# Oxidative cyclization of *N*-alkyl-2-arylhydrazonothioacetamides*

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Oxidative cyclization of *N*-alkyl-2-arylhydrazono-2-cyanothioacetamides by the action of *N*-chlorosuccinimide, bromine, or iodine affords 4-cyano-5-imino-1,2,3-thiadiazoles.

**Key words:** hydrazones, thioacetamides, oxidation, 1,2,3-thiadiazoles, heterocyclization.

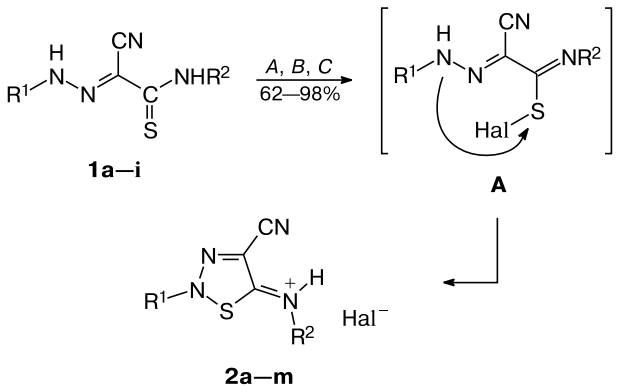
1,2,3-Thiadiazoles have a broad spectrum of biological effect,[1—9] in particular, antimicrobial,[1,2] fungicidal,[3,4] and insecticidal[5] activity.

Systematic studies of oxidative cyclization of 2-arylhydrazononthioacetamides made it possible to develop a new preparative method for the synthesis of 5-imino-2,5-dihydro-1,2,3-thiadiazoles[10,11] and 2*H*-1,2,3-thiadiazoloindoles.[12] In order to refine the area of application of this method, we studied the oxidative cyclization of arylhydrazonothioacetamides containing the alkyl substituent in the thioamide group.

Arylhydrazonothioacetamides **1a**—**i** were transformed at room temperature by the addition to their solutions of crystalline *N*-chlorosuccinimide, a solution of bromine in acetic acid, or a iodine solution in ethanol. As a result, we obtained 2*H*-1,2,3-thiadiazoliminium salts **2a**—**m** as chlorides, bromides, and iodides in good yields (Scheme 1). We have earlier[10] shown that for the oxidative dehydrogenation of arylhydrazonothioacetamides containing the primary thioamide group the enhancement of the electron-withdrawing properties of the substituent in the aromatic ring decreases the yield of the final product or even changes the direction of cyclization forming intermolecular oxidation products, *viz.*, 1,2,4-thiadiazoles. Such a drastic substrate dependence was not observed in the series of *N*-alkyl-substituted arylhydrazonothioacetamides **1a**—**i**. However, for arylhydrazonothioacetamides **1a**—**c** bearing the electron-donating methoxy group in the aromatic ring, the reaction is ceased with a yield of 90—97% using a twofold reagent excess and storing for 1—2 h, whereas an increase in the amount of the oxidant and the elongation of the reaction duration to 15 h are necessary for a similar transformation of 4-nitrophenylhydrazones **1h**,**i**.

This fact can be explained by the electronic effect of the substituent in the aromatic ring, which for compounds **1h**,**i** decreases the nucleophilicity of both the nitrogen atom of the hydrazone group and the sulfur atom, preventing both the formation of adduct **A** (see Scheme 1) and its cyclization to final product **2j**,**k**,**m**.

**Scheme 1**




2a—m

*A*: NCS, EtOAc; *B*: $Br_2$, AcOH; *C*: $I_2$, EtOH

| Compound | $R^1$ | $R^2$ | Hal |
|---|---|---|---|
| **1a** | 4-$MeOC_6H_4$ | Me | — |
| **1b** | 4-$MeOC_6H_4$ | Bn | — |
| **1c** | 4-$MeOC_6H_4$ | *cyclo*-$C_6H_{11}$ | — |
| **1d** | Ph | Me | — |
| **1e** | Ph | Bn | — |
| **1f** | Ph | *cyclo*-$C_6H_{11}$ | — |
| **1g** | 4-$CF_3C_6H_4$ | Me | — |
| **1h** | 4-$NO_2C_6H_4$ | Bn | — |
| **1i** | 4-$NO_2C_6H_4$ | *cyclo*-$C_6H_{11}$ | — |
| **2a** | 4-$MeOC_6H_4$ | Me | Cl |
| **2b** | 4-$MeOC_6H_4$ | Bn | Cl |
| **2c** | Ph | Me | Cl |
| **2d** | Ph | Bn | Cl |
| **2e** | Ph | *cyclo*-$C_6H_{11}$ | Cl |
| **2f** | 4-$CF_3C_6H_4$ | Me | Cl |
| **2g** | 4-$MeOC_6H_4$ | Me | Br |
| **2h** | 4-$MeOC_6H_4$ | *cyclo*-$C_6H_{11}$ | Br |
| **2i** | 4-$CF_3C_6H_4$ | Me | Br |
| **2j** | 4-$NO_2C_6H_4$ | Bn | Br |
| **2k** | 4-$NO_2C_6H_4$ | *cyclo*-$C_6H_{11}$ | Br |
| **2l** | 4-$MeOC_6H_4$ | Bn | I |
| **2m** | 4-$NO_2C_6H_4$ | Bn | I |

