 Hz); 10.98 (d, 1 H, NH, ^3J = 13.7 Hz). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 170 $[M + H]^+$ (11.2), 169 $[M]^+$ (97.7), 168 $[M - H]^+$ (11.5), 142 $[M - HCN]^+$ (12.9), 104 $[M - 65]^+$ (32.2), 77 $[M - 92]^+$ (100), 66 $[M - 103]^+$ (16.7), 65 $[M - 104]^+$ (56.1), 64 $[M - 105]^+$ (16.7), 52 $[M - 117]^+$ (19.0), 51 $[M - 118]^+$ (80.4), 50 $[M - 119]^+$ (19.2). Compound **7a** is identical with a sample obtained from aniline, triethyl orthoformate, and malononitrile[12] (TLC data).

[(4-Ethylphenyl)aminomethylidene]malononitrile (7b). Yield 56%, cream-colored fine crystalline powder, m.p. 248—250 °C (EtOH—acetone). Found (%): C, 72.91; H, 5.66; N, 21.51. $C_{12}H_{11}N_3$ (M = 197.24). Calculated (%): C, 73.07; H, 5.62; N, 21.30. IR, ν/cm^{-1}: 3200—3160 (NH), 2207 and 2223 (2 C≡N), 1665 (C=C). ^{1}H NMR (500 MHz, CCl_4—DMSO-d_6), δ: 1.21 (t, 3 H, $CH_2C\underline{H}_3$, ^3J = 7.6 Hz); 2.60 (q, 2 H, $C\underline{H}_2CH_3$, ^3J = 7.6 Hz); 7.11 and 7.26 (both d, 2 H each, Ar, ^3J = 8.3 Hz); 8.25 (d, 1 H, HC=, ^3J = 13.5 Hz); 10.87 (d, 1 H, NH, ^3J = 13.5 Hz). ^{13}C NMR (125 MHz, CCl_4—DMSO-d_6), δ: 15.226 ($CH_2\underline{C}H_3$); 27.652 ($\underline{C}H_2CH_3$); 52.178 (C=$\underline{C}(CN)_2$); 113.578 (C≡N); 115.730 (C≡N); 117.662 (C_{Ar}); 128.183 (C_{Ar}); 136.980 (C_{Ar}); 140.192 (C_{Ar}); 154.460 ($\underline{C}$=$C(CN)_2$).

For an X-ray diffraction experiment, the crystals of (*E*)-3-(2-chlorophenyl)-2-cyano-1-iminioprop-2-ene-1-sulfenate (**4b**) were obtained by its recrystallization from EtOH—Me_2CO (1 : 2). The crystals are monoclinic, $C_{10}H_7N_2OSCl$; at 20 °C, *a* = = 15.0992(8) Å, *b* = 9.0095(5) Å, *c* = 7.7519(5) Å, β = 101.878(6)°, *V* = 1032.0(1) Å^3, M_r = 238.69, *Z* = 4, space group $P2_1/c$, d_{calc} = = 1.536 g cm^{-3}, μ(Mo-Kα) = 0.543 mm^{-1}, *F*(000) = 488. The intensities of 6253 reflections (2351 independent reflections, R_{int} = 0.024) were measured on an Xcalibur-3 diffractometer (Mo-Kα radiation, a CCD detector, graphite monochromator, ω scan mode, $2\theta_{max}$ = 55°). The unit cell parameters were calculated from the collected data. The structure was solved by the direct methods with the SHELXTL program package.[35] The hydrogen atoms were located in the difference electron-density maps and refined isotropically. The structure was refined on F^2 by the full-matrix least-squares method in the anisotropic approximation for the non-hydrogen atoms. Final residuals are wR_2 = 0.103 for 2308 reflections and R_1 = 0.037 for 1699 reflections with $F > 4\sigma(F)$ (S = 0.980). Comprehensive data for structure **4b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 842953).

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* The integral intensity of the signal is lowered because of partial deuterium exchange.

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