* Dedicated to Academician V. N. Charushin on the occasion of his 60th birthday.

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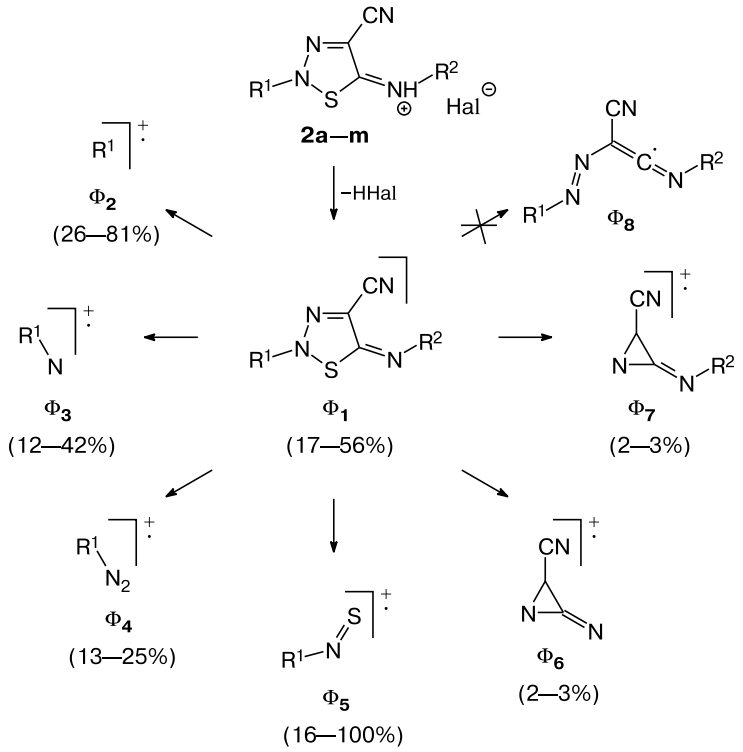
**Scheme 2**



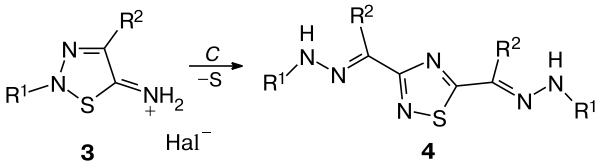

Elemental analysis data showed that compounds **2a—m** are monochlorides, monobromides, and monoiodides. In the $^1$H NMR spectra of synthesized compounds **2a—m** (DMSO-$d_6$), the signals of protons of the aromatic ring and alkyl substituent exhibit the downfield shift by 0.10—0.50 ppm compared to the signals of arylhydrazonothioacetamdes **1a—i**. The signals of protons of the Me and CH groups of the iminium substituent in the $^1$H NMR spectra of compounds **2f—h** in $CDCl_3$ are presented as a doublet and the signals of the NH proton represent a quartet (**2f**,**g**) and a doublet (**2h**).

It should be mentioned that the $^1$H NMR spectra of thiadiazoles **2** (DMSO-$d_6$) are characterized by the presence of a double set of signals of proton-containing groups. This indicates that in DMSO-$d_6$ solutions these compounds exist as *Z*- and *E*-isomers relative to the exocyclic bond C(5)=N.

The mass spectra of salts **2** contain the peak of the molecular ion (**Φ$_1$**) and the peaks of stable fragments formed upon the destruction of the thiadiazole cycle (**Φ$_3$—Φ$_7$**) (Scheme 2). In this case, the mass spectrum exhibits no peak of the fragmentation ion (**Φ$_8$**), which is related to sulfur elimination from the 1,2,3-thiadiazole cycle and is detected in considerable amounts in the mass spectra of thiadiazolimines ($R^2$ = H)[10] (Scheme 2).

It is known that 1,2,3-thiadiazole derivatives easily undergo rearrangements and in the presence of strong bases or on heating they are susceptible to ring destruction with the ejection of nitrogen and sulfur and formation of alkynes.[1] On heating in pyridine or in the presence of a base unsubstituted 5-imino-2*H*-1,2,3-thiadiazoles **3** are easily transformed into 1,2,4-thiadiazoles **4** (Scheme 3).[10]

**Scheme 3**

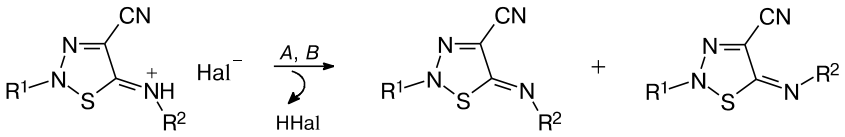



*C*: TEA, Py, NaOH
$R^1$ = Ar, $R^2$ = CN, CONHAlk

Salts of 5-alkyliminosubstituted derivatives of 2,5-dihydro-1,2,3-thiadiazoles **2** in solution in the presence of a base only lose a hydrohalide molecule and are transformed into 5-alkylimino-2-aryl-2,5-dihydro-1,2,3-thiadiazoles **5a—d** as mixtures of two isomers (Scheme 4).

It should be mentioned that the $^1$H NMR spectra of 2,5-dihydro-1,2,3-thiadiazoles **5a—d** contains no signal from the proton of the imino group characteristic of the corresponding hydrohalides **2a—c,h**. The signals of protons of the groups NMe, $NCH_2$, and NCH of thiadiazoles **5** are presented as upfield singlets compared to analogous signals in the starting salts **2**. The IR spectra of com-

**Scheme 4**




**2a,b,d,h** *Z*-Isomer *E*-Isomer

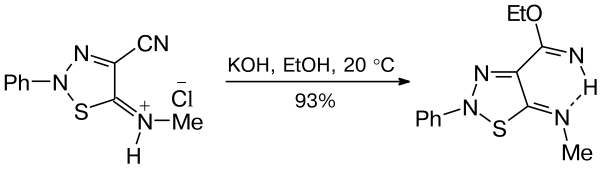
**5a—d**

*A*: TEA, EtOH, 20 °C; *B*: Py, Δ
**5:** $R^1$ = 4-$MeOC_6H_4$, $R^2$ = Me (**a**), Bn (**b**), *cyclo*-$C_6H_{11}$ (**c**); $R^1$ = Ph, $R^2$ = Me (**d**)

pounds **5** exhibit the shift of the absorption band corresponding to stretching vibrations of the cyano group by 29—38 $cm^{-1}$ to the region of lower frequencies compared with the IR spectra of chlorides, bromides, and iodides of 5-alkylimino-1,2,3-thiadiazoles **2**.

A new compound (TLC) is formed upon storing salt **2c** in an ethanol solution in the presence of KOH for 2 h at room temperature. According to the data of spectroscopy and elemental analysis, this compound turned out to be ethyl 1,2,3-thiadiazole-4-carbimidate **6** (Scheme 5).

**Scheme 5**




**2c** **6**

The $^1H$ NMR spectrum of ethyl carbimidate **6** contains one set of proton-containing groups. It can be assumed that this is the *Z*,*cis*-isomer, because this structure can be stabilized due to the formation of an intramolecular hydrogen bond between the hydrogen atom of the imino group and the nitrogen atom of the 5-methylimino group.

As a result of the study of oxidation of *N*-alkyl-2-arylhydrazono-2-cyanothioacetamides **1**, we synthesized new *N*-alkyl derivatives of 2-aryl-5-imino-2,5-dihydro-1,2,3-thiadiazoles **2** as their hydrohalides and free bases **5**. It should be mentioned that the reaction occurs rather successfully regardless of the substituent in the aromatic ring or at the nitrogen atom of the thioamide group. In the case of substrates with the alkyl substituent in the 5-imino group, the corresponding 2,5-dihydro-1,2,3-thiadiazoles are so stable that even in the presence of strong bases (for example, KOH) the transformation involves only side substituents, whereas the heterocyclic fragment remains unchanged.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded on Bruker WM-250 and Bruker AVANCE II 400 instruments (250.13 and 400.00 MHz for $^1H$ and 100.00 MHz for $^{13}C$) in DMSO-$d_6$ or $CDCl_3$ solutions using $Me_4Si$ as an internal standard. IR spectra were measured on a Bruker Alpha FTIR spectrometer (Frustrated Total Internal Reflection, ZnSe). Mass spectra were recorded on a Varian MAT 311A spectrometer (accelerating voltage 3 kV, ionization potential 70 eV, direct sample inlet). The reaction course and individual character of the synthesized substances were monitored by TLC on Sorbfil UV-254 plates in ethyl acetate—hexane (1 : 1); chloroform—acetone (30 : 1); and chloroform—hexane—acetone (5 : 4 : 1) systems. Solvents were purified according to a standard procedure.

Arylhydrazonothioacetamides were synthesized by the method described earlier.[13]

**Oxidative cyclization of *N*-alkyl-2-arylhydrazonothioacetamides 1 (general procedures). Method *A*.** *N*-Chlorosuccinimide (0.25 g, 6 mmol) was added to a solution of arylhydrazonothioacetamide **1a**,**b**,**d**—**g** (2 mmol) in ethyl acetate (100 mL), and the mixture was stirred at ~20 °C for 1—15 h (TLC). The precipitate was filtered off and washed with ethyl acetate.

**Method *B*.** A solution of $Br_2$ (0.1 mL, 6 mmol) in acetic acid (5 mL) was added to a solution of arylhydrazonothioacetamide **1a**,**c**,**g**—**i** (2 mmol) in acetic acid (100 mL) heated to 40 °C. The reaction mixture was stirred for 5 h at ~20 °C. The precipitate was filtered off and recrystallized from ethanol.

**Method *C*.** A solution of $I_2$ (8 mmol) in EtOH (5 mL) was added to a solution of arylhydrazonothioacetamide **1b,h** (2 mmol) in EtOH (100 mL). The reaction mixture was stirred for 5 h at ~20 °C. The precipitate was filtered off and washed with EtOH.

***N*-[4-Cyano-2-(4-methoxyphenyl)-1,2,3-thiadiazol-5-ylidene]-*N*-methylammonium chloride (2a).** Method *A*, the yield was 0.462 g (82%), m.p. 167—168 °C. IR, ν/$cm^{-1}$: 2231 (C≡N); 2845, 2935 (C—H); 3144 (NH). $^1H$ NMR (DMSO-$d_6$), δ: 3.15, 3.59 (both s, 3 H, NMe); 3.86, 3.92 (both s, 3 H, OMe); 7.09, 7.69, 7.17, 7.72 (two systems AA′XX′, 4 H, Ar, $J$ = 8.8 Hz); 10.88 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio 1 : 1. $^{13}C$ NMR (DMSO-$d_6$), δ: 33.1, 47.8, 55.4, 55.5, 112.6, 112,8, 114.8, 115.1, 118.2, 118.4, 119.1, 121.5, 133.6, 135.1, 157.5, 159.6, 160.60, 168.63. MS, $m/z$ ($I_{rel}$ (%)): 246 $[M - HCl]^+$ (43). Found (%): C, 46.52; H, 4.08; Cl, 12.84; N, 20.03; S, 11.19. $C_{11}H_{11}ClN_4OS$. Calculated (%): C, 46.73; H, 3.92; Cl, 12.54; N, 19.81; S, 11.34.

***N*-Benzyl-*N*-[4-cyano-2-(4-methoxyphenyl)-1,2,3-thiadiazol-5-ylidene]ammonium chloride (2b).** Method *A*, the yield was 0.523 g (73%), m.p. 162—163 °C. IR, ν/$cm^{-1}$: 2229 (C≡N); 2836, 2920, 3000 (C—H); 3150, 3440 (NH). $^1H$ NMR (DMSO-$d_6$), δ: 3.75, 3.86 (both s, 3 H, OMe); 4.50, 6.02 (both s, 2 H, $CH_2$); 6.85—7.12 (m, 4 H, Ar); 7.20—7.40 (m, 4 H, Ar); 7.53—7.69 (m, 1 H, Ar); 11.33 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers

in the ratio 1 : 1. $^{13}$C NMR (DMSO-$d_6$), δ: 49.9, 56.0, 56.2, 56.3, 112.9, 113.7, 115.4, 115.9, 120.6, 121.3, 123.1, 126.0, 127.1, 127.9, 128.2, 128.8, 129.1, 129.2, 129.4, 129.6, 132.8, 135.6, 160.4, 161.2, 166.5, 168.4. MS, *m/z* ($I_{rel}$ (%)): 322 [M – HCl]$^+$ (17). Found (%): C, 56.72; H, 4.01; N, 15.89; S, 8.65. $C_{17}H_{15}ClN_4OS$. Calculated (%): C, 56.90; H, 4.21; N, 15.61; S, 8.94.

***N*-(4-Cyano-2-phenyl-1,2,3-thiadiazol-5-ylidene)-*N*-methylammonium chloride (2c).** Method *A*, the yield was 0.403 g (80%), m.p. 241—242 °C. IR, ν/cm$^{-1}$: 2230 (C≡N); 2850, 2920, 2960, 3000 (C—H); 3360 (NH). $^1$H NMR (DMSO-$d_6$), δ: 3.57, 4.31 (both s, 3 H, Me); 7.34—7.38 (m, 1 H, Ph); 7.54—7.65 (m, 3 H, Ph); 7.78—7.84 (m, 1 H, Ph); 10.99 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio 1 : 1. MS, *m/z* ($I_{rel}$ (%)): 216 [M – HCl]$^+$ (56). Found (%): C, 47.75; H, 3.32; Cl, 13.85; N, 22.46; S, 12.92. $C_{10}H_9ClN_4S$. Calculated (%): C, 47.53; H, 3.59; Cl, 14.03; N, 22.17; S, 12.69.

***N*-Benzyl-*N*-(4-cyano-2-phenyl-1,2,3-thiadiazol-5-ylidene)-ammonium chloride (2d).** Method *A*, the yield was 0.485 g (74%), m.p. 179—180 °C. IR, ν/cm$^{-1}$: 2238 (C≡N); 2855, 2920, 2963, 3010 (C—H); 3460 (NH). $^1$H NMR (DMSO-$d_6$), δ: 3.91, 4.42 (both s, 2 H, $CH_2$); 7.37—7.35 (m, 1 H, Ph); 7.40 (d, 2 H, Ph, *J* = 7.6 Hz); 7.46 (t, 2 H, Ph, *J* = 7.6 Hz); 7.53 (d, 2 H, Ph, *J* = 7.7 Hz); 7.65—7.63 (m, 1 H, Ph); 7.81 (d, 2 H, Ph, *J* = 7.6 Hz); 11.47 (br.s, 1 H, =NH). MS, *m/z* ($I_{rel}$ (%)): 282 [M – HCl]$^+$ (7). Found (%): C, 52.92; H, 3.74; Cl, 9.58; N, 15.11. $C_{16}H_{13}ClN_4S$. Calculated (%): C, 52.67; H, 3.57; Cl, 9.74; N, 15.36.

***N*-(4-Cyano-2-phenyl-1,2,3-thiadiazol-5-ylidene)-*N*-cyclohexylammonium chloride (2e).** Method *A*. The yield was 0.531 g (83%), m.p. 170—171 °C. IR, ν/cm$^{-1}$: 2228 (C≡N); 2929 (C—H); 3440 (NH). $^1$H NMR (DMSO-$d_6$), δ: 1.35—2.12 (m, 10 H, 5 $CH_2$); 3.95, 4.57 (both m, 1 H, CH); 7.46—7.78 (m, 5 H, Ph); 10.99, 11.37 (both s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio (1 : 1). MS, *m/z* ($I_{rel}$ (%)): 284 [M – HCl]$^+$ (34). Found (%): C, 42.58; H, 4.39; Cl, 8.62; N, 13.52. $C_{15}H_{17}ClN_4S$. Calculated (%): C, 42.81; H, 4.04; Cl, 8.44; N, 13.32.

***N*-[4-Cyano-2-(4-trifluoromethylphenyl)-1,2,3-thiadiazol-5-ylidene]-*N*-methylammonium chloride (2f).** Method *A*, the yield was 0.416 g (65%), m.p. 193—194 °C. $^1$H NMR ($CDCl_3$), δ: 3.67 (d, 3 H, Me, *J* = 5.5 Hz); 7.98—7.80 (m, 4 H, Ar); 11.26 (br.q, 1 H, =NH, *J* = 5.5 Hz). MS, *m/z* ($I_{rel}$ (%)): 284 [M – HCl]$^+$ (5). Found (%): C, 41.31; H, 2.34; Cl, 11.34; N, 17.25. $C_{11}H_8ClF_3N_4S$. Calculated (%): C, 41.19; H, 2.50; Cl, 11.08; N, 17.47.

***N*-[4-Cyano-2-(4-methoxyphenyl)-1,2,3-thiadiazol-5-ylidene]-*N*-methylammonium bromide (2g).** Method *B*, the yield was 0.403 g (62%), m.p. 208—209 °C. IR, ν/cm$^{-1}$: 2228 (C≡N); 2929 (C—H), 3445 (NH). $^1$H NMR ($CDCl_3$), δ: 3.65 (d, 3 H, Me, *J* = 5.6 Hz); 3.91 (s, 3 H, OMe); 7.04, 7.64 (AA´XX´ system, 4 H, Ar, *J* = 9.2 Hz); 10.52 (br.q, 1 H, =NH, *J* = 5.6 Hz). MS, *m/z* ($I_{rel}$ (%)): 246 [M – HBr]$^+$ (16). Found (%): C, 40.61; H, 3.22; Br, 24.20; N, 17.45. $C_{11}H_{11}BrN_4OS$. Calculated (%): C, 40.38; H, 3.39; Br, 24.42; N, 17.12.

***N*-[4-Cyano-2-(4-methoxyphenyl)-1,2,3-thiadiazol-5-ylidene]-*N*-cyclohexylammonium bromide (2h).** Method *B*, the yield was 0.670 g (85%), m.p. 160—161 °C. IR, ν/cm$^{-1}$: 2231 (C≡N); 2854, 2928 (C—H); 3445 (NH). $^1$H NMR ($CDCl_3$), δ: 1.55—2.16 (m, 10 H, 5 $CH_2$); 3.91 (s, 3 H, OMe); 4.53 (m, 1 H, CH); 7.05, 7.65 (AA´BB´ system, 4 H, Ar, *J* = 8.6 Hz); 10.56 (br.d, 1 H, =NH, *J* = 7.0 Hz). $^{13}$C NMR ($CDCl_3$), δ: 23.0, 24.4, 31.9, 55.4, 55.9, 112.2, 113.7, 115.5, 122.8, 132.3, 160.8, 166.3. MS, *m/z* ($I_{rel}$ (%)): 314 [M – HBr]$^+$ (18). Found (%): C, 48.86; H, 4.50; Br, 20.61; N, 14.41. $C_{16}H_{19}BrN_4OS$. Calculated (%): C, 48.61; H, 4.84; Br, 20.21; N, 14.17.

***N*-[4-Cyano-2-(4-trifluoromethylphenyl)-1,2,3-thiadiazol-5-ylidene]-*N*-methylammonium bromide (2i).** Method *B*, the yield was 0.518 g (71%), m.p. 208—209 °C. $^1$H NMR (DMSO-$d_6$), δ: 3.76, 4.37 (both s, 3 H, NMe); 7.62, 7.65 (both s, 4 H, Ar); 10.9 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio 1 : 1. MS, *m/z* ($I_{rel}$ (%)): 284 [M – HBr]$^+$ (85). Found (%): C, 36.45; H, 2.48; Br, 22.03; N, 15.10. $C_{11}H_8BrF_3N_4S$. Calculated (%): C, 36.18; H, 2.21; Br, 21.88; N, 15.30.

***N*-Benzyl-*N*-[4-cyano-2-(4-nitrophenyl)-1,2,3-thiadiazol-5-ylidene]ammonium bromide (2j).** Method *B*, the yield was 0.443 g (53%), m.p. 180—181 °C. IR, ν/cm$^{-1}$: 2235 (C≡N), 3440 (NH). $^1$H NMR (DMSO-$d_6$), δ: 4.55, 5.3 (both s, 2 H, $CH_2$); 7.35—7.47 (m, 5 H, Ph); 7.75—8.10 (m, 4 H, Ar); 11.1 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio 1 : 3. MS, *m/z* ($I_{rel}$ (%)): 337 [M – HBr]$^+$ (16). Found (%): C, 46.22; H, 3.01; Br, 19.51; N, 16.15. $C_{16}H_{12}BrN_5O_2S$. Calculated (%): C, 45.93; H, 2.87; Br, 19.14; N, 16.75.

***N*-[4-Cyano-2-(4-nitrophenyl)-1,2,3-thiadiazol-5-ylidene]-*N*-cyclohexylammonium bromide (2k).** Method *B*, the yield was 0.435 g (53%), m.p. 198—199 °C. IR, ν/cm$^{-1}$: 2237 (C≡N); 2854, 2940 (C—H); 3400 (NH). $^1$H NMR (DMSO-$d_6$), δ: 1.21—1.88 (m, 10 H, 5 $CH_2$); 4.41 (m, 1 H, CH); 7.26, 8.05, 8.36, 8.42 (AA´BB´ system, 4 H, Ar, *J* = 8.9 Hz); 11.99 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio 1 : 1. MS, *m/z* ($I_{rel}$ (%)): 329 [M – HBr]$^+$ (70). Found (%): C, 43.76; H, 3.65; Br, 19.85; N, 16.81. $C_{15}H_{16}BrN_5O_2S$. Calculated (%): C, 43.90; H, 3.90; Br, 19.51; N, 17.07.

***N*-Benzyl-*N*-[4-cyano-2-(4-methoxyphenyl)-1,2,3-thiadiazol-5-ylidene]ammonium iodide (2l)**. Method *C*, the yield was 0.756 g (84%), m.p. 203—204 °C. IR, ν/cm$^{-1}$: 2226 (C≡N); 3440 (NH). $^1$H NMR (DMSO-$d_6$), δ: 3.86, 3.92 (both s, 3 H, OMe); 5.2, 6.5 (both s, 2 H, $CH_2$); 7.01, 7.09, 7.24, 7.22 (two AA´XX´ systems, 4 H, Ar, *J* = 9.0 Hz); 7.25—7.65 (m, 5 H, Ph); 10.85 (br.s, 1 H, =NH). A mixture of *Z*- and *E*-isomers in the ratio 1 : 1. MS, *m/z* ($I_{rel}$ (%)): 322 [M – HI]$^+$ (18). Found (%): C, 45.10; H, 3.01; I, 28.53; N, 12.18. $C_{17}H_{15}IN_4OS$. Calculated (%): C, 45.33; H, 3.33; I, 28.22; N, 12.45.

***N*-Benzyl-*N*-[4-cyano-2-(4-nitrophenyl)-1,2,3-thiadiazol-5-ylidene]ammonium iodide (2m).** Method *C*, the yield was 0.512 g (55%), m.p. 176—177 °C. IR, ν/cm$^{-1}$: 2234 (C≡N); 3440 (NH). $^1$H NMR (DMSO-$d_6$), δ: 4.56 (s, 2 H, $CH_2$); 7.35—7.47 (m, 5 H, Ph); 7.74, 8.41 (AA´BB´ system, 4 H, Ar, *J* = 8.0 Hz); 10.90 (br.s, 1 H, =NH). MS, *m/z* ($I_{rel}$ (%)): 337 [M – HI]$^+$ (14). Found (%): C, 41.56; H, 2.35; I, 27.05; N, 15.31. $C_{16}H_{12}IN_5O_2S$. Calculated (%): C, 41.30; H, 2.60; I, 27.28; N, 15.05.

**Bases 5a—d (general procedures). Method *A*.** Triethylamine (0.139 mL, 1 mmol) was added to a solution of thiadiazolium salts **2a**,**b**,**g**,**h** in EtOH (20 mL). The reaction mixture was stirred for 1 h at ~20 °C, and the precipitate was filtered off.

**Method *B*.** Iminium chloride **2a** (1 mmol) in pyridine (4 mL) was refluxed for 10 min, and then the reaction mixture was poured into ice with water. The precipitate was filtered off.

**Method *C*.** Potassium hydroxide (0.26 g, 4 mmol) was added to a solution of iminium chloride **2c** (2 mmol) in EtOH (20 mL), the mixture was stirred for 2 h at ~20 °C, then ice was added, and the precipitate was filtered off.

**2-(4-Methoxyphenyl)-5-methylimino-2,5-dihydro-1,2,3-thiadiazole-4-carbonyl (5a).** Methods *A* and *B*, the yield was 0.354 g (72 and 73%), m.p. 203—204 °C. IR, ν/cm$^{-1}$: 2200 (C≡N); 2840,

2930, 2960 (C—H). $^1$H NMR (DMSO-$d_6$), δ: 3.17, 4.13 (both s, 3 H, Me); 3.81, 3.84 (both s, 3 H, OMe); 6.96—7.02 (m, 2 H, Ar); 7.40 (d, 1 H, Ar, $J$ = 9.1 Hz); 7.73 (d, 1 H, Ar, $J$ = 9.0 Hz). A mixture of *Z*- and *E*-isomers in the ratio 1 : 1. $^{13}$C NMR (DMSO-$d_6$), δ: 37.5, 40.1, 55.4, 55.5, 110.2, 110.3, 113.3, 114.8, 115.1, 118.6, 119.1, 121.5, 133.6, 135.1, 156.2, 157.5, 159.4, 159.6. MS, $m/z$ ($I_{rel}$ (%)): 246 $[M]^+$ (66). Found (%): C, 53.82; H, 4.27; N, 22.54; S, 13.28. $C_{11}H_{10}N_4OS$. Calculated (%): C, 53.64; H, 4.09; N, 22.75; S, 13.02.

**5-Benzylimino-2-(4-methoxyphenyl)-2,5-dihydro-1,2,3-thiadiazole-4-carbonitrile (5b).** Method *A*, the yield was 0.470 g (75%), m.p. 162—163 °C. IR, ν/cm$^{-1}$: 2200 (C≡N); 2840, 2920, 3040, 3060 (C—H). $^1$H NMR (DMSO-$d_6$), δ: 3.79, 3.85 (both s, 3 H, OMe); 4.50, 6.03 (both s, 2 H, $CH_2$); 6.86—7.10 (m, 4 H, Ar); 7.20—7.38 (m, 4 H, Ph); 7.76 (d, 1 H, Ph, $J$ = 7.7 Hz). A mixture of *Z*- and *E*-isomers in the ratio 1 : 3. MS, $m/z$ ($I_{rel}$ (%)): 322 $[M]^+$ (29). Found (%): C, 63.59; H, 4.61; N, 17.57; S, 9.61. $C_{17}H_{14}N_4OS$. Calculated (%): C, 63.34; H, 4.38; N, 17.38; S, 9.95.

**5-Cyclohexylimino-2-(4-methoxyphenyl)-2,5-dihydro-1,2,3-thiadiazole-4-carbonitrile (5c).** Method *A*, the yield was 0.340 g (54%), m.p. 74—75 °C. $^1$H NMR (DMSO-$d_6$), δ: 1.20—1.36 (m, 3 H, $CH_2$); 1.44—1.55 (m, 2 H, $CH_2$); 1.60—1.66 (m, 1 H, $CH_2$); 1.78—1.87 (m, 4 H, $CH_2$); 2.39—2.45 (m, 1 H, CH); 3.81 (s, 3 H, OMe); 7.70, 7.37 (AA´XX´ system, 4 H, Ar, $J$ = 8.8 Hz). MS, $m/z$ ($I_{rel}$ (%)): 314 $[M]^+$ (42). Found (%): C, 60.90; H, 5.54; N, 17.60. $C_{16}H_{18}N_4OS$. Calculated (%): C, 61.12; H, 5.77; N, 17.82.

**5-Methylimino-2-phenyl-2,5-dihydro-1,2,3-thiadiazole-4-carbonitrile (5d).** Method *A*, the yield was 0.260 g (60%), m.p. 241—242 °C. IR, ν/cm$^{-1}$: 2200 (C≡N); 2850, 2920, 2960, 3000 (C—H). $^1$H NMR (DMSO-$d_6$), δ: 3.25, 4.25 (both s, 3 H, Me); 7.29—7.34 (m, 1 H, Ph); 7.42—7.60 (m, 3 H, Ph); 7.77 (d, 1 H, Ph, $J$ = 7.3 Hz). A mixture of *Z*- and *E*-isomers in the ratio 1 : 3. MS, $m/z$ ($I_{rel}$ (%)): 216 $[M]^+$ (54). Found (%): C, 55.35; H, 3.53; N, 26.14; S, 15.07. $C_{10}H_8N_4S$. Calculated (%): C, 55.54; H, 3.73; N, 25.91; S, 14.83.

**Ethyl 5-methylimino-2-phenyl-2,5-dihydro-1,2,3-thiadiazole-4-carbimidate (6).** Method *C*, the yield was 0.49 g (93%), m.p. 92—93 °C. $^1$H NMR (DMSO-$d_6$), δ: 1.33 (t, 3 H, $OCH_2C\underline{H}_3$, $J$ = 7.2 Hz); 3.20 (s, 3 H, Me); 4.30 (q, 2 H, $OC\underline{H}_2CH_3$, $J$ = 7.2 Hz); 7.21—7.17 (m, 1 H, Ph); 7.44—7.30 (m, 4 H, Ph); 9.56 (s, 1 H, NH). MS, $m/z$ ($I_{rel}$ (%)): 262 $[M]^+$ (45). Found (%): C, 55.15; H, 5.23; N, 21.15; S, 12.38. $C_{12}H_{14}N_4OS$. Calculated (%): C, 54.96; H, 5.34; N, 21.37; S, 12.21.

